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

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S Supporting Information

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 4.3×10^{-12} , 4.0×10^{-12} , 6.4×10^{-12} , 1.3×10^{-12} , and 1.0×10^{-11} cm³·molecule⁻¹·s⁻¹, respectively, and their corresponding atmospheric lifetimes range from several minutes to half an hour at the NO₃ radical concentration of 5×10^8 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.^{1,2} 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).^{1,2} 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.^{8,10,11,13–26} 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.^{12,23,24,27,28} Shiraiwa et al.²³ 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 NO_3 radicals. Besides, some studies on the uptake coefficients and reaction products of heterogeneous reactions between PAHs and NO_3 radicals have been performed.^{12,24,27,28} However, to our knowledge, few reaction rate data for the reactions of suspended PAH particles with NO_3 radicals have been determined.

In this study, effective rate constants for heterogeneous reactions of NO_3 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 NO_3 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) $\times$ 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 NO_3 radicals. Pure azelaic acid particles are exposed to NO_3 radicals at a concentration of $\sim 5 \times 10^9$ 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 N_2 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 composed of a differential mobility analyzer (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3010). The measured mean diameters of BaA, Ch, Py, 1-NP, and 1-OHP particles are 310, 324, 292, 280, and 285 nm, respectively, and their corresponding mass concentrations are 274 ± 17 , 424 ± 38 , 211 ± 15 , 421 ± 33 , and 396 ± 29 $\mu\text{g}\cdot\text{m}^{-3}$. The geometric standard deviations of particles are 1.2–1.4. The thicknesses of the coatings are 33, 40, 34, 29, and 27 nm for BaA, Ch, Py, 1-NP, and 1-OHP, respectively, calculated according to the size distributions of particles before and after coating by 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 $\sim 5\%$ 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 $\sim 1.5 \times 10^{14}$ 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 (C_5H_7^+). Then, a N_2 stream with a volumetric flow rate of 0.6 L·min⁻¹ passes through a flask containing N_2O_5 powder and introduces N_2O_5 vapor into the reaction chamber. NO_3 radicals are generated by thermal decomposition of N_2O_5 at the room temperature of ~ 287 K. The concentrations of NO_3 radicals employed in the experiment are $(1.4\text{--}18) \times 10^9$ 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 $\sim 5 \times 10^{14}$ 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 $\mu\text{g}\cdot\text{m}^{-3}$ 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%), P_2O_5 (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 (99.99%) is purchased from Beijing Huayuan Gas Chemical Industry Co. Ltd.

■ RESULTS AND DISCUSSION

The maximum average concentrations of NO_2 and N_2O_5 in this work are estimated to be 3.0×10^{13} and 2.8×10^{15} molecules·cm⁻³, respectively, according to the maximum loss of isoprene and the thermal decomposition rate of N_2O_5 at ~ 287 K.³⁴ In order to evaluate the possible effects of the reactions between PAH aerosols and NO_2 on the decays of PAHs in the experiment, PAH particulates exposed to NO_2 with a concentration of $\sim 4.6 \times 10^{13}$ molecules·cm⁻³ are investigated. The results show that there are no apparent

Table 1. Polycyclic Aromatic Hydrocarbons Used in the Experiment

Name	Formula	Structure	MW	Purity	Supplier
BaA	C ₁₈ H ₁₂		228	98%	TIC-GR
Ch	C ₁₈ H ₁₂		228	98%	Sigma-Aldrich
Py	C ₁₆ H ₁₀		202	98%	Sigma-Aldrich
1-NP	C ₁₆ H ₉ NO ₂		247	97%	Matrix Scientific
1-OHP	C ₁₆ H ₁₀ O		218	98%	Sigma-Aldrich

products produced after PAH particulates are exposed to NO₂ 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 NO₂.¹² 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. Kamens et al.³⁵ have reported that the heterogeneous rate constants for reactions of PAHs with N₂O₅ ($\sim 2.5 \times 10^{14}$ molecules·cm⁻³) 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.¹² 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.²⁸ 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.²⁸ 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 the injection of NO₃ radicals into the reaction chamber, and there are two new mass peaks appearing at *m/z* 273 and 318, which are assigned as mononitrochrysene and dinitrochrysene, respectively, on the basis of the ratios of mass to charge (*m/z*). The mononitrochrysene is further identified as 6-nitrochrysene on the basis of GC/MS analysis, which has been observed in the atmospheric particulate matter.²⁹ As reported in the literature, the reaction of NO₃

Figure 1. TOF mass spectra of (a) Ch particles and (b) their oxidation products after reaction with NO₃ radicals. 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 4.0×10^9 molecules·cm⁻³.

radicals with PAH begins with an initial addition of the NO₃ radical to the aromatic rings to form a nitratocyclohexadienyl-type radical, which then either decomposes back to reactants or reacts exclusively with NO₂ to form NPAHs.^{36–38} The oxidation products observed in this study are mutagenic and carcinogenic and are recognized to be secondary air toxics.^{1,2,19,39}

Effective Rate Constants. According to the mixed-phase relative rate expression presented in the previous studies, the effective mixed-phase ratio of rate constants ($k_{\text{PAH}}/k_{\text{ref}}^{\text{m}}$) can be typically expressed as follows:^{40,41}

$$\ln(C_{\text{PAH}}/C_{\text{PAH}0}) = (k_{\text{PAH}}/k_{\text{ref}}^{\text{m}})_{\text{eff}} \ln(C_{\text{ref}}/C_{\text{ref}0}) \quad (1)$$

Here C_{PAH} and C_{ref} are the real-time concentrations of particle-bound PAH and gas-phase reference species, $C_{\text{PAH}0}$ and $C_{\text{ref}0}$ are the initial concentrations of PAH particles and gas-phase reference species, $(k_{\text{PAH}})_{\text{eff}}$ 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^{-13} cm³·molecule⁻¹·s⁻¹.⁴² As the average NO₃ radical exposure $\bar{C}_{\text{NO}_3}$, $t = -\ln(C_{\text{ref}}/C_{\text{ref}0})/k_{\text{ref}}$,⁴³ eq 1 can be transformed into eq 2:⁴⁴

$$\ln(C_{\text{PAH}}/C_{\text{PAH}0}) = -(k_{\text{PAH}})_{\text{eff}} \bar{C}_{\text{NO}_3} t \quad (2)$$

Here $\bar{C}_{\text{NO}_3}$ is the time-averaged concentration of NO₃ radicals in the gas phase, and t is the exposure time. By plotting $\ln(C_{\text{PAH}}/C_{\text{PAH}0})$ versus $\bar{C}_{\text{NO}_3} t$, the effective rate constant $(k_{\text{PAH}})_{\text{eff}}$ can be obtained.

Figure 2 shows the plots of $\ln(C_{\text{PAH}}/C_{\text{PAH}0})$ 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

Figure 2. Plots of $\ln(C_{\text{PAH}}/C_{\text{PAH0}})$ versus NO_3 radical exposure for (a) BaA, (b) Ch, (c) Py, (d) 1-NP, and (e) 1-OHP particles. The average concentrations of NO_3 radicals exposed to BaA, Ch, Py, 1-NP, and 1-OHP particles are approximately 1.7×10^9 , 4.0×10^9 , 1.6×10^9 , 6.1×10^9 , and 1.7×10^9 molecules·cm $^{-3}$, respectively.

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 NO_3 radicals, which are 4.3×10^{-12} , 4.0×10^{-12} , 6.4×10^{-12} , 1.3×10^{-12} , and 1.0×10^{-11} cm 3 ·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 NO_3 radicals are similar, both of which are ~ 3 times faster than that of 1-NP. The effective rate constant for Py particles is ~ 1.5 times larger than those of BaA and Ch. Miet et al.¹⁴ reported that 1-OHP was more reactive than Py in the reaction with O_3 , whereas 1-NP was less reactive than Py. The reactivities of Py, 1-NP, and 1-OHP toward NO_3 radicals in this study are similar to their results. The heterogeneous reaction rates of Py and fluoranthene (Fl) with NO_3 radicals estimated by Gross and Bertram¹² were 8×10^{-11} and 9×10^{-12} cm 3 ·molecule $^{-1}$ ·s $^{-1}$, respectively. The effective rate constants obtained in this study are basically consistent with their results.

NO_3 Uptake Coefficients. The uptake coefficients (γ) of NO_3 radicals on PAH particles are calculated with the following equation, the detailed derivation of which is shown in Supporting Information:

$$\gamma = \frac{(R_p^3 - R_c^3)\rho_{\text{PAH}}N_A\eta_{\text{PAH}}}{3M_{\text{PAH}}R_pD_{\text{NO}_3}\bar{C}_{\text{NO}_3}t} \quad (3)$$

Here R_p is the particle radius (centimeters), R_c is the radius of the inner core (centimeters), ρ_{PAH} is the PAH density (1.2–1.4 g·cm $^{-3}$), N_A is Avogadro's number, η_{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_{NO_3} is the diffusion coefficient of NO_3 radicals (~ 0.12 cm 2 ·s $^{-1}$),⁴⁵ and $\bar{C}_{\text{NO}_3}t$ is the average NO_3 exposure (molecules per cubic centimeter second).

According to eq 3, the uptake coefficients for NO_3 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.^{12,27} Lambe et al.⁴⁴ 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^{-4} Pa and their gas-phase reaction rates with NO_3 radicals are on the order of 10^{-17} – 10^{-16} cm 3 ·molecule $^{-1}$ ·s $^{-1}$.^{1,12,37,38} Therefore, the influences of gas-phase reactions of the 4-ring PAHs on the uptake coefficients could be neglected. The diffusion coefficient

Table 2. Comparison of Rate Constants^a for Heterogeneous Reactions between Particulate PAHs and Different Atmospheric Oxidants

compd	NO_2		O_3		OH radicals		NO_3 radicals
	graphite ^b	silica	graphite ^c	silica	graphite compds	SRM 1650a ^d	azelaic acid ^e
BaA	3.2×10^{-17}	6.7×10^{-18f}	2.8×10^{-17}	8.7×10^{-17c}	5.6×10^{-12}	3.2×10^{-13}	4.3×10^{-12}
Ch	3.7×10^{-17}	6.0×10^{-19f}	1.5×10^{-17}	3.1×10^{-17c}	5.0×10^{-12}	4.4×10^{-13}	4.0×10^{-12}
Py	5.1×10^{-17}	2.0×10^{-17f}	2.5×10^{-17}	5.9×10^{-17c}	3.1×10^{-12}	4.1×10^{-13}	6.4×10^{-12}
1-NP		6.2×10^{-18g}		2.2×10^{-17h}			1.3×10^{-12}
1-OHP				7.7×10^{-16h}			1.0×10^{-11}

^aIn units of cubic centimeters per molecule per second. ^bData derived from Esteve et al.¹⁷ ^cData derived from Perraudin et al.⁸ ^dData derived from Esteve et al.¹⁸ ^eThis work. ^fData derived from Perraudin et al.²⁰ ^gData derived from Miet et al.¹⁹ ^hData derived from Miet et al.¹⁴

($\sim 0.12 \text{ cm}^2 \cdot \text{s}^{-1}$) 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 NO_3 radicals in the reaction chamber are forcedly 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 NO_3 uptake coefficients on PAHs surfaces,^{12,27} a derived diffusion coefficient of $\sim 1.0 \text{ cm}^2 \cdot \text{s}^{-1}$ is obtained for NO_3 radicals under the experimental condition. Calculated with this diffusion coefficient, the corresponding uptake coefficients of NO_3 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 NO_2 with PAHs adsorbed on various carrier surfaces have been performed intensively, and the rate constants for heterogeneous reactions of NO_2 with PAHs are in the range 10^{-19} – $10^{-17} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (Table 2).^{17–21} The results obtained in this study show that the effective reaction rate constants of PAHs with NO_3 radicals are about 5–7 orders of magnitude faster than those of adsorbed PAHs oxidized by NO_2 . Heterogeneous reactions of O_3 with particulate PAHs also attracted much attention, and the rate constants for heterogeneous reactions of PAHs with O_3 range from 10^{-18} to $10^{-16} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (Table 2).^{8,10,13–15} Thus, the obtained reaction rate constants of PAHs aerosols with NO_3 radicals are about 4–6 orders of magnitude faster than those of adsorbed PAHs oxidized by O_3 . Shiraiwa et al.²³ reported that the surface layer reactions of PAHs with NO_3 radicals were much faster (by 2–6 orders of magnitude) than those of PAHs with NO_2 and O_3 . 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^{-13} to $10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (Table 2),^{17,18,22} which are close to the effective reaction rate constants for PAHs in the reactions with NO_3 radicals obtained in this study. However, compared with NO_3 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 NO_3 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 NO_3 radicals were on the order of 10^{-17} – $10^{-16} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$.^{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 NO_3 radicals are about 4–5 orders of magnitude slower than the heterogeneous reaction rates. Thereby, under typical atmospheric conditions at nighttime, NO_3 radicals could be the most important oxidant for the degradation of atmospheric PAHs.

The concentrations of NO_3 radicals employed in the experiment are close to the atmospheric concentration of NO_3 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 NO_3 radical concentration of $5 \times 10^8 \text{ molecules} \cdot \text{cm}^{-3}$ in the lower troposphere at nighttime.³⁷ To our knowledge, 1-OHP is rarely observed in the atmosphere,³⁰ 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 NO_3 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 PAHs aerosols may vary under different circumstances.

■ ASSOCIATED CONTENT

Supporting Information

Additional text, one table, and two figures with information on reaction products, TOF mass spectra, and uptake calculations. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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