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# KINETICS AND MECHANISM OF HYDROLYSIS OF MONO-4-CHLOROTHIOPHENYL PHOSPHATE ESTER VIA CONJUGATE ACID SPECIES

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## ABSTRACT

Hydrolysis of Mono-4-chlorothiophenyl phosphate ester has been carried out in acid region from 0.1- 6.0 mol dm$^{-3}$ HCl at 98$^0$C in aqueous dioxan medium 10 percent (V/V). Ionic strength data exhibits different contribution of conjugate acid species and presence of acid catalysis. Theoretical rates agree well with the experimentally observed rates. Bimolecularity of the reaction is supported by using various concepts and hypothesis like Hammet acidity function, Zucker-Hammet, Bunnet, Bunnet –Olsen, Arrhenius parameters and solvent effect. The monoester involves P-S bond fission which is strengthened by comparative kinetic data.

**KEYWORDS:** Mono-4-chlorothiophenyl phosphate, conjugate acid species, bimolecularity, monoester.

## INTRODUCTION

Organothiophosphates are a subclass of organophosphorus compounds. Compounds with C-S-P linkage are used as insecticides, some of them have applications in medical field as antitumor agents[1], cancer chemotherapeutics[2] and as antibiotics. Keeping this in view, the hydrolysis of mono-4-chlorothiophenyl phosphate has been investigated.

## EXPERIMENTAL

Mono-4-chlorothiophenyl phosphate was prepared by treating 4-chlorothiophenol with $POCl_3$ in pyridine.[3] Kinetic study of hydrolysis of the monoester was carried out in aqueous HCl medium at 98$^0$C using 5.0×10$^{-4}$ mol dm$^{-3}$ of the ester which was then followed by colorimetric estimation of inorganic phosphate by Allen's modified method[4].Values of pseudo first order rate coefficients were obtained from the standard equation. Constant ionic strength was maintained by using appropriate mixtures of NaCl and HCl.

## RESULTS AND DISCUSSION

Pseudo first order rate coefficients for the hydrolysis of present monoester in the range of 0.1to 6.0 mol $dm^{-3}$ HCl are found to increase with the increase in acid molarity upto 4.0 mol $dm^{-3}$ HCl (Table 1). Further increase in acid molarity decreases the rate. The rate maxima found to be at 4.0 molarity may be attributed to complete conversion of the ester into its conjugate acid species. After 4.0 molarity the decrease in the rate is attributed to the lowering of concentration of the attacking nucleophile taking part in the chemical reaction (i.e) due to variation in a parameter known as water activity.[5,6]

**Table 1: Estimated and Experimental rates for the hydrolysis of Mono-4-chlorothiophenyl phosphate at $98^0$c**

| **HCl mol $dm^{-3}$** | **$K_N \times 10^3$ $min^{-1}$** | **$K_N \times 10^3$ $min^{-1}$ Eq- ix** | **$a(H_2O)^n$** | **$K_{H^+}.C_{H^+} \times 10^3$ $min^{-1}$** | **$K_{H^+}.C_{H^+} \times 10^3$ $min^{-1}$ Eq- viii** | **$a(H_2O)^n$** | **$K_e \times 10^3$ $min^{-1}$ Estmd.** | **$K_e \times 10^3$ $min^{-1}$** | **3+log $K_e$ estmd** | **3+log $K_e$ Exp** |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.1 | 8.044 | | | -2.961 | | | 5.083 | 5.092 | 0.706 | 0.706 |
| 0.5 | 8.482 | | | 1.744 | | | 10.226 | 10.232 | 1.009 | 1.009 |
| 1.0 | 9.036 | | | 3.631 | | | 12.667 | 12.665 | 1.103 | 1.102 |
| 1.5 | 9.620 | | | 5.669 | | | 15.289 | 15.381 | 1.184 | 1.186 |
| 2.0 | 10.26 | | | 7.852 | | | 18.112 | 18.115 | 1.257 | 1.258 |
| 2.5 | 10.92 | | | 10.22 | | | 21.14 | 21.35 | 1.325 | 1.329 |
| 3.0 | 11.64 | | | 12.79 | | | 24.43 | 24.44 | 1.387 | 1.388 |
| 3.5 | 12.40 | | | 15.54 | | | 27.94 | 27.94 | 1.446 | 1.446 |
| 4.0 | 13.21 | | | 18.49 | | | 31.70 | 31.73 | 1.501 | 1.5014 |
| 5.0 | 15.00 | 10.51 | **0.155** $^1$ | 25.00 | 17.50 | **0.155** $^1$ | 28.01 | 28.79 | 1.447 | 1.459 |
| 6.0 | 17.02 | 10.47 | **0.211** $^1$ | 32.58 | 12.33 | **0.211** $^2$ | 22.8 | 23.54 | 1.358 | 1.372 |
| 7.0 | 19.32 | 10.16 | **0.279** $^1$ | 41.21 | 5.998 | **0.279** $^3$ | 16.158 | 17.01 | 1.208 | 1.230 |

To examine the effect of ionic strength on the rate of hydrolysis in acid medium, kinetic runs were made at three different ionic strengths (1.0. 2.0 and 3.0µ).

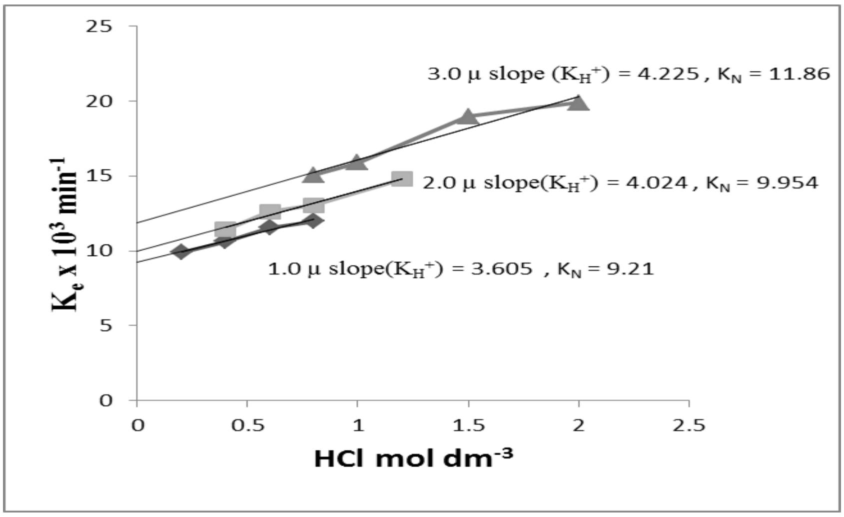


**Figure 1: Rates of hydrolysis of Mono-4-chlorothiophenyl phosphate at constant Ionic strength at 98°C**

Hydrolysis at each ionic strength is represented by a linear curve that makes a positive slope with the acid axis, indicating the presence of acid catalysis. Since the slopes ($K_H^+$ = 3.605, 4.024, 4.225 for 1.0, 2.0 and 3.0 μ respectively) increase with the increase in ionic strength, acid catalysed hydrolysis is subjected to positive salt effect.

Plot of Mono-4-chlorothiophenyl phosphate shows three different lines intersect the rate axis at different points. Therefore, in addition to conjugate acid species, the presence of some other species can't be ignored. It may be expected that there is participation of neutral species along with conjugate acid species. Hence the overall rate of hydrolysis may be represented by the equation,

$K_e$ = Acid Rate + Neutral Rate

$K_e = K_H^+ . C_H^+ + K_N$ ……………… (I)

In the above equation, the terms **$K_e$, $K_H^+$** and **$K_N$** are the observed rate constants, specific acid catalysed rate and neutral rate respectively at that ionic strength.

$K_e = K_{H0}^+ . C_H^+ .\exp. b'_H . \mu \, (a\, H_2O)^n + K_{N0} . \exp. b'_N . \mu \, (aH_2O)^n$ .... (II)

Where $aH_2O$ is water activity and n is an integer. The revised estimated rates now agree well with the experimentally observed rates (Table 1).

Solvent effect on the rate of hydrolysis indicates the formation of a transition state in which charge is dispersed (Table not shown).

Arrhenius parameters[7] determined for the acid hydrolysis at 3.0 and 5.0 molarity (Table 2) favour bimolecular nature of the reaction.[8]

**Table 2: Arrhenius parameters for the hydrolysis of Mono-4-chlorothiophenyl Phosphate in acid medium.**

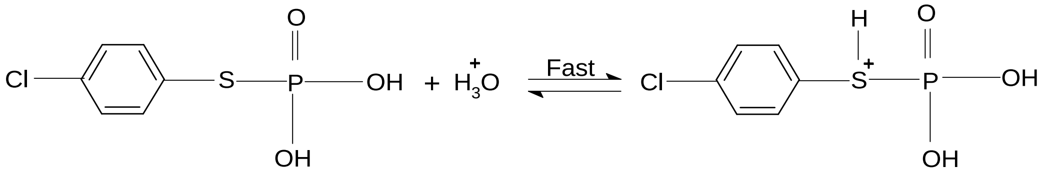
| HCl mol dm$^{-3}$ | Parameters | | |
|---|---|---|---|
| | Energy of Activation "E" K.Cal mol$^{-1}$ | Frequency factor "A" Sec$^{-1}$ | Entropy of Activation $-\Delta S^{\neq}$ e.u |
| 3.0 | 18.12 | $2.0 \times 10^{-3}$ | 54.60 |
| 5.0 | 22.6 | $2.35 \times 10^{-3}$ | 54.278 |

Bimolecularity is further supported by Zucker-Hammmet[9] (0.441),Hammmet(0.122), Bunnet ($\omega = 9.296$, $\omega^{*} = 2.55$) plots.

Bunnet – Olsen parameter[10] ($\phi$=1.4) which is greater than 0.58 suggests water is involved in rate limiting step and it behaves as a proton transfer agent in the reaction pathway. The effect of concentration on the rate of hydrolysis of the present ester confirms first order kinetics with respect to the monoester. Comparative kinetic data (not shown) also supports bimolecular nature of hydrolysis involving attack of water on phosphorus of the monoester.

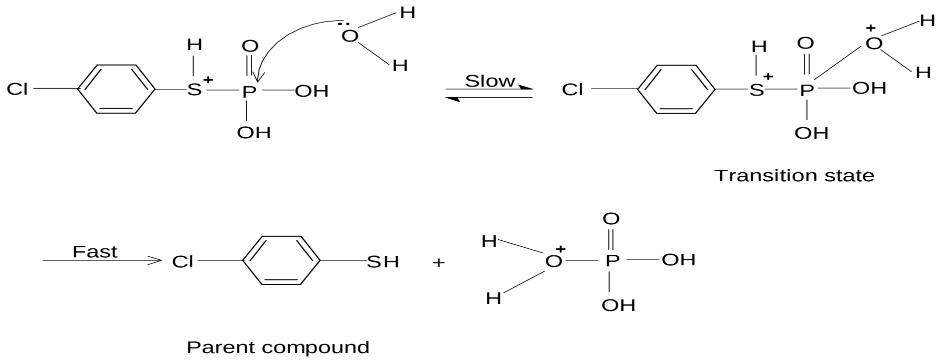
### Probable mechanism

**(A) Formation of conjugate acid species**

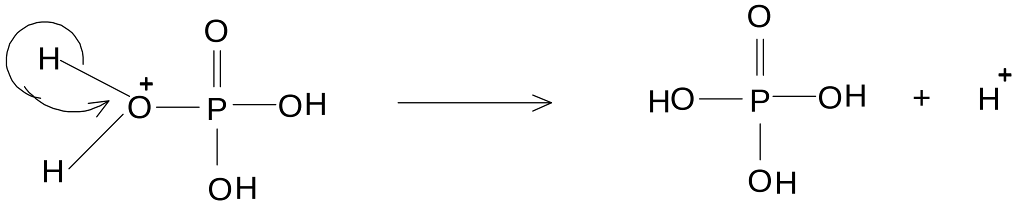


**(Neutral species)** **(Conjugate acid species)**

**(B) Bimolecular nucleophillic attack of water on phosphorus through conjugate acid species, $S_N2(P)$:**



**(C)**



## CONCLUSION

Kinetics and mechanism of hydrolysis of orthophosphate esters (mono, di and triesters) in neutral, alkaline and acidic media have been reviewed from time to time. The hydrolysis of orthophosphate esters follows several patterns depending upon the solvent, range of pH or catalytically active additives. Modern synthetic methods for the derivatives of phosphoric acid have made an easy access to a variety of compounds of biological and agricultural interest, which are otherwise, inaccessible from classical synthetic procedures. This has resulted in accelerating the studies on biological and agricultural significance.

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