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Kinetics and mechanistic study of hydrolysis of mono 4-chloro, 3-methyl phenyl phosphate (In acidic medium) is applicable for the environment

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Abstract

Phosphate having C-O-P linkage is widely used as fertilizers, pesticides etc. pesticides are generally poisonous or toxic and adversely affected the environment. Study of relative eco-friendly nature of pesticides depends on their bond cleavage and stability during hydrolysis in this connection and investigation of hydrolysis of Mono-4-Chloro-3-Methyl Phenyl Phosphate was carried out by using "Allen's Modified Method" of colorimetry in aqueous medium from 0.1 to 6.0 mol dm⁻³ HCl at 98°. Ionic strength data exhibits different contribution of natural species and presence of acid catalysis. Theoretical rates estimated from second empirical term of Debye-Hickel equation have been found in close agreement with experimental rates. The effect of ionic strength, temperature, solvent and concentration are provided to identify the reactive species and molecularity. Bimolecular behavior has been decided by the Arrhenius parameters and by the analysis of molecularity data. The monoester involves P-O Bond fission which is strengthened by comparative kinetic data's.

Keywords: hydrolysis, phosphate esters, phosphate with C-O-P linkage, conjugate species

Introduction

Organic compounds of phosphorus are essential constituent of protoplasm and DNA and play an important role for the maintenance of life. Phosphates having C-O-P linkage are widely used as Fertilizers, flame retardants, pesticides, chemosterilants, Herbicides, Fungicides, Plasticizers, Lubricants, Defoliant, Cancer chemotherapeutic agents, Antitumor agents, Antibiotic and in the treatment of Myasthenia. There are sculpture containing Para thion phosphate series used as pesticide series but because phosphate having C-O-P linkage have wide range of application in different scientific discipline and also to assess its eco-friendly behavior, the knowledge regarding their bond cleavage and stability during hydrolysis is important. Keeping the above objectives in view the hydrolysis of Mono 4-chloro 3-methyl phenyl phosphate ester has been investigated.

Material and Methods

Mono 4-Chloro 3-Methyl Phenyl phosphate was prepared by Auger and Dupis method in ratio of 1:1 of 4-Chloro 3-Methyl Phenol (Sigma Aldrich) and Phosphorus oxy Chloride in pyridine. The hydrolytic reaction was carried out at 98° employing 5.0 × 10⁻⁴ mol dm⁻³ aqueous solution of mono ester which was subsequently followed by the Allen's modified method of colorimetric estimation of inorganic phosphate by means of HCl and NaCl. All the chemicals are used of BDH quality.

Results and Discussion

The rate of hydrolysis of mono 4-Chloro 3-Methyl Phenyl Phosphate was studied in HCl (0.1 to 6.0 mol dm⁻³) at 98°. In table-1 the pseudo- first order rate constants are summarized, from which it is quite clear that the rate of hydrolysis increases up to 4.0 mol dm⁻³, further increase in acid molarities decreases the rate as it can be attributed to the complete conversion of the ester molecule into their respective conjugate acid species with the lowering of concentration of a nucleophile (water), which play its role in rate determining step of bimolecular hydrolytic reaction. In order to determine whether or not there is effect of ionic strength or presence of acid catalysis, kinetic runs were made at three different ionic strength (1.0μ, 2.0μ and 3.0μ) which were maintained by adequate mixture of NaCl and HCl. Hydrolysis of each ionic strength is denoted by linear curve that makes a positive slope with the acid axis indicating the

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presence of acid catalysis. Since the slopes ($K_H+9.00 \times 10^{-3} \text{min}^{-1} \text{mol dm}^{-3}$, $10.16 \times 10^{-3} \text{min}^{-1} \text{mol dm}^{-3}$ and $12.00 \times 10^{-3} \text{min}^{-1} \text{mol dm}^{-3}$) for 1.0 μ , 2.0 μ and 3.0 μ respectively increases with increase in ionic strength, three curves make intercepts on the rate axis indicating the presence of side reaction of neutral species. From the study of ionic strength effect, the total rates contributed by conjugate acid species and neutral species can be calculated by the following second empirical term of Debye Huckel equation

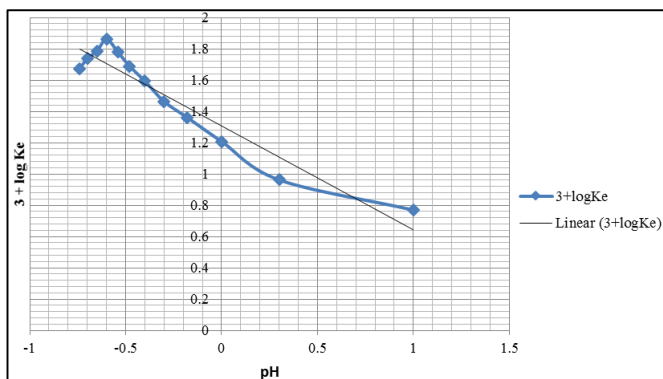


Fig 1: pH log rate profile for the hydrolysis of Mono-4 Chloro-3 Methyl Phenyl Phosphate at 98°

Table 5.A-1: Rates of hydrolysis of Mono-4-chloro, 3-methyl phenyl phosphate at 98°

HCl Mol dm ⁻³	pH	K _e × 10 ³ min ⁻¹	3+ log K _e
0.10	1.00	5.89	0.7701
0.50	0.30	9.18	0.9628
1.00	0.00	16.14	1.2096
1.50	-0.18	23.02	1.3621
2.00	-0.30	29.12	1.4641
2.50	-0.40	39.29	1.5942
3.00	-0.48	48.94	1.6896
3.50	-0.54	60.14	1.7791
4.50	-0.60	72.65	1.8612
5.00	-0.65	61.25	1.7871
5.50	-0.70	54.86	1.7392
6.00	-0.74	47.12	1.6732

a = 0.0 % (v/v) Dioxan b = 5.0% (v/v) Dioxan c = 0.0(v/v) Dioxan

$$K_e = K_H^+ + C_H^+ K_N \quad \dots (i)$$

In the above equation the term K_e, K_H⁺, K_N are observed rate constant the specific rate and neutral rates of the ionic strength respectively. The sum of the specific and neutral rates agrees well with the experimentally observed rates (Table: 1) up to 4.0 Mol dm⁻³ HCl. The lowering in rates in higher acid region (> 4.0 Mol dm⁻³ HCl) can be explained by considering the water activity as additional parameter respectively as:

$$K_e = K_{H_0^+} + C_H^+ \exp. b_H^+ \mu (\alpha H_2O)^n + K_{N_0} \exp. b_N \mu (\alpha H_2O)^n \quad \dots (ii)$$

Where, K_{H₀⁺ and K_{N₀} are specific conjugate acid and specific neutral rate coefficients at zero ionic strength respectively, b⁺H⁺ and b⁺N are constants, and α H₂O is water activity and is an integer. It is clear from the above results that mono-4-Chloro 3-Methyl Phenyl phosphate in aqueous acid solution occurs via both conjugate acid species and neutral species and their rates are subjected to water activity. Effect solvent dioxan (Table) on the rate of hydrolysis may, therefore, taken to}

indicate the formation transition state in which charge is dispersed.

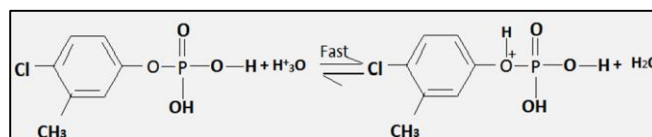
Table 2: Calculated Arrhenius parameter

HCl Mol dm ⁻³	Temp.t°	K _e × 10 ³ (Min ⁻¹)	Parameters		
			'E' K. cal/mol	'A' Sec ⁻¹	Δs [‡] e.u.
3.0	80	22.00	11.80	0.82 × 10 ⁻³	61.33
	90	35.57			
5.0	80	48.94	9.88	0.29 × 10 ⁻³	61.11
	90	24.23			
	90	39.81			
	98	54.86			

Arrhenius parameters determined for the hydrolysis at 3.0 and 5.0 mol dm⁻³ HCl. (Table 2) the magnitude of Arrhenius parameter fall in the range of bimolecular reaction. Biomolecular nature of reaction is further supported by Zuker-Hammett parameter (slope-1.25) Hammett acidity function (slope-0.444) Bunnett parameter (G = 4.807 and G* = 2.272) and Bunnett-Olsen parameter (Φ=1.000) which is greater than 0.58 suggests that value is involved as a proton transfer agent in the rate determining step. The effect of concentration of monoester on the rate of hydrolysis also confirms the order of reaction to be on with respect to monoester by reducing either half (K_e=72.12 × 10⁻³min⁻¹) or double (K_e = 72.95 × 10⁻³min⁻¹) and the normal concentration (K_e=72.65 × 10⁻³min⁻¹) at 4.0 mol dm⁻³ HCl.

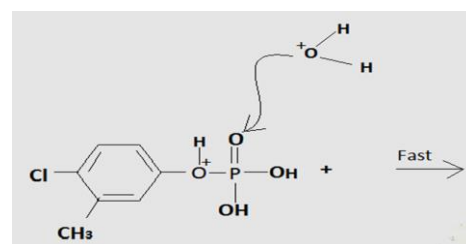
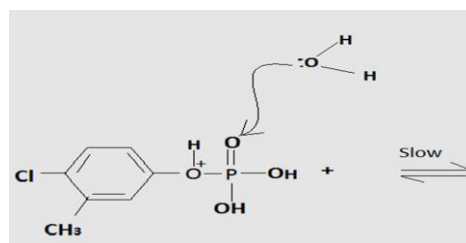
Comparative kinetic data of other mono phenyl phosphates also support the bimolecular nature of hydrolysis involving the attack of water on phosphorus of mono ester. On the bases of above evidence and discussion, the most tentative mechanistic rote of mono 4-Chloro 3-Methyl phenyl phosphate may be formulated as.

a) Formation of conjugate Acid Species

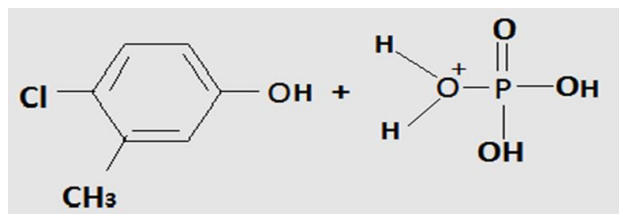


(Neutral Species) (Conjugated acid Species)

b) Bimolecular nucleophilic attack of water on phosphorus via conjugate acid species: S_N2 (P)

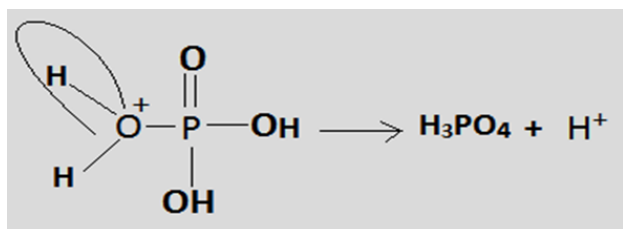


Transition State



Parent Compound

(c)



Conclusion

The hydrolysis of organophosphates follows several patterns depending upon the type of esters, the solvent and pH range or upon catalytically additives. A qualitative knowledge or the various grades of reactivity in relationships to structure facilitates the synthesis of product with special properties for practical application e.g. for use in rather strong alkaline dip in acid soils to regulate the rate of degradation in plants or animals (residue tolerance, waiting periods, toxicological effects etc.). Organic compounds of phosphorus having C-O-P linkages are widely used as fertilizers, flame-retardants, pesticides, herbicides, chemosterilants, plasticizers and antitumourous agents. But the mechanism and kinetic study of hydrolysis Mono-4-Chloro-3-Methyl Phenyl Phosphate in acidic medium reveals that these chemicals may easily hydrolysis with respect to others and hence has least toxic effect than other series of compounds used as Pesticides/herbicides etc. Therefore on the bases of this study may be concluded that Mono-4-Chloro-3-Methyl Phenyl Phosphate are more effective and eco-friendly pesticides. Its eco-friendly nature does not affect or dilutes its pesticide behavior and after acting effectively as pesticides or agrochemical or economic poisons phosphates having C-O-P linkage i.e., Mono-4-Chloro-3-Methyl Phenyl Phosphate easily degrades/hydrolysis and becomes least harmful or eco-friendly.

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