Heterogeneous ozonation of suspended malathion and chlorpyrifos particles

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ABSTRACT

The heterogeneous ozonation of suspended malathion and chlorpyrifos particles are studied in real-time with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS). The pesticide particles with the diameter of hundreds of nanometers are generated by the homogeneous nucleation method using azelaic acid as nucleus. The reactions are carried out in an aerosol reaction chamber under ambient pressure (1 atm) and room temperature (298 K), respectively. The time-of-flight mass spectra of the solid-state ozonation products of malathion and chlorpyrifos are obtained. The assignments of the mass spectra reveal that the major ozonation products of malathion particles are *s*-(1,2-diethoxycarbonyl)ethyl-O,O-dimethylphosphorothioate (malaoxon), 2-mercapto-succinic acid diethylester, 1,2-dicarbethoxyethyl-dimethoxyphosphinyldisulfide and bis(1,2-bis-ethoxycarbonyl-ethyl)disulfide. The experimental results reveal that water vapor can enhance the formation of malaoxon, 2-mercapto-succinic acid diethylester and bis(1,2-bis-ethoxycarbonyl-ethyl)disulfide. In the case of chlorpyrifos, the sole ozonation product observed is 3,5,6-trichloro-2-pyridyl-diethylphosphate (chlorpyrifos oxon). The pathways of heterogeneous ozonation of malathion and chlorpyrifos particles are proposed. The atmospheric lifetimes of malathion and chlorpyrifos particles towards ozone reaction are estimated based on the time-dependent mass spectrometric signals obtained.

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1. Introduction

The wide use of organophosphorous pesticides has led to severe contamination of the environment. The atmosphere is considered as an important medium for dispersion of organophosphorus pesticides (Van Dijk and Guicherit, 1999; Van Pul et al., 1999). They can be released into atmosphere directly by spraying during application and indirectly via evaporation or soil erosion (Van den Berg et al., 1999; Gil and Sinfort, 2005; Luo and Zhang, 2009). The organophosphorus pesticides in the atmosphere exist in gas-phase or adsorbed on atmospheric particles depending on their physicochemical properties (Atkinson et al., 1999; Bedos et al., 2002). Besides wet and dry deposition, the organophosphorus pesticides can be removed via reactions with nitrate radicals (NO_3), hydroxyl radicals (OH) and ozone, as well as the direct photolysis during the atmospheric transport (Atkinson et al., 1999; Sabljic and Peijnenburg, 2001). These chemical conversions strongly affect the toxic properties and transport distances of the organophosphorus pesticides in the atmosphere (Van Pul et al., 1999). However, data on their atmospheric fate especially in the particle phase are limited (Atkinson et al., 1999).

Malathion and chlorpyrifos are two widely used organophosphorus pesticides. Both of them are toxic to humans. Exposure to

them could lead to acute cholinergic poisoning and affect the central nervous system (Jamal, 1997). In the environment, the thiophosphoryl bonds ($\text{P}=\text{S}$) of malathion and chlorpyrifos can be oxidized to their corresponding ($\text{P}=\text{O}$) oxons by various oxidizing agents such as ozone, dinitrogen tetroxide, peracid and chlorine (Berkelhammer et al., 1963; Bellet and Casida, 1974; Ohashi et al., 1994; FinlaysonPitts and Pitts, 1997; Duirk et al., 2008). Chlorpyrifos oxon, the transformation product of chlorpyrifos, has been detected in the atmosphere (Aston and Seiber, 1997; Le-Noir et al., 1999; Goel et al., 2007). The corresponding oxons are substantially more toxic, typically more potent in inhibition of acetylcholinesterase (AChE) than their parent compounds (Ryan and Fukuto, 1985; Wu and Laird, 2003; Kralj et al., 2007). There are extensive studies on the oxidation of malathion and chlorpyrifos in the soil and water (Mulla et al., 1981; Miles and Takashima, 1991; Racke, 1993). Besides oxidation, the hydrolysis reaction can also take place during the degradation of malathion and chlorpyrifos and play an important role in their degradation in soil (Mulla et al., 1981; Miles and Takashima, 1991; Racke, 1993) and water (Mulla et al., 1981; Liu et al., 2001; Pehkonen and Zhang, 2002; Duirk et al., 2008). In the atmosphere, gas-phase malathion can be oxidized to malaoxon by atmospheric oxidants such as ozone, nitrate radicals and OH radicals (Brown et al., 1993). Malathion and chlorpyrifos can also be found in the particle phase in the atmosphere (Vincent et al., 1997; Van Dijk and Guicherit, 1999) due to their low vapor pressures (1.78×10^{-4} Pa for malathion

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and 2.5×10^{-3} Pa for chlorpyrifos at 25 °C, respectively (Tomlin, 2006)). However, no data on the oxidation of malathion and chlorpyrifos particles in the atmosphere are available.

Ozone is one of the most common atmospheric oxidants and plays an important role in the chemistry of the atmosphere (Ade-niji et al., 1981). The annual average background ozone concentrations over the midlatitude of the Northern Hemisphere range between 20 ppb and 45 ppb (Vingarzan, 2004) and it is present during day and night. Ozone can react with many organic compounds, such as unsaturated hydrocarbons, aromatics and sulfur-containing organics in the atmosphere (Atkinson and Carter, 1984; Ljubic and Sabljic, 2002).

In this paper, the heterogeneous ozonation of suspended malathion and chlorpyrifos particles by gaseous ozone is investigated utilizing a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) under the pseudo-first-order conditions in an aerosol reaction chamber. The VUV-ATOFMS is an instrument developed for analyzing the chemical composition of suspended organic particles on-line (Shu et al., 2008). Combining with gas chromatography, the electron-impact mass spectrometer is used to identify organics. However, the mass spectra of complex organic aerosols obtained with aerosol mass spectrometer equipped with an electron-impact ionizer are usually too complicated to identify organics. Utilizing a VUV photoionization source, the VUV-ATOFMS is capable of acquiring mass spectra of organic particles with less fragments or even fragment free, which are easier to assign than the ones obtained with an electron-impact source (Shu et al., 2008; Gao et al., 2009). The real-time analysis of the solid-state products is conducted and reaction products are speculated based on the mass spectra obtained. The pathways of heterogeneous ozonation of malathion and chlorpyrifos particles are proposed in the paper.

2. Experimental

The experimental setup has been described in detail elsewhere (Gao et al., 2009; Meng et al., 2009). Briefly, the aerosol 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 volume of the reaction chamber is $\sim$ 200 L when the film bag is fully filled. A small fan is set at the bottom of the aerosol reaction chamber to mix the reactants quickly. Prior to each experiment, the reaction chamber is rinsed with ethanol, dried with hot air and then filled with filtered air. The relative humidity in the chamber is estimated to be $\sim$ 5% due to the residual filtered ambient air in the chamber. The size distribution of the particles is measured with a scanning mobility particle sizer (SMPS) composed of a differential mobility analyzer (DMA, TSI model 3081) and a condensation particle counter (CPC, TSI model 3776). Ozone is generated with an ozone generator (NIPPON, model NPF8 W). Pure O₂ (99.99%) is used as discharging gas. The flow of discharging gas is maintained at 5 L min⁻¹. The concentration of ozone in the reaction chamber is controlled by adjusting the feed-in time of the discharged gas and detected with an ozone monitor (2B technologies Inc., model 201 M). The VUV-ATOFMS used to analyze the malathion, chlorpyrifos and their ozonation products is home-built. Its detailed description has been given elsewhere (Shu et al., 2008). Only information directly related to the present work is described here. The sample rate of the VUV-ATOFMS is 1.3 cm³ s⁻¹. An 8 mm diameter copper rod coupled to a cartridge heater driven by a DC power supply is used to vaporize organic particles. The heater temperature is $\sim$ 400 K. The vapor generated from particles is photoionized with light radiated from a home-assembled RF-powered VUV lamp. Then, the ions produced by VUV photoionization are de-

tected with a reflectron mass spectrometer. The reflectron mass spectrometer is characterized with a field-free flight distance of 1.4 m, an ion mirror and a chevron multichannel plate detector.

The suspended malathion or chlorpyrifos particles with azelaic acid as nucleus are generated by the homogeneous nucleation method. The aerosol generator consists of two tandem 3 cm (outer diameter) $\times$ 40 cm (length) quartz tubes equipped with heating tapes and thermometers. About 0.2 g azelaic acid used to generate nucleus is put in a small boat-shaped ceramic container positioned at the center of the first quartz tube. Azelaic acid is chosen as the nucleus because it has little reactivity with ozone (Kwamena et al., 2007). The temperature of the first quartz tube is set at 413 K. Fig. 1 shows the size distributions of the azelaic acid particles (line with open circles) in the aerosol reaction chamber after $\sim$ 20 min filling. Meanwhile, $\sim$ 0.1 g malathion or chlorpyrifos used to coat the azelaic acid nucleus is placed into the center of the second quartz tube. The temperature of the second tube is set at 358 K for malathion and 385 K for chlorpyrifos, respectively. The particle concentration and coating thickness are controlled by adjusting the temperature of the quartz tubes during the experiments. Pure nitrogen passes through the two tubes sequentially at a volumetric flow of $\sim$ 0.5 L min⁻¹. The temperature of each quartz tube is optimized to produce particles with expected size and mass concentration to meet the detection limit of the VUV-ATOFMS. Fig. 1 shows the size distributions of the malathion (line with triangles) and chlorpyrifos (line with closed circles) coated azelaic acid particles in the aerosol reaction chamber measured with SMPS before the ozone injection. The size distribution of the pure azelaic acid particles has a mean diameter of 148 nm and the mass concentration of azelaic acid particles is $\sim$ 779 μ g m⁻³. The density of azelaic acid is 1.2 g cm⁻³ (Lide and Milne, 1994). The size distributions of the malathion and chlorpyrifos coated particles shift to the mean diameters of 216 nm and 376 nm. The mass concentrations of malathion and chlorpyrifos coated particles are $\sim$ 1308 μ g m⁻³ and $\sim$ 2744 μ g m⁻³ respectively. The densities of malathion and chlorpyrifos are 1.2 g cm⁻³ and 1.4 g cm⁻³ (Tomlin, 2003), respectively. On the assumption that the azelaic acid core is spheric and the pesticide coating is uniform, the masses of particulate malathion and chlorpyrifos are estimated roughly at $\sim$ 179 μ g and 521 μ g in the $\sim$ 200 L reaction chamber. The masses of saturated malathion and chlorpyrifos vapor in the reaction chamber are estimated at $\sim$ 4.7 μ g and $\sim$ 70.5 μ g according the pesticide vapors mentioned above and the equation $PV = nRT$. This ensures that the concentra-

Fig. 1. Particle size distributions of azelaic acid (line with open circles), malathion (line with triangles), and chlorpyrifos (line with closed circles) particles measured by SMPS.

tion of particulate pesticides in the reaction chamber is higher compared to corresponding concentrations in the gas-phase.

Chlorpyrifos (~99.5%, Dikma Inc. Beijing), malathion (~99.5%, Dikma Inc. Beijing), azelaic acid (99%, China North Region Special Chemical Reagent Development Center), oxygen (99.99%, Beijing Huayuan Gas Chemical Industry Co. Ltd.) and nitrogen (99.99%, Beijing Huayuan Gas Chemical Industry Co. Ltd.) are used in the experiment.

3. Results and discussion

The time-of-flight mass spectrum of malathion particles and the molecular structure of malathion ($C_{10}H_{19}O_6PS_2$, mol. wt. 330 Da) are shown in Fig. 2A. The mass spectrum of malathion particles is acquired before ozone is injected into the reaction chamber. The acquisition time for the mass spectrum is 30 s. The prominent mass peak is at m/z 173. The intensities of all the mass peaks are normalized to the mass peak at 173. The mass peak at m/z 330 is assigned to the molecular ion of malathion. The mass peaks at m/z

Table 1

The intensities and assignments of the mass peaks of malathion and its ozonation products. The symbol η stands for the relative intensities of the mass peaks shown in Figs. 2A, 3A and 3B.

m/z	Ions	η		
		Malathion ^a	Products ^b	Products ^c
410	$C_{16}H_{26}O_8S_2^+$		0.008	0.016
346	$C_{10}H_{19}O_7PS_2^+$		0.004	0.005
330	$C_{10}H_{19}O_6PS_2^+$	0.046		
314	$C_{10}H_{19}O_7PS^+$		0.007	0.020
284	$C_8H_{13}O_5PS_2^+$	0.026		
268	$C_8H_{13}O_6PS^+$		0.008	0.016
256	$C_7H_{13}O_4PS_2^+$	0.005		
204	$C_8H_{12}O_4S^+$		0.015	0.021
173	$C_8H_{13}O_4^+$	1.000		
158	$C_2H_7O_2PS_2^+$	0.031		

All of the peak intensities are normalized to the mass peak at m/z 173.

^a Mass peaks in Fig. 2A.

^b Mass peaks in Fig. 3A.

^c Mass peaks in Fig. 3B.

Fig. 2. (A) TOF mass spectrum of malathion particles, (B–D) TOF mass spectra of the ozonation products of malathion particles acquired 20, 40 and 60 min after the ozone injection. The acquisition time for each mass spectrum is 30 s. The intensities of all mass peaks are normalized to the mass peak at m/z 173.

m/z 158, 173, 256 and 284 are assigned to the daughter ions of malathion $C_2H_7O_2PS_2^+$, $C_8H_{13}O_4^+$, $C_7H_{13}O_4PS_2^+$ and $C_8H_{13}O_5PS_2^+$. The ion $C_8H_{13}O_4^+$ (m/z 173) results from the simple cleavage of the C–S bond of malathion during the VUV photoionization. Malathion loses 2-butenedioic acid (Z)-, diethyl ester ($C_8H_{12}O_4$), formic acid, ethyl ester ($C_3H_6O_2$) and ethanol (C_2H_6O) forming $C_2H_7O_2PS_2^+$ (m/z 158), $C_7H_{13}O_4PS_2^+$ (m/z 256) and $C_8H_{13}O_5PS_2^+$ (m/z 284) during the VUV photoionization, respectively. The small mass peaks at m/z 220 and 223 (Fig. 2) are the background noise of VUV-ATOFMS which appears during the experiments. The mass peak at m/z 152 is contributed from the azelaic acid nucleus and is not discussed in the paper. The tentative assignments of the mass peaks discussed above are listed in Table 1.

The time-of-flight mass spectra of solid-state ozonation products of malathion particles are shown in Fig. 2B–D, which are acquired 20, 40 and 60 min after ozone is injected into the reaction chamber. The acquisition time for each spectrum is 30 s. Each spectrum is normalized with the intensity of the mass peak at m/z 173. The initial concentration of ozone is ~95 ppm (2.6×10^{15} molecule cm^{-3}). The main mass peaks of the ozonation products of malathion particles located at m/z 204, 206, 268, 314, 346 and 410 arise 20 min after ozone is injected into the reaction chamber (Fig. 2B). The intensities of the mass peaks of the ozonation products increase with the reaction time. The mass peaks at m/z 314 and 346 are assigned to malaoxon ($C_{10}H_{19}O_7PS$, mol. wt. 314 Da) and 1,2-dicarbethoxyethyl-dimethoxyphosphinyldisulfide ($C_{10}H_{19}O_7PS_2$, mol. wt. 346 Da), respectively. Malaoxon and 1,2-dicarbethoxyethyl-dimethoxyphosphinyldisulfide were reported as products of oxidation of malathion by Bellet and Casida (1974). Miyamoto and Yamamoto (1977) also reported the similar analogues from the oxidation of O,O-diethyl-s-(4-chlorophenyl)phosphorodithioate. Malaoxon, the main oxidation product of malathion, was observed in the ozonation and the degradation of malathion in water and soil (Laplanche et al., 1984; Reynolds et al., 1989; Miles and Takashima, 1991; Bavcon et al., 2003; Ikehata and El-Din, 2005; Bavcon Kralj et al., 2007; Zhao and Hwang, 2009). The mass peak at m/z 268 is assigned to $C_8H_{13}O_6PS^+$, the malaoxon daughter ion after losing ethanol (C_2H_6O) group during the VUV photoionization. The mass peaks at m/z 204 and 410 are tentatively assigned to 2-mercapto-succinic acid diethylester ($C_8H_{14}O_4S$, mol. wt. 206 Da) and bis(1,2-bis-ethoxycarbonyl-ethyl)disulfide ($C_{16}H_{26}O_8S_2$, mol. wt. 410 Da), respectively. 2-Mercapto-succinic acid diethylester may form $C_8H_{12}O_4S^+$ (m/z 204) by losing one hydrogen molecule during the VUV photoionization. There is also a minor mass peak at m/z 206, which may be

contributed from the molecular ion of 2-mercapto-succinic acid diethylester directly. 2-Mercapto-succinic acid diethylester was reported as an environmental transformation product of malathion (Brown et al., 1993). Bis(1,2-bis-ethoxycarbonyl-ethyl)disulfide may be produced by the oxidation of 2-mercapto-succinic acid diethylester, which is similar to the formation of bis(4-chlorophenyl)disulfide observed in the oxidation of O,O-diethyl-s-(4-chlorophenyl)phosphorodithioate (Miyamoto and Yamamoto, 1977). The minor mass peaks at m/z 160, 188, 236, 254 and 283 cannot be assigned.

In order to evaluate the influence of water vapor on the heterogeneous ozonation of malathion particles, additional experiments are conducted under extremely dry (RH < 1% estimated) and wet (RH ~ 80% measured) conditions. In the experiment with the extremely dry condition, nitrogen is used as the balance gas in the reaction chamber. The RH in the reaction chamber is estimated as <1% under this condition. In the experiment with high RH, the reaction chamber was injected with filtered water vapor and the RH in the reaction chamber is measured with a hygrometer. Fig. 3A and 3B show the time-of-flight mass spectra of solid-state ozonation products of malathion particles obtained under RH < 1% and RH ~ 80%, respectively. The relative intensities of the mass peaks (Fig. 3) are listed in Table 1. Compared with Fig. 3A, the relative intensities of the mass peaks at m/z 204, 314 and 410 shown in Fig. 3B are greatly enhanced under the extremely wet condition (Table 1). The relative intensities of mass peaks at m/z 204, 314 and 410 are increased by 40%, 200% and 100% under the high RH condition, respectively. These experimental results show that water vapor have a strong influence on the ozonation of malathion particles.

The time-of-flight mass spectra of chlorpyrifos particles ($C_9H_{11}Cl_3NO_3PS$, mol. wt. 349 Da) and its ozonation products are shown in Fig. 4. The mass spectrum of chlorpyrifos particles shown in Fig. 4A is collected before ozone is injected into the reaction chamber. The initial concentration of ozone is ~55 ppm (1.5×10^{15} molecule cm^{-3}). The time-of-flight mass spectra of the chlorpyrifos ozonation products shown in Fig. 4B and 4C are collected 30 and 60 min after the ozone injection. The acquisition time for each mass spectrum is 30 s and each mass spectrum is

Fig. 3. TOF mass spectra of the ozonation products of malathion particles under low (<1%) (A) and high (~80%) (B) RH. The mass spectra are acquired 20 min after the ozone injection and the acquisition time for each mass spectrum is 30 s. The intensities of all mass peaks are normalized to the mass peak at m/z 173.

Fig. 4. (A) TOF mass spectra of chlorpyrifos particles, (B and C) TOF mass spectra of the ozonation products of chlorpyrifos particles acquired 30 and 60 min after the ozone injection. The acquisition time for each mass spectrum is 30 s. The intensities of all mass peaks are normalized to the mass peak at m/z 314.

normalized to its most intense mass peak at m/z 314. The mass spectrum of chlorpyrifos is composed of three clusters of mass peaks (Fig. 4A). The mass peaks at m/z 349, 351 and 353 are from molecular ions of chlorpyrifos with $^{35}Cl_3$, $^{35}Cl_2^{37}Cl$ and $^{35}Cl^{37}Cl_2$, respectively. The mass peaks at 314, 316 and 318 are assigned to the daughter ions of chlorpyrifos after losing a Cl atom during the VUV photoionization. The mass peaks at m/z 208 and 210 cannot be assigned. The new mass peaks at m/z 298, 300, 333 and 335 shown in Fig. 4B and 4C arise after the ozone injection. Referring to the previous studies by Racke (1993), Glotfelty et al. (1987), Liu et al. (2001), Duirk et al. (2008) and Bellet and Casida (1974), the mass peak at m/z 333 is assigned to chlorpyrifos oxon ($C_9H_{11}Cl_3NO_4P$, mol. wt. 333 Da), which is regularly found as the transformation product of chlorpyrifos in the atmosphere (Glotfelty et al., 1987; Aston and Seiber, 1997; LeNoir et al., 1999). The mass peak at m/z 335 is contributed from chlorpyrifos oxon with one isotope ^{37}Cl atom. The mass peaks at m/z 298 and 300 are assigned to the daughter ions of chlorpyrifos oxon after losing a Cl atom during the VUV photoionization. Besides chlorpyrifos oxon, a few of new weak mass peaks from m/z 190 to 290 arise during the ozonation of chlorpyrifos (Fig. 4C), which may be contributed from some minor products formed in the ozonation processes. The relative intensities and tentative assignments of the mass peaks discussed are listed in Table 2.

It has been reported that the m-chloroperoxybenzoic acid oxidation of thionophosphorus compounds is initiated by addition of oxygen to the P=S moiety (Bellet and Casida, 1974), forming unstable phosphorus oxythionate intermediates with a cyclic P—S—O group. The unstable oxidized intermediates undergo the

Table 2

The intensities and assignments of the mass peaks of chlorpyrifos and its ozonation products. The symbol η stands for the intensities of the mass peaks shown in Fig. 4.

m/z	Ions	η	
		Chlorpyrifos ^a	Products ^b
349	$C_9H_{11}Cl_3NO_3PS^+$	0.507	
333	$C_9H_{11}Cl_3NO_4P^+$		0.210
314	$C_9H_{11}Cl_2NO_3PS^+$	1.000	
298	$C_9H_{11}Cl_2NO_4P^+$		0.128

All of the peak intensities are normalized to the mass peak at m/z 314.

^a Mass peaks in Fig. 4A.

^b Mass peaks in Fig. 4C.

rearrangement to form the stable products. The ozonation of malathion and chlorpyrifos may undergo the reaction pathways similar to the *m*-chloroperoxybenzoic acid oxidation of thiono-phosphorus compounds and the ozonation may be initiated by the attack of ozone on the P=S double bond. Based on the assignments of the mass spectra above, the mechanisms for the heterogeneous ozonation of malathion and chlorpyrifos are proposed. Fig. 5 shows the pathways of the heterogeneous ozonation of malathion. The ozonation of malathion undergoes three different pathways. Pathway I is the loss of sulfur, which yields malaoxon. This pathway is also the common pathway of the oxidation of thionophosphorous compounds. Pathway II is the formation of

1,2-dicarbethoxyethyl-dimethoxyphosphinyldisulfide through the intramolecular rearrangement of atoms.

Pathway III of the malathion ozonation is hydrolysis of the unstable phosphorus oxythionate intermediates, which is suggested by the observation of the intense signals at m/z 204 and 410. The mass peak at m/z 410 is assigned to bis(1,2-bis-ethoxycarbonyl-ethyl)disulfide ($C_{16}H_{26}O_8S_2$, mol. wt. 410 Da). It has been reported that the disulfide can be formed from oxidation of thiols (Bellet and Casida, 1974; Miyamoto and Yamamoto, 1977). Therefore, we speculate that bis(1,2-bis-ethoxycarbonyl-ethyl)disulfide observed may be produced through the oxidation of 2-mercapto-succinic acid diethylester ($C_8H_{14}O_4S$, mol. wt. 206 Da). A small mass peak at m/z 206 is observed, which may be attributed to the molecular ion of 2-mercapto-succinic acid diethylester. The intense mass peak at m/z 204 is tentatively assigned to the daughter ion of 2-mercapto-succinic acid diethylester after losing one hydrogen molecule during the VUV photoionization. Additionally, a small mass peak at m/z 142 is also observed, which can be assigned to O,O'-dimethylphosphorothioic acid, the counterpart of 2-mercapto-succinic acid diethylester formed during hydrolysis. A similar phenomenon has been observed by Miyamoto and Yamamoto (1977). Their experimental results indicate that the hydrolysis of the unstable phosphorus oxythionate intermediates might take place in the 3-chlorobenzoic acid oxidation of O,O-diethyl-s-(4-chlorophenyl)phosphorodithioate. The hydrolysis of

Fig. 5. Proposed pathways of the heterogeneous ozonation of particulate malathion.

the unstable phosphorus oxythionate intermediates results in the formation of thiol compounds, which forms bis(4-chlorophenyl)disulfide by further oxidation. The signal of bis(1,2-bis-ethoxycarbonyl-ethyl)disulfide is observed enhanced greatly under the extremely wet condition, which might be an evidence for Pathway III of the malathion ozonation. Since the formation of bis(1,2-bis-ethoxycarbonyl-ethyl)disulfide needs the collision of two 2-mercapto-succinic acid diethylester molecules, we speculate that there may be a certain amount of gas-phase 2-mercapto-succinic acid diethylester formed in the ozonation of malathion vapor (vapor pressure = 1.78×10^{-4} Pa at 25 °C). The phenomenon observed in this experiment is also consistent with the results by Warren et al. (2009) which indicate that the water vapor may react with the Crigee intermediate in the ozonation of gas-phase cyclohexane to form hydrolysis products.

Compared with malathion, the pathway of the ozonation of chlorpyrifos is very simple. Chlorpyrifos oxon is the sole product observed in the ozonation of chlorpyrifos, which corresponds to the product formed in the pathway of the sulfur loss.

The atmospheric lifetimes of malathion and chlorpyrifos particles due to reaction with ozone can be roughly estimated based on the decay rates of the reactants and the growth rates of products derived from the time-dependent mass spectrometric signals obtained in the experiment. The decay rate of malathion particles and the growth rate of malaoxon (the main ozonation product) measured are $\sim 8.0 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹. Using the formula of $\tau_{O_3} = 1/(k_{O_3} \times [O_3])$ and $[O_3] = 7 \times 10^{11}$ molecule cm⁻³ (Logan, 1985), the atmospheric lifetimes of malathion particles towards ozone reaction is ~ 18 d. The decay rate of chlorpyrifos particles and the growth rate of chlorpyrifos oxon (the main ozonation product) measured are $\sim 1.5 \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹, which corresponds to an atmospheric lifetime of ~ 9 d. Compared with the atmospheric lifetimes of the gas-phase O,O,S-trimethylphosphorodithioate (83 d, the analogue of malathion) and the O,O,O-trimethylthiophosphate (55 d, the analogue of chlorpyrifos) due to reaction with ozone (Goodman et al., 1988), the atmospheric lifetime of malathion and chlorpyrifos particles due to reaction with ozone are relatively shorter. The discrepancies between these atmospheric lifetimes may result from the different molecular structures of the analogues or the different circumstances of the reactions.

During the experiments, the high concentrations of ozone and organophosphorous pesticide particles are applied for producing the signals of ozonation products strong enough to meet the sensitivity of the VUV-ATOFMS. These experimental conditions are apparently different from those in the atmosphere, which may lead to some discrepancies in the product yields and the ozonation pathways of organophosphorous pesticides particles. Nevertheless, these experimental data provide a useful reference for understanding the ozonation mechanism of organophosphorous pesticide particles under realistic atmospheric conditions.

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