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# 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

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The interaction of NO<sub>3</sub> free radical and N<sub>2</sub>O<sub>5</sub> with laboratory flame soot was investigated in a Knudsen flow reactor at  $T = 298$  K equipped with beam-sampling mass spectrometry and in situ REMPI detection of NO<sub>2</sub> and NO. Decane (C<sub>10</sub>H<sub>22</sub>) has been used as a fuel in a co-flow device for the generation of gray and black soot from a rich and a lean diffusion flame, respectively. The gas-phase reaction products of NO<sub>3</sub> reacting with gray soot were NO, N<sub>2</sub>O<sub>5</sub>, HONO, and HNO<sub>3</sub> with HONO being absent on black soot. The major loss of NO<sub>3</sub> is adsorption on gray and black soot at yields of 65 and 59%, respectively, and the main gas-phase reaction product is N<sub>2</sub>O<sub>5</sub> owing to heterogeneous recombination of NO<sub>3</sub> with NO<sub>2</sub> and NO according to NO<sub>3</sub> + {C} → NO + products. HONO was quantitatively accounted for by the interaction of NO<sub>2</sub> with gray soot in agreement with previous work. Product N<sub>2</sub>O<sub>5</sub> was generated through heterogeneous recombination of NO<sub>3</sub> with excess NO<sub>2</sub>, and the small quantity of HNO<sub>3</sub> was explained by heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub>. The reaction products of N<sub>2</sub>O<sub>5</sub> on both types of soot were equimolar amounts of NO and NO<sub>2</sub>, which suggest the reaction N<sub>2</sub>O<sub>5</sub> + {C} → N<sub>2</sub>O<sub>3(ads)</sub> + products with N<sub>2</sub>O<sub>3(ads)</sub> decomposing into NO + NO<sub>2</sub>. The initial and steady-state uptake coefficients  $\gamma_0$  and  $\gamma_{ss}$  of both NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> based on the geometric surface area continuously increase with decreasing concentration at a concentration threshold for both types of soot.  $\gamma_{ss}$  of NO<sub>3</sub> extrapolated to [NO<sub>3</sub>] → 0 is independent of the type of soot and is  $0.33 \pm 0.06$  whereas  $\gamma_{ss}$  for [N<sub>2</sub>O<sub>5</sub>] → 0 is  $(2.7 \pm 1.0) \times 10^{-2}$  and  $(5.2 \pm 0.2) \times 10^{-2}$  for gray and black soot, respectively. Above the concentration threshold of both NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>,  $\gamma_{ss}$  is independent of concentration with  $\gamma_{ss}(\text{NO}_3) = 5.0 \times 10^{-2}$  and  $\gamma_{ss}(\text{N}_2\text{O}_5) = 5.0 \times 10^{-3}$ . The inverse concentration dependence of  $\gamma$  below the concentration threshold reveals a complex reaction mechanism for both NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. The atmospheric significance of these results is briefly discussed.

## 1. Introduction

Atmospheric aerosols are recognized to be important as a global climate factor whose uncertainty has given rise to numerous climate change scenarios for time horizons of 50–100 years.<sup>1</sup> In addition, they may affect the atmospheric composition through their interaction with trace gases in cases where they attain significant surface-to-volume ratios that enable many heterogeneous or multiphase reactions. Soot is a significant component of many atmospheric aerosols<sup>2–4</sup> that plays a unique role for several reasons. Despite the hydrophobic nature of freshly emitted soot, it is thought to cause cloud formation processes by providing cloud condensation (CCN) or ice (IN) nuclei depending on the age, and thus surface composition, of the aerosol particles<sup>5</sup> and is therefore an important factor in global climate change.<sup>6</sup> In addition, it is the only globally occurring aerosol that has strong absorbing properties from the near IR to the UV spectral range and therefore significantly affects the global radiative balance by absorbing both terrestrial (long wave) as well as solar (short wave) components of the actinic spectrum.<sup>7,8</sup> Soot particles have reducing properties and therefore generate interesting reaction products such as HONO not normally resulting from gas-phase processes in the oxidizing

atmosphere.<sup>9–12</sup> These reaction products of intermediate oxidation state can then bring about other redox reactions not possible without the occurrence of reducing soot particles. There exist many heterogeneous chemical reactions involving carbonaceous particles of soot substrates of potential relevance to the atmosphere that have been compiled and evaluated in the past.<sup>13</sup> Last, combustion aerosol emitted into the boundary layer has been recently recognized to be a public health issue.<sup>14,15</sup>

Soot is a carbon-containing aerosol resulting from incomplete combustion of hydrocarbon fuel of varying stoichiometry, defined by the  $\lambda$ -ratio of fuel to oxygen. Soot usually implies only the condensed phase and excludes the volatile organic fraction as well as the surrounding gas phase. It is formed through a complex network of chemical processes from small C<sub>2</sub>–C<sub>4</sub> hydrocarbon fragment free radicals that results in large stacked molecular condensates that in part contain substituted aromatic structures depending on the combustion conditions.<sup>16–18</sup> Despite long-standing efforts at elucidating the soot formation mechanism, the molecular details have not emerged yet even though useful structural models have been proposed.<sup>18</sup> Soot particles are composed of insoluble amorphous carbon, sometimes called elemental (EC) or black carbon (BC), and a soluble organic fraction (OC) containing up to 50% of the soot particle mass under certain conditions, of partially oxidized hydrocarbons as a bulk phase associated with the EC core or forming an adsorbed layer on the particle surface.<sup>16</sup> This soluble OC fraction

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may span the gamut of high molecular weight compounds from complex organic matter such as humic acid-like substances (HULIS) to highly annellated polycyclic aromatic hydrocarbons whose reactivity with trace gases has been the recent focus of research.<sup>19,20</sup> This organic fraction may play a significant role in the reactivity of soot and may take an active part in the formation of reaction products such as HONO resulting from the reduction of NO<sub>2</sub> on soot according to eq 1.



HONO formation is an example of an interesting reaction product that previous studies have identified as a result of a heterogeneous reaction of NO<sub>2</sub> with soot.<sup>16,21,22,31–39</sup> However, it was conjectured that there must be additional sources of HONO in the atmosphere because the quantities of soot necessary to support the observed levels of atmospheric HONO are not sufficient. Three recent examples are the light-supported (actinic) formation of HONO in the presence of humic acids that are ubiquitous in the environment,<sup>40</sup> the generation of HONO from irradiated nitrate-containing ice in a hitherto unknown reaction mechanism,<sup>41</sup> and the interaction of NO<sub>2</sub> with NH<sub>4</sub>Cl aerosol.<sup>42</sup> It is very likely that there are several significant additional day and/or nighttime sources of HONO. The present work contributes an additional mechanism of HONO formation in the presence of N<sub>2</sub>O<sub>5</sub> and a specific type of soot substrate.

The primary particle size of soot aerosol may range from 10 to 150 nm and a lifetime of several to tens of days before being scavenged in wet deposition processes. During their lifetime as suspended aerosol they are actively partaking in heterogeneous chemical reactions with gaseous pollutants such as HNO<sub>3</sub>, NO<sub>2</sub>, and O<sub>3</sub>.<sup>9,21–23</sup> and therefore reduce oxidized species in the atmosphere. These processes are noncatalytic, consume the reactive sites of soot and thus modify its structure through surface oxidation in a typical aging process that generally leads to an increase of soot surface oxygen functionalities.<sup>16,24–29</sup> Until now, no experimental work has been reported on the interaction of NO<sub>3</sub> on soot in contrast to laboratory experiments of N<sub>2</sub>O<sub>5</sub> reacting with soot.<sup>11,47</sup>

The present work deals with the interaction of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> with soot substrates from a laboratory combustion aerosol simulating an exhaust gas plume of a combustion engine. Active nitrogen or NO<sub>y</sub>, which includes NO<sub>x</sub>, is connected to the abundance of global ozone because NO<sub>x</sub> directly partakes in atmospheric oxidation processes being a catalytic species, whereas NO<sub>y</sub> species act as NO<sub>x</sub> reservoir. The relative abundance of NO<sub>x</sub> and NO<sub>y</sub> in the planetary boundary layer can change significantly with altitude even within 10 m, and with it its characteristic influence on tropospheric ozone.<sup>30</sup>

## 2. Experimental Method

A custom-designed co-flow system has been used to produce flame soot from decane fuel in a reproducible way.<sup>22</sup> It leads to a diffusion flame maintained in a controlled flow of air. To regulate the fuel flow feeding the flame by capillary forces, two types of ceramics of different porosity were used. One type of soot has been generated in a lean flame (low fuel/oxygen ratio) and will be referred to as “black” soot; the second has been generated in a rich (high fuel/oxygen ratio) and will be referred to as “gray” soot. These correspond to two types of soot obtained under two limiting flame conditions for the given combustion device used whose internal surface measured by BET and elemental composition have been given.<sup>22</sup> Table 1 displays the characteristic parameters we have used to produce the two types

**TABLE 1: Characteristic Parameters of Flame Soot Used To Produce Decane Soot**

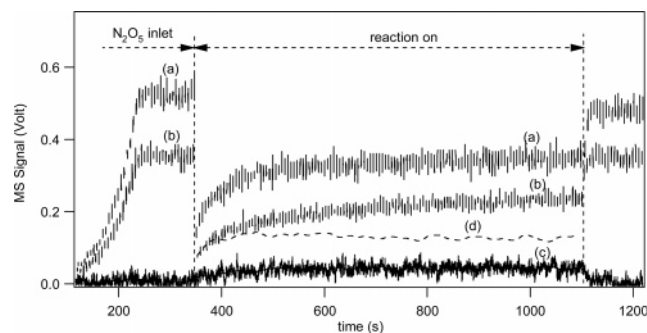
flame type (decane)	air flow [L min <sup>-1</sup> ]	fuel duct (pore Ø) [μm]	soot type	BET surface area [m <sup>2</sup> g <sup>-1</sup> ] <sup>22</sup>	diam of soot particle [nm] <sup>21</sup>
rich	1.2–1.4	17–40	“gray”	69	40
lean	1.3–1.5	11–16	“black”	218	20

of flame soot. The samples were collected from the burnt gases at 1 cm above the visible flame on ambient temperature Pyrex glass plates of 19.6 cm<sup>2</sup> surface area. The different soot substrates used in this work are meant to show the change in the chemical and physical properties of fresh soot emitted into the atmosphere by combustion sources when two limiting conditions of combustion, such as rich vs lean, are chosen.

The reactivity of the soot samples toward NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> was examined in a low-pressure (Knudsen) flow reactor using modulated molecular beam mass spectrometry (MMBMS) for the measurement of the rate of reactant uptake and product release into the gas phase. To unambiguously monitor the concentration of NO and NO<sub>2</sub> in situ, resonance enhanced multiphoton ionization (REMPI) was employed as part of a multi-diagnostic experimental technique in addition to MMBMS. Design and operation of the Knudsen flow reactor have been described in detail in the literature<sup>43</sup> as well as the in situ REMPI detection of NO and NO<sub>2</sub><sup>44</sup> performed using a Nd:YAG-pumped dye laser. The gas-kinetic parameters of the Knudsen flow reactor as well as details pertaining to in situ REMPI detection of NO and NO<sub>2</sub> may be found in refs 43 and 44. The measurement of molecular flux and concentration was performed using MS and REMPI detection, as reported in previous work.<sup>44</sup>

The mass of soot was varied between 1.5 and 20 mg spread out over 19.6 cm<sup>2</sup>. Each sample was pumped for 10 min before performing an uptake experiment. The gas under study, NO<sub>3</sub>, was generated by thermal decomposition of N<sub>2</sub>O<sub>5</sub> at 530 K in a 6 mm diameter glass tube that directly extends into the reactor. Due to the low residence time and pressure in the reactor, there is no recombination of NO<sub>3</sub> with NO<sub>2</sub> to form N<sub>2</sub>O<sub>5</sub>. Production of NO<sub>3</sub> and characterization of the NO<sub>3</sub> source have been reported in detail in a recent study.<sup>44</sup> Hydrolysis of N<sub>2</sub>O<sub>5</sub> may occur on internal surfaces of the inlet line before flowing across the hot glass tube thus generating HNO<sub>3</sub> as an impurity on the order of a few to 15%. However, HNO<sub>3</sub> does not thermally decompose inside the hot glass tube of the NO<sub>3</sub> source because we did not observe any change in the MS signal amplitude at *m/e* 63 (HNO<sub>3</sub><sup>+</sup>) when increasing the source temperature from ambient to 530 K. Both NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> were introduced into the reactor as a continuous flow from the NO<sub>3</sub> source which was heated for NO<sub>3</sub> and was run at ambient temperature for N<sub>2</sub>O<sub>5</sub>. The used free radical NO<sub>3</sub> source consistently generated a 3-fold excess of NO<sub>2</sub> owing to heterogeneous secondary processes of NO<sub>3</sub> to NO<sub>2</sub> within the source, as reported before.<sup>44</sup> This associated and unfortunately unavoidable NO<sub>2</sub> flow is in part responsible for the obtained reaction products (see below).

**2.1. NO<sub>3</sub>.** The relative concentration of NO<sub>3</sub> decreases with decreasing escape orifice diameter because it undergoes increasing wall loss with increasing residence time in the Knudsen reactor. The measured first-order loss of NO<sub>3</sub> given by *k'* at a given escape orifice size of the reactor may be expressed as the sum of two components, namely, *k*<sub>esc</sub> and *k*<sub>dec</sub>, representing escape, that is, physical, and chemical loss, respectively: *k'* = *k*<sub>esc</sub> + *k*<sub>dec</sub>. As reported in recent work,<sup>44</sup> the measurement of *k'* at three different aperture sizes enabled the determination of *k*<sub>dec</sub> = 0.6 ± 0.27 s<sup>-1</sup> at 300 K. NO<sub>3</sub> has a measurable parent



**Figure 1.**  $\text{N}_2\text{O}_5$  uptake on a sample of 10 mg of gray soot at  $[\text{N}_2\text{O}_5] = (8.0 \pm 1.3) \times 10^{12} \text{ cm}^{-3}$  and at an orifice diameter of 4 mm. Curves a and b correspond to the raw MS signals monitored at  $m/e$  46 and 30, respectively. Curve c corresponds to the raw REMPI signal for  $\text{NO}_2$  at  $\lambda_{\text{NO}_2} = 511 \text{ nm}$  (Coumarin 307, Radiant Dyes) scaled to a MS signal at  $m/e$  46. Curve d corresponds to the excess MS signal at  $m/e$  30 related to the production of NO.

peak at  $m/e$  62 ( $\text{NO}_3^+$ ) denoted as  $I_0^{62(\text{NO}_3)}$  and  $I_r^{62(\text{NO}_3)}$  corresponding to the MS signal before and during reaction, respectively. The measured rate constant  $k_{\text{obs}}$  for  $\text{NO}_3$  disappearance from the gas phase is given by eq 2.

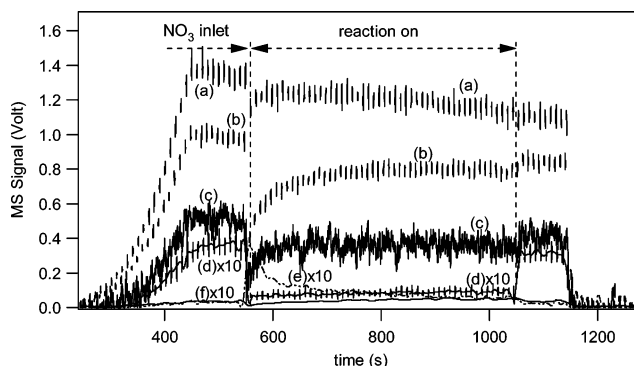
$$k_{\text{obs}} = \left( \frac{I_0^{62(\text{NO}_3)}}{I_r^{62(\text{NO}_3)}} - 1 \right) (k_{\text{esc}} + k_{\text{dec}}) \quad (2)$$

In the following, the subscripts 0 and  $r$  will refer to continuous gas uptake experiments in the absence and presence, respectively, of the sample.  $\text{N}_2\text{O}_5$  does not have a measurable parent and fragment peak at  $m/e$  108 ( $\text{N}_2\text{O}_5^+$ ) and 62 ( $\text{NO}_3^+$ ), respectively, under the present experimental conditions; the most intense peaks are its fragment  $\text{NO}_2^+$  at  $m/e$  46 followed by the less intense fragment  $\text{NO}^+$  at  $m/e$  30. The details regarding the contribution of the  $\text{HNO}_3$  impurity to the MS amplitude at  $m/e$  46 and 30 may be found in Appendix A1. In the  $\text{NO}_3$  uptake experiments only  $[\text{NO}_2]$  was detected by REMPI whereas  $[\text{NO}]$  was evaluated at  $m/e$  30 after successive subtraction of the detected reaction products contributing at  $m/e$  30 (see eq A2 in Appendix A1).

**2.2.  $\text{N}_2\text{O}_5$ .** When  $\text{N}_2\text{O}_5$  is exposed to soot, it is taken up and undergoes a heterogeneous reaction which results in a decrease of the MS signal from  $I_0^{46(\text{N}_2\text{O}_5)}$  to  $I_r^{46(\text{N}_2\text{O}_5)}$ . Upon  $\text{N}_2\text{O}_5$  uptake on both gray and black soot, we observe the formation of both NO and  $\text{NO}_2$  in the gas phase as detected by in situ REMPI at  $\lambda = 452.5$  and 511 nm, respectively. For  $\text{NO}_2$  REMPI detection a Coumarin 307 (Radiant Dyes) methanol solution was used whereas NO was multiphoton ionized using a methanol solution of Coumarin 47 (Radiant Dyes). We have determined the rate constant  $k_{\text{obs}}$  for the disappearance of  $\text{N}_2\text{O}_5$  following eq 3, assuming that the rate law is first order in  $\text{N}_2\text{O}_5$ ,

$$k_{\text{obs}} = \left( \frac{I_0^{46(\text{N}_2\text{O}_5)}}{I_r^{46(\text{N}_2\text{O}_5)}} - 1 \right) k_{\text{esc}} \quad (3)$$

where  $I_0^{46(\text{N}_2\text{O}_5)}$  and  $I_r^{46(\text{N}_2\text{O}_5)}$  are the intensities of the  $\text{NO}_2^+$  fragment of  $\text{N}_2\text{O}_5$  before and during heterogeneous reaction, respectively, and  $k_{\text{esc}}$  is the measured rate constant of effusion for  $\text{N}_2\text{O}_5$  out of the flow reactor. To determine  $I_r^{46(\text{N}_2\text{O}_5)}$ , the raw MS signal at  $m/e$  46 was corrected for the product  $\text{NO}_2$  generated during uptake of  $\text{N}_2\text{O}_5$  on soot because  $\text{NO}_2$  contributes to the total MS signal  $I_r^{46}$  at  $m/e$  46, its parent peak.<sup>45</sup> Figure 1 shows the raw REMPI signal at  $\lambda = 511 \text{ nm}$



**Figure 2.**  $\text{NO}_3$  uptake on a sample of 10 mg of gray soot at  $[\text{NO}_3] = (7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  in the 8 mm aperture reactor. Curves a, b, and d–f correspond to the raw MS signals monitored at  $m/e$  30, 46, 62, 47, and 63, respectively. Curve c corresponds to the raw REMPI signal for  $\text{NO}_2$  at  $\lambda_{\text{NO}_2} = 511 \text{ nm}$  scaled to a MS signal at  $m/e$  46.

corresponding to  $\text{NO}_2$  production for a typical uptake experiment of  $\text{N}_2\text{O}_5$  on soot scaled to a MS signal amplitude and thus to a flow rate. For both uptake experiments performed with  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  the absolute  $\text{NO}_2$  concentration,  $[\text{NO}_2]_{0,r}$ , in the absence and presence of the soot sample, respectively, has been determined by means of in situ REMPI detection of  $\text{NO}_2$ <sup>44</sup>. The procedure used to calculate its MS signal contribution  $I_{0,r}^{46(\text{NO}_2)}$  at  $m/e$  46 in the absence (subscript “0”) and presence (subscript “r”) of the soot sample has been reported in Appendix A2.

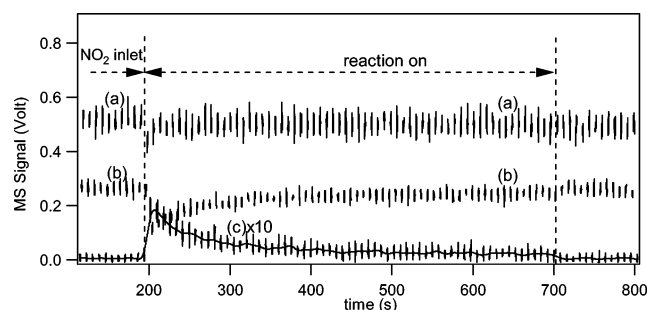
If one assumes that the rate law for uptake is first order, the uptake coefficient  $\gamma_{\text{obs}}$  for  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  is given by  $\gamma_{\text{obs}} = k_{\text{obs}}/\omega$ , where  $\omega$  is the collision frequency of  $\text{N}_2\text{O}_5$  or  $\text{NO}_3$  with the soot sample. In the present data analysis  $\gamma_{\text{obs}}$  was calculated using the geometric surface area  $A_s$  of the sample holder which will be justified below;  $\gamma_{\text{obs}}$  became  $\gamma_{\text{ss}}$ , the steady-state uptake coefficient, once steady-state conditions were achieved after an exposure time of 500 s or so;  $\gamma_{\text{obs}}$  is  $\gamma_0$  at  $t = 0 \text{ s}$ , that is, immediately after lifting the plunger and thus exposing the soot sample to  $\text{N}_2\text{O}_5$ . The details of the product analysis arising from the heterogeneous reaction of  $\text{N}_2\text{O}_5$  on soot may be found in Appendix A2.

Continuous flow uptake experiments were carried out at ambient temperature ( $298 \pm 2 \text{ K}$ ) under molecular flow conditions. The concentration of  $\text{NO}_3$  inside the Knudsen reactor ranged between  $(2.7 \pm 0.5) \times 10^{11} \text{ cm}^{-3}$  and  $(2.4 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ . The associated  $[\text{NO}_2]$  without reaction on soot determined by REMPI was  $(8.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  for the lower limit of  $[\text{NO}_3] = (2.7 \pm 0.5) \times 10^{11} \text{ cm}^{-3}$  and  $(6.2 \pm 1.5) \times 10^{12} \text{ cm}^{-3}$  for the upper limit of  $[\text{NO}_3] = (2.4 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ .

### 3. Results and Discussion

**3.1.  $\text{NO}_3$  Reaction with Gray Decane Soot: Reaction Products.** The interaction of  $\text{NO}_3$  with gray decane soot was investigated in a series of uptake experiments performed at different masses of soot and at different  $[\text{NO}_3]$ . Figure 2 shows a typical uptake experiment of  $\text{NO}_3$  on 10 mg of gray soot at  $[\text{NO}_3] = (7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$ . Once a steady flow of  $\text{NO}_3$  was established, the isolation plunger was lifted at  $t = 550 \text{ s}$  and the substrate exposed to the  $\text{NO}_3$  flow. Because of the uptake of  $\text{NO}_3$  on soot, the number of molecules effusing through the escape orifice and thus the MS signal at  $m/e$  62 immediately decreases (curve d). At  $t = 1050 \text{ s}$  the sample compartment is sealed by lowering the plunger and the MS signal at  $m/e$  62 returns to its initial value. The slight decrease





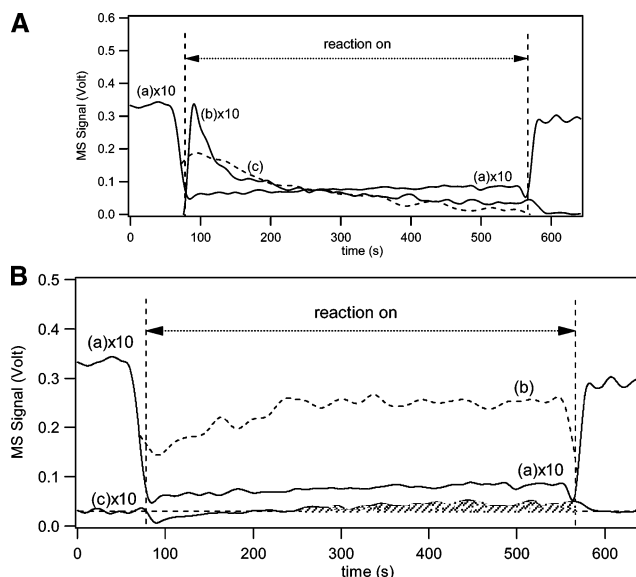
**Figure 3.** NO<sub>2</sub> uptake on a sample of 10 mg of gray soot at [NO<sub>2</sub>] =  $(2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$  (orifice diameter = 8 mm). Curves a–c correspond to the raw MS signals monitored at *m/e* 30, 46, and 47, respectively. Curve c describes HONO production.

of  $I_0^{62}(\text{NO}_3)$  over extended periods of time such as displayed in Figure 2 may be explained by a slight decrease of the corresponding flow rate into the reactor. In all experiments we observed uptake of NO<sub>2</sub> that only occurred in the presence of NO<sub>3</sub>, which led to a net decrease of the REMPI signal for NO<sub>2</sub> at  $\lambda_{\text{NO}_2} = 511 \text{ nm}$  (Figure 2, curve c). The major loss of NO<sub>3</sub> is simple adsorption on gray and black soot. We did not perform experiments at higher temperatures to measure the reversibility of the reaction of NO<sub>3</sub> with soot.

NO<sub>2</sub> in the absence of soot arises from the thermal decomposition of N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> in the NO<sub>3</sub> source or in the flow reactor. Reference uptake experiments with pure NO<sub>2</sub> in the presence of gray soot were performed at [NO<sub>2</sub>] =  $(2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$  (Figure 3). A large and instantaneous rate of uptake was observed and attained steady-state conditions after 3 min of interaction. The initial and steady-state uptake coefficients were  $\gamma_0 = (3.0 \pm 0.6) \times 10^{-2}$  and  $\gamma_{\text{ss}} = (1.3 \pm 0.2) \times 10^{-3}$ , respectively, and were similar to previous results.<sup>32,34</sup> Simultaneously to the uptake of NO<sub>2</sub> a large product peak of HONO appears, which shows that the conversion of NO<sub>2</sub> into HONO is a fast process (Figure 3, curve c). The observed HONO yields defined as the ratio of the integral of HONO released to the amount of NO<sub>2</sub> taken up during the reaction time tended toward  $100 \pm 10\%$  and were independent of integration time (Figure 3). No significant formation of NO was observed.

Identical behavior has been observed at low [NO<sub>2</sub>] in recent work on the reactivity of NO<sub>2</sub> on decane flame soot<sup>22</sup> and confirms that NO<sub>2</sub> strongly interacts with flame soot. This is in contrast to uptake experiments of NO<sub>2</sub> on mineral dust, which showed that NO<sub>2</sub> does not significantly adsorb on dust except on Saharan dust.<sup>44</sup> In that case NO<sub>2</sub> reacted only on NO<sub>3</sub> that was previously adsorbed on the substrate which has also been observed on the present soot substrate (see below).

During the uptake of NO<sub>3</sub> on gray soot the MS signal at *m/e* 62 (Figure 4a, curve a) partially recovered as the exposure time increases, indicating a decrease in the rate of uptake of NO<sub>3</sub>, presumably owing to a decrease of the net number of available surface sites for reaction. As a consequence, we observe an apparent reduction of the uptake coefficient  $\gamma_{\text{ss}}$ . As displayed in Figure 4a, a large burst of HONO at *m/e* 47 co-incident with the uptake of NO<sub>3</sub> has been observed immediately after the exposure of the sample which reaches steady state after 500 s (Figure 4a, curve b). NO has been observed at the beginning of the reaction and tended to small values at steady-state conditions (Figure 4a, curve c). A fast initial rate of formation of HONO and NO is observed immediately after exposure of soot to NO<sub>3</sub> as displayed in Figure 4a, curves b and c. Following results with pure NO<sub>2</sub> interacting with the same type of soot as displayed in Figure 3 the observed HONO formation is attributed



**Figure 4.** (a) Uptake of NO<sub>3</sub> on 10 mg of gray decane soot and resulting reaction products at [NO<sub>3</sub>] =  $(7.0 \pm 1.0) \times 10^{11} \text{ molecule cm}^{-3}$  from data displayed in Figure 2 that are electronically smoothed and interpolated (orifice diameter = 8 mm). Curve a represents the raw MS signal at *m/e* 62 for the NO<sub>3</sub> uptake on the soot sample. Curve b represents the raw MS signal at *m/e* 47 related to the production of gas-phase HONO. Curve c represents the corrected MS signal at *m/e* 30 corresponding to the production of gas-phase NO. (b) Uptake of NO<sub>3</sub> on 10 mg of gray soot and resulting reaction products at [NO<sub>3</sub>] =  $(7.0 \pm 1.0) \times 10^{11} \text{ molecule cm}^{-3}$  (from experiment displayed in Figure 2 but electronically smoothed and interpolated, orifice diameter = 8 mm). Curve a represents the raw MS signal at *m/e* 62 for the NO<sub>3</sub> uptake on the soot sample. Curve b is the calculated MS signal at *m/e* 46,  $I_{\text{exc}}^{46}$ , corresponding to N<sub>2</sub>O<sub>5</sub> formation. Curve c represents the raw MS signal at *m/e* 63 for the impurity HNO<sub>3</sub> uptake on soot. Positive flow MS signal at *m/e* 63 indicated by the hatched area under curve c represents the net amount of generated HNO<sub>3</sub>.

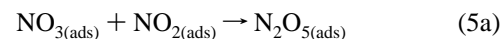
to the reduction of NO<sub>2</sub> by reducing sites on gray soot according to reactions 4a and 4b.<sup>34,46</sup>



The species listed in curved brackets refer to surface adsorbates.  $\{\text{C-H}\}_{\text{red}}$  represents a surface site on gray soot that reduces NO<sub>2</sub> to HONO and  $\{\text{C}\}_{\text{ox}}$  is the reaction product after surface oxidation by NO<sub>2</sub> on soot. The interaction of NO<sub>2</sub> with an adsorption site in reaction 4a must be weak to be sufficiently mobile to subsequently interact with other surface sites for reaction 4b in a Langmuir–Hinshelwood mechanism.

For all gray and black soot samples we have observed the formation of small amounts of gas-phase N<sub>2</sub>O<sub>5</sub>. We have calculated the yield of N<sub>2</sub>O<sub>5</sub> from the increase of the corrected MS signal at *m/e* 46,  $I_{\text{exc}}^{46}$ , discussed in Appendix A2 and displayed in Figure 4b (curve b). The yield of N<sub>2</sub>O<sub>5</sub> following the uptake of NO<sub>3</sub> continuously increases and reaches steady state after 500 s.

Under our experimental conditions the formation of N<sub>2</sub>O<sub>5</sub> may be explained by NO<sub>2</sub> reacting with adsorbed NO<sub>3</sub> on the soot substrate. It is important to note that NO<sub>2</sub> itself reacts both on gray and on black decane soot.<sup>22,32</sup> The observed simultaneous uptake for both NO<sub>3</sub> and NO<sub>2</sub> suggests the formation of N<sub>2</sub>O<sub>5(ads)</sub> through the heterogeneous recombination reaction 5a.



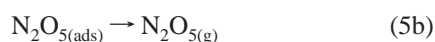
**TABLE 2: Summary Yields of Reaction Products during the Heterogeneous Reaction of NO<sub>3</sub> on Decane Soot Samples of 19.6 cm<sup>2</sup> Geometric Surface Area at [NO<sub>3</sub>]<sub>0</sub> = (2.3 ± 0.5) × 10<sup>12</sup> cm<sup>-3</sup> and [NO<sub>2</sub>]<sub>0</sub> = (6.0 ± 1.0) × 10<sup>12</sup> cm<sup>-3</sup> (Orifice Diameter = 8 mm)<sup>e,f</sup>**

gray soot (decane)	5 mg	% yield	10 mg	% yield	20 mg	% yield	average yield <sup>d</sup>	% yield <sup>g</sup>
NO <sub>3(lost)</sub>	(3.2 ± 0.7) × 10 <sup>18</sup>		(3.3 ± 0.7) × 10 <sup>18</sup>		(3.3 ± 0.7) × 10 <sup>18</sup>		(3.3 ± 0.7) × 10 <sup>18</sup>	
N <sub>2</sub> O <sub>5(g)</sub>	(7.0 ± 1.7) × 10 <sup>17 a</sup>	22	(8.5 ± 1.4) × 10 <sup>17 a</sup>	25	(8.4 ± 1.2) × 10 <sup>17 a</sup>	22	(8.5 ± 1.4) × 10 <sup>17 a</sup>	23 ± 7
NO <sub>2(lost)</sub>	(2.4 ± 0.6) × 10 <sup>18</sup>		(2.5 ± 0.5) × 10 <sup>18</sup>		(3.7 ± 0.7) × 10 <sup>18</sup>		(3.1 ± 0.6) × 10 <sup>18</sup>	
NO <sub>(g)</sub>	(3.2 ± 0.5) × 10 <sup>17 a</sup>	10	(3.3 ± 0.7) × 10 <sup>17 a</sup>	10	(4.6 ± 1.0) × 10 <sup>17 a</sup>	13	(4.0 ± 0.9) × 10 <sup>17 a</sup>	11 ± 5
HNO <sub>3(g)</sub>	(4.8 ± 0.5) × 10 <sup>16 a</sup>	1.5	(5.0 ± 0.3) × 10 <sup>16 a</sup>	1.5	(6.6 ± 0.6) × 10 <sup>16 a</sup>	2	(5.8 ± 1.0) × 10 <sup>16 a</sup>	1.8 ± 0.5
HONO <sub>(g)</sub>	(1.6 ± 0.2) × 10 <sup>18 b</sup>	94	(1.6 ± 0.5) × 10 <sup>18 b</sup>	98	(2.5 ± 0.8) × 10 <sup>18 b</sup>	87	(2.0 ± 0.7) × 10 <sup>18 b</sup>	96 ± 8
black soot (decane)	5 mg	% yield	10 mg	% yield	20 mg	% yield	average yield <sup>d</sup>	% yield <sup>g</sup>
NO <sub>3(lost)</sub>	(3.2 ± 0.5) × 10 <sup>18</sup>		(3.4 ± 0.8) × 10 <sup>18</sup>		(3.5 ± 0.5) × 10 <sup>18</sup>		(3.5 ± 0.5) × 10 <sup>18</sup>	
N <sub>2</sub> O <sub>5(g)</sub>	(1.0 ± 0.6) × 10 <sup>18 a</sup>	31	(7.2 ± 1.2) × 10 <sup>17 a</sup>	20	(7.0 ± 1.0) × 10 <sup>17 a</sup>	20	(7.0 ± 1.0) × 10 <sup>17 a</sup>	24 ± 7
NO <sub>2(lost)</sub>	(2.8 ± 0.4) × 10 <sup>18</sup>		(3.0 ± 0.6) × 10 <sup>18</sup>		(3.0 ± 0.8) × 10 <sup>18</sup>		(3.0 ± 0.6) × 10 <sup>18</sup>	
NO <sub>(g)</sub>	(4.5 ± 0.7) × 10 <sup>17 a</sup>	14	(5.1 ± 0.4) × 10 <sup>17 a</sup>	15	(6.3 ± 0.5) × 10 <sup>17 a</sup>	18	(5.7 ± 0.5) × 10 <sup>17 a</sup>	16 ± 6
HNO <sub>3(g)</sub>	(4.8 ± 0.5) × 10 <sup>16 a</sup>	1.5	(6.8 ± 0.7) × 10 <sup>16 a</sup>	2	(5.2 ± 0.5) × 10 <sup>16 a</sup>	1.5	(6.0 ± 0.7) × 10 <sup>16 a</sup>	1.6 ± 0.4
HONO <sub>(g)</sub>	— <sup>c</sup>	—	—	—	—	—	—	—

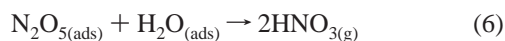
<sup>a</sup> Yield of NO<sub>y</sub> given as percentage with respect to the total number of molecules of NO<sub>3</sub> taken up on soot during a reaction time of 500 s. <sup>b</sup> Yield of HONO given as a percentage with respect to the total number of molecules of NO<sub>2(lost)</sub> — N<sub>2</sub>O<sub>5(g)</sub> taken up during a reaction time of 500 s. <sup>c</sup> Dash (—) indicates that no reaction product has been observed. <sup>d</sup> The average yield is calculated on the basis of the results obtained for 10 and 20 mg of soot corresponding to a coherent soot layer. <sup>e</sup> The average uncertainty of the yields is ±20%. <sup>f</sup> Uncertainty includes systematic error. <sup>g</sup> Includes a potential systematic uncertainty for N<sub>2</sub>O<sub>5</sub> and NO owing to successive subtraction (see eqs A1 and A2).

The conversion of NO<sub>3</sub> to N<sub>2</sub>O<sub>5</sub> occurs via a Langmuir–Hinshelwood mechanism where NO<sub>3</sub> and NO<sub>2</sub> first adsorb onto the soot surface and subsequently react forming N<sub>2</sub>O<sub>5</sub> which in part desorbs from the surface.

Once N<sub>2</sub>O<sub>5</sub> has been formed in the adsorbed state, a fraction may desorb into the gas phase, and another may subsequently react, as will be discussed below in section 3.3.



HNO<sub>3</sub>, present as an impurity, reacts on the soot substrate as well. This reaction has been studied in recent laboratory work using the same experimental apparatus.<sup>23</sup> As displayed in Figure 4b, a significant initial uptake of HNO<sub>3</sub> was observed at *m/e* 63 (curve c). After a reaction time of 170 s, an excess in the MS signal at *m/e* 63 corresponding to formation rather than loss of HNO<sub>3</sub> is observed, as indicated by the hatched area in Figure 4b, curve c. The increasing rate of formation of HNO<sub>3</sub> in the presence of soot coincides with the trend of N<sub>2</sub>O<sub>5</sub> formation displayed in Figure 4b, curve b and shows that part of N<sub>2</sub>O<sub>5(ads)</sub> formed in reaction 5a undergoes hydrolysis on the surface of soot. HNO<sub>3</sub> is then released back into the gas phase after heterogeneous hydrolysis, reaction 6.

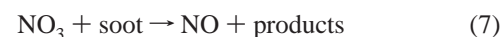


The yield of HNO<sub>3</sub> observed in uptake experiments performed at [NO<sub>3</sub>] = (2.5 ± 0.5) × 10<sup>12</sup> cm<sup>-3</sup> on different amounts of gray and black soot is only 1.5–2% of the total number of NO<sub>3</sub> molecules taken up (see Table 2).

An increase of gas-phase HNO<sub>3</sub> formation in the presence of soot aerosol has been observed in recent experimental work at very low humidities in which NO<sub>2</sub>, HNO<sub>3</sub>, and NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> reacted on soot particles in a large aerosol chamber.<sup>11</sup> In the same study the reaction probability for reaction 6 was assumed to be time independent and resulted in  $\gamma = (4.0 \pm 2.0) \times 10^{-5}$ . Apparently there exists sufficient adsorbed water even at low relative humidity to enable reaction 6 such that H<sub>2</sub>O is not the limiting reagent.

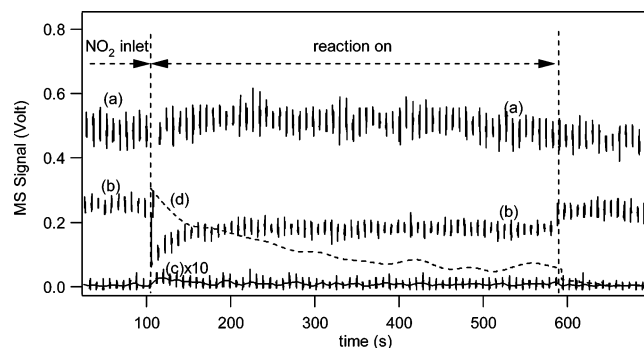
In Table 2 we report the product yields for the NO<sub>3</sub> reaction on three different masses of gray soot at [NO<sub>3</sub>] = (2.5 ± 0.5) × 10<sup>12</sup> and an excess of NO<sub>2</sub> of (6.0 ± 1.0) × 10<sup>12</sup> cm<sup>-3</sup>. We

point out that the experimental uncertainties for N<sub>2</sub>O<sub>5</sub> and NO reported in the last column of Table 2 also include potential systematic errors owing to the evaluation of the product yields by successive subtraction (see eqs A1 and A2). The mass balance reveals that 16–30% of NO<sub>2</sub> taken up on gray soot has been converted into gas-phase N<sub>2</sub>O<sub>5</sub> according to reactions 5a and 5b under the assumption of excess adsorbed NO<sub>3</sub> that is converted only in moderate yields to gas-phase NO (see below). The remaining 70–84% of reacted NO<sub>2</sub> equals the yield of HONO produced due to reaction 4b according to the NO<sub>2</sub> mass balance, namely  $N(\text{N}_2\text{O}_5) + N(\text{HONO}) = N(\text{NO}_2)$ , where *N* is the number of molecules taken up after a given reaction time. The essentially 100% yield of HONO resulting from pure NO<sub>2</sub>/gray soot experiments, in agreement with previous results,<sup>22</sup> leads to the amount of generated N<sub>2</sub>O<sub>5</sub> calculated from the amount of NO<sub>2</sub> taken up minus the yield of N<sub>2</sub>O<sub>5</sub>. We may conclude that NO<sub>3</sub> reacting on gray soot does not generate HONO because the amount of HONO may be entirely accounted for by the loss of NO<sub>2</sub>. Therefore, the slow production of NO must be attributed to the reaction of NO<sub>3</sub> with gray soot. Previous work has shown that HONO is the only gas-phase product from the reaction of pure NO<sub>2</sub> with gray soot<sup>22,34</sup> in contrast to NO formation resulting from the NO<sub>2</sub> reaction on amorphous carbon<sup>32</sup> or black soot (see below). Therefore, we attribute the slow formation of NO exclusively to the heterogeneous reaction of NO<sub>3</sub> on gray soot according to reaction 7 knowing that NO<sub>2</sub> does not lead to NO on gray soot.



The amount of NO released into the gas phase has been calculated from the excess MS signal at *m/e* 30,  $I_{\text{exc}}^{30}$  according to eq A2. The yield of NO did not show a significant variation with [NO<sub>3</sub>] and the amount of soot. Table 2 displays the fact that NO corresponds to nearly 6–16% of NO<sub>3</sub> taken up on the substrate. In addition, NO is nonreactive toward fresh unexposed soot samples,<sup>22,32</sup> a result obtained in ancillary experiments for the present soot samples.

To explain the temporal trend of the observed product yields on gray soot displayed in Figure 4, we need to analyze the time dependence of reactants and products at the beginning (between



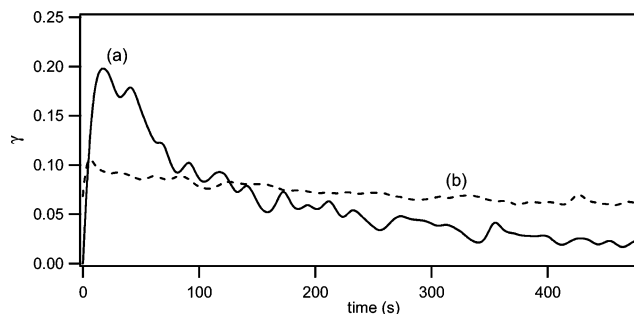
**Figure 5.** NO<sub>2</sub> uptake on a sample of 10 mg of black soot at [NO<sub>2</sub>] =  $(2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$  (orifice diameter = 8 mm). Curves a–c correspond to the raw MS signals monitored at *m/e* 30, 46 and 47, respectively. Curve d (broken line) reports the NO formation.

$t = 62$  and  $210 \text{ s}$ ) and at  $t > 210 \text{ s}$  of the uptake process, respectively. At first the fast disappearance of gas-phase NO<sub>2</sub> leads to fast HONO production (curve b in Figure 4a, reaction 4b). Concurrently, the fast uptake of NO<sub>3</sub> leads to rapid decomposition on the substrate resulting in a significant rate of formation of NO (curve c in Figure 4a, reaction 7). Therefore, owing to competitive reactions 4b and 7, only a fraction of NO<sub>3(ads)</sub> reacts with NO<sub>2</sub> and recombines to N<sub>2</sub>O<sub>5</sub> according to reaction 5a whereas all of the NO<sub>2</sub> reacts either to HONO or to N<sub>2</sub>O<sub>5</sub>. At  $t > 210 \text{ s}$  the number of adsorbed NO<sub>3</sub> molecules increases, thereby leading to partial saturation of the NO<sub>3</sub> uptake and thus inhibiting the turnover of available surface sites where NO<sub>3</sub> decomposition can take place. Therefore, reactions 5a and 5b become predominant with respect to reactions 4b and 7 at later reaction times. On the other hand, HONO production is ongoing in the steady state by continuous NO<sub>2</sub> reaction on gray soot, in contrast to NO production according to reaction 7.

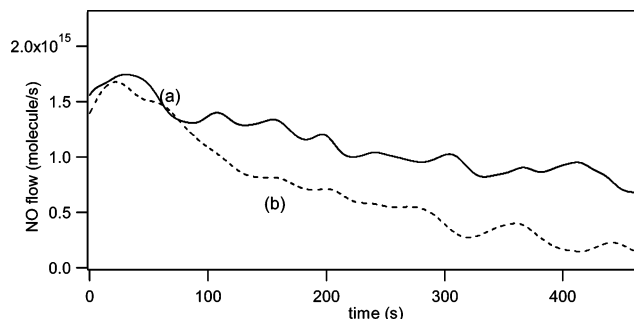
We therefore conclude that according to Table 2 approximately  $35 \pm 10\%$  of NO<sub>3</sub>, which reacted on gray soot has been converted to N<sub>2</sub>O<sub>5</sub> and NO. The remaining amount of NO<sub>3</sub>, that is,  $65 \pm 10\%$ , is irreversibly taken up on the substrate. However, no saturation of the uptake of NO<sub>3</sub> has been observed under the current experimental conditions despite the vanishing NO production at late reaction times, as displayed in Figure 4a.

**3.2. NO<sub>3</sub> Reaction with Black Decane Soot.** The reaction of NO<sub>3</sub> on black soot was examined in the same manner as gray soot discussed above. A fast initial uptake coefficient  $\gamma_0$  was observed for all experiments performed within [NO<sub>3</sub>], which ranged between  $(2.7 \pm 0.5) \times 10^{11}$  and  $(2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ , as reported in Table 2.

Ancillary uptake experiments with pure NO<sub>2</sub> in the presence of black soot were performed at [NO<sub>2</sub>] =  $(2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ . As observed in the companion experiment with gray soot, the observed uptake of NO<sub>2</sub> attained steady-state conditions after 3 min of interaction. The initial and steady-state uptake coefficient was  $\gamma_0 = (1.5 \pm 1.0) \times 10^{-2}$  and  $\gamma_{ss} = (2.7 \pm 0.6) \times 10^{-3}$ , respectively, similar to previous results.<sup>22,32</sup> Simultaneous to the uptake of NO<sub>2</sub> a significant quantity of product NO appears. The amount of product NO has been calculated from the excess MS signal at *m/e* 30,  $I_{\text{exc}}^{30}$ , according to eq A2. This signal has been converted to a flow rate using a calibration factor for pure NO and subsequently integrated over the reaction time. The observed NO yields defined as the ratio of the amount of NO released to the amount of NO<sub>2</sub> taken up during the reaction time tended toward 40% in contrast to the vanishing yield of HONO (Figure 5). Similar behavior at low [NO<sub>2</sub>] was



**Figure 6.** Uptake coefficient  $\gamma$  vs time for NO<sub>3</sub> on 10 mg of black (a) and gray (b) soot. [NO<sub>3</sub>] =  $(7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  (orifice diameter = 8 mm).



**Figure 7.** NO rate of formation vs time for NO<sub>3</sub> on 10 mg of (a) black and (b) gray soot. [NO<sub>3</sub>] =  $(7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  (orifice diameter = 8 mm).

observed in recent work on the reactivity of NO<sub>2</sub> on black decane flame soot.<sup>22</sup>

Figure 6 shows the temporal variation of  $\gamma$  for NO<sub>3</sub> on a 10 mg sample of black and gray soot at [NO<sub>3</sub>] =  $(7.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  in the presence of NO<sub>2</sub>. The value of  $\gamma_0$  for black soot is twice that observed for gray soot, as will be discussed below. At steady-state conditions the situation is reversed, where  $\gamma_{ss}$  for black soot is smaller by a factor of 2 with respect to  $\gamma_{ss}$  for gray soot. However, the number of NO<sub>3</sub> molecules taken up on both substrates during the exposure time of 500 s is approximately the same. As already observed for gray soot, simultaneous uptake of both NO<sub>3</sub> and NO<sub>2</sub> on black soot leads to the formation of small amounts of gas-phase N<sub>2</sub>O<sub>5</sub> according to reactions 5a and 5b.

Figure 7 displays the NO product flow generated during uptake of NO<sub>3</sub> on 10 mg of black and gray decane soot at the same experimental conditions. NO<sub>2</sub> effusing from the hot NO<sub>3</sub> source reacts with black soot to produce mainly NO, as observed in the interaction of NO<sub>2</sub> with amorphous carbon<sup>32</sup> or black decane soot.<sup>22</sup> NO<sub>2</sub> presumably interacts with black soot, resulting in the formation of HONO akin to the reaction on gray soot, which to a large extent decomposes into NO according to the following reaction mechanism proposed by Stadler and Rossi:<sup>22</sup>



The difference in the NO yields between black and gray decane flame soot following reaction with NO<sub>3</sub>, curves a and b in Figure 7 is related to the NO formation from HONO decomposition, reactions 4b and 8. NO from HONO decomposition, reaction 8, may therefore occur in addition to the NO formation from heterogeneous decomposition of NO<sub>3</sub> on black soot according to reaction 7 in contrast to gray soot where



**TABLE 3: Summary of NO Yield Resulting from the Uptake of NO<sub>3</sub> on 10 mg of Gray and Black Soot at Different [NO<sub>3</sub>] (Orifice Diameter = 8 mm)**

[NO <sub>3</sub> ] <sub>0</sub> , cm <sup>-3</sup>	NO (gray soot) <sup>a</sup>	% yield	NO (black soot) <sup>a</sup>	% yield
$(2.7 \pm 0.5) \times 10^{11}$	$(1.6 \pm 0.4) \times 10^{17}$	13	$(2.0 \pm 0.5) \times 10^{17}$	20
$(3.8 \pm 1.8) \times 10^{11}$	$(2.0 \pm 0.6) \times 10^{17}$	11	$(2.6 \pm 0.7) \times 10^{17}$	19
$(7.0 \pm 1.0) \times 10^{11}$	$(2.6 \pm 0.5) \times 10^{17}$	9	$(4.3 \pm 0.4) \times 10^{17}$	16
$(1.5 \pm 0.5) \times 10^{12}$	$(3.0 \pm 0.7) \times 10^{17}$	8	$(5.8 \pm 0.8) \times 10^{17}$	14
$(2.3 \pm 0.5) \times 10^{12}$	$(3.3 \pm 0.4) \times 10^{17}$	10	$(5.1 \pm 0.7) \times 10^{17}$	15

<sup>a</sup> Yield of NO given as a percentage with respect to the total number of molecules of NO<sub>3</sub> taken up during the reaction time of 500 s.

HONO is kinetically stable and where NO exclusively stems from reaction 7. Therefore, contributions of NO formation from HONO and NO<sub>3</sub> decomposition cannot be experimentally separated for black in contrast to gray decane soot. Table 4 reveals a NO yield higher by approximately 50% for black compared to gray decane soot that is consistent with the HONO decomposition leading to additional NO in the case of black decane soot.

In recent work performed by Stadler,<sup>22</sup> black decane soot was exposed to a flow of pure HONO to decide whether or not HONO produced on black soot may irreversibly adsorb on the surface or decompose to NO. In that work fast uptake of HONO and production of NO was observed according to reaction 8. The total NO product yield at limiting high concentration was 50% with respect to HONO taken up, whereas for [HONO] =  $(3.7 \pm 0.4) \times 10^{11}$  cm<sup>-3</sup> the total product yield consisted of 40% NO and 10% NO<sub>2</sub>. The open balance of nitrogen was attributed to a reservoir of HONO or its reaction product adsorbed on the soot substrate. The NO rate of formation resulting from NO<sub>3</sub> decomposition on gray soot tends to zero under steady-state conditions, as shown in Figure 7, whereas the rate of NO formation on black soot is sustained owing to continuous HONO decomposition following reaction 8. Table 2 reveals that the sum of the yields of NO and N<sub>2</sub>O<sub>5</sub> directly attributable to the reaction of NO<sub>3</sub> on black soot amounts to 40 ± 10% based on NO<sub>3</sub> taken up, a value that is quite comparable to that on gray soot when the contribution of HNO<sub>3</sub> is ignored (1.8% yield). The remainder of adsorbed NO<sub>3</sub>, namely 60 ± 10% must stay adsorbed on the black soot substrate.

Table 3 reports the NO yield resulting from the uptake of NO<sub>3</sub> on 10 mg of gray and black decane soot at [NO<sub>3</sub>] between  $(2.7 \pm 0.5) \times 10^{11}$  and  $(2.3 \pm 0.5) \times 10^{12}$  cm<sup>-3</sup>. The yield of NO for black soot over an integration period of 500 s was 5–8% larger than for gray soot. There is no significant dependence of the NO yields on [NO<sub>3</sub>]. The NO yield expressed as a percentage with respect to the total number of molecules of NO<sub>3</sub> taken up during the same reaction time resulted in a value of 10.2 ± 1.9% for gray and 16.8 ± 2.6% for black soot when averaged over uptake experiments at different values of [NO<sub>3</sub>]. We attribute the larger value of the NO yield found for black compared to gray soot to HONO decomposition on black soot. The small difference in the NO yields reported in Table 3 suggests that most of the putative HONO remains adsorbed on black soot rather than decompose to form NO. In agreement with this conclusion, the HONO rate of formation is negligible for the interaction of NO<sub>2</sub> with black soot, as displayed in Figure 5, curve c.

### 3.3. N<sub>2</sub>O<sub>5</sub> Reaction with Decane Soot: Reaction Products.

As far as the experimental arrangement is concerned, the only difference between the NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> uptake experiments was that the source temperature was raised to 530 K for NO<sub>3</sub> whereas

it was kept at ambient temperature for N<sub>2</sub>O<sub>5</sub>. Figures 1 and 8 display typical uptake experiments of N<sub>2</sub>O<sub>5</sub> on gray and black soot, respectively. Both NO and NO<sub>2</sub> were detected as the only reaction products resulting from the interaction of N<sub>2</sub>O<sub>5</sub> with soot. Figure 1 shows that the NO<sub>2</sub> concentration measured using REMPI detection is zero within experimental uncertainty before exposure of N<sub>2</sub>O<sub>5</sub> to soot at  $t = 350$  s, which is proof for the absence of NO<sub>2</sub> in the N<sub>2</sub>O<sub>5</sub> flow emanating from the source. The same is true for the NO displayed in Figure 8 where REMPI detection of NO was employed. Owing to the dye change for the REMPI detection of NO and NO<sub>2</sub>, simultaneous REMPI detection of both reaction products was not possible such that separate uptake experiments using identical [NO<sub>3</sub>] had to be undertaken, one set for NO and another for NO<sub>2</sub> detection. However, analysis of the MS signal amplitudes at  $m/e$  30 and 46 after correction for the contribution of N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub> detected by REMPI following the procedure outlined in Appendix A2 based on  $I_{\text{exc}}^{30}$ , revealed the presence of NO as a reaction product (see eq A6). Conversely, the MS signal amplitudes at  $m/e$  30 and 46 revealed the presence of NO<sub>2</sub> as a reaction product once the contribution of N<sub>2</sub>O<sub>5</sub> and NO whose absolute concentration was measured using REMPI were accounted for (see eq A5). Qualitatively one observes an increase of both NO and NO<sub>2</sub> during the first 100 s or so after exposing the soot to the N<sub>2</sub>O<sub>5</sub> flow that is roughly co-incident with the establishment of steady-state conditions of the MS signal at  $m/e$  46. This indicates that a certain amount of N<sub>2</sub>O<sub>5</sub> must first be adsorbed onto soot before the rate of product desorption becomes significant. We also note that unlike the situation for NO<sub>3</sub> the differences between gray and black soot are minimal.

Table 4 displays the quantitative aspects in terms of the yields of NO and NO<sub>2</sub> using REMPI detection referenced to the number of N<sub>2</sub>O<sub>5</sub> molecules taken up within a given time, usually 500 s. The corresponding twin product not directly detected by REMPI, for instance NO in the case of REMPI detection of NO<sub>2</sub>, was evaluated as described above from the MS spectra. At low concentrations up to [N<sub>2</sub>O<sub>5</sub>] =  $2.0 \times 10^{12}$  molecule cm<sup>-3</sup> the yields of both NO and NO<sub>2</sub> are identical within experimental uncertainty and equal to between 80 and 100%. Beyond this threshold value of [N<sub>2</sub>O<sub>5</sub>] the NO<sub>2</sub> yield detected by REMPI and the NO yield inferred from the MS spectra seem to decrease significantly. This decrease by roughly a factor of 2 seems to depend primarily on the concentration and not on the dose of N<sub>2</sub>O<sub>5</sub> taken up by soot, as revealed by a comparison between lines 3 and 4 for gray soot, and between lines 5 and 6 for black soot of Table 4. The subtle difference between the effect of concentration and dose undoubtedly points toward a complex mechanism for the heterogeneous interaction of N<sub>2</sub>O<sub>5</sub> with soot. A similar situation prevails for the interaction of N<sub>2</sub>O<sub>5</sub> with ice at low temperatures. We conclude that both the NO and NO<sub>2</sub> yields tend toward 100% for the reaction of N<sub>2</sub>O<sub>5</sub> on soot under atmospheric conditions, that is, for small N<sub>2</sub>O<sub>5</sub> concentrations.

In addition, neither HNO<sub>3</sub> nor HONO was observed in any of the uptake experiments on both gray and black soot. The absence of significant amounts of HNO<sub>3</sub> is somewhat of a surprise because N<sub>2</sub>O<sub>5</sub> is known for its efficient hydrolysis in the presence of small amounts of adsorbed water. On Norit A, a commercial carbon black product that holds important quantities of adsorbed water, the reaction of N<sub>2</sub>O<sub>5</sub> generated a large yield of HNO<sub>3</sub><sup>47</sup> that was generated through heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> in addition to the reduction of N<sub>2</sub>O<sub>5</sub> resulting in NO. The equimolar formation of NO and NO<sub>2</sub> in the uptake



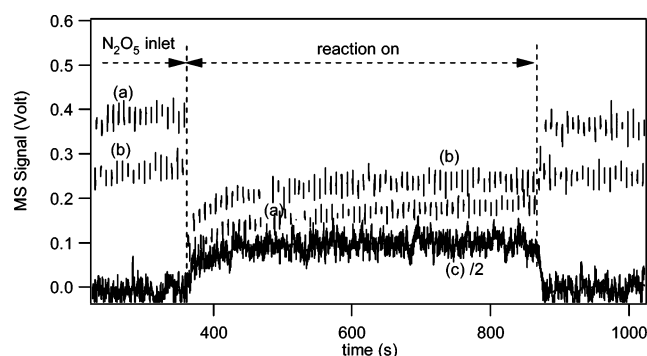
**TABLE 4:** Yield of NO<sub>2</sub> and NO Given as Percentage with Respect to the Total Number of Molecules of N<sub>2</sub>O<sub>5</sub> Taken up on Gray and Black Soot during a Reaction Time of 500 s (19.6 cm<sup>2</sup> Geometric Surface Area)<sup>a</sup>

[N <sub>2</sub> O <sub>5</sub> ] <sub>0</sub> , cm <sup>-3</sup>	N <sub>2</sub> O <sub>5(lost)</sub> (gray soot)	NO <sub>2(g)</sub> (gray soot)	% yield	NO <sub>(g)</sub> (gray soot)	% yield
(1.0 ± 0.5) × 10 <sup>12 b</sup>	(6.0 ± 1.5) × 10 <sup>17</sup>	(4.8 ± 1.2) × 10 <sup>17</sup>	80	(4.3 ± 1.3) × 10 <sup>17</sup>	72
(1.6 ± 0.5) × 10 <sup>12 b</sup>	(8.9 ± 1.3) × 10 <sup>17</sup>	(7.7 ± 1.6) × 10 <sup>17</sup>	86	(8.0 ± 1.1) × 10 <sup>17</sup>	90
(2.0 ± 0.7) × 10 <sup>12 b</sup>	(9.8 ± 1.1) × 10 <sup>17</sup>	(9.3 ± 1.5) × 10 <sup>17</sup>	94	(8.6 ± 0.9) × 10 <sup>17</sup>	88
(2.7 ± 1.0) × 10 <sup>12 b</sup>	(1.0 ± 0.2) × 10 <sup>18</sup>	(4.5 ± 0.2) × 10 <sup>17</sup>	45	(3.8 ± 0.7) × 10 <sup>17</sup>	38
(8.0 ± 1.3) × 10 <sup>12 c</sup>	(2.0 ± 0.3) × 10 <sup>18</sup>	(7.0 ± 1.2) × 10 <sup>17</sup>	33	(7.0 ± 1.0) × 10 <sup>17</sup>	35

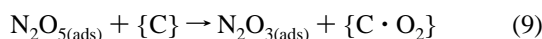
  

[N <sub>2</sub> O <sub>5</sub> ] <sub>0</sub> , cm <sup>-3</sup>	N <sub>2</sub> O <sub>5(lost)</sub> (black soot)	NO <sub>2(g)</sub> (black soot)	% yield	NO <sub>(g)</sub> (black soot)	% yield
(1.0 ± 0.5) × 10 <sup>12 b</sup>	(5.3 ± 1.4) × 10 <sup>17</sup>	(5.2 ± 1.3) × 10 <sup>17</sup>	98	(5.2 ± 1.5) × 10 <sup>17</sup>	100
(1.3 ± 0.7) × 10 <sup>12 b</sup>	(9.5 ± 1.5) × 10 <sup>17</sup>	(8.2 ± 1.3) × 10 <sup>17</sup>	87	(7.7 ± 1.2) × 10 <sup>17</sup>	81
(1.5 ± 0.5) × 10 <sup>12 b</sup>	(1.0 ± 0.7) × 10 <sup>18</sup>	(9.5 ± 1.9) × 10 <sup>17</sup>	95	(9.9 ± 0.5) × 10 <sup>17</sup>	100
(1.9 ± 0.8) × 10 <sup>12 b</sup>	(9.7 ± 1.2) × 10 <sup>17</sup>	(8.7 ± 1.0) × 10 <sup>17</sup>	90	(8.2 ± 1.0) × 10 <sup>17</sup>	84
(2.0 ± 0.8) × 10 <sup>12 b</sup>	(1.0 ± 0.2) × 10 <sup>18</sup>	(9.6 ± 1.1) × 10 <sup>17</sup>	92	(8.7 ± 1.7) × 10 <sup>17</sup>	87
(2.9 ± 1.0) × 10 <sup>12 b</sup>	(1.0 ± 0.3) × 10 <sup>18</sup>	(4.2 ± 1.2) × 10 <sup>17</sup>	45	(5.0 ± 1.5) × 10 <sup>17</sup>	50
(8.0 ± 1.3) × 10 <sup>12 c</sup>	(1.7 ± 0.5) × 10 <sup>18</sup>	(6.6 ± 1.1) × 10 <sup>17</sup>	39	(7.1 ± 2.1) × 10 <sup>17</sup>	42

<sup>a</sup> The data for NO and NO<sub>2</sub> given in straight font correspond to yields obtained by REMPI detection whereas data listed in italics have been obtained using the analysis of MS signals at *m/e* 30 and 46 (see Appendix A2). <sup>b</sup> Orifice diameter = 8 mm. <sup>c</sup> Orifice diameter = 4 mm.

**Figure 8.** N<sub>2</sub>O<sub>5</sub> uptake on a sample of 15 mg of black soot at [N<sub>2</sub>O<sub>5</sub>] = (2.0 ± 0.7) × 10<sup>12</sup> cm<sup>-3</sup> and at an orifice diameter of 8 mm. Curves a and b correspond to the raw MS signals monitored at *m/e* 46 and 30, respectively. Curve c corresponds to the raw REMPI signal for NO detection at λ<sub>NO</sub> = 452.6 nm (Coumarin 47, Radiant Dyes) scaled to a MS signal at *m/e* 30.

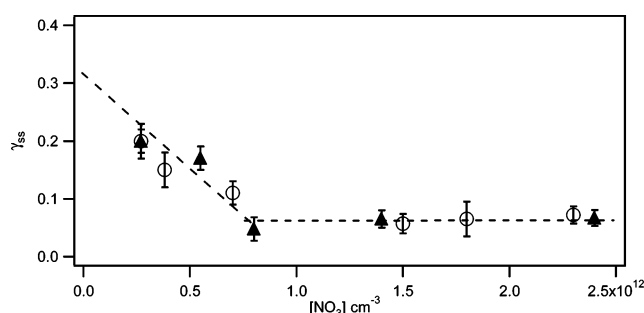
of N<sub>2</sub>O<sub>5</sub> on both gray and black soot suggests the occurrence of reactions 9 and 9a.



This mode of decomposition is similar to NO<sub>3</sub> decomposition according to eq 7 in that two O atoms are transferred to the soot substrate after reaction corresponding to a reduction involving the transfer of two electrons per N atom in the case of N<sub>2</sub>O<sub>5</sub>. In case the reduction of N<sub>2</sub>O<sub>5</sub> on soot occurs via NO<sub>2</sub> and subsequent secondary reduction of NO<sub>2</sub> to NO akin to NO<sub>2</sub> reduction on amorphous carbon<sup>32</sup> it would be highly improbable to observe equimolar amounts of NO and NO<sub>2</sub>.

**3.4. Uptake Kinetics of NO<sub>3</sub> on Decane Soot.** The interaction of NO<sub>3</sub> with gray and black decane soot shows that after an initial fast uptake of NO<sub>3</sub> there is no saturation of the sample at steady-state conditions. Figure 9 and Table 5 display the values of γ<sub>ss</sub> as a function of [NO<sub>3</sub>] for gray and black soot based on the geometric sample surface of 19.6 cm<sup>2</sup>. The uncertainties for NO<sub>3</sub> uptake experiments were determined from the signal-to-noise ratio of the MS signal at *m/e* 62.

We note that for a variation of [NO<sub>3</sub>] between (2.7 ± 0.5) × 10<sup>11</sup> and (7.0 ± 1.0) × 10<sup>11</sup> cm<sup>-3</sup> γ<sub>ss</sub> decreases from 0.2 ± 0.03 to 0.11 ± 0.01 for both types of soot. Variations of [NO<sub>3</sub>]

**Figure 9.** Uptake coefficient γ<sub>ss</sub> of NO<sub>3</sub> based on the geometric sample surface as a function of [NO<sub>3</sub>] (orifice diameter = 8 mm): NO<sub>3</sub> on black (triangles) and gray soot (open circles).**TABLE 5: Summary of Uptake Experiments of NO<sub>3</sub> on 10 mg of Gray and Black Decane Soot<sup>a</sup>**

[NO <sub>3</sub> ] <sub>0</sub> , cm <sup>-3</sup>	γ <sub>0</sub> (gray soot)	γ <sub>ss</sub> (gray soot)
(2.7 ± 0.5) × 10 <sup>11</sup>	0.44 ± 0.05	0.2 ± 0.02
(3.8 ± 1.8) × 10 <sup>11</sup>	0.35 ± 0.06	0.15 ± 0.03
(7.0 ± 1.0) × 10 <sup>11</sup>	0.15 ± 0.07	0.11 ± 0.02
(1.5 ± 0.5) × 10 <sup>12</sup>	0.12 ± 0.05	(5.7 ± 1.3) × 10 <sup>-2</sup>
(1.8 ± 0.5) × 10 <sup>12</sup>	0.12 ± 0.05	(6.5 ± 1.0) × 10 <sup>-2</sup>
(2.3 ± 0.5) × 10 <sup>12</sup>	0.12 ± 0.04	(7.2 ± 1.5) × 10 <sup>-2</sup>

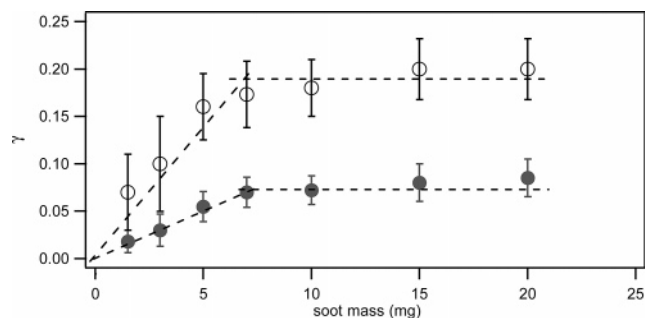
  

[NO <sub>3</sub> ] <sub>0</sub> , cm <sup>-3</sup>	γ <sub>0</sub> (black soot)	γ <sub>ss</sub> (black soot)
(2.7 ± 0.5) × 10 <sup>11</sup>	0.5 ± 0.07	0.2 ± 0.03
(5.5 ± 1.0) × 10 <sup>11</sup>	0.35 ± 0.08	0.17 ± 0.02
(8.0 ± 0.5) × 10 <sup>11</sup>	0.3 ± 0.04	(6.7 ± 1.4) × 10 <sup>-2</sup>
(1.4 ± 0.5) × 10 <sup>12</sup>	0.2 ± 0.05	(6.5 ± 1.5) × 10 <sup>-2</sup>
(2.3 ± 0.5) × 10 <sup>12</sup>	0.18 ± 0.03	(4.8 ± 1.0) × 10 <sup>-2</sup>

<sup>a</sup> Initial (γ<sub>0</sub>) and steady-state (γ<sub>ss</sub>) uptake coefficients (orifice diameter = 8 mm, 19.6 cm<sup>2</sup> geometric surface area).

between (7.0 ± 1.0) × 10<sup>11</sup> cm<sup>-3</sup> and (2.3 ± 0.5) × 10<sup>12</sup> cm<sup>-3</sup> result in a constant value of γ<sub>ss</sub> = (6.5 ± 1.5) × 10<sup>-2</sup>, independent of [NO<sub>3</sub>]. In addition, there is no significant difference in γ<sub>ss</sub> between gray and black soot.

From this series of measurements it is evident that γ<sub>ss</sub> follows a rate law pseudo first order in NO<sub>3</sub> for [NO<sub>3</sub>] > (7.0 ± 1.0) × 10<sup>11</sup> cm<sup>-3</sup>. Conversely, for [NO<sub>3</sub>] < (7.0 ± 1.0) × 10<sup>11</sup> cm<sup>-3</sup> the inverse dependence of γ<sub>ss</sub> on [NO<sub>3</sub>] suggests that the mechanism of NO<sub>3</sub> uptake is complex and does not correspond to a simple first-order rate law for uptake. A similar behavior has been observed for the interaction of NO<sub>3</sub> with mineral dust substrates such as Kaolinite.<sup>44</sup> Akin to γ<sub>ss</sub>, γ<sub>0</sub> for black and



**Figure 10.** Uptake coefficient of  $\text{NO}_3$  on gray soot based on the geometric sample surface: dependence of the initial (open circles) and steady-state (full circles) uptake coefficient on sample mass at  $[\text{NO}_3] = (2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$  (orifice diameter = 8 mm).

gray soot seems to follow the same trend as a function of  $[\text{NO}_3]$  within experimental uncertainty.

Figure 10 displays the steady-state uptake coefficient  $\gamma_{ss}$  of  $\text{NO}_3$  as a function of the mass of gray and black soot (Table 6). A linear dependence of  $\gamma_{ss}$  as a function of the substrate mass is clearly visible for soot masses up to 7 mg. The identical situation holds for black soot (not shown). We note that for the interaction pair  $\text{NO}_3$ –soot there is no mass dependence beyond the mass of 7 mg, which we interpret as the minimum mass required for forming a coherent monolayer of soot. The alternative interpretation of  $\text{NO}_3$  penetrating into deeper layers of the sample is less applicable owing to the large absolute values of  $\gamma$ . This value of 7 mg corresponds to a soot loading of  $7/19.6 = 0.37 \text{ mg/cm}^2$  and is identical to that for black soot. In earlier work<sup>21</sup> a value for the threshold loading of  $0.41 \pm 0.1 \text{ mg/cm}^2$  has been determined. Soot is a porous material, and on the time scale of a few seconds given by the orifice diameter of the flow reactor, we do not expect  $\text{NO}_3$  to explore the internal surface of the pores as given for instance by the BET surface area. We do not think that the surface porosity of soot plays an important role in the determination of the uptake coefficient in view of the large value of  $\gamma_{ss}$  of  $\text{NO}_3$  on gray and black soot. In contrast, for the reaction of  $\text{N}_2\text{O}_5$  on soot we may have to take into account possible diffusion of  $\text{N}_2\text{O}_5$  into deeper sample layers due to smaller values of  $\gamma_{ss}$  with respect to  $\text{NO}_3$ .

We therefore take the geometric surface area for the evaluation of the gas–surface collision frequency  $\omega$  under the constraint of the present experimental conditions of low gas-phase residence times for  $\text{NO}_3$ . The linear mass dependence of  $\gamma_0$  and  $\gamma_{ss}$  observed below 7 mg for gray and black soot and displayed in Figure 10 is interpreted that no coherent layer of soot on the sample holder has been formed at those sample masses yet. Beyond 7 mg of soot the initial uptake coefficient  $\gamma_0$  is very large and stays constant at approximately 0.2 such that  $\text{NO}_3$  does not have sufficient time to explore the internal surface area of the substrate given by the BET surface. Therefore, as already discussed for  $\text{N}_2\text{O}_5$  on mineral dust substrates, we do not think that the pore diffusion model<sup>18</sup> should be applied to correct  $\gamma_0$  or  $\gamma_{ss}$ . At steady-state conditions we note that  $\gamma_{ss}$  follows the same trend as  $\gamma_0$  as a function of mass of the soot sample. The correction to  $\gamma_{ss}$  afforded by the pore diffusion theory, if feasible, may serve as a lower limit for  $\gamma$  whereas  $\gamma_{ss}$  based on the geometrical surface area may be regarded as an upper limit to the true value of  $\gamma$ . In addition, it is noteworthy that the pore diffusion theory has never been successfully applied to soot substrates in view of their structural complexity. If we use the BET surface area to provide a lower bound for  $\gamma_{ss}$  of  $\text{NO}_3$  reacting on 20 mg of soot, we obtain

$\gamma_{\text{BET}} = 1.2 \times 10^{-7}$  and  $\gamma_{\text{BET}} = 3.7 \times 10^{-8}$  for gray and black soot, respectively.

The amount of adsorbed  $\text{NO}_3$  during an uptake experiment on gray and black soot turned out to be the same. At  $[\text{NO}_3] = (2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$  ( $3.3 \pm 0.7) \times 10^{18}$  molecules of  $\text{NO}_3$  were adsorbed on 10 mg of soot during a reaction time of 500 s. During this time the samples did not saturate. As discussed in recent work on the interaction of  $\text{NO}_3$  on mineral dust,<sup>44</sup>  $\text{NO}_3$  may be represented by a  $4.5 \text{ \AA}$  diameter sphere with a projected surface area of  $1.6 \times 10^{-15} \text{ cm}^2/\text{molecule}$ , which leads to a full surface coverage of  $6.3 \times 10^{14} \text{ molecules cm}^{-2}$ . The 10 mg sample of gray soot has a total surface area of  $6.9 \times 10^3 \text{ cm}^2$  based on a BET surface area of  $69 \text{ m}^2/\text{g}$  (see Table 1). This leads to  $1.3 \times 10^{16}$  and  $3.5 \times 10^{19}$   $\text{NO}_3$  forming a monolayer on 10 mg of soot based on the geometric and BET surface area, respectively. Therefore, the total number of  $\text{NO}_3$  taken up on the substrate during 500 s has consumed  $3.3 \times 10^{18}/3.5 \times 10^{19} = 9.4\%$  of reactive sites based on the BET surface area. On the basis of this estimate, we may expect to observe increasing levels of saturation of  $\text{NO}_3$  uptake on soot beyond 50% coverage at 2500 s of exposure at  $[\text{NO}_3] = (2.3 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ .

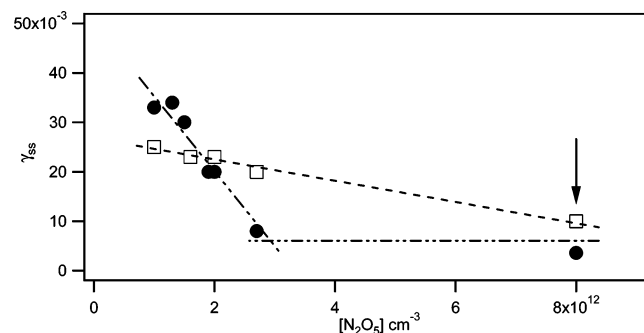
**3.5. Uptake Kinetics of  $\text{N}_2\text{O}_5$  on Decane Soot.** Figure 11 and Table 7 display the kinetic results of the heterogeneous reaction of  $\text{N}_2\text{O}_5$  on gray and black soot in terms of  $\gamma_0$  and  $\gamma_{ss}$  based on the geometric sample surface. We note from Figure 11 that both  $\gamma_0$  and  $\gamma_{ss}$  decrease with increasing  $[\text{N}_2\text{O}_5]$  down to a constant value of  $5$  to  $10 \times 10^{-3}$  that is independent of  $[\text{N}_2\text{O}_5]$  for both  $\gamma_0$  and  $\gamma_{ss}$ . The concentration dependence of  $\gamma_0$  and  $\gamma_{ss}$  shows the same trend as for  $\text{NO}_3$  albeit with two differences: for one the threshold value for  $[\text{N}_2\text{O}_5]$  below which the uptake coefficient increases with decreasing  $[\text{N}_2\text{O}_5]$  in an inverse  $\gamma/\text{concentration}$  dependence is higher than for  $\text{NO}_3$ . This threshold value for black soot seems to lie around  $[\text{N}_2\text{O}_5] = 3 \times 10^{12} \text{ molecule cm}^{-3}$ , whereas it lies around  $(7\text{--}8) \times 10^{11} \text{ molecule cm}^{-3}$  for  $\text{NO}_3$  according to Figure 9. The situation is less clear for gray soot, which seems to follow an inverse  $\gamma/\text{concentration}$  relationship throughout the examined concentration range where the values of  $\gamma_0$  and  $\gamma_{ss}$  coincide at the highest examined  $[\text{N}_2\text{O}_5]$  of  $8 \times 10^{12} \text{ molecule cm}^{-3}$ . The second difference with  $\text{NO}_3$  is the fact that the  $\gamma$  dependence on  $[\text{N}_2\text{O}_5]$  for gray and black soot is different from that with  $\text{N}_2\text{O}_5$  whereas it is identical for both types of soot in the case of  $\text{NO}_3$  as displayed in Figure 9. In any case, the concentration independent  $\gamma$  value for  $\text{N}_2\text{O}_5$  beyond the threshold value is a factor of 10 lower than for the corresponding  $\gamma$  value for  $\text{NO}_3$ . As for  $\text{NO}_3$  we report the calculated value of  $\gamma$  using the BET surface area thus regarding it as a lower bound. The steady-state uptake coefficient for  $\text{N}_2\text{O}_5$  reacting on 20 mg of soot is  $\gamma_{\text{BET}} = 3.2 \times 10^{-8}$  for gray and black soot (see Table 7).

#### 4. Conclusions and Atmospheric Significance

The reaction products resulting from the heterogeneous reaction of  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  with soot support the reduction of both trace gases according to reactions 9, 9a, and 7.  $\text{N}_2\text{O}_5$  yields an equimolar amount of  $\text{NO} + \text{NO}_2$  whereas  $\text{NO}_3$  exclusively leads to  $\text{NO}$  independent of the type of decane soot. The nature of the reaction products reveals a heterogeneous renoxification reaction following a mechanism that effectively converts  $\text{NO}_y$  to  $\text{NO}_x$ . The science community is looking for renoxification pathways other than the photolysis of  $\text{HNO}_3$  to adjust the  $[\text{HNO}_3]/[\text{NO}_x]$  concentration ratio downward, as all models substantially overpredict  $\text{HNO}_3$ .<sup>49</sup> The present work does not lay any claim to the importance of these renoxification pathways but does emphasize its potential importance in certain situations.

**TABLE 6: Summary of Uptake Experiments with NO<sub>3</sub> on Gray and Black Soot as a Function of Sample Mass ([NO<sub>3</sub>] = (2.3 ± 0.5) × 10<sup>12</sup> cm<sup>-3</sup>, Orifice Diameter = 8 mm)**

mass (mg)	γ <sub>0</sub> (gray soot)	γ <sub>ss</sub> (gray soot)	γ <sub>0</sub> (black soot)	γ <sub>ss</sub> (black soot)
1.5	(7.0 ± 4.0) × 10 <sup>-2</sup>	(1.8 ± 1.2) × 10 <sup>-2</sup>	(5.0 ± 3.5) × 10 <sup>-2</sup>	(1.5 ± 1.3) × 10 <sup>-2</sup>
3	0.1 ± 0.05	(3.0 ± 1.7) × 10 <sup>-2</sup>	(8.0 ± 3.0) × 10 <sup>-2</sup>	(2.5 ± 1.3) × 10 <sup>-2</sup>
5	0.16 ± 0.035	(5.5 ± 1.6) × 10 <sup>-2</sup>	0.15 ± 0.035	(5.0 ± 1.5) × 10 <sup>-2</sup>
7	0.17 ± 0.035	(6.5 ± 1.6) × 10 <sup>-2</sup>		
10	0.12 ± 0.030	(7.2 ± 1.2) × 10 <sup>-2</sup>	0.18 ± 0.03	(6.7 ± 1.4) × 10 <sup>-2</sup>
15	0.2 ± 0.032	(8.0 ± 2.0) × 10 <sup>-2</sup>	0.2 ± 0.03	(7.5 ± 2.3) × 10 <sup>-2</sup>
20	0.2 ± 0.032	(8.5 ± 2.0) × 10 <sup>-2</sup>	0.2 ± 0.03	(8.4 ± 2.0) × 10 <sup>-2</sup>

**Figure 11.** Uptake coefficient  $\gamma_{ss}$  of N<sub>2</sub>O<sub>5</sub> based on the geometric sample surface as a function of [N<sub>2</sub>O<sub>5</sub>]: N<sub>2</sub>O<sub>5</sub> on black (circles) and gray soot (open squares). For all measurements we used the 8 mm orifice diameter except for the point marked by the arrow where a 4 mm orifice diameter has been used.**TABLE 7: Summary of Results for Uptake Experiments of N<sub>2</sub>O<sub>5</sub> on 10 mg of Gray and Black Decane Soot<sup>a</sup>**

[N <sub>2</sub> O <sub>5</sub> ] <sub>0</sub> , cm <sup>-3</sup>	γ <sub>0</sub> (gray soot)	γ <sub>ss</sub> (gray soot)
(1.0 ± 0.5) × 10 <sup>12</sup> <sup>a</sup>	(8.5 ± 0.7) × 10 <sup>-2</sup>	(2.5 ± 1.0) × 10 <sup>-2</sup>
(1.6 ± 0.5) × 10 <sup>12</sup> <sup>a</sup>	(5.4 ± 0.3) × 10 <sup>-2</sup>	(2.3 ± 0.7) × 10 <sup>-2</sup>
(2.0 ± 0.7) × 10 <sup>12</sup> <sup>a</sup>	(5.2 ± 0.2) × 10 <sup>-2</sup>	(2.3 ± 0.4) × 10 <sup>-2</sup>
(2.7 ± 1.0) × 10 <sup>12</sup> <sup>a</sup>	(4.6 ± 0.5) × 10 <sup>-2</sup>	(2.0 ± 0.3) × 10 <sup>-2</sup>
(8.0 ± 1.3) × 10 <sup>12</sup> <sup>b</sup>	(4.4 ± 0.7) × 10 <sup>-2</sup>	(1.0 ± 0.5) × 10 <sup>-2</sup>

[N <sub>2</sub> O <sub>5</sub> ] <sub>0</sub> , cm <sup>-3</sup>	γ <sub>0</sub> (black soot)	γ <sub>ss</sub> (black soot)
(1.0 ± 0.5) × 10 <sup>12</sup> <sup>a</sup>	0.1 ± 0.05	(3.3 ± 0.8) × 10 <sup>-2</sup>
(1.3 ± 0.7) × 10 <sup>12</sup> <sup>a</sup>	0.1 ± 0.05	(3.4 ± 0.5) × 10 <sup>-2</sup>
(1.5 ± 0.5) × 10 <sup>12</sup> <sup>a</sup>	0.1 ± 0.08	(3.0 ± 0.6) × 10 <sup>-2</sup>
(1.9 ± 0.8) × 10 <sup>12</sup> <sup>a</sup>	(8.9 ± 0.5) × 10 <sup>-2</sup>	(2.0 ± 0.8) × 10 <sup>-2</sup>
(2.0 ± 0.8) × 10 <sup>12</sup> <sup>a</sup>	(7.5 ± 0.5) × 10 <sup>-2</sup>	(2.0 ± 0.5) × 10 <sup>-2</sup>
(2.9 ± 1.0) × 10 <sup>12</sup> <sup>a</sup>	(7.3 ± 0.5) × 10 <sup>-2</sup>	(8.0 ± 1.4) × 10 <sup>-3</sup>
(8.0 ± 1.3) × 10 <sup>12</sup> <sup>b</sup>	(4.4 ± 0.5) × 10 <sup>-2</sup>	(3.6 ± 1.0) × 10 <sup>-3</sup>

<sup>a</sup> Initial (γ<sub>0</sub>) and steady-state (γ<sub>ss</sub>) uptake coefficients (orifice diameter = 8 mm; orifice diameter = 4 mm).

In contrast to NO<sub>2</sub><sup>21</sup> and HNO<sub>3</sub><sup>23</sup> the mass balance for both N<sub>2</sub>O<sub>5</sub> (Table 4) and NO<sub>3</sub> (Table 2) indicates that the yields of reaction products are independent of the type of soot, in agreement with the measured uptake coefficients that are also essentially independent of the type of soot, as displayed in Figures 9 and 11. We attribute the higher NO yield in the case of NO<sub>3</sub> reacting with black compared to gray decane soot to the decomposition of HONO that is formed as a consequence of the presence of NO<sub>2</sub> on black soot. This is an artifact of the used NO<sub>3</sub> source that delivers 3 times as much NO<sub>2</sub> compared to NO<sub>3</sub> and that forces us to take into account the interaction of NO<sub>2</sub> with soot in detail. In contrast to NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, the type of soot matters for the NO<sub>2</sub>/soot interaction.<sup>32</sup>

The N<sub>2</sub>O<sub>5</sub> yield of 23% is observed to be independent of the type of soot and is a consequence of the presence of adsorbed NO<sub>3</sub> reacting with excess gaseous NO<sub>2</sub>. Adsorbed NO<sub>2</sub> is reacting to HONO and NO on gray and black decane soot, respectively.<sup>22</sup> We conclude that the extents of adsorption of

NO<sub>3</sub> are identical on both types of soot. Somewhat surprisingly, only a very low rate of hydrolysis of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> is observed on both types of soot, which is at variance with results on N<sub>2</sub>O<sub>5</sub> reacting on carbon black, Norit A, a carbonaceous material produced from pyrolysis.<sup>47</sup> For both trace gases significant amounts remain adsorbed on the soot substrate. Only 11 and 16% of the lost NO<sub>3</sub> are converted to NO on gray and black decane soot, respectively. We attribute the difference of 5% “excess” yield of NO on black vs gray soot to HONO decomposition (see above). Considering the fraction of NO<sub>3</sub> that goes on to yield N<sub>2</sub>O<sub>5</sub> we see that approximately two-thirds of the lost NO<sub>3</sub> remains adsorbed on soot during uptake vs 1/3 generating gaseous N<sub>2</sub>O<sub>5</sub>. In contrast, we observe an essentially quantitative conversion of N<sub>2</sub>O<sub>5</sub> to an equimolar mixture of NO + NO<sub>2</sub> for concentrations lower than 3 × 10<sup>12</sup> molecules cm<sup>-3</sup>, which means that no significant amounts of N<sub>2</sub>O<sub>5</sub> remain adsorbed on both types of soot, as indicated in Table 4. At higher concentrations of N<sub>2</sub>O<sub>5</sub> the rate of surface reaction according to reactions 9 and 9a obviously slows down compared to N<sub>2</sub>O<sub>5</sub> adsorption which leads to a significant reduction of the product yield.

In contrast to the interaction of NO<sub>2</sub> and HNO<sub>3</sub> with gray and black hexane and decane soot<sup>21,23</sup> whose product branching ratio strongly depended on the type of soot, we see the opposite behavior, namely a lack of dependence on the type of soot in the case of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>. This finding is somewhat unexpected compared to both the behavior of NO<sub>2</sub> and HNO<sub>3</sub> and is in disagreement with the results of Smith and co-workers<sup>24</sup> who have observed a strong correlation of the reactivity of O<sub>3</sub> and of the interaction of H<sub>2</sub>O vapor with several types of combustion soot as a function of the air/fuel ratio that is comparable to the fuel/oxygen ratio used in the present work. In general agreement with the present results Longfellow et al.<sup>50–52</sup> find a yield of NO<sub>2</sub> of 104 ± 10% and a small HONO yield on the order of 1% for the interaction of N<sub>2</sub>O<sub>5</sub> on propane soot whose fuel to oxygen ratio was not controlled. The small HONO yield was believed to originate from the secondary reaction of NO<sub>2</sub> on propane soot. On the side, the present work yields additional confirmation of HONO formation of NO<sub>2</sub> on decane soot compared to previous results obtained on hexane soot<sup>21</sup> and lends support to the importance of the fuel to oxygen ratio  $\lambda$  in determining the reactivity of soot toward NO<sub>2</sub>.<sup>21–24</sup>

Finally, we would like to point out that the heterogeneous reduction reaction of both NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> on both types of soot formally corresponds to a 4 electron transfer in regard to NO formation from NO<sub>3</sub> and NO + NO<sub>2</sub> formation from N<sub>2</sub>O<sub>5</sub>. This is accompanied with the formal transfer of two O atoms from the reacting trace gas to the reducing soot substrate. In contrast, HONO formation from NO<sub>2</sub> implies a formal transfer of one electron,<sup>21,22,40,41</sup> whereas HONO formation from HNO<sub>3</sub>/soot interaction<sup>21</sup> requires the transfer of two electrons. In this analysis we regard the NO formation from the NO<sub>2</sub>/black decane soot interaction as a secondary product of HONO decomposition on soot,<sup>22</sup> i.e., a one-electron reduction.



From the present kinetic uptake experiments performed on gray and black decane soot, we may extrapolate  $\gamma$  to vanishing  $\text{NO}_3$  concentration as displayed in Figure 9 and obtain an estimate of  $\gamma_{ss}$  for  $[\text{NO}_3] < 7.0 \times 10^{11}$  molecule  $\text{cm}^{-3}$  independent of the type of soot. With tropospheric  $[\text{NO}_3]$  at a typical value of  $2.0 \times 10^9$  molecule  $\text{cm}^{-3}$ ,<sup>30</sup>  $\gamma_{ss}$  tends toward values larger than 0.3 according to the results displayed in Figure 9. The  $\text{NO}_3$  loss rate constant ( $k_{\text{het}}$ ) due to heterogeneous uptake onto aerosols is given by  $k_{\text{het}} = \tau^{-1}(\text{NO}_3) = \gamma A \bar{c} / 4V$  as far as the surface resistance is concerned without consideration of mass transfer, where  $\gamma$  is the uptake coefficient of  $\text{NO}_3$ ,  $A/V$  is the surface-to-volume ratio of the aerosol, and  $\bar{c}$  is the mean molecular speed of  $\text{NO}_3$ .

The uptake of  $\text{NO}_3$  on soot was studied in a large aerosol chamber and yielded an upper limit of  $\gamma \leq 3.0 \times 10^{-4}$  at very low relative humidity (rh) ( $\text{H}_2\text{O} < 10$  ppm), whereas at 50% rh an upper limit of  $\gamma \leq 1.0 \times 10^{-3}$  was obtained. These values are 2 (50% rh) and 3 orders of magnitude lower than the  $\gamma$  value of 0.3 for  $[\text{NO}_3] < 7.0 \times 10^{11}$  molecule  $\text{cm}^{-3}$ . The impact of soot aerosol surface reactions on the rate of formation of photochemical ozone was also investigated using a box model.<sup>11</sup> The results showed that soot has a minor impact on ozone formation at low  $[\text{NO}_y]$ . In contrast, soot may cause an ozone reduction of up to 10% at high  $[\text{NO}_y]$ . However, we must point out that the nature of the carbonaceous aerosol from a spark ignition generator<sup>11</sup> is significantly different from flame soot used in the present study. At variance, the work of Saathoff et al.<sup>11</sup> shows that the uptake of  $\text{NO}_3$  on soot seems to saturate and tend to a small  $\gamma_{ss}$  value at steady state. This may perhaps be due to the graphitic core of the used soot that proves to be unreactive toward  $\text{NO}_3$  free radical attack once the reactive “soot” surface functionalities are consumed and the “bare” graphitic core is exposed. On the other hand, the present experiments are not sensitive to saturation phenomena owing to the shorter time scale used such that critical comparison of results has to await further experiments.

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## Appendix A: Data Analysis for the Detection of Reaction Products

**A1.  $\text{NO}_3$  Reaction and Detection.** The absolute  $\text{NO}_2$  concentration  $[\text{NO}_2]_{0(\text{REMPI})}$  originating from the  $\text{NO}_3$  source has been determined by means of in situ REMPI detection akin to the method outlined in ref 44. Subsequently, the corresponding MS signal of  $\text{NO}_2$  at  $m/e$  46,  $I_{0(\text{REMPI})}^{46(\text{NO}_2)}$ , was calculated according to eq A3 (see below). We point out that in contrast to MS signals that are proportional to an ion current, and thus to flux, the REMPI signals scale with the concentration of the detected trace gas as explained in detail in ref 44.

Through a calibrated mass spectrum of pure  $\text{HNO}_3$  we have accurately determined the contribution of the  $\text{HNO}_3$  impurity at  $m/e$  46 and 30 by using the fragmentation pattern expressed as the ratios

$$f_{46} = \frac{I_0^{46(\text{HNO}_3)}}{I_0^{63(\text{HNO}_3)}} = 52 \pm 8 \quad f_{30} = \frac{I_0^{30(\text{HNO}_3)}}{I_0^{63(\text{HNO}_3)}} = 33 \pm 4$$

In the absence of a substrate,  $f_{46}I_0^{63(\text{HNO}_3)}$  and  $f_{30}I_0^{63(\text{HNO}_3)}$  have been subtracted from the total MS signals  $I_0^{46}$  and  $I_0^{30}$  at  $m/e$  46 and 30, respectively, to assign the remaining MS amplitude to the  $\text{NO}_2^+$  and  $\text{NO}^+$  fragments of  $\text{N}_2\text{O}_5$ :  $I_0^{46(\text{N}_2\text{O}_5)} = I_0^{46} - f_{46}I_0^{63(\text{HNO}_3)}$  and  $I_0^{30(\text{N}_2\text{O}_5)} = I_0^{30} - f_{30}I_0^{63(\text{HNO}_3)}$ . The same type of procedure has been used for experiments in the presence of a sample once all the reaction products were known, starting at the high mass end ( $\text{HNO}_3$ ,  $\text{NO}_3$ ,  $\text{HONO}$ ,  $\text{N}_2\text{O}_5$ ,  $\text{NO}_2$ , and  $\text{NO}$ ).

In the absence of the soot substrate,  $I_{0(\text{REMPI})}^{46(\text{NO}_2)}$  and  $f_{46}I_0^{63(\text{HNO}_3)}$  have been subtracted from the total MS signal  $I_0^{46}$  at  $m/e$  46 to attribute the remaining signal to the  $\text{NO}_2^+$  fragment of the electron-impact ionization of  $\text{NO}_3$  once the absence of nondissociated  $\text{N}_2\text{O}_5$  from the  $\text{NO}_3$  source was established. The temperature of the  $\text{NO}_3$  source was increased to the point where all non dissociated  $\text{N}_2\text{O}_5$  fell below the detection limit. The resulting MS signal at  $m/e$  46 pertaining to  $\text{NO}_3$  is  $I_0^{46(\text{NO}_3)} = I_0^{46} - I_{0(\text{REMPI})}^{46(\text{NO}_2)} - f_{46}I_0^{63(\text{HNO}_3)}$ .

When soot is exposed to the effluents of the  $\text{NO}_3$  source,  $\text{NO}_3$  is taken up and reacts on soot, resulting in a decrease of  $[\text{NO}_3]$  that leads to a concomitant decrease of the MS signal  $I_0^{46}$  at  $m/e$  46. To correct for the contribution of  $\text{NO}_3$  at  $m/e$  46 for the following series of uptake experiments, we have determined  $r_{46} = I_0^{46(\text{NO}_3)} / I_0^{62(\text{NO}_3)} = 8.5 \pm 1.5$  as the ratio of the MS signal  $I_0^{46(\text{NO}_3)}$  at  $m/e$  46 ( $\text{NO}_2^+$ ) and  $I_0^{62(\text{NO}_3)}$ , the molecular ion peak at  $m/e$  62 ( $\text{NO}_3^+$ ), both for  $\text{NO}_3$  free radical in the absence of the soot sample.

As a result of the exposure of the sample to  $\text{NO}_3$  in the presence of  $\text{NO}_2$ , we expect four possible reaction products besides changes of  $\text{NO}_2$ :  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HONO}$ , and  $\text{NO}$ . Under our experimental conditions  $\text{HNO}_3$  may possibly be formed at high densities by heterogeneous recombination of  $\text{NO}_2$  and  $\text{NO}_3$  to  $\text{N}_2\text{O}_5$  and subsequent heterogeneous hydrolysis. To find other possible reaction products contributing to the  $I_{\text{exc}}^{46}$  MS signal intensity at  $m/e$  46 not due to  $\text{HNO}_3$ , we have subtracted the following known contributions from the total MS signal  $I_{\text{exc}}^{46}$ : (a)  $I_{\text{r(REMPI)}}^{46(\text{NO}_2)}$  for  $\text{NO}_2$ , (b)  $r_{46}I_{\text{r}}^{62(\text{NO}_3)}$  for  $\text{NO}_3$ , and (c)  $f_{46}I_{\text{r}}^{63(\text{HNO}_3)}$  for the possible  $\text{HNO}_3$  formation during the reaction which result in the following remaining MS signal called excess MS intensity at  $m/e$  46:

$$I_{\text{exc}}^{46} = I_{\text{r}}^{46} - I_{\text{r(REMPI)}}^{46(\text{NO}_2)} - r_{46}I_{\text{r}}^{62(\text{NO}_3)} - f_{46}I_{\text{r}}^{63(\text{HNO}_3)} \quad (\text{A1})$$

It is reasonable to expect that  $\text{N}_2\text{O}_5$  may be the only reaction product contributing to an excess at  $m/e$  46, as will be discussed below. Therefore, in the following  $I_{\text{exc}}^{46}$  will be named  $I_{\text{exc}}^{46(\text{N}_2\text{O}_5)}$ .

Using REMPI detection at  $\lambda_{\text{NO}} = 452.6$  nm, we could not detect any  $\text{NO}$  product formation because its concentration dropped below the detection limit given by the chosen experimental conditions. Therefore, to establish the amount of  $\text{NO}$  from the excess MS signal intensity at  $m/e$  30,  $I_{\text{exc}}^{30}$ , during the exposure of soot to  $\text{NO}_3$ , we have accurately determined all the possible contributions to the total MS signal  $I_{\text{r}}^{30}$  at  $m/e$  30. The major contribution to  $I_{\text{r}}^{30}$  comes from the mixture of  $\text{NO}_2$  and  $\text{NO}_3$  originating from the hot  $\text{NO}_3$  source given that the amount of  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$  in the presence of the sample is small. Using a reference mass spectrum of pure  $\text{NO}_2$ , we have calculated the effective contribution of  $\text{NO}_2$  at  $m/e$  30 by using the fragmentation pattern expressed as the ratio

$$z_1 = \frac{I_0^{30(\text{NO}_2)}}{I_0^{46(\text{NO}_2)}} = 2.0 \pm 0.2$$

The ratio of the MS signal  $I_0^{30(\text{NO}_3)}$  at  $m/e$  30 (NO<sup>+</sup>) and  $I_0^{62(\text{NO}_3)}$  at  $m/e$  62 (NO<sub>3</sub><sup>+</sup>) for NO<sub>3</sub> radical has been defined as follows:

$$r_{30} = \frac{I_0^{30(\text{NO}_3)}}{I_0^{62(\text{NO}_3)}} = \frac{I_0^{30} - z_1 I_0^{46(\text{NO}_2)} - f_{30} I_0^{63(\text{HNO}_3)}}{I_0^{62(\text{NO}_3)}} = 6.3 \pm 0.8$$

where  $I_0^{30}$  is the total MS signal at  $m/e$  30 and  $z_1 I_0^{46(\text{NO}_2)}$  and  $f_{30} I_0^{63(\text{HNO}_3)}$  are the contributions of NO<sub>2</sub> and HNO<sub>3</sub>, both at  $m/e$  30, respectively.

As explained above, it is reasonable to expect that N<sub>2</sub>O<sub>5</sub> will be a reaction product of the reaction of NO<sub>3</sub> on soot. However, we have to consider that pure N<sub>2</sub>O<sub>5</sub> has fragment peaks at  $m/e$  46 and 30 that are correlated by the fragmentation pattern expressed as the ratio  $r_{\text{N}_2\text{O}_5} = I_0^{46(\text{N}_2\text{O}_5)}/I_0^{30(\text{N}_2\text{O}_5)} = 1.36 \pm 0.3$ .

This ratio was established after extensive passivation of the inlet system and running the NO<sub>3</sub> source at ambient temperature to afford a stabilized flow of N<sub>2</sub>O<sub>5</sub>. As shown in previous studies on soot,<sup>23</sup> HNO<sub>3</sub> reacts on the soot surface resulting in the formation of volatile products such as HONO and NO that contribute to the total MS signal  $I_r^{30}$  at  $m/e$  30. At the present experimental conditions HONO has a measurable, albeit low intensity, parent peak at  $m/e$  47 (HONO<sup>+</sup>). Therefore, the effective contribution of HONO at  $m/e$  30 has been determined by using its fragmentation pattern expressed as the ratio  $h = I_0^{30(\text{HONO})}/I_0^{47(\text{HONO})} = 22 \pm 0.5$ . As already explained above, HNO<sub>3</sub> present in the hot NO<sub>3</sub> source also provides a contribution to the MS amplitude at  $m/e$  30 as expressed by  $f_{30}$ .

Finally, during the exposure of soot to NO<sub>3</sub> we have subtracted the following known contributions from the total MS signal  $I_r^{30}$  at  $m/e$  30: (a)  $I_{\text{exc}}^{46}/r_{\text{N}_2\text{O}_5}$  for the contribution owing to the presence of N<sub>2</sub>O<sub>5</sub>, (b)  $z_1 I_{\text{r(REMPI)}}^{46(\text{NO}_2)}$  for the contribution of NO<sub>2</sub> (see eq A3, next paragraph), (c)  $r_{30} I_r^{62(\text{NO}_3)}$  for the contribution of NO<sub>3</sub>, (d)  $h I_r^{47(\text{HONO})}$  for HONO, (e)  $f_{30} I_r^{63(\text{HNO}_3)}$  for HNO<sub>3</sub>. The final expression for the residual (=excess) MS signal amplitude  $I_{\text{exc}}^{30}$  attributed to the presence of NO resulted from the following equation:

$$I_{\text{exc}}^{30} = I_r^{30} - \frac{I_{\text{exc}}^{46(\text{N}_2\text{O}_5)}}{r_{\text{N}_2\text{O}_5}} - z_1 I_{\text{r(REMPI)}}^{46(\text{NO}_2)} - r_{30} I_r^{62(\text{NO}_3)} - h I_r^{47(\text{HONO})} - f_{30} I_r^{63(\text{HNO}_3)} \quad (\text{A2})$$

It is reasonable to expect that N<sub>2</sub>O<sub>5</sub> and NO may be the only reaction products contributing to  $m/e$  46 and 30, respectively, after subtraction of all known contributions to these masses displayed in eqs A1 and A2.

**A2. N<sub>2</sub>O<sub>5</sub> Reaction and Detection.** For N<sub>2</sub>O<sub>5</sub> uptake experiments performed on gray and black soot, both NO<sub>2</sub> and NO could be observed in the gas phase. The NO REMPI detection sensitivity was increased in the N<sub>2</sub>O<sub>5</sub> uptake experiments such that both products could be detected in situ in back-to-back experiments, albeit not concurrently. The reaction product not determined using REMPI was quantified using MS signal analysis of amplitudes at  $m/e$  30 and 46. The absolute NO and NO<sub>2</sub> concentrations obtained using REMPI detection were then scaled to the corresponding flow rates using eq A3 for NO<sub>2</sub> and the analogous expression for NO. The relevant MS calibration factors were previously established in ancillary experiments (see above).

The corresponding MS signal contribution  $I_{0,\text{r(REMPI)}}^{46(\text{NO}_2)}$  at  $m/e$  46 in the absence (subscript “0”) and presence (subscript “r”)

of the soot sample, the NO<sub>2</sub> REMPI signal was scaled to a MS signal using the following equation:

$$I_{0,\text{r(REMPI)}}^{46(\text{NO}_2)} = \frac{F_{0,\text{r}}^{\text{NO}_2}}{C_{\text{cal}(\text{NO}_2)}} = \frac{[\text{NO}_2]_{0,\text{r(REMPI)}} k_{\text{esc}(\text{NO}_2)} V_{\text{cell}}}{C_{\text{cal}(\text{NO}_2)}} \quad (\text{A3})$$

where  $C_{\text{cal}(\text{NO}_2)}$  is the NO<sub>2</sub> calibration factor that was directly determined from an absolute measurement of [NO<sub>2</sub>] in an ancillary experiment using a suitably calibrated MS signal for pure NO<sub>2</sub>.  $k_{\text{esc}(\text{NO}_2)}$  is the NO<sub>2</sub> effusive loss rate constant. One should be reminded that the conversion following eq A3 is necessary because the REMPI signal scales with the concentration whereas the MS signal corresponds to a flux (see above).

Equation A3 allows one to calculate the fraction of the MS signal at  $m/e$  46 owing to the presence of NO<sub>2</sub> using the measured REMPI signal for NO<sub>2</sub> to establish its absolute concentration. Therefore, we have corrected the MS signal at  $m/e$  46 for the presence of NO<sub>2</sub> according to eq A4 when the sample is exposed to N<sub>2</sub>O<sub>5</sub> and obtained the MS signal at  $m/e$  46 for pure N<sub>2</sub>O<sub>5</sub> under the assumption that there are no additional contributions to  $I_r^{46}$ .

$$I_r^{46(\text{N}_2\text{O}_5)} = I_0^{46} - I_{\text{r(REMPI)}}^{46(\text{NO}_2)} \quad (\text{A4})$$

which thus exclusively corresponds to N<sub>2</sub>O<sub>5</sub> for this experiment after correction of the MS signal  $I_r^{46}$  at  $m/e$  46 for the contribution of NO<sub>2</sub> produced during uptake of N<sub>2</sub>O<sub>5</sub> on the soot substrate. Specifically, significant amounts of HNO<sub>3</sub> were not detected in the present experiments.

To calculate the amount of NO<sub>2</sub> formed during the reaction of N<sub>2</sub>O<sub>5</sub> on gray and black soot, we have subtracted the contribution of N<sub>2</sub>O<sub>5</sub> from the total MS signal at  $m/e$  46. The MS signal at  $m/e$  30 was corrected for its NO contribution when NO was detected by REMPI, namely,  $I_{\text{r(REMPI)}}^{30(\text{NO})}$ , after scaling to a flow rate or MS signal. Therefore, the total contribution of N<sub>2</sub>O<sub>5</sub> to the MS signal at  $m/e$  46 was  $r_{\text{N}_2\text{O}_5}(I_r^{30} - I_{\text{r(REMPI)}}^{30(\text{NO})})$ . The final expression for  $I_{\text{exc}}^{46}$  attributed to the presence of NO<sub>2</sub> is given by eq A5.

$$I_{\text{exc}}^{46} = I_r^{46} - r_{\text{N}_2\text{O}_5}(I_r^{30} - I_{\text{r(REMPI)}}^{30(\text{NO})}) \quad (\text{A5})$$

Conversely, to calculate the amount of NO formed during the reaction of N<sub>2</sub>O<sub>5</sub> on gray and black soot, we have subtracted the contribution of N<sub>2</sub>O<sub>5</sub> from the total MS signal at  $m/e$  30. The MS signal at  $m/e$  46 was corrected for its NO<sub>2</sub> contribution when NO<sub>2</sub> was detected by REMPI, namely,  $I_{\text{r(REMPI)}}^{46(\text{NO}_2)}$  after scaling to a flow rate or MS signal. Therefore, the total contribution of N<sub>2</sub>O<sub>5</sub> to the MS signal at  $m/e$  30 was  $(I_r^{46} - I_{\text{r(REMPI)}}^{46(\text{NO}_2)})/r_{\text{N}_2\text{O}_5}$ . The final expression for  $I_{\text{exc}}^{30}$  attributed to the presence of NO is given by eq A6.

$$I_{\text{exc}}^{30} = I_r^{30} - \frac{(I_r^{46} - I_{\text{r(REMPI)}}^{46(\text{NO}_2)})}{r_{\text{N}_2\text{O}_5}} \quad (\text{A6})$$

This analysis makes use of the observation that both HNO<sub>3</sub> and HONO were undetectable during uptake of N<sub>2</sub>O<sub>5</sub> on gray and black soot.

## References and Notes

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