



Ozonation of trifluralin particles: An experimental investigation with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer

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ABSTRACT

The ozonation of trifluralin coated on azelaic acid particles is investigated with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer. The suspended trifluralin particles with the mean diameter of 270 nm react with ~ 100 ppm ozone in an aerosol reaction chamber under ambient pressure and room temperature (1 atm, 298 K). The time-of-flight mass spectra of the trifluralin particles and the solid state ozonides are obtained. The assignments of the mass spectra reveal that the major primary ozonides of trifluralin particles are 2,6-dinitro-*N*-propyl-*N*-propanoyl-4-(trifluoromethyl) benzamine and 2,6-dinitro-*N*-(propan-2-(and 3)-ol)-*N*-propyl-4-(trifluoromethyl) benzamine. The major secondary ozonides of trifluralin 2-ethyl-7-nitro-5-(trifluoromethyl) benzimidazole-3-oxide, 2,6-dinitro-*N*-propyl-4-(trifluoromethyl) benzenamine and 2,6-dinitro-*N*-(formyl)-*N*-propyl-4-(trifluoromethyl) benzamine are observed. The primary ozonides are directly resulted from the oxidation of *N*-propyl groups. The pathways of the primary ozonation are proposed in the paper.

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1. Introduction

Pesticides are emitted into the atmosphere directly during application and indirectly through volatilization from ground, leaf surface and water. In the atmosphere, these organics not only exist in gaseous phase, some of them, especially for those with low vapor pressure, also may attach to the surface of aerosols or form secondary aerosols [1–5]. These compounds are mainly removed from the atmosphere by dry and wet deposition and chemical reactions including photolysis and reaction with oxidants [1,6,7].

Trifluralin, a selective pre-sowing and pre-emergence herbicide, is one of the most common herbicides used to control many annual grasses and broadleaf weeds for agricultural crops [8]. Once applied in the field, trifluralin immediately volatilizes into air with a large flux before soil incorporation [9]. Seasonal trifluralin releases into the atmosphere can be as high as 25% of that applied and the maximum residues of trifluralin in the air above treated fields are in the range of 2–3 $\mu\text{g m}^{-3}$ following application [10]. Trifluralin, a persistent compound in the atmosphere [11], was found in air, rainwater and microlayer [12,13]. The particle phase of trifluralin accounted for $\sim 3\%$ of total trifluralin in the atmosphere [14].

The early studies mainly focused on the environmental fate of trifluralin under various physical and biological conditions [15–19]. These research results showed that the two *N*-propyl groups of

trifluralin are relatively reactive and the oxidation of the propyl groups resulted in the formation of the hydroxyl and carbonyl groups [18,19]. Recently, the degradation of trifluralin by Fe(II) in solution and the reaction of trifluralin with ozone in the trifluralin-contaminated soil and the OH radical in the gas phase have been reported [8,20,21]. Pierpoint et al. reported the observation of the oxidation and cleavage of the *N*-propyl groups and several ozonides in trifluralin-contaminated soil treated with ozone [20]. The photolysis of trifluralin in the gas phase and coated on the fly ash and kaolin was reported [21,22]. Ozone is one of the major oxidants in the atmosphere which can degrade many compounds. The ozonation of trifluralin absorbed on the surface of the ambient aerosol particles may affect the total environmental fate of trifluralin. However, to the best of our knowledge, no investigation on the ozonation of particle-phase trifluralin has been reported yet.

In the present study, we have conducted a real-time investigation on the ozonation of trifluralin particles with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS). The time-of-flight mass spectra of the trifluralin particles and the solid state ozonides are acquired with the VUV-ATOFMS. Combining with the previous studies on the trifluralin, the mass spectra are tentatively assigned. The major pathways of ozonation of trifluralin are proposed in the paper.

2. Experimental

The schematic diagram of the experimental setup is shown in Fig. 1. The aerosol reaction chamber consists of a cylindrical

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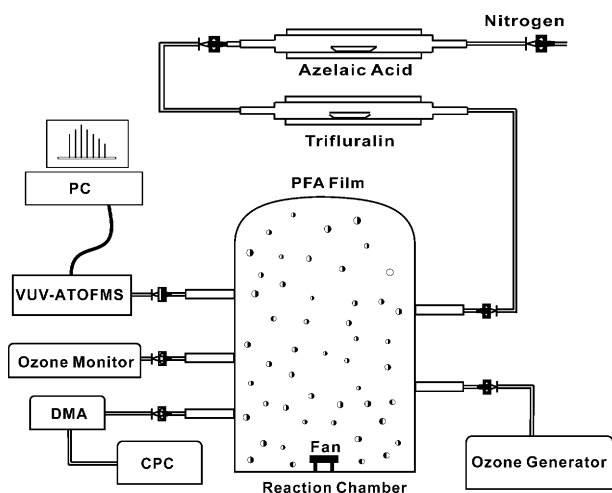


Fig. 1. Schematic diagram of the experimental set-up.

stainless steel chamber ($\varnothing 50 \text{ cm} \times \text{H}60 \text{ cm}$) and a thin perfluoroalkoxy (PFA) film ($\varnothing 51 \text{ cm} \times \text{H}50 \text{ cm}$) bag on the top of the chamber. The PFA bag is used to keep one atmospheric pressure in the aerosol reaction chamber during the experiment. 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 cleaned for several hours with filter 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 distributions and concentrations of the particles are measured with a scanning mobility particle sizer (SMPS), which is composed of a differential mobility analyzer (DMA, TSI model 3081) and a condensation particle counter (CPC, TSI model 3776). Conductive silicone tubes (TSI) are used to deliver particles between each instrument in order to minimize the wall loss of the particles during transportation. Ozone is generated with an ozone generator (NIPPON, model NPF8W). Pure oxygen (99.99%) is used as the discharging gas. The flow of the discharging gas is maintained at 5 lpm with a ball-float flowmeter. 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 201M).

The VUV-ATOFMS used to analyze the trifluralin and the ozonides is home-built and a detailed description has been given elsewhere [23]. Information only directly related to the present work is described here. A nozzle of $\sim 0.12 \text{ mm}$ orifice combined with an aerodynamic lens assembly and a three stage differential pumping system is used to sample particles directly at atmospheric pressure. The sample rate of the VUV-ATOFMS is $1.3 \text{ cm}^3 \text{ atm}^{-1} \text{ s}^{-1}$. 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 used in the experiment is $\sim 400 \text{ K}$. The vapor generated from particles is photoionized with light radiated from a home-assembled RF-powered VUV lamp. The VUV irradiation is achieved by exciting a 210 Pa mixture of 5% krypton in helium (v/v) with a copper coil driven by a 13.56 MHz RF power supply. It outputs $\sim 5 \times 10^{14}$ VUV photons per second with $\sim 30\%$ photons confined in 0.01 sr. Then, the ions produced by VUV photoionization are detected 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 cost of the VUV-ATOFMS is about US\$ 150K. The main payout is made on the purchase of the turbo pumps, the multiscaler, the RF power supply, the high voltage pulser, the pulse delay generator, and machining of the vacuum apparatus. The cost to build the VUV-ATOFMS is more expensive than buy a regular GC/MS. Never-

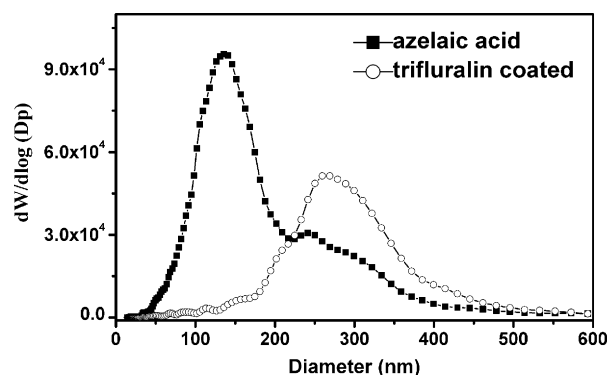


Fig. 2. Particle size distributions of azelaic acid particles and trifluralin-coated particles measured by SMPS.

theless, its capability of the on-line analysis is a good supplement to the traditional off-line analytical instruments.

The suspended trifluralin particles are generated by the homogeneous nucleation method. The aerosol generator consists of two tandem 40 cm long quartz tubes with OD 3 cm wrapped with heating tapes and equipped with 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 [24]. The temperature of the first quartz tube is at 408 K. Meanwhile, $\sim 0.1 \text{ g}$ trifluralin 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 375 K. 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 $\sim 0.5 \text{ lpm}$ controlled by a ball-float flowmeter. The temperature of each quartz tube is optimized to produce aerosol particles with the expected size and mass concentration to meet the detection limit of the VUV-ATOFMS. Fig. 2 shows the polydisperse size distributions of the generated particles measured with the SMPS. The size distribution of the pure azelaic acid particles has a mean diameter of 136 nm and the mass concentration of azelaic acid particles is $\sim 930 \mu\text{g}/\text{m}^3$. The size distribution of the trifluralin-coated particles shifts to the mean diameters of 270 nm with the mass concentration of $\sim 4900 \mu\text{g}/\text{m}^3$. The large shift of the size distributions of the trifluralin particles indicates a multilayer coating of the trifluralin on the azelaic acid nucleus.

Trifluralin ($\sim 95\%$, Kongfeng Chemical Co. Ltd., China), azelaic acid (99%, China North Region Special Chemical Reagent Development Center), 1-butanol ($>99\%$, Beijing Chemical works) and 2-butanone ($>99\%$, Beijing Chemical Works) are used in the experiment. Oxygen (99.99%) and nitrogen (99.99%) are purchased from Beijing Huayuan Gas Chemical Industry Co. Ltd.

3. Results and discussion

The time-of-flight mass spectrum of trifluralin ($\text{C}_{13}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_4$, mol. wt 335) particles is shown in Fig. 3. The mass spectrum of trifluralin particles is acquired before ozone is injected into the reaction chamber. The acquisition time for the mass spectrum is 60 s. The mass spectrum is normalized with the intensity of the mass peak at m/z 335 which is assigned to the molecular ion of trifluralin ($\text{C}_{13}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_4^+$, mol. wt 335). Other prominent mass peaks shown in Fig. 3 are at m/z 318 and 306. The minor mass peaks are at m/z 290, 277, 260, 248, and 232. The intensities and tentative assignments of the mass peaks are listed in the Table 1. The prominent fragment mass peaks at m/z 306 and 318 are assigned to $\text{C}_{11}\text{H}_{11}\text{F}_3\text{N}_3\text{O}_4^+$ (C_2H_5 lose) and $\text{C}_{13}\text{H}_{15}\text{F}_3\text{N}_3\text{O}_3^+$ (OH lose), respectively. The assignments of other minor mass peaks are speculated according to the number

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