



# Homogeneous and heterogeneous reactions of phenanthrene with ozone

Yang Zhang, Bo Yang, Junwang Meng, Shaokai Gao, Xinyu Dong, Jinian Shu\*

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

## ARTICLE INFO

### Article history:

Received 13 May 2009

Received in revised form

30 October 2009

Accepted 6 November 2009

### Keywords:

Phenanthrene

Ozonation

Homogeneous reaction

Heterogeneous reaction

Aerosol mass spectrometer

## ABSTRACT

The reactions of gas-phase phenanthrene and suspended phenanthrene particles with ozone were conducted in a 200l chamber. The secondary organic aerosol formation was observed in the reaction of gas-phase phenanthrene with ozone and simultaneously the size distribution of the secondary organic aerosol was monitored with a scanning mobility particle sizer during the formation process. The particulate ozonation products from both reactions were analyzed with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer. 2,2'-Diformylbiphenyl was identified as the dominant product in both homogeneous and heterogeneous reactions of phenanthrene with ozone. GC/MS analysis of ozonation products of phenanthrene in glacial acetic acid was carried out for assigning time-of-flight mass spectra of reaction products formed in the homogeneous and heterogeneous reactions of phenanthrene with ozone.

© 2009 Elsevier Ltd. All rights reserved.

## 1. Introduction

The homogeneous reaction of gas-phase volatile organic compounds (VOCs) and heterogeneous reaction of surface-bound organics with atmospheric oxidants such as OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> are important atmospheric chemistry processes in the troposphere. The secondary organic aerosol (SOA) that results from the homogeneous reactions of VOCs effects particle pollution directly (human health, visibility, light scattering, and light absorption) and indirectly (cloud and haze formation) (Chuong et al., 2004; Kanakidou et al., 2005; Ervens and Kreidenweis, 2007). The heterogeneous reactions of surface-bound organics alter the chemical composition and hence may change the hygroscopic and toxic properties of aerosols (Rudich, 2003).

Polycyclic aromatic compounds (PAHs) and their derivatives are mainly derived from incomplete combustion of organic compounds and fossil fuels (Herner et al., 2001; Emmenegger et al., 2005; Kou et al., 2008). Three- to four-ring PAHs are semi-volatile and these compounds partition between the gas and solid phases in the atmosphere (Sitaras et al., 2004). Five and more rings PAHs tend to be mainly associated with particles having size <1 μm (Kahan et al., 2006; Gross and Bertram, 2008; Pitts et al., 1980; Vione et al., 2004). These pollutants have received considerable research attention since they have mutagenic and carcinogenic effects on humans (Pitts et al., 1980; Kou et al., 2008). The oxidized PAH derivatives are more toxic than their parent compounds because hydrophilic molecules are

more easily reabsorbed in the alveolus (Barring et al., 2002). Thus PAHs reactions with atmospheric oxidants have been reported in the literature. Homogeneous reactions of ozone and hydroxyl radicals with low molecular weight PAHs have been investigated (Kwok et al., 1994; Atkinson and Aschmann, 1988; Wang et al., 2007). Heterogeneous ozonation was also studied with PAHs associated with different organic and inorganic substrates, such as soot, fly ash, water droplets, etc. (Murray and Singh, 1997; Kamens et al., 1985; Raja and Valsaraj, 2006; Kwamena et al., 2004; Perraudin et al., 2007a,b; Beltran et al., 1995, 1999; Kahan et al., 2006).

Three-ring member phenanthrene exists mainly in gas phase in ambient air (May and Wise, 1984; Niles and Tan, 1989; Arey et al., 1987; Helmig and Harger, 1994; Vasilakos et al., 2007) because of its high vapor pressure at room temperature ( $1.6 \times 10^{-2}$  Pa, 298 K, Osborn and Douslin, 1975). Kinetic studies and product identifications of gas-phase phenanthrene reactions with atmospheric oxidants were carried out by many groups. Kwok et al. (1994) obtained rate constants for the gas-phase reactions of phenanthrene with OH radicals and O<sub>3</sub>. Helmig and Harger (1994) investigated the OH radical-initiated reaction of gas-phase phenanthrene and identified the reaction products by high-performance liquid chromatography. Wang et al. (2007) investigated the formation of 9,10-phenanthrenequinone from the reactions of gas-phase phenanthrene with OH radicals and ozone. Though there is relatively little particle-phase phenanthrene in the atmosphere, the heterogeneous reaction of phenanthrene is of significance in atmospheric chemistry due to the potential higher efficiency of the heterogeneous reaction. Perraudin et al. measured the pseudo-first and second order rate constants for the reactions of ozone with phenanthrene adsorbed on

\* Corresponding author. Tel.: +86 010 6284 9508; fax: +86 010 6292 3563.

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

different types of particles (Perraudin et al., 2007b) and the identification of phenanthrene gas-surface heterogeneous ozonation products was also reported (Perraudin et al., 2007a).

This paper reports an investigation on the homogeneous and heterogeneous reactions of phenanthrene with ozone utilizing a vacuum ultraviolet photoionization time-of-flight aerosol mass spectrometer (VUV-ATOFMS). The reactions of gas and particulate phase phenanthrene with ozone were conducted under pseudo-first-order conditions. The SOA formation from the reaction of gas-phase phenanthrene with ozone was observed with a scanning mobility particle sizer. The time-of-flight mass spectra of the solid state ozonation products from reactions of gas and particulate phase phenanthrene with ozone were obtained with the VUV-ATOFMS. The main ozonation products were assigned via GC/MS analysis of ozonation products of phenanthrene in glacial acetic acid.

## 2. Experimental section

### 2.1. Description of the instruments

The schematic diagram of the experimental setup is shown in Fig. 1. 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 flexible PVF bag is used to keep one atmospheric pressure in the aerosol reaction chamber. The volume of the chamber is  $\sim$ 200 l when the PVF bag is fully filled. A muffle fan is set at the bottom of the aerosol reaction chamber to ensure rapid and sufficient mixing of reactants. The concentrations of gas-phase phenanthrene were measured by a gas chromatograph with a flame ionization detection (GC-FID, East & West Analytical Instruments, Inc., China), which was equipped with a coil of 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m fused silica capillary as a column. The particle size and number in the reaction chamber were measured using a scanning mobility particle sizer (SMPS, TSI 3080) equipped with a long differential mobility analyzer electrode (TSI 3081) and a condensation particle counter (CPC, TSI 3010). The organic particles were postulated to be spherical particles and its density was assumed to be 1.0 g cm $^{-3}$ . The mass concentrations of organic particles were calculated from the size distribution and the particle density. Ozone was produced by an ozone generator (Shandong NIPPON, China) with an oxygen stream of

4.0 l min $^{-1}$ . The concentration of ozone was measured with an ozone monitor (Model 202, 2B technologies Inc.). The aerosol reaction chamber was flushed with filtered air before each reaction experiment was carried out.

The VUV-ATOFMS utilized to analyze the chemical composition of particles in real-time is home-built and described in detail elsewhere (Shu et al., 2008). Therefore, only a brief description is presented here. A nozzle of  $\sim$ 0.15 mm orifice combined with an aerodynamic lens assembly and a three stage differential pumping system is used to sample particles directly at a flow rate of  $\sim$ 1.3 cm $^3$  atm s $^{-1}$  under atmospheric pressure. The particles sampled are focused into a particle beam with a diameter of  $\sim$ 1 mm by an aerodynamic lens assembly. An 8 mm diameter copper rod coupled with a cartridge heater placed in the detection chamber is used to vaporize the particles and the nascent vapor is photoionized with light radiated from a VUV lamp. The photon energy of the main output is 10 eV (123.6 nm, Kr atom resonance line) and the total photon flux output is about  $5 \times 10^{14}$  photon s $^{-1}$ . The ions generated by VUV photoionization are then detected with a reflectron mass spectrometer with a field free flight distance of 1.4 m, an ion mirror and a chevron multichannel plate detector.

### 2.2. Homogeneous reaction experiment

The phenanthrene vapor used for the homogeneous reaction was generated by heating  $\sim$ 0.5 g of phenanthrene contained in a 3 cm (inner diameter)  $\times$  40 cm (length) quartz tube at  $383 \pm 2$  K. The phenanthrene vapor was introduced into the chamber by flushing nitrogen at a constant flow rate of 1.0 l min $^{-1}$  controlled by a ball-float flowmeter. The introduction lasted  $\sim$ 180 min. The mass of the phenanthrene vapor introduced was  $\sim$ 55  $\mu$ g, which was estimated based on the GC-FID measurement of the same volume of nitrogen and phenanthrene vapor mixture prepared under the same conditions. Phenanthrene in the reaction chamber was collected by pumping the mixture through a filter containing resin (200 g Amberlite XAD-2 macroporous resin (Sigma–Aldrich)). The resin was extracted ultrasonically. The concentrated extract was measured with the GC-FID. Then ozone was added into the chamber and its initial concentration reached  $\sim$ 23.50 ppmv. The size distributions of the SOA particles were measured with the SMPS and the chemical composition of the SOA particles was analyzed with the VUV-ATOFMS.

### 2.3. Heterogeneous reaction experiment

The phenanthrene particles were generated by the homogeneous nucleation method. Two tandem 3 cm (outer diameter)  $\times$  40 cm (length) quartz tubes heated with heating tapes were used as an aerosol generator. Azelaic acid was chosen as the model nucleus because it was almost inert to ozone (Kwamena et al., 2007). A small ceramic container containing  $\sim$ 0.4 g azelaic acid was positioned at the center of the first tube. A ball-float flowmeter was used to send a volumetric flow of 0.5 l min $^{-1}$  nitrogen through the first tube containing azelaic acid. The flow then passed through the second tube containing  $\sim$ 0.4 g phenanthrene. The thickness of the phenanthrene coating was controlled by adjusting the temperature of the second tube. The temperature of two tubes was  $413 \pm 2$  K. 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  $\sim$ 285 nm and the mass concentration of azelaic acid particles was  $\sim$ 1530  $\mu$ g m $^{-3}$ . The size distributions of the phenanthrene coated particles shifted to a mean diameter of  $\sim$ 350 nm and the mass concentration was  $\sim$ 2000  $\mu$ g m $^{-3}$ . The mass of particulate phenanthrene was estimated roughly at  $\sim$ 90  $\mu$ g in the reaction chamber. Ozone was introduced into the chamber and its

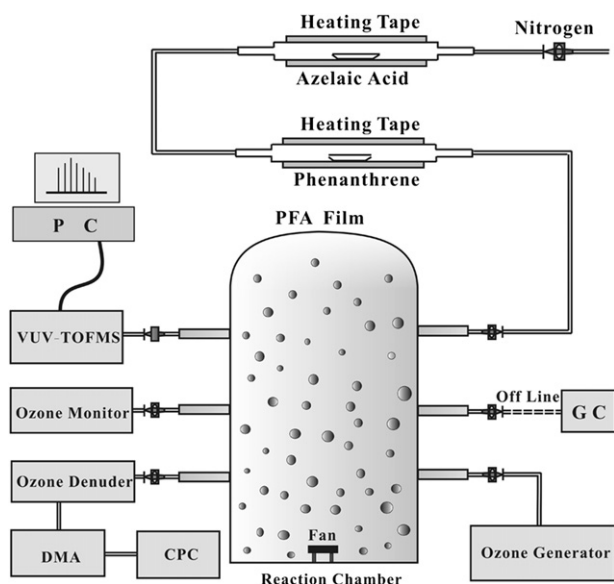


Fig. 1. Schematic diagram of the experimental setup.

Download English Version:

<https://daneshyari.com/en/article/4441246>

Download Persian Version:

<https://daneshyari.com/article/4441246>

[Daneshyari.com](https://daneshyari.com)