Kinetic and product study of the heterogeneous reactions of NO₃ radicals with suspended resmethrin, phenothrin, and fenvalerate particles

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HIGHLIGHTS

- ▶ Heterogeneous reactions of three typical pyrethroids with NO₃ radicals are studied.
- ▶ The effective reaction rate constants and uptake coefficients are measured.
- ▶ The reaction products are observed with VUV-ATOFMS and GC-MS.
- ▶ Molecular structures of the products and the degradation pathways are proposed.

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ABSTRACT

Resmethrin, phenothrin, and fenvalerate are the synthetic pyrethroids that have been used widely against groundling or flying insect pests both indoors and outdoors. In this study, the heterogeneous reactions of the three pyrethroid particles with NO₃ radicals are investigated with a mixed-phase relative rate method. The reactions are performed in a reaction chamber equipped with a vacuum ultraviolet photo-ionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) and an atmospheric gas analysis mass spectrometer. The uptake coefficients of NO₃ radicals on resmethrin, phenothrin, and fenvalerate particles are ~0.20, 0.04, and 0.03 respectively, calculated with a spherical shell model. And the atmospheric lifetimes of the three pyrethroid particles toward NO₃ radicals are estimated to be ~2.6, 7.5, and 9.3 h, respectively. The molecular structures of reaction products and the reaction pathways are suggested based on the measurements of VUV-ATOFMS and off-line GC-MS.

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1. Introduction

Pyrethroids are synthetic pyrethrins, which are used widely for de-insectization in agriculture and controlling mosquitoes in and around households. Due to their low avian and mammalian toxicity, the use of pyrethroids has increased greatly during the past decade with the declining use of organophosphate pesticides. However, the application of pyrethroid pesticides has brought new issues to the environment and human health. Residues in run-off from agricultural application of pyrethroids (Erstfeld, 1999), have potentially resulted in exposure of aquatic lives to harmful levels in water and sediment (Weston et al., 2004, 2005). Exposure to pyrethroids can cause dermal irritation and paresthesia for its prolongation of sodium channel currents in the nervous system (Cagen et al., 1984), and induce pronounced repetitive activity characterized grossly by tremor, hypersensitivity, choreoathetosis, and salivation (Miyamoto et al., 1995). Most agricultural pyrethroids have low vapor pressures, around 10⁻³ h Pa at an ambient

temperature (Laskowski, 2002). Thus, pyrethroids mainly exist in condensed phase after they are emitted into the atmosphere (Atkinson et al., 1999) through spray drift from treatments and post-application emissions including volatilization and wind erosion (Van den Berg et al., 1999; Kosikowska and Biziuk, 2010). Pyrethroids adsorbed on atmospheric interfaces will interact with solar irradiation and atmospheric oxidants, such as hydroxyl (OH) radicals, ozone (O₃), and nitrate (NO₃) radicals (Atkinson, 2007), yielding products that may still pose health and environmental concerns (Segal-Rosenheimer and Dubowski, 2007, 2008).

The NO₃ radical is an important oxidant and controls the chemistry of the nighttime troposphere (Wayne et al., 1991). In urban polluted environments nighttime NO₃ concentrations can reach up to 400 ppt (i.e. ~9.9 × 10⁹ molecules cm⁻³) (Pitts et al., 1984; Brown et al., 2006). Rural concentrations less than 10 ppt and up to 34 ppt (i.e. 2.4 × 10⁸–8.4 × 10⁹ molecules cm⁻³) have been reported (Heintz et al., 1996; Geyer et al., 2001; McLaren et al., 2004). The higher atmospheric abundance of NO₃ radicals can render its heterogeneous oxidation pathway atmospherically important and competitive to OH radicals (Knopf et al., 2011). Indoors, given the absence of direct sunlight, NO₃ radicals may be of

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Table 1

Structures and vapor pressures (VPs) of resmethrin, phenothrin, and fenvalerate.

Pyrethroid	Formula	Structure	MW	VP (Pa, 25 °C)
Resmethrin	C ₂₂ H ₂₆ O ₃		338.4	1.0 × 10 ⁻⁵ (Ref. 1)
Phenothrin	C ₂₃ H ₂₆ O ₃		350.5	2.5 × 10 ⁻⁴ (Ref. 2)
Fenvalerate	C ₂₅ H ₂₂ ClNO ₃		419.9	2.0 × 10 ⁻⁷ (Ref. 3)

Ref. 1 is NPIC, 1997, Ref. 2 Katagi, 2012, and Ref. 3 Adelsbach and Tjeerdema, 2003.

comparable importance to outdoors at night. The NO₃ indoor concentrations ranging from 0.15 to 18 ppt (i.e. 3.6×10^7 – 4.4×10^9 molecules cm⁻³) were measured using different models and conditions (Nazaroff and Cass, 1986; Sarwar et al., 2002; Nøjgaard, 2010). Other studies also indicated the potential key role of NO₃ in heterogeneous oxidation of particulate organic matters in a polluted urban environment (Shiraiwa et al., 2009; Kaiser et al., 2011). However, to the best of our knowledge, the heterogeneous reactions of airborne pyrethroids with NO₃ radicals have not been conducted yet.

Resmethrin (5-benzyl-3-furylmethyl (1RS,3RS;1RS,3SR)-2,2-dimethyl-3-(2-methylpropyl-1-enyl) cyclopropanecarboxylate), phenothrin ((3-phenoxyphenyl) methyl 2,2-dimethyl-3-(2-methylpropyl-1-enyl) cyclopropane-1-carboxylate), and fenvalerate (4-chloro- α -(1-methylethyl) benzeneacetic acid cyano (3-phenoxyphenyl) methyl ester) (shown in Table 1) selected as the samples in this study are the three representative kinds of pyrethroids, which are widely used in agriculture and households to control flying and crawling insects. Despite of their high insecticidal activity and low hazard potential to humans, resmethrin is classified by the US EPA as “likely to be carcinogenic to humans” (EPA, 2005). Resmethrin and phenothrin belong to the type I pyrethroids both having the chrysanthemate moiety, while fenvalerate is the classic type II pyrethroid characterized by the α -cyano group. They are all low-vapor pressure insecticides and susceptible to reside in the atmosphere in its aerosolized form or adsorbed upon atmospheric aerosols. Great efforts have been made into the studies on the three pyrethroids, which mainly focus on their toxicity activities, hydrolysis, photolysis, and their metabolites in plants, waters, and soils (Nambu et al., 1980; Samsonov and Makarov, 1996; Katagi, 2002; Sánchez-Fortún and Barahona, 2005; Suzuki et al., 2011). The aim of this study is to investigate the heterogeneous reactions of the suspended resmethrin, phenothrin, and fenvalerate particles with NO₃ radicals. The effective reaction rate constants are measured using a mixed-phase relative rate method. The reaction products are observed with VUV-ATOFMS and off-line GC-MS. The results may help to reveal the degradation processes of these pyrethroids in the atmosphere through oxidation by NO₃ radicals.

2. Experimental section

2.1. Experimental setup

The aerosol generator is an electric tubular oven comprising two tandem quartz tubes, each of which is 50 cm (length) × 4 cm (outer diameter), equipped with an independent temperature controller (from the room temperature up to 523 K). The suspended

particles are generated through homogeneous nucleation method. Azelaic acid located at the center of the first tube (433 ± 1 K for resmethrin, 443 ± 1 K for phenothrin, and 463 ± 1 K for fenvalerate) is used to produce nuclei. Pure azelaic acid particles have had similar exposure to the NO₃ radicals as pyrethroid particles and no apparent products are observed with ATOFMS. The pesticide sample in the second tube (443 ± 1 K for resmethrin and fenvalerate, 453 ± 1 K for phenothrin) is gasified and coated on azelaic acid nuclei. N₂ flows through the two quartz tubes sequentially at 0.6 L min⁻¹ bringing the nuclei into the second tube and then introducing the generated coated pesticide particles into the reaction chamber. The size and distribution of particles in the chamber are monitored with a scanning mobility particle sizer (SMPS, TSI 3080). The coating thicknesses of the suspended pesticide particles are controlled by adjusting the temperature of the quartz tubes and the flow rate of N₂. The particles used in the experiment are polydisperse: the geometric mean diameters of resmethrin, phenothrin, and fenvalerate coated particles are 390.5, 338.2, and 323.4 nm, respectively, and the corresponding geometric standard deviations of the particle size distributions are 1.6, 1.4, and 1.7. The initial mass concentrations of condensed-phase resmethrin, phenothrin, and fenvalerate in the chamber are 255.6 ± 18.8 , 146.8 ± 4.2 , and 179.7 ± 15.6 $\mu\text{g m}^{-3}$ respectively, calculated with the density of pyrethroids (1.1 g cm^{-3} for resmethrin, 1.1 g cm^{-3} for phenothrin, and 1.2 g cm^{-3} for fenvalerate). The number concentrations of the particles are measured to be $(1.1\text{--}2.0) \times 10^4$ particles cm⁻³.

The reaction chamber is a thin-walled open head stainless steel drum (50 cm (out diameter) × 60 cm (height)), covered with a thin Tedlar Polyvinyl Fluoride (PVF) film bag (50 cm (length) × 50 cm (diameter)) to maintain one atmospheric pressure in the reaction chamber. The volume of the chamber is ~200 L when the PVF bag is fully filled. The experiments are conducted under atmospheric pressure and room temperature (~298 K). The relative humidity in the chamber is estimated to be 5% due to the residual filtered air in the chamber. After the concentration of particulate pyrethroid within the reaction chamber reaches the desired value, isoprene is injected into the chamber as the reference compound. The concentration of the gas-phase isoprene is monitored with an atmospheric gas analysis mass spectrometer (QIC-20-HAL3F-RC, Hiden). The concentrations of isoprene measured in the experiments are in the range of $(2.8\text{--}4.9) \times 10^{14}$ molecules cm⁻³. When the concentration of gas-phase isoprene in the chamber becomes stable, a N₂ flow at the rate of 0.6 L min⁻¹ passes through a flask which contains N₂O₅ powder placed at room temperature, and introduces gaseous N₂O₅ continuously into the chamber during the reaction. Before the experiment, the flask containing N₂O₅ powder is kept in a liquid nitrogen Dewar. A magnetic driven stain-

less steel fan at the bottom keeps rotating during the reactions. The particles (including reactants and products) and the gas-phase isoprene are monitored synchronously by a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) (Shu et al., 2008) and an atmospheric gas analysis mass spectrometer, respectively. Since the concentration of pyrethroid particle is linear with respect to the signal intensity of the mass peak measured by VUV-ATOFMS, the decay rate of signal intensity is equal to the decay rate of pyrethroid concentration. The laboratory-built VUV-ATOFMS has been described elsewhere (Shu et al., 2008). Only a brief description is presented here. 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. The mass resolution of VUV-ATOFMS is ~ 1000 and the detection limit is $\sim 1 \mu g m^{-3}$ for the pyrethroids.

The NO_3 radicals are generated by thermal decomposition of N_2O_5 , which is synthesized by dehydrating fuming nitric acid with P_2O_5 powder (Yang et al., 2011). During the experiment, the gaseous N_2O_5 in the reaction chamber thermally decomposes into NO_2 and NO_3 radical at room temperature (Finlayson-Pitts and Pitts, 2000). The concentrations of NO_3 radicals used in the experiment are $(1.5\text{--}10.2) \times 10^9$ molecules cm^{-3} , estimated with the loss rates of isoprene ($\sim 10^{-3} s^{-1}$) and the reported reaction rate constant of isoprene with NO_3 radicals $((7.0 \pm 2.0) \times 10^{-13} cm^3 \text{ molecules}^{-1} s^{-1}$ at 298 K) (www.iupac-kinetic.ch.cam.ac.uk). The detailed calculation of the NO_3 radical concentrations with the simple box model is elaborated in Supporting Information.

2.2. GC–MS analysis

GC–MS analysis is conducted to help to identify the reaction products. 10 mg pure pesticide is scattered in a conical flask. A N_2 flow at $0.6 L min^{-1}$ introduces gaseous N_2O_5 continuously into the conical flask for ~ 5 min. After reaction, 100 mL CH_2Cl_2 is added into the conical flask and then ultrasonic-washed for ~ 3 min. A part of the solution is atomized into suspended droplets and analyzed directly with VUV-ATOFMS, as the auxiliary experiment for contrasting with the TOF mass spectra obtained from the reaction of suspended particles. The mass spectra of the products obtained from the reaction in the conical flask are similar to those from the reaction in the chamber. Meanwhile, another part of the solution is analyzed with GC–MS for products identification.

The Agilent 6890 GC–MS is equipped with a $30 m \times 0.25 mm \times 0.25 \mu m$ HP-5 capillary column and an HP-5973 quadrupole mass filter with a 70 eV electron impact ionizer. 1 μL sample is injected via the pulsed splitless mode. The injector temperature and transfer line temperature are both $280^\circ C$. The capillary column is set at $100^\circ C$ for 2 min with an increase of $15^\circ C min^{-1}$ to $130^\circ C$, $2^\circ C min^{-1}$ up to $220^\circ C$, and $10^\circ C min^{-1}$ up to $310^\circ C$. The temperature is held at $310^\circ C$ for 4 min.

2.3. Chemicals

Resmethrin (Dikma, 99.5% cis and trans), phenothrin (ACROS, 96.5%), fenvalerate (Sigma, 98.6%), azelaic acid (NRSCRD, China, 99%), isoprene (99%, Alfa Aesar), fuming nitric acid (Beijing Lisui Chemical Factory, 95%), P_2O_5 (Sinopharm Chemical Reagent Co., Ltd., 98%), and absolute ethyl alcohol (Sinopharm Chemical Reagent Co., Ltd., 99.7%) 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.

3. Results and discussion

The reactivities of the three pyrethroids toward NO_2 are verified by exposing the pyrethroid particles to NO_2 with concentration of 2.5×10^{14} molecules cm^{-3} . The pyrethroid particles are online analyzed with ATOFMS. There are no apparent new mass peaks observed after exposure to NO_2 for 10 min. Since the reaction time of the pyrethroid particles with NO_3 radicals is less than 10 min, the direct reaction between NO_2 and the pyrethroid particles is neglected in this study.

3.1. Effective rate constants

The effective rate constants of the reaction between NO_3 radicals and pyrethroid particles are studied using the mixed-phase relative rate method (Donahue et al., 2005; Hartz et al., 2007). The loss of particle-phase pyrethroids is compared with the loss of the gas-phase reference compound, using

$$\ln(C_{pyre}^a/C_{pyre0}^a) = (k_{pyre}^a/k_{ref}^g)_{eff}^m \ln(C_{ref}^g/C_{ref0}^g). \quad (1)$$

where C_{pyre}^a and C_{ref}^g are the respective concentrations of aerosol-phase pyrethroids and gas-phase reference species (molecules cm^{-3}), and C_{pyre0}^a and C_{ref0}^g are the respective initial concentrations of pyrethroid particles and gas-phase reference compound in the reaction chamber (molecules cm^{-3}). k_{pyre}^a represents the corresponding effective particle-phase reaction rate constant ($cm^3 \text{ molecules}^{-1} s^{-1}$), k_{ref}^g is the reaction rate constant of the gas-phase reference species $((7.0 \pm 2.0) \times 10^{-13} cm^3 \text{ molecules}^{-1} s^{-1}$ for isoprene at 298 K) (www.iupac-kinetic.ch.cam.ac.uk).

Whereas $\frac{\ln(C_{ref}^g/C_{ref0}^g)}{-k_{ref}^g} = \int_0^t C_{NO_3}^g dt = \overline{C_{NO_3}^g} t$ (Smith et al., 2009), Eq. (1) can be represented as Eq. (2) (Lambe et al., 2009).

$$\ln(C_{pyre}^a/C_{pyre0}^a) = -k_{pyre}^a \overline{C_{NO_3}^g} t. \quad (2)$$

Here $C_{NO_3}^g$ and $\overline{C_{NO_3}^g}$ are the time dependent and averaged concentrations of NO_3 radicals in the gas phase (molecules cm^{-3}) respectively. Therefore, the effective rate constants of particles can be determined by measuring the decay rates of particles and the gas-phase reference compound concurrently in the mixed-phase reaction.

Fig. 1 shows the plots of the measured $\ln(C_{pyre}^a/C_{pyre0}^a)$ as the function of NO_3 exposure ($\overline{C_{NO_3}^g} t$) for the three pyrethroids. Error bars represent the standard deviations of three reduplicate experiments for each pyrethroid. The wall losses ($< 5\%$) of the three pyrethroid particles are ignored in the data processing. The data points are well fitted with a linear equation ($R^2 > 0.98$). According to Eq. (2), the slopes of the fitting lines represent the effective rate constants of the pyrethroid particles. Thereby, the rate constants (k_{eff}) obtained for resmethrin, phenothrin, and fenvalerate aerosols are $(5.54 \pm 0.14) \times 10^{-12}$, $(1.61 \pm 0.03) \times 10^{-12}$, and $(1.86 \pm 0.04) \times 10^{-12} cm^3 \text{ molecules}^{-1} s^{-1}$, respectively. The uncertainty in the reaction rate of the reference compound is 28.5%, which is higher than the uncertainties due to the linear fit quality to the data. The particle's sizes and structures might also influence the effective reaction rates since the relative loss of particles decreases as the mean size increases (McNeill et al., 2008). It is obvious that the reactivity of resmethrin towards NO_3 radicals is higher than those of phenothrin and fenvalerate, which may be due to its reactive furan ring structure. Additionally, it should be stated that the effective rate constants obtained are the apparent degradation rates of the particulate pyrethroids in the presence of NO_3 radicals. The actual reaction is a complicated process which includes the gas to particle surface reaction, uptake of NO_3 radicals, diffusion of NO_3 radicals from surface to the bulk, and reactions inside of particles.

Fig. 1. Plots of $\ln(C_{\text{pyre}}^a/C_{\text{pyre0}}^a)$ versus NO_3 exposure ($\overline{C_{\text{NO}_3}^g} t$) for the reactions of NO_3 radicals with resmethrin (A), phenothrin (B), and fenvalerate (C) particles.

3.2. NO_3 uptake coefficients

The uptake coefficients (γ) of NO_3 radicals on pyrethroid particles are calculated with a spherical shell model. The core of the particle is inert to NO_3 radicals and the shell comprises multilayered pyrethroid molecules which are permeable to NO_3 radicals. The total flux of NO_3 radicals toward the particle (J_c , molecules s^{-1}) can be typically expressed as follows (Sander, 1999):

$$J_c = 4\pi R_p D_g \overline{C_{\text{NO}_3}^g} \quad (3)$$

Here R_p is the particle radius (cm). D_g is the diffusion coefficient of NO_3 radicals ($\sim 1.0 \text{ cm}^2 \text{ s}^{-1}$) under forced diffusion (Liu et al., 2012). The influence of surface NO_3 radicals on the total flux of NO_3 radicals toward the particle is neglected due to forced diffusion employed in the experiment. The total number of pyrethroid molecules consumed by NO_3 radicals during the reaction (N_{tot}) is calculated with the following equation:

$$N_{\text{tot}} = \frac{4\pi(R_p^3 - R_c^3)\rho_{\text{pyre}}N_A\eta_{\text{pyre}}}{3M_{\text{pyre}}} \quad (4)$$

Here R_c is the radius of the inner core (cm), ρ_{pyre} the pyrethroid density (1.1 g cm^{-3} for resmethrin, 1.1 g cm^{-3} for phenothrin, and 1.2 g cm^{-3} for fenvalerate), N_A the Avogadro's number, η_{pyre} the ratio of consumption (~ 0.8 in the experiment), and M_{pyre} the pyrethroid molecular weight (g mol^{-1}). Assuming that one NO_3 radical consumes one pyrethroid molecule, the uptake coefficient (γ) of NO_3 radicals on pyrethroid particles is expressed as follows.

$$\gamma = \frac{N_{\text{tot}}}{J_c t} = \frac{(R_p^3 - R_c^3)\rho_{\text{pyre}}N_A\eta_{\text{pyre}}}{3M_{\text{pyre}}R_p D_g \overline{C_{\text{NO}_3}^g} t} \quad (5)$$

Here t is the reaction time (s).

According to Eq. (5), the uptake coefficients for NO_3 radicals on resmethrin, phenothrin, and fenvalerate particles are about 0.20, 0.04, and 0.03 respectively, indicating that 20%, 4%, and 3% of the collisions between NO_3 radicals and resmethrin, phenothrin, and fenvalerate particles yield reactions. Since Eq. (5) is based on the loss of particulate pyrethroid during the reaction, the loss of pyrethroid induced by reactive intermediates and evaporation followed by oxidation might influence the uptake coefficients. However, these influences are hard to quantify under the experimental conditions. Nevertheless, the obtained uptake coefficients offer a general knowledge on the particle size-independent reactivities for NO_3 radicals towards particulate resmethrin, phenothrin, and fenvalerate.

The lifetimes of the three pyrethroid particles at the lower tropospheric concentration of NO_3 radicals at night ($5 \times 10^8 \text{ molecules cm}^{-3}$) (Atkinson, 1991; Shu and Atkinson, 1995) are calculated to be ~ 2.6 , 7.5 , and 9.3 h , respectively (the calculation of the atmospheric lifetime is described in the Supporting information). However, the real atmospheric lifetimes of the three pyrethroid particles may have a deviation due to the different concentrations of oxidants in certain places and complex morphology of atmospheric particles (Gross et al., 2009; Knopf et al., 2011; Shiraiwa et al., 2012). The degradation rates of the pyrethroid aerosol also relate to the surface area of the atmospheric particles and the availability of the pyrethroids to react with NO_3 radicals. The atmospheric lifetimes of the pyrethroids toward NO_3 radicals would be longer if the pyrethroids are trapped inside or coexist in the particles under the real atmospheric environment. And the inefficient diffusion flux of NO_3 radicals to the pyrethroid films/particles and the lower steady-state concentrations of NO_3 in the ambient air would cause the longer lifetime of pyrethroids in the environment. Assuming that every NO_3 radical uptaken on the particles could react with one pyrethroid molecule, the particles with diameter of $3\text{--}4 \mu\text{m}$ versus $0.3\text{--}0.4 \mu\text{m}$ used in this experiment, the lifetimes toward NO_3 radicals would be ~ 11 , 31 , and 39 d for resmethrin, phenothrin, and fenvalerate respectively.

3.3. Reaction products

The heterogeneous reaction products of resmethrin, phenothrin, and fenvalerate particles with NO_3 radicals are analyzed with VUV-ATOFMS and off-line GC-MS. Since there are no standard EI mass spectra of the reaction products available, the molecular structures of the reaction products are suggested based on the molecular ions obtained from VUV-ATOFMS, the EI mass spectra obtained from GC-MS, and reported degradation products of these pesticides. The suggested reaction products of the pyrethroids with NO_3 radicals are listed in Table 2.

3.3.1. Reaction products of resmethrin particles

Fig. 2A shows a typical VUV-ATOFMS spectrum of unreacted resmethrin particles before exposure to NO_3 radicals. The mass peak at m/z 338 corresponds to the parent molecular ion of resmethrin. The mass peaks at m/z 166 and 171 are its dominating daughter ions. The new mass peaks at m/z 168, 188, 354, 383, 399, 446, and 506 appear in the mass spectrum (Fig. 2B), which is acquired after exposure of 105 s to NO_3 radicals. These new mass peaks are assigned to Products I^a–VII^a of resmethrin particles reaction with NO_3 radicals (see Table 2). The EI spectra of Products I^a–IV^a are obtained by GC-MS analyses.

Table 2

Products detected and suggested based on the molecular ion peaks from VUV-ATOFMS, EI characteristic ions peaks of GC–MS analyses, and reported degradation products.

Products	Formula	<i>m/z</i>	RT	η	Ref.
Resmethrin + NO₃					
I ^a	C ₁₀ H ₁₆ O ₂	168	6.42	0.25	1, 2, 3
II ^a	C ₁₂ H ₁₂ O ₂	188	48.94	0.17	1, 2, 3
III ^a	C ₂₂ H ₂₆ O ₄	354	53.59	0.10	
IV ^a	C ₂₂ H ₂₅ NO ₆	399	54.12	0.08	
V ^a	C ₂₂ H ₂₅ NO ₅	383	–	0.08	
VI ^a	C ₂₂ H ₂₆ N ₂ O ₈	446	–	0.08	
VII ^a	C ₃₂ H ₄₂ O ₅	506	–	0.25	
Phenothrin + NO₃					
I ^b	C ₁₄ H ₁₂ O ₃	228	–	0.31	
II ^b	C ₂₃ H ₂₆ NO ₅	395	–	0.39	
III ^b	C ₂₃ H ₂₆ N ₂ O ₈	458	–	0.30	
Fenvalerate + NO₃					
I ^c	C ₁₃ H ₁₀ O ₃	214	–	0.22	4, 5, 6
II ^c	C ₁₂ H ₁₀ O ₂	186	–	0.16	7
III ^c	C ₁₃ H ₁₀ O ₄	230	–	0.31	4, 5, 8
IV ^c	C ₂₅ H ₂₁ ClN ₂ O ₅	464	59.55	0.31	

RT is the retention time (min) of the product observed by GC/MS and η represents the relative peak intensities of the mass peaks shown in Figs. 2B, 3B, and 4B. The column Ref. lists the references which reported the products. Ref. 1 is Ueda et al., 1975, 2 is the Ridlen et al., 1984, 3 is the Christopher et al., 1989, 4 is the Akhtar, 1983, 5 is the Lee, 1985, 6 is the Lee et al., 1988, 7 is the Katagi, 1992, and 8 is the Fujisawa et al., 2009. The molecular structures of the products are as shown in Fig. 5.

Fig. 2. TOF mass spectra of resmethrin aerosols, before (A) and after (B) exposure to NO₃ radicals ($\sim 1.70 \times 10^9$ molecules cm⁻³). The mass spectra are normalized to the mass peak at *m/z* 338 shown in Fig. 2A and the acquisition time for each mass spectrum is 10 s.

Product I^a is considered as chrysanthemic acid, and Product II^a is assigned as 5-benzyl-3-furylmethanol, both of which are the main metabolites of resmethrin in organisms and might be more toxic than resmethrin (Ueda et al., 1975; Ridlen et al., 1984; Christopher et al., 1989). The EI mass spectra of both Products III^a and IV^a are characterized by a mass peak at *m/z* 123 resulting from the alkyl fragment of the acid moiety, which is the typical functional group of chrysanthemates. Pyrethroid chemistry studies showed that 5-benzyl-3-furylmethyl derivatives usually undergo oxidation of the isobutenyl substituent and furan ring, and the latter is likely to be more reactive (Ueda et al., 1974; Ruzo et al., 1985). Thus, Product

Fig. 3. TOF mass spectra of phenothrin aerosols, before (A) and after (B) exposure to NO₃ radicals ($\sim 6.17 \times 10^9$ molecules cm⁻³). The mass spectra are normalized to the mass peak at *m/z* 350 shown in Fig. 3A and the acquisition time for each mass spectrum is 10 s.

Fig. 4. TOF mass spectra of fenvalerate aerosols, before (A) and after (B) exposure to NO₃ radicals ($\sim 4.93 \times 10^9$ molecules cm⁻³). The mass spectra are normalized to the mass peak at *m/z* 419 shown in Fig. 4A and the acquisition time for each mass spectrum is 10 s.

III^a is assigned as 5-benzyl-2-oxo-2,5-dihydro-3-furylmethyl chrysanthemate. Products IV^a and V^a are assigned as the nitro-Product III^a and nitro-resmethrin, respectively, based on the mass spacing of 45 Da between the nitro-products and their respective precursors. The mass spacing of 45 Da indicates one nitro group (NO₂, mol. wt 46) is added and one hydrogen atom (H, mol. wt 1) is removed at the substitution position. The nitro substitution sites of Products IV^a and V^a are speculated to be on benzene ring since the benzene ring is the active sites of the nitro substitution reaction (Atkinson and Arey, 1994). The mass spacing between Product VI^a and resmethrin is 108 Da, which may result from the 2,5-additions of one nitro group (–NO₂, mol. wt 46) and one nitrate group (–ONO₂, mol. wt 62) to the furan ring of resmethrin.

The similar additions have been reported in the NO_3 -initiated reactions of naphthalene (Sasaki et al., 1997). Product VII^a might be due to the 2,5-additions of one hydroxy group ($-\text{OH}$, mol. wt 17) and one chrysanthemate moiety ($-\text{R}$, mol. wt 151) to the furan ring in resmethrin since the mass spacing between Product VII^a and resmethrin is 168 Da. Product VII^a has not been reported in the previous literatures to our knowledge.

3.3.2. Reaction products of phenothrin particles

The TOF mass spectra of phenothrin particles shown in Fig. 3A and B are obtained before and after exposure of 120 s to NO_3 radicals. The most intense mass peak at m/z 350 shown in Fig. 3A corresponds to the molecular ion of phenothrin. The mass peak at m/z 252 is assigned to the daughter ion of phenothrin. The

three new mass peaks at m/z 228, 395, and 458 shown in Fig. 3B are assigned to the molecular ions of its Products I^b–III^b, respectively. The mass peaks at m/z 256 cannot be assigned due to the limit of our knowledge. Product I^b is speculated to be 3-phenoxybenzyl formate, which may be formed via cleavage of the $\text{C}-\text{C}(\text{O})$ bond followed by abstraction of an H atom. Product II^b is assigned to a nitro-substitution product of phenothrin according to the mass spacing of 45 Da between phenothrin and Product II^b. Similar to Product VI^a, Product III^b has a mass spacing of 108 Da to phenothrin, which suggests the additions of one nitro group ($-\text{NO}_2$, mol. wt 46) and one nitrato group ($-\text{ONO}_2$, mol. wt 62) to the isobutenyl of phenothrin. The oxidation of the isobutenyl has been reported in water and on plant foliage for phenothrin (Nambu et al., 1980).

Fig. 5. Proposed pathways for the reactions of resmethrin particles (A), phenothrin particles (B), and fenvalerate particles (C) with NO_3 radicals.

3.3.3. Reaction products of fenvalerate particles

The TOF mass spectra of fenvalerate particles shown in Fig. 4A and B are obtained before and after exposure of 140 s to NO₃ radicals. The mass peaks at *m/z* 419, 225, and 202 correspond to the molecular ions of fenvalerate and its two daughter ions. The new mass peaks at *m/z* 186, 214, 230, and 464 shown in Fig. 4B are assigned to the molecular ions of Products I^c–IV^c of fenvalerate particles, respectively. Other new mass peaks including that at *m/z* 252 shown in Fig. 4B cannot be assigned and are not discussed in this paper. Product I^c is assigned as 3-phenoxybenzoic acid (PBacid), which is a common metabolic product in soil, wheat plants, and organisms (Akhtar, 1983; Lee, 1985; Lee et al., 1988). Products II^c and III^c are speculated to be 3-phenoxyphenol and 4'-OH-PBacid respectively, both of which might be the secondary products of Product I^c since the intensities of their mass peaks increase synchronously all the way to the maximum while that of Product I^c increases at first and then decreases. Product II^c was reported as a minor photoproduct of Product I^c in water, but the detailed formation mechanism is not clear (Katagi, 1992). Product III^c was shown to be probably formed by the enzymatic oxidation of Product I^c in leaf cell and chicken liver (Akhtar, 1983; Fujisawa et al., 2009). Both Products I^c and III^c are the principle soil degradation products of fenvalerate and have a lesser accumulation potential than the parent molecule (Lee, 1985). Product IV^c is likely to be the nitro-fenvalerate. Since the OH-substitution of the phenothrin and fenvalerate in soil or plant foliage dominantly proceeds at the 2',4'-position of the 3-phenoxybenzyl moiety (Katagi, 2012), the site of the nitro-substitution is speculated to be on the phenoxy moiety and the chemical structures of Products II^b and IV^c are shown in Fig. 5.

3.4. Degradation pathways

Based on the suggested molecular structures of the reaction products, the heterogeneous reaction pathways of resmethrin, phenothrin, and fenvalerate particles with NO₃ radicals are proposed in Fig. 5.

Fig. 5A shows the reaction pathways of resmethrin particles with NO₃ radicals. The first pathway is the ester cleavage that results in the formation of corresponding acid and alcohol (Products I^a and II^a), which is a well known enzymatic hydrolysis pathway for most pyrethroids having an ester linkage in plants (Katagi, 2012). The second pathway includes the formation of Products III^a, V^a, VI^a, and VII^a, which is special for resmethrin in reaction with NO₃ radicals. And both Products III^a and V^a may react with NO₃ radicals further to produce Product IV^a.

Fig. 5B shows the three reaction pathways of phenothrin particles with NO₃ radicals, respectively producing Products I^b, II^b, and III^b. Product I^b is initiated by NO₃-induced bond cleavage and followed by abstraction of an H atom. Product II^b is the classical nitro-substitution product and Product III^b results from the additions of a NO₃ radical and a NO₂ molecule to the C=C double bond.

Fig. 5C shows the degradation pathways for the reaction of fenvalerate particles. The first pathway is the formation of Product I^c. It is speculated that the NO₃-induced cleavage of O–C(CN) bond occurs first and then the 3-phenoxybenzyl moiety generated could be finally oxidized to Product I^c via elimination of hydrogen cyanide. Product I^c may transform into Products II^c and III^c, and the similar pathway has been reported elsewhere (Akhtar, 1983; Katagi, 1992; Fujisawa et al., 2009). Product II^c might also be formed directly via the NO₃-induced 3-phenoxyphenyl cleavage from fenvalerate. The second pathway is the classic nitration pathway resulting in the formation of Product IV^c.

The nitro-substitution pathway is a typical and common reaction pathway in the reactions of NO₃ radicals with organics. The

nitro-substitution products (Products V^a, VI^a, II^b, IV^c) are observed in the title reactions. The previous studies have shown that the reaction is initiated by the electrophilic addition of NO₃ radical. Then a free NO₂ molecule is added and a HNO₃ molecule is removed (Sasaki et al., 1997; Atkinson and Arey, 1994). Ambient concentrations of NO₂ at Blodgett Forest varied from below 50 ppt (i.e. $\sim 1.2 \times 10^9$ molecules cm⁻³) to 4000 ppt (i.e. $\sim 9.8 \times 10^{10}$ molecules cm⁻³) were detected (Thornton et al., 2000). Therefore, the yield of these reaction pathways should be influenced by the NO₂ level of the local areas.

4. Conclusions

Combined online particle-phase and gas-phase chemical composition analyses with off-line GC–MS analyses, the reaction kinetics and products of resmethrin, phenothrin, and fenvalerate particles with NO₃ radicals are investigated. The effective rate constants for the corresponding heterogeneous reactions are measured for the first time in the laboratory. The experimental results indicate that the heterogeneous reactions with NO₃ radicals are an important degradation pathway for the pyrethroid particles in the atmosphere. Considering that the chemical composition and the structure of the atmospheric aerosols are much more complicated than the particles used in the experiment, there would be some discrepancies in extrapolating the experimental results into the real atmospheric environment. Nevertheless, the results in this study are helpful in understanding the atmospheric degradation of the pyrethroids.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2012.09.096>.

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