Heterogeneous reactions of particulate benzo[b]fluoranthene and benzo[k]fluoranthene with NO₃ radicals

Peng Zhang, Youfeng Wang, Bo Yang*, Changgeng Liu, Jinian Shu

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

HIGHLIGHTS

- Heterogeneous reactions of B[b]F and B[k]F with NO₃ radicals are studied.
- Reaction products of the PAHs particles are observed.
- Effective rate constants for the reactions are obtained using a relative method.
- Effective NO₃ uptake coefficients for the reactions are calculated.

ARTICLE INFO

Article history:

Received 13 April 2013

Received in revised form 19 August 2013

Accepted 22 August 2013

Available online 7 November 2013

Keywords:

Polycyclic aromatic hydrocarbons

Heterogeneous reactions

NO₃ radicals

Aerosol mass spectrometry

ABSTRACT

Benzo[b]fluoranthene (B[b]F) and benzo[k]fluoranthene (B[k]F) are widespread priority pollutants of polycyclic aromatic hydrocarbons (PAHs), which can react with atmospheric oxidants during transport in the troposphere and lead to the formation of more toxic compounds. At present, the rates of heterogeneous reactions of B[b]F and B[k]F aerosols with NO₃ radicals, an important atmospheric oxidant, are not fully understood. Thus, this study investigated the products and kinetics of heterogeneous reactions of suspended B[b]F and B[k]F particles with NO₃ radicals in an aerosol reaction chamber at room temperature (293 ± 2 K) under atmospheric pressure. The reactions are monitored online using a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) and an atmospheric gas analysis mass spectrometer. The mono-nitro-, di-nitro-, tri-nitro-products, and those products containing both nitro and ketone groups are observed with VUV-ATOFMS. The effective rate constants for heterogeneous reactions of particulate B[b]F and B[k]F with NO₃ radicals under the experimental conditions are respectively estimated to $(1.2 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(5.8 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ using a mixed-phase relative rate method, and the corresponding effective uptake coefficients are respectively estimated to 0.22 and 0.65. The lifetimes of particulate B[b]F and B[k]F at a typical concentration of NO₃ radicals ($5 \times 10^8 \text{ molecule cm}^{-3}$) in the lower troposphere during the night are estimated to 3.0 and 3.9 h, respectively. The experimental results of these heterogeneous reactions in the aerosol state provide supplementary knowledge for kinetic behaviors of airborne PAHs particles.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Benzo[b]fluoranthene (B[b]F) and benzo[k]fluoranthene (B[k]F) are among the 16 priority pollutants of polycyclic aromatic hydrocarbons (PAHs) recommended by the United States Environment Protection Agency (USEPA). Due to incomplete fossil fuel combustion and biomass burning, B[b]F and B[k]F widely occur in the environment (Zielinska et al., 2004; Xu et al., 2006; Lin et al., 2008; Watanabe and Noma, 2009; Inomata et al., 2012). The toxic equivalent factors (TEFs) of B[b]F and B[k]F are both 0.1, right following that of B[a]P (Albinet et al., 2008). In a potential toxicity risk assessment of PAHs in different types of ashes, the B[a]P-based TEF values

of B[b]F and B[k]F (13.72–45.15% and 2.88–9.61%, respectively) are substantially higher than those of other PAHs with less than 6 rings (Kong et al., 2011). In addition to B[a]P, B[b]F and B[k]F are reported among the most important PAHs emitted from coal combustion (Chen et al., 2004). B[b]F and B[k]F are also considered to be the most abundant particle-bound PAHs adsorbed on inhalable particles (PM_{2.5} and PM₁₀ fractions, particularly the latter) in urban (24.4%), rural (23.3%), and industrial areas (24.8%) (Varea et al., 2011). Therefore, B[b]F and B[k]F are important atmospheric aerosol constituents of human health concerns. More recently, the observed B[b]F and B[k]F concentrations have been respectively reported to $10100 \pm 6940 \text{ pg m}^{-3}$ and $3050 \pm 2280 \text{ pg m}^{-3}$ at the Beijing monitoring site, where B[b]F occurs at the highest level among the 9 PAHs investigated (Inomata et al., 2012). The vapor pressures of B[b]F and B[k]F are $6.7 \times 10^{-5} \text{ Pa}$ (Coover and Sims,

* Corresponding author. Tel.: +86 010 6284 9087; fax: +86 010 6292 3563.

E-mail address: boyang@rcees.ac.cn (B. Yang).

1987) and 1.3×10^{-7} Pa at 25 °C (Howard and Meylan, 1997), respectively. According to the model for gas/particle partitioning of semi-volatile organic compounds (Bidleman, 1988), B[b]F is typically distributed in both gas and particulate phases while B[k]F may mainly exist in particulate phase in the ambient atmosphere.

When transported in the troposphere, particle-phase PAHs can react with atmospheric oxidants such as NO₃ radicals, OH radicals, and O₃ (Perraudin et al., 2007; Gross and Bertram, 2008; Bedjanian and Nguyen, 2010; Zhang et al., 2011), leading to degradation of PAHs and formation of more toxic compounds such as nitro-PAHs and oxygenated PAHs derivatives (Pitts et al., 1985a,b; Umbuzeiro et al., 2008). Therefore, research of heterogeneous reactions between PAHs and atmospheric oxidants is of great importance to the understanding of PAH environmental behaviors (transportation and transformation) and their potential impacts on human health. In recent years, a large body of work has been conducted on the rates of heterogeneous reactions between condensed-phase PAHs (B[b]F and B[k]F) and gas-phase oxidants (OH, NO₂, and O₃) using different substrates such as diesel, graphite, silica, and simulated kerosene combustion soot particles (Alebic-Juretic et al., 1990; Esteve et al., 2004, 2006; Perraudin et al., 2007; Bedjanian et al., 2010). These studies show that the reactivity of PAHs tested toward OH radicals is approximately 4 orders of magnitude greater than that toward NO₂ and O₃.

As compared with other atmospheric oxidants such as NO₂ and O₃, NO₃ radicals also are a more important sink of PAHs which impact the tropospheric lifetimes of surface-bound PAHs (Karagulian and Rossi, 2005; Gross and Bertram, 2008). The mono-nitro-, di-nitro-, and poly-nitro-products as well as oxygenated products of anthracene, phenanthrene, pyrene, benzo[a]anthracene (B[a]A), anthrone, 9-nitroanthracene, 1-hydroxypyrene (1-HP), and 1-nitropyrene (1-NP) particles have been studied due to their heterogeneous reactions with NO₃ radicals (Zhang et al., 2011). The kinetics of heterogeneous reactions of B[a]A, chrysene, pyrene, 1-NP, and 1-HP particles with NO₃ radicals have recently been investigated and the corresponding effective rate constants range from 1.3×10^{-12} to 1.0×10^{-11} cm³ molecule⁻¹ s⁻¹ (Liu et al., 2012). Considering the fact listed above, although heterogeneous reactions of PAHs with NO₃ radicals may be important loss processes for PAHs, we realize that former studies focused mainly on the products and kinetics for the heterogeneous reaction of NO₃ radicals with lower molecular containing 2 and 3-ring PAH and middle molecular weight PAHs (4-ring). To our knowledge, few studies have investigated the heterogeneous reaction between NO₃ radicals and higher molecular weight PAHs (5-, 6-, and 7-ring) particles such as B[b]F and B[k]F, which shows that our understanding of their kinetics and products is incomplete. To fill this gap, it is necessary to clarify their chemical conversion during the heterogeneous reaction process occurring in the atmospheric environment.

To this end, this study focus on heterogeneous reactions of suspended B[b]F and B[k]F particles with gas-phase NO₃ radicals in an aerosol reaction chamber. The reactions are monitored online using a vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) and an atmospheric gas analysis mass spectrometer, and the reaction products are observed with VUV-ATOFMS and gas chromatography-mass spectrometry (GC-MS). The effective rate constants and uptake coefficients for heterogeneous reactions of particulate B[b]F and B[k]F with NO₃ radicals are obtained using a mixed-phase relative rate method.

2. Materials and methods

2.1. Experimental setup

The experimental setup mainly consists of an aerosol reaction chamber, a laboratory-built VUV-ATOFMS (Shu et al., 2008), and

an atmospheric gas analysis mass spectrometer (QIC-20-HAL3F-RC, Hiden). The 120-L reaction chamber is comprised of a thin-walled open head stainless steel drum (50 cm outside diameter, 60 cm height) and a thin Tedlar polyvinyl fluoride film bag (50 cm diameter, 50 cm height). A magnetically driven stainless steel fan is set at the bottom of the reaction chamber to ensure rapid mixing of the reactants during the reaction. Before each experiment, the reaction chamber is rinsed with absolute ethanol, dried with hot air, and then filled with filtered air. The relative humidity is estimated to ~10% with the residual filtered ambient air in the chamber. The experiment is conducted at room temperature (293 ± 2 K) under atmospheric pressure.

The VUV-ATOFMS is used to monitor PAH particles (Shu et al., 2008). Briefly, aerosol particles are loaded into the VUV-ATOFMS under atmospheric pressure with a 3-stage differential pumping system. An 8-mm diameter copper rod coupled with a cartridge heater (~520 K) is placed in the detection chamber to vaporize the particle, and the nascent organic vapor is photoionized with a VUV light lamp. The photon flux is $\sim 5 \times 10^{14}$ photons s⁻¹ and the photon energy is 10 eV. Each ATOFMS took 10 s for acquisition and 1 s for saving data files.

The atmospheric gas analysis mass spectrometer is used to monitor the concentration of reference compound (isoprene, 99%, Alfa Aesar) with a 70 eV EI ionization source and a quadrupole detector.

2.2. Generation of PAH particles and NO₃ radicals

Particle-phase PAHs are generated via homogeneous nucleation in an electric tube furnace comprised of two tandem quartz tubes (3 cm diameter, 40 cm length). The temperature of each tandem quartz tube is controlled with an independent temperature controller. The first quartz tube containing 0.1 g of azelaic acid (99%, NRSCRD, China) is maintained at 443 ± 1 K, and the second quartz tube is kept at 473 ± 1 K and 493 ± 1 K for B[b]F and B[k]F, respectively. The azelaic acid in the first tube vaporized and nucleated into particles as it encountered a decreasing temperature gradient. The azelaic acid particles are introduced into the second tube by a N₂ flow at a volumetric flow rate of 0.6 L min⁻¹ and then coated with B[b]F (>95%, Acros) and B[k]F (99%, Acros). The generated PAH particles entrained in N₂ flow are filled into the reaction chamber. The particle size and concentration are controlled by adjusting the temperatures of quartz tubes and the flow rate of N₂, and monitored with a scanning mobility particle sizer (SMPS) composed of a differential mobility analyzer (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3010). The measured mean diameters of B[b]F and B[k]F particles are 381 nm and 431 nm, respectively. The geometric standard deviations of the particle diameter are 1.2–1.4. The initial mass concentrations of particulate B[b]F and B[k]F in the chamber are respectively estimated to 100 ± 6 µg m⁻³ and 347 ± 42 µg m⁻³ according to the corresponding size distributions and mass concentrations of azelaic acid and PAH-coated particles.

Finally, NO₃ radicals are generated from thermal decomposition of N₂O₅ that is synthesized by dehydration of nitric acid (Zhang et al., 2011). The N₂O₅ powder is kept in a flask in liquid nitrogen prior to use. In the experiment, the flask is placed at room temperature and warmed up via ambient air convection. According to the NO₃ concentration calculated from the loss rate of isoprene in the chamber, the temperature of N₂O₅ powder in the flask is estimated to ~ -20 °C.

2.3. Experimental procedure

Isoprene is injected into the chamber after a certain amount of PAH particles are introduced. The average isoprene concentration

in the reaction chamber is estimated to $\sim 3.3 \times 10^{14}$ molecules cm^{-3} by detecting the mass peak at m/z 67 (C_5H_7^+) using atmospheric gas analysis mass spectrometer. Then, N_2O_5 vapor is continuously flushed into the chamber with a N_2 flow of 0.6 L min^{-1} and thermally decomposed into NO_2 and NO_3 radicals at room temperature ($293 \pm 2 \text{ K}$) (Tuazon et al., 1984). The decays of particle-phase PAHs and gaseous isoprene are synchronously monitored with VUV-ATOFMS and atmospheric gas analysis mass spectrometer, respectively.

2.4. GC–MS assay

The particulate products formed during the reactions of PAH particles with NO_3 radicals in the absence of isoprene are directly captured with a glass microfiber filter (25 mm diameter, $0.7 \mu\text{m}$ pore-size, Whatman), extracted with dichloromethane (Chromatographic grade, J.T. Baker Co., Ltd.), and then analyzed with GC–MS (Agilent 6890–5973). The GC–MS is comprised of a gas chromatography (DB-5MS $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ capillary column) and a mass spectrometer (quadrupole mass filter with a 70 eV electron impact ionizer). The aliquot of samples ($1 \mu\text{L}$) is introduced into the GC–MS system in the pulsed splitless mode. The temperature of the programmed temperature vaporizer is held at 270°C . The initial oven temperature is set to 40°C for 2 min, then step-by-step increased to 150°C (by $20^\circ\text{C min}^{-1}$), 220°C (by $10^\circ\text{C min}^{-1}$), and 300°C (by 5°C min^{-1}) and held for 10 min at each of the 3 levels. Helium (99%, Beijing Huayuan Gas Chemical Industry Co., Ltd.) is used as the carrier gas at a constant flow rate of 1 mL min^{-1} . The interface temperature is kept at 280°C throughout GC–MS assay.

3. Results and discussion

3.1. Reaction products of B[b]F and B[k]F

The VUV-TOF mass spectra of B[b]F particles exposed to NO_3 radicals are obtained at 0, 110, 170, and 260 s, respectively (Fig. 1A–D). The mass peak at m/z 252 (Fig. 1A) is attributed to the molecular ion of B[b]F, and the new mass peaks at m/z 282 and 297 (Fig. 1B) are assigned to the molecular ions of reaction products, benzo[b]fluoranthenequinone (B[b]F-quinone) and mono-nitrobenzo[b]fluoranthene (NB[b]F), respectively. The mass peak at m/z 267 (Fig. 1B) is likely attributed to the daughter ion of NB[b]F by losing a NO during VUV photoionization. Compared with Fig. 1B, there are new mass peaks at m/z 312, 327, 342, 357, 372, and 387 in Fig. 1(C and D). The mass peaks at m/z 327 and 372 are assigned to the molecular ion peaks of mono-NB[b]F-quinone and di-NB[b]F-quinone formed in further nitration of B[b]F-quinone, and the mass peaks at m/z 342 and 387 are attributed to the molecular ions of di-NB[b]F and tri-NB[b]F, respectively. The mass peaks at m/z 312 and 357 are respectively assigned to the daughter ions of di-NB[b]F and tri-NB[b]F by losing a NO during VUV photoionization. At the reaction time of 200 s, there are 9 mono-NB[b]F isomers (retention time at 49.57, 50.60, 51.42, 51.68, 52.23, 52.33, 52.62, 53.06, and 54.07 min, respectively) and two di-NB[b]F isomers (retention time at 55.6 and 56.1 min, respectively) observed with GC–MS (Fig. 3A). However, none of B[b]F-quinone, mono/di-NB[b]F-quinone, or tri-NB[b]F are observed by GC–MS in this experiment, possibly because these products are difficult to be gasified.

The VUV-TOF mass spectra of B[k]F particles in the chamber before exposed to NO_3 radicals are also obtained (Fig. 2A). The mass peak at m/z 252 is attributed to the molecular ion of B[k]F. In addition, several new mass peaks appear and rise at m/z 282, 297, 327, 342, and 387, respectively (Fig. 2B and C). The mass peaks at m/z 297, 342, and 387 are attributed to the molecular ions of mono-

Fig. 1. Time-of-flight mass spectra of B[b]F particle (A) and their reaction products due to reaction with NO_3 radicals in the reaction time of 110 s (B), 170 s (C), and 260 s (D).

NB[k]F, di-NB[k]F, and tri-NB[k]F, respectively, and those at m/z 282 and 327 are assigned to the molecular ions of B[k]F-quinone and mono-NB[k]F-quinone, respectively. At the reaction time of 200 s, 4 mono-NB[k]F isomers (retention time at 50.0, 51.4, 52.2, and 53.4 min, respectively) and 1 di-NB[k]F isomer (retention time at 59.5 min) are detected by GC–MS (Fig. 3B). Other products are not detected by GC–MS during the experiment. The relative yields of products are estimated from their chromatographic peak areas obtained by GC–MS and the relative peak intensities of their mass peaks obtained by VUV-ATOFMS (Table 1). It should be noted that the after-reaction on the filter surface during sampling may affect the products and their yields. The GC/MS analyses showed that the abundances of NPAHs in captured particles increased by 19% and 12% for NB[b]F and NB[k]F compared with the online measurements with VUV-TOFMS before collection. Nevertheless, we speculate that the reaction products should mainly be contributed from the suspended state reaction.

The majority of previous studies indicated that heterogeneous nitration of PAHs follows a similar pathway as the gas-phase mechanism. NO_3 radicals add predominantly to the aromatic ring to form NO_3 -PAH adducts, which then either thermally decompose or react with NO_2 to form nitro-PAH and with O_2 to form, at least in part, other products (Gross and Bertram, 2008; Kwamena and Abbatt, 2008; Wang et al., 2010). We speculate that the products containing both nitro and ketone groups came from the secondary reaction of B[b]F-quinone with NO_3 radicals because the mass peaks of these two reactants appear and rise sequentially during the reaction. Due to lack of the standard EI mass spectra, the products such as nitro-PAH, PAH-quinone, and those containing both nitro and ketone groups cannot be identified. To our knowledge, no study has reported such products formed in heterogeneous or homogeneous reactions of B[b]F and B[k]F with NO_3 radicals. Further examination of these products is necessary to illustrate their potential threats to human health.

Fig. 2. Time-of-flight mass spectra of B[k]F particle (A) and their reaction products due to reaction with NO₃ radicals in the reaction time of 280 s (B) and 590 s (C).

Fig. 3. GC-MS total ion chromatograms of the reaction products formed from the B[b]F (A) and B[k]F (B) in the reaction chamber.

3.2. Effective rate constants

The concentrations of NO₃ radicals employed in this study are estimated to be $(0.9\text{--}2.4) \times 10^{10}$ molecules cm⁻³ in accordance

with the loss rates of isoprene. The concentration uncertainty of NO₃ radicals applied in this study (36%) is dependent on the uncertainty of the rate coefficients for the reactions of isoprene and NO₃ radicals. The maximal concentrations of NO₂ are estimated to $(1.6\text{--}2.7) \times 10^{14}$ molecules cm⁻³. The initial N₂O₅ concentrations in the chamber are calculated to be $(2.8\text{--}3.3) \times 10^{14}$ molecules cm⁻³. The detailed calculation processes of the concentrations of N₂O₅, NO₂, and NO₃ radicals are shown in Supporting Information. In order to evaluate the possible effects of NO₂ on reaction products and the decay of isoprene, PAHs particles and isoprene are exposed to 10 ppm NO₂ ($\sim 2.46 \times 10^{14}$ molecules cm⁻³) for 10 min, respectively. As no reaction products and apparently decay of isoprene are observed, the influence of NO₂ on the products and kinetics of the reactions between PAHs aerosols and NO₃ radicals are ignored in this study. The potential influence of N₂O₅ on the reactions is tested under experimental conditions. The 0.6 L min⁻¹ N₂ flow containing N₂O₅ vapor is heated to promote N₂O₅ dissociation before it entered the chamber. The results indicate that the effective rate constants for the reactions between PAHs and NO₃ radicals had no substantial variations between 60 °C and 90 °C. Thus, the degradation of PAHs particles may mainly occur by reacting with NO₃ radicals. Because the effective rate constants for heterogeneous reactions of B[b]F and B[k]F with N₂O₅ are on the order of 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹ (Kamens et al., 1990) and the corresponding reactive uptake coefficients are reported to 4 orders of magnitude lower than those for heterogeneous reactions of B[b]F and B[k]F with NO₃ radicals (Gross and Bertram, 2008), the influence of N₂O₅ can be negligible in this study. In addition, at most ~ 1 ppm gas-phase HNO₃ may be formed in the chamber estimated by the relative humidity and the maximal concentration of N₂O₅. The previous studies showed that HNO₃ (~ 50 ppb–1.5 ppm) has little effect on PAHs (Pitts et al., 1985a,b; Gross and Bertram, 2008). Therefore, we speculate that the HNO₃ present in exposures may not result in the large amount of NB[b]F and NB[k]F. The wall losses of gaseous isoprene and PAHs particles (<5%) are ignored during data processing. The longest data acquisition time for each kinetic study is less than 160 s to mitigate the influence of the secondary reactions.

The effective rate constants for heterogeneous reactions of B[b]F and B[k]F with NO₃ radicals are measured using a mixed-phase relative rate method (Smith et al., 2009). The time averaged concentration of NO₃ radicals ($\overline{C_{\text{NO}_3}^g}$) is derived from the measured decay of the reference gas (isoprene) using the following equation:

$$\frac{\ln(C_{\text{ref}}^g/C_{\text{ref}0}^g)}{-k_{\text{ref}}^g} = \int_0^t C_{\text{NO}_3}^g dt = \overline{C_{\text{NO}_3}^g} t \quad (1)$$

where $\overline{C_{\text{ref}}^g}$ and $\overline{C_{\text{ref}0}^g}$ are the time-dependent and initial concentrations of the reference gas, and k_{ref}^g is the reaction rate constant for the reactions of gas-phase reference gas and NO₃ radicals (7.0×10^{-13} cm³ molecule⁻¹ s⁻¹ at 298 K) (www.iupac-kinetic.ch.cam.ac.uk/). The effective rate constant (k_{PAH}^a) is expressed in the following equation:

$$\ln(C_{\text{PAH}}^a/C_{\text{PAH}0}^a) = -k_{\text{PAH}}^a \overline{C_{\text{NO}_3}^g} t \quad (2)$$

where C_{PAH}^a and $C_{\text{PAH}0}^a$ are the time-dependent and initial concentrations of particle-phase PAHs, respectively.

By plotting $\ln(C_{\text{PAH}}^a/C_{\text{PAH}0}^a)$ versus NO₃ exposure ($\overline{C_{\text{NO}_3}^g} t$), the effective rate constants (k_{PAH}^a) are obtained from the slopes of the lines (Fig. 4A and B). The correlation coefficients (R^2) of the linear regressions are 0.98 (B[b]F) and 0.97 (B[k]F). The effective reaction rates of heterogeneous reactions of the PAHs particles toward NO₃ radicals are $(1.2 \pm 0.1) \times 10^{-12}$ and $(5.8 \pm 0.3) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, respectively. The uncertainties are standard errors generated in the linear regression of the data points.

Table 1Products of the heterogeneous reactions of NO₃ radicals with particulate B[b]F and B[k]F.

Product	Formula	MW	η_1	η_2
x-Nitrobenzo[b]fluoranthene	C ₂₀ H ₁₁ NO ₂	297	1 ^b	
x,y-Dinitrobenzo[b]fluoranthene	C ₂₀ H ₁₀ N ₂ O ₄	342	0.043	1 ^b
x,y,z-Trinitrobenzo[b]fluoranthene*	C ₂₀ H ₉ N ₃ O ₆	387		0.78
Bezon[b]fluoranthenequinone*	C ₂₀ H ₁₀ O ₂	282		0.22
x-Nitrobenzo[b]fluoranthenequinone*	C ₂₀ H ₉ NO ₄	327		0.67
x,y-Dinitrobenzo[b]fluoranthenequinone*	C ₂₀ H ₈ N ₂ O ₆	372		0.22
x-Nitrobenzo[k]fluoranthene	C ₂₀ H ₁₁ NO ₂	297	1 ^k	
x,y-Dinitrobenzo[k]fluoranthene	C ₂₀ H ₁₀ N ₂ O ₄	342	0.12	0.58
x,y,z-Trinitrobenzo[k]fluoranthene*	C ₂₀ H ₉ N ₃ O ₆	387		1 ^k
Bezon[k]fluoranthenequinone*	C ₂₀ H ₁₀ O ₂	282		0.37
x-Nitrobenzo[k]fluoranthenequinone*	C ₂₀ H ₉ NO ₄	327		0.42

MW is the molecular weight. η_1 represents the total relative abundances of mono-NPAH isomers and di-NPAH isomers respectively obtained from GC–MS, which is shown in Fig. 3. η_2 represents the relative peak intensities of the mass peaks shown in Fig. 1D and Fig. 2C. The products labeled with the superscript * are only observed by VUV-ATOFMS, otherwise observed by both VUV-ATOFMS and GC–MS.

Table 2 lists the kinetic data of the reactions between the PAHs (B[b]F and B[k]F) and atmospheric oxidants (OH radicals, O₃ radicals, NO₂, and N₂O₅) reported in previous studies. The rate constants for the reactions of PAHs with NO₃ radicals are significantly larger than those with O₃, NO₂, and N₂O₅, and slightly lower than those with OH radicals (Kamens et al., 1990; Esteve et al., 2004; Perraudin et al., 2005). Compared with the data reported by Kamens et al., the reaction rates obtained in our studies are apparently greater. We speculate that the discrepancy may result from the different types of particles investigated. It was reported that different substrates would result in different reaction rates when the particulate PAHs react with atmospheric oxidants (Inazu et al., 1997; Pöschl et al., 2001; Kwamena et al., 2004; Kahan et al., 2006). Especially, the degradation rates of atmospheric PAHs particles may be smaller when the PAHs are trapped inside diesel and wood soot particles. Compared with OH radicals, NO₃ radicals feature higher atmospheric concentrations, thus can act a more important atmospheric oxidant in the degradation and transformation of particle-phase PAHs during the nighttime.

3.3. Effective uptake coefficients

In atmospheric chemistry, the uptake coefficient (γ) is most widely used to describe heterogeneous processes. The γ is defined as the fraction of NO₃–particle collisions that result in a reaction. Given that it is not practical to directly measure the gas-phase loss of NO₃ radicals in the experiment, γ is determined by monitoring the reactive loss of PAHs in particle-phase. Assuming that the measured loss of PAHs is caused completely by reactions with NO₃ radicals, the effective uptake coefficients (γ_{eff}) can be calculated with the equation $\gamma_{eff} = N_{tot}/N_{coll}$, where N_{tot} is the number of reacted PAHs molecules per unit volume (cm³), and N_{coll} is the total number of NO₃ radicals colliding with the particles per unit volume (cm³).

The total number of PAH molecules (N_{tot}) consumed by NO₃ radicals per unit volume (cm³) are expressed as follows:

$$N_{tot} = \frac{C_{PAH0} \eta_{PAH}}{M_{PAH}} N_A \quad (3)$$

where C_{PAH0} is the initial mass concentration of particle-phase PAH (g cm^{−3}). η_{PAH} is the consumption ratio of PAHs for producing mono-nitro-PAHs (0.45–0.55, depending on the PAH sample), which was measured before di-nitro-PAHs were observed. M_{PAH} is the PAH molecular weight (g mol^{−1}), and N_A is the Avogadro's number (molecules mol^{−1}). The total number of collisions (N_{coll}) of NO₃ radicals towards the particles per unit volume (cm³) is denoted as follows:

$$N_{coll} = J_{coll}[SA]t = \frac{\bar{c}}{4}[\text{NO}_3][SA]t \quad (4)$$

Fig. 4. Plots of $\ln(C_{PAH0}/C_{PAH})$ versus the NO₃ exposure ($\bar{C}_{NO_3}^0 t$) for the reactions of NO₃ radicals with B[b]F (A) and B[k]F (B) aerosols.

where J_{coll} is the gas kinetic flux of reactant gas colliding with the surface (number of molecules per unit area and unit time, molecules cm^{−2} s^{−1}), expressed as $\frac{\bar{c}}{4}[\text{NO}_3]$; $\bar{c}$ is the mean thermal velocity of NO₃ (cm s^{−1}); $[\text{NO}_3]$ denotes the concentration of NO₃ radicals in the gas phase (molecule cm^{−3}); $[SA]$ is the total surface area of particles per volume of gas phase directly measured by SMPS (2.8×10^{-5} and 6.7×10^{-5} cm² cm^{−3} for B[b]F and B[k]F particles, respectively); and t is the reaction time (s). The effective uptake coefficient (γ_{eff}) of NO₃ radicals on PAH particles is expressed using the following equation:

$$\gamma_{eff} = \frac{N_{tot}}{N_{coll}} = \frac{4C_{PAH0} \eta_{PAH} N_A}{M_{PAH} \bar{c} [\text{NO}_3] [SA] t} \quad (5)$$

According to Eq. (5), the effective uptake coefficients (γ_{eff}) for NO₃ radicals on B[b]F and B[k]F particles under the experimental conditions are 0.22 and 0.65, respectively. It should be noted that

Table 2The second-order reaction rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of particulate B[b]F and B[k]F with different atmospheric oxidants.

PAHs	Graphite			Silica S5-70-500		Wood soot	Diesel soot	This study
	OH ^a	NO ₂ ^a	O ₃ ^b	NO ₂ ^c	O ₃ ^b	N ₂ O ₅ ^d	N ₂ O ₅ ^d	NO ₃ ^e
B[b]F						1.7×10^{-18}	5.3×10^{-18}	$1.2 \pm 0.1 \times 10^{-12}$
B[k]F	3.5×10^{-12}	2.5×10^{-17}	$(1.9 \pm 0.6) \times 10^{-17}$	$(1.5 \pm 0.3) \times 10^{-18}$	$(3.6 \pm 0.8) \times 10^{-17}$	1.8×10^{-18}	9.8×10^{-18}	$5.8 \pm 0.3 \times 10^{-13}$

^a Results are reported by Esteve et al. (2004).^b Results are reported by Perraudin et al. (2007).^c Results are reported by Perraudin et al. (2005).^d Results are reported by Kamens et al. (1990).^e Results are obtained in the experiment.

[NO₃] is the average concentration during the reaction time, and the uptake coefficients (γ_{eff}) obtained in our experiments represent the mean uptake coefficient within ~ 110 s and ~ 130 s for B[b]F and B[k]F, respectively. Additionally, compared to those obtained by monitoring the decay of gas-phase reactant in some previous studies, the γ_{eff} in this study may be overestimated at a certain extent. The volatilization of particulate PAHs may occur in the reactions, and the radical intermediates generated in the reaction may consume some particulate PAHs (Hearn et al., 2007; McNeill et al., 2008; Lambe et al., 2009). Taken together, these factors can lead to increases in the γ_{eff} .

The oxidation lifetimes of particulate B[b]F and B[k]F are estimated from the obtained effective uptake coefficient using the following equation:

$$\tau = \frac{4C_{\text{PAH}_0}N_A}{M_{\text{PAH}}\bar{c}[\text{SA}][\text{NO}_3]\gamma_{\text{eff}}} \quad (6)$$

According to Eq. (6), the oxidation lifetimes of B[b]F and B[k]F at a typical concentration of NO₃ radicals in the continental boundary layer ($5 \times 10^8 \text{ molecules cm}^{-3}$) (Shu and Atkinson, 1995) are 3.0 and 3.9 h, respectively. However, because real atmospheric aerosols have more complex components with different concentrations and physical morphologies, the lifetime of organics adsorbed on the atmospheric relevant particles is affected by other factors mentioned above. For instance, the lifetimes of atmospheric PAH particles may be longer when the PAHs are trapped in solids and not accessible to NO₃ radicals. Therefore, discrepancy may exist between the estimated lifetimes of PAH particles reported in this study and those in the real atmosphere.

4. Conclusions

This study investigates the heterogeneous reactions of NO₃ radicals with B[b]F and B[k]F adsorbed on azelaic acid particles under laboratory conditions. The mono-nitro-, di-nitro-, tri-nitro-products, and those products containing both nitro and ketone groups are firstly observed with VUV-ATOFMS. On the basis of the obtained total relative abundances measured using GC-MS and the relative peak intensities of the mass peaks observed using VUV-ATOFMS, we speculate that some mono-nitro-B[b]F and mono-nitro-B[k]F isomers may be distributed in the atmospheric particles. Using the mixed-phase relative rate method, the second-order rate constants of B[b]F and B[k]F particles under the experimental conditions are estimated to $(1.2 \pm 0.1) \times 10^{-12}$ and $(5.8 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Based on a comparison between the measured second-order rate constants obtained from the heterogeneous reactions of some atmospheric oxidants (OH radicals, O₃ radicals, NO₂, and N₂O₅) with particulate PAHs and those in this study, the results indicate that NO₃ radicals play a significant role in chemical transformation of particulate B[b]F and B[k]F in the atmosphere. Additionally, the lifetimes for particulate B[b]F and

B[k]F calculated using the effective uptake coefficients obtained in this study are 3.0 and 3.9 h, respectively. These results may help improve our understanding of the chemical transformation of particulate B[b]F and B[k]F in the atmosphere. However, because the chemical composition and the morphology of atmospheric aerosols are more complex than the single-component of PAH particles used under experimental conditions, further study is needed to focus on heterogeneous reactions of PAHs with oxidants involving more atmospheric-relevant aerosols.

Acknowledgements

This work is supported by the co-funding of the State Key Laboratory of Environmental Aquatic Chemistry of China (No. 12L04ESPC) and the National Natural Science Foundation of China (No. 21207143).

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.2013.08.093>.

References

- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., Jaffrezzo, J.L., 2008. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys – Part 1: Concentrations, sources and gas/particle partitioning. *Atmos. Environ.* 42, 43–54.
- Alebic-Juretic, A., Cvitas, T., Klasinc, L., 1990. Heterogeneous polycyclic aromatic hydrocarbon degradation with ozone on silica gel carrier. *Environ. Sci. Technol.* 24, 62–66.
- Bedjanian, Y., Nguyen, M.L., 2010. Kinetics of the reactions of soot surface-bound polycyclic aromatic hydrocarbons with O₃. *Chemosphere* 79, 387–393.
- Bedjanian, Y., Nguyen, M.L., Le Bras, G., 2010. Kinetics of the reactions of soot surface-bound polycyclic aromatic hydrocarbons with the OH radicals. *Atmos. Environ.* 44, 1754–1760.
- Bidleman, T.F., 1988. Atmospheric processes – wet and dry deposition of organic-compounds are controlled by their vapor particle partitioning. *Environ. Sci. Technol.* 22, 361–367.
- Chen, Y.J., Bi, X.H., Mai, B.X., Sheng, G.Y., Fu, J.M., 2004. Emission characterization of particulate/gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. *Fuel* 83, 781–790.
- Coover, M.P., Sims, R.C., 1987. The effect of temperature on polycyclic aromatic hydrocarbon persistence in an unacclimated agricultural soil. *Waste Hazard. Mater.* 4, 69–82.
- Esteve, W., Budzinski, H., Villenave, E., 2004. Relative rate constants for the heterogeneous reactions of OH, NO₂ and NO radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 1: PAHs adsorbed on 1–2 μm calibrated graphite particles. *Atmos. Environ.* 38, 6063–6072.
- Esteve, W., Budzinski, H., Villenave, E., 2006. Relative rate constants for the heterogeneous reactions of NO₂ and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a. *Atmos. Environ.* 40, 201–211.
- Gross, S., Bertram, A.K., 2008. Reactive uptake of NO₃, N₂O₅, NO₂, HNO₃, and O₃ on three types of polycyclic aromatic hydrocarbon surfaces. *J. Phys. Chem. A* 112, 3104–3113.
- Hearn, J.D., Renbaum, L.H., Wang, X., Smith, G.D., 2007. Kinetics and products from reaction of Cl radicals with dioctyl sebacate (DOS) particles in O₂: a model for radical-initiated oxidation of organic aerosols. *Phys. Chem. Chem. Phys.* 9, 4803–4813.

- Howard, P.H., Meylan, W.M., 1997. Prediction of physical properties, transport, and degradation for environmental fate and exposure assessments. *Quant. Struct.-Act. Rel. Environ. Sci.* 7, 185–205.
- Inazu, K., Kobayashi, T., Hisamatsu, Y., 1997. Formation of 2-nitrofluoranthene in gas-solid heterogeneous photoreaction of fluoranthene supported on oxide particles in the presence of nitrogen dioxide. *Chemosphere* 35, 607–622.
- Inomata, Y., Kajino, M., Sato, K., Ohara, T., Kurokawa, J.-I., Ueda, H., Tang, N., Hayakawa, K., Ohizumi, T., Akimoto, H., 2012. Emission and atmospheric transport of particulate PAHs in northeast Asia. *Environ. Sci. Technol.* 46, 4941–4949.
- Kahan, T., Kwamena, N.-O., Donaldson, D., 2006. Heterogeneous ozonation kinetics of polycyclic aromatic hydrocarbons on organic films. *Atmos. Environ.* 40, 3448–3459.
- Kamens, R.M., Guo, J., Guo, Z., McDow, S.R., 1990. Polynuclear aromatic hydrocarbon degradation by heterogeneous reactions with N_2O_5 on atmospheric particles. *Atmos. Environ. Part A. General Topics* 24, 1161–1173.
- Karagulian, F., Rossi, M.J., 2005. The heterogeneous chemical kinetics of NO_3 on atmospheric mineral dust surrogates. *Phys. Chem. Chem. Phys.* 7, 3150–3162.
- Kong, S., Shi, J., Lu, B., Qiu, W., Zhang, B., Peng, Y., Zhang, B., Bai, Z., 2011. Characterization of PAHs within PM_{10} fraction for ashes from coke production, iron smelt, heating station and power plant stacks in Liaoning Province, China. *Atmos. Environ.* 45, 3777–3785.
- Kwamena, N.O.A., Abbatt, J.P.D., 2008. Heterogeneous nitration reactions of polycyclic aromatic hydrocarbons and n-hexane soot by exposure to $\text{NO}_3/\text{NO}_2/\text{N}_2\text{O}_5$. *Atmos. Environ.* 42, 8309–8314.
- Kwamena, N.-O.A., Thornton, J.A., Abbatt, J.P., 2004. Kinetics of surface-bound benzo [a] pyrene and ozone on solid organic and salt aerosols. *J. Phys. Chem. A* 108, 11626–11634.
- Lambe, A.T., Miracolo, M.A., Hennigan, C.J., Robinson, A.L., Donahue, N.M., 2009. Effective rate constants and uptake coefficients for the reactions of organic molecular markers (n-alkanes, hopanes, and steranes) in motor oil and diesel primary organic aerosols with hydroxyl radicals. *Environ. Sci. Technol.* 43, 8794–8800.
- Lin, C.C., Chen, S.J., Huang, K.L., Lee, W.J., Lin, W.Y., Tsai, J.H., Chaung, H.C., 2008. PAHs, PAH-induced carcinogenic potency, and particle-extract-induced cytotoxicity of traffic-related nano/ultrafine particles. *Environ. Sci. Technol.* 42, 4229–4235.
- Liu, C., Zhang, P., Yang, B., Wang, Y., Shu, J., 2012. Kinetic studies of heterogeneous reactions of polycyclic aromatic hydrocarbon aerosols with NO_3 radicals. *Environ. Sci. Technol.* 46, 7575–7580.
- McNeill, V., Yatavelli, R., Thornton, J., Stipe, C., Landgrebe, O., 2008. The heterogeneous OH oxidation of palmitic acid in single component and internally mixed aerosol particles: vaporization, secondary chemistry, and the role of particle phase. *Atmos. Chem. Phys.* 8, 6035–6068.
- Perraudin, E., Budzinski, H., Villenave, E., 2005. Kinetic study of the reactions of NO_2 with polycyclic aromatic hydrocarbons adsorbed on silica particles. *Atmos. Environ.* 39, 6557–6567.
- Perraudin, E., Budzinski, H., Villenave, E., 2007. Kinetic study of the reactions of ozone with polycyclic aromatic hydrocarbons adsorbed on atmospheric model particles. *J. Atmos. Chem.* 56, 57–82.
- Pitts Jr, J.N., Zielinska, B., Sweetman, J.A., Atkinson, R., Winer, A.M., 1985a. Reactions of adsorbed pyrene and perylene with gaseous N_2O_5 under simulated atmospheric conditions. *Atmos. Environ.* 19, 911–915.
- Pitts, J.N., Sweetman, J.A., Zielinska, B., Atkinson, R., Winer, A.M., Harger, W.P., 1985b. Formation of nitroarenes from the reaction of polycyclic aromatic-hydrocarbons with dinitrogen pentoxide. *Environ. Sci. Technol.* 19, 1115–1121.
- Pöschl, U., Letzel, T., Schauer, C., Niessner, R., 2001. Interaction of ozone and water vapor with spark discharge soot aerosol particles coated with benzo [a] pyrene: O_3 and H_2O adsorption, benzo [a] pyrene degradation, and atmospheric implications. *J. Phys. Chem. A* 105, 4029–4041.
- Shu, J., Gao, S., Li, Y., 2008. A VUV photoionization aerosol time-of-flight mass spectrometer with a RF-powered VUV lamp for laboratory-based organic aerosol measurements. *Aerosol Sci. Technol.* 42, 110–113.
- Shu, Y., Atkinson, R., 1995. Atmospheric lifetimes and fates of a series of sesquiterpenes. *Journal of Geophysical Research: Atmospheres* (1984–2012), 100(D4), 7275–7281.
- Smith, J.D., Kroll, J.H., Cappa, C.D., Che, D.L., Liu, C.L., Ahmed, M., Leone, S.R., Worsnop, D.R., Wilson, K.R., 2009. The heterogeneous reaction of hydroxyl radicals with sub-micron squalane particles: a model system for understanding the oxidative aging of ambient aerosols. *Atmos. Chem. Phys.* 9, 3209–3222.
- Tuazon, E.C., Sanhueza, E., Atkinson, R., Carter, W.P.L., Winer, A.M., Pitts, J.N., 1984. Direct determination of the equilibrium-constant at 298 K for the NO_2+NO_3 reversible N_2O_5 reactions. *J. Phys. Chem.* 88, 3095–3098.
- Umbuzeiro, G.A., Franco, A., Martins, M.H., Kummrow, F., Carvalho, L., Schmeiser, H.H., Leykauf, J., Stiborova, M., Claxton, L.D., 2008. Mutagenicity and DNA adduct formation of PAH, nitro-PAH, and oxy-PAH fractions of atmospheric particulate matter from Sao Paulo, Brazil. *Mutat. Res., Genet. Toxicol. Environ. Mutagen.* 652, 72–80.
- Varea, M., Galindo, N., Gil-Molto, J., Pastor, C., Crespo, J., 2011. Particle-bound polycyclic aromatic hydrocarbons in an urban, industrial and rural area in the western Mediterranean. *J. Environ. Monit.* 13, 2471–2476.
- Wang, L., Atkinson, R., Arey, J., 2010. Comparison of alkylnitronaphthalenes formed in NO_3 and OH radical-initiated chamber reactions with those observed in ambient air. *Environ. Sci. Technol.* 44, 2981–2987.
- Watanabe, M., Noma, Y., 2009. Influence of combustion temperature on formation of nitro-PAHs and decomposition and removal behaviors in pilot-scale waste incinerator. *Environ. Sci. Technol.* 43, 2512–2518.
- <http://www.iupac-kinetic.ch.cam.ac.uk/>.
- Xu, S., Liu, W., Tao, S., 2006. Emission of polycyclic aromatic hydrocarbons in China. *Environ. Sci. Technol.* 40, 702–708.
- Zhang, Y., Yang, B., Gan, J., Liu, C., Shu, X., Shu, J., 2011. Nitration of particle-associated PAHs and their derivatives (nitro-, oxy-, and hydroxy-PAHs) with NO_3 radicals. *Atmos. Environ.* 45, 2515–2521.
- Zielinska, B., Sagebiel, J., Arnott, W., Rogers, C., Kelly, K., Wagner, D., Lighty, J., Sarofim, A., Palmer, G., 2004. Phase and size distribution of polycyclic aromatic hydrocarbons in diesel and gasoline vehicle emissions. *Environ. Sci. Technol.* 38, 2557–2567.