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PHOTOLYTIC DEGRADATION OF CHLORPYRIFOS INDUCED BY AN ARTIFICIAL LIGHT SOURCE

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Abstract

Chlorpyrifos dissolved in methanol was illuminated by the Xe polychromatic light source, which is commonly used as artificial solar radiation source. Photolytic degradation of the parent compound was followed by UV/Vis spectrophotometry and GC/MS technique. GC/MS measurements indicated that very few pyridine containing intermediates are formed during the degradation process. After 2 hours of illumination almost no chlorpyrifos could be observed and significant mineralization (formation of carbon dioxide, water, alkyl phosphates and sulfates) was achieved.

Introduction

Organophosphate esters are an important class of pesticides. The pathways of their decomposition such as hydrolysis, photolytic oxidation, microbial transformations and other biological processes have been intensively investigated recently [1]. The photodecomposition of organophosphorous pesticides and other man-made pollutants in environment occurs in both direct and indirect photochemical processes. Direct photolysis involves direct absorption of light by pollutants followed by chemical reactions, while indirect photolysis may be initiated by natural substances or solvents.

Chlorpyrifos, O,O-diethyl(O-3,5,6-trichloropyrid-2-yl)phosphorothioate (trade names Dursban, Lorsban), belongs to organophosphate pesticides. It is widely used in a variety of agricultural and urban pest control scenarios. It is used at the rate of over 50,000 kg per year in Europe and in amounts exceeding 5 million kg per year in US agriculture [2]. Chlorpyrifos is a broadly active insecticide, effective by ingestion and contact, being absorbed through skin, gut and pulmonary membranes. It is strongly adsorbed by soil and sediment, the extent being greater with organic soil and sandy loams due to liophylic nature of chlorpyrifos [3]

In this work the products of photolytic degradation of chlorpyrifos by UV/Vis spectrophotometry and GC/MS technique, using a Xe lamp as light source, were studied. The goal was to determine if any pyridine and chlorine containing products are formed during direct photolysis of chlorpyrifos.

Experimental

All chemicals used in the experiments were of reagent grade and were used without further purification. Chlorpyrifos was purchased from Sigma-Aldrich. Methanol used as a solvent was HPLC grade produced by JTBaker. All experiments were performed at $21 \pm 1^\circ\text{C}$

Photodegradation procedure

Experiments have been carried out in a 1 cm × 1 cm quartz cuvette using an Osram XBO 150 W Xenon lamp. The absorbed light intensity was $8.73 \times 10^{-5} \text{ ein} \cdot \text{min}^{-1} \cdot \text{ml}^{-1}$, for 200–400 nm illumination measured with monochloroacetic acid actinometry. Methanol solutions containing 0.1 mM (35 ppm) of chlorpyrifos were used for all photodegradation experiments.

Analytical procedure

Absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV/Vis spectrophotometer.

A HP 5890 series II+ gas chromatograph (Hewlett Packard) equipped with a HP 5891 mass spectrometer (Hewlett Packard) and J&W DB-5MS capillary column (30 m, 0.25 mm, 0.25 μm) was used for measurements. The temperature program started at 50 °C for 1 min, then increased at 10 °C·min⁻¹ to 300 °C. The injector was operated in split mode at 250 °C. Helium was used as carrier gas at flow rate of 1 ml·min⁻¹.

Results and Discussion

The changes of the absorption spectra of chlorpyrifos during the illumination are shown in Fig 1. Chlorpyrifos has three distinct absorption peaks at 206, 230 and 288 nm. It can be seen that the change in the absorbance during illumination is the most significant at 288 nm; after 120 min of illumination the absorbance is almost zero. The absorbance at 208 and 230 nm is significantly higher than zero even after 4 hours of illumination. This indicates that some intermediates and/or degradation products formed during photolysis also absorb in this region.

GC/MS technique was used to determine which products are formed during illumination. Chromatogram of the starting solution of chlorpyrifos as well as chroma-

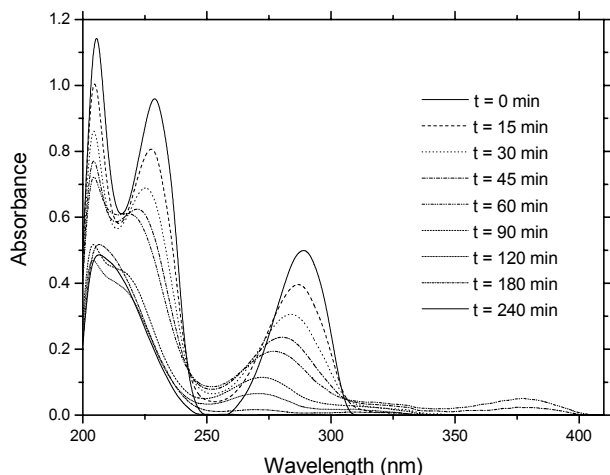


Figure 1. Absorption spectra of chlorpyrifos solutions illuminated for the indicated time by the Xe light source.

tograms of the solutions after designated time of illumination are shown in Fig. 2. Peak 1 corresponds to chlorpyrifos. Its intensity decreases with increasing of illumination time; after 120 min of illumination it could be hardly detected - almost all chlorpyrifos was degraded. The peak of the major intermediate degradation product is marked with number 2. It corresponds to O-(3,6-dichloro-2-pyridyl)-O,O-diethylphosphorothioate according to MS spectra. Its concentration increases until

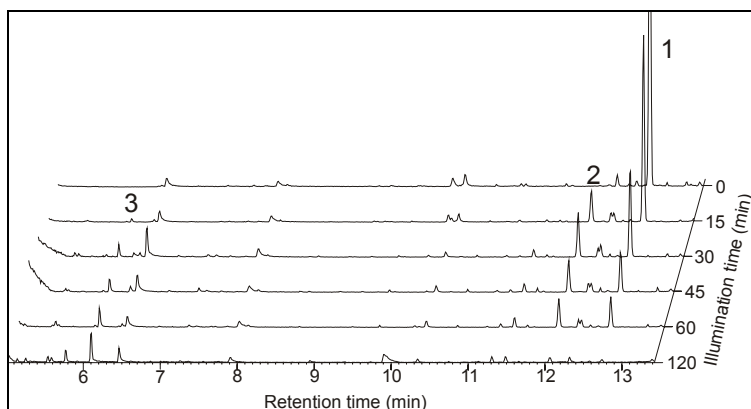


Figure 2. Chromatograms of chlorpyrifos solutions illuminated for the indicated time by the Xe light source.

60 minutes of illumination and then starts to decrease. After 2 hours of illumination it could hardly be detected just like chlorpyrifos. On the other hand some O,O-diethyl-O-methylphosphorothioate could be detected ($t_r = 6.45$ min) even before illumination and additional amounts are formed during illumination. Also, there are several alkylphosphates detected at retention times ≤ 6.1 min (marked with number 3 in Fig. 2) suggesting the nature of the final degradation products. These findings are somewhat different than the literature [2, 4] where the major degradation products were identified as 3,5,6-trichloropyridin-2-ol (TCP) and O,O-diethyl-O-methylphosphorothioate, and as a secondary product 3,5,6-trichloro-2-methoxypyridine (TMP). We could not detect any TCP or TMP in the illuminated solutions. According to our results, photolytic degradation pathway of chlorpyrifos, using Xe lamp as a light source, has only one major intermediate product: O-(3,6-dichloro-2-pyridyl)-O,O-diethylphosphorothioate which is further degraded to smaller molecules.

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