



ORIGINAL ARTICLE

Metal ion promoted degradation mechanism of chlorpyrifos and phoxim



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Abstract This study evaluate the degradation of the two organophosphorus pesticides: chlorpyrifos and phoxim in the presence of Ag⁺ at fixed initial concentration and temperature. Chlorpyrifos and phoxim were used as model compounds to develop experimental methods for the investigation of kinetic and degradation pathways. In order to determine what metabolites will be formed after degradation we used ³¹P NMR. Chlorpyrifos and phoxim were found to degrade in the presence of Ag⁺ and the result shown in lower chlorpyrifos to Ag⁺ ratio (<8), only one product formed and its concentration increased versus time. Degradation of chlorpyrifos and phoxim in methanolic solution in the presence of Ag⁺ followed first-order exponential decay kinetics, and the half-life (*t*_{1/2}) of chlorpyrifos and phoxim are 693 and 1155, respectively.

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1. Introduction

Organophosphorus pesticides (OPPs) are a large group of highly effective pesticides. The widespread use of OPPs has led to severe environmental pollution because these compounds are often transported from their target sites (Liang et al., 2011). Phoxim and chlorpyrifos which have been widely used to control insects are organophosphate pesticides that kill

insects by inhibiting cholinesterase, an enzyme necessary for nerve function (Health Risk From the Insecticide Phoxim). The persistence of pesticides can generally be termed as its lasting power in the environment. Their persistence in the environment is controlled by a number of different factors, specifically the different routes by which a pesticide can degrade. Some of these often show higher toxicity than the parent compound. Therefore, toxicological evaluation of these decomposed products is important from the viewpoint of their effect on human health (Hirahara et al., 2003). Recent decades have witnessed increases in the levels of contamination of water with toxic organic compounds. Among those highly toxic compounds dissolved in water are pesticides, which, through their extensive use, have become increasingly present in water. Thus pesticides removal from the aquatic environment has become a high priority (Derbalbala et al., 2004). Degradation of organophosphorothioate (OP) compounds occurs by either of the following path-

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ways: hydrolysis (Benoit-Marqui et al., 2004), oxidation (Acero et al., 2000), ultrasonic radiation (Zhang et al., 2011), electrical field (Chen et al., 2009) and photolysis (Menager et al., 2007).

Homogeneous process applies when a nucleophile interacts with the OP compound in solution with or without the presence of dissolved metal ions or other catalysts. Dissolved metal ions are known to play a wide and varied role in enhancing the rate of many significant hydrolysis reactions. A number of studies have shown that dissolved metal ions can play an important role in catalysis of organophosphorus pesticides. In most cases the catalytic enhancement is attributed to metal co-ordination with the substrate. Understanding the degradation of OPPs (such as chlorpyrifos and phoxim) is important for removing this substance assessing its potential risk to non-targets. In this work we investigate the catalytic effect of Ag^+ ions on the hydrolysis of two pesticides chlorpyrifos and phoxim. In addition, the degradation products were identified by ^{31}P NMR technique in order to establish the possible mechanism for degradation.

2. Experimental

2.1. Reagent

HPLC grade methanol was purchased from Merck (Darmstadt, Germany). Methanol- CD_3OD (Cambridge Isotope Laboratories, Inc.) was employed in the ^{31}P NMR studies. Water was distilled and purified by a Direct-Q 3 UV with a pump system (Millipore, Molsheim, France). Silver nitrate (Merck) solution (0.050 M) was prepared by dissolving the weighed amount of AgNO_3 in 3.5 mL of methanol and 1.5 mL of water. Ortho-phosphoric acid as an internal standard was prepared from Merck and standard stock of phosphoric acid (0.2 mol L^{-1}) as an internal standard was obtained by dissolving appropriate amount of phosphoric acid in methanol. Chlorpyrifos and phoxim were prepared from Ehrnestorfer (Augsburg, Germany) and the working solutions (0.05 mol L^{-1}) were prepared in methanol.

2.2. Hydrolysis experiments

In the kinetic studies, fixed volumes of the pesticide (0.200 mL of 0.05 mol L^{-1}), fixed volumes of Ag^+ (0.05 mL of 0.05 mol L^{-1}) and 0.05 mL of internal standards (H_3PO_4) were mixed in NMR tube and used to obtain metal to pesticide mole ratio of 0.25 in NMR tube. In all ^{31}P NMR measurements 20% v/v to final volume of CD_3OD was also added to lock the field frequency of the instrument. Kinetics was followed by ^{31}P NMR and for each treatment samples were analyzed on 0, 1, 2, 3 and 4 h after mixing.

3. Instrumentation

3.1. ^{31}P NMR spectroscopy

All ^1H -decoupled ^{31}P NMR spectra were recorded on a Bruker DRX 500 Avance operating at 202.456 MHz for the phosphorus-31 nucleus with a dedicated 5-mm QNP probe and running XWINNMR2.6 software using 500 μL of samples. The chemical shifts (δ) are reported in parts per million (ppm) with respect to the resonance peak of 85% H_3PO_4 used as an external chem-

ical shift reference. The spectra were acquired using 90° pulses with 16–512 scans collected into 128 k data points over a spectral width. The acquisition time was 0.328 s followed by a 10 s relaxation time delay to ensure full T1 relaxation. The probe temperature was 25°C for quantitative analysis of OP compounds.

NMR processing for final solutions of all samples included phase correction (performed manually for each replicate) and baseline correction over the entire spectral range. In all instances, the baseline was additionally corrected over the integrated regions. Areas of the peaks were determined by electronic integration of expanded regions around diagnostic resonances, using an integral limit of ± 0.5 ppm around the corresponding signals. The T1 measurements of the ^{31}P nuclei were carried out by the inversion-recovery method, using the standard sequence of $180^\circ\text{-F-}90^\circ\text{-D1}$ with a relaxation delay D1 of 10 s and T1 cal Bruker program. It should be noted that, in the process of T1 measurements, the minimal spectral windows required for each analyte were employed.

4. Results and discussion

In our previous work, the degradation of chlorpyrifos and phoxim with Ag^+ led to the formation of *O,O*-diethyl-*O*-methyl phosphorothionate at metal ion/pesticide ratio \leq stoichiometry and completely decomposed at higher ratio. Thus for kinetic investigation, pesticide to ion ratio of 4 or less was selected.

4.1. Degradation kinetics

4.1.1. First-order reactions

A first-order reaction depends on the concentration of only one reactant (a unimolecular reaction). Other reactants can be present, but each will be zero-order. The rate law for an elementary reaction that is first order with respect to a reactant A is:

$$C_t = C_0 e^{-kt}$$

where C_t represents the concentration of the chemical of interest at a particular time, and C_0 represents the initial concentration and k is the first order rate constant, which has units of time^{-1} . The integrated first-order rate law is:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt$$

A plot of $\ln\left(\frac{C_t}{C_0}\right)$ versus time t gives a straight line with a slope of $-k$. The half-life of a reaction describes the time needed for half of the reactant to be depleted (same as the half-life involved in nuclear decay). The half life of a first-order reaction is independent of the starting concentration and is given by:

$$t_{1/2} = \frac{\ln(2)}{k}$$

The degradation of OPPs over time in the presence of Ag^+ was monitored by using ^{31}P NMR. As shown in Fig. 1, chlorpyrifos degraded with increasing of time and resulting new products formation at 25°C . It is important to note that in lower pesticide to Ag^+ ratio (< 8), the product 2 was not formed and only product 1 was formed and its concentration increased versus time.

Chlorpyrifos itself shows a change in the chemical shifts of the phosphorus nuclei with addition of Ag^+ , establishing an

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