Short communication

Heterogeneous reaction of particle-associated triphenylene with NO$_3$ radicals

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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$_3$ 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$_3$ 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.

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 (Bonnefoy et al., 2011; Ovrevik 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^{-3} for urban areas, but they can reach as high as 800 pg m^{-3} 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$_3$, NO$_2$, N$_2$O$_5$, and NO$_3$ 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$_3$, NO$_2$, N$_2$O$_5$ (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$_3$ 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$_3$ radicals can be a more important sink for PAHs than NO$_2$, HNO$_3$, N$_2$O$_5$, or O$_3$. Therefore, NO$_3$ 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$_3$ 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$_3$ may be more atmospherically important than reactions with N$_2$O$_5$. Thus, heterogeneous reactions with NO$_3$ 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$_3$

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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_2 in dichloromethane was conducted by Pryor et al. (1984). In addition, work by Nielsen (1984) investigated nitration of triphenylene by dinitrogen tetraoxide, 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_3 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%, $HOOC(CH_2)_7COOH$, Molecular Weight 188, purchased from China North Region Special Chemical Reagent Development Center) are used in the experiment. N_2 (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_3 radicals (Yang et al., 2011), is placed in the first tube (413 ± 2 K), while triphenylene in the second (393 ± 2 K). A volumetric flow of 0.5 L min^{-1} of N_2 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_2. 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 ~ 280 nm and ~ 310 nm, respectively. The thickness of triphenylene adsorbed on azelaic acid particles is ~ 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 L min^{-1}) and NO_3 radicals (0.8 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_3 radicals and aerosols is varied by changing the position of injector.

NO_3 radical is generated by the thermal decomposition of N_2O_5, which detailed synthesizing method was given elsewhere (Zhang et al., 2011). HNO_3 can be formed from the reaction between N_2O_5 and H_2O. If the system contains any H_2O, then HNO_3 may also be present. Therefore, all lines are purged with dry gas for 3 h before synthesis to minimize water contamination. The pure N_2O_5 powder is white. If traces of yellow appeared, as arises with HNO_3 contamination, the sample is discarded.

A synthetic air flow (0.8 L min^{-1}) passes through a flask containing N_2O_5 powder and introduces N_2O_5 vapor into the reactor. N_2O_5 quickly decomposes at room temperature and is in dynamic equilibrium with NO_2 and NO_3 radicals. The concentration of NO_3 radicals in the flow tube is estimated to be $10^{10}-10^{11}$ molecule cm^{-3}, according to heterogeneous rate constants for reactions of PAHs with NO_3 radicals on the order of $\sim 10^{-12}$ cm^{-3} molecule^{-1} s^{-1} (Liu et al., 2012) and the loss rate of triphenylene ($K = 0.083$ s^{-1}, the pseudo-first-order rate coefficient, See below). The concentrations of NO_2 and N_2O_5 are $\sim 10^{14}$ and $\sim 10^{15}$ molecule 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_3 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 g L^{-1} triphenylene/CH_2Cl_2 solution in the conical flask. A synthetic air flow of 0.2 L min^{-1} mixed with N_2O_5 vapor flows through the conical flask for ~ 3.5 min using a 2.5-m-long Teflon tube. Then, 50 mL of CH_2Cl_2 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 m $\times$ 0.25 mm $\times$ 0.25 μm 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]$^+$), 243 ([M-NO]$^+$), 226 ([M-HNO$_2$]$^+$), and 215 ([M-CNO$_2$]$^+$) 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 ($C_{18}H_{12}$ mol. wt 228) and ^{13}C triphenylene ($^{13}CC_{17}H_{12}$. 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_3 for 16.3 s. The newly arising mass peak located at m/z 273 is contributed from NTP ($C_{18}H_{11}NO_2$. 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_3 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.
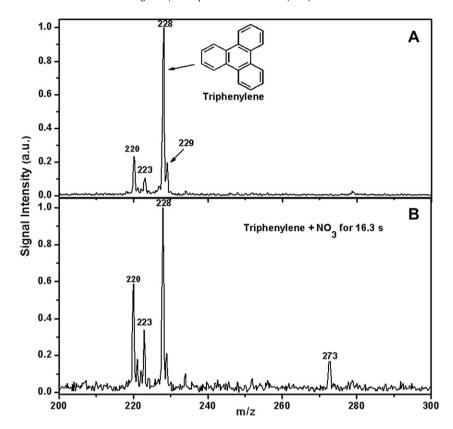
Fig. 1. Time-of-flight mass spectra of triphenylene particles (A) and its products (B) after reaction with NO$_3$ for 16.3 s. The peak intensities for each spectrum are normalized to its highest peak at *m*/*z* 228.

In contrast, previous laboratory experiments had shown that the nitration of triphenylene presents high selectivity at the 2-position (Ishii et al., 2000; Kameda et al., 2006). The 2-NTP/1-NTP ratios of 1.22 and >1.5 obtained respectively from OH and NO$_3$ radical-initiated nitration of gas-phase triphenylene suggested that 2-NTP was predominantly produced (See Table 1). These experimental results may indicate that there are some discrepancies in the nitration pathways between heterogeneous and homogeneous reactions of triphenylene. However, 2-NTP as the predominant product was identified from heterogeneous reaction of triphenylene deposited on a filter with NO$_2$/O$_3$ (Ishii et al., 2000). The difference isomers distribution may be due to much higher
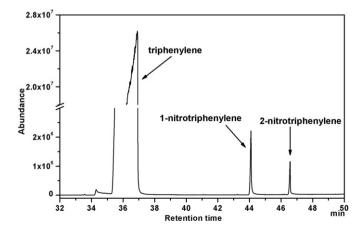
concentrations of nitrogen oxides ([TN] = [N$_2$O$_5$] + [NO$_2$] + [NO$_3$]) employed in this work (>50 ppm) than those of Ishii's (10 ppm, ignore the wall loss). Recently, work by Zimmermann et al. (2012) found that the yield of 1-NTP-d$_{11}$ (deuterated 1-NTP) was slight higher than that of 2-NTP-d$_{11}$ during the N$_2$O$_5$/NO$_3$ and NO$_3$ reactions (16.4 ppm, [TN]). It was suggested that the formations of deuterated NTPs were mainly from heterogeneous reaction by N$_2$O$_5$. In addition, 1-nitropyrene was observed as the only mononitrated product from the heterogeneous reaction of particulated pyrene with NO$_3$ radicals (>15 ppm, [TN]) by our group (Liu et al., 2012; Zhang et al., 2011). All of these researches may reveal that initial concentrations of NO$_2$, N$_2$O$_5$, and NO$_3$ radicals will alter the product distributions, especially in the case of extremely high concentrations. In this study, high concentrations of NO$_2$ and N$_2$O$_5$ were involved in the reaction, which may alter the product distributions.

Nevertheless, it has reported that the rate constants of degrading particle-bound PAHs by N$_2$O$_5$ (~2.5 × 10^{14} molecule cm^{-3}) are on the order of 10^{-18} cm^3 molecule^{-1} s^{-1} (Kamens et al., 1990), while these by NO$_3$ (~5 × 10^9 molecule cm^{-3}) are on the order of 10^{-12} cm^3 molecule^{-1} s^{-1} (Liu et al., 2012). Besides, the reported reactive uptake coefficients of N$_2$O$_5$ on PAHs surface were 4 orders of magnitude lower than compared to NO$_3$ radicals, though the concentrations of N$_2$O$_5$ is 200 times higher than that of NO$_3$ radicals (Gross and Bertram, 2008). It is therefore possible that the formations of NTPs in this study are dominantly contributed from the NO$_3$-radical reaction. In order to evaluate the possible effect of NO$_2$, triphenylene particles exposed to NO$_x$ (NO + NO$_2$) with a concentration of ~3.7 × 10^{15} molecule cm^{-3} for 1 h was investigated in a chamber, suggesting no nitrated product formation (See Supporting information). There is limited available data on heterogeneous reaction of triphenylene with N$_2$O$_5$ or NO$_3$ and the
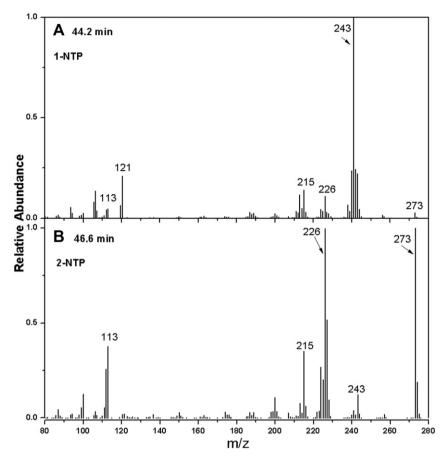

Fig. 2. GC–MS total ion chromatogram (TIC) of triphenylene and its nitration products by NO$_3$ radicals.

Fig. 3. EI mass spectra of the reaction products with retention time at 44.2 (A) and 46.6 min (B).

Table 1

Concentrations of nitrotriphenylene (NTP) in airborne particles and diesel exhaust particles (DEP) and the relative abundances of NTPs resulted from the laboratory experiments.

	1-NTP	2-NTP	2-NTP/1-NTP
Relative abundance of reaction products			
Gas-phase reaction			
OH	1[a]	1.22[a]	1.22[a]
NO$_3$	1[a]	>1.5[a]	>1.5[a]
Gas−Solid-phase reaction			
NO$_3$	1[b]	1.67[b]	1.67[b]
NO$_3$ (N$_2$O$_5$)	1[c]	~1[c]	~1[c]
NO$_3$	1[e]	0.46[e]	0.46[e]
Concentrations			
DEP (pmol mg^{-1})	2.1−7.7[a]	0.28−3.3[a]	0.37[a] (n = 4)
Osaka (fmol m^{-3})	NQ−26.4[a]	7.2−56.4[a]	>1.55[a] (n = 31)
Tokyo nighttime (ng m^{-3})	0.4−0.5[b]	0.3−0.4[b]	~0.75[b] (n = 2)
Tokyo daytime (ng m^{-3})	0.1−0.25[b]	0.25−0.4[b]	~2.5[b] (n = 2)
Riverside nighttime (pg m^{-3})	0.2−1.8[c]	0.1−0.9[c]	0.67[c] (n = 4)
Riverside daytime (pg m^{-3})	0.3−1.7[c]	0.2−1.1[c]	0.76[c] (n = 4)
Tokyo summer (pg m^{-3})	9.3[c]	6.2[c]	0.67[c] (n = 1)
Tokyo winter (pg m^{-3})	33[c]	17[c]	0.52[c] (n = 1)
Mexico city (pg m^{-3})	0.1−0.8[c]	0.2−0.6[c]	1.12[c] (n = 5)
Tokyo nighttime (ng m^{-3})	0.02−0.44[d]	0.03−0.31[d]	0.7−1.5[d] (n = 4)
Tokyo daytime (ng m^{-3})	0.01−0.04[d]	0.02−0.36[d]	2−3.6[d] (n = 4)

NQ, Not quantified.
[a] From Kameda et al. (2006).
[b] From Ishii et al. (2000).
[c] From Zimmermann et al. (2012).
[d] From Ishii et al. (2001).
[e] From this work.

mechanisms for NO$_3$−PAH surface reactions are still unclear. It is therefore difficult to explain the reason for the product distribution differences between this work and other studies (Ishii et al., 2000; Zimmermann et al., 2012). So, much more efford on NO$_3$ radicals-initiated heterogeneous reactions should be undertaken.

As listed in Table 1, 1- and 2-NTP occur widely in particles. Their ambient concentrations are influenced by emissions, meteorology, and atmospheric oxidizing capacity. 1- and 2-NTP as well as tri-phenylene were directly emitted mainly from diesel engine, they should be presented at higher levels in the daytime than in the nighttime because traffic is usually much heavier during daytime. The concentrations of NTPs obtained from Riverside were slight higher in the daytime (6.6 pg m^{-3}, $\sum$ NTPs) than in the nighttime (5.4 pg m^{-3}, $\sum$ NTPs) (Zimmermann et al., 2012). In contrast, the ambient concentrations of NTPs in Tokyo were higher in the nighttime than in the daytime (Ishii et al., 2001, 2000), probably due to atmospheric reaction of triphenylene to form NTPs.

Previous studies also showed the concentration ratios of 2-NTP/1-NTP were higher in airborne particles than in diesel exhaust particles (See Table 1), which suggest the formation of airborne NTPs, especially 2-NTP, are contributed significantly from atmo-spheric reactions. Ambient measurements showed higher value of 2-NTP/1-NTP ratio in the daytime than in the nighttime suggesting that 2-NTP is predominantly formed via the OH-chemistry in the daytime (Ishii et al., 2001, 2000; Zimmermann et al., 2012). As mentioned above, the higher concentration of NTPs occurred in the nighttime in Tokyo, while the concentration of triphenylene was much higher in the daytime than in the nighttime (Ishii et al., 2000), indicating that NTPs in the nighttime are significantly

formed from atmospheric reactions. Further, 2-NTP was reported as the predominantly product from atmospheric reactions. Thus, under the hypothesis of homogeneous gas-phase reactivity, it is easy to conclude that the concentration of 2-NTP in the nighttime should be higher than that of 1-NTP. In contrast, field observation results showed that the concentration of 1-NTP in the nighttime was much higher than that of 2-NTP (Ishii et al., 2000). The reason may be that significant amounts of airborne 1-NTP might originate from heterogeneous nitration reactions during the nighttime, as observed in this work. Beyond that, 1- and 2-NTP could undergo transformation reactions in the atmosphere, which may alter the concentration ratio on particles independently of the emission/formation rates.

In order to further understand the fate of triphenylene in atmospheric environment, the kinetics studies of heterogeneous reaction of particulate triphenylene with NO_3 radicals was conducted in the flow-tube-reactor. Fig. 4 illustrates plot of $\ln([TP]_t/[TP]_0)$ as a function of reaction time (t).

$$\ln \frac{[TP]_t}{[TP]_0} = -K \cdot t \tag{1}$$

where $[TP]_0$ and $[TP]_t$ represent the particulate triphenylene concentration at the initial and real-time during the experiment, respectively. The reactions between aerosol-associated triphenylene and NO_3 radicals are well described by first-order kinetics given the linearity of the plot (Equation (1)). The slope of the linear least-squares fit provided the pseudo-first-order rate coefficient, K. Error bars represent the standard deviation of the triplicate analysis performed every time ($n = 3$). The pseudo-first-order reaction rate of (0.083 ± 0.012) s^{-1} is obtained. The lifetime of triphenylene (τ) is calculated to be $\sim$12 s based on the rate constant according to Equation (2). It should be pointed out that the concentrations of NO_3 radicals, NO_2, and N_2O_5 greatly exceed the corresponding concentration in the ambient atmosphere, thus, more works must be carried out to make clear the product yield and kinetics of heterogeneous nitration of triphenylene.
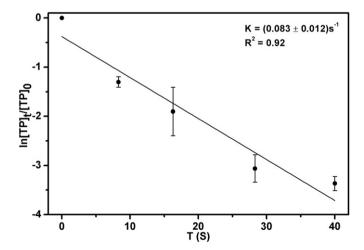
$$\tau = \frac{1}{K} \tag{2}$$

Fig. 4. Plot of $\ln([TP]_t/[TP]_0)$ versus T (reaction time) for the reaction of NO_3 radicals (10^{10}–10^{11} molecule cm^{-3}) with particulate-phase triphenylene at room temperature ($n = 3$, error bars represent the standard deviation of the triplicate analysis performed every time). Where $[TP]_0$ and $[TP]_t$ represent the particulate triphenylene concentration at the initial and real-time during the experiment, respectively.

4. Conclusion

The heterogeneous reactions of triphenylene particles with NO_3 radicals were investigated in this study. Experimental results show that the reactivity of triphenylene towards NO_x is very low when high concentration of NO_x was used. The observation of NTPs formation suggests that triphenylene in the atmosphere can be converted into NTPs via nitration reaction by NO_3 radicals. 1- and 2-NTP were identified as the products by GC–MS and 1-NTP was the major product. Heterogeneous reaction of triphenylene particles with NO_3 radicals was observed to be very fast with the pseudo-first-order rate constants of (0.083 ± 0.012) s^{-1}. These results may help improve our understanding of the chemical transformation of triphenylene particles in the atmosphere.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2012.11.052.

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