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Spectroscopic Methods for the Detection of Organophosphate Pesticides –A Preview

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ABSTRACT

Organophosphate pesticides are the ester forms of phosphoric acid usually considered as secure for agriculture uses due to their relatively fast degradation rates. Organophosphorus pesticides have been extensively used in the area of agriculture to manage insect or pests of a number of economically important crops. Organophosphate pesticides are well-known as the inhibitor of acetylcholinesterase activity, not in insects only, but can also affect the nervous system of other organisms as well as humans. Organophosphorus pesticides are not restricted to anticholinesterase action, but comprise genotoxicity and teratogenicity including other environmental and ecological adverse impact. Such severe health and ecological consequences signify a requirement for a better understanding of the fate of organophosphates in the environment. By kept all these things in mind we have written a review on organophosphorus pesticides. In this review we have previewed the different methods of spectroscopic methods of detection including UV-visible, X-ray, Mass analysis, NMR, electrochemical analysis (sensor based) and FTIR. Among all these mass and electrochemical studies were flourished till date and considered as advanced techniques for the analysis of other pesticides also.

Key words: Organophosphate Pesticides, UV-visible, X-ray, Mass analysis, NMR, electrochemical and FTIR.

INTRODUCTION

Organophosphate pesticides (OPs) are the ester forms of phosphoric acid usually considered as secure for agriculture uses due to their relatively fast degradation rates.[1] Although the degradation of OPs is a linear function of microbial composition, pH, temperature, structural arrangement etc. OPs inhibit acetylcholinesterase (AChE) activity not only in insects only, but can also affect the nervous system of other organisms as well as humans.[1-3] Literature data illustrated the OPs persistence in soils years after their application.[4] But the reason behind this environmental persistence is not very clear. Pesticides has been transferred to humans through the food chain[4,7-9] and number of environmental[4-6] and health[10-14] issues have aroused the public concern during last few years. By kept all these views in mind we are going to carve a review on OPs, divided into following parts.

Structural Properties of OPs

Organophosphate pesticides derived from phosphorus analog PH_3 having phosphorus as a core nuclei involved in oxidation states III and V. Basically organophosphate is the general name for esters of phosphoric acid. Hydrolyzed derivatives of phosphorus formal incorporation of additional oxygen atoms gives phosphinic acid ($O=PH_2OH$) and phosphonic (phosphorus) acid [$O=PH(OH)_2$]. Notably, these species may tautomerize between P(V) and P(III), that is, $H_2P(O)OH$ to $HP(OH)_2$. Also a tetrahedral structure [$O=PH(OH)_2$] is more

established than its isomer phosphonic acid, $P(OH)_3$. This form can be stabilized by coordination with some metals.[16]

Methods of Detection of OPs

The combination of FTIR, NMR and Mass data is often sufficient to determine completely the structure of an unknown molecule. There has been a longstanding interest, first among inorganic chemists, about how organophosphates bind to metals, and next by analytical chemists, about how an adequate detection device can be engineered. Ligand optimization and reporting media continue to be explored in OPs detection efforts that involve various spectroscopic techniques such as UV-Visible, FTIR, Mass and NMR spectroscopy.

UV- Visible Spectroscopy

In the field of pesticides UV-Vis. Spectroscopy play the vital role in the detection and interaction of metal ions with organic ligands i.e. pesticides, especially with transition metal ions. P=O can obscure absorbance. Agents themselves are not significant absorbers or emitters in the UV-Vis spectral region[17] unless they are specifically modified with a fluorescent coumarin-type leaving group.[18] With the inclusion of a photoabsorber material, such as a porphyrin, photocatalytic degradation of acephate and monocrotophos in the presence of TiO_2 indicated that the decomposition of acephate begin from the destruction of C-N and P-N bonds.[19-23] The $ZnFe_2O_4$-TiO_2 composite photocatalyst is prepared by sol-gel method and used to degrade acephate successfully.[24] Cu(II)-Glyphosate complex was studied in tea at pH 5 at absorbance 250 nm.[25] A UV-Visible based study to detection of monocrotophos at 490 nm included the effect of temperature and different regent *viz*. 2, 4, dinitrophenylhydrazine and NaOH at different pH level.[26] The photolysis of phorate has been studied as a thin film on a glass surface and in a solution of methanol water (60:40) by ultraviolet light ($\lambda > 290$ nm). The rate of disappearance of phorate in the solution show first order kinetics with a rate constant of 4.9×10^{-5} s^{-1}.[27] Metal complexes of Fe(III), Al(III), Co(II) and Zn(II) studied by using UV-Spectrophotometer, it observed that the complexes of methylphosphonic acid, formed the M-$(CH_3PO_3)_3 \cdot 3H_2O$, and aminomethylphosphonic acid, formed the M-OH$(NH_3CH_2PO_3)_2 \cdot H_2O$. Also complexes of *N*-phosphonomethylglycine were prepared and the formula was M-OH(–OOC–CH_2–NH_2^+–CH_2–PO_3^{2-})$\cdot 2.25H_2O$ is proposed. UV-Vis. study indicating that the complexes form by the chelation of P=O and N-H bonds by consuming two ligands and two water molecules.[28]

FTIR Spectroscopy

IR spectroscopy is indispensible for many systems mentioned herein; direct access to monitoring the phosphoryl stretch is very useful. Electron-poor ions such as Fe(III) and Cu(II) favor stronger coordination and give [P=O] stretching frequencies concomitantly lower by 30-100 cm^{-1}. Some other functionality, such as perchlorate Cl-O stretches, can obscure P=O absorbance. In OPs from literature following main stretching and bending frequencies observed in different solvents.[29,30] OPs having the thio as well as amino salts, for the thio group ν(S-H) and ν(C-S) observed at 2550 and 730 cm^{-1}. Ammonium salts are divided into following parts as per their IR frequencies; these are primary, secondary and tertiary ammonium salts. In all these salts ν(C-N) observed between the region 1380 – 1250 cm^{-1} and ν(N-H) between the 1550 – 1630 cm^{-1}. For the ammonium salt a strong band of ν(N-H) at 1430cm^{-1} also reported in literature. In the FTIR study of copper complexes, for the yellow complex; [$Cu(Ph_3P=O)_2Cl_2$] the ν(P=O) observed at 1142 cm^{-1}. For the dark red complex; [$Cu(Ph_3P=O)_2Br_2$] the ν(P=O) observed at 1145,1169 cm^{-1}. For free $Ph_3P=O$, ν(P=O) is 1195 cm^{-1}. These compounds were found to be *tetrahedral*. The cation moiety Cu(II)-$(Me_3PO)_4$ was *square planar*. Arsenic analogs were yellow-brown ν(P=O) at 840 cm^{-1} and olive green ν(P=O) at 842 cm^{-1}. Perchlorate species were also obtained, but the C=O stretching bands in the IR spectrum obscured the P=O stretches. In MgI_2 complex with diphenylphosphinates; it was found that the PO-C bond, not the P-OC bond, was cleaved.[15] In the interaction of Cu(II) with DIMP the IR frequency of ν(P-O) and ν(P-O…H) observed at 1016 and 1206 cm^{-1}.[31] Metal complexes of Fe(III), Al(III), Co(II) and Zn(II) studied by using FTIR, it observed that the complexes of methylphosphonic acid, formed the M-$(CH_3PO_3)_3 \cdot 3H_2O$, and aminomethylphosphonic acid, formed the M-OH$(NH_3CH_2PO_3)_2 \cdot H_2O$. Also complexes of *N*-phosphonomethylglycine, were prepared and the formula was M-OH(—OOC–CH_2–

NH_2^+–CH_2–PO_3^{2-})·2.25H_2O is proposed. FTIR study indicating that the complexes form by the chelation of P=O and N-H bonds.[28] In the FTIR study of interaction of OPs herbicide glyphosate with Fe(III) in aqueous solution at pH 4, suggests that coordination of Fe(III), or more likely $Fe(OH)^{2+}$ species, occurs through the phosphonic group, glyphosate shows no evidence of coordinating the metal through the carboxylate anion or the amino group; however, significant changes are observed in the range for the phosphonic group vibrations as expected for metal-phosphonate coordination.[32]

NMR Spectroscopy

Nuclear magnetic resonance (NMR) is a spectroscopic method that is even more important to the structure elucidation than other spectroscopic techniques. Many nuclei may be studied by NMR techniques *viz*. ^{13}C, ^{1}H, ^{31}P, ^{15}N, and ^{19}F. Any atomic nucleus that possesses either *odd* mass, *odd* atomic number split in the radiofrequency region. NMR gives information about the number of magnetically distinct atoms of the type being studied.[28] NMR spectroscopy supports many areas of chemistry and science. NMR spectra have found great utility in monitoring reactions and characterizing new compounds and also in detection of OPs and their fragments.[33,34] There are numerous nuclei that can be brought to bear in OPs studies, especially the ^{31}P nucleus. Analytes that contain characteristic ^{13}C, ^{1}H, and ^{31}P, as well as ^{15}N and ^{19}F, NMR signals can be probed.[35] Other NMR active nuclei and related experiments also are found in the literature. The types of experiments have involved HSQC NMR, as well as magic angle spinning.[15] Next, shift reagents can change the phosphorus δ value.[15] One early study involved mixtures of $(Me_2N)_3P=O$, DMMP, or $(MeO)_3P=O$, in the presence of Be^{2+} and Al^{3+} ionic centers and a series of phosphates was treated with Co^{2+} and Fe^{3+}.[36] The species$(MeO)_3P=O$, $(EtO)_3P=O$, and $(MeO)_2P=O(Me)$ were all found to give shifts upon binding; also P-H decoupling was observed. With this technique, changes in P-S bonding can be monitored.[37] Variable-temperature ^{31}P NMR spectroscopy was used in studying resin-based systems with two DMMP adsorption sites, the macro-reticular region and the quaternary ammonium hydroxide ion-exchange sites.[38] It was found that DMMP may migrate from one site to another. There is also a report of lanthanide-induced shifts from authors who have also been active in the organophosphonate sensor area.[39] An NMR spectroscopic assay was also developed to conveniently determine the purity of live agents of OPs derivatives. ^{31}P NMR spectroscopy can also be used in studies that involve enzymes that degrade agents. Studies that successfully determine discrete cleavage events have used ^{31}P.[40] Nuclei other than ^{13}C, ^{1}H, and ^{31}P NMR also occasionally hold prominence. The ^{27}Al, ^{113}Cd, and ^{199}Hg nuclei have been utilized in terms of monitoring the adducts and mineralization.[15] A ^{1}H-NMR study of phorate deals to photodegredation of phorate, indicated the P-S bond destruction.

X-ray Diffraction

X-ray diffraction is among the unswerving techniques to studies and elucidates the intricacies of metal ligand structure and probable binding possibilities that help open up a casement for future sensing possibilities. In study of $[R_3P=O—M^{n+}]$ moieties (R = alkyl, aryl) and (M = any metal), the mean P=O bond length in [P=O—Mn^+] interactions is 1.48 Å and the mean M—O bond length is 2.33 Å.[15] The importance of these structures is that they resemble a deprotonated acid fragment bound through three atoms to one metal center. $(CH_2)_2$ could be thought of as holding the place of [-P=OMe(OR)-]. This motif is pragmatic with respect to a degraded sample in which the (-OR) has been hydrolyzed off. Metal complexes of Fe(III), Al(III), Co(II) and Zn(II) studied by using XRD-Spectrophotometer, it observed that the complexes of methylphosphonic acid formed the M-$(CH_3PO_3)_3$·3H_2O, and aminomethylphosphonic acid, formed the M-OH$(NH_3CH_2PO_3)_2$·H_2O. Also complexes of *N*-phosphonomethylglycine were prepared and the formula was M-OH(-OOC–CH_2–NH_2^+–CH_2–PO_3^{2-})·2.25H_2O is proposed. X - ray study representing that metal ions concerned in octahedral structure.[28]

Electrochemical

Almost all current instrumental techniques that explicitly determine the presence of pesticides are generally exclusive and non-portable, such as FTIR, mass chromatography and NMR spectrophotometer etc. But electrochemical methods are simple, versatile, in terms of controlling

and altering the behavior of redox materials. Transition metal ions here have vulnerable properties. Such equipment is not too bulky and has a portable device, principally in regards to recent lab-on-a-chip research efforts. Reviews in this area mostly deal with biosensing. Organophosphonate electrochemistry with sarin, $(EtO)_2(EtSCH_2\text{-}CH_2S)P=O$, parathion, and malathion. There were reports of a mercury surface with which polaragram data was recorded. Chemical groups point outward and waters are replaced stepwise in a Cu^{2+}-complex by the surface-active compounds $R_3P=O$. In the late 1990s, there are outstanding electrochemistry papers concerning with organophosphorus hydrolase.[41-43] Also, some studies involve the use of phthalocyanines. Thus, this section involves structurally positioned redox active metal ions that do not directly bind with OPs donor atoms. Recently, electronic tongue array, consisting of an eight working electrodes (Au, Pt, Ir, Rh, Cu, Co, Ni, and Ag) was used to detect nerve agent stimulants DCP and DECP in aqueous environments.[44,15]

Mass Spectrometric

The fundamental principles of mass spectroscopy (MS) to determined the mass-to-charge ratio of the molecule by ionizing it by using different procedures. The number of ions with a particular mass-to-charge ratio is plotted as a function of that ratio. The types of MS techniques include MALDI-TOF, GC-MS, ESI, SPAMS, and desorption electrospray. MALDI-TOF and MS-TOF was presented as an effective way of determining widespread emergency events.[40] A detection by MS of species that include $(RO)_2P=O(R_1)$, $(RO)P=O(R_1)F$, $(RO)P=O(R_1)(SR_2)$, and $(R_2N)P=O(OR_1)(CN)$.[44] MS also provides support for some surface-based studies. A study include the development and inter-laboratory verification of LC–MS libraries for organic chemicals of environmental concern, includes the 129 pesticides in which the monocrotophos and phorate having the m/z at 193, 98 and 75. In the study it was observed that more than 90% data was accepted in both modes.[15] The determination of OPs in human blood and water using solid-phase microextraction and gas chromatography with mass (GC-MS) spectrometric detection performed.[45,46] A Multiresidue detection of pesticide in fishery products was conducted by using the tandem solid-phase extraction technique. Study includes more than 50 OPs. Zero recovery was obtained from samples fortified with acephate and monocrotophos and 118.2 and 125.4 % in sample amino-propyl, the maximum label spiked (mg/L) for both is 5.[47] Method validation and comparison of acetonitrile and acetone extraction for the analysis of 169 pesticides in soya grain by liquid chromatography–tandem mass spectrometry.[45-47]

The interesting disulfide derivative [bis (diisopropylaminoethyl) disulfide] was determined from a soil sample (detected at 1 µg per 1.0 g of soil).[15] Secondary ionization (IM-TOF-MS) was used in detecting pinacolyl methylphosphonate, diethyl phosphoramidate, and 2-(butylamino) ethanethiol.[15] Some reports involve the mention of pesticides: malathion was studied with GC-FID.[47] ES-MS was used to support microsynthesis of various O,Odialkyl- N,N-dialkylphosphoramidates to generate a library of mass spectra.[48] Additionally the methyl esters of N,N-dialkylaminoethane- 2-sulfonic acids, $R_2NCH_2CH_2S(O)_2OCH_3$, were analyzed by GC-EI mass spectroscopy.[49] Rapid determination of pesticide residues in Chinese materia medica using QuEChERS sample preparation followed by gas chromatography–mass spectrometry.[50] In a minipig model, plasma was used in studying (iPrO(P=O)Me-(OH)) and cyclohexyl-O(P=O)Me(OH). In another study, albumin was studied; peptide fragments of human serum albumin were analyzed in response to chlorpyrifos oxon, dichlorvos, diisopropylfluorophosphate, and sarin.[50-53] Complexes of Ni, Co, and Fe, were evaluated for the OPs sensing, but Cu^{2+} gave the best response indicating that the ligand had to accommodate enough vacancy. Thus, at this early point it was concluded that "copper complexes may adsorb and desorb phosphorus esters in air."[15]

CONCLUSION

Among the all methods of detections mass and electrochemical based methods are flourished in recent years but there is slow development in FTIR and UV based sensing and detection of OPs which is highlighting a gap in study. Even OPs have the short life time of decomposition but they persist and leach out in soil and environment which is the

matter of huge concern, so there is need to develop the new moieties which minimize all these risks and hazards. For the future safeguard, there is need to development of antidotes for intoxication with neurotoxic is one of the most important task, not only because their potential use as chemical warfare defense agents, but also for the treatment of intoxication with organophosphorus pesticides, which are very intensively used in agriculture. There is the need to develop quicker, cheapest, portable methods for agent and pesticides sensing..

REFERENCES

1. Chambers W. H., Organophosphorus compounds: An overview in Organophosphates Chemistry Fate and Effects, Academic Press, New York, (1961).
2. Racke K. D., Degradation of organophosphorus insecticides in environmental matrices in Organophosphates Chemistry, Academic Press, New York, (1992).
3. Frank M. R., *Nature*, **469**: 310 (2011).
4. Vala-Ragnarsdottir K. J., *Geological Soc.,* **157**: 859 (2000).
5. David T., *Nature*, **396**: 211 (1998).
6. Guo J. H., Liu X. J., Zhang Y., Shen J. L., Han W. X., Zhang W. F., Christie P., Goulding K. W. T. and Zhang F. S., *Science*, **327**: 1008 (2010).
7. Stefan M. W., Violeta T. P., Krysztof N. W. and Jorge N. C., *Rev. Int. Contam. Ambient.*, **13**: 41 (1997).
8. Crentsil K. B., Jacob A., Daniel A. A., Juliana B. and Stephen B. A., *Emir. J. Food Agric.,* **24**: 293 (2012).
9. Md. Alamgir Z. C., Sanjoy B., Borhan U., Mohammed M., Nurul K. and Siew H. G., Int. *J. Environ. Res., Public Health.,* **9**: 3318 (2012).
10. Vandana S., The Violence of the Green Revolution: Third World Agriculture Ecology and Politics, Zed Books Ltd. New Jersey Third World Network, Penang, 72 (1991).
11. Maele-Fabry G. V. and Willems J. L., *Occup. Environ. Med.*, **60**: 634 (2003).
12. Kori B. F., Jane A. H., Charles F. L., Aaron B., Charles K., David L. S. and Dale P. S., *Environ. Health Perspect.,* **112**: 631 (2004).
13. Lee W. J., Lijinsky W., Heineman E. F., Markin R. S., Weisenburger D. D. and Ward M. H., *Occup. Environ. Med.*, **61**: 743 (2004).
14. Jan D., Shelia H. Z., Annika H. and Hans A., *Cancer Causes and Control.*, **8**: 420 (1997).
15. Kibong K., Olga G. T., David A. A. and David G. C., *Chem. Rev.* **111**: 5345 (2011).
16. Sokolov M. N., Virovets A. V., Dybtsev D. N., Chubarova E. V., Fedin V. P. and Fenske D., *Inorg. Chem.*, **40**: 4816 (2001).
17. Timperley C. M., Casey K. E., Notman S., Sellers D. J., Williams N. E., Williams N. H. and Williams G. R., *J. Fluorine Chem.*, **127**: 1554 (2006).
18. Briseno-Roa L., Hill J., Notman S., Sellers D., Smith A. P., Timperley C. M., Wetherell J., Williams N. H., Williams G. R., Fersht A. R. and Griffiths A. D., *J. Med. Chem.*, **49**: 246 (2006).
19. Doong R. and Chang W., *Chemosphere,* **37**: 2563 (1998).
20. Doong R. and Chang W. Photochem. Photobiol. A, 107, 239 (1997).
21. Konstantinou I. K., Sakellarides T. M., Sakkas V. A. and Albanis T. A., *Environ. Sci. Technol.,* **35**: 398 (2001).
22. Young K. and Liang J., *Chemosphere,* **37**: 2589 (1998).
23. Sivagami R., Krishna R. R. and Swaminathan T. J., *Water Sustain.*, **1**: 75 (2011).
24. Fu Weina, Wang Y., He C. and Zhao J., *J. Adv. Oxi. Tech.*, **15**: 1 (2012).
25. Shuji K J., *Health Sci.*, **54**: 602 (2008).
26. Prasanna K. S. and Surendra K. R., *Inter. J. Sci. & Eng. Res.,* 3: 1 (2012).
27. Sharma B. K. and Navindu G., *Toxi. & Envir. Chem.,* **41**: 249 (1994).
28. Barja, B. C. and Santos A. M., *Environ. Sci. Technol.,* **32**: 3331 (1998).
29. Kim C. S., Lad R. J. and Tripp C. P., *Sens. Actuators*, **B76**: 442 (2001).
30. Moss J. A., Szczepankiewicz S. H., Park E. and Hoffmann M. R., *J. Phys. Chem.* B, **109**: 19779 (2005).
31. Rauk A., Shishkov I. F. and Kostyanovsky R.

G., *J. Am. Chem. Soc.*, **117**: 7180 (1995).
32. Koskela H. J., *Chromatogr.* B, **878**: 1365 (2010).
33. He W. Y., Du F. P., Wu Y. and Zhao X. D., *J. Fluorine Chem.*, **127**: 809 (2006).
34. Koskela H., Rapinoja M. L., Kuitunen M. L. and Vanninen P., *Anal. Chem.*, **79**: 9098 (2007).
35. Gab J., Melzer M., Kehe K., Wellert S., Hellweg T. and Blum M. M., *Anal. Bioanal. Chem.,* **396**: 1213 (2010).
36. Kolakowski J. E., DeFrank J. J., Harvey S. P., Szafraniec L. L., Beaudry W. T., Lai K. H. and Wild J., *Biocatal. Biotransform.,* **15**: 297 (1997).
37. Beaudry W. T., Wagner G. W. and Ward J. R., *J. Mol. Catal.*, **73**: 77 (1992).
38. Henderson T. J., *Anal. Chem.,* **74**: 191 (2002).
39. Amitai G., Adani R., Sod-Moriah G., Rabinovitz I., Vincze A., Leader H., Chefetz B., Leibovitz-Persky L., Friesem D. and Hadar Y. *FEBS Lett.*, **438**: 195 (1998).
40. Hartmann T. C., Hu J., Kaganove S. N., Keinath S. E., Keeley D. L. and Dvornic P. R., *Chem. Mater.*, **16**: 5357 (2004).
41. Mulchandani P., Mulchandani A., Kaneva I. and Chen W., *Biosens. Bioelectron.*, **14**: 77 (1999).
42. Mulchandani P., Mulchandani A., Kaneva I. and Chen W., *Anal. Chem.*, **70**: 4140 (1998).
43. Gahlaut A., Gothwal A., Chhillar A. K. and Hooda V., *Open J. Appl. Biosens.,* **1**: 1 (2012).
44. Charlita R., Betowski D., Romano J., Neukom J., Dennis W. and Lawrence Z., Talanta, **79**: 810 (2009).
45. Frank M., Heike J. and Burkhard M., *J. Chromatgr. Sci.*, **40**: 18 (2002).
46. Feei S., Sue S. W., Gwo C. L. and Shiu N. C., *J. Food and Drug Anal.*, **13**: 151 (2005).
47. Noradoun C. E., Mekmaysy C. S., Hutcheson R. M. and Cheng I. F*., Green Chem.*, **7**: 426 (2005).
48. Palit M., Pardasani D., Gupta A. K., Shakya P. and Dubey D. K*., Anal. Bioanal. Chem.*, **381**: 477 (2005).
49. Pardasani D., Gupta A. K., Palit M., Shakya P., Kanaujia P. K., Sekhar K. and Dubey D. K., *Rapid Commun. Mass Spectrom.*, **19**: 3015 (2005).
50. Yichen H., Wan L., Jinming Z., Fang Y. and Jiliang C., *Acta Pharmaceutica Sinica* B, **2**: 286 (2012).
51. Li B., Ricordel I., Schopfer L. M., Baud F., Megarbane B., Nachon F., Masson P. and Lockridge O., *Toxicol. Sci.*, **116**: 23 (2010).
52. Li B., Schopfer L. M., Hinrichs S. H., Masson P. and Lockridge O., *Anal. Biochem.*, **361:** 263 (2007).
53. Grigoryan H., Schopfer L. M., Thompson C. M., Terry A. V., Masson P. and Lockridge O., *Chem-Biol. Interact.*, **175**: 180 (2008).