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# Heterogeneous conversion of NO<sub>2</sub> on secondary organic aerosol surfaces: A possible source of nitrous acid (HONO) in the atmosphere?

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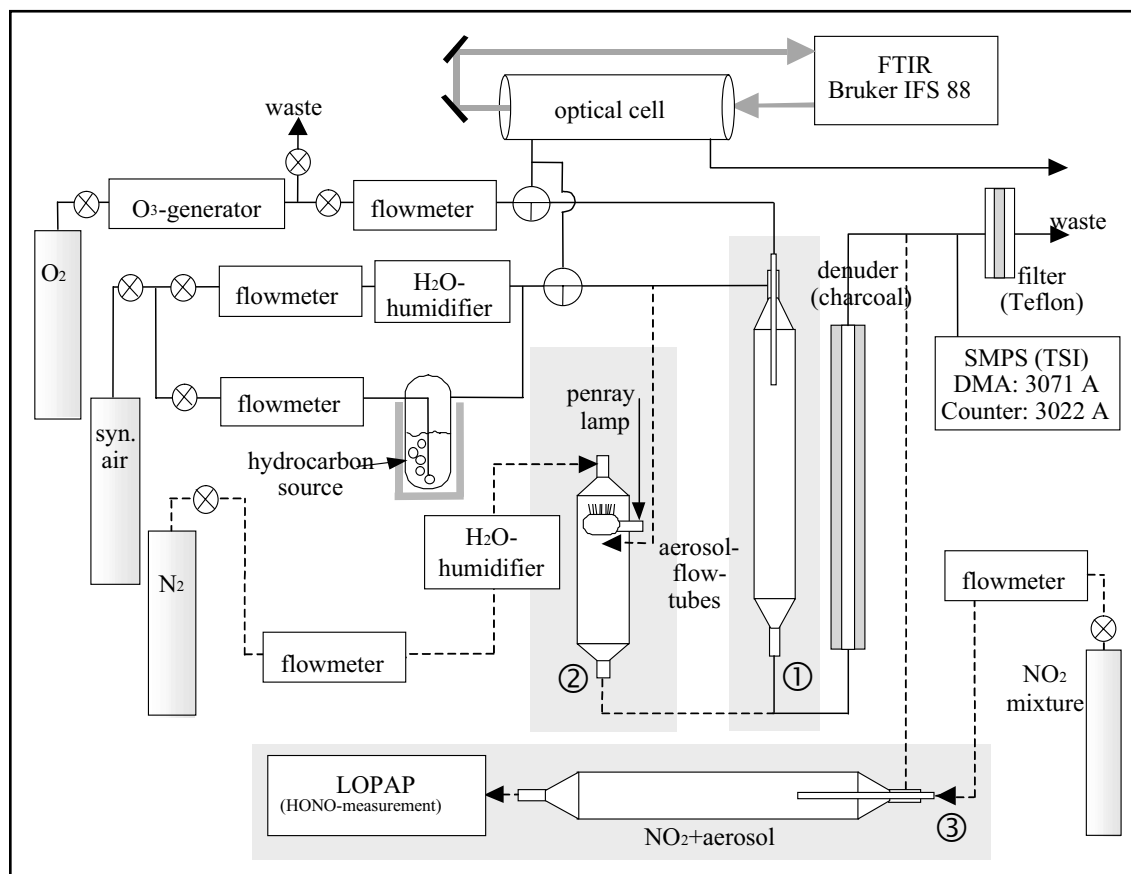
**Abstract.** The heterogeneous conversion of NO<sub>2</sub> on different secondary organic aerosols (SOA) was investigated with the focus on a possible formation of nitrous acid (HONO). In one set of experiments different organic aerosols were produced in the reactions of O<sub>3</sub> with  $\alpha$ -pinene, limonene or catechol and OH radicals with toluene or limonene, respectively. The aerosols were sampled on filters and exposed to humidified NO<sub>2</sub> mixtures under atmospheric conditions. The estimated upper limits for the uptake coefficients of NO<sub>2</sub> and the reactive uptake coefficients NO<sub>2</sub>→HONO are in the range of 10<sup>-6</sup> and 10<sup>-7</sup>, respectively. The integrated HONO formation for 1 h reaction time was < 10<sup>13</sup> cm<sup>-2</sup> geometrical surface and < 10<sup>17</sup> g<sup>-1</sup> particle mass. In a second set of experiments the conversion of NO<sub>2</sub> into HONO in the presence of organic particles was carried out in an aerosol flow tube under atmospheric conditions. In this case the aerosols were produced in the reaction of O<sub>3</sub> with  $\beta$ -pinene, limonene or catechol, respectively. The upper limits for the reactive uptake coefficients NO<sub>2</sub>→HONO were in the range of 7 × 10<sup>-7</sup> – 9 × 10<sup>-6</sup>. The results from the present study show that heterogeneous formation of nitrous acid on secondary organic aerosols (SOA) is unimportant for the atmosphere.

formation by the reaction of NO<sub>2</sub> with soot surfaces was postulated to be of potential importance (Ammann et al., 1998; Gerecke et al., 1998; Longfellow et al., 1999). However, other studies have demonstrated that the integrated HONO yield of the non-catalytic reaction is too small to explain significant HONO formation in the atmosphere (Kleffmann et al., 1999; Arens et al., 2001). It is assumed that adsorbed organic compounds are responsible for the HONO formation on soot surfaces (Stadler and Rossi, 2000; Arens et al., 2002). In a recent study, significant HONO formation was observed on aqueous or humid surfaces in the reaction of NO<sub>2</sub> with semi-volatile hydrocarbons emitted from a diesel engine (Gutzwiller et al., 2002). Different groups of compounds were postulated, although the exact nature of the hydrocarbons is still unknown. Different reactions of NO<sub>2</sub> with organic hydrocarbons were reviewed by Huie (1994). In the reaction of NO<sub>2</sub> with aromatic amines (Saltzman, 1954; Huie and Neta, 1986), hydroxy-substituted aromatic hydrocarbons (Alfassi et al., 1986; Alfassi, et al., 1990), alkenes and polyunsaturated fatty acids (Pryor and Lightsey, 1981; Giamalva et al., 1987) nitrite formation was observed in the liquid phase. In addition, heterogeneous HONO formation was observed in the reaction of NO<sub>2</sub> with adsorbed hydroxy-substituted aromatics (Arens et al., 2002). In the atmosphere these reactions might also take place on similar organic surfaces e.g. on secondary organic particles. The organic species mentioned above are formed, at least in part, in the reaction of volatile organic compounds with O<sub>3</sub> or OH radicals (Seinfeld and Pandis, 1998). Since the organic fraction of the atmospheric aerosol can significantly exceed the black carbon fraction (Raes et al., 2000), secondary organic aerosols could be an important HONO source in the atmosphere. However, the conversion of NO<sub>2</sub> into HONO in the presence of such particles is still unknown and was investigated in the present study using two different experimental approaches, namely in an aerosol flow tube and in aerosol filter experiments.

## 1 Introduction

HONO is an important precursor for OH radicals in the atmosphere due to the photolysis HONO + *hν* → OH + NO. In addition, HONO is supposed to be an important indoor pollutant. It can form either carcinogenic nitrosamines (e.g. Pitts et al., 1978) or interhelical DNA cross-links (e.g. Harwood et al., 2000). Different formation pathways in the atmosphere were proposed during the last decades (e.g. Lammer and Cape, 1996). Recently, the heterogeneous HONO

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**Fig. 1.** Experimental set-up for the generation and sampling of secondary organic particles (part 1: O<sub>3</sub>+hydrocarbon, part 2: OH+hydrocarbon) and for the reaction of NO<sub>2</sub> with organic particles in an aerosol flow tube (part 3).

## 2 Experimental

Two flow systems were used in which the aerosols were generated by the reaction of different hydrocarbons with O<sub>3</sub> or OH radicals. The experimental set-up used for the preparation and the sampling of the aerosols is shown in Fig. 1. The particle size distribution was measured by a SMPS-system (TSI 3071 electrostatic classifier and TSI 3022A condensation particle counter).

### 2.1 Aerosol formation by O<sub>3</sub> reaction

The aerosols were produced by the reaction of O<sub>3</sub> with  $\alpha$ -pinene (99%, Aldrich), limonene (99%, Aldrich) or 1,2-dihydroxybenzene (catechol, 99%, Aldrich), respectively. Ozone was prepared in pure oxygen (O<sub>2</sub> 99.95%, Messer Griesheim) with a silent discharge generator (Fig. 1, part 1). The initial concentrations of the gas phase compounds were in the range of a few ppmv to get a weighable particle mass. O<sub>3</sub> and the different hydrocarbons were measured in a separate optical cell (optical path length 46 cm) by FTIR spectroscopy (Bruker IFS 88). All mass flows were controlled

with calibrated mass flowmeters (Tylan, FM 360) and needle valves. A humidified mixture of the organic compounds in synthetic air was added to a flow of O<sub>3</sub>. The reaction time in the flow system could be varied between a few seconds and two minutes by the use of a movable injector. During this time a fast formation of particles took place. The particle number and the maximum of the size distribution could be varied by using different initial concentrations and reaction times. To exclude a deactivation of the freshly prepared aerosols due to a former reaction with excess O<sub>3</sub>, a charcoal denuder was placed behind the flow tube. O<sub>3</sub> and the organic gas phase compounds were captured with >98% and >90% efficiency, respectively, whereas the particles were unaffected.

### 2.2 Aerosol formation by OH reaction

For generating aerosols by reaction with OH radicals a second flow system was built up (Fig. 1, part 2). OH radicals were produced by the UV photolysis of H<sub>2</sub>O. A flow of  $\sim 500 \text{ ml min}^{-1}$  N<sub>2</sub> (99.999%, Messer Griesheim) was humidified and irradiated with a Hg penray lamp (Oriol).

Mixtures of toluene (99,8%, Fluka) or limonene (99%, Aldrich) in synthetic air were added behind the radiation source. By this experimental set-up the photolysis of the hydrocarbons by the penray lamp was prevented. Thus, in experiments performed with dry N<sub>2</sub> no particle formation was observed. From the absence of particle formation when dry N<sub>2</sub> was used and e.g. limonene was added behind the Hg penray lamp, we exclude significant formation of O<sub>3</sub> with this experimental set-up.

### 2.3 NO<sub>2</sub> filter experiments

The aerosols were sampled on Teflon filters (Schleicher & Schuell TE 37, 1 μm or Millipore Type FH, 0.5 μm). The collected particle masses varied in the range 0.5–6 mg. After the determination of the particle mass, the filter samples were placed into a PFA filter holder and were exposed to humidified NO<sub>2</sub> mixtures (100–300 ppbv, Messer Griesheim, 9.98 ppmv NO<sub>2</sub> in N<sub>2</sub>) under atmospheric conditions (1 atm, 298 K, ~50% r.h.) at flow rates of 300–500 ml min<sup>-1</sup>. HONO concentrations in the gas phase were measured using a stripping coil and ion chromatography (Shimadzu) after pre-concentration on a Dionex, TAC LP1 column. NO and NO<sub>2</sub> concentrations in the gas phase were determined by a luminol nitrogen oxide analyser (Unisearch, LMA-3D).

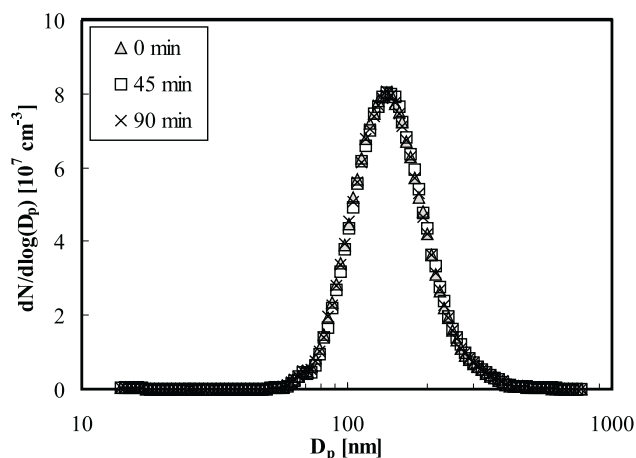
### 2.4 Flow tube experiments with NO<sub>2</sub>

In addition to the filter experiments, the conversion of NO<sub>2</sub> into HONO in the presence of organic particles was also investigated in an aerosol flow tube (length 80 cm, i.d. 5 cm, conic entrance and exit junctions) placed behind the charcoal denuder (Fig. 1, part 3). The aerosols were generated as described above. After passing the charcoal denuder, the aerosols were exposed to ~20 ppbv NO<sub>2</sub> (Messer Griesheim, 9.98 ppmv NO<sub>2</sub> in N<sub>2</sub>) under atmospheric conditions (1 atm, 298 K, 50% r.h.) at laminar flow (Reynolds number ~15) and a flow rate of ca. 1 l min<sup>-1</sup>. For the sensitive detection of the HONO concentration the LOPAP instrument (Heland et al., 2001; Kleffmann et al., 2002) was used with a time resolution of 1 min and a detection limit of 10 pptv. The particle size distribution was measured simultaneously as described above.

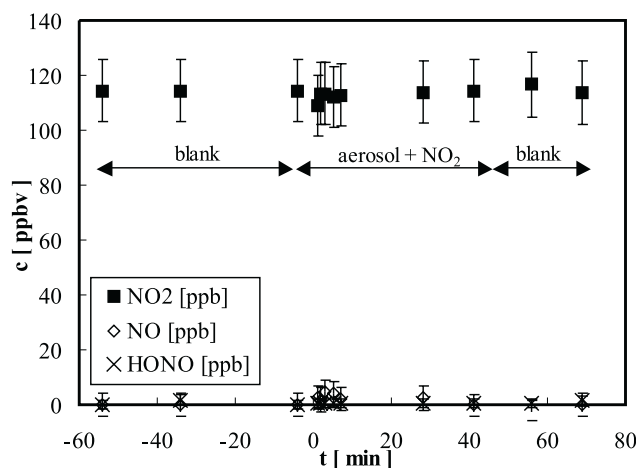
## 3 Results and discussion

### 3.1 Aerosol generation

In the experiments, high initial concentrations of the aerosol precursors were used to get a weighable aerosol mass in the filter experiments and high surface area densities in the aerosol flowtube experiments. The comparison between the weight of the filter and the calculated aerosol mass from the SMPS data, assuming an aerosol density of 1 g cm<sup>-3</sup>, agree within 90±5%. The particle number and the maximum of



**Fig. 2.** Size distribution of particles generated in the reaction of  $\alpha$ -pinene with O<sub>3</sub>. ([O<sub>3</sub>] = 33 ppm, [ $\alpha$ -pinene] = 34 ppm,  $T = 298$  K, [ $particles$ ] =  $2.7 \times 10^7$  [cm<sup>-3</sup>], 55% r.h.,  $T = 298$  K).



**Fig. 3.** Example of the concentration-time profiles for the conversion of NO<sub>2</sub> on organic particle surfaces (limonene/O<sub>3</sub>,  $m_{aerosol} = 2.1$  mg, [NO<sub>2</sub>] = 115 ppbv, 57% r.h.,  $T = 298$  K).

the size distribution could be varied by the use of different initial concentrations and reaction times. The secondary organic particles were produced under very different experimental conditions, e.g. the particles were produced with an excess of O<sub>3</sub> and an excess of the different hydrocarbons in different experiments. In addition, the humidity was varied. For constant experimental conditions it was observed, that the generated particle size was constant over a long period of time (Fig. 2).

### 3.2 Filter experiments

After the particle collection, the filter samples were exposed to humid NO<sub>2</sub> mixtures. Before and after the experiments, blank measurements were performed to determine the NO<sub>2</sub>,

**Table 1.** Summary of the filter experiments with NO<sub>2</sub> and organic particles. The uptake coefficients were determined using the geometric filter surface

aerosol system	uptake coefficients		integrated HONO formation (t = 1 h)	
	NO <sub>2</sub>	NO <sub>2</sub> →HONO	cm <sup>-2</sup> (geometric)	g <sup>-1</sup>
α-pinene/O <sub>3</sub>	< 5 × 10 <sup>-7</sup>	< 1 × 10 <sup>-7</sup>	< 1.0 × 10 <sup>13</sup>	< 3.0 × 10 <sup>16</sup>
limonene/O <sub>3</sub>	< 1.5 × 10 <sup>-6</sup>	< 8.5 × 10 <sup>-8</sup>	< 7.7 × 10 <sup>12</sup>	< 1.3 × 10 <sup>17</sup>
catechol/O <sub>3</sub>	< 1.5 × 10 <sup>-6</sup>	< 8.5 × 10 <sup>-8</sup>	< 7.7 × 10 <sup>12</sup>	< 6.0 × 10 <sup>17</sup>
limonene/OH	< 1.5 × 10 <sup>-6</sup>	< 8.5 × 10 <sup>-8</sup>	< 7.7 × 10 <sup>12</sup>	< 2.8 × 10 <sup>17</sup>
tolouene/OH	< 1.5 × 10 <sup>-6</sup>	< 8.5 × 10 <sup>-8</sup>	< 7.7 × 10 <sup>12</sup>	< 6.1 × 10 <sup>17</sup>

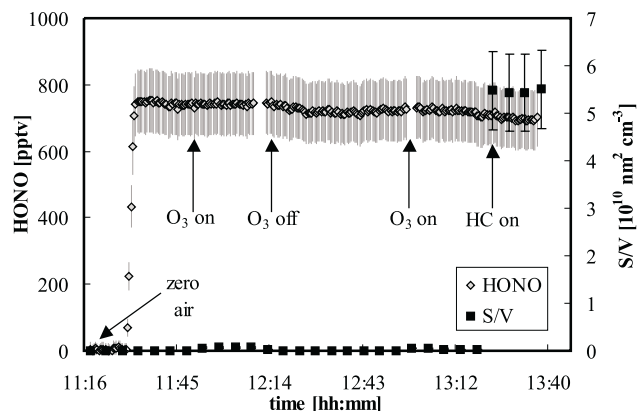
NO and HONO background concentrations. For these blank measurements a filter without the aerosol sample was used. A typical behaviour of the HONO, NO<sub>2</sub> and NO concentrations during the blank experiments and in the presence of the aerosol is shown in Fig. 3. Neither a NO<sub>2</sub> loss nor a HONO or NO formation was observed in any of the filter experiments on the different secondary organic particle surfaces for different humidities. Accordingly, from the precision of the instruments for Δ[NO<sub>2</sub>] of < 10 ppbv and for Δ[HONO] of < 1 ppbv upper limits for the NO<sub>2</sub> uptake coefficient, the reactive uptake coefficient (NO<sub>2</sub>→HONO) and the integrated HONO formation for reaction time of 1 h was estimated, using Eq. (1):

$$\gamma_{geo} = \frac{4 \times \Delta[\text{NO}_2] \text{ (or } \Delta[\text{HONO}]) \times \Phi}{[\text{NO}_2]_0 \times \bar{v} \times S} \quad (1)$$

in which [NO<sub>2</sub>]<sub>0</sub>, Δ[NO<sub>2</sub>] and Δ[HONO] reflect the initial and consumed NO<sub>2</sub> or formed HONO, respectively, Φ the gas flow rate, S the geometric surface of the filter and  $\bar{v}$  the mean molecular velocity of NO<sub>2</sub>. For the calculations, the geometric surface of the filters was taken as a lower limit leading to only upper limits of the uptake coefficients. The estimated upper limits for the uptake coefficients of NO<sub>2</sub> and the reactive uptake coefficients NO<sub>2</sub>→HONO are in the range of 10<sup>-6</sup> and 10<sup>-7</sup>, respectively. The integrated HONO formation for 1 h reaction time was < 10<sup>13</sup> cm<sup>-2</sup> geometrical surface and < 10<sup>17</sup> g<sup>-1</sup> particle mass (see Table 1).

### 3.3 Aerosol flow tube experiments

A lower HONO formation was expected in the aerosol flow tube experiments caused by the lower total particle surface area. Therefore, the sensitive LOPAP instrument was used for the detection of HONO. In separate experiments it was shown that particles in the size range investigated are not taken up by the LOPAP instrument. Accordingly, only HONO in the gas phase is detected by the instrument. The aerosols were produced only by reactions with O<sub>3</sub>, since the aerosol yields in the OH reactions were too low. A typical plot of the HONO concentration and the surface area density of the particles during an experiment is shown in Fig. 4. A constant flow of 19 ppbv humidified NO<sub>2</sub> led to the formation of ~800 pptv HONO, the so-called background HONO,

**Fig. 4.** Example of the conversion of NO<sub>2</sub> on secondary organic particles in the aerosol flow tube, generated in the reaction of β-pinene with O<sub>3</sub>, ([NO<sub>2</sub>] = 19 ppbv, 50% r.h., T = 298 K, Δt<sub>reac</sub> = 60 s).

due to the heterogeneous NO<sub>2</sub> conversion on the walls of the flow reactor (e. g. Kleffmann et al., 1998). The addition of ppmv levels of only O<sub>3</sub> led to a minor particle formation. This could be explained with the reaction of O<sub>3</sub> with impurities sticking on the surface of the reaction system. Only in the presence of both, O<sub>3</sub> and hydrocarbons a large bulk of particles was immediately formed. As shown in Fig. 4 the HONO concentration is independent of the particle concentration. The upper limits for the reactive uptake coefficients NO<sub>2</sub>→HONO could be estimated using Eq. (2):

$$\gamma = \frac{4 \times \Delta[\text{HONO}]_{max}}{[\text{NO}_2] \times \bar{v} \times S/V \times \Delta t_{reac}} \quad (2)$$

S/V is the surface area density of the particles, [NO<sub>2</sub>] the NO<sub>2</sub> gas phase concentration, Δt<sub>reac</sub> the reaction time of 60 s,  $\bar{v}$  the mean velocity of NO<sub>2</sub>. Using the upper limit of the HONO formation Δ[HONO]<sub>max</sub> of < 10 pptv, based on the 1% precision of the LOPAP instrument, upper limits for the uptake coefficients in the range of 10<sup>-6</sup> were estimated (see Table 2). These values are in good agreement with the upper limits from the filter experiments.

**Table 2.** Summary of the experiments on organic particles in the aerosol flow tube ([NO<sub>2</sub>] = 20 ppbv, 30–60% r. h., T = 298 K)

aerosol system	$\Delta S/V_{max}$ [nm <sup>2</sup> cm <sup>-3</sup> ]	reactive uptake coefficients (NO <sub>2</sub> →HONO)
$\beta$ -pinene/O <sub>3</sub>	$5.4 \times 10^{10}$	$< 2 \times 10^{-6}$
limonene/O <sub>3</sub>	$8.5 \times 10^{10}$	$< 7 \times 10^{-7}$
catechol/O <sub>3</sub>	$0.7 \times 10^{10}$	$< 9 \times 10^{-6}$

#### 4 Implications for the atmosphere

For the reaction of NO<sub>2</sub> with secondary organic particles an upper limit for the reactive uptake coefficient (NO<sub>2</sub>→HONO) of  $< 10^{-7}$  was determined. Accordingly, the reaction kinetics is much slower compared to the reaction of NO<sub>2</sub> with soot aerosols for which a reactive uptake coefficient of  $\sim 10^{-4}$  was determined under similar conditions, such as e. g. [NO<sub>2</sub>], humidity and reaction time (Ammann et al., 1998). Besides the reaction kinetics, also the upper limit of the integrated HONO yield in the reaction of NO<sub>2</sub> with secondary organic aerosols of  $< 10^{13}$  cm<sup>-2</sup> is 1–2 orders of magnitudes smaller than for the reaction of NO<sub>2</sub> with soot (Kalberer et al., 1999; Kleffmann et al., 1999; Arens et al., 2001). This leads to the conclusion that the functional groups on the surface of secondary organic particles are different from those on soot. This might be explained by the oxidative atmosphere under which the aerosols were produced. For soot surfaces it was shown that e.g. the HONO formation capacity could be significantly reduced by a treatment with ozone (Kalberer et al., 1999). The results from the present study show that the reaction of NO<sub>2</sub> with secondary organic aerosols can be excluded as an important source of HONO in the atmosphere.

#### 5 Conclusions

The heterogeneous conversion of NO<sub>2</sub> into HONO in the presence of different organic aerosols was studied under atmospheric conditions in filter experiments and in an aerosol flow tube. No NO<sub>2</sub> uptake and no HONO formation was observed for any of the aerosol systems investigated independent of the experimental conditions. Upper limits of the uptake coefficients of NO<sub>2</sub> and the reactive uptake coefficients NO<sub>2</sub>→HONO in the range of  $10^{-6}$  and  $10^{-7}$ , respectively, have been determined. The upper limits of the integrated HONO formation for a reaction time 1 h of  $< 10^{13}$  cm<sup>-2</sup> geometrical surface and  $< 10^{17}$  g<sup>-1</sup> particle mass indicate that the reaction of NO<sub>2</sub> with secondary organic particles does not represent an important HONO source in the atmosphere.

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