Chemosphere 87 (2012) 470–476

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Heterogeneous reactions of suspended parathion, malathion, and fenthion particles with NO_3 radicals

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ARTICLE INFO

Article history:
Received 19 September 2011
Received in revised form 12 December 2011
Accepted 13 December 2011
Available online 5 January 2012

Keywords:
Organophosphorus pesticides
Heterogeneous reaction
NO_3 radicals
GC/MS
Aerosol mass spectrometry

ABSTRACT

Organophosphorus pesticides (OPPs) emit into the atmosphere in both gas and particulate phases via spray drift from treatments and post-application emission, but most of their degradations in the atmosphere are not well known. In this study, the heterogeneous reactions of nitrate (NO_3) radicals with three typical OPPs (parathion, malathion, and fenthion) absorbed on azelaic acid particles are investigated using an online vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS). The reaction products observed with the VUV-ATOFMS are identified on the basis of GC/MS analysis of the products in the reaction between NO_3 radicals and the coating of the pesticide. Paraoxon is identified as the only product of parathion; malaoxon and bis(1,2-bis-ethoxycarbonylethyl)disulfide as the products of malathion; fenoxon, fenoxon sulfoxide, fenthion sulfoxide, fenoxon sulfone, and fenthion sulfone as the products of fenthion. The degradation rates of parathion, malathion, and fenthion under the experimental conditions are 5.5×10^{-3}, 5.6×10^{-2}, and $3.3 \times 10^{-2}\ s^{-1}$, respectively. The pathways of the heterogeneous reactions between the three OPPs and NO_3 radicals are proposed. The experimental results reveal the possible transformations of these OPPs through the oxidation of NO_3 radicals in the atmosphere.

1. Introduction

Organophosphorus pesticides (OPPs) are a group of very effective compounds widely used in agriculture and residence as insecticides and herbicides (Jauregui et al., 2003). OPPs are regarded as less persistent in the environment than organochlorine pesticides (OCPs) (Ferrando et al., 1992), and this family of chemicals is one of the substitutes for OCPs, which was banned for use in the 1970s (Vonderheide et al., 2003). It is well known that OPPs have genotoxicity (Cakir and Sarikaya, 2005), cytotoxicity (Giordano et al., 2007), reproductive toxicity (Pina-Guzman et al., 2005), and irreversible inhibitory activity to acetylcholinesterase (Jauregui et al., 2003). In addition, not only OPPs themselves but also their degradation products put humans at risk, because their degradation products in the environment may be more toxic than their parent chemicals (van den Berg et al., 1999). As a result of wide application, not only waters and soils but also the air is contaminated with OPPs (Kosikowska and Biziuk, 2010). This is due to spray drift from the application (van den Berg et al., 1999) and the post-application emission including volatilization (van den Berg et al., 1999) and wind erosion (Kosikowska and Biziuk, 2010). Besides their wet and dry deposition, OPPs in the atmosphere can be removed by the photolysis and the reactions with atmospheric oxidants, such as hydroxyl (OH) radicals, ozone (O_3), and nitrate (NO_3) radicals (Atkinson, 1995).

The NO_3 radical plays an important role in the nighttime atmosphere, its reactivity is comparable to that of OH radicals in the daytime atmosphere (Karagulian and Rossi, 2005). The concentration of NO_3 radicals is reported to reach values of up to 4.0×10^7 molecules cm^{-3} in the stratosphere (Naudet et al., 1989) and 2.0×10^9 molecules cm^{-3} in the troposphere at nighttime (Platt et al., 1980). Despite these significant concentrations, few studies on the heterogeneous reactions of airborne OPPs with NO_3 radicals have hitherto been performed (Liu et al., 2011).

Parathion (*O*,*O*-diethyl *O*-(4-nitrophenyl) phosphorothioate), malathion (*S*-[1,2-bis(carbethoxy)ethyl]-*O*,*O*-dimethyl dithiophosphate), and fenthion (*O*,*O*-dimethyl *O*-[3-methyl-4-(methylthio)-phenyl] phosphorothioate) selected as the samples in this study are three representative kinds of OPPs, widely used in agrochemical applications. These OPPs are expected to exist in both gas and particle phases in the atmosphere on the basis of their vapor pressures ranging from 10^{-3} to 10^{-4} Pa at room temperature. Great efforts have been made into the studies on the three OPPs, but most of which focused on the treatment technologies, toxic effects, and the metabolites in plants, waters and soils (Cabras et al., 1993; Minelli et al., 1996; Kaur et al., 1997; Bavcon et al., 2003; Pico et al., 2007; Wu and Linden, 2008; Slotkin et al., 2009; Fan et al.,

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doi:10.1016/j.chemosphere.2011.12.031

2011). The aim of this study is to identify the products of suspended parathion, malathion, and fenthion particles in the reactions with NO_3 radicals, and explore their reaction pathways. The results may help reveal the transformation processes of these OPPs in the atmosphere through oxidation by NO_3 radicals, and provide fundamental information for evaluating the harmful effects of the three OPPs and their products in the atmosphere.

2. Experimental section

2.1. Chemicals

Parathion (98.3%, Dikma), malathion (98.4%, Dikma), fenthion (98.9%, Dikma), azelaic acid (99%, NRSCRD, China), fuming nitric acid (95%, Beijing Lisui Chemical Factory), P_2O_5 (98%, Sinopharm Chemical Reagent Co., Ltd.), and absolute ethyl alcohol (99.7%, Sinopharm Chemical Reagent Co., Ltd.) are used in the experiment. Nitrogen (99.99%) is purchased from Beijing Huayuan Gas Chemical Industry Co. Ltd. and dichloromethane (chromatographic grade) from J. T. Baker Co.

2.2. Experimental setup

The experimental setup has been described in detail elsewhere (Zhang et al., 2010a). Briefly, it consists of an aerosol generator, a reaction chamber, and analytic instruments.

The suspended pesticide particles are generated through the homogeneous nucleation. The aerosol generator is an electric tube furnace equipped with two tandem quartz tubes (50 cm (length) × 3 cm (inner diameter)), each with an independent temperature controller (from the room temperature up to 523 K). Azelaic acid is employed to produce nuclei due to its little reactivity with NO_3 radicals in the previous studies (Yang et al., 2011). Azelaic acid is placed in the first tube (418 ± 1 K for fenthion, 428 ± 1 K for malathion and parathion), while the pesticide sample in the second tube (403 ± 1 K for fenthion, 413 ± 1 K for malathion and parathion). A N_2 stream with a volumetric flow rate of 0.6 L min^{-1} flows through the first tube bringing the nuclei into the second tube. In the second tube, the azelaic acid nuclei are coated by the pesticide. The thickness of the coating is controlled by adjusting the temperature of the quartz tube and the flow rate of N_2. The size and concentration of particles are monitored with a scanning mobility particle sizer (SMPS), which is composed of a differential mobility analyzer (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3010). The geometric mean diameters of parathion, malathion, and fenthion particles are 390, 395, and 373 nm, respectively. The initial mass concentrations of parathion, malathion, and fenthion in the chamber are 572, 654, and 407 μg m^{-3}, respectively, which are calculated on the basis of the mass concentrations and size distributions of particles before and after coated by the pesticide.

The reaction chamber consists of a thin-walled open head stainless steel drum (50 cm (outer diameter) × 60 cm (height)) and a thin Tedlar polyvinyl fluoride (PVF) film bag (50 cm (diameter) × 50 cm (length)). The PVF bag is used to keep one atmospheric pressure in the aerosol reaction chamber. The volume of the chamber is ~200 L when the PVF bag is fully filled. A magnetic-driven fan is set at the bottom of the reaction chamber to ensure that the reactants could be mixed rapidly and sufficiently. The experiments are performed under the atmosphere pressure with the room temperature of ~293 K. The relative humidity in the chamber is roughly estimated to be ~5% due to the residual filtered air in the chamber. After the concentration of suspended pesticide particles within the reaction chamber reaches the desired value, a N_2 stream with a volumetric flow rate of 0.6 L min^{-1} passes through the flask containing N_2O_5 powder that is placed at the room temperature, and introduces gaseous N_2O_5 continuously into the chamber during the particulate reaction with the fan turned on.

The TOF mass spectra of particulate OPPs and their reaction products are obtained in real-time with the VUV-ATOFMS (Shu et al., 2008). Only a brief description of the VUV-ATOFMS is presented here. It consists of three collimated chambers: a source chamber, a differential chamber, and a detection chamber. An 8 mm diameter copper rod coupled with a cartridge heater placed in the detection chamber is used to vaporize the particles, the nascent organic vapor is photoionized with VUV light emitted from a VUV light lamp with a photon flux of 5×10^{14} photons s^{-1} and a photon energy of 10 eV (Shu et al., 2008).

The NO_3 radicals are generated by thermal decomposition of N_2O_5. During the experiment, the flask containing N_2O_5 powder is placed at room temperature of ~293 K. The vapor pressure of N_2O_5 at 293 K is ~2.12 kPa (Yaws, 1999). N_2O_5 quickly decomposes at room temperature and is in the dynamic equilibrium with NO_2 and NO_3 radicals, the concentrations of gaseous N_2O_5 and NO_3 radicals are respectively estimated about 10^{12}–10^{13} and 10^{11}–10^{12} molecules cm^{-3} in the reaction chamber using an equilibrium constant of 2.9×10^{-11} cm^3 $molecule^{-1}$ (Finlayson-Pitts and Pitts, 1999).

2.3. Gas chromatography/mass spectrometry (GC/MS)

In order to assign the TOF mass spectra of reaction products, GC/MS analysis is performed to identify the products in the reaction between NO_3 radicals and the coating of the pesticide. The coating is prepared by nitrogen-purging of the pesticide solution with ~2 mL (~15 g L^{-1} in CH_2Cl_2) in a 150 mL conical flask. During the reaction, a synthetic air flow of 0.6 L min^{-1} containing gaseous N_2O_5 passes through the conical flask for ~5 min. After reaction, 100 mL CH_2Cl_2 is added into the conical flask. Then, the conical flask is ultrasonic-washed for ~5 min. A part of the solution is atomized into suspended droplets, and the generated droplets are directly analyzed with the VUV-ATOFMS, which serves as the auxiliary experiment for product identification by contrast with the TOF mass spectra obtained from the particulate reaction. In this experiment, the TOF mass spectra of the products from the reaction between NO_3 radicals and the coating of the pesticide are similar to those from the particulate reaction. Meanwhile, another part of the solution is used for product identification by GC/MS.

An Agilent 6890 GC/MS equipped with a 30 m × 0.25 mm × 0.25 um HP-5 capillary and an HP-5973 quadrupole mass filter with a 70 eV electron impact ionizer is used to identify the products. 1 μL sample is injected via the pulsed splitless mode. The temperature settings of GC/MS for the measurements of the three OPPs and their derivates are adopted from the previous studies (Gallardo et al., 2006; Tsakirakis and Machera, 2007; Zhang et al., 2010b). The reaction products are analyzed by GC/MS in the total ion chromatogram (TIC) mode and identified by comparing the EI mass spectra of the products with those from a Mass Spectral Library (the National Institute of Standards and Technology (NIST) 2005). Compared with the available mass spectra in the NIST 2005 library, the product with the match rate over 85% could be identified. The mass range from 50 to 500 amu is used in the process of data acquisition. The scanning times for parathion, malathion, and fenthion are 17.9, 44, and 24.9 min, respectively. Data acquisition and processing are controlled by a HP Chemstation data system. Table 1 shows the reaction products detected and identified by GC/MS.

3. Results and discussion

3.1. Reaction of parathion particles with NO_3 radicals

The TOF mass spectrum of parathion particles shown in Fig. 1A is obtained before exposure to NO_3 radicals. The most intense mass