Kinetic Studies of Heterogeneous Reactions of Polycyclic Aromatic Hydrocarbon Aerosols with NO₃ Radicals

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are mutagenic and carcinogenic substances widely distributed in the atmospheric environment. In this study, effective rate constants for heterogeneous reactions of NO₃ radicals with five 4-ring PAHs [benzo[a]anthracene (BaA), chrysene (Ch), pyrene (Py), 1-nitropyrene (1-NP), and 1-hydroxypyrene (1-OHP)] adsorbed on suspended azelaic acid particles are investigated by a mixed-phase relative rate method with gas-phase isoprene as the reference substance. The concentrations of suspended PAH particles and gas-phase isoprene are monitored concurrently by a real-time vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) and an online atmospheric gas analysis mass spectrometer, respectively. The obtained effective rate constants for the reactions of BaA, Ch, Py, 1-NP, and 1-OHP particles with NO₃ radicals are $4.3 \times 10^{-12}$, $4.0 \times 10^{-12}$, $6.4 \times 10^{-12}$, $1.3 \times 10^{-12}$, and $1.0 \times 10^{-11}$ cm³·molecule⁻¹·s⁻¹, respectively, and their corresponding atmospheric lifetimes range from several minutes to half an hour at the NO₃ radical concentration of $5 \times 10^{10}$ molecules·cm⁻³. In addition, the NO₃ uptake coefficients on particulate PAHs are estimated according to the consumption of PAHs under the exposure of NO₃ radicals. The experimental results of these heterogeneous reactions in the aerosol state provide supplementary knowledge for kinetic behaviors of airborne PAHs particles.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants in the atmospheric environment with mutagenic and carcinogenic properties.¹² These compounds principally originate from incomplete combustion and are released into the atmosphere by sources such as vehicles, coal-fired power plants, and wood burning.³ The atmospheric concentrations of particulate PAHs are in the range of a few to several hundred nanograms per cubic meter for urban areas,³,⁴ and about 90% of PAHs emissions are anthropogenic.⁵ In the atmosphere, low molecular weight PAHs are mainly present in the gas phase, while PAHs with more than four rings are primarily found adsorbed on particulate matter, especially on particles with a diameter below 3 μm.⁶ After their emission into the atmosphere, PAHs can undergo photolysis or chemical transformation processes in both gas and particulate phases due to interactions with atmospheric trace gases. Heterogeneous reactions of particulate PAHs are an important degradation pathway, which frequently lead to the formation of some reaction products showing more toxicity than their parent chemicals, such as nitrated polycyclic aromatic hydrocarbons (NPAHs).¹² Therefore, understanding the atmospheric lifetime and fate of PAH aerosols is very important for health risk assessments.

In order to document their lifetimes in the atmosphere, substantial efforts have been made on the homogeneous chemistry between PAHs and gas-phase oxidants since a few decades ago.⁷,⁸ However, the kinetics and mechanism of heterogeneous reaction can differ dramatically from those of homogeneous reaction.¹,⁹ The previous studies revealed that heterogeneous reactions of adsorbed PAHs were much faster (by several orders of magnitude) than their corresponding gas-phase reactions.⁸,¹⁰–¹² Besides, PAHs with high molecular weights are mainly associated with particles in the atmosphere due to their low volatility. Thus, the heterogeneous reactions of these compounds may be the main degradation pathway in the atmosphere.¹⁰ In the past decade, kinetics of heterogeneous reactions between gas-phase oxidants (NO₂, O₃, and OH radicals) and PAHs adsorbed on various carrier surfaces (soot, mineral particles, organic aerosols, etc.) have been studied intensively.⁸,¹⁰,¹¹,¹³–¹⁶ Additionally, because NO₃ radicals play an important role in the atmospheric chemistry at nighttime, heterogeneous reactions of surface-bound PAHs with NO₃ radicals have been investigated by a few groups in recent years.¹²,¹³,¹⁴,¹⁶–²¹ Shiraiwa et al.²¹ reported that the rate constants for surface layer reactions of PAHs with NO₃ radicals were in the range from $10^{-15}$ to $10^{-12}$ cm²·s⁻¹. Kaiser et al.²⁴

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indicated that PAHs were degraded rapidly at nighttime due to gas-surface reactions with NO3 radicals. Besides, some studies on the uptake coefficients and reaction products of heterogeneous reactions between PAHs and NO3 radicals have been performed.12,24,27,28 However, to our knowledge, few reaction rate data for the reactions of suspended PAH particles with NO3 radicals have been determined.

In this study, effective rate constants for heterogeneous reactions of NO3 radicals with five 4-ring PAHs adsorbed on suspended azelaic acid particles are determined via a mixed-phase relative rate approach. The five 4-ring PAHs used in the experiment are benzo[a]anthracene (BaA), chrysene (Ch), pyrene (Py), and two derivatives of Py [1-nitropyrene (1-NP) and 1-hydroxypyrene (1-OHP)]. All of them have been observed in the atmosphere.3,4,29–31 During the reaction process, the concentration changes of suspended PAH particles and gas-phase isoprene are measured synchronously by a real-time vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS) and an online atmospheric gas analysis mass spectrometer, respectively.

**EXPERIMENTAL SECTION**

The experimental setup of the heterogeneous reaction between PAH aerosols and NO3 radicals has been described in detail elsewhere.32 Briefly, it consists of an aerosol generator, a reaction chamber, and analytical instruments.

PAH aerosols are generated through homogeneous nucleation. The aerosol generator is an electric tube furnace equipped with two tandem quartz tubes [50 cm (length) × 3 cm (inner diameter)], each with an independent temperature controller. Azelaic acid is used to produce nuclei in this study due to its limited reactivity toward NO3 radicals. Pure azelaic acid particles are exposed to NO3 radicals at a concentration of ~5 × 1010 molecules·cm−3 for 10 min, and no reaction product is observed with ATOFMS. Azelaic acid is placed in the first tube while the PAH sample in the second tube. A N2 stream with a volumetric flow rate of 0.6 L·min−1 flows through the first tube, bringing the nuclei into the second tube. In the second tube, the azelaic acid nuclei are coated by the PAH sample. The size and concentration of particles are monitored by a scanning mobility particle sizer (SMPS), which is determined via a mixed-phase relative rate approach. The five 4-ring PAHs used in the experiment are BaA, Ch, Py, 1-NP, and 1-OHP, respectively, calculated according to the size distributions of particles before and after coating with the PAH sample.

The reaction chamber with a volume of ~180 L consists of a thin-walled open head stainless steel drum and a thin Tedlar poly(vinyl fluoride) (PVF) film bag. A magnetic-driven fan is set at the bottom of the reaction chamber to ensure that the reactants could be mixed rapidly and sufficiently. The experiments are performed under atmospheric pressure at room temperature of ~287 K. The relative humidity in the chamber is roughly estimated to be ~5% from the residual filtered air in the chamber. After the concentration of PAH particles within the reaction chamber reaches the desired value, isoprene is injected into the reaction chamber. The initial concentration of isoprene in the chamber is ~1.5 × 1014 molecules·cm−3, measured with an atmospheric gas analysis mass spectrometer (QIC-20-HAL3F-RC, Hiden) via detection of the mass peak at m/z 67 (C5H9O·). Then, a N2 stream with a volumetric flow rate of 0.6 L·min−1 passes through a flask containing N2O5 powder and introduces NO3 vapor into the reaction chamber. NO3 radicals are generated by thermal decomposition of N2O5 at the room temperature of ~287 K. The concentrations of NO3 radicals employed in the experiment are (1.4–18) × 1014 molecules·cm−3, estimated according to the loss rates of isoprene. The 400 s wall losses of PAHs and isoprene in the absence of oxidants are below 5%, monitored with the VUV-ATOFMS and the atmospheric gas analysis mass spectrometer, respectively.

The concentrations of PAH aerosols are measured in real time with VUV-ATOFMS via detection of their molecular ion mass peaks. Detailed descriptions of VUV-ATOFMS have been presented elsewhere.32,33 Therefore, only a brief description of VUV-ATOFMS is presented here. It consists of three collimated chambers: a source chamber, a differential chamber, and a detection chamber.33 An 8 mm diameter copper rod coupled with a cartridge heater (~523 K) placed in the detection chamber is used to vaporize the particles; the nascent organic vapor is photoionized with VUV light emitted from a VUV light lamp with a photon flux of ~5 × 1014 photons·s−1 and a photon energy of 10 eV.33 The pulsed electric field of the ion repeller runs at 15 kHz. Each time-of-flight mass spectrum takes 10 s of acquisition and 1 s of saving data files. The mass resolution of VUV-ATOFMS is ~1000 and the detection limit is ~0.5 µg·m−3 for PAHs.

Three duplicate experiments are performed for the heterogeneous reaction of each PAH sample. Before every single experiment, the reaction chamber is rinsed thoroughly with absolute ethyl alcohol and dried with hot air. During the experiment, the atmospheric gas analysis mass spectrometer and VUV-ATOFMS respectively monitor the concentrations of isoprene and PAH particles every 11 s. The data are recorded continuously until the end of the reaction. Since the concentration of PAH particles is linear with respect to the signal intensity of the mass peak measured by VUV-ATOFMS,33 the decay rate of signal intensity is equal to the decay rate of PAH concentration. In addition, the reaction products are identified with an Agilent 6890 GC/MS and the analysis method has been described in detail elsewhere.28

The PAHs samples used in the experiment are listed in Table 1. Azelaic acid (Sinopharm Chemical Reagent Co., Ltd., 99%), fuming nitric acid (Beijing Lisui Chemical Factory, 95%), P2O5 (Sinopharm Chemical Reagent Co., Ltd., 98%), absolute ethyl alcohol (Sinopharm Chemical Reagent Co., Ltd., 99.7%), and dichloromethane (J. T. Baker Co., chromatographic grade) are used in the experiment. Nitrogen (99.999%) is purchased from Beijing Huayuan Gas Chemical Industry Co. Ltd.

**RESULTS AND DISCUSSION**

The maximum average concentrations of NO3 and N2O5 in this work are estimated to be 3.0 × 1012 and 2.8 × 1013 molecules·cm−3, respectively, according to the maximum loss of isoprene and the thermal decomposition rate of N2O5, at ~287 K.34 In order to evaluate the possible effects of the reactions between PAH aerosols and NO3 on the decays of PAHs in the experiment, PAH particulates exposed to NO3 with a concentration of ~4.6 × 1013 molecules·cm−3 are investigated. The results show that there are no apparent
products produced after PAH particulates are exposed to NO₃ for 400 s. Besides, it was reported that the reactive uptake coefficients of NO₃ radicals on PAH surfaces were 4 orders of magnitude higher than those of NO₂. Considering that the maximum acquisition time of the kinetic data in the experiment is less than 300 s, the direct loss of PAH aerosols due to the reaction with NO₂ is neglected in this study. Kaments et al. have reported that the heterogeneous rate constants for reactions of PAHs with N₂O₅ (≈2.5 × 10¹⁴ molecules·cm⁻³⁻¹·s⁻¹) are on the order of 10⁻¹⁸ cm³·molecule⁻¹·s⁻¹. These results suggest that PAH heterogeneous reactions with N₂O₅ to degrade particle-bound PAHs are not important. Besides, the reported reactive uptake coefficients of N₂O₅ on PAH surfaces were 4 orders of magnitude lower than those of NO₃ radicals. Therefore, the effects of N₂O₅ on the loss of PAHs are also ignored in the experiment.

**Reaction Products.** The mononitro, dinitro, and polynitro products from successive nitro-substitution reactions of PAH particles are observed in real time with VUV-ATOFMS. 7-Nitrobenzo[a]anthracene, benzo[a]anthracene-7,12-dione, 1-nitropyrene, and 1,3-, 1,6-, and 1,8-dinitropyrene are identified as the main reaction products of BaA, Py, and 1-NP by GC/MS analysis (Table S1 in Supporting Information). Polynitro products of 1-OHP observed with VUV-ATOFMS are not identified successfully by GC/MS analysis. The failure may be due to the polarity and thermal instability of the reaction products. These experimental results are consistent with our previous studies. TOF mass spectra of BaA, Py, 1-NP, and 1-OHP particles and their products in the reactions with NO₃ radicals are shown in Figures S1 and S2 in Supporting Information, which have been reported and discussed in detail in earlier studies. Figure 1a shows the TOF mass spectrum of Ch particles in the reaction chamber before exposure to NO₃ radicals. The ion peak at m/z 228 corresponds to the molecular ion peak of Ch. The mass spectrum shown in Figure 1b is acquired 200 s after exposure to NO₃ radicals. The acquisition time for each mass spectrum is 10 s. The concentration of NO₃ radicals exposed to Ch particles is approximately 4.0 × 10⁹ molecules·cm⁻³⁻¹.

**Effective Rate Constants.** According to the mixed-phase relative rate expression presented in the previous studies, the effective mixed-phase ratio of rate constants (κ_PAH/κₜₚₑᵢₙ) can be typically expressed as follows: ⁴⁰⁻⁴¹

\[
\ln \left( \frac{C_{PAH}}{C_{PAH0}} \right) = \ln \left( \frac{k_{PAH}}{k_{ref}} \right)_{eff} \ln \left( \frac{C_{ref}}{C_{ref0}} \right)
\]

Here C_PAH and C_ref are the real-time concentrations of particle-bound PAH and gas-phase reference species, C_PAH₀ and C_ref₀ are the initial concentrations of PAH particles and gas-phase reference species, (k_PAH/κₜₚₑᵢₙ) eff is the effective reaction rate constant of particulate PAH, and k_ref is the reaction rate constant of the gas-phase reference species. Isoprene served as the reference substance in the experiment, and the reaction rate constant of gas-phase isoprene with NO₃ radicals adopted in this study is 7.0 × 10⁻¹⁵ cm³·molecule⁻¹·s⁻¹. ⁴² As the average NO₃ radical exposure C_NO₃ = −ln (C_ref/C_ref₀)/k_ref, the effective reaction rate constant (κ_PAH/κₜₚₑᵢₙ) eff can be transformed into eq 2: ⁴⁴

\[
\ln \left( \frac{C_{PAH}}{C_{PAH0}} \right) = -\left( k_{PAH} \right)_{eff} C_{NO₃} t
\]

Here C_NO₃ is the time-averaged concentration of NO₃ radicals in the gas phase, and t is the exposure time. By plotting ln (C_PAH/C_PAH₀) versus C_NO₃ t, the effective rate constant (κ_PAH/κₜₚₑᵢₙ) eff can be obtained.

Figure 2 shows the plots of ln (C_PAH/C_PAH₀) versus NO₃ radical exposure for BaA, Ch, Py, 1-NP, and 1-OHP particles. The wall losses (<5%) of PAH particulates are ignored in the
The experimental results show that 1-OHP is ~8 times more reactive than 1-NP. The reactivities of BaA and Ch toward NO₃ radicals are similar, both of which are ~3 times faster than that of 1-NP. The effective reaction constant for Py particles is ~1.5 times larger than those of BaA and Ch. Miet et al. reported that 1-OHP was more reactive than Py in the reaction with O₃, whereas 1-NP was less reactive than Py. The reactivities of Py, 1-NP, and 1-OHP toward NO₃ radicals in this study are similar to their results. The heterogeneous reaction rates of Py and fluoranthene (Fl) with NO₃ radicals estimated by Gross and Bertram were 8 × 10⁻¹² and 9 × 10⁻¹² cm²·molecule⁻¹·s⁻¹, respectively. The effective reaction constants obtained in this study are basically consistent with their results.

**NO₃ Uptake Coefficients.** The uptake coefficients (γ) of NO₃ radicals on PAH particles are calculated with the following equation, the detailed derivation of which is shown in Supporting Information:

\[
γ = \frac{(R_p^3 - R_c^3)\rho_{PAH} N_A \eta_{PAH}}{3M_{PAH} R_p D_{NO₃}}
\]

Here, \(R_p\) is the particle radius (centimeters), \(R_c\) is the radius of the inner core (centimeters), \(\rho_{PAH}\) is the PAH density (1.2–1.4 g·cm⁻³), \(N_A\) is Avogadro’s number, \(\eta_{PAH}\) is the ratio of consumption (0.8–0.9, depending on each PAH sample), \(M_{PAH}\) is the PAH molecular weight (grams per mole), \(D_{NO₃}\) is the diffusion coefficient of NO₃ radicals (~0.12 cm²·s⁻¹), and \(C_{NO₃}\) is the average NO₃ exposure (molecules per cubic centimeter second).

According to eq 3, the uptake coefficients for NO₃ radicals on BaA, Ch, Py, 1-NP, and 1-OHP particles are 2.4, 1.5, 3.1, 0.5, and 4.8, respectively, which are much larger than the reported data. Lambe et al. reported that evaporation followed by gas-phase oxidation was the main reason resulting in the uptake coefficients greater than unity observed in their experiment. In this experiment, the vapor pressures of the 4-ring PAHs are less than 6 × 10⁻⁸ Pa and their gas-phase reaction rates with NO₃ radicals are on the order of 10⁻¹⁷–10⁻¹⁶ cm³·molecule⁻¹·s⁻¹. Therefore, the influences of gas-phase reactions of the 4-ring PAHs on the uptake coefficients could be neglected. The diffusion coefficient data processing. Error bars represent the standard deviation of three duplicate experiments. The five plots shown in Figure 2 are fitted well with linear least-squares fitting (\(R^2 > 0.96\)). The obtained slopes of linear regressions correspond to the effective reaction rate constants (\(k_{eff}\)) for BaA, Ch, Py, 1-NP, and 1-OHP particle reactions with NO₃ radicals, which are 4.3 × 10⁻¹², 4.0 × 10⁻¹², 6.4 × 10⁻¹², 1.3 × 10⁻¹², and 1.0 × 10⁻¹¹ cm³·molecule⁻¹·s⁻¹, respectively (Table 2). The experimental results show that 1-OHP is ~8 times more reactive than 1-NP. The reactivities of BaA and Ch toward NO₃ radicals are similar, both of which are ~3 times faster than that of 1-NP. The effective reaction constant for Py particles is ~1.5 times larger than those of BaA and Ch. Miet et al. reported that 1-OHP was more reactive than Py in the reaction with O₃, whereas 1-NP was less reactive than Py. The reactivities of Py, 1-NP, and 1-OHP toward NO₃ radicals in this study are similar to their results. The heterogeneous reaction rates of Py and fluoranthene (Fl) with NO₃ radicals estimated by Gross and Bertram were 8 × 10⁻¹² and 9 × 10⁻¹² cm²·molecule⁻¹·s⁻¹, respectively. The effective reaction constants obtained in this study are basically consistent with their results.

**Table 2. Comparison of Rate Constants**

<table>
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<tr>
<th>compd</th>
<th>NO₂</th>
<th>O₃</th>
<th>OH radicals</th>
<th>NO₃ radicals</th>
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<td></td>
<td>graphite</td>
<td>silica</td>
<td>graphite</td>
<td>silica</td>
</tr>
<tr>
<td>BaA</td>
<td>3.2 × 10⁻¹⁷</td>
<td>6.7 × 10⁻¹⁸</td>
<td>2.8 × 10⁻¹⁷</td>
<td>8.7 × 10⁻¹⁷</td>
</tr>
<tr>
<td>Ch</td>
<td>3.7 × 10⁻¹⁷</td>
<td>6.0 × 10⁻¹⁹</td>
<td>1.5 × 10⁻¹⁷</td>
<td>3.1 × 10⁻¹⁷</td>
</tr>
<tr>
<td>Py</td>
<td>5.1 × 10⁻¹⁷</td>
<td>2.0 × 10⁻¹⁸</td>
<td>2.5 × 10⁻¹⁷</td>
<td>5.9 × 10⁻¹⁷</td>
</tr>
<tr>
<td>1-NP</td>
<td>6.2 × 10⁻¹⁸</td>
<td>2.2 × 10⁻¹⁷</td>
<td>1.1 × 10⁻¹⁶</td>
<td>1.3 × 10⁻¹⁰</td>
</tr>
</tbody>
</table>

In units of cubic centimeters per molecule per second. aData derived from Esteve et al. bData derived from Perraudin et al. cData derived from Esteve et al. dThis work. eData derived from Perraudin et al. fData derived from Miet et al. gData derived from Miet et al.
(~0.12 cm²·s⁻¹) applied in the calculation above is the value used to describe natural diffusion resulting from the gradient in the concentration. When it is considered that NO₃ radicals in the reaction chamber are forcibly diffused with a mixing fan, the diffusion coefficient under this circumstance should be much greater than that of natural diffusion. By use of the reported NO₃ uptake coefficients on PAHs surfaces,¹²,²⁷ a derived diffusion coefficient of ~1.0 cm²·s⁻¹ is obtained for NO₃ radicals under the experimental condition. Calculated with this diffusion coefficient, the corresponding uptake coefficients of NO₃ radicals on BaA, Ch, Py, 1-NP, and 1-OHP particles are 0.29, 0.18, 0.37, 0.06, and 0.57, respectively. We speculate that the corrected values are more reasonable.

**Atmospheric Implications.** Heterogeneous reactions of NO₃ with PAHs adsorbed on various carrier surfaces have been performed intensively, and the rate constants for heterogeneous reactions of NO₃ with PAHs are in the range 10⁻¹⁵–10⁻¹⁷ cm³·molecule⁻¹·s⁻¹ (Table 2).¹⁷⁻²¹ The results obtained in this study show that the effective reaction rate constants of PAHs with NO₃ radicals are about 5–7 orders of magnitude faster than those of adsorbed PAHs oxidized by NO₂. Heterogeneous reactions of O₃ with particulate PAHs also attracted much attention, and the rate constants for heterogeneous reactions of PAHs with O₃ range from 10⁻¹⁸ to 10⁻¹⁶ cm³·molecule⁻¹·s⁻¹ (Table 2).⁸,¹⁰,¹³–¹⁵ Thus, the obtained reaction rate constants of PAHs aerosols with NO₃ radicals are about 4–6 orders of magnitude faster than those of adsorbed PAHs oxidized by O₃. Shiraiwa et al.⁵ reported that the surface layer reactions of PAHs with NO₃ radicals were much faster (by 2–6 orders of magnitude) than those of PAHs with NO₂ and O₃. The results obtained in the experiment are consistent with those presented by Shiraiwa et al.²³

In addition, the estimated rate constants of adsorbed PAHs with OH radicals range from 10⁻¹⁳ to 10⁻¹² cm³·molecule⁻¹·s⁻¹ (Table 2),¹⁷,¹⁸,²² which are close to the effective reaction rate constants for PAHs in the reactions with NO₃ radicals obtained in this study. However, compared with NO₃ radicals, the effect of OH radicals on the degradation of atmospheric particle-bound PAHs may not be remarkable due to its lower concentration in the atmosphere.²⁴ Recently, Kaiser et al.²⁴ reported that PAH half-lives at nighttime were on the order of seconds due to rapid oxidation by gas–surface reactions with NO₂ radicals, while half-lives of PAH aerosols at daytime were longer (on the order of minutes). The reported reaction rates of the homogeneous reactions between gas-phase 4-ring PAHs and NO₂ radicals were on the order of 10⁻¹⁷–10⁻¹⁶ cm³·molecule⁻¹·s⁻¹.³⁷,³⁸ According to the effective rate constants obtained in this work and previous data,¹² the gas-phase reaction rates of PAHs with NO₂ radicals are about 4–5 orders of magnitude slower than the heterogeneous reaction rates. Thereby, under typical atmospheric conditions at nighttime, NO₂ radicals could be the most important oxidant for the degradation of atmospheric PAHs.

The concentrations of NO₃ radicals employed in the experiment are close to the atmospheric concentration of NO₃ radicals at nighttime.³⁷ Therefore, the kinetic data obtained with eq 2 can be directly used to estimate the atmospheric lifetime of PAH aerosols. The corresponding lifetimes of BaA, Ch, Py, 1-NP, and 1-OHP are 7.8, 8.3, 5.2, 25.6, and 3.3 min, respectively, calculated from a NO₃ radical concentration of 5 × 10⁶ molecules·cm⁻³ in the lower troposphere at nighttime.³⁷ To our knowledge, 1-OHP is rarely observed in the atmosphere,⁷⁰ while the other four PAHs are reported in many field studies.³,⁴,²⁹,³¹ These observations may partly reflect the lifetimes of these five PAHs. Under real atmospheric conditions, the phase and morphology of atmospheric particles may be quite complex, and those PAHs distributed in the particle bulk may not be accessible for oxidation by NO₃ radicals (or other gas-phase oxidants). In addition, other factors such as atmospheric relative humidity,²⁴ particle sizes,⁴¹ and concentrations of particulate reactants and gas-phase oxidants⁴⁶ can affect heterogeneous reaction. As a result, the lifetimes of atmospheric PAH aerosols may vary under different circumstances.

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