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Kinetics and Mechanism of Hydrolysis of Tri-2-chloro-4-Nitrophenyl Phosphate

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Hydrolysis of tri-2-chloro-4-nitrophenyl phosphate has been investigated in 20% aqueous-dioxan medium (V/V) at 98°C in acid region of 0.01–7.0 mol dm^3. Acid log rate profile has a rate maxima at 4.0 mol dm^3. The lowering in rates after 4.0 mol dm^3 may be attributed to the lowering in concentration of the nucleophile (water activity) or due to negative salt effect or both simultaneously. Ionic strength effect data upto 3.0 μ requires the participation of conjugate acid species and to determine theoretical rates, which are estimated from second empirical terms of Debye-Hückel equation, have been found in close aggrement with observed rates.

INTRODUCTION

Hydrolysis of Tri-2-chloro-4-Nitrophenyl Phosphate

The vital part of living cell includes deoxyribonucleic acid (D.N.A.) and ribonucleic acid (R.N.A.) which involve C—O—P linkages like those of simple organic phosphate esters. They are used for antiviral activity[1], radioactive tracer techniques[2], plasticisers[3], polymers[4], pressure-lubricants impregnating agents, self-extinguishing agents. Keeping this in view the hydrolysis of tri-2-chloro-4-nitrophenyl phosphate has been under taken for study.

EXPERIMENTAL

Tri-2-chloro-4-nitrophenyl phosphate was prepared by treating 2-chloro-4-nitrophenol with PCl_5 method. % Analysis

Calc., C = 38.26, H = 1.59, N = 7.44, P = 5.49,
Found, C = 37.45, H = 1.75, N = 6.85, P = 5.50.

Tri-2-chloro-4-nitrophenyl phosphate was hydrolysed in 20% aqueous-dioxane at 98°C, in acid region from 0.01 mol dm^3 to 7.0 mol dm^3 HCl, followed by colorimetric estimation of phosphate by Allen's[5] modified method.

RESULTS AND DISCUSSION

The pseudo first order rate-coefficients for the hydrolysis of tri-2-chloro-4-nitrophenyl phosphate in the range from 0.01 mol dm^{-3} to 7.0 mol dm^{-3} HCl are found to increase with the increase in acid molarity upto 4.0 mol dm^{-3}, beyond this there is decrease in rates, such a maxima has been attributed due to the lowering in concentration of the nucleophile *i.e.*, water-activity or negative salt effect or due to the presence of both effects simultaneously. Hydrolysis at each ionic strength (1, 2 and 3 μ) is denoted by a linear curve, that make positive slopes (Fig. not shown) which indicate the reaction to be acid-catalysed. Since the linear curves meet at origin shows no contribution of the neutral rate in the overall rate of the reaction, specially in strong acid medium. From the study of ionic strength effect, the total rates contributed by conjugate acid species can be calculated by the following second empirical term of Debye-Hückel[5, 6] equation, (Table 1).

$$K_{H^+} = K_{HO^+} + \exp b_{H^+} \cdot \mu$$

or,

$$\log K_{H^+} = \log K_{HO^+} + b_{H^+}/2.303\mu$$

Or, we can calculate specific acid catalysed rates for any molarity,

$$K_{H^+} \cdot C_{H^+} = K_{HO^+} \cdot \exp \cdot b_{H^+} \cdot \mu \cdot C_{H^+}$$

TABLE–1

CALCULATED AND OBSERVED RATES FOR THE HYDROLYSIS OF TRI-2-CHLORO-4-NITROPHENYL PHOSPHATE AT 98°C

S. No.	HCl (mol dm^{-3})	$K \times 10^3 = K_{H^+} \cdot C_{H^+}$ (min^{-1})	$K \times 10^3$ (min^{-1}) estimated	$K \times 10^3$ (min^{-1}) experimental
1.	0.01	0.159	0.159	0.536
2.	0.05	0.800	0.800	1.180
3.	0.1	1.612	1.612	1.996
4.	0.2	3.280	3.280	3.921
5.	0.3	5.001	5.001	5.040
6.	0.4	6.784	6.784	6.870
7.	0.5	8.625	8.625	9.000
8.	1.0	18.770	18.770	19.650
9.	2.0	44.460	44.460	44.820
10.	3.0	78.990	78.030	77.690[a] 77.030[b] 76.720[c]
11.	4.0	124.760	87.360	87.110
12.	5.0	180.500	73.300	62.700[a] 61.840[b] 61.030[c]
13.	6.0	262.500	57.500	57.310
14.	7.0	362.810	28.720	28.690

a = 20% dioxane; b = 40% dioxane, c = 50% dioxane.

There is slight deviation in rates of feebly acidic runs (0.01 to 0.05 mol dm^3) this is due to the incursion of inert neutral species[7]. In higher acid medium (> 3.0 mol dm^{-3} HCl) the effect of water activity is seen, thus the hydrolysis of the present ester is formulated as,

$$K_{H^+} \cdot C_{H^+} = K_{HO^+} \cdot C_{H^+} \cdot \exp \cdot b_{H^+} \cdot \mu \cdot (aH_2O)^n$$

(aH_2O is water activity and n is an integer)

Arrehenius[8] parameters determined for the hydrolysis at 3.0 and 5.0 mol dm^{-3} HCl (Table 2) at different series of temperature *i.e.*, 98°, 90° and 80°C. Magnitudes of the Arrhenius parameters clearly fall in the range of bimolecular reaction.

TABLE-2
CALCULATED ARRHENIUS PARAMETERS

S.No.	HCl (mol dm^{-3})	Temp. °C	K × 10^3 (min^{-1})	'E' Kcal/mol	'A' (Sec^{-1})	$-\Delta S^{\neq}$ (e.u.)
1.	3	98	77.69			
2.	3	90	44.41	18.31	7.802×10^7	24.85
3.	3	70	12.09			
4.	5	98	62.70			
5.	5	90	35.13	18.31	6.298×10^7	25.27
6.	5	70	8.09			

Bimolecular nature of reaction is further supported by Zücker-Hammett[9] (0.75), Hammett[10] (0.50) and Bunnett[11] ($w = 8.0$ and $w^* = 2.4$) slopes of the plots.

Bunnett-Olsen[12] parameter ($\phi = 1.5$ which is greater than 0.58) suggests the water is involved as a proton-transfer agent in the rate determining step.

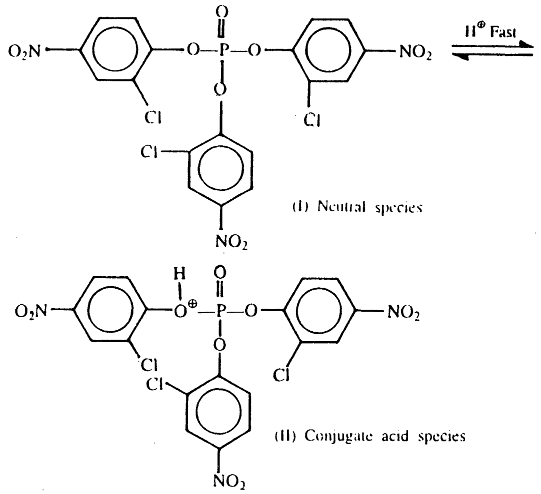
The effect of solvent (Table–1) shows a decrease in the rate of reaction with the increase in dioxane content of the medium *i.e.*, with decrease in polarity of the solvent, as according to the qualitative theory of solvent effect, but forwarded by Hughes and Ingold, is used for predicting the nature of transition state, indicating that change is unchanged but will be dispersed in transition state.

The concentration[13] 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 ($K_e = 19.72 \times 10^{-3}$ min^{-1}) or double ($K_e = 19.69 \times 10^{-3}$ min^{-1}) the normal concentration ($K_e = 19.63 \times 10^3$ min^{-1}) at 1.0 mol dm^3 HCl.

Bimolecular nature of the hydrolysis of triester involving P—O bond fission is further supported by comparative kinetic data[13, 14] for the hydrolysis of other esters and isokinetic relationship.

Mechanism of Hydrolysis

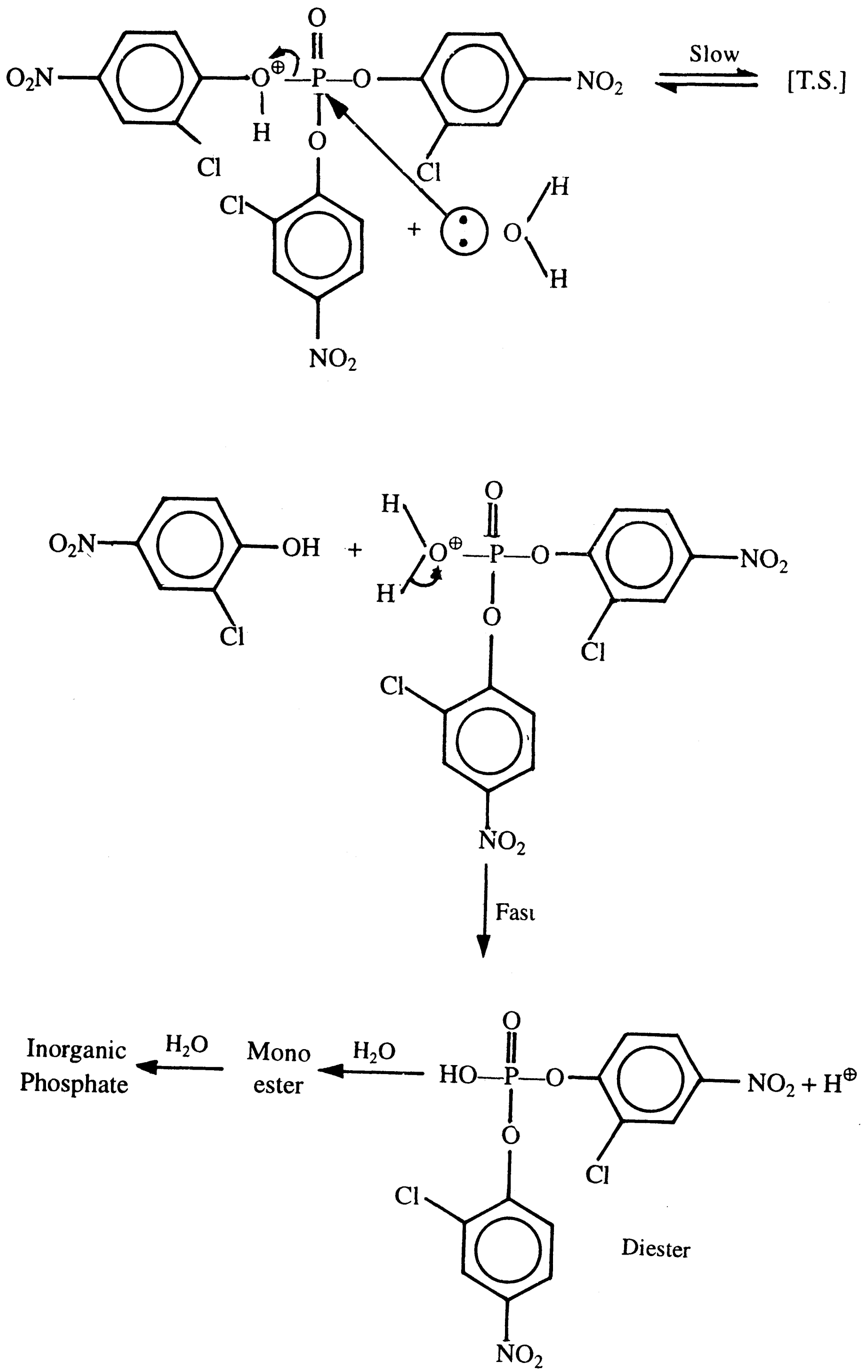
(a) Formation of conjugate acid species (II) of the triester (I) by the fast pre-equilibrium proton-transfer



(I) Neutral species

(II) Conjugate acid species

(b) Bimolecular attack of water on phosphorus of the conjugate acid species



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