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A Review: General Base Catalysis Hydrolysis of Organophosphorus Insectisides by Different Amines

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Abstract: ***Esters of pentavalent phosphorus acids are the most important class of organophosphorus (OP) compounds. They are derivatives of the following three parent acids, viz. phosphinic acid, phosphonic acid and phosphoric acid. Phosphorus compounds may be classified as anhydride, aliphatic, aromatic, and heterocyclic. The majority of OP insecticides are derivatives of phosphoric acid. Triesters of phosphoric acid (phosphates) are considered the prototype of the entire family of OP compounds, in which phosphorous is surrounded by 4 atoms of oxygen. Phosphorothionates (parathion, methyl parathion, diazinon, chlorpyrifos) and phosphorothioates contain a P=S bond. Cationic polyelectrolytes have also been employed for the substrate, which accelerate the hydrolysis. The reactivity of nucleophilic reagents (amines) towards the chlorpyrifos suggested that the reaction proceeds via both nucleophilic and general base catalysis. When substrate is catalysis by amines like ammonia, hydrazine and ethanolamine, etc. suggests that amines also react via nucleophilic attack at phosphorus to catalyze substrate. Nucleophilic cleavage of chlorpyrifos has been reported in the presence of hydroximate nucleophiles to release 3,5,6 trichloro 2-pyridinol with second order rate constants. Various amines like ethanolamine, hydrazine, imidazole, n-butylamine and ammonia etc. have been reported to catalyze chlorpyrifos via general base catalysis, in contrast to phosphonate diesters which undergo nucleophilic catalysis by amines. The hydrolytic study of substrate was performed in the presence of amine catalyst, at the temperature of 80^oC. The concentration of substrates and amine catalyst in all kinetic runs unless otherwise specified. All the measurement was done on the LC-20AD (ULFA Prominence Liquid Chromatography (Shimadzu) equipped with a UV/Vis detector (HPLC). The Kinetics was found to be of first order with respect to substrate concentration in both the free amine as well as in amine catalyzed reactions. In this study we found that amines catalysis reaction more efficiently at mild acidic regions and ammonia is better catalyst than the other amines. These results are quite encouraging for using ammonia as a powerful decontaminating agent for phosphorothinate ester pesticides at around neutral to slightly acidic pH range i.e. by water from any available source.***

Keywords: Organophosphorus insecticides, Chlorpyrifos, General base catalysis hydrolysis, HPLC, ammonia, ethanolamine, imidazole, n-butylamine

1. Introduction

Phosphorus is placed on the second row of group V elements in the periodic table. The electronic configuration of the neutral phosphorus atom is denoted as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$. This means that the phosphorus atom has 5 valence electrons in the M- shell; 1 electron pair in the 3-s orbital and 3 electrons in the 3-p orbitals. The activation energy to promote electrons from 3s to 3p and 3p to 3d is relatively low, 7.5 and 9eV respectively [52]. Therefore, in phosphorus compounds the d- orbital can be used much more easily for binding hybrid orbitals. The compounds of trivalent phosphorus exihibit the pyramidal symmetry consisting of sp^3–hybridization and a certain degree of sp^3 character [35]. Phosphine PH_3 may be regarded as the parent compound of trivalent phosphorus compounds. There are many organic phosphines derived by the replacement of the hydrogen with various alkyl and aryl groups. Pentavalent phosphorus compounds may be divided into two classes based on the number of σ-bonds connected to phosphorus. All the naturally occurring phosphorus compounds have a characteristic “phosphoryl” bond P=O or P-O. Esters of pentavalent phosphorus acid are the most important class of organophosphorus compounds. They are derivatives of the following three parent acids, viz., phosphinic acid, phosphonic acid and phosphoric acid. The majority of Organophosphorus insecticides [33],[21],[50],[39],[4],[47] is derivatives of phosphoric acids. Triesters of phosphoric acid (phosphates) are considered the prototype of the entire family of OP compounds, in which all 4 atoms surrounding the phosphorus are oxygen. Sulfur containing OP compounds also exist. Phosphorothionates (parathion, diazinon, chlorpyrifos.) and phosphorothioates contain a P=S bond. The phosphorothionothiolates (e.g. phosphorodithioates) constitute a subclass, where one S atom is a P=S, and the other is a thioester. Thioesters can be linked to an alkyl substituent, or the leaving group can be attached via S atom (e.g., Malathion, dimethoate). Phosphoramides constitute another class of OP compounds, where amides are formed instead of esters. Todayseven phosphoamides are being used as insecticides, out of them, there are three phosphoramidates (fenamiphos, phospholan and mephospholan), two are phosphoramidothionates (propetamphos and isofenphos) and two are phosphoramidothiolates (metamidophos, acephate). OP compounds that have one substituent attached by a phosphorus-carbon bond are classified as phosphonates (e.g., trichlorfon), phosphonothionothiolates (fonophos) and phosphonothionates.

Organophosphates are widely employed both in natural and synthetic applications because of the ease with which organic groups can be linked together. Organophosphorus compounds play a central role in life processes [54] in living growth development and maintenance of all plants [23] and animals [63].They are also used as defoliants [8], cancer chemotherapeutic agents [31], antitumor agents [27] and also is the treatment of glaucoma [9],[59]. Organophosphate pesticides as well as sarin [20] and VX nerve agents irreversibly inactive acetylcholinesterase (AChE), which are essential to nerve function in insects, humans and many others animals. For instance, parathion, one of the first commercialized organophosphate, is many times more potent than malathion. Malathion is an insecticide used in combating the Mediterranean fruit fly. Some organophosphate esters cause delayed neuropathy termed as “Organophosphorus ester induced delayed neurotoxicity” (OPIDN) [46],[60]. Delayed neuropathy is initiated by attack on a nervous tissue esterase distinct from Ache. The target has esterase activity and is called neuropathy target esterase [formerly neurotoxic esterase (NTE)] [45].

The nucleophilicity of many organophosphorus forms lends itself readily to electron transfer reactions. It is no surprise that organophosphorus compounds are also key components in terrestrial life. They mainly acts as an energy carrier or transfer point (i.e. ATP), but also forms important cellular lipid structure and function. They provide the basic bone structure in vertebrates, and serve an important nerve function in animals and insects in the form of phosphates. However, the toxicological properties of many current and previous organophosphorus pesticide formulations have shown mammalian effect. This has given rise to numerous investigations intended to understand pesticide fate [62],[10],[55],[36],[3],[58],[43]. The biological action of organophosphorus pesticides targets the central nervous system of insects, arachnids, and invertebrates which have an acetylcholinesterase-based nerve response mechanism. In mammals, this mechanism involves the irreversible binding of organophosphorus to receptor sites in acetylcholinesterase and inhibits hydrolysis of acetylcholine. Acetylcholine chemically transmits sodium and potassium ion charge across the synapse that initiates nerve impulse. If acetylcholinesterase is neutralized, then acetylcholine maintains a charge potential on the postsynaptic side of the neural transmitting membrane forcing permanent nerve stimulation. The potency of an organophosphorus compound can be qualitatively estimated by its ability and rate to hydrolyze, phosphorylate with an enzyme, or undergo detoxification. These changes depend on the physio-chemical properties of the organophosphorus formulation. Consequently, formulations developed early on in organophosphorus pesticide chemistry had both acute insect and mammalian toxicities mainly due to the fact that they had excellent phosphorylating properties. Later attention given to differences inherent in mammalian physiology exploited formulations that had reduced phosphorylating activity, but that were readily hydrolytically detoxified [15].

2. Insectcides Chemistry

Organophosphate insecticides are usually esters, amides, or thiol derivatives of phosphoric acids or phosphonic acids, general formula is as follows: fig 1 is showing general formula.

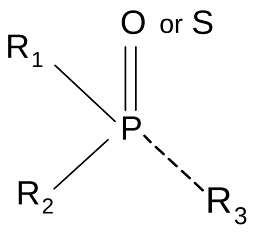
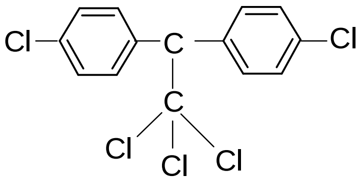


Figure 1

In fig 1. R_1 and R_2 are usually simple alkyl or aryl groups. Group “X”, referred to as the “leaving group” may be one of a wide variety of substituted or branched aliphatic, aromatic or heterocyclic groups linked to phosphorus via a bond of some liability, usually -O- or -S- . The double bonded atom may be O or S and the related compound termed as a phosphate or phosphorothioate. The P=S from is intrinsically more stable and many insecticides are manufactured in this form, which may be converted subsequently in vivo to the biologically active oxon. Insecticides are the dominant group of pesticides used in most rice growing countries like India [37]. In this the categories are as follows:

2.1. Organochlorines

The Organochlorines are insecticides that contain carbon (thus organo-) hydrogen, and chlorine. They are also known by other names: Chlorinated hydrocarbons, chlorinated organic, chlorinated insecticides; the oldest group of the organochlorines is the diphenyl aliphatics, which induced DDT, dicofol, etc. DDT (dichloro-diphenyl-trichloroethane, fig.2) is probably the best known and most notorious chemical of the 20th century.



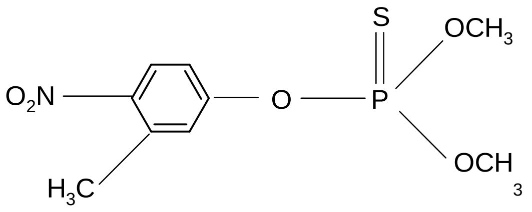
Dichloro-diphenyl-trichloroethane

Figure 2

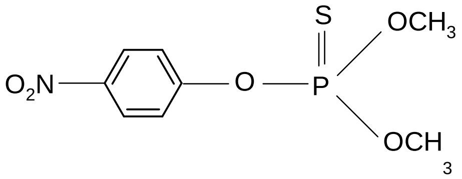
It is used in the control of malaria, yellow fever and many other insectivore disease.

2.2 Organic phosphate or Organophosphate

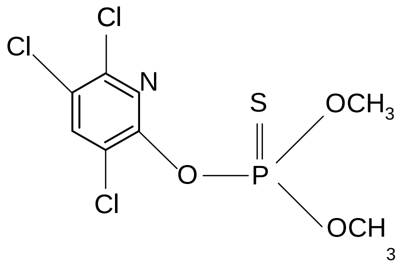
All organophosphates are derived from one of the phosphorus acids, and generally this class is the most toxic pesticide to vertebrates. Schrader and co-workers prepared the first organophosphours pesticides, O,O-diethyl-O-(4-nitrophenyl)thiophosphate, more commonly known as parathion [29].



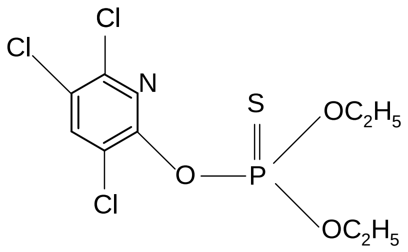
Fenitrothion



Methyl parathion



Methyl Chloropyrifos

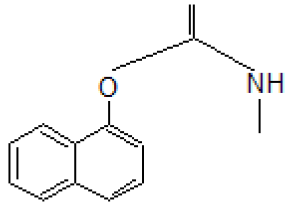


Chloropyrifos

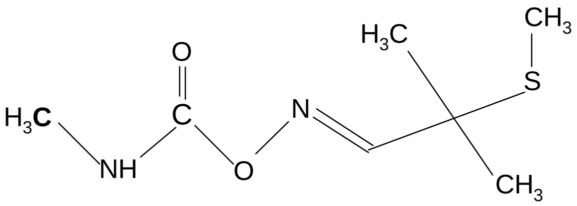
Figure 3

2.3 Carbamates

The Carbamate insecticides are derivatives of carbamic acid (as the Organophosphate are derivatives of phosphoric acid), NH_2COOH, an unstable Compound with $R^1 = R^2 = R^3 = H$.



A



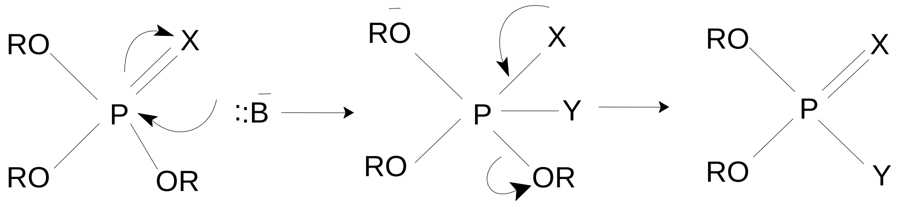
B

Figure 4

Carbamic acid is an unstable compound because of the labiaility of the H-groups, leading upon exposure to water to rearrangements that lead to the decomposition of ammonium bicarbonate. The first successful Carbamate insecticide, carbaryl was introduced in 1956.

2. Hydrolysis of Organophophates

The reaction of hydrolysis of OP compounds is similar to that of phosphorylation, in which attacking nucleophile $(:B^-)$ is water (H_2O) or hydroxide ion (OH^-). The hydrolysis of OP compounds follows several patterns, depending upon type of ester, the solvent, the *p*H range or upon the catalytically active additives.



Scheme 1

A qualitative knowledge of various grades of reactivity, in relation to structure, facilitates the synthesis of products with practical applications, to study the rate of degradation, in monitoring toxicological effect on plants and animals etc. The hydrolysis of OP insecticides and their metabolites are of great importance, because the hydrolysis results in detoxication of pesticides and their susceptibility to alkaline hydrolysis relates to their biological activity. Moreover, variety of derivatives of phosphoric and phosphonic esters were synthesized and their biological properties- such as pesticidal, fungicidal and medicinal properties were discovered. Apart from this, a few of them were found to be highly toxic and were selected for being used for defense purposes. The information about their stability in aqueous media as well as during storage, was an utmost important task for the phosphorus chemist, and in this connection, efforts were made on studies of kinetics and mechanism of these compounds under different conditions. The reaction between a phosphate ester (A) and water, base or acid (B) obeys second order kinetics as:

$$A + B \longrightarrow C \text{ (products)}$$

The rate equation may be represented as in Equation-1

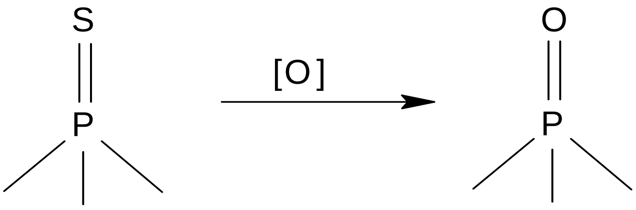
$$dx / dt = k_2 (a\text{-}x) (b\text{-}x) \text{ --------------- } (1)$$

where a & b are the initial concentration of reactants A & B and x is the decrease in concentration after time t, in conditions where one reactant B is in large excess, or where its concentration is held constant, the reaction may be regarded as pseudo-first order reaction and the equation reduces to

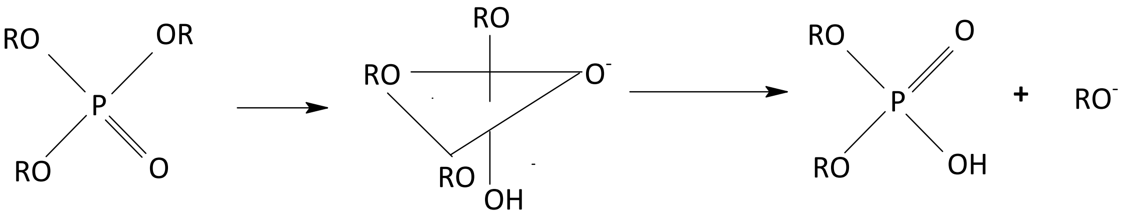
$$dx / dt = k_1 (a\text{-}x) \text{ --------------- } (2)$$

Where, k_1 is pseudo-first order rate constant. Often rate is dependent upon the chemical structure and reaction conditions such as *p*H, temperature, the kind of solvent used, and the existence of catalytic agents. In aqueous solutions, many organophosphorus pesticides are most stable between *p*H 1 to 5 [24]. In this range, the variation in *p*H of the medium has practically no effect on the hydrolysis rate. The organophosphates are much more unstable under alkaline conditions. The hydrolysis rates increase steeply at *p*H higher than 7. Since, the hydrolysis is primarily catalyzed by the hydroxide ion under alkaline conditions; the hydrolysis rates increase almost 10 fold with each additional *p*H unit [25]. The effect of temperature is also an important parameter. The average temperature quotient (k_{30}°C / k_{20}°C) of hydrolysis rates of 21 phosphate esters is about 3.75 [24], *i.e.*, the hydrolysis rates increase about 4 times by the temperature raise of each 10°C.

Kinetics and Mechanism: Earlier, phosphate ester hydrolysis mechanisms have been characterized as S_N1 or S_N2. It is interesting to note that the mechanism, which involves concerted entry and departure of reagent and hydrolysis product at a tetrahedral atom, is not expected mechanism at phosphoryl centre. However, bimolecular P-O hydrolysis reactions are not S_N2, but instead, involve a more stable pentacoordinated T.S. as shown in Scheme-2.



Scheme-2



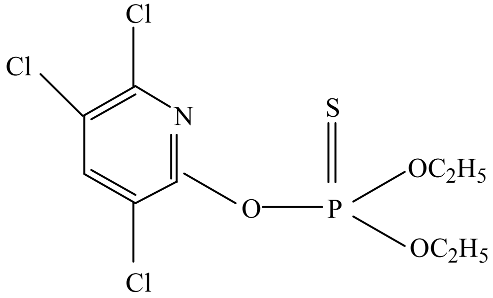
Scheme 3

Thus, it was hypothesized that all hydrolysis at phosphate tetrahedral occurs by two types of mechanisms: (1) S_N1 and (2) pentacoordinated. It is also possible that S_N2 mechanism is also present under certain conditions. The key evidence for occurrence of bimolecular hydrolysis at phosphorus through pentacoordinated T.S. is that, strained five membered ring of ethylene phosphate enormously increases not only the rate of ring opening but also the rate of oxygen exchange with the solvent at the phosphoryl oxygen and the rate of methoxyl loss from methyl ethylene phosphate. For an S_N1 or S_N2 mechanism, the ring strain influence only the rate of ring opening. In a pentacoordinated T.S. the ring strain is relieved, and the oxygen exchange and methoxyl elimination reactions are facilitated via pseudorotation. The mechanism is discussed in detail in above. The transition state is presumed to have a trigonal bipyramidal configuration having sp^3d hybrid orbital's of the phosphorus.

All hydrolysis at phosphorus tetrahedron found to be first order with respect to the reactant. For a given species, the rate expression determined in very dilute solutions and at a given *p*H, is either genuinely first order or a pseudo first order. Molecularity of the reaction is determined generally by entropy of activation ($S^{\neq}$). Small values of $S^{\neq}$, near to zero, indicate unimolecular reactions, while larger negative values *e.g.* -15 to -30 e.u. or greater (entropy units) shows bimolecular reactions [40],[12],[57]. Changes in the hydrolysis rates with *p*H have generally been attributed to changing degrees of protonation of the phosphate tetrahedral. Linear free energy relationships (slope of plots between log *k* versus *p*Ka of the leaving group) are being used for showing relative importance of the leaving group in determining rate. Metal salts reportedly increase the rates significantly above *p*H 4 [42],[17]. The metal cations increase electrophilic character of phosphorus atom, there by facilitating attack of nucleophile [13]. The point of cleavage is an important parameter for establishing a mechanism. Generally the cleavage will be either C-O or P-O, depends on the pH and nature of substituent.

3.CHlORPYRIFOS

Chloropyrifos, a model compound representative of the organophosphorothioate insecticides, was first introduced and patented by Dow chemical company in 1965 [61]. It is produced by the reaction of 3,5,6–trichloro-2-pyridinol (TCP) with O,O-diethyl phosphorochlorodithioate. It is used to control chewing and sucking insects in wide range of crops including cereals, fruits, vines, vegetables, ornamentals. It is a broadly active insecticide, effective by ingestion and contact, being absorbed through skin, gut and pulmonary membranes. It has no systemic action and in insecticidal concentration is nonphytotoxic[16]. Chloropyrifos acts by phosphorylating acetylcholinesterase 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.

Chloropyrifos 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]. Chloropyrifos has a half life in water of 90days, and 200 days in soil [56]. When large concentrations of chloropyrifos 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 chloropyrifos has been studied using various kinetic parameters.

3.3 Hydrolysis of chloropyrifos

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 H_2O at the phosphorus atom which is a "hard" electrophilic site, and attack by H_2O 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 chloropyrifos 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 $C_3H_4N_2$. Imidazole is a heterocyclic aromatic organic compound [22]. This ring system is present in important biological building blocks such as histidine and histamine [64]. Idazoles 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 NH_3 [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 N_2H_4. 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 $CH_3CH_2CH_2CH_2NH_2$. 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 slop 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 *p*H. 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 slop 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.

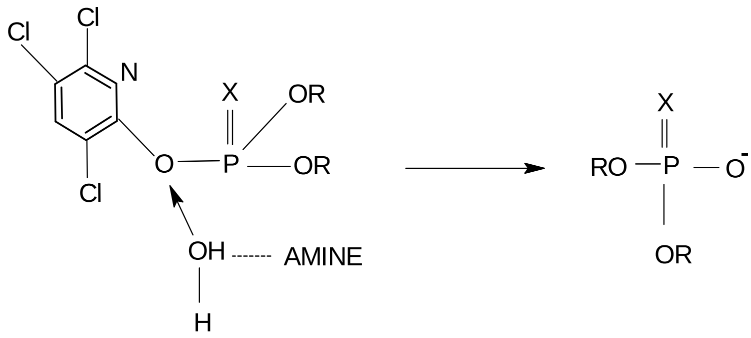
8. Effect of Substrate Concentration

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 chlorpyrifos 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 *p*H ca. 9. Our data below *p*H 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 nucleophilies. 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 trimoleculer 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 *p*H, 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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