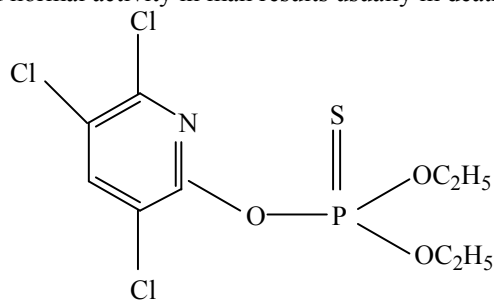


both at the synapse of neurons and in the plasma. The inactivation of the acetylcholine (ACh) which is normally hydrolysed by the enzyme, paralyzing the synaptic site. The manifestations of organophosphate poisoning are associated with the increase in concentration of ACh at the neuron synapse [34] reduction in acetylcholinesterase activity to 10-20% of normal activity in man results usually in death.



Chlorpyrifos, fig-4.

Chlorpyrifos is metabolized by fish and excreted in a changed form that is not an inhibitor of acetylcholinesterase [7]. The uptake by plants is much faster than in fish [26]. Chlorpyrifos has a half life in water of 90 days, and 200 days in soil [56]. When large concentrations of chlorpyrifos reach in soil, as in accidental spill, degradation will occur only after many years. As a hazardous OP pesticide, it is regularly misused in developing countries and the problem related to it also persists. Thus there is an urgent need to find the solution for its toxicity and in this connection the catalytic hydrolysis of chlorpyrifos has been studied using various kinetic parameters.

3.3 Hydrolysis of chlorpyrifos

Hydrolysis is a major degradation pathway for thionate ester pesticides and their corresponding oxonates. Many thionate and oxonate esters hydrolyze quickly in alkaline solution [38],[18],[53], but persist under the neutral and slightly acidic conditions typical of surface waters and soils. There is growing evidence that these toxic pollutants may interact with dissolved and particulate chemical constituents of environments [44],[19]. In particular, the role of metal ions in catalyzing hydrolytic reactions merits consideration [14],[6]. The pesticides examined here can hydrolyze via two distinct pathways: attack by OH⁻ and H₂O at the phosphorus atom which is a "hard" electrophilic site, and attack by H₂O at the carbon atoms within the alcoholate linkages, which are "soft" electrophilic sites [18]. Each hydrolysis step may involve loss of either phenolate leaving group or one of the alcoholate leaving groups. Measurement of phenolate product concentrations during the hydrolysis reaction can provide information regarding mechanism. If the phenolate product is less than the amount of parent lost, then a significant fraction of the triester hydrolysis must occur through alcoholate leaving group. If the phenolate product is equal to the amount of parent lost, then triester hydrolysis exclusively via the phenolate group. To fully understand the mechanism of the amine catalyzed hydrolysis, various parameters have to be used in studying the hydrolysis. The work is done by the C. P. Shinde and his coworkers, hydrolysis of chlorpyrifos catalyzed by different amine, at 80°C.

4. Chemistry of Amines

Amines are organic compounds which contain and are often actually based on one or more atoms of nitrogen. In an amine, one or more of the hydrogen atoms from ammonia are replaced by organic substituent like alkyl (alkane chain) and aryl (aromatic ring) groups. Some of the amines we are used in the experiment which are as follows: Imidazole, ammonia, hydrazine, ethanolamine, n-butyl amine.

a) **Imidazole:** Imidazole is an organic compound with the formula C₃H₄N₂. Imidazole is a heterocyclic aromatic organic compound [22]. This ring system is present in important biological building blocks such as histidine and histamine [64]. Imidazole exists in two tautomeric forms with a hydrogen atom moving between the two nitrogens.

b) **Ammonia:** Ammonia is a compound of nitrogen and hydrogen (and so is covalently-bonded) with the formula NH₃ [11]. It is a colourless gas with a characteristic pungent odor [48]. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals. Although in wide use, ammonia is both caustic and hazardous [32].

c) **Hydrazine:** Hydrazine is an inorganic chemical compound [49] with the formula N₂H₄. It is a colourless flammable liquid [30], [1] with an ammonia-like odor and is derived from the same industrial chemistry processes that manufacture ammonia. However, hydrazine has physical properties that are closer to those of water. Hydrazine is used within both nuclear and conventional electrical power plant steam cycles to control concentrations of dissolved oxygen in an effort to reduce corrosion.

d) **Ethanolamine:** Ethanolamine, also called 2-aminoethanol or mono-ethanolamine (often abbreviated as ETA or MEA), is an organic chemical compound [51] that is both a primary amine (due to an amino group in its molecule) and a primary alcohol (due to a hydroxyl group). Like other amines, mono-ethanolamine [32] acts as a weak base. Ethanolamine is a toxic, flammable, corrosive, colorless, viscous liquid with an odor similar to that of ammonia. Ethanolamine is the second-most-abundant head group for phospholipids, substances found in biological membranes [2].

e) **n-Butylamine:** n-Butylamine is an organic compound [51] (specifically, an amine) with the formula CH₃CH₂CH₂CH₂NH₂. This colourless liquid is one of the four isomeric amines of butane, the others being *sec*-butylamine, *tert*-butylamine and isobutylamine. At standard temperature and pressure, n-butylamine is a liquid having the fishy, ammonia-like odor common to amines. The liquid acquires a yellow color upon storage in air. It is soluble in all organic solvents.

5. Effect of Catalyst Concentration on Hydrolysis of Chlorpyrifos

The effect of catalyst concentrations (0.10 to 0.90 M) on the rate of hydrolysis of chlorpyrifos was studied. Apparently, the binding constant (*K*) and amine catalyzed hydrolysis rate constants (*k_M*) values amine were calculated for each

reaction by the method described by *C.P. Shinde* and co-workers.

6. Second Order Rate Constant

k_2 (second order rate constant) values are obtained for all amines from the slope of the observed pseudo-first order rate constants plotted as a function amine existing in the free base form. Values of k_2 are independent of pH . Second order rate constant were determined by plotting observed pseudo-first order constants against catalyst concentration. The slope was taken as the second order rate constant and intercept as the first order constant in the absorbance of added catalyst [28].

7. Brønsted correlation

Brønsted plot is pK_a v/s $\log k_2 + 7$. Most of amine follow a Brønsted relation graph with a slope of 0.215 ($r = 0.196$). *C.P. Shinde* and co-workers also showed the general base catalysis reaction of amine, when slope is less than 0.50.

8. Effect of Substrate Concentration

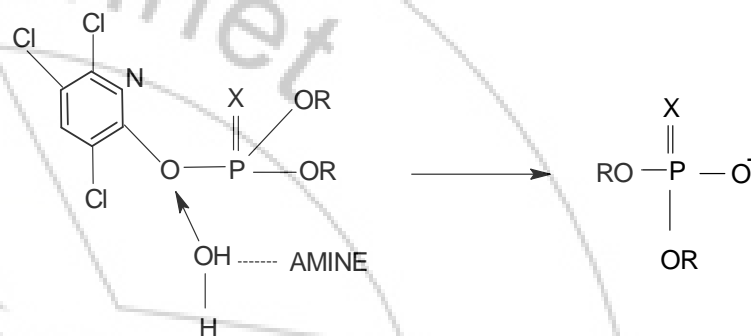
The effect of substrate concentrations (1.0×10^{-5} to 3.5×10^{-5} M) on the rates of amine catalyzed hydrolysis of chloropyrifos was studied. The k_{obs} values in the reactions remains practically unchanged, suggested that the reactions followed pseudo-first order kinetics [28].

9. Discussion & Conclusion

Reaction of chloropyrifos with amines proceeds exclusively by a general base pathway. The stoichiometry, rate law, Brønsted correlation are completely consistent with this interpretation. The kinetically equivalent general acid-hydroxide ion reaction can be excluded. Substrates are the few examples of an acyclic organophosphorus ester showing general base behavior in its reaction with amines. The fit and slope of the Brønsted plot are of interest. The apparent fit to a Brønsted plot of amines of widely varying structure is likely fortuitous. The magnitude of the Brønsted slope, ca. 0.215, is consistent with a general base mechanism. It has been shown that toward the same or similar neutral substrates a nucleophilic mechanism yields a higher value of the Brønsted slope than a general base path [41]. The reaction of hydroxide ion and water with substrate produce 3,5,6 trichloro 2-pyridinol, which is stable under reaction conditions. The reaction of water becomes important below pH ca. 9. Our data below pH 9 are limited and subject to error in intercept estimation in plots of the form k_{obs} v/s general base or nucleophilic concentration. However, it appears that the reaction of water involves general base catalysis by a second (or more) water molecule(s).

The data in this investigation are consistent with concerted reaction at the phosphorus center, i.e., for water attack catalyzed by amines, for the water reaction catalyzed by water, and for $SN^2(P)$ bimolecular reaction of nucleophiles. No direct evidence has been obtained to indicate the existence of a pentacoordinate intermediate though it cannot be excluded. Jencks [5] has pointed out for displacement at

tetrahedral carbon that an asymmetric transition state can be involved rather than a tetrahedral intermediate in some cases. This would mean that "tetrahedral intermediate could be close to a transition state rather than a discrete intermediate" [41]. That reaction coordinates for displacements at phosphorus (or carbon) may represent a continuum depending on substrate and nucleophile. This continuum can range from the pure $SN^2(P)$ case (or the concerted trimolecular general base case), to an asymmetric transition state, to a stable pentacoordinate intermediate. One can speculate that a sterically crowded substrate would favor the asymmetric transition state rather than a pentacoordinate intermediate if a pure $SN^2(P)$ case does not obtain. Therefore, the rate determining step and mechanism for the catalytic hydrolysis reactions has been proposed.



Where, $R = CH_3$ Or C_2H_5 and $X = S$ Or O

The work had been done in keeping view following aims.

- To distinguish the reaction of amines towards proposed compounds is via nucleophilic or general base mechanism.
- To examine the relation of alkali medium and acidic medium with Brønsted correlation.
- To examine effect of pH , catalysis concentration and temperature, And the future scope of this work is determine the catalytic activity of amines towards the chloropyrifos.

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