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Development of high performance liquid chromatography Method for the hydrolysis of chloropyrifos with different Amines

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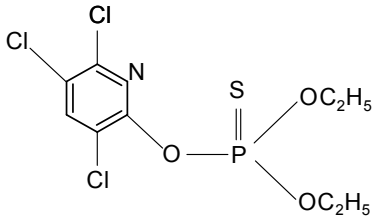
Abstract: High-performance liquid chromatographic methods were developed for the effect of amines on the hydrolysis of chloropyrifos [O,O-diethyl (O-3,5,6-trichloropyrid-2-yl) phosphorothioate] have been studied in different pH medium. The hydrolysis study was monitored measuring phenolate product appear and the substrate disappear during the hydrolysis reaction.
Key words: High performance liquid chromatography, hydrolysis of chloropyrifos with different Amines.

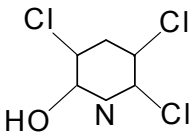
INTRODUCTION

Organophosphorus compounds are play a central role in life processes[1] in living growth development and maintenance of all plants[2] and animals[3]. Organophosphates are widely employed both in natural and synthetic applications because of the ease with which organic groups can be linked together. These compounds are also used in agriculture and household applications as pesticides.

Chlorpyrifos O,O-diethyl (O-3,5,6- trichloropyrid-2-yl) phosphorothioate is a crystalline organophosphate insecticide that inhibits acetylcholinesterase and is used to control insect pest. It is formed by the reaction of 3,5,6-trichloropyridin-2-ol with O, O-diethyl phosphorochlorothioate.



Chloropyrifos

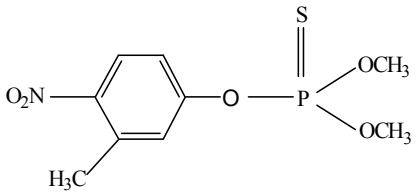


3,5,6-trichloropyrid-2-yl.

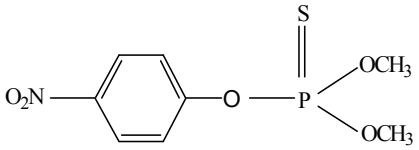
Fig - 1

The crops with the most intense chloropyrifos use are cotton almond corn. Chloropyrifos is readily soluble in acetone, benzene, chloroform and methanol and slightly soluble in water. It is highly toxic to mammals; the oral LD_{50} in rats being 2.9mg/kg.

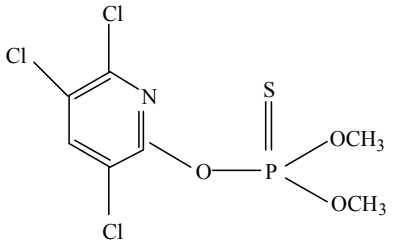
These pesticides are toxic to human but do not remain in the environment for long periods of time especially in comparison to organochlorine pesticides. Schrader and co-workers prepared the first organophosphorus pesticides O,O-diethyl-O-(4-nitrophenyl) thio phosphate, more commonly known as parathion[4,5]. In the 1970's and 1980's the use of organophosphorus pesticides accelerated to the point that over 200 organophosphorus pesticides were marked worldwide[5]. An array of organophosphorus compounds is shown in figure 2, paying particular attention to those previously studied with regards to degradation processes including chloropyrifos and some chlorinated compounds. It is interesting to note the similarity in the structure but also the distinct differences such as the availability and location of Lewis base sites.



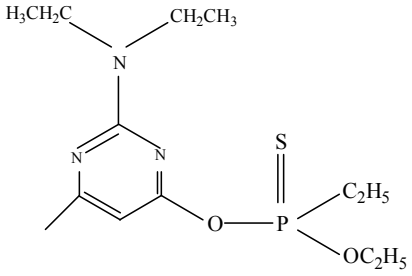
Fenitrothion



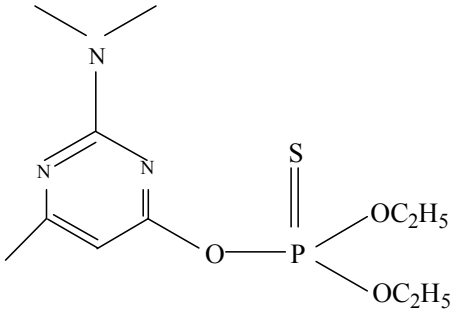
Methyl parathion



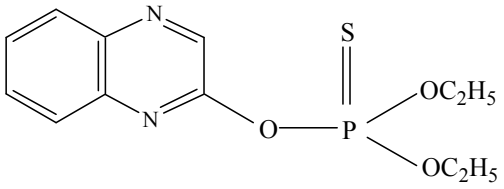
Chlorpyrifos- Methyl



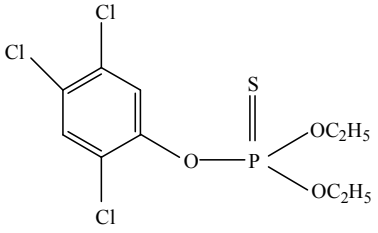
Primos methyl



Diazinon



Quinalphos



Ronnel

Fig - 2

MATERIALS AND METHODS

EXPERIMENTAL

The hydrolysis of chloropyrifos in the presence of amines such as n-butyl amine[6], Imidazole[7], hydrazine[8], ammonia[9], and ethanolamine[10] was examined. Commercial grade chloropyrifos was obtained from India Pesticides Ltd. and were of (> 98% pure) technical grade and its degradation product was supplied by Aldrich (Sigma-Aldrich chemie, Germany). KCL was used AR grade and was obtained from Central drug house (P) Ltd. Mumbai.

HPLC ANALYSIS

Chloropyrifos were analyzed[11-13] using an LC-20AD (ULFA Prominence Liquid Chromatography (Shimadzu) equipped with a UV/V is a detector (at 280nm)). Analysis were chromatographed with a pre-mixed mobile phase comprised of 50% acetonitrile/ 45% water/ 5% 1mM acetic acid (pH 4.30) at room temperature.

Method: Injection of 20µl at a flow rate of 2ml/min for 15 minute. Retention time of chloropyrifos 5.6 min and its degradation product 3,5,6-trichloro-2-pyridinol is 2.0 min.

RESULTS AND DISCUSSION

The results of the investigation of kinetics and hydrolysis of chloropyrifos catalyzed with n-butylamine, Imidazole, hydrazine, ammonia, and ethanolamine. Reactions of chloropyrifos with amines proceed exclusively by general base pathway[14].

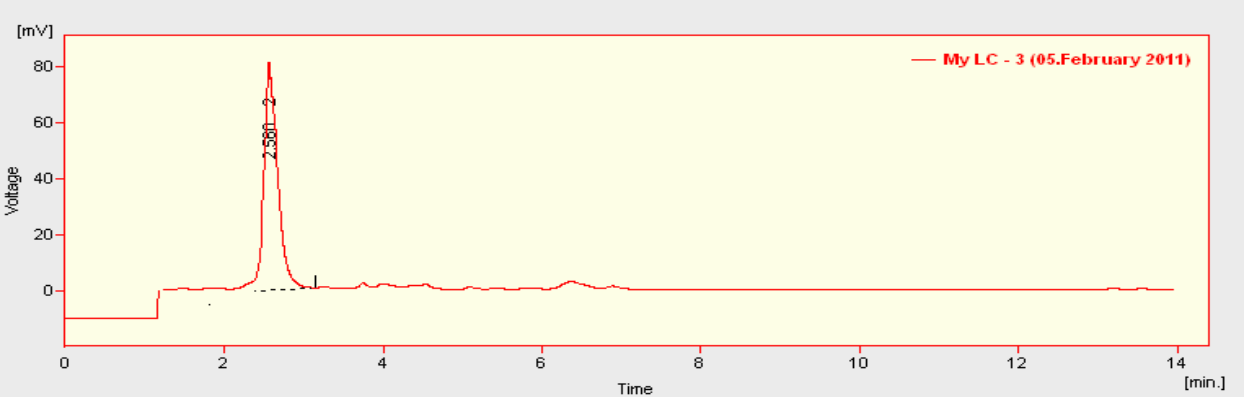
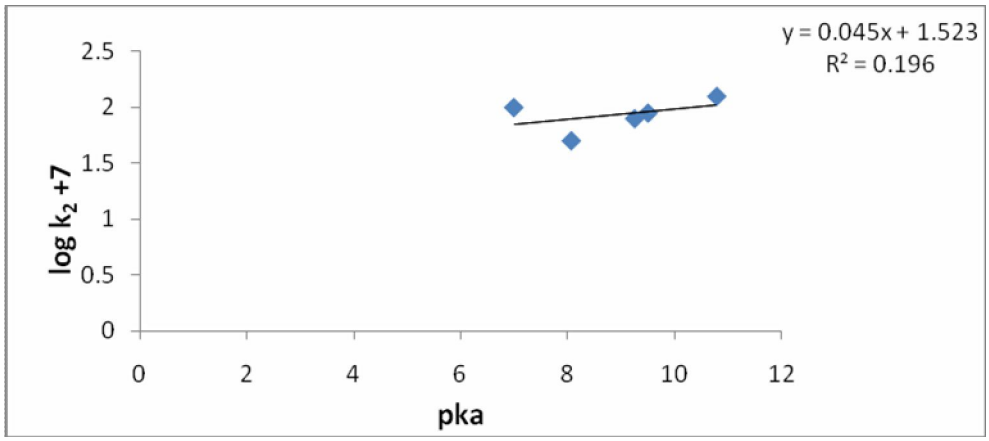


Fig - 3

3.3 Table - BrØnsted plot for the general base-catalyzed reaction of amines with chloropyrifos at 80ºC.

Amine	pK_a	log k_2+7
n- Butylamine	10.78	2.1
Ethanol amine	9.50	1.95
Ammonia	9.25	1.9
Hydrazine	8.07	1.7
Imidazole	7.00	2



BrØnsted plot for the general base-catalyzed reactions of amines with chloropyrifos at 80ºC.

CONCLUSION

HPLC methods were developed for the separation of the chloropyrifos amines catalysis reaction more efficiently at mild pH regions. Ammonia is better catalyst than other Amines. These results are quite encouraging for using ammonia as a powerful decontaminating agent for phosphorothionate ester pesticides at around neutral to slightly acidic pH range i.e. by water from any available source.

REFERENCES:

1. Clayton,R.K.,"Photosynthesis:Physical mechanism and Chemical patterns".Cambridge U.Jniversity Press(1980).
2. Nestler,E.J. and Greengard "Protein Phosphorylation in the Nervous system", Wiley New York (1983).
3. Tonaka,Y., Kano,S. and Odawara,K., Nipponsoda Co.Ltd., D.O.S. 2.416.178 (1974).
4. Plimmer J r, Kreiger R, Handbook of pesticides toxicity, Acedamic Press, London, 2 (2001) 2nd edithion.
5. Kim M, Picot A & Gabbaï F P, Inorg Chem, 45 (2006) 5600.
6. Brown, E.G. Ring Nitrogen and Key Biomolecules. Kluwer Academic Press, (1998).
7. Hall, H.K., J. Am. Chem. Soc., 1957, 79, 5441.
8. Pradyot Patnaik. Handbook of Inorganic Chemicals. McGraw-Hill, 2002.
9. Toy A D F & Beck T M, J Am Chem Soc, 72 (1950) 3191.
10. Batra B S & Purnanand, Indian J Chem, 40 B (1991) 57.
11. Ott R & Krämer R, Angew Chem, Int Ed Eng, 37 (1998)1529.
12. Richard E M, Thomas M P,Theresa A B, and John J J,J Liquidchromatography & Related Technology, 29 (2006) 339-348.
13. Hendry P & Sargeson A M, Prog Inorg Chem, 38 (1990) 201.
14. Green A J , Sainsbury G L , Saville B & Stansfield M, J Chem Soc, (1958) 1583.

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