



## Uptake of NO<sub>3</sub> on soot and pyrene surfaces

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[1] The reaction of NO<sub>3</sub> with methane soot, hexane soot, and solid pyrene was investigated using a flow tube reactor. The uptake of NO<sub>3</sub> on fresh soot was fast (uptake coefficient >0.1). Based on this result and an assumed density of reactive sites on soot, the time to process or oxidize 90% of a soot surface in the atmosphere would take only approximately five minutes. This suggests that NO<sub>3</sub> chemistry can rapidly oxidize soot surfaces under atmospheric conditions. After exposing soot films to NO<sub>3</sub> for approximately 180 minutes in the laboratory, the uptake reaches a steady-state value. The steady state uptake coefficients (assuming a geometric surface area) were  $0.0054 \pm 0.0027$  and  $0.0025 \pm 0.0018$  for methane and hexane soot, respectively. These numbers are used to show that heterogeneous reactions between NO<sub>3</sub> and soot are not likely a significant sink of gas-phase NO<sub>3</sub> under most atmospheric conditions. The uptake of NO<sub>3</sub> on fresh pyrene surfaces was also fast (uptake coefficient >0.1), and much faster than previously suggested. We argue that under certain atmospheric conditions reactions between NO<sub>3</sub> and surface-bound polycyclic aromatic hydrocarbons (PAHs) may be an important loss process of PAHs in the atmosphere. **Citation:** Mak, J., S. Gross, and A. K. Bertram (2007), Uptake of NO<sub>3</sub> on soot and pyrene surfaces, *Geophys. Res. Lett.*, 34, L10804, doi:10.1029/2007GL029756.

### 1. Introduction

[2] Reactions between NO<sub>3</sub> and gas-phase species have received a significant amount of attention, and this research has shown that NO<sub>3</sub> is an important nighttime gas-phase oxidant [Finlayson-Pitts and Pitts, 2000]. While the chemistry between NO<sub>3</sub> and gas-phase species is relatively well understood, the chemistry between NO<sub>3</sub> and atmospheric particles remains basically unexplored with a few exceptions.

[3] Heterogeneous reactions between NO<sub>3</sub> and atmospheric particles may be important for several reasons. For example, these reactions could be a sink of NO<sub>3</sub> in the atmosphere, and they may also change the chemical composition and toxicity of aerosol particles [Finlayson-Pitts and Pitts, 2000; Moise et al., 2002].

[4] Heterogeneous reactions between NO<sub>3</sub> and aqueous solutions, mineral dust, and organic substrates have previously been studied [Docherty and Ziemann, 2006; Hung et al., 2005; Imamura et al., 1997; Karagulian and Rossi, 2005; Knopf et al., 2006; Moise et al., 2002; Rudich et al., 1996a; Rudich et al., 1996b; Rudich et al., 1998; Schutze and Herrmann, 2005]. Also the uptake of NO<sub>3</sub> on decane

soot and soot produced with a graphite spark generator was recently explored [Saathoff et al., 2001; Karagulian and Rossi, 2007]. To add to this short list, we have carried out measurements of the reactive uptake coefficient of NO<sub>3</sub> on methane and hexane soot surfaces and on solid pyrene surfaces (pyrene is a polycyclic aromatic hydrocarbon consisting of four aromatic rings). The reactive uptake coefficient is defined as the ratio of the molecules removed from the gas-phase by reactions to the total gas-surface collisions. These are the first measurements of the reactive uptake coefficient of NO<sub>3</sub> on methane soot, hexane soot, and pyrene. For both soot and pyrene, we measured the uptake coefficient on fresh surfaces, and for soot we also measured the reactive uptake of NO<sub>3</sub> as a function of exposed time to NO<sub>3</sub> to assess whether or not the NO<sub>3</sub> reaction modifies the soot surface.

[5] The studies involving solid pyrene were carried out to better understand the chemistry of NO<sub>3</sub> with polycyclic aromatic hydrocarbons (PAHs) adsorbed on or absorbed in atmospheric particles. PAHs while in the atmosphere can be adsorbed on or absorbed in atmospheric particles where they can undergo heterogeneous reactions with gas-phase oxidants. There has only been one study that has looked at the reaction of NO<sub>3</sub> and PAHs adsorbed on a substrate, but the reactive uptake coefficient of NO<sub>3</sub> on the surface was not determined [Pitts et al., 1985]. Our measurements with solid pyrene surfaces are a starting point to understanding the reactivity of NO<sub>3</sub> with PAHs adsorbed on and absorbed in atmospheric particles. Our studies with solid PAH surfaces are also related to the soot measurements since soot is believed to contain a significant amount of PAH material.

[6] In this manuscript we show that NO<sub>3</sub> is efficiently taken up by fresh soot and fresh pyrene surfaces and the possible atmospheric implications are discussed.

### 2. Experimental

[7] The apparatus used in this work was similar to that previously used in our laboratory to study heterogeneous loss processes [Knopf et al., 2005; Knopf et al., 2006]. It consisted of a coated-wall flow tube reactor coupled to a chemical ionization mass spectrometer. The flow tube was constructed of borosilicate glass and included a movable injector through which NO<sub>3</sub> was introduced. The main carrier gas, which was a mixture of He (80%) and O<sub>2</sub> (20%), was introduced through a port at the upstream end of the flow reactor. The inside wall of a Pyrex tube (1.75 cm inside diameter and 15 cm in length) was coated with either soot or a pyrene film and then inserted into the flow tube reactor. These coatings provided the surfaces for the heterogeneous studies.

[8] The reactive uptake coefficients were determined by first measuring the loss of NO<sub>3</sub> on the surfaces as a function of injector position. This data was then used to calculate the

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**Table 1.** Summary of the Uptake Measurements for Fresh and Oxidized Methane and Hexane Soot and Fresh Pyrene Surfaces

| Surface      | $\gamma_g$ (Fresh Surface) | $\gamma_g$ (Oxidized Surface) |
|--------------|----------------------------|-------------------------------|
| Methane soot | >0.1                       | 0.0054 ± 0.0027               |
| Hexane soot  | >0.1                       | 0.0025 ± 0.0018               |
| Solid pyrene | >0.1                       | -                             |

observed first-order loss rate coefficient,  $k_{\text{obs}}$ . Next  $k_{\text{obs}}$  was corrected for concentration gradients that form close to the flow-tube wall by using the procedure developed by *Brown* [1978]. The diffusion coefficients of NO<sub>3</sub> reported by *Rudich et al.* [1996a] were used when correcting for concentration gradients. The reactive uptake coefficient,  $\gamma$ , was calculated from the corrected  $k_{\text{obs}}$  using a standard procedure [*Knopf et al.*, 2005]. This procedure assumes that the surface area available for reaction is equal to the geometric surface area of the Pyrex tubes. To indicate that the reactive uptake coefficient was based on a geometric surface area we use the symbol  $\gamma_g$ . The effect of the porosity of the films on the reactive uptake coefficient is addressed below.

[9] The flow tube technique utilized in this research is typically capable of accessing reactive uptake coefficients greater than  $10^{-6}$ . However, for our flow rates and pressures, reactive uptake coefficients greater than approximately 0.1 are greatly influenced by gas-phase diffusion to the reactive surface. In this case, a small uncertainty in  $k_{\text{obs}}$  or the diffusion coefficient results in a large uncertainty in the reactive uptake coefficients. For this reason, when the reactive uptake coefficient is >0.1 we are only able to report a lower limit of 0.1.

[10] NO<sub>3</sub> radicals were produced by passing N<sub>2</sub>O<sub>5</sub> through a Teflon coated glass oven held at 423–433 K [*Knopf et al.*, 2006]. At the exit of the flow cell, NO<sub>3</sub> was detected using chemical ionization with I<sup>-</sup> as the reagent ion. NO<sub>3</sub> concentration used in these studies ranged from  $0.7 \times 10^{11}$  to  $4 \times 10^{11}$  molecule cm<sup>-3</sup> and NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> ratios ranged from 20 to 100.

[11] Solid pyrene films were prepared by first melting pyrene crystals on the inside of the Pyrex tubes and then rotating the tubes while the liquid pyrene recrystallized. This resulted in an even distribution of the pyrene and a relatively flat surface – the surface area was within 2 % of the geometric surface area of the Pyrex tube based on measurements with a profilometer. The profilometer measurements were performed using Pyrex slides rather than Pyrex tubes. However, the slides were prepared using the same techniques that were used to prepare the tubes. For the soot experiments, two types of soot surfaces were used: methane soot and hexane soot. Methane soot was generated by exposing the inner wall of the glass tube to a methane flame produced with a standard torch. Hexane soot was generated by combusting hexane in an open glass container. An inverted glass funnel was placed above the glass container to limit the amount of air during combustion. A glass tube was held above the narrow opening of the funnel until a coating of soot covered the inner wall. The total mass of methane or hexane soot deposited in our experiments ranged from 1.6 to 6.4 mg.

[12] Soot and pyrene experiments were conducted at a temperature of 298 K and 293 K respectively. The total

pressures used in the uptake measurements ranged from 2–4 Torr with a total flow rate ranging from 450–4000 sccm in the flow reactor.

### 3. Results and Discussion

#### 3.1. Soot Studies

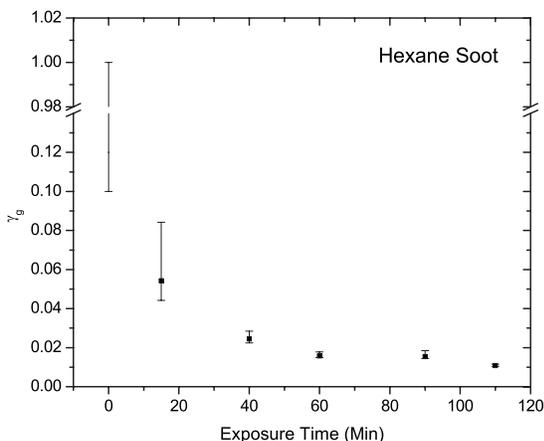
[13] Shown in the auxiliary material are examples of results from NO<sub>3</sub> uptake measurements on soot.<sup>1</sup> Displayed are several uptake measurements made on the same sample of hexane soot after exposing the sample to NO<sub>3</sub> at a concentration of approximately  $1.1 \times 10^{11}$  molecule cm<sup>-3</sup> for 0 to 110 minutes. The data show that the uptake decreases with NO<sub>3</sub> exposure time.

[14] The uptake coefficient,  $\gamma_g$ , on fresh methane and hexane soot in both cases is >0.1 (see Table 1). The reported values take into account the uncertainty in the measurements and the uncertainty in the diffusion coefficient used when calculating  $\gamma_g$ . Since  $\gamma_g$  is based on the geometric surface area, it is an upper limit to the true uptake coefficient. However, when  $\gamma_g$  is >0.1, the correction factor for porous films is typically small (between 1/3 and 1) [*Keyser et al.*, 1991]. Hence, our measured  $\gamma_g$  is close to the true uptake coefficient. Our results are in good agreement with the reactive uptake coefficients measured by *Karagulian and Rossi* [2007] for decane soot.

[15] Shown in Figure 1 are results from the measurements of  $\gamma_g$  on a hexane soot film as a function of time of exposure to NO<sub>3</sub>. Methane soot shows a similar trend. The data show that the NO<sub>3</sub> uptake decreases with exposure, suggesting the uptake process is reactive. At long exposure times (approximately 180 minutes) the uptake reaches a steady-state rate. The values for the reactive uptake coefficient associated with the steady-state loss are  $0.0054 \pm 0.0027$  and  $0.0025 \pm 0.0018$  for methane and hexane soot, respectively. These values are based on several measurements at an exposure time of approximately 180 minutes. The steady-state loss values are included in Table 1 for comparison. *Karagulian and Rossi* [2007] also observed a decrease in uptake with exposure time for decane soot, but they used relatively short exposures, so a direct comparison is not possible.

[16] As discussed above, when  $\gamma_g$  is >0.1, the correction for porosity is small; however, the porosity correction for the steady-state uptake coefficients may be large. The correction depends on the fraction of the soot film sampled by NO<sub>3</sub>. As a lower limit to the true steady-state uptake coefficient we can assume NO<sub>3</sub> samples the entire film and use the BET surface area to calculate a lower limit. Methane soot has a BET surface area of 25 m<sup>2</sup> g<sup>-1</sup> [*Tesner and Shurupov*, 1995] and hexane soot has a BET surface area of 46 m<sup>2</sup> g<sup>-1</sup> [*Choi and Leu*, 1998]. Based on these values and the mass of soot used for the experiments, the actual surface areas are 5 and 20 times greater than the geometric areas of methane and hexane soot, respectively. This translates to lower limits to the true steady-state reactive uptake coefficients of  $0.00083 \pm 0.00046$  and  $0.000124 \pm 0.000006$  for methane and hexane soot, respectively. These numbers are consistent with the numbers reported by *Saathoff et al.* [2001] for soot generated by a graphite spark generator.

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2007GL029756.



**Figure 1.** Plot of the NO<sub>3</sub> uptake coefficient as a function of exposure time on hexane soot. The soot sample was exposed to a NO<sub>3</sub> concentration of approximately  $1.1 \times 10^{11}$  molecule cm<sup>-3</sup> for 0–110 minutes.

### 3.2. Atmospheric Implications of the Soot Studies

[17] The time required for the reactive uptake coefficient to reach a steady-state value in the soot experiments was approximately 180 minutes for an NO<sub>3</sub> concentration of  $10^{11}$  molecule cm<sup>-3</sup>. We assume this corresponds to the time to process or oxidize the soot surface. It is rather difficult to calculate the time to process or oxidize the surface of a soot particle in the atmosphere from our exposure studies. This is because the laboratory experiments were carried out using multiple layers of soot particles and also because the laboratory experiments involve both reaction and diffusion into the pores for all cases except at the very start of the exposure studies. Under these conditions, the NO<sub>3</sub> exposure level ( $[\text{NO}_3] \times \text{time}$ ) needed for processing in the laboratory will be larger than the NO<sub>3</sub> exposure level needed in the atmosphere.

[18] Nevertheless, we can estimate the time required for the processing of a soot particle in the atmosphere using our measured NO<sub>3</sub> reactive uptake coefficients and the following equation:[Bertram *et al.*, 2001]

$$\begin{aligned} & \text{fraction of surface processed in the atmosphere} \\ &= \exp\left(-\frac{\gamma_0 Z t}{N_{\text{total}}}\right) \end{aligned} \quad (1)$$

where  $\gamma_0$  represents the reactive uptake coefficient of NO<sub>3</sub> on a fresh soot surface,  $Z$  represents the collision frequency of NO<sub>3</sub> with the surface (molecule cm<sup>-2</sup> s<sup>-1</sup>),  $t$  represents time (s), and  $N_{\text{total}}$  represents the total number of surface sites available for reaction (reactive sites cm<sup>-2</sup>). We assume  $\gamma_0 = 0.5$ , which is consistent with our measurements. For  $N_{\text{total}}$  we used  $7 \times 10^{14}$  reactive sites cm<sup>-2</sup> which is an average of the  $N_{\text{total}}$  values reported in the literature from measurements of O<sub>3</sub> uptake on soot [Kamm *et al.*, 1999; Lelievre *et al.*, 2004; Poschl *et al.*, 2001]. In these calculations we used an NO<sub>3</sub> concentration of 50 ppt, which corresponds to polluted urban conditions. Using these values the time to process 90 % of a soot particle in the atmosphere would take only approximately 5.5 minutes. However, keep in mind that these calculations are an

estimate and include several assumptions. Nevertheless, this calculation does suggest that NO<sub>3</sub> chemistry can rapidly oxidize soot surfaces in the atmosphere. This may have implications for the CCN properties and hygroscopic properties of atmospheric particles.

[19] We have also carried out preliminary measurements of the surface functional groups produced by this NO<sub>3</sub> chemistry on soot using Fourier Transform infrared spectroscopy. Preliminary results show the formation of oxygen and nitrogen containing functional groups on the soot surface after exposure. These functional groups may alter the infrared light absorption properties of soot particles in the atmosphere as well as their health effects.

[20] To determine if the reaction between NO<sub>3</sub> and soot is a significant sink of gas-phase NO<sub>3</sub> in the troposphere, we compare the lifetime of NO<sub>3</sub> with respect to heterogeneous loss,  $\tau_{\text{het}}$ , with the lifetime of NO<sub>3</sub> estimated from field measurements.  $\tau_{\text{het}}$  can be calculated with the following equation:

$$\tau_{\text{het}} = \frac{4}{\omega \gamma A} \quad (2)$$

where  $\omega$  is the average thermal velocity,  $\gamma$  is the reactive uptake coefficient and  $A$  is the soot area density in the atmosphere. For these calculations we assume  $\gamma = 3 \times 10^{-3}$ , which is consistent with the steady-state reactive uptake coefficients determined in our measurements. Here we use the steady-state values since the initial fast uptake likely only applies to very fresh plumes in the atmosphere as mentioned above. For  $A$ , we assume  $\sim 2.5 \times 10^{-6}$  cm<sup>2</sup> cm<sup>-3</sup> based on soot concentrations of  $5 \mu\text{g m}^{-3}$  [Sloane *et al.*, 1991] and a surface to mass ratio of  $50 \text{ m}^2 \text{ g}^{-1}$ , which is consistent with BET surface areas for methane and hexane soot. Soot surface area densities of  $\sim 2.5 \times 10^{-6}$  cm<sup>2</sup> cm<sup>-3</sup> correspond roughly to polluted conditions. Using these values we get a  $\tau_{\text{het}}$  of >4.5 hours. In contrast, field measurements suggest the lifetime of NO<sub>3</sub> in the continental boundary layer is typically much less [see e.g., Geyer *et al.*, 2001; Platt *et al.*, 1984]. Hence, the loss of NO<sub>3</sub> on soot is likely not a significant sink of NO<sub>3</sub> under most atmospheric conditions except close to soot sources. However, keep in mind that the values for  $\tau_{\text{het}}$  discussed above are order of magnitude estimates, which rely on published BET surface areas for similar soot samples. Because soot structure and composition are dependent on the mode of generation, BET surface areas and reactive surface species will be different for different soot sources.

### 3.3. Pyrene Studies

[21] Also shown in Table 1 is the uptake coefficient of NO<sub>3</sub> on a fresh pyrene surface. In this case the pyrene surface is not porous so  $\gamma_g$  should be within a few percent of the true uptake coefficient.

[22] To the best of our knowledge this is only the third study of the reactive uptake coefficient of NO<sub>3</sub> on organic material. Moise *et al.* [2002] studied the uptake of NO<sub>3</sub> on a range of organics including alkanes, alkenes, an alcohol, and carboxylic acids with conjugated and nonconjugated unsaturated bonds, and they observed uptake coefficients ranging from  $1.5 \times 10^{-2}$  to  $3.8 \times 10^{-4}$ . The largest uptake coefficients were observed for molecules with unsaturated

**Table 2.** Reactive Uptake Coefficients of NO<sub>3</sub> and O<sub>3</sub> on PAH Surfaces

| Oxidant         | Surface  | $\gamma$                                      | Atmospheric Concentration, <sup>a</sup><br>[Oxidant] | $\gamma \times [\text{Oxidant}] / \text{molecule cm}^{-3}$ |
|-----------------|--|---|--|--|
| NO <sub>3</sub> | Solid pyrene   | >0.1  | 50 ppt   | $(12-1.1) \times 10^8$                                     |
| O <sub>3</sub>  | Benzo[a]pyrene on soot [Poschl et al., 2001] <sup>b</sup>  | $\sim 2 \times 10^{-5}$ to $5 \times 10^{-6}$ | 100 ppb  | $\sim (4.9-1.2) \times 10^7$                               |
| O <sub>3</sub>  | Benzo[a]pyrene on solid organic aerosol [Kwamena et al., 2004] <sup>b</sup>                        | $\sim 2 \times 10^{-6}$ to $5 \times 10^{-7}$ | 100 ppb  | $\sim (4.9-1.2) \times 10^6$                               |
| O <sub>3</sub>  | Anthracene at air-water interface [Mmereki and Donaldson, 2003; Mmereki et al., 2004] <sup>c</sup> | $\sim 3 \times 10^{-7}$ to $2 \times 10^{-8}$ | 100 ppb  | $\sim (7.4-0.5) \times 10^5$                               |

<sup>a</sup>Taken from Finlayson-Pitts and Pitts [2000].

<sup>b</sup>The reactive uptake coefficient depended on relative humidity and O<sub>3</sub> concentrations.

<sup>c</sup>The reactive uptake coefficient depended on O<sub>3</sub> concentration and whether or not the air-water interface was coated with an organic monolayer.

bonds and also octanol. Knopf et al. [2006] investigated the uptake of NO<sub>3</sub> on alkane monolayers and obtained a value of  $8.8 \times 10^{-4}$ . A comparison between the previous measurements and our current results suggests that the heterogeneous reactivity of polycyclic aromatic hydrocarbons is significantly enhanced compared to other organic groups. This suggests that NO<sub>3</sub> will preferentially oxidize polycyclic aromatic hydrocarbon material in atmospheric particles.

[23] The only other study that we are aware of that investigated NO<sub>3</sub> with surface-bound PAHs is the work by Pitts et al. [1985]. These authors carried out a preliminary study of the reaction of NO<sub>3</sub> with pyrene adsorbed on glass fiber filters in an environmental chamber. The authors monitored the decay of pyrene rather than the loss of NO<sub>3</sub> and concluded that adsorbed pyrene did not react to any observable extent with the NO<sub>3</sub> radicals. A possible reason for the apparent discrepancy may be the difference in experimental conditions. The experiments by Pitts et al. were carried out in the presence of large concentrations of N<sub>2</sub>O<sub>5</sub> ( $2.5 \times 10^{13}$  molecule cm<sup>-3</sup>). These large concentrations may have interfered with the surface reaction between NO<sub>3</sub> and pyrene by blocking reaction sites.

### 3.4. Atmospheric Implications of the Pyrene Studies

[24] Recently the reaction between O<sub>3</sub> and PAHs adsorbed on surfaces has received considerable attention [see e.g., Finlayson-Pitts and Pitts, 2000; Kwamena et al., 2004; Mmereki and Donaldson, 2003; Mmereki et al., 2004; Perraudin et al., 2007; Poschl et al., 2001; Raja and Valsaraj, 2005, and references therein]. This research has shown that under certain conditions, these reactions may be an important loss process of PAHs in the atmosphere [see e.g., Alebicjuretic et al., 1990; Finlayson-Pitts and Pitts, 2000; Mmereki et al., 2004; Poschl et al., 2001, and references therein]. To assess whether or not loss of PAHs by heterogeneous reactions with NO<sub>3</sub> is comparable to heterogeneous reactions with O<sub>3</sub> we first compare reactive uptake coefficients (see Table 2). Note the reactive uptake coefficient of O<sub>3</sub> on solid pyrene has not been measured so instead we have compared our uptake coefficients for NO<sub>3</sub> with the O<sub>3</sub> uptake coefficients on other PAH surfaces. In Table 2, we have also included approximate atmospheric concentrations of NO<sub>3</sub> and O<sub>3</sub>. In addition we have included the product  $\gamma \times [\text{oxidant}]$  where [oxidant] is the approximate atmospheric concentration in units of molecule cm<sup>-3</sup>.  $\gamma \times [\text{radical}]$  is a more relevant parameter for comparing the loss of PAHs by heterogeneous reactions, since the number

of PAH molecules lost by reaction should be proportional to  $\gamma \times [\text{radical}]$ . The  $\gamma \times [\text{radical}]$  values for NO<sub>3</sub> are greater than the  $\gamma \times [\text{radical}]$  values for O<sub>3</sub>, which suggests that NO<sub>3</sub> could potentially be more important than O<sub>3</sub> as a heterogeneous sink of PAH molecules. If the heterogeneous reaction of O<sub>3</sub> with adsorbed PAHs is important under certain conditions, as mentioned above, NO<sub>3</sub> heterogeneous reactions with PAHs should be important as well.

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### References

- Alebicjuretic, A., T. Cvitas, and L. Klasinc (1990), Heterogeneous polycyclic aromatic hydrocarbon degradation with ozone on silica-gel carrier, *Environ. Sci. Technol.*, *24*(1), 62–66.
- Bertram, A. K., A. V. Ivanov, M. Hunter, L. T. Molina, and M. J. Molina (2001), The reaction probability of OH on organic surfaces of tropospheric interest, *J. Phys. Chem. A*, *105*, 9415–9421.
- Brown, R. L. (1978), Tubular flow reactors with first-order kinetics, *J. Res. Natl. Bur. Stand. U.S.*, *83*, 1–8.
- Choi, W., and M. T. Leu (1998), Nitric acid uptake and decomposition on black carbon (soot) surfaces: Its implications for the upper troposphere and lower stratosphere, *J. Phys. Chem. A*, *102*, 7618–7630.
- Docherty, K. S., and P. J. Ziemann (2006), Reaction of oleic acid particles with NO<sub>3</sub> radicals: Products, mechanism, and implications for radical-initiated organic aerosol oxidation, *J. Phys. Chem. A*, *110*, 3567–3577.
- Finlayson-Pitts, B. J., and J. N. Pitts (2000), *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications*, 969 pp., Academic, San Diego, Calif.
- Geyer, A., R. Ackermann, R. Dubois, B. Lohrmann, T. Muller, and U. Platt (2001), Long-term observation of nitrate radicals in the continental boundary layer near Berlin, *Atmos. Environ.*, *35*(21), 3619–3631.
- Hung, H. M., Y. Katrib, and S. T. Martin (2005), Products and mechanisms of the reaction of oleic acid with ozone and nitrate radical, *J. Phys. Chem. A*, *109*, 4517–4530.
- Imamura, T., Y. Rudich, R. K. Talukdar, R. W. Fox, and A. R. Ravishankara (1997), Uptake of NO<sub>3</sub> on water solutions: Rate coefficients for reactions of NO<sub>3</sub> with cloud water constituents, *J. Phys. Chem. A*, *101*, 2316–2322.
- Kamm, S., O. Mohler, K. H. Naumann, H. Saathoff, and U. Schurath (1999), The heterogeneous reaction of ozone with soot aerosol, *Atmos. Environ.*, *33*(28), 4651–4661.
- Karagulian, F., and M. J. Rossi (2005), The heterogeneous chemical kinetics of NO<sub>3</sub> on atmospheric mineral dust surrogates, *Phys. Chem. Chem. Phys.*, *7*(17), 3150–3162.
- Karagulian, F., and M. J. Rossi (2007), Heterogeneous chemistry of the NO<sub>3</sub> free radical and N<sub>2</sub>O<sub>5</sub> on decane flame soot at ambient temperature: Reaction products and kinetics, *J. Phys. Chem. A*, *111*, 1914–1926.
- Keyser, L. F., S. B. Moore, and M. T. Leu (1991), Surface reaction and pore diffusion in flow-tube reactors, *J. Phys. Chem.*, *95*, 5496–5502.
- Knopf, D. A., L. M. Anthony, and A. K. Bertram (2005), Reactive uptake of O<sub>3</sub> by multicomponent and multiphase mixtures containing oleic acid, *J. Phys. Chem. A*, *109*, 5579–5589.

- Knopf, D. A., J. Mak, S. Gross, and A. K. Bertram (2006), Does atmospheric processing of saturated hydrocarbon surfaces by NO<sub>3</sub> lead to volatilization?, *Geophys. Res. Lett.*, *33*, L17816, doi:10.1029/2006GL026884.
- Kwamena, N. O. A., J. A. Thornton, and J. P. D. Abbatt (2004), Kinetics of surface-bound benzo[a]pyrene and ozone on solid organic and salt aerosols, *J. Phys. Chem. A*, *108*, 11,626–11,634.
- Lelievre, S., Y. Bedjanian, N. Pouvesle, J. L. Delfau, C. Vovelle, and G. Le Bras (2004), Heterogeneous reaction of ozone with hydrocarbon flame soot, *Phys. Chem. Chem. Phys.*, *6*(6), 1181–1191.
- Mmereki, B. T., and D. J. Donaldson (2003), Direct observation of the kinetics of an atmospherically important reaction at the air-aqueous interface, *J. Phys. Chem. A*, *107*, 11,038–11,042.
- Mmereki, B. T., D. J. Donaldson, J. B. Gilman, T. L. Eliason, and V. Vaida (2004), Kinetics and products of the reaction of gas-phase ozone with anthracene adsorbed at the air-aqueous interface, *Atmos. Environ.*, *38*(36), 6091–6103.
- Moise, T., R. K. Talukdar, G. J. Frost, R. W. Fox, and Y. Rudich (2002), Reactive uptake of NO<sub>3</sub> by liquid and frozen organics, *J. Geophys. Res.*, *107*(D2), 4014, doi:10.1029/2001JD000334.
- Perraudin, E., H. Budzinski, and E. Villenave (2007), Kinetic study of the reactions of ozone with polycyclic aromatic hydrocarbons adsorbed on atmospheric model particles, *J. Atmos. Chem.*, *56*(1), 57–82.
- Pitts, J. N., B. Zielinska, J. A. Sweetman, R. Atkinson, and A. M. Winer (1985), Reactions of adsorbed pyrene and perylene with gaseous N<sub>2</sub>O<sub>5</sub> under simulated atmospheric conditions, *Atmos. Environ.*, *19*(6), 911–915.
- Platt, U. F., A. M. Winer, H. W. Biermann, R. Atkinson, and J. N. Pitts (1984), Measurement of nitrate radical concentrations in continental air, *Environ. Sci. Technol.*, *18*(5), 365–369.
- Poschl, U., T. Letzel, C. Schauer, and R. Niessner (2001), Interaction of ozone and water vapor with spark discharge soot aerosol particles coated with benzo[a]pyrene: O<sub>3</sub> and H<sub>2</sub>O adsorption, benzo[a]pyrene degradation, and atmospheric implications, *J. Phys. Chem. A*, *105*, 4029–4041.
- Raja, S., and K. T. Valsaraj (2005), Heterogeneous oxidation by ozone of naphthalene adsorbed at the air-water interface of micron-size water droplets, *J. Air Waste Manage. Assoc.*, *55*(9), 1345–1355.
- Rudich, Y., R. K. Talukdar, T. Imamura, R. W. Fox, and A. R. Ravishankara (1996a), Uptake of NO<sub>3</sub> on KI solutions: Rate coefficient for the NO<sub>3</sub> + I<sup>-</sup> reaction and gas-phase diffusion coefficients for NO<sub>3</sub>, *Chem. Phys. Lett.*, *261*(4–5), 467–473.
- Rudich, Y., R. K. Talukdar, and A. R. Ravishankara (1996b), Reactive uptake of NO<sub>3</sub> on pure water and ionic solutions, *J. Geophys. Res.*, *101*, 21,023–21,031.
- Rudich, Y., R. K. Talukdar, and A. R. Ravishankara (1998), Multiphase chemistry of NO<sub>3</sub> in the remote troposphere, *J. Geophys. Res.*, *103*, 16,133–16,143.
- Saathoff, H., K. H. Naumann, N. Riemer, S. Kamm, O. Mohler, U. Schurath, H. Vogel, and B. Vogel (2001), The loss of NO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub>, and HO<sub>2</sub>/HOONO<sub>2</sub> on soot aerosol: A chamber and modeling study, *Geophys. Res. Lett.*, *28*, 1957–1960.
- Schutze, M., and H. Herrmann (2005), Uptake of the NO<sub>3</sub> radical on aqueous surfaces, *J. Atmos. Chem.*, *52*(1), 1–18.
- Sloane, C. S., J. Watson, J. Chow, L. Pritchett, and L. W. Richards (1991), Size-segregated fine particle measurements by chemical-species and their impact on visibility impairment in Denver, *Atmos. Environ., Part A*, *25*(5–6), 1013–1024.
- Tesner, P. A., and S. V. Shurupov (1995), Some physico-chemical parameters of soot formation during pyrolysis of hydrocarbons, *Combust. Sci. Technol.*, *105*(1–3), 147–161.

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