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

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ABSTRACT

Kinetic study Di-4-chlorothiophenyl phosphate has been carried out at 98^{0}C in acid region from 0.1 – 7.0 mol dm^{-3} HCl and in buffer medium (1.24-7.46pH). The kinetic study was performed in 10% aqueous dioxan (V/V). The study has yielded pseudo first order rate coefficients. Theoretical and experimental rates have been found to be in close agreement as estimated from second empirical term of Debye-Huckle equation. Arrhenius parameters and comparative kinetic rate data have been used to propose the tentative mechanism.

KEYWORDS: Di-4-chlorothiophenyl phosphate, Debye-Huckle equation, Arrhenius parameters.

INTRODUCTION

The chemistry of phosphate esters continues to draw attention of chemists due to their versatile applications in analytical.[1,2], biological[3,4] and industrial fields.[5,6] Phosphates with C-S-P linkages have great importance. They represent an important class of environmental chemicals that are mostly used in the field of agriculture as insecticides. Their hydrolysis generally involves conversion of phosphate trimesters to their corresponding diester derivatives.

EXPERIMENTAL

Di-4-chlorothiophenyl phosphate was prepared by Auger and Dupis[7] method using pyridine as solvent. Kinetic study of acid hydrolysis of di-4-chlorothiophenyl phosphate was carried out at 98^{0}C using 5.0 ×10^{-4} mol dm^{-3} solution of the present diester, followed by colorimetric estimation of inorganic phosphate by Allen's modified method[8]. Kinetic runs were carried out at different constant ionic strengths using appropriate mixtures of NaCl and HCl. All the chemicals used were of AR grade.

RESULTS AND DISCUSSION

A thorough kinetic study of the present diester reveals pseudo first order rate coefficients in the range of 0.1 to 7.0 mol dm^{-3} HCl (Table 1). Further increase in acidity decreases the rate uniformly upto 7.0 mol dm^{-3} HCl. The rise in rate with increasing acidity upto 4.0 mol dm^{-3} may be due to acid catalysed hydrolysis and lowering of rates after 4.0 mol dm^{-3} which may be attributed to water activity.[9]

Table 1: Estimated and experimental rates of hydrolysis of Di-4-chlorothiophenyl phosphate at 98^0C.

HCl mol dm^{-3}	$K_N \times 10^3$ min^{-1}	$K_H{}^+C_H{}^+ \times 10^3$ min^{-1}	$K_H{}^+C_H{}^+ \times 10^3$ min^{-1}	$(aH_2O)^n$	$K_e \times 10^3$ min^{-1} (Estm)	$K_e \times 10^3$ min^{-1} (Expt.)	3+log K_e Estm.	3+log K_e Expt.
0.1	24.00	13.60			37.6	38.83	1.575	1.5891
0.5	24.00	61.09			85.09	85.15	1.929	1.930
1.0	24.00	107.4			131.40	131.20	2.118	2.118
1.5	24.00	140.6			164.40	164.67	2.216	2.217
2.0	24.00	166.0			190.00	191.01	2.278	2.281
2.5	24.00	182.0			206.00	206.7	2.313	2.314
3.0	24.00	192.30			216.30	216.92	2.335	2.336
3.5	24.00	197.20			221.2	220.00	2.344	2.342
4.0	24.00	198.2			222.2	223.15	2.346	2.348
5.0	24.00	191.4	133.7	$\mathbf{(0.155)^1}$	157.7	158.39	2.197	2.198
6.0	24.00	177.4	67.14	$\mathbf{(0.211)^2}$	91.14	93.20	1.959	1.969
7.0	24.00	173.8	25.88	$\mathbf{(0.279)^3}$	49.88	50.37	1.967	1.702

The rate of hydrolysis increases with the increase in acidity upto 4.0 molarity and then decreases. This decrease may be attributed to negative salt effect and water activity.

In order to determine the effect of ionic strength or presence of acid catalysis, kinetic runs were made at three different ionic strengths (1.0, 2.0 and 3.0 µ) which were maintained by using appropriate mixtures of NaCl and HCl. Hydrolysis at each ionic strength is denoted by a linear curve that makes a negative slope with the acid axis indicating negative salt effect. This suggests that the reaction obeys the following equation.

$$K_e = K_H{}^+ . C_H{}^+ ({}^aH_2O)^n + K_N ({}^aH_2O)^n \quad \ldots\ldots\ldots\ldots..(1)$$

Where $({}^{a}H_2O)^n$ is water activity and n is an integer. The estimated and observed rates now agree well with each other (Table 1). It is clear from the above results that hydrolysis of Di-4-chlorothiophenyl phosphate ester occurs via both conjugate acid species and neutral species and their rates are subjected to both ionic strength and water activity.

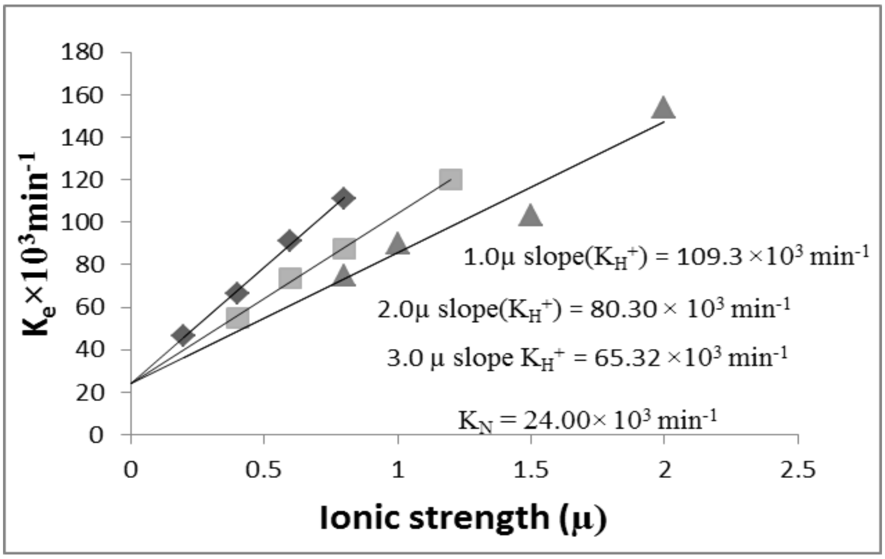


Figure 1: Rates of hydrolysis of Di-4-chlorothiophenyl phosphate at constant Ionic strength at 98°C.

Solvent effect shows a significant rise in rates by varying the percentage of dioxan as it acts as a better proton donor than water. This indicates formation of a transition state in which charge is dispersed (Table 2).

Table 2: Effect of change in Dioxan content on the rates of hydrolysis of, Di-4-chlorothiophenyl phosphate at 98^0 c

HCl mol dm^{-3}	Percentage of Dioxan (V/V)	$K_e \times 10^3 min^{-1}$
4.0	40	246.31
	50	269.46
	60	295.93

Arrhenius parameters[10] at 3.0 and 5.0 mol dm^{-3} HCl for the hydrolysis of present diester fall in the range of bimolecular reaction (Table 3).

Bimolecularity is further supported by Zucker- Hammet[11] (0.293), Hammet[12] (0.169), and Bunnet[13] ($\omega = 10.33$, $\omega^* = 4.196$) parameters. Bunnet – Olsen[14] parameter ($\phi = 1.674$) which is greater than 0.58 suggests that water is involved as proton transfer agent in the rate determining step.

Table 3: Arrhenius parameters for the the hydrolysis of Di-4-chlorothiophenyl phosphate in acid medium.

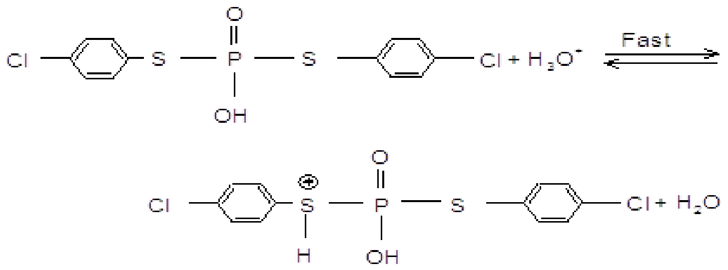
HCl mol dm^{-3}	Parameters		
	Energy of Activation "E" K.Cal mol^{-1}	Frequency factor "A" Sec^{-1}	Entropy of Activation-$\Delta S^{\neq}$ e.u
3.0	13.72	2.33×10^{-3}	50.271
5.0	13.72	2.19×10^{-3}	50.90

Comparative kinetic data further suggests P-S bond cleavage.

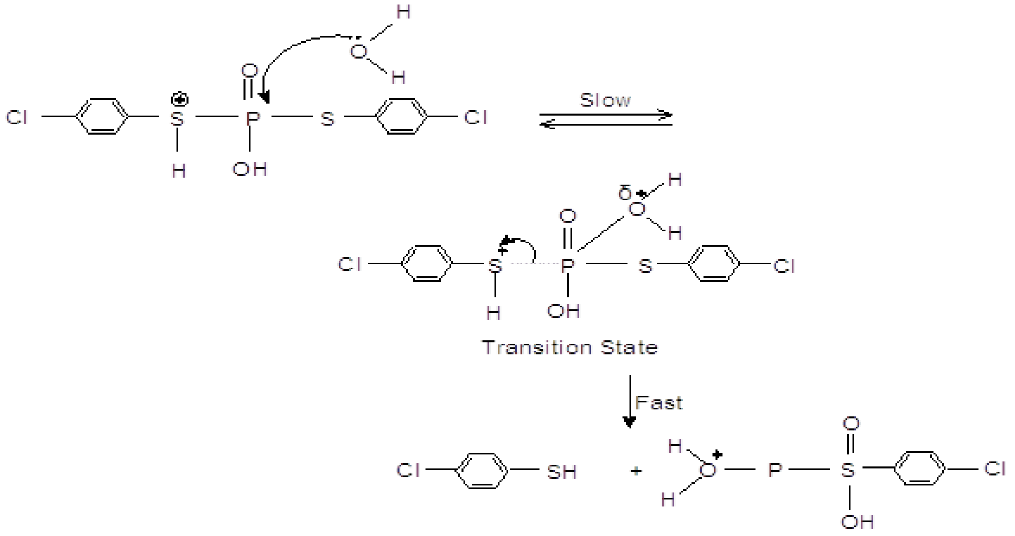
Mechanism

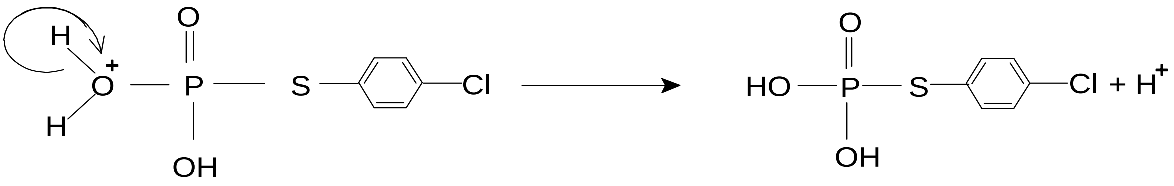
Hydrolysis of Di-4-chlorothiophenyl phosphate via conjugate acid species.

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



B) Bimolecular attack of H_2O on P atom involving P-S bond fission.





Note: This is followed by the hydrolysis of monoester into inorganic phosphate.

CONCLUSION

Kinetics deals with the rates of a chemical reaction and with how the rates depend on certain factors like concentration and temperature. Such studies are important in providing necessary evidence as to the mechanism of any chemical process. One can also get valuable evidence about the mechanism by non kinetic investigation by the detection of reaction intermediates and isotope exchange studies.

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