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ScienceDirect

Chemosphere 70 (2008) 1653–1659

CHEMOSPHERE

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Decomposition of ^{14}C-fenitrothion under the influence of UV and sunlight under tropical and subtropical conditions

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Received 4 April 2007; received in revised form 25 July 2007; accepted 25 July 2007
Available online 5 September 2007

Abstract

The decomposition of ^{14}C-fenitrothion on silica gel chromatoplates as well as in polar and non polar solvents under sunlight and ultraviolet light was investigated, Its stability to sunlight on leaf surfaces of bean plants and on different surfaces (such as glass, quartz and plastic) was also determined. The main photoproducts were identified as carboxyfenitrothion, fenitrooxon, carboxyfenitrooxon and 3-methyl-4-nitrophenol and a small amount 3-caboxy-4-nitrophenol and methyl parathion. The addition of carbaryl and deltamethrin insecticides slightly accelerated the photodecomposition of fenitrothion on silica gel plates and in solution.

Keywords: Fenitrothion; Photodecomposition; Sun and UV lights; Different surfaces; Different solvents

1. Introduction

Organophosphorus compounds have recently been used as an alternative to organochlorine compounds for pest control. The widespread use of organophosphorus insecticides results in the release of their residues into natural water, thus inducing an environmental problem (Derbalah et al., 2004a).

Fenitrothion, first prepared by Sumitomo Chemical Co. has the structural formula [*O*,*O*-dimethyl-*O*-(3-methyl-4-nitrophenyl) phosphorothioate, I] is marketed under different trade names, e.g., Sumithion, Novathion and Metathion. It is a broad-spectrum organophosphorus insecticide that has been in use since 1959. It is considered to be a common river water pollutant, and its residues in natural water undergo photodegradation, resulting in the release of many toxic metabolites, some being more toxic than the parent compound to aquatic organisms (Eto, 1974; Amoros et al., 2000; Derbalah et al., 2004b).

Fenitrothion is considered somewhat toxic to fish (Thomson, 1989). And it is also employed in agriculture to control insects on rice, cereals, fruits, vegetables, stored grains and cotton. It is applied in public health measures to control flies, mosquitoes and cockroaches (WHO, 1992). It has been also used for the control of stored product insect pests in a number of countries (Snelson, 1987). The insecticide is non-systemic and non-persistent (Spencer, 1981; Hassall, 1990; Briggs and Council, 1992). The acute toxicity of fenitrothion to mammal is considered to be low (Spencer, 1981; Hayes, 1982; Hayes and Laws, 1990).

In Egypt, fenitrothion is used on cotton and other plants. Cotton receives, other than fenitrothion, insecticides such as carbaryl and deltamethrin, so the soil under the plant usually contain a mixture of the used insecticides. Therefore, we found it important to investigate the stability of fenitrothion in presence of carbaryl and deltamethrin in solution.

This paper studies the decomposition of fenitrothion by ultraviolet (UV) and sun light on silica gel surface and on bean foliage and when dissolved in organic solvents and water. Also, the effect of some pesticide chemicals usually used for spraying cotton plants (carbaryl and deltamethrin) on the photodecomposition of fenitrothion and stability of the insecticide fenitrothion on surfaces of glass, quartz and plastic was examined.

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doi:10.1016/j.chemosphere.2007.07.063

The photodecomposition of fenitrothion has been reported by several authors (Durand et al., 1990, 1994; Barcelo et al., 1993; Burrows et al., 2002; Sakellarides et al., 2003; Matsushita et al., 2006). All these studies were carried out in temperate regions. In the present work we studied the photodecomposition under local conditions which are almost tropical (or subtropical), where the temperature reaches 37–41° in summer which is accompanied with a high degree of relative humidity (90–100%).

2. Materials and methods

2.1. Chemicals

^{14}C-methanol was obtained from Amersham International Corporation, United Kingdom. Thiophosphorylchloride was obtained from Fluka AG. All solvents and silica gel used were of chemical grades. (Merck Darmstadt, Germany). Labelled fenitrothion I (Nishizawa et al., 1963) Fenitrooxon II (Kim et al., 2000), 3-methyl-4-nitrophenol III (Akintonwa and Hutson, 1967), carboxyfenitrothion (IV) (Bowden et al., 1946) and carboxyfenitrooxon (V) (Greenhalgh and Marshall, 1976) were synthesized in the laboratory according to the procedures indicated.

2.1.1. Synthesis of fenitrothion (*I*)

^{14}C-fenitrothion labelled at the carbon atoms of the methyl groups was synthesized by a single vesseled reaction that involved the condensation of 0.28 ml (0.007 M) of ^{14}C-methanol in toluene with 0.315 ml (0.003 M) of thiophosphorylchloride in presence of triethylamine 0.81 ml (0.006 M) and the mixture was stirred at 5–10 °C for 30 min. After removal of the separated triethylamine hydrochloride by filtration, the filtrate was evaporated in a vacuum. The obtained (*O*,*O*-dimethylthiophosphoryl chloride) in toluene was allowed to react with 0.58 g (0.003 M) of potassium salt of 3-methyl-4-nitrophenol while stirring for 30 min at room temperature. This mixture was refluxed for 2–3 h at 60–80 °C, cooled, diluted with cold water and the organic layer was separated and dried over anhydrous sodium sulphate. Under reduced pressure the solvent was evaporated to give yellow-brown liquid bp 140–145 °C, 0.1 mmHg). The product was purified by preparative thin layer chromatography (TLC) (Silica gel 60 F_{254} pre-coated plates 20×20 cm; layer thickness 0.5 mm Art. 5744). The prepared ^{14}C-fenitrothion had a specific activity 2.96 MBq (0.08 µci/mg) and a radiometric purity 98% (Nishizawa et al., 1963).

Non-labelled fenitrothion was prepared as described above and its main degradation products were synthesized in our laboratory according to known procedures for comparison purposes (Fig. 1).

2.1.2. Synthesis of fenitrooxon (*II*)

Oxidation of fenitrothion was obtained by mixing fenitrothion solution (2 mM) in acetonitrile with a 10 times excess of bromine solution (20 mM) in acetonitrile followed by vortexing the mixture for a few seconds. The completion of the reaction was checked by silica gel TLC by using suitable mobile phases (Hexane: Benzene 1:2).

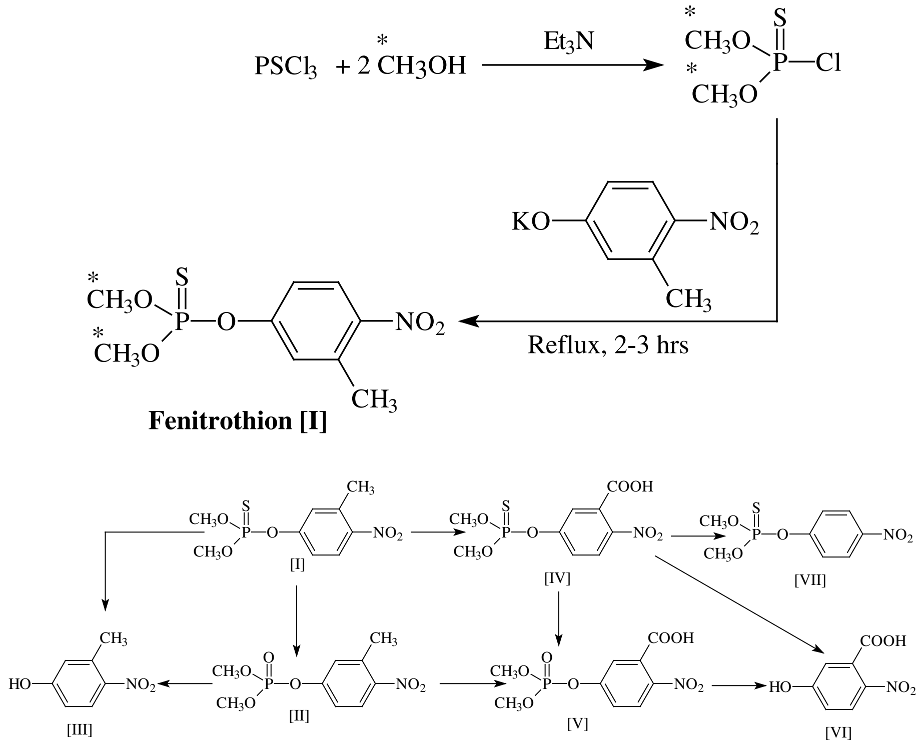

Fig. 1. Synthesis of ^{14}C-fenitrothion and its main degradation products by photodecomposition.