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The gas-phase degradation of chlorpyrifos and chlorpyrifos-oxon towards OH radical under atmospheric conditions

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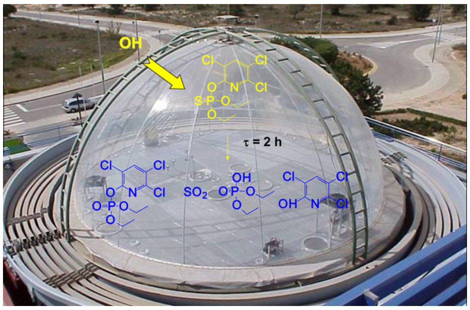
HIGHLIGHTS

- The gas phase atmospheric degradation of chlorpyrifos was investigated at EUPHORE.
- The gas phase atmospheric degradation of chlorpyrifos-oxon was also investigated.
- First experimental value for the rate constant of chlorpyrifos-oxon with respect to OH.
- The atmospheric lifetime with respect to OH of chlorpyrifos is 2 h.
- The atmospheric lifetime with respect to OH of chlorpyrifos-oxon is 11 h.

GRAPHICAL ABSTRACT



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ABSTRACT

The OH initiated oxidation of chlorpyrifos (a widely used insecticide) and its photooxidation product chlorpyrifos-oxon were investigated at the large outdoor European Photoreactor (EUPHORE). The rate constants for reaction of chlorpyrifos and chlorpyrifos oxon with OH radicals were measured using a conventional relative rate method. The value of the OH reaction rate constants with chlorpyrifos and chlorpyrifos-oxon were determined to be $k = (9.1 \pm 2.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(1.7 \pm 0.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 303 ± 5 K and atmospheric pressure. They gave an atmospheric lifetime in relation to the reaction with OH of approximately 2 h and 11 h for chlorpyrifos and chlorpyrifos-oxon, respectively. Photolysis was found to be unimportant relative to reaction with OH. The main products detected in the gas phase from the reaction of OH with chlorpyrifos were SO$_2$, chlorpyrifos-oxon, 3,5,6-trichloro-2-pyridinol and diethylphosphate with molar yields of 17 ± 5%, ~10%, 8 ± 4% and 30 ± 9%, respectively.

1. Introduction

Pesticides are extensively used in agriculture, horticulture and a variety of household applications. The wide use of pesticides is of some concern since they may have a significant environmental impact (Hamir et al., 2012). Like other synthetic organic chemicals used in large volumes, their intensive worldwide use has led to contamination of soil, water and air in both exposed and remote areas. Once a plant protection product is applied to the field, the active ingredient can be partitioned into the soil, water, biota and the atmosphere. The amount emitted depends on their physical properties and their form of application. In the atmosphere, pesticides are distributed among the gas, particle and aqueous phases, depending on their physicochemical properties and environmental conditions (Tsal and Cohen, 1991; Espallardo et al., 2012).

Chlorpyrifos (CAS: 2921-88-2 (O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate)

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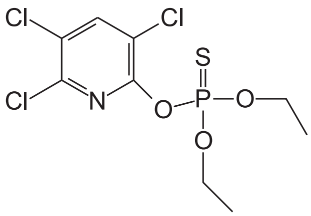
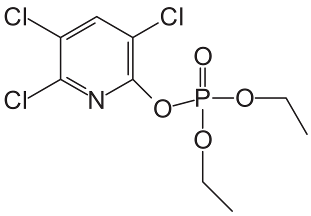
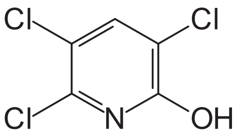


is an organophosphorous insecticide, and is among the most widespread insecticides for agricultural crop protection worldwide. Concentrations of chlorpyrifos (CHL) of up to 1428 ng m^{-3} have been reported in ambient air in both the gas and particle phases (Yusa et al., 2009; Borrás et al., 2011).

The major pathways for the tropospheric degradation of volatile organic compounds involve photolysis and reactions with ozone, and hydroxyl and nitrate radicals (Atkinson and Arey, 2003). Hence, it is expected that the gas-phase atmospheric oxidation of CHL is initiated by one or more of these processes. The photodegradation of CHL has been previously studied in the liquid phase in methanol, hexane and water, and on soil and leaf surfaces (i.e, Chukwudebe et al., 1989; Barceló et al., 1993; Bavcon Kralja et al., 2007). These studies suggest that photo-oxidation results in mainly desulphuration or dehalogenation. Hebert et al. (2000) investigated the OH radical initiated oxidation of CHL in the gas phase at elevated temperatures (333–353 K) using a solar simulator as the radiation source. The atmospheric lifetime in relation to reaction with OH radicals was found to be 2.0 h. In this study, no information on the possible products of degradation in air was reported. Muñoz et al. (2011a) investigated the atmospheric degradation of the analogous compound chlorpyrifos-methyl (CHLM) in air using natural sunlight at 300 ± 5 K. The atmospheric lifetime of CHLM was found to be 3.5 h, mainly due to reaction with OH radicals. From the data available on the degradation of organophosphorothioate- and phosphonothioate-based pesticides (Barceló et al., 1993; Muñoz et al., 2011a,b), it is likely that the atmospheric oxidation of CHL leads to the formation of the corresponding oxon (CAS 5598-15-2) phosphoric acid, diethyl 3,5,6-trichloro-2-pyridyl ester)



and 3,5,6-trichloro-2-pyridinol (PYRIDOL).



CHLO has been detected in air at concentration ranges of 0.196–0.189 ng m^{-3} (Yusa et al., 2009)

The present series of experiments were carried out to determine the major reaction pathways for CHL degradation in the troposphere. The studies were performed at the outdoor European Photoreactor (EUPHORE). The results provide information on the atmospheric lifetime of CHL. The main primary products of the OH radical initiated oxidation of CHL were also determined and mechanisms for their formation were proposed. To the best of our knowledge, experimental determination of the rate constant of OH with CHL and chlorpyrifos-oxon (CHLO) in gas-phase at ambient temperature and the identification of the main degradation products have not been previously determined in the peer reviewed literature.

2. Experimental section

The experiments were performed under sunlight conditions at EUPHORE photoreactor in Valencia, Spain, following the same procedures previously used to determine the atmospheric fate of other pesticides (i.e: Muñoz et al., 2011a, 2012, 2014; Vera et al., 2011). Technical information concerning the facility has previously been reported in the literature (Becker, 1996), and only a brief description of the system is given here. The experiments were performed in a hemispherical reaction chamber (volume ~200 m^3) fabricated of FEP foil, which transmits greater than 80% of the solar radiation in the wavelength range 290–500 nm. The time of exposure to solar radiation was controlled with a retractable steel housing which surrounds the chamber.

A FTIR spectrometer (NICOLET 6700) coupled to a White-type mirror system (optical path-length 554 m) was used to monitor reactants and products. Infrared spectra were derived from the co-addition of 280 scans, collected over a 5 min period, and recorded using 1 cm^{-1} resolution. The IR absorption cross-sections used to analyze the FTIR data were determined in separate calibration experiments. Complex infrared spectra were analyzed with a fitting routine developed at CEAM (Ródenas, 2008). Table S.I.1 summarizes the compounds analyzed in the present work.

Solid-phase microextracion (SPME) was also use to monitor reactants and products. The SPME device consisted in a holder assembly with 65-μm fibres coated with polydimethylsiloxane/divinylbenzene (PDMS/DVB), from Supelco. These fibres were conditioned at 250 °C to eliminate any impurities. Exposing the fibre to the air of the chamber was achieved by means of an aluminium adapter located in one of the flanges in the chamber floor. Calibrations were done by introducing known amounts of the compounds of interest in the EUPHORE chambers. Concentration was calculated from the corresponding regression curve. Validation of the methodology for CHL, CHLO and PYRIDOL was made by comparison with FTIR in dark conditions. Correlations better than 0.98 were obtained (Fig. S.I.1). Samples were taken for 5 min and were analyzed by gas-chromatography equipped with a flame ionization detector (GC-FID) by injecting the fibre directly into the GC injector. An HP 6890 Gas Chromatograph equipped with an HP-5MS column of 30 m × 0.25 mm × 0.25 mm, was used. The chromatograph was programmed at 190 °C for 0 min, then ramped at a rate of 4 °C min^{-1} to 225 °C.

Additionally, gas-phase samples were taken through C-18 solid phase cartridges at a sampling flow rate of 1 L min^{-1} and aerosol samples were collected at a sampling flow rate of 23 L min^{-1} at the end of experiment with a pre-heated 47 mm-diameter glass fibre filter (0.45 μm, pore size) and then extracted, derivatized and analyzed by gas chromatography-mass spectrometry. Treatment was the same for both, filters and C-18 cartridges. Detailed information on this methodology was described by Borrás and Tortajada-Genaro (2012). The sulphur dioxide concentrations was measured using a Thermo Scientific 43i monitor.

Due to their relatively low vapour pressure, CHL (Dow AgroSciences), CHLO (Dow AgroSciences), and the standards PYRIDOL (Dow AgroSciences) and diethylphosphate (Acros Organics, 75%) were gently heated to accelerate their introduction into the chamber. The vapour pressures of CHL, CHLO, and Pyridol are 2.7, 1.0