Heterogeneous reactions of suspended parathion, malathion, and fenthion particles with NO₃ radicals

Changgeng Liu, Bo Yang, Jie Gan, Yang Zhang, Miao Liang, Xi Shu, Jinian Shu *

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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

NO₃ 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 (NO₃) 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 NO₃ radicals and the coating of the pesticide. Paraaxon is identified as the only product of parathion; malaoxon and bis(1,2-bis-ethoxycarbonyl)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 $3.3 \times 10^{-2} \text{ s}^{-1}$, respectively. The pathways of the heterogeneous reactions between the three OPPs and NO₃ radicals are proposed. The experimental results reveal the possible transformations of these OPPs through the oxidation of NO₃ radicals in the atmosphere.

© 2011 Elsevier Ltd. All rights reserved.

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 (O₃), and nitrate (NO₃) radicals (Atkinson, 1995).

The NO₃ 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 NO₃ radicals is reported to reach values of up to $4.0 \times 10^7 \text{ molecules cm}^{-3}$ in the stratosphere (Naudet et al., 1989) and $2.0 \times 10^9 \text{ molecules cm}^{-3}$ in the troposphere at nighttime (Platt et al., 1980). Despite these significant concentrations, few studies on the heterogeneous reactions of airborne OPPs with NO₃ 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.,

* Corresponding author. Tel.: +86 10 62849508; fax: +86 10 62923563.

E-mail address: jshu@rcees.ac.cn (J. Shu).

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) $\times$ 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 $407 \mu\text{g m}^{-3}$, 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) $\times$ 60 cm (height)) and a thin Tedlar polyvinyl fluoride (PVF) film bag (50 cm (diameter) $\times$ 50 cm (length)). The PVF bag is used to keep one atmospheric pressure in the aerosol reaction chamber. The volume of the chamber is $\sim 200 \text{ L}$ 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 $\sim 293 \text{ K}$. The relative humidity in the chamber is roughly estimated to be $\sim 5\%$ 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 $5 \times 10^{14} \text{ photons s}^{-1}$ 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 $\sim 293 \text{ K}$. The vapor pressure of N_2O_5 at 293 K is $\sim 2.12 \text{ kPa}$ (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} – $10^{12} \text{ molecules cm}^{-3}$ in the reaction chamber using an equilibrium constant of $2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ (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 $\sim 2 \text{ mL}$ ($\sim 15 \text{ g L}^{-1}$ 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 $\sim 5 \text{ min}$. After reaction, 100 mL CH_2Cl_2 is added into the conical flask. Then, the conical flask is ultrasonic-washed for $\sim 5 \text{ min}$. 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 $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ 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 derivatives 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

Table 1

Products detected and identified with GC/MS and VUV-ATOFMS.

Compounds	Formula	MW	RT	η_1	η_2
Paraoxon (Product I ^a)	C ₁₀ H ₁₄ NO ₆ P	275	14.4	0.38 ^a	1 ^a
Malaoxon (Product I ^b)	C ₁₀ H ₁₉ O ₇ PS	314	21.5	1 ^b	1 ^b
1,2-Dicarbethoxyethyl-dimethoxyphosphinyldisulfide (Product II ^b)	C ₁₀ H ₁₉ O ₇ PS ₂	346	–	–	0.12 ^b
2-Mercapto-succinic acid diethylester (Product III ^b)	C ₈ H ₁₄ O ₄ S	206	–	–	0.14 ^b
Bis(1,2-bis-ethoxycarbonylethyl)disulfide (Product IV ^b)	C ₁₆ H ₂₆ O ₈ S ₂	410	26.9	0.017 ^b	0.075 ^b
Fenoxon (Product I ^c)	C ₁₀ H ₁₅ O ₄ PS	262	11.0	0.28 ^c	–
Fenthion sulfoxide (Product II ^c)	C ₁₀ H ₁₅ O ₄ PS ₂	294	15.4	1 ^c	0.17 ^c
Fenoxon sulfoxide (Product III ^c)	C ₁₀ H ₁₅ O ₅ PS	278	14.2	0.072 ^c	1 ^c
Fenthion sulfone (Product IV ^c)	C ₁₀ H ₁₅ O ₅ PS ₂	310	16.4	0.001 ^c	–
Fenoxon sulfone (Product V ^c)	C ₁₀ H ₁₅ O ₆ PS	294	14.5	0.1 ^c	0.17 ^c
Nitro-fenoxon sulfoxide (Product VI ^c)	C ₁₀ H ₁₄ NO ₇ PS	323	–	–	0.075 ^c

MW is the molecular weight and RT the retention time of compounds in minutes. η_1 represents the relative abundances of the products from the results of GC/MS analysis, and η_2 denotes the relative peak intensities of the mass peaks shown in Figs. 1B, 2B, and 4C. The superscripts indicate the date from the reactions of NO₃ radicals with parathion (a), malathion (b), and fenthion (c).

peak at m/z 291 corresponds to the molecular ion of parathion, and the ion peak at m/z 275 is assigned as its daughter ion formed by losing an oxygen atom through VUV photoionization. The mass spectrum shown in Fig. 1B is acquired 200 s after the injection of NO₃ radicals. The intensity of the mass peak at m/z 291 decreases along with the reaction time, while the intensity of the ion peak at m/z 275 increases. GC/MS analyses (See Fig. 1C and Table 1) show that paraoxon (Product I^a, C₁₀H₁₄NO₆P, mol. wt 275) is the only

reaction product in the reaction between NO₃ radicals and the coating of parathion. Thus, it suggests that the phenomena result from the formation of Product I^a, a common degradation product of parathion through photolysis, biological metabolism, and advanced oxidation process (Gallardo et al., 2006; Wu and Linden, 2008; Fan et al., 2011). As a derivate of parathion, its intoxication symptoms are similar to those produced by other cholinesterase inhibitors (Gallardo et al., 2006).

3.2. Reaction of malathion particles with NO₃ radicals

Fig. 2A shows the TOF mass spectrum of malathion particles before exposure to NO₃ radicals. The mass peak at m/z 330 is contributed from the molecular ion of malathion, and the most intense mass peak at m/z 173 is assigned as its daughter ion formed by removing a C₂H₆O₂PS₂ group (mol. wt 157) via the cleavage of the C–S bond through VUV photoionization. The ion peaks at m/z 256 and 284 are tentatively assigned to the daughter ions of malathion, which may be respectively produced by the losses of an ethyl ester group (C₃H₆O₂, mol. wt 74) and an ethanol group (C₂H₆O, mol. wt 46) through VUV photoionization. The ion peak at m/z 188 is not successfully assigned, which may be the daughter ion of malathion. The small mass peak at m/z 220 is contributed from the pump oil in the instrument and is not discussed in the paper.

The TOF mass spectrum shown in Fig. 2B is acquired 60 s after the injection of NO₃ radicals into the reaction chamber. Compared with the TOF mass spectrum shown in Fig. 2A, some new mass peaks appear at m/z 204, 206, 224, 268, 300, 314, 346, and 410. Based on GC/MS analyses (see Fig. 2C and Table 1), malaoxon (Product I^b, C₁₀H₁₉O₇PS, mol. wt 314) and bis(1,2-bis-ethoxycarbonylethyl)disulfide (Product IV^b, C₁₆H₂₆O₈S₂, mol. wt 410) are identified as the two products in the reaction between NO₃ radicals and the coating of malathion, and their retention times are 21.5 and 26.9 min, respectively.

Thus, the mass peaks at m/z 314 and 410 are assigned to the molecular ions of Products I^b and IV^b, respectively. Product I^b is the main oxidative degradation product of malathion in the natural environment (Kaur et al., 1997; Bavcon et al., 2003), and shows approximately 10-fold more toxic than its parent chemical (Snawder and Chambers, 1989). The ion peak at m/z 268 is tentatively assigned to the daughter ion of Products I^b, which may be formed by removing an ethanol group (C₂H₆O, mol. wt 46) through VUV photoionization. The mass peak at m/z 346 is tentatively assigned to the molecular ion of 1,2-dicarbethoxyethyl-dimethoxyphosphinyldisulfide (Product II^b, C₁₀H₁₉O₇PS₂, mol. wt 346), and the ion peak at m/z 300 is assigned as its daughter ion, formed by the loss of an ethanol group (C₂H₆O, mol. wt 46) through VUV photoionization.

Fig. 1. TOF mass spectra of parathion particles (A) and its oxidation products in the reaction with NO₃ radicals (B), and GC/MS total ion chromatograms (C) of the oxidation products in the reaction between NO₃ radicals and the coating of parathion. The spectrum shown in Fig. 1B is acquired 200 s after NO₃ radicals are introduced into the reaction chamber. The acquisition time for each mass spectrum is 10 s. The TOF mass spectra and the GC/MS total ion chromatogram are normalized to their most intense peaks, respectively.

Fig. 2. TOF mass spectra of malathion particles (A) and its oxidation products in the reaction with NO₃ radicals (B), and GC/MS total ion chromatograms (C) of the oxidation products in the reaction between NO₃ radicals and the coating of malathion. The spectrum shown in Fig. 2B is acquired 60 s after NO₃ radicals are introduced into the reaction chamber. The acquisition time for each mass spectrum is 10 s. The GC/MS total ion chromatogram is normalized to its most intense peak.

Products I^b and II^b are both reported as the products of malathion through peracid oxidation (Bellet and Casida, 1974). The ion peak at m/z 204 is tentatively assigned to the daughter ion of 2-mercapto-succinic acid diethylester (Product III^b, C₈H₁₄O₄S, mol. wt 206), which is a common hydrolytic product of malathion in water and soil (Kaur et al., 1997). The mass peak at m/z 204 may result from the loss of one hydrogen molecule from Product III^b through VUV photoionization (Meng et al., 2010). The mass peaks at m/z 188 and 224 are not assigned successfully, which may be the daughter ion of the reaction products. Products II^b and III^b are not detected by GC/MS, which may be due to their thermal instability (Bellet and Casida, 1974) and chemical polarity. The four assigned products are also observed in the heterogeneous reaction of suspended malathion particles with ozone (Meng et al., 2010).

The EI mass spectrum of Product IV^b shown in Fig. 3 is obtained by GC/MS, of which the standard EI mass spectrum is not available yet in NIST library. Thus, the mass peak at m/z 410 in the EI mass spectrum is deemed to be the molecular ion of Product IV^b. The specific fragment ion at m/z 365 might be formed by the loss of an ethoxy group (C₂H₅O, mol. wt 45) from the molecular ion, and the successive losses of an ethoxy group (C₂H₅O, mol. wt 45) and an ethyl group (C₂H₅, mol. wt 29) from the daughter ion at m/z 365 may produce the dominant fragment ion at m/z 291. The mass peak at m/z 205 could be formed via the cleavage of S–S bond of the molecular ion at m/z 410. The loss of an ethyl ester group (C₃H₆O₂, mol. wt 74) via the breakage of C–C bond of the fragment ion at m/z 205 might produce fragment ion at m/z 131 (C₅H₇O₂S,

Fig. 3. EI mass spectrum of bis(1,2-bis-ethoxycarbonyl)disulfide (Product IV^b) obtained in the experiments.

mol. wt 131). The fragment ion at m/z 99 (C₅H₇O₂, mol. wt 99) might be formed by removing a sulfur atom from the fragment ion at m/z 131.

3.3. Reaction of fenthion particles with NO₃ radicals

Fig. 4A shows the TOF mass spectrum of fenthion particles in the absence of NO₃ radicals. The mass peak at m/z 278 corresponds to the molecular ion of fenthion. The mass spectra shown in Fig. 4B and C are acquired 60 and 140 s after the injection of NO₃ radicals into the chamber. Compared with the mass spectrum shown in Fig. 4A, there are new mass peaks appearing at m/z 220, 247, 263, 279, 294, 307, and 323 in the TOF mass spectra shown in Fig. 4B and C.

Through GC/MS analyses, fenoxon (Product I^c, C₁₀H₁₅O₄PS, mol. wt 262), fenthion sulfoxide (Product II^c, C₁₀H₁₅O₄PS₂, mol. wt 294), fenoxon sulfoxide (Product III^c, C₁₀H₁₅O₅PS, mol. wt 278), fenthion sulfone (Product IV^c, C₁₀H₁₅O₅PS₂, mol. wt 310), and fenoxon sulfone (Product V^c, C₁₀H₁₅O₆PS, mol. wt 294) are obtained as the five products in the reaction between NO₃ radicals and the coating of fenthion. Their retention times are 11.0, 15.4, 14.2, 16.4, and 14.5 min (see Fig. 4D and Table 1), respectively. Thus, the mass peaks at m/z 294 shown in Fig. 4B and C might be contributed from both Products II^c and V^c, and the mass peaks at m/z 278 possibly from Product III^c and residual fenthion. These five products are common degradation products of fenthion in the natural environment (Cabras et al., 1993; Minelli et al., 1996; Pico et al., 2007; Tsakirakis and Machera, 2007), and show higher toxicity than fenthion (Cabras et al., 1993).

It was reported that fenthion was converted into Product II^c rapidly during sunlight photolysis (Minelli et al., 1996). Besides, GC/MS analyses show that the yield of Product II^c is one order of magnitude more than that of Product V^c. Therefore, the first mass peak (m/z 294) appearing in the reaction process shown in Fig. 4B is mainly contributed from the molecular ion of Product II^c. The mass peaks at m/z 247, 263, and 279 in Fig. 4B are tentatively assigned to the daughter ions of Product II^c. The fragment at m/z 279 may be formed by the loss of a methyl group (CH₃, mol. wt 15) through VUV photoionization, and the successive loss of oxygen atom from the fragment ion at m/z 279 yields fragment ions at m/z 263 and 247.

Since the EI mass spectrum in NIST library of Product III^c shows a strong daughter ion mass peak at m/z 263, the most intense mass peak at m/z 263 shown in Fig. 4C is assigned as the daughter ion of Product III^c, produced by losing a methyl group (CH₃, mol. wt 15)

Fig. 4. TOF mass spectra of the fenthion particles (A) and its oxidation products in the reaction with NO_3 radicals (B and C), and GC/MS total ion chromatograms (D) of the oxidation products in the reaction between NO_3 radicals and the coating of fenthion. The spectra shown in Fig. 3B and C are acquired 60 and 140 s after NO_3 radicals are introduced into the reaction chamber. The acquisition time for each mass spectrum is 10 s. The TOF mass spectra and the GC/MS total ion chromatogram are normalized to their most intense peaks, respectively.

through VUV photoionization. Considering the mass spacing of 45 amu between m/z 278 and 323, we speculate that the mass peak at m/z 323 results from the nitro-substituted product of Product III^c (Liu et al., 2011). Thus, the mass peak at m/z 323 is tentatively assigned to the molecular ion of nitro-fenoxon sulfoxide (Product VI^c, $\text{C}_{10}\text{H}_{14}\text{NO}_7\text{PS}$, mol. wt 323), and the ion peak at m/z 307 is tentatively assigned as its daughter ion formed by removing an oxygen atom through VUV photoionization. Products I^c and IV^c are only detected by GC/MS while the confirmation of Product VI^c by GC/MS is not successfully achieved. These inconsistencies may result from the different detection limits of two analytical instruments (Gao et al., 2008).

3.4. Degradations of parathion, malathion, and fenthion

The initial mass concentrations of parathion, malathion, and fenthion in the chamber are 572, 654, and 407 $\mu\text{g m}^{-3}$, respectively. Since the concentrations of the particles are linear to their signal intensities obtained by the VUV-ATOFMS (Shu et al., 2008), the decay rates of the signal intensities are equal to the decay rates of the concentrations of OPPs particles. Therefore, the residual concentrations of parathion, malathion, and fenthion in the chamber are calculated to be 5.7, 5.8, and 2.1 $\mu\text{g m}^{-3}$, respectively. The data points shown in Fig. 5 are the time-dependent signal intensities of OPPs particles normalized to their initial intensities. The

Fig. 5. Decay curves of parathion, malathion, and fenthion particles at the concentration of NO_3 radicals about 10^{11} – 10^{12} molecules cm^{-3} .

Fig. 6. Proposed pathways for the reactions of NO_3 radicals with parathion, malathion, and fenthion particles.

degradation rates of parathion, malathion, and fenthion under the experimental conditions are 5.5×10^{-3} , 5.6×10^{-2} , and $3.3 \times 10^{-2} \text{ s}^{-1}$, respectively, obtained by fitting the data points with an exponential decay via non-linear least square fitting ($R^2 > 0.98$). These experimental results suggest that the reactivity of parathion toward NO_3 radicals is much less than those of malathion and fenthion.

3.5. Reaction pathways of parathion, malathion, and fenthion

It has been reported that the reactions of organothiophosphorus compounds are usually initiated by the addition of oxidants to the sulfur atom or to the P=S double bond, giving one or more unstable intermediates (Bellet and Casida, 1974). Thus, Intermediates I^a, I^b, and I^c are speculated to be formed by the addition of NO₃ radicals to the P=S moiety, accompanying with the loss of a NO₂ molecule (Liu et al., 2011). These intermediates respectively yield Products I^a, I^b, and I^c via the loss of a sulfur atom from the cyclic P—O—S group (See Fig. 6A–C) (Liu et al., 2011). Product II^b of malathion is formed through the intermolecular rearrangement of Intermediate I^b (Bellet and Casida, 1974). Product III^b might result from the cleavage of P—S bond from Intermediate I^b and subsequent radical-molecule reaction, and Product III^b might be further oxidized into Product IV^b (Meng et al., 2010). The formation mechanism of Product IV^b may be similar to that of bis(4-chlorophenyl)disulfide in the oxidation of O,O-diethyl S-(4-chlorophenyl) phosphorodithioate (Miyamoto and Yamamoto, 1977). The degradation pathways of malathion particles toward NO₃ radicals obtained in this study are similar to that of ozonation of malathion particles (Meng et al., 2010).

Product I^c of fenthion could be converted into Products III^c and V^c by the oxidation of the sulfur atom on the methylthio group (Cabras et al., 1993; Minelli et al., 1996; Pico et al., 2007). Product II^c of fenthion observed in the experiment suggests that Intermediate II^c could be formed in the reaction of fenthion particles with NO₃ radicals (See Fig. 6C). It might be formed by the attack of the NO₃ radical on the sulfur atom on the methylthio group of fenthion, then yielding Product II^c by losing a NO₂ molecule. Products II^c undergoes subsequent oxidation of the sulfur atom on the methylthio group by NO₃ radicals, forming Products IV^c. In addition, the oxidation of Products II^c and IV^c could lead to the formations of Products III^c and V^c, respectively (Cabras et al., 1993; Minelli et al., 1996). Product III^c can be converted into Product VI^c via further reaction with the NO₃ radical, of which the formation mechanism may be similar to that of nitro-substituted products of carbaryl particles in the reaction with NO₃ radicals (Yang et al., 2011). There are some discrepancies between the proposed pathways in this study and those of fenthion in oranges (Pico et al., 2007), which might be mainly due to the difference in degradation circumstances.

4. Conclusions

In this study, the VUV-ATOFMS is used to online analyze the particulate products of heterogeneous reactions of NO₃ radicals with parathion, malathion, and fenthion adsorbed on azelaic acid particles. Assisted with GC/MS analysis, paraoxon is identified as the only reaction product of parathion. Malaoxon and bis(1,2-bis-ethoxycarbonyl)disulfide are identified in the reaction of malathion with NO₃ radicals. Fenoxon, fenoxon sulfoxide, fenthion sulfoxide, fenoxon sulfone, and fenthion sulfone are detected and identified as the reaction products of fenthion. Meanwhile, 2-mercapto-succinic acid diethylester, 1,2-dicarbethoxyethyl-dimethoxyphosphinyldisulfide, and nitro-fenoxon sulfoxide are observed by the VUV-ATOFMS but not identified by GC/MS. It was reported that the oxygen analog (P=O) of OPPs had more effective toxicity than its thiophosphoryl function (P=S) (Yan et al., 2008). Then, we speculate that the potential risks of these products to human health are much severer than their parent chemicals. Under the experimental conditions, the degradation rates of parathion, malathion, and fenthion are 5.5×10^{-3} , 5.6×10^{-2} , and $3.3 \times 10^{-2} \text{ s}^{-1}$, respectively. The degradation pathways of the three OPPs in the reactions with NO₃ radicals are proposed. The experimental results might shed light on the chemical transformations of the three OPPs through oxidation by NO₃ radicals in the atmosphere.

Acknowledgements

This research is funded by Creative Research Groups of China (Grant No. 50921064) and National Natural Science Foundation of China (Grant No. 21077115).

References

- Atkinson, R. (Ed.), 1995. Gas Phase Tropospheric Chemistry of Organic Compounds. Royal Society of Chemistry, London.
- Bavcon, M., Trebse, P., Zupancic-Kralj, L., 2003. Investigations of the determination and transformations of diazinon and malathion under environmental conditions using gas chromatography coupled with a flame ionisation detector. Chemosphere 50, 595–601.
- Bellet, E.M., Casida, J.E., 1974. Products of peracid oxidation of organothiophosphorus compounds. J. Agric. Food Chem. 22, 207–211.
- Cabras, P., Garau, V.L., Melis, M., Pirisi, F.M., Spanedda, L., 1993. Persistence and fate of fenthion in olives and olive products. J. Agric. Food Chem. 41, 2431–2433.
- Cakir, S., Sarikaya, R., 2005. Genotoxicity testing of some organophosphate insecticides in the *Drosophila* wing spot test. Food. Chem. Toxicol. 43, 443–450.
- Fan, C.H., Tsui, L., Liao, M.C., 2011. Parathion degradation and its intermediate formation by Fenton process in neutral environment. Chemosphere 82, 229–236.
- Ferrando, M.D., Alarcon, V., Fernandezcasalderrey, A., Gamon, M., Andreumoliner, E., 1992. Persistence of some pesticides in the aquatic environment. B. Environ. Contam. Tox. 48, 747–755.
- Finlayson-Pitts, B.J., Pitts, J.N., Jr. (Eds.), 1999. Chemistry of the Upper and Lower Atmosphere. Academic Press, NYC, USA.
- Gallardo, E., Barroso, M., Margallo, C., Cruz, A., Vieira, D.N., Lopez-Rivadulla, M., 2006. Determination of parathion in biological fluids by means of direct solid-phase microextraction. Anal. Bioanal. Chem. 386, 1717–1726.
- Gao, S.K., Zhang, Y., Li, Y., Meng, J.W., He, H., Shu, J.N., 2008. A comparison between the vacuum ultraviolet photoionization time-of-flight mass spectra and the GC/MS total ion chromatograms of polycyclic aromatic hydrocarbons contained in coal soot and multi-component PAH particles. Int. J. Mass Spectrom. 274, 64–69.
- Giordano, G., Afsharinejad, Z., Guizzetti, M., Vitalone, A., Kavanagh, T.J., Costa, L.G., 2007. Organophosphorus insecticides chlorpyrifos and diazinon and oxidative stress in neuronal cells in a genetic model of glutathione deficiency. Toxicol. Appl. Pharmacol. 219, 181–189.
- Jauregui, J., Valderrama, B., Albores, A., Vazquez-Duhalt, R., 2003. Microsomal transformation of organophosphorus pesticides by white rot fungi. Biodegradation 14, 397–406.
- Karagulian, F., Rossi, M.J., 2005. The heterogeneous chemical kinetics of NO₃ on atmospheric mineral dust surrogates. Phys. Chem. Chem. Phys. 7, 3150–3162.
- Kaur, I., Mathur, R.P., Tandon, S.N., Dureja, P., 1997. Identification of metabolites of malathion in plant, water and soil by GC–MS. Biomed. Chromatogr. 11, 352–355.
- Kosikowska, M., Bizziuk, M., 2010. Review of the determination of pesticide residues in ambient air. Trac-Trend Anal. Chem. 29, 1064–1072.
- Liu, C.G., Gan, J., Zhang, Y., Liang, M., Shu, X., Shu, J.N., Yang, B., 2011. Heterogeneous reaction of suspended phosmet particles with NO₃ radicals. J. Phys. Chem. A 115, 10744–10748.
- Meng, J.W., Yang, B., Zhang, Y., Dong, X.Y., Shu, J.N., 2010. Heterogeneous ozonation of suspended malathion and chlorpyrifos particles. Chemosphere 79, 394–400.
- Minelli, E.V., Cabras, P., Angioni, A., Garau, V.L., Melis, M., Pirisi, F.M., Cabitza, F., Cubeddu, M., 1996. Persistence and metabolism of fenthion in orange fruit. J. Agric. Food Chem. 44, 936–939.
- Miyamoto, T., Yamamoto, I., 1977. Mechanism of phosphinyl disulfide formation from a phosphorodithioate ester. J. Pestic. Sci. 2, 303–310.
- Naudet, J.P., Rigaud, P., Pirre, M., 1989. Altitude distribution of stratospheric NO₃. 1. observation of NO₃ and related species. J. Geophys. Res.-Atmos. 94, 6374–6382.
- Pico, Y., Farre, M., Soler, C., Barcelo, D., 2007. Confirmation of fenthion metabolites in oranges by IT-MS and QqTOF-MS. Anal. Chem. 79, 9350–9363.
- Pina-Guzman, B., Solis-Heredia, M.J., Quintanilla-Vega, B., 2005. Diazinon alters sperm chromatin structure in mice by phosphorylating nuclear protamines. Toxicol. Appl. Pharmacol. 202, 189–198.
- Platt, U., Perner, D., Harris, G.W., Winer, A.M., Pitts, J.N., 1980. Observations of nitrous-acid in an urban atmosphere by differential optical-absorption. Nature 285, 312–314.
- Shu, J.N., Gao, S.K., Li, Y., 2008. A VUV photoionization aerosol time-of-flight mass spectrometer with a RF-powered VUV lamp for laboratory-based organic aerosol measurements. Aerosol Sci. Technol. 42, 110–113.
- Slotkin, T.A., Levin, E.D., Seidler, F.J., 2009. Developmental neurotoxicity of parathion: progressive effects on serotonergic systems in adolescence and adulthood. Neurotoxicol. Teratol. 31, 11–17.
- Snawder, J.E., Chambers, J.E., 1989. Toxic and developmental effects of organophosphorus insecticides in embryos of the South African clawed frog. J. Environ. Sci. Health B 24, 205–218.
- Tsakirakis, A., Machera, K., 2007. Determination of fenthion and oxidation products in personal protection equipment by gas chromatography. J. Chromatogr. A 1171, 98–103.

- van den Berg, F., Kubiak, R., Benjey, W.G., Majewski, M.S., Yates, S.R., Reeves, G.L., Smelt, J.H., van der Linden, A.M.A., 1999. Emission of pesticides into the air. *Water Air Soil Pollut.* 115, 195–218.
- Vonderheide, A.P., Meija, J., Montes-Bayon, M., Caruso, J.A., 2003. Use of optional gas and collision cell for enhanced sensitivity of the organophosphorus pesticides by GC–ICP–MS. *J. Anal. Atom. Spectrom.* 18, 1097–1102.
- Wu, C.L., Linden, K.G., 2008. Degradation and byproduct formation of parathion in aqueous solutions by UV and UV/H₂O₂ treatment. *Water Res.* 42, 4780–4790.
- Yan, D.Y., Jiang, X., Xu, S.H., Wang, L.G., Bian, Y.R., Yu, G.F., 2008. Quantitative structure-toxicity relationship study of lethal concentration to tadpole (*Bufo vulgaris formosus*) for organophosphorous pesticides. *Chemosphere* 71, 1809–1815.
- Yang, B., Meng, J.W., Zhang, Y., Liu, C.G., Gan, J., Shu, J.N., 2011. Experimental studies on the heterogeneous reaction of NO₃ radicals with suspended carbaryl particles. *Atmos. Environ.* 45, 2074–2079.
- Yaws, C.L. (Ed.), 1999. *Chemical Properties Handbook*. McGraw-Hill, Columbus.
- Zhang, Y., Yang, B., Meng, J.W., Gao, S.K., Dong, X.Y., Shu, J.N., 2010a. Homogeneous and heterogeneous reactions of phenanthrene with ozone. *Atmos. Environ.* 44, 697–702.
- Zhang, Y.Y., Xiao, Z.Y., Chen, F., Ge, Y.Q., Wu, J.H., Hu, X.S., 2010b. Degradation behavior and products of malathion and chlorpyrifos spiked in apple juice by ultrasonic treatment. *Ultrason. Sonochem.* 17, 72–77.