Heterogeneous reactions of particulate benzo[b]fluoranthene and benzo[k]fluoranthene with NO$_3$ radicals

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HIGHLIGHTS

- Heterogeneous reactions of B[b]F and B[k]F with NO$_3$ radicals are studied.
- Reaction products of the PAHs particles are observed.
- Effective rate constants for the reactions are obtained using a relative method.
- Effective NO$_3$ uptake coefficients for the reactions are calculated.

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 NO$_3$ 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 NO$_3$ radicals in an aerosol reaction chamber at room temperature (293 ± 2 K) under atmospheric pressure. The reactions are monitored online using a vacuum ultra-violet 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 NO$_3$ radicals under the experimental conditions are respectively estimated to $(1.2 ± 0.1) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $(5.8 ± 0.3) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ 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 NO$_3$ radicals $(5 \times 10^8$ 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.

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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 PM$_{10}$ 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 10 100 ± 6940 pg m$^{-3}$ and 3050 ± 2280 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 $6.7 \times 10^{-5}$ Pa (Coover and Sims,
and 35/C0 radicals also are a more important sink of PAHs which im-
radicals have recently been inves-
cessary to clarify their chemical conversion during the heteroge-
etic reactions between condensed-phase PAHs (B
cals and higher molecular weight PAHs (5-, 6-, and 7-ring) particles
strates such as diesel, graphite, silica, and simulated kerosene com-
bustion soot particles (Alebic-Juretic et al., 1990; Esteve et al., 2004,
Perraudin et al., 2007; Bedjanian et al., 2010). These studies show that the reactivity of PAHs tested toward OH radicals is approxi-
ately 4 orders of magnitude greater than that toward NO2 and O3.
As compared with other atmospheric oxidizers such as NO2 and O3, NO3 radicals also are a more important sink of PAHs which im-
pact 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), anthrane, 9-nitroanthracene, 1-hydroxypyrene (1-HP), and 1-
nitropyrene (1-NP) particles have been studied due to their hetero-
genous 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 investi-
gated 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 reac-
tions 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[1]F and B[k]F, which shows that our understanding of their kinetics and products is incomplete. To fill this gap, it is neces-
sary to clarify their chemical conversion during the heteroge-
neous reaction process occurring in the atmospheric environment.
To this end, this study focuses on heterogeneous reactions of sus-
pended B[1]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 analy-
sis 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[1]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-HAL3FRC, 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 ra-
pid mixing of the reactants during the reaction. Before each exper-
iment, 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 ~5 × 1011 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 con-
troller. 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[1]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

2.3. Experimental procedure

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

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[1]F is typi-
cally 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,

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When transported in the troposphere, particle-phase PAHs can react with atmospheric oxidants such as NO3 radicals, OH radicals,
in the reaction chamber is estimated to \( \sim 3.3 \times 10^{14} \text{ molecules cm}^{-3} \) by detecting the mass peak at m/z 67 (C\(_6\)H\(_7^+\)) using atmospheric gas analysis mass spectrometer. Then, N\(_2\)O\(_5\) 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 K) (Tuzason 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 m \( \times \) 0.25 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°C min\(^{-1}\)), 220°C (by 10°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[\( k \)]F and B[\( k \)]F

The VUV-TOF mass spectra of B[\( k \)]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[\( k \)]F, and the new mass peaks at m/z 282 and 297 (Fig. 1B) are assigned to the molecular ions of reaction products, benzo[\( k \)]fluoranthenequinone (B[\( k \)]F-quinone) and mono-nitrobenzo[\( k \)]fluoranthene (NB[\( k \)]F), respectively. The mass peak at m/z 267 (Fig. 1B) is likely attributed to the daughter ion of NB[\( k \)]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. 1C and D. The mass peaks at m/z 327 and 372 are assigned to the molecular ion of mono-NB[\( k \)]F-quinone and di-NB[\( k \)]F-quinone formed in further nitration of B[\( k \)]F-quinone, and the mass peaks at m/z 342 and 387 are attributed to the molecular ions of di-NB[\( k \)]F and tri-NB[\( k \)]F, respectively. The mass peaks at m/z 312 and 357 are respectively assigned to the daughter ions of di-NB[\( k \)]F and tri-NB[\( k \)]F by losing a NO during VUV photoionization. At the reaction time of 200 s, there are 9 mono-NB[\( k \)]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[\( k \)]F isomers (retention time at 55.6 and 56.1 min, respectively) observed with GC–MS (Fig. 3A). However, none of B[\( k \)]F-quinone, mono-di-NB[\( k \)]F-quinone, or tri-NB[\( k \)]F is the products observed by GC–MS (Fig. 3A). Therefore, no study has reported such products formed in heterogeneous or homogeneous reactions of B[\( k \)]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. 1.** Time-of-flight mass spectra of B[\( k \)]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).
3.2. Effective rate constants

The concentrations of NO₃ radicals employed in this study are estimated to be (0.9–2.4) × 10¹⁴ 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 (1.6–2.7) × 10¹⁴ molecules cm⁻³. The initial N₂O₅ concentrations in the chamber are calculated to be (2.8–3.3) × 10¹⁴ 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 (~2.46 × 10¹⁴ 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 NO₂ 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 NO₂ and NO₃ radicals are on the order of 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹ (Kamins et al., 1990) and the corresponding reactive uptake coefficients are reported to 4 orders of magnitude lower than those for heterogeneous reactions of NO₂ and 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 NO₂ and NO₃ radicals are estimated using a mixed-phase relative rate method (Smith et al., 2009). The time averaged concentration of NO₃ radicals (C₃NO₃) is derived from the measured decay of the reference gas (isoprene) using the following equation:

\[
\frac{\ln(C_{ref}^g/C_{ref}^{g0})}{-k_{ref}^g} = \int_0^t C_{NO_3}^g dt = C_{NO_3}^{g0} e^{-k_{ref}^g t}
\]

(1)

where \(C_{ref}^g\) and \(C_{ref}^{g0}\) 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 (\(k_{PAH}^g\)) is expressed in the following equation:

\[
\ln(C_{PAH}^g/C_{PAH0}^g) = -k_{PAH}^g C_{NO_3}^{g0} t
\]

(2)

where \(C_{PAH}^g\) and \(C_{PAH0}^g\) are the time-dependent and initial concentrations of particle-phase PAHs, respectively.

By plotting \(\ln(C_{PAH}^g/C_{PAH0}^g)\) versus NO₃ exposure (\(\overline{C}_{NO_3}^g\)), the effective rate constants (\(k_{PAH}^g\)) are obtained from the slopes of the lines (Fig. 4A and B). The correlation coefficients (R²) 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 ± 0.1) × 10⁻¹² and (5.8 ± 0.3) × 10⁻¹³ cm² molecule⁻¹ s⁻¹, respectively. The uncertainties are standard errors generated in the linear regression of the data points.
Table 1

<table>
<thead>
<tr>
<th>Product</th>
<th>Formula</th>
<th>MW</th>
<th>$\eta_1$</th>
<th>$\eta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-Nitrobenzo[k]fluoranthene</td>
<td>C_{20}H_{11}NO_2</td>
<td>297</td>
<td>1$^a$</td>
<td></td>
</tr>
<tr>
<td>x,y-Dinitrobenzo[k]fluoranthene</td>
<td>C_{20}H_{10}N_2O_4</td>
<td>342</td>
<td>0.043</td>
<td>1$^b$</td>
</tr>
<tr>
<td>x,y,2-Trinitrobenzo[k]fluoranthene</td>
<td>C_{20}H_{10}N_3O_4</td>
<td>387</td>
<td>0.78</td>
<td>0.78</td>
</tr>
<tr>
<td>Benzon[k]fluoranthenquinone$^e$</td>
<td>C_{20}H_{9}N_3O_4</td>
<td>327</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>x-Nitrobenzo[k]fluoranthenquinone$^e$</td>
<td>C_{20}H_{9}N_2O_4</td>
<td>372</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>x-Nitrobenzo[k]fluoranthene</td>
<td>C_{20}H_{11}NO_2</td>
<td>297</td>
<td>1$^e$</td>
<td></td>
</tr>
<tr>
<td>x,y-Dinitrobenzo[k]fluoranthene</td>
<td>C_{20}H_{10}N_2O_4</td>
<td>342</td>
<td>0.12</td>
<td>0.58</td>
</tr>
<tr>
<td>x,y,2-Trinitrobenzo[k]fluoranthene</td>
<td>C_{20}H_{9}N_3O_4</td>
<td>387</td>
<td>1$^e$</td>
<td></td>
</tr>
<tr>
<td>Benzon[k]fluoranthenquinone$^e$</td>
<td>C_{20}H_{9}N_2O_4</td>
<td>327</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>x-Nitrobenzo[k]fluoranthenquinone$^e$</td>
<td>C_{20}H_{9}N_2O_4</td>
<td>327</td>
<td>0.42</td>
<td>0.42</td>
</tr>
</tbody>
</table>

MW is the molecular weight. $\eta_1$ represents the total relative abundances of mono-NPAH isomers and di-NPAH isomers respectively obtained from GC–MS, which is shown in Fig. 3. $\eta_2$ represents the relative peak intensities of the mass peaks shown in Fig. 1D and Fig. 2C. The products labeled with the superscript $^e$ are only observed by VUV-ATOFMS, otherwise observed by both VUV-ATOFMS and GC–MS.

3.3. Effective uptake coefficients

In atmospheric chemistry, the uptake coefficient ($\gamma$) is most widely used to describe heterogeneous processes. The $\gamma$ is defined as the fraction of NO$_3$ particle collisions that result in a reaction. Given that it is not practical to directly measure the gas-phase loss of NO$_3$ radicals in the experiment, $\gamma$ 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 NO$_3$ radicals, the effective uptake coefficients ($\gamma_{\text{eff}}$) can be calculated with the equation

\[
\gamma_{\text{eff}} = \frac{N_{\text{tot}}}{N_{\text{col}}} \frac{N_A}{N_0}
\]

where $N_{\text{tot}}$ is the number of reacted PAHs molecules per unit volume (cm$^3$), and $N_{\text{col}}$ is the total number of NO$_3$ radicals colliding with the particles per unit volume (cm$^3$).

The total number of PAH molecules ($N_{\text{tot}}$) consumed by NO$_3$ radicals per unit volume (cm$^3$) are expressed as follows:

\[
N_{\text{tot}} = \frac{C_{\text{PAH}} \eta_{\text{PAH}} N_A}{M_{\text{PAH}}}
\]

where $C_{\text{PAH}}$ is the initial mass concentration of particle-phase PAH (g cm$^{-3}$), $\eta_{\text{PAH}}$ 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. $M_{\text{PAH}}$ is the PAH molecular weight (g mol$^{-1}$), and $N_A$ is the Avogadro’s number (molecules mol$^{-1}$). The total number of collisions ($N_{\text{col}}$) of NO$_3$ radicals towards the particles per unit volume (cm$^2$) is denoted as follows:

\[
N_{\text{col}} = \frac{J_{\text{coll}} |S| t}{4[NO_3]|S| t}
\]

where $J_{\text{coll}}$ 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 $\frac{\xi}{N_0}$, $\xi$ is the mean thermal velocity of NO$_3$ (cm s$^{-1}$); $[NO_3]$ denotes the concentration of NO$_3$ radicals in the gas phase (molecule cm$^{-3}$); $\{S\}$ is the total surface area of particles per volume of gas phase directly measured by SMPS (2.8×10$^{-5}$ and 6.7×10$^{-5}$ cm$^2$ cm$^{-3}$ for B[b]F and B[k]F particles, respectively); and $t$ is the reaction time (s). The effective uptake coefficient ($\gamma_{\text{eff}}$) of NO$_3$ radicals on PAH particles is expressed using the following equation:

\[
\gamma_{\text{eff}} = \frac{N_{\text{tot}}}{N_{\text{col}}} \frac{4C_{\text{PAH}} \eta_{\text{PAH}} N_A}{M_{\text{PAH}} |S| t [NO_3] |S| t}
\]

According to Eq. (5), the effective uptake coefficients ($\gamma_{\text{eff}}$) for NO$_3$ 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
[NO₃] is the average concentration during the reaction time, and the uptake coefficients (κₑff) obtained in our experiments represent the mean uptake coefficient within ~110 s and ~130 s for B[bf] and B[kf], respectively. Additionally, compared to those obtained by monitoring the decay of gas-phase reactant in some previous studies, the κₑff in this study may be overestimated at a certain extent. The volatility 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 κₑff.

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

\[ \tau = \frac{4\mu_{PAH} N_A}{M_{PAH} [S] [NO_3]^{κ_{eff}}} \]  

(6)

According to Eq. (6), the oxidation lifetimes of B[bf] and B[kf] at a typical concentration of NO₃ radicals in the continental boundary layer (5 × 10⁴ 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[bf] and B[kf] 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[bf] and mono-nitro-B[kf] isomers may be distributed in the atmospheric particles. Using the mixed-phase relative rate method, the second-order rate constants of B[bf] and B[kf] particles under the experimental conditions are estimated to (1.2 ± 0.1) × 10⁻¹² and (5.8 ± 0.3) × 10⁻¹³ cm³ molecule⁻¹ 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, NO₃, and N₂O₅) with particulate PAHs and those in this study, the results indicate that NO₃ radicals play a significant role in the chemical transformation of particulate B[bf] and B[kf] in the atmosphere. Additionally, the lifetimes for particulate B[bf] and B[kf] 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[bf] and B[kf] 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

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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


