Asian Journal of Chemistry Vol. 7, No. 4 (1995), 877–880

Reactivity of Tri-3-Phenyl Propyl Phosphate in the Form of its Conjugate Acid Species

C.P. SHINDE and R. PATIL*
School of Postgraduate Studies in Chemistry
Jiwaji University, Gwalior-474 011, India

Kinetics of hydrolysis of tri-3-phenyl propyl phosphate has been investigated from 0.1 to 7.0 mol dm^{-3} in HCl at 98°C in 20% dioxane-water mixture (v/v). Ionic strength data exhibit the participation of conjugate acid species. Unimolecular behaviour has been decided by molecularity data studies. Solvent isotope effect study favours specific acid catalysis. The formation of a transition state has been observed by solvent effect study. Carbon-oxygen bond fission has been further strengthened by comparative kinetic data.

INTRODUCTION

Esters of *ortho*-phosphoric acid with amines and hydroxy compounds have been found to be very potent agricultural chemicals of high insecticidal and acaricidal activity[1–3], wide spectrum and rapidity of action on plant pests, relatively rapid breakdown in the absence of accumulation in the animal organism. The present work is in continuation of the previous work[4].

EXPERIMENTAL

Tri-3-phenylpropyl phosphate was prepared by phosphorus oxytrichloride[5]. % Analysis, Found (Calcd.): C = 71.65 (71.68), H = 7.30 (7.30) and p = 6.86 (6.85)

The hydrolysis of tri-3-phenyl propyl phosphate (0.0005 mol dm^{-3}) was followed by colorimetric estimation of Allen's[5] modified method.

RESULTS AND DISCUSSION

The first order rate co-efficients for the hydrolysis of the present triester in the range 0.1 to 7.0 mol dm^{-3} HCl are found to increase in acid molarity up to 7.0 mol dm^{-3} (Table-1). The overall rise in rates in acid media may be attributed to the incursion of more reactive conjugate acid species or the (+)ve salt effect or due to both. Neutral electrolyte effect study has been performed at different constant ionic strengths using mixtures of HCl and NaCl. The increase in rates with the increase in acid concentration (Table-2) at each ionic strength (μ) indicates specific acid catalysis. This is further supported by the fact that the rates are slightly increased ($K_{D_2O}/K_{H_2O} = 1.30$) when water is replaced by D_2O. This also suggests a fast pre-equilibrium proton transfer generally observed for acid catalysed reactions. However, (+)ve effect of ionic strength on the rates of hydrolysis has also been observed (Table-3). Contribution of neutral species is negligibly small in acid medium.

TABLE-1
ESTIMATED AND EXPERIMENTAL RATE CO-EFFICIENTS FOR THE HYDROLYSIS OF TRI-3-PHENYL PROPYL PHOSPHATE AT 98°C

HCl (mol dm^{-3})	$K_e \times 10^5$ min^{-1} estimated	$K_e \times 10^5$ min^{-1} experimental
0.1	0.27	0.95
0.2	0.57	1.14
0.5	1.65	1.42
1.0	4.16	4.10
2.0	13.24	13.52 18.12[a]
3.0	31.42	32.32
4.0	66.39	66.37 74.64[b] 100.10[c] 22.18 (90°) 7.70 (50°)
5.0	77.00*	70.96
6.0	94.66*	89.00
7.0	127.90*	103.60

a = in D_2O; b = in 30% dioxane; c = in 40% dioxane
*From 1

TABLE-2
THE RATE COEFFICIENTS OF ACID HYDROLYSIS OF TRI-3-PHENYL PROPYL PHOSPHATE AT CONSTANT IONIC STRENGTH (μ) AT 98°C

Ionic strength (μ)	HCl (mol dm^{-3})	NaCl (mol dm^{-3})	$K_e \times 10^5$ min^{-1} experimental
2.0	1.8	0.2	11.44
	1.5	0.5	10.32
	1.0	1.0	5.82
	0.7	1.3	4.10
3.0	2.5	0.5	25.16
	2.0	1.0	20.57
	1.5	1.5	15.17
	1.0	2.0	10.31
4.0	3.5	0.5	57.73
	3.0	1.0	50.42
	2.5	1.5	41.64

TABLE-3
SPECIFIC ACID CATALYSED (K_{H^+}) RATES OF TRI-3-PHENYL PROPYL PHOSPHATE AT DIFFERENT IONIC STRENGTHS AT 98°C

Ionic Strength (μ)	10^5 K_{H^+} min^{-1} mol^{-1}	$5 + \log K_{H^+}$
2.0	6.50	0.8129
3.0	10.00	1.0000
4.0	16.00	1.2041

The overall rate of hyrolysis has been governed by the following rate law:

$$K_e = K_{H^+} \cdot C_{H^+} = 2.630 \times 10^{-5} \times C_{H^+} \exp(0.2\mu) + (aH_2O)^n$$

where n = 1, 2 and 2 respectively for 5, 6 and 7.0 mol dm^{-3} HCl.

The unit slope (1.17) of Hammett[8] plot (not shown) and Arrhenius parameters[9] (E = 36.55 Kcals/mole, $A = 3.835 \times 10^{16}$ sec^{-1}, $\Delta S^* = +14.91$ e.u.) for 4.0 mol dm^{-3} HCl indicate unimolecular nature of hydrolytic reaction. Bunnett-Olsen parameter[10] 0 as –0.4 (< 0.0) suggests that water is not involved in rate determining step.

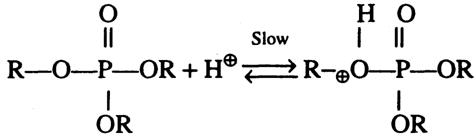
Solvent effect studies (Table-1) show that rate increases with increase in dioxane content. This is in accord with Chanley's[11] observation. It indicates the formation of a transition state in which charge is dispersed.

The effect of variation of concentration on the reaction rate in case of present triester shows that it is kinetically first order with respect to the ester by reducing either half ($K_e = 66.320 \times 10^{-5}$ min^{-1}) or double ($K_e = 66.260 \times 10^{-5}$ min^{-1}) the normal concentration (66.370×10^{-5} min^{-1}) at 4.0 mol dm^{-3}.

Comparative kinetic data for other esters[12] and isokinetic relationship[13] supports C—O bond fission.

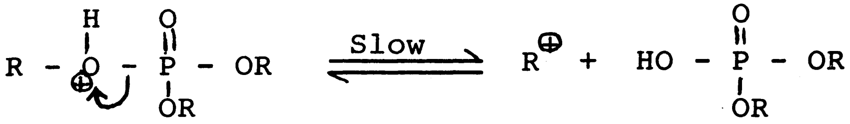
By considering all the above effects we can predict unimolecular C—O bond fission for the present triester.

(1) Formation of conjugate acid species by fast pre-equilibrium proton transfer

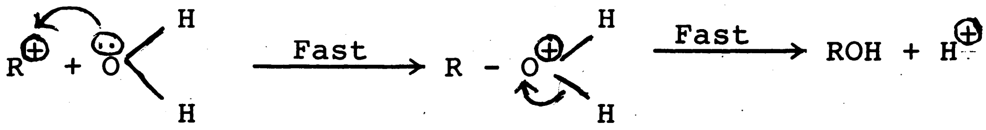


$$R{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{OR}{|}}{P}}{-}OR + H^{\oplus} \xrightleftharpoons{\text{Slow}} R{-}\overset{\overset{H}{|}}{{}_{\oplus}O}{-}\overset{\overset{O}{\|}}{\underset{\underset{OR}{|}}{P}}{-}OR$$

(2) Unimolecular hydrolysis of tri-3-phenyl propyl phosphate with C—O bond fission.



$$R{-}\overset{\overset{H}{|}}{\overset{\oplus}{O}}{-}\overset{\overset{O}{\|}}{\underset{\underset{OR}{|}}{P}}{-}OR \xrightleftharpoons{\text{Slow}} R^{\oplus} + HO{-}\overset{\overset{O}{\|}}{\underset{\underset{OR}{|}}{P}}{-}OR$$



$$R^{\oplus} + O\!\begin{array}{l} H \\ H \end{array} \xrightarrow{\text{Fast}} R{-}\overset{\oplus}{O}\!\begin{array}{l} H \\ H \end{array} \xrightarrow{\text{Fast}} ROH + H^{\oplus}$$

where, $R = C_6H_5CH_2{-}CH_2{-}$.

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(*Received*: 16 February 1995; *Accepted*: 27 April 1995) AJC-970