Effects of Humidity and $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ Ratio on the Heterogeneous Reaction of Fluoranthene and Pyrene with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$

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S Supporting Information

ABSTRACT: Atmospheric 2-nitrofluoranthene (2-NFL) and 2-nitropyrene (2-NPY) were two important nitro-polycyclic aromatic hydrocarbons (NPAHs). Especially, 2-NFL was recognized to be the most abundant particle-associated NPAH (Ramdahl et al., 1986). In previous studies, these two products were observed in the gas-phase reaction between $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ and their parent polycyclic aromatic hydrocarbons (PAHs), while the heterogeneous reaction generated other nitro-PAH isomers (1, 3, 7, 8-NFL and 1-NPY) (Atkinson et al. 1990). To clarify the possible reasons for this difference, the heterogeneous reactions of suspended fluoranthene (FL) and pyrene (PY) particles under different relative humidity (RH; 0.5%–43%) and $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ ratios were carried out. Under low humidity (0.5% RH) or a relatively high ratio of $[\text{NO}_3]/[\text{N}_2\text{O}_5]$, 2-NFL and 2-NPY were observed as the major nitro-FL isomers for the first time in the heterogeneous reaction. Decreasing the humidity or increasing the $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ ratio in the reaction essentially increases the concentration ratio of $[\text{NO}_3(\text{g})]/[\text{NO}_2^+(\text{aq})]$ on the particle surface (NO_2^+ is derived from the ionization of N_2O_5). Thus, it can be concluded that under different atmospheric conditions, the change of $[\text{NO}_3(\text{g})]/[\text{NO}_2^+(\text{aq})]$ in the particle surface has an influence on the product distribution of FL and PY in the atmosphere. The experimental results provide evidence for the heterogeneous formations of particle-bound 2-NFL and 2-NPY. However, relative to the gas-phase formation, they will be negligible in the real atmosphere. 2-NFL and 2-NPY observed in the ambient particles should mainly derive from deposition of gas-phase reactions. Additionally, this study also clarifies the reason for different nitro-PAHs isomers observed between gas and particulate reactions.

INTRODUCTION

The atmospheric chemistry between polycyclic aromatic hydrocarbons (PAHs) and gas-phase oxidants (O_3 , OH, NO_3 , and NO_2) is the most important source of toxic and mutagenic PAH derivatives (nitro-PAHs and oxy-PAHs) in the atmosphere.^{1–6} Nitro-PAHs (NPAHs) have mutagenic potencies up to 100 000 times greater than PAHs^{7–10} and constitute 10% of the total mutagenicity of inhalable particles in the ambient atmosphere.^{11,12} Additionally, these nitrated species especially have strong narrow band adsorption bands in the UV–visible range, which may enhance the radiative forcing in the atmosphere and therefore contribute to significant climate effects.^{13,14} Both 2-nitrofluoranthene (2-NFL) and 2-nitropyrene (2-NPY) are two ubiquitous nitro-PAH pollutants and ambient 2-NFL/2-NPY ratio is generally used to assess the contribution of the NO_3 radical chemistry for NPAHs formation.^{15–18}

Considering that neither 2-NFL nor 2-NPY have been directly observed from combustion emissions,^{19–21} most research has focused on the contribution of the atmospheric reactions of FL and PY with gas-phase oxidants (OH or NO_3 radicals in the presence of NO_2). Some studies have suggested that these two nitro-PAHs were formed exclusively via

atmospheric gas-phase reactions of FL and PY.^{22,23} The production of 2-NFL involves the gas-phase reaction between FL and either OH or NO_3 radicals in the presence of NO_2 , whereas the production of 2-NPY mainly involves the gas-phase reaction of PY initiated by OH radical.^{24–27} The formation of both 2-NFL and 2-NPY in the gas phase is a multistep addition–elimination reaction initiated by OH or NO_3 radical species. This radical-initiated reaction is postulated to proceed by an initiated-addition of OH radical (present during the day time) or the NO_3 radical (present during evening and night time) to the position with the highest electron density (the 3-position in FL and 1-position in PY), followed by the ortho addition of NO_2 (2-position) and subsequent loss of H_2O or HNO_3 .^{27–31} By contrast, many reports have also focused on the heterogeneous reactions of FL and PY with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$, but only 1-, 3-, 7-, 8-NFL, and 1-NPY have been observed as the reaction products.^{1,16,31,32} The formation of these NPAHs via heterogeneous chemistry has been proposed to occur via an ionic electrophilic nitration by the nitronium ion (NO_2^+).³¹

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Table 1. Initial Experimental Conditions

oxidants	estimated NO ₃ /N ₂ O ₅	PAH	heterogeneous reaction at RH (%)					gas-phase reaction at RH (%)	
			~43	<9	<5	<2	<0.5	~43	<0.5
N ₂ O ₅ ~12 ppm	~1.0 × 10 ⁻⁴	FL	✓	✓	✓	✓	✓	✓	✓
		PY	✓		✓		✓	✓	✓
N ₂ O ₅ /O ₃ ~9 ppm/~10 ppm	~(8–10) × 10 ⁻³	FL	✓				✓		
		PY	✓				✓		

Given the abundant existence of a liquid layer on wood and diesel soot particle surfaces in the atmosphere, it is speculated that N₂O₅ is ionized on particle surfaces to give NO₂⁺ as the nitration species prior to the reaction with PAHs.^{31,33,34} Therefore, both 2-NFL and 2-NPY are proposed as markers for radical-initiated reactions.^{17,35}

Since these specific radical-initiated nitro-isomers (2-NFL and 2-NPY) are not observed in heterogeneous reactions, whether the NO₃ radical-initiated reactions can result in the formation of nitro-PAHs in a heterogeneous environment is unclear. Furthermore, the exact cause of the difference between the products of the homogeneous and heterogeneous reactions of PAHs with NO₃ radicals is still a controversy. Two potential explanations have been put forward to explain these issues. First, some studies have suggested that the reaction proceeds by a different mechanism depending on if it is carried out under heterogeneous or gas-phase condition.^{1,27,31,33} Alternatively, some recent studies suggested that high concentrations of N₂O₅ and NO₂ in the ambient atmosphere may block the accommodation and reaction of the NO₃ radical on the particle surfaces.^{27,30,36} Unfortunately, these speculations have not yet been scientifically proven.

In order to clarify these speculations, the heterogeneous reaction of suspended FL and PY aerosol particles and N₂O₅/NO₃/NO₂ was analyzed in detail to determine if humidity has an impact on the heterogeneous mechanism. The second set of experiment described here focuses on the effect of the ratio of [NO₃]/[N₂O₅] on the heterogeneous reaction. The results added to the understanding of atmospheric transformations of PAHs, especially for systems containing N₂O₅/NO₃/NO₂.

EXPERIMENTAL METHODS

Experimental Setup. The experimental setup used in this work is similar to that reported in previous studies.² The schematic diagram of the experimental setup is shown in Supporting Information (SI) Figure S1. It consisted of an aerosol reaction chamber, online and offline analytical instruments, an aerosol generator, an ozone generator, and a N₂O₅ vapor manipulator. The online and offline analytical instruments included a laboratory-built vacuum ultraviolet photoionization aerosol time-of-flight mass spectrometer (VUV-ATOFMS), a laboratory-built vacuum ultraviolet photoionization gas time-of-flight mass spectrometer (VUV-GTOFMS), a scanning mobility particle sizer (SMPS) composed of a differential mobility analyzer (DMA, TSI 3081) and a condensation particle counter (CPC, TSI 3010), an ozone monitor (model 202), a Vaisala Humicap (HMM100), an atmospheric gas analysis mass spectrometer (QIC-20-HAL3F-RC, Hiden), and a gas chromatograph/mass spectrometer (GC-MS). The Vaisala Humicap was used to monitor the relative humidity (RH; > 5%) in the chamber online, while QIC-20-HAL3F-RC was employed to monitor the RH < 5% via detection of the ion at *m/z* 18. The measured mean diameters

of the FL and PY particles (with azelaic acid as the substrate) were 327 ± 34 and 364 ± 20 nm, respectively. The geometric standard deviation of the particle diameter was 1.2. The coating thicknesses of FL and PY are 57 and 96 nm, respectively. They are estimated according to the size distributions of particles before and after coating by the PAH sample.² The initial mass concentrations of particulate FL and PY in the chamber were estimated to be 112 ± 9 and 143 ± 17 μg m⁻³, respectively.

N₂O₅ was synthesized according to the literature and kept in a glass trap in liquid nitrogen prior to use.³⁷ N₂O₅ was eluted by passing a stream of N₂ (~0.6 lpm) over N₂O₅ crystals held in a cooling bath (243 K). A digital refrigerated circulator bath (−40–100 °C, DCW-4006, China) was used to maintain a constant temperature of the cooling bath. The concentration of N₂O₅ in the chamber was controlled via adjusting the temperature of the bath. O₃ was prepared by passing O₂ through a commercial ozonizer (NBF30/W) and its initial concentration in the mixture was measured with an ozone monitor. All experiments were conducted in the dark at room temperature and atmospheric pressure. It should be noted that the gas-phase control experiments were conducted at 298 K, whereas the heterogeneous experiments were conducted at 286 K. The experimental conditions were summarized in Table 1.

Exposure Experiments. Effect of Humidity on the Heterogeneous Chemistry. Heterogeneous Exposures. The exposures of FL and PY particles to the N₂O₅/NO₃/NO₂ system in the range of 0.5%–43% RH (0.06–5.6 g m⁻³) were conducted in the chamber at 286 K. The mixture of N₂O₅/NO₃/NO₂ was generated by the thermal decomposition of N₂O₅ according to eq R1. The thermal dissociation rate of N₂O₅ was ~0.01 s⁻¹ at 286 K.^{38–40} In order to change the humidity in the chamber, two glass culture dishes containing phosphorus pentoxide power were placed at the bottom of the chamber. Before each reaction experiment, the chamber was flushed with nitrogen three times and then filled with compressed air. The initial concentration of N₂O₅ was estimated to be ~12 ppm in the chamber. After each reaction, the particles were collected by a filter and off-line analysis with GC-MS. Since the gas-phase N₂O₅/NO₃/NO₂ was not denuded upstream of the filter sampling line, the subsequent reaction occurring on the surface of the filter during sampling could not be excluded. Additionally, there might be some HNO₃ molecules formed in the chamber. However, the previous references have suggested that the HNO₃ present in these exposures could not be responsible for the high degrees of nitration observed in these exposures for PY and FL.¹⁶

Gas-Phase Control Exposures. In order to evaluate the mass transfer from the gas phase to the heterogeneous reaction products, the gas-phase experiments of FL and PY by exposure to N₂O₅/NO₃/NO₂ were conducted at 298 K under 0.5% and 43% RH. The chamber was flushed with clean compressed air

for several times until the mass concentration of particle in the chamber decreased to $\sim 0.7 \pm 0.3 \mu\text{g m}^{-3}$ prior to each experiment. A N_2 stream with a volumetric flow rate of 0.2 L min^{-1} flowed through a heated PAH-contained quartz tube bringing PAHs vapor/particles into the reaction chamber until the mass concentrations of PAHs particles in the chamber reached $20 \pm 5 \mu\text{g m}^{-3}$. Then, the PAHs gas/particles were exposed to $\sim 12 \text{ ppm}$ of $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ for $\sim 5 \text{ min}$. Both gas phase and particle-phase substances in the reaction chamber were collected by liquid nitrogen washing after exposure. The corresponding schematic diagram of the collecting setup was shown in SI Figure S1. Five mL sodium bicarbonate solution ($\sim 1 \text{ mg mL}^{-1}$) was placed at the bottom of the round-bottomed flask prior to collecting, which could prevent trapped PAHs from nitration by trapped nitric acid during the process of thermal balance. After the temperature of round-bottomed flask restored up to room temperature, the reaction products formed in the gas-phase and particle phase were extracted using $\sim 5 \text{ mL}$ dichloromethane via supersonic wave-assisted extraction method. According to similarity-intermiscibility theory, it was very easy to separate the dichloromethane with extracted reaction product and sodium bicarbonate solution.

The concentrations of gas-phase FL in the chamber were investigated using VUV-GTOFMS at 298 K. The experimental result showed that the concentration of gas-phase FL in the chamber filled with $\sim 20 \pm 5 \mu\text{g m}^{-3}$ FL particles was $\sim 10 \text{ ppbv}$ ($\sim 117.4 \mu\text{g m}^{-3}$) which was close to the saturated concentration of gaseous FL at 298 K. Therefore, we speculated that the concentration of gas-phase PAH in the presence of a large amount of PAH particles in the reaction chamber was determined by their vapor pressure. The detailed experiment process was described in SI.

Effect of $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ Ratio on the Heterogeneous Chemistry. FL and PY particles were exposed to the $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2/\text{O}_3$ system in the chamber under ambient humidity ($\sim 43\% \text{ RH}$). The mixture of $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ and O_3 was prepared by simultaneously introducing O_3 and N_2O_5 into the reaction chamber through two independent mass flow controllers (MFC, D08–2F), respectively. In order to decrease the concentration of N_2O_5 , the $\text{N}_2\text{O}_5/\text{N}_2$ mixture was flowed through a quartz tube (heated at 430 K) at the entrance of the reaction chamber. As such, the N_2O_5 decomposed completely to NO_3 radical and NO_2 , and 20% of NO_3 thermally dissociated in the quartz tube according to the literature.^{41,42} In the presence of O_3 , the ratio of $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ should increase significantly according to R2. These measures decreased the initial N_2O_5 concentration and increased the $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ ratio in the chamber. The initial concentrations of N_2O_5 and O_3 in the chamber were estimated to be ~ 9 and 10 ppm , respectively.

RESULTS AND DISCUSSION

Effect of Humidity on the Heterogeneous Chemistry. Particulate FL Exposed to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$. The heterogeneous reaction of FL particles with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ in the reaction chamber was monitored online via VUV-ATOFMS. TOF mass spectra of FL particles and their particle-associated products in the reaction with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ under different RH are shown in Figure 1. All peak intensities were normalized to that of the initial mass peak at m/z 202 (FL particles) shown in Figure 1A. Figure 1B showed the TOF mass spectrum of NFL

Figure 1. Time-of-flight mass spectrum of FL particles and the reaction products from the reaction between FL particles and a mixture of $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ under atmospheric humidity: 43% RH (B) and 0.5% RH (C). The reaction time was 300 s.

(m/z 247) under ambient humidity (43% RH; $\sim 5.6 \text{ g m}^{-3}$). By contrast, the mass peaks at m/z 218, 232, and 277 were observed in addition to the mass peaks at m/z 247 (Figure 1C) when a low humidity (0.5% RH; $\sim 0.06 \text{ g m}^{-3}$) was employed in the chamber. The mass peaks at m/z 218 and 232 were assigned to hydroxyl-fluoranthene (HFL) and fluoranthene-quinone (FLQ), respectively. These two products were consistent with two oxygenated PAHs (OPAHs) observed in the reaction of N_2O_5 with FL in CCl_4 at 25°C .³¹ The mass peak at m/z 277 was tentatively assigned to mono-NFL-quinone (NFLQ). NFLQ contains a nitro and ketone group and may come from the secondary reaction of FLQ with NO_3 radical. The experimental results show that the NFL formed/FL reacted ratio (0.24) at 43% RH is greater than that (0.07) at 0.5% RH. This phenomenon may result from the additional formation of oxy-FLs in the heterogeneous reaction of FL at 0.5% RH.

These reactions products observed using VUV-ATOFMS were analyzed and identified using offline GC-MS. The NFL isomers identified with GC-MS are shown in Figure 2A. As shown in Figure 2A, four isomers of mono-NFLs (1-, 3-, 7-, and 8-NFLs) formed under ambient humidity (43% RH) was consistent with the reported reaction products of adsorbed FL with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$.^{22,31} However, in addition to the four NFL isomers, 2-NFL was observed to be the major NFL at 0.5% RH. It should be noted that the relative yield of 3-NFL at 43% RH was a factor of ~ 13 higher than that at 0.5% RH by comparing the signal intensities of 3-NFL observed using GC/MS under different RH.

To further investigate the sources of 2-NFL observed in Figure 2A, the gas-phase control experiment of FL with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ were conducted in the reaction chamber at 0.5% and 43% RH. The obtained results showed that the amount of 2-NFL formed at 43% RH was almost equal to that formed at 0.5% RH (Figure 2B). Additionally, 1-, 3-, 7-, and 8-NFL

Figure 2. Gas chromatogram of the reaction products from the reaction of particulate FL (A) and gaseous FL (B) by exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ under different RH, 43% RH (black line) and 0.5% RH (red line).

isomers were also observed under both humidity conditions. We concluded that these four NFL isomers (1-, 3-, 7-, and 8-NFL) were formed from the heterogeneous reaction of FL particles in the chamber. The results shown in Figure 2(A and B) also revealed that the relative amount of 2-NFL observed in the heterogeneous reaction was 1 order of magnitude more than that in the gas-phase reaction. Since the heterogeneous experiments were conducted at 286 K which is lower than the temperature of gas-phase experiments (298 K), the yield of 2-NFL formed in the gas-phase reaction at 286 K should be even less than that at 298 K due to the lower vapor pressure for FL ($\sim 3.0 \times 10^{-4}$ Pa at 286 K). Therefore, the 2-NFL observed in the reaction of particulate FL with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ at 0.5% RH (presented as the red line in Figure 2A) should be mainly contributed from the heterogeneous reaction.

Particulate PY Exposed to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$. The heterogeneous reaction of PY particles with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ was also investigated in detail under different humidity. Only a small amount of NPY was observed using VUV-ATOFMS under different RH (shown in SI Figure S5). The NPY was identified using offline GC-MS (Figure 3). As shown in Figure 3A, 1-NPY was the sole product observed under ambient humidity (43% RH), which was consistent with some recent studies.^{1,24,35,43} Additionally, this experimental result was also consistent with the observation reported by Zimmermann et al.²⁴ They found that under actual ambient conditions where $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ was present, very little possible formation of 1-NPY occurred in comparison with 2-NFL formation.²⁷ Thereby, we concluded that only small amount of 1-NPY may be formed through the heterogeneous processing of PY with atmospheric oxidants in the real atmosphere. Besides 1-NPY, 2-NPY, and a trace amount of 4-NPY were also observed in the heterogeneous reaction of PY under low humidity (0.5% RH).

Figure 3. Gas chromatogram of the reaction products from the reaction of particulate PY (A) and gaseous PY (B) by exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ under different RH, 43% RH (black line) and 0.5% RH (red line).

The control experiment of gas-phase reactions between PY and $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ at 0.5% RH was also conducted to evaluate the contribution of the gas-phase 2-NPY. However, as shown in Figure 3B, only a large amount of 1-NPY and trace amount of 4-NPY (without 2-NPY) were observed in the gas-phase reaction at 0.5% RH. Thereby, the contribution of 2-PY from gas-phase reaction to the heterogeneous reaction could be negligible.

Additionally, as shown in Figure 4, a decreasing ratio of 2-NFL/3-NFL and 2-NPY/1-NPY was observed with increasing humidity in the chamber. Under $\sim 0.5\%$ RH, the ratio of 2-NFL/3-NFL and 2-NPY/1-NPY were $\sim 1.8 \pm 0.3$ and $\sim 0.25 \pm 0.03$, respectively. However, when the ambient humidity was increased to 43% RH, the ratio of 2-NFL/3-NFL and 2-NPY/1-NPY were close to zero. This phenomenon might be explained by the fact that under a low RH ($\sim 0.5\%$) the absence of water in the particle phase suppresses the ionization of N_2O_5 at 0.5% RH and subsequently suppresses the NO_2^+ -initiated electrophilic nitration reaction, leading to an abundant formation of NO_3 radical-derived products, 2-NFL or 2-NPY. Another critical factor for this phenomenon was that the effective uptake coefficients of N_2O_5 on the surface of organic/inorganic particles increased apparently with increasing humidity.^{44–46} In our experiment, when the RH was increased to 43% the N_2O_5 -initiated ionization may be dominated in the reaction process and only NO_2^+ -initiated reaction products (1-, 3-, 7-, 8-NFL and 1-NPY) were produced, which provided direct evidence that the N_2O_5 -initiated ionization was inextricably linked with liquid water in the atmospheric particle or ambient RH. The experimental results not only suggested that humidity has a significant impact on the heterogeneous reaction mechanism, but also explained why both 2-NFL and 2-NPY were hardly produced in the heterogeneous reaction under real atmospheric condition.

Effect of $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ Ratio on the Heterogeneous Reaction. Particulate FL Exposed to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2/\text{O}_3$. The

Figure 4. Ratio of 2-NFL/3-NFL (A) and 2-NPY/1-NPY (B) versus the relative humidity obtained from reactions between particulate FL and PY and $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ (300 s reaction time with RH in the range of 0.5–43% in the chamber). The error bars are $\pm 7\%$ (FL) and $\pm 4.5\%$ (PY), respectively.

heterogeneous reaction of particulate FL and $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ in the presence of O_3 was investigated in the reaction chamber at both 43% and 0.5% RH, which is shown in Figure 5A. The peak intensities of the m/z of 218, 232, and 247 were more comparable to m/z 202 as compared with those shown in Figure 1C. This may be because the heterogeneous reaction between particulate FL and O_3 also produces oxy- and HFL products.^{35,47,48} Similar with that in Figure 2A, the similar NFL isomer distributions (2- > 3- > 8- > 7- > 1-NFL) in the presence of O_3 under different RH were observed (Figure 5B). The decreasing amount of NFL and the increasing ratio of 2-NFL/3-NFL with the decreasing RH were also observed in the presence of O_3 , which was similar to that exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ only (shown in Figure 2A). Comparing with that in Figure 2A, it should be noted that the amount of 3-NFL formed in the presence of O_3 was lower and the ratio of 2-NFL/3-NFL was higher comparing with that in the $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ at a given relative humidity (43% RH or 0.5% RH). A possible reason for the differences may be that the addition of O_3 not only increased the concentration ratio of $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ in the gas phase but also caused the formation of more particle-bound NO_3 radical due to the surface reaction of O_3 with NO_2 under either higher or lower RH.⁴⁹

Particulate PY Exposed to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2/\text{O}_3$. The heterogeneous reaction of particulate PY and $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ in the presence of O_3 was also investigated in the reaction chamber under different RH. The TOF mass spectra of both NPAHs and OPAHs were observed after 230 s exposure (Figure 6A), which was different with that in the reaction with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ only (SI Figure S5). The mass peaks at m/z 202 and 247 corresponded to the molecular ions of PY and

Figure 5. Time-of-flight mass spectrum (A) of reaction products from the reaction between FL particles and $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2/\text{O}_3$ for 160 s. The corresponding gas chromatogram (B) of reaction products under different RH: 43% RH (black line) and 0.5% RH (red line).

NPY, respectively. The mass peaks at m/z 218 and 250 were assigned to hydroxypyrene (HPY) and 4-carboxy-5-phenanthrene-carboxaldehyde, respectively. These two products may be produced through the heterogeneous reaction of PY with O_3 , which is consistent with that reported by Gao et al.⁴⁷ The mass peaks at m/z 232 and 277 were assigned to 4,5-pyrenequinone (4,5-PYQ) and mononitro-4,5-pyrenequinone (mononitro-4,5-PYQ). The product mononitro-4,5-PYQ may come from the secondary reaction of 4,5-PYQ with the NO_3 radical on the particle surface. However, these secondary products should be unlikely formed in the real atmosphere due to very lower level of NO_3 radical (and 10–400 ppt) and trace amount of 4,5-PYQ.⁵⁰

Figure 6B showed the corresponding products identified using GC-MS. In addition to 1-NPY, both 2-NPY and 4-NPY were formed in the presence of O_3 under different humidity. The decreasing amount of 1-NPY and increasing ratio of 2-NPY/1-NPY with the decreasing RH were also observed in the presence of O_3 (Figure 6B), which was consistent with that exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ only (Figure 3A). Similar with FL, the ratio of 2-NPY/1-NPY was also higher than that exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ only at either 43% RH or 0.5% RH. Whereas, unlike FL, the amount of NPY formed in the presence of O_3 was higher than that exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ only. This may result from that a significant amount of 2-NPY and 4-NPY were formed in the $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2/\text{O}_3$ exposure due to the higher concentration ratio of $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ (~ 0.01 in Table 1) at either 43% RH or 0.5% RH.

Figure 6. Time-of-flight mass spectrum (A) of reaction products from the reaction between PY particles and $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2/\text{O}_3$ for 230 s. The corresponding gas chromatogram (B) of reaction products under different RH: 43% RH (black line) and 0.5% RH (red line).

The experimental results showed that both 2-NFL and 2-NPY were formed in the heterogeneous reactions of FL and PY particles, respectively, by exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2/\text{O}_3$ under different RH, which was apparently different from exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ only under ambient humidity (43% RH). Thereby, we concluded that the concentration ratio of $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ has a significant impact on the heterogeneous reaction mechanism under either higher RH or lower RH.

■ ATMOSPHERIC IMPLICATIONS

This study provides evidence for the NO_3 radical-initiated heterogeneous reactions. The distribution of the reaction products of particulate FL and PY with the $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ system was influenced by humidity and the concentration ratio of $[\text{NO}_3]/[\text{N}_2\text{O}_5]$. NO_2^+ (derived from the ionization of N_2O_5 on the particle surface) and NO_3 radical-initiated reactions are a pair of competing reactions on the particle surface, leading to formation of 1-, 3-, 7-, 8-NFL/1-NPY, and 2-NFL/2-NPY, respectively. Since the absence of water adsorbed on particles can suppress the ionization of N_2O_5 and formation of NO_2^+ , decreasing the humidity or increasing the $[\text{NO}_3]/[\text{N}_2\text{O}_5]$ ratio in our experiments, essentially increases the concentration ratio of $[\text{NO}_3(\text{g})]/[\text{NO}_2^+(\text{aq})]$ on the particle surface, thereby promoting the formation of the NO_3 radical-initiated reaction markers, 2-NFL and 2-NPY. However, in the real atmosphere, a low humidity (<5% RH) hardly exists and the concentration of NO_3 radicals ranges from <10 to 430 ppt, which is far less than the concentration of N_2O_5 (up to ~10 ppb).^{50–54} Under these conditions, the concentration ratio of $[\text{NO}_3(\text{g})]/[\text{NO}_2^+(\text{aq})]$ on the particle surface would be much lower than those in our experiments. This might explain why 2-NFL and 2-NPY are

hardly observed in the heterogeneous reactions of atmospheric particles and why 1-, 3-, 7-, 8-NFL and 1-NPY are observed as the dominant nitro-products. Thereby, we conclude that the formation of 2-NFL or 2-NPY from heterogeneous NO_3 chemistry, relative to that in the gas-phase reaction, is not expected to be an important process under ambient conditions.²⁷ And 2-NFL and 2-NPY observed in the ambient particles should mainly derive from deposition of gas-phase reactions.

Recently, some studies reported that the indirect sinks of NO_3 radical in the atmosphere were closely related to the heterogeneous loss of N_2O_5 , which increased apparently with increasing RH.^{55,56} This result may well support our speculation that on the atmospheric particles, N_2O_5 would ionize in the adsorbed water, leading to a sink of NO_3 and the generation of NO_2^+ . As a result, the low ratio of $[\text{NO}_3(\text{g})]/[\text{NO}_2^+(\text{aq})]$ on the particle surface would make the heterogeneous reaction of PAHs significantly different from that in the gas phase, causing different nitro-PAHs isomers to be produced. In other words, the change in atmospheric humidity would alter the amount of $[\text{NO}_3(\text{g})]/[\text{NO}_2^+(\text{aq})]$ on the particle surface and has an influence on the product distribution of the reaction between particulate PAHs and NO_3 and N_2O_5 . The influence of humidity on the heterogeneous reaction is also reflected by decay rate of the particulate PAHs. In the experiments, the signal intensities of particulate FL and PY decayed much more quickly when the low humidity (~0.5% RH) was applied, or in the presence of O_3 , as compared with the exposure to $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ at ambient humidity (~43% RH). Shiraiwa et al. also showed that the degradation rates of PAHs increased with increasing NO_3 radical concentrations in the presence of O_3 at 25% RH.⁴⁹ Therefore, it can be concluded that when the atmospheric humidity is changed (the concentration of $[\text{NO}_3(\text{g})]/[\text{NO}_2^+(\text{aq})]$ on the particle surface is altered), the transformation rates and lifetimes of particulate PAHs is also influenced. These results may deepen our understanding of the migration and transformation of PAHs in the atmosphere.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section, additional control experiments, estimation of oxidants concentrations in different experiments, and TOF mass spectra. 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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