



## Short communication

Heterogeneous reaction of particle-associated triphenylene with NO<sub>3</sub> radicalsYang Zhang<sup>a,b,\*</sup>, Jinian Shu<sup>b</sup>, Changgeng Liu<sup>b</sup>, Yuanxun Zhang<sup>a</sup>, Bo Yang<sup>b</sup>, Jie Gan<sup>b</sup><sup>a</sup> University of Chinese Academy of Sciences, Beijing 100049, China<sup>b</sup> Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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## ABSTRACT

Although heterogeneous reactions of polycyclic aromatic hydrocarbons (PAHs) with atmospheric oxidants may be important loss processes for PAHs, our understanding of their kinetics and products is incomplete. The study of heterogeneous reaction of suspended triphenylene particles with NO<sub>3</sub> radicals is undertaken in a flow-tube-reactor. The time-of-flight mass spectra of particulate triphenylene and its nitration products are obtained with vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer. 1- and 2-nitrotriphenylene are identified by GC–MS analysis of the products formed from the reaction of NO<sub>3</sub> radicals with triphenylene coated on the inner bottom surface of a conical flask. 1-Nitrotriphenylene is formed in larger yield than 2-nitrotriphenylene. This phenomenon is different from what had been observed in previous studies of the gas-phase triphenylene nitration, showing that 2-nitrotriphenylene is the major nitration product. The experimental results may reveal the discrepancies between heterogeneous and homogeneous nitrations of triphenylene.

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## 1. Introduction

Nitro-polycyclic aromatic hydrocarbons (NPAHs) are ubiquitous pollutants found in airborne particulate matters. Their occurrence in the atmosphere could bring potential health threats to humans and animals due to their allergenic, strongly mutagenic and highly carcinogenic properties (Bonney et al., 2011; Ovreik et al., 2010; Pitts et al., 1978). Sources of NPAHs are incomplete combustion processes such as emissions from diesel and gasoline engines and biomass or coal burning (Bamford and Baker, 2003; Hien et al., 2007; Reisen and Arey, 2005; Schuetzle, 1983). Concentrations of individual particle-phase NPAHs in atmospheric samples are usually in the range of a few pg m<sup>-3</sup> for urban areas, but they can reach as high as 800 pg m<sup>-3</sup> during heavy traffic conditions (Isabel Barrado et al., 2012; Vasconcellos et al., 2008). In addition to their direct emission into the atmosphere, particle-associated NPAHs are also produced from heterogeneous reactions of parent PAHs with atmospheric oxidants such as HNO<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, and NO<sub>3</sub> radicals. Recently, it has been found that such reactions may be a significant source for atmospheric NPAHs (Karagulian and Rossi, 2007; Mak et al., 2007). Therefore, heterogeneous reactions between atmospheric oxidants and aerosol-associated PAHs

attracted considerable interest (Ammar et al., 2010; Esteve et al., 2004; Gross and Bertram, 2008; Kaiser et al., 2011; Knopf et al., 2011; Kwamena and Abbatt, 2008; Lu et al., 2011; Miet et al., 2009; Zhang et al., 2011).

Most previous studies focused on heterogeneous nitration reactions of PAHs by nitrogen-containing compounds such as HNO<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub> (Ammar et al., 2010; Carrara et al., 2010; Ma et al., 2011; Miet et al., 2009; Nguyen et al., 2009; Springmann et al., 2009). There is only limited reliable and consistent data for nitration reactions between particulate PAHs and NO<sub>3</sub> radicals. However, work by Gross and Bertram (2008) investigating the reactions of three types of solid PAHs (pyrene, fluoranthene, and benz[a]anthracene) with nitrating agents suggested that under certain atmospheric conditions, NO<sub>3</sub> radicals can be a more important sink for PAHs than NO<sub>2</sub>, HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, or O<sub>3</sub>. Therefore, NO<sub>3</sub> can impact tropospheric lifetimes of surface-bound PAHs. Further, Mak et al. (2007) report a reactive coefficient greater than 0.1 for the uptake of NO<sub>3</sub> on solid pyrene films using a coated-wall flow tube apparatus. The high reactivity observed in these studies suggests that heterogeneous reaction of PAHs with NO<sub>3</sub> may be more atmospherically important than reactions with N<sub>2</sub>O<sub>5</sub>. Thus, heterogeneous reactions with NO<sub>3</sub> radicals may be the dominant loss process of atmospheric PAHs at night and a significant source for NPAHs in the atmosphere.

Triphenylene, a 4-ring PAH, is very abundant in airborne particles. However, only few studies on the reactions of triphenylene with nitrating agents have been conducted. Gas-phase OH or NO<sub>3</sub>

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radical-initiated reactions of triphenylene were performed using a flow reactor system by Kameda et al. (2006); 1- and 2-nitrotriphenylene (1- and 2-NTP) were identified and their concentrations determined. The reaction of triphenylene with NO<sub>2</sub> in dichloromethane was conducted by Pryor et al. (1984). In addition, work by Nielsen (1984) investigated nitration of triphenylene by dinitrogen tetroxide, nitric and nitrous acid in solutions. All these studies show that 2-NTP was formed in larger yield than 1-NTP. The fact that triphenylene in the atmosphere is found mainly in condensed phase indicates the need to investigate the reactions between gas-phase nitrogen oxides and triphenylene adsorbed on or in aerosol particles. Such reactions may dramatically differ from homogeneous reactions in reaction rates, mechanisms, and products. However, heterogeneous reactions between condensed phase triphenylene and gas-phase nitrogenous species are not well documented. To our knowledge, the two studies on such reactions were performed by Ishii et al. (2000) and Zimmermann et al. (2012) up to now.

In this paper, experimental investigation on the heterogeneous reaction of triphenylene adsorbed on azelaic acid particles with NO<sub>3</sub> radicals is carried out. The particle-phase triphenylene and its reaction products are analyzed in real time with a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS). Two reaction products are observed and identified.

## 2. Experimental section

### 2.1. Chemicals

Triphenylene (97%, Acros) and azelaic acid (99%, HOOC(CH<sub>2</sub>)<sub>7</sub>-COOH, Molecular Weight 188, purchased from China North Region Special Chemical Reagent Development Center) are used in the experiment. N<sub>2</sub> (99.99%) and synthetic air are purchased from Beijing Huayuan Gas Chemical Industry Co. Ltd.

### 2.2. Aerosol generation

The aerosol generator is an electric tube furnace equipped with two tandem quartz tubes ( $l = 50$  cm,  $id = 3$  cm), each with an independent temperature controller. Azelaic acid, employed to produce nuclei due to its little reactivity with NO<sub>3</sub> radicals (Yang et al., 2011), is placed in the first tube ( $413 \pm 2$  K), while triphenylene in the second ( $393 \pm 2$  K). A volumetric flow of  $0.5 \text{ L min}^{-1}$  of N<sub>2</sub> flows through the first tube, bringing the nuclei into the second tube, where the nuclei are coated by triphenylene. The thickness of the coating is controlled by adjusting the temperature of quartz tube and flow rate of N<sub>2</sub>. The size and concentration of particles are monitored with a scan mobility particle sizer (SMPS) composed of a differential mobility analyzer (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3010). The mean diameter of pure azelaic acid particles and triphenylene coated particles is  $\sim 280$  nm and  $\sim 310$  nm, respectively. The thickness of triphenylene adsorbed on azelaic acid particles is  $\sim 15$  nm.

### 2.3. Flow-tube experiment

The flow-tube-reactor setup has been described in detail elsewhere (Zhang et al., 2011). Only a brief description is given here. The setup consists of a quartz tube ( $l = 100$  cm,  $id = 65.4$  mm) and a moveable stainless steel injector ( $l = 120$  cm,  $id = 4.3$  mm). Aerosol ( $0.5 \text{ L min}^{-1}$ ) and NO<sub>3</sub> radicals ( $0.8 \text{ L min}^{-1}$ ) flows are fed into the stainless steel injector and quartz tube, respectively. The flow-tube-reactor is operated under laminar flow condition at ambient pressure and temperature (1 atm, 298 K). The reaction

time between NO<sub>3</sub> radicals and aerosols is varied by changing the position of injector.

NO<sub>3</sub> radical is generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>, which detailed synthesizing method was given elsewhere (Zhang et al., 2011). HNO<sub>3</sub> can be formed from the reaction between N<sub>2</sub>O<sub>5</sub> and H<sub>2</sub>O. If the system contains any H<sub>2</sub>O, then HNO<sub>3</sub> may also be present. Therefore, all lines are purged with dry gas for 3 h before synthesis to minimize water contamination. The pure N<sub>2</sub>O<sub>5</sub> powder is white. If traces of yellow appeared, as arises with HNO<sub>3</sub> contamination, the sample is discarded.

A synthetic air flow ( $0.8 \text{ L min}^{-1}$ ) passes through a flask containing N<sub>2</sub>O<sub>5</sub> powder and introduces N<sub>2</sub>O<sub>5</sub> vapor into the reactor. N<sub>2</sub>O<sub>5</sub> quickly decomposes at room temperature and is in dynamic equilibrium with NO<sub>2</sub> and NO<sub>3</sub> radicals. The concentration of NO<sub>3</sub> radicals in the flow tube is estimated to be  $10^{10}$ – $10^{11}$  molecule  $\text{cm}^{-3}$ , according to heterogeneous rate constants for reactions of PAHs with NO<sub>3</sub> radicals on the order of  $\sim 10^{-12}$   $\text{cm}^{-3}$  molecule<sup>-1</sup> s<sup>-1</sup> (Liu et al., 2012) and the loss rate of triphenylene ( $K = 0.083 \text{ s}^{-1}$ , the pseudo-first-order rate coefficient, See below). The concentrations of NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> are  $\sim 10^{14}$  and  $\sim 10^{15}$  molecule  $\text{cm}^{-3}$ , respectively, according to the equilibrium constant at 298 K (Tuazon et al., 1984).

### 2.4. Product identification

The time-of-flight (TOF) mass spectra of triphenylene and its products are obtained with VUV-ATOFMS in real time. In order to assign the TOF mass spectra of products, GC-MS analysis is conducted to identify the products from the reaction of NO<sub>3</sub> radicals with triphenylene coated on the inner bottom surface of a 150 mL conical flask. The coatings are made by nitrogen-purging 2 mL of  $25 \text{ g L}^{-1}$  triphenylene/CH<sub>2</sub>Cl<sub>2</sub> solution in the conical flask. A synthetic air flow of  $0.2 \text{ L min}^{-1}$  mixed with N<sub>2</sub>O<sub>5</sub> vapor flows through the conical flask for  $\sim 3.5$  min using a 2.5-m-long Teflon tube. Then, 50 mL of CH<sub>2</sub>Cl<sub>2</sub> is added into the conical flask after the reaction stops. The solution containing the products and remained reactant is analyzed by GC-MS.

The GC-MS is a Hewlett-Packard (HP) 6890 gas chromatograph equipped with a  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$  HP-5 capillary column and an HP-5973 quadrupole mass filter with 70 eV electron impact ionizer. The chromatography conditions are the same as already reported (Zhang et al., 2011). Mass spectra for NTP analysis are drawn for ions with  $m/z = 273$  ([M]<sup>+</sup>), 243 ([M-NO]<sup>+</sup>), 226 ([M-HNO<sub>2</sub>]<sup>+</sup>), and 215 ([M-CNO<sub>2</sub>]<sup>+</sup>) to identify the NTP peaks (Svendsen et al., 1983; Zimmermann et al., 2012).

## 3. Results and discussion

Fig. 1 shows the TOF mass spectra obtained from experiments in the flow-tube-reactor. The acquisition time for each TOF mass spectrum is 20 s and all the peak intensities are normalized to its highest mass peak at  $m/z$  228. Fig. 1(A) shows the TOF mass spectrum of triphenylene particles and the mass peaks at  $m/z$  228 and 229 are contributed from molecular ions of triphenylene (C<sub>18</sub>H<sub>12</sub> mol. wt 228) and <sup>13</sup>C triphenylene (<sup>13</sup>CC<sub>17</sub>H<sub>12</sub>, mol. wt 229), while mass peaks at  $m/z$  220 and 223 may be contributed from impurities of triphenylene. Fig. 1(B) shows the TOF mass spectrum of triphenylene particles exposed to NO<sub>3</sub> for 16.3 s. The newly arising mass peak located at  $m/z$  273 is contributed from NTP (C<sub>18</sub>H<sub>11</sub>NO<sub>2</sub>, mol. wt 273), the heterogeneous reaction products.

As seen in Fig. 2, the formations of 1- and 2-NTP are clearly shown by GC-MS analysis of the products of heterogeneous reaction of triphenylene film with NO<sub>3</sub> radicals. The EI mass spectra of the products with retention time at 44.2 and 46.6 min are shown in Fig. 3(A and B), respectively. The 2-NTP/1-NTP ratio (0.46) was obtained, indicating that 1-NTP is the major product in this study.

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