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Laboratory Studies of Sources of HONO in Polluted Urban Atmospheres

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Abstract. Laboratory studies reported here and in previous work show that the reaction of NO(g) with surface adsorbed HNO_3 may be a significant source of HONO in polluted urban atmospheres. If these laboratory studies can be extrapolated to ambient conditions, this heterogeneous reaction may generate HONO to about the same extent as the hydrolysis of NO_2 on surfaces, which is greater than the heterogeneous reaction of NO, NO_2 and water. It may also be involved in generating HONO in snowpacks, and important in reconciling the discrepancy between measured and modeled HNO_3/NO_x ratios in the troposphere.

1. Introduction

Nitrous acid (HONO) is a major source of tropospheric OH radicals. The highest concentrations have been detected at dawn in a number of polluted urban air [*Winer and Biermann*, 1994; *Finlayson-Pitts and Pitts*, 2000, and references therein]. Despite the importance of HONO, its sources are not well understood. It is found in direct emissions from non-catalyst equipped automobiles [*Pitts et al.*, 1984b; *Vecera and Dasgupta*, 1994; *Kirchstetter et al.*, 1996], and as a product of the heterogeneous reactions of nitrogen oxides on surfaces [*Wayne and Yost*, 1951; *Graham and Tyler*, 1972; *Chan et al.*, 1976a; b; *Sakamaki et al.*, 1983; *Pitts et al.*, 1984a; *Akimoto et al.*, 1987; *Svensson et al.*, 1987; *Jenkin et al.*, 1988; *Lammel and Perner*, 1988; *Febo and Perrino*, 1991; *Bambauer et al.*, 1994; *Mertes and Wahner*, 1995; *Kleffmann et al.*, 1998a; b]. Laboratory studies suggest that the surface hydrolysis of NO_2

$$2\,NO_2 + H_2O \xrightarrow{surface} HONO + HNO_3 \qquad (1)$$

is a major source of HONO in air, while the heterogeneous reaction (2) of NO, NO_2 and water,

$$NO + NO_2 + H_2O \xrightarrow{surface} 2\,HONO \qquad (2, -2)$$
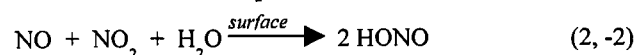
is of little or no importance in HONO generation [*Wayne and Yost*, 1951; *Graham and Tyler*, 1972; *Cox and Derwent*, 1976/77; *Chan et al.*, 1976a; b; *Kaiser and Wu*, 1977; *Sakamaki et al.*, 1983; *Pitts et al.*, 1984a; *Atkinson*, 1986]. NO_2 has also been shown to react with soot, generating HONO and NO [*Tabor et al.*, 1994; *Rogaski et al.*, 1997; *Ammann et al.*, 1998; *Gerecke et al.*, 1998; *Aumont et al.*, 1999; *Kalberer et al.*, 1999; *Longfellow et al.*, 1999].

However, a number of field measurements of HONO and associated nitrogen oxides have shown that HONO concentrations are better correlated with the product

$[NO][NO_2][H_2O]$ than with $[NO_2][H_2O]$ [*Sjodin and Ferm*, 1985; *Notholt et al.*, 1992; *Calvert et al.*, 1994; *Winer and Biermann*, 1994]. As a result, reaction (2) has been proposed as a possible HONO source.

Recent studies in this laboratory have shown that gas phase NO reacts with surface-adsorbed HNO_3 to generate NO_2 as a product, and HONO as an intermediate rapidly removed by secondary reactions [*Mochida and Finlayson-Pitts*, 2000a]. Due to experimental limitations, the lowest NO concentration studied was in the low Torr range, about four orders of magnitude higher than that found in polluted atmospheres.

In this paper, we extend our studies of the heterogeneous reaction of HNO_3 with NO two orders of magnitude. If we extrapolate the results further to ambient conditions, this reaction may be an important source of HONO in polluted urban areas. This is consistent with the suggestion [*Fairbrother et al.*, 1997] that the HNO_3 reaction with NO may occur during the day in the troposphere via heterogeneous catalysis. This reaction also explains the observed correlation of HONO with NO and may contribute to reconciling the discrepancy between measured and modeling ratios of HNO_3 to NO_x in the troposphere [*Chatfield*, 1994; *Hauglustaine et al.*, 1996].

2. Experimental

Two different borosilicate glass cells, were used for these experiments.

Long Path Gas Cell: The long path cell consisted of a 7.6 L cylinder, equipped with White cell optics, giving an optical path of 38.4 m. This permitted monitoring gases but not surface-adsorbed species. The metal holders for the optics were coated with halocarbon wax (Halocarbon Products Corp. Series 1500). The cell was located in the sampling compartment of a Mattson FTIR spectrometer (Research Series). HNO_3, obtained from the vapor above an HNO_3/H_2SO_4 mixture (1:2 v:v 69.3% HNO_3, Fisher and 95.7% H_2SO_4, Fisher), was added to the cell and then pumped out, leaving HNO_3 adsorbed on the cell walls. This was repeated several times and then water vapor (generated from Nanopure water, 18 MΩ cm) in N_2 was added to the cell to a total pressure of approximately 550 Torr. NO (Matheson 99%) in N_2 (99.999%, Oxygen Services Company) was added and the relative humidity and total pressure adjusted to 50% RH at 1 atm. The loss of NO and formation of gaseous products were followed using FTIR.

Porous Glass Cell: The porous glass cell of volume 79 cm^3 and surface area $\sim$ 240 cm^2, described in detail elsewhere [*Mochida and Finlayson-Pitts*, 2000a], was fixed in the sampling compartment of an FTIR spectrometer (Mattson, Research Series). A 2 x 3 cm porous glass plate (Corning) with original thickness 1 mm was etched in a 3 cm^2 area in the center using an HF solution to make it sufficiently thin to transmit infrared radiation down to $\sim$1500 cm^{-1}. This plate,

with a BET surface area of 28.5 m^2, was suspended in the cell and could be moved in and out of the infrared beam so that spectra of either the surface plus the gas phase, or the gas phase alone, could be measured. The difference gives the surface-adsorbed species. The pathlength was 6.7 cm so that only higher gas concentrations could be followed. The porous glass was not heated so that the surface held a significant amount of physisorbed water observed by its broad band around 3500 cm^{-1} [*Kiselev and Lygin*, 1975]. Gaseous HNO$_3$ was admitted to the cell to adsorb on the "wet" porous glass and the cell walls; the cell was then pumped out to remove the gas, leaving HNO$_3$ on the glass surfaces. Adsorbed HNO$_3$ on the porous glass was followed using the infrared band at 1677 cm^{-1}. After NO was added to the cell, the loss of HNO$_3$ on the surface and the formation of NO$_2$ in the gas phase were followed using FTIR.

3. Results

Porous glass was used primarily as a means of supporting a thin water film, which could be interrogated using transmission infrared spectroscopy. Uptake and reactions of HNO$_3$ in this water film determine the chemistry, and hence surfaces in the atmosphere holding appropriate amounts of water are expected to behave similarly. However, since silica is a significant component of soil dust [*Finlayson-Pitts and Pitts*, 2000, and references therein], this surface is also directly relevant to the atmosphere.

Mochida and Finlayson-Pitts [*Mochida and Finlayson-Pitts*, 2000a] showed that HNO$_3$ preadsorbed onto the porous glass surface decayed when NO(g) was added to the cell; NO$_2$ and small amounts of HONO were generated. Figure 1 shows a typical set of HNO$_3$ decays at different initial NO concentrations. The stoichiometry $\Delta NO_2/\Delta NO$ averaged over 6 runs was 2.2 ± 0.3 (2σ) [*Mochida and Finlayson-Pitts*, 2000a]. This calculation does not account for the N$_2$O$_4$ in the gas phase and on the surface, where its concentration is enhanced [*Barney and Finlayson-Pitts*, 2000].

The decay of HNO$_3$ and the formation of NO$_2$ as the major gas phase product are consistent with the following reaction:

$$HNO_3 + NO \rightarrow HONO + NO_2 \qquad (3)$$
$$\Delta H_r(298 \text{ K}) = -1.7 \text{ kJ mol}^{-1}, \Delta G_r(298 \text{ K}) = -5.4 \text{ kJ mol}^{-1}$$
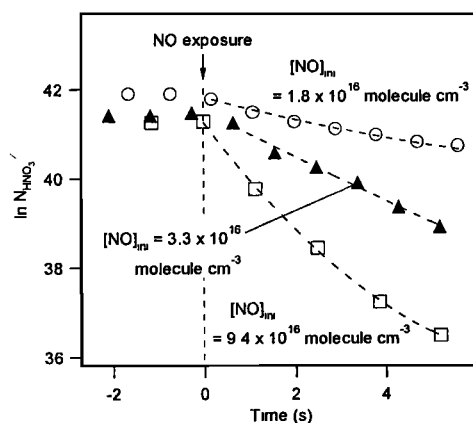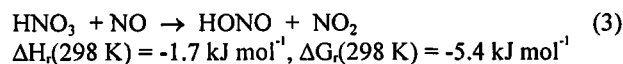

Figure 1. Decay of HNO$_3$ adsorbed on a porous glass surface before and after addition of gas phase NO at the initial concentrations indicated. The initial number of HNO$_3$ adsorbed on the porous glass was 8×10^{17} molecules (data from Mochida and Finlayson-Pitts, 2000a).
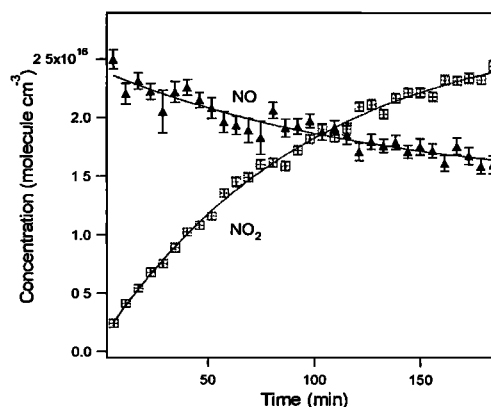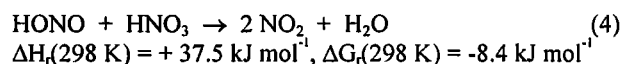

Figure 2. Typical decay of gas phase NO and formation of NO$_2$ at 50% RH in the long path cell whose walls had first been exposed to HNO$_1$. Data are shown for run #6, Table 1

followed by the heterogeneous reaction (-2) of HONO, or by:

$$HONO + HNO_3 \rightarrow 2 NO_2 + H_2O \qquad (4)$$
$$\Delta H_r(298 \text{ K}) = + 37.5 \text{ kJ mol}^{-1}, \Delta G_r(298 \text{ K}) = -8.4 \text{ kJ mol}^{-1}$$

The cited enthalpies and free energies are for all species as gases. Reaction (3) is near thermoneutral in the gas phase, and reaction (4) is endothermic. Thus, in the atmosphere, reaction (3) is likely to proceed to give HONO, while secondary reactions of HONO such as reaction (-2) or (4) maybe important under lab conditions. This is consistent with the studies of Fairbrother *et al.* (1997), who suggested that a heterogeneous form of reaction (3) is a potential source of HONO in the troposphere, and Besemer and Nieboer (1985) who reported that the photochemical oxidation of CO and organics in a mixture with NO$_x$ and air could be quantitatively modeled only if it was assumed that gas phase NO reacted with HNO$_3$ on the walls to form HONO.

In order to extend these initial studies to lower concentrations, FTIR studies of the decay of NO and formation of NO$_2$ were also carried out in the long path cell. The relative humidity in these experiments was ~50% to simulate the porous glass experiments where surface-adsorbed water was present. Figure 2 shows a typical concentration-time profile for the decay of NO and formation of NO$_2$. Small HONO (~10^{14} cm^{-3}) concentrations were observed, suggesting that it was removed by secondary reactions such as (-2) or (4). Table 1 summarizes the stoichiometry, $\Delta NO_2/\Delta NO$, which averaged 3.5 ± 0.5 (2σ). At small NO$_2$ concentrations and without a high-surface area substrate such as the porous glass which enhanced N$_2$O$_4$ concentrations [*Barney and Finlayson-Pitts*, 2000], corrections to N$_2$O$_4$ stoichiometry are not important.

Table 1. Summary of the Long Path Cell FTIR Measurements of the Decay of NO and Formation of NO$_2$ in the Reaction of NO with HNO$_3$ Adsorbed on the Cell Walls

Run #	[NO]$_0$	Δ[NO]	Δ[NO$_2$]	Δ[NO$_2$]/Δ[NO]
1	0.6	0.50	1.03	2.05
2	3.2	0.70	2.70	3.86
3	7.0	1.50	5.50	3.67
4	8.20	2.20	6.90	3.14
5	14.30	2.80	10.0	3.57
6	22.00	5.00	16.0	3.20
7	40.00	8.00	26.8	3.35
			Average (±2σ)	3.5 ± 0.5

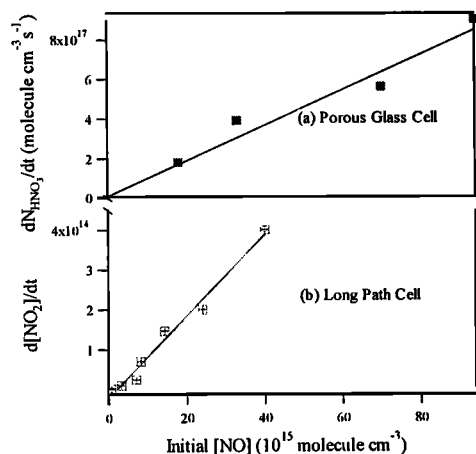All concentrations are expressed in (10^{15} molecule cm^{-3})

Figure 3. Rate as a function of initial NO concentration of (a) decay of surface HNO_3 on the porous glass, and (b) NO_2 formation in the long path cell at 1 atm pressure and 50% RH

The initial rate of decay of HNO_3 adsorbed on the porous glass and the rate of NO_2 formation in the long path cell show (Fig. 3) that the reaction is first-order in NO. This consistency in the kinetics and stoichiometry over approximately four orders of magnitude in the NO concentration suggests that it is reasonable to extrapolate further to atmospheric levels.

4. Discussion

For the purposes of comparing HONO formation from reactions (1), (2) and (3) at night in polluted urban atmospheres, we assume an air mass containing 10^4 particles cm^{-3} having a diameter of 1 μm. We also assume that NO and NO_2 concentrations are 100 ppb, typical of polluted urban areas at night, and a relative humidity of 50%. The mixing height is taken to be 100 m, and the ground is also considered available for these heterogeneous reactions. The surface area for the particles is 3.1×10^{-4} cm^2 per cm^3 air or 3.1 cm^2 total particle surface in a column of air of 100 m high and area 1 cm^2. The ground geometric surface area of 1 cm^2 is multiplied by two because of the increased area associated with the porosity of the soil and the buildings in urban areas. The total surface area (S) in this column is thus 5 cm^2. Clearly this assumption, and indeed the size and concentration of suspended particles, is somewhat arbitrary but provides a consistent set of conditions to compare the three mechanisms.

Reaction (3) of Surface-Adsorbed HNO_3 with NO:. The measured pseudo-first order rate constant for the decay of surface-adsorbed HNO_3 in the presence of 3.3×10^{16} molecule cm^{-3} of NO (Fig. 1) is 0.49 s^{-1}. Scaling this rate constant down to 2.5×10^{12} molecule cm^{-3} (100 ppb), gives a pseudo-first order rate constant of 3.7×10^{-5} s^{-1}. The rate constant for HONO generation would be half of this if it were not removed in subsequent reactions. If there are 1×10^{14} HNO_3 per cm^2, then the total rate of HNO_3 decay in the air column is 9.3×10^5 HNO_3 cm^{-3} s^{-1}, which if sustained, would generate about 1 ppb HONO in 8 hours.

Clearly this involves many assumptions, including that the surface coverage of HNO_3 on the particles and ground is similar to that on the porous glass and that HONO is not removed by secondary reactions in air as is the case in our laboratory system. However, even this crude estimate of potential HONO production is of the same order of magnitude as that measured for HONO in air [*Finlayson-Pitts and Pitts,*

2000, and references therein]. Thus, this surface reaction of NO with adsorbed HNO_3 cannot be discounted as a source of HONO in air. Furthermore, it would be consistent with the field observations that HONO concentrations often appear to correlate better with [NO][NO_2][H_2O] rather than [NO_2][H_2O] [*Sjodin and Ferm,* 1985; *Notholt et al.,* 1992; *Calvert et al.,* 1994; *Winer and Biermann,* 1994].

Reaction (2) of NO and NO_2 with Water on Surfaces: In a separate set of studies carried out in the porous glass cell, [*Mochida and Finlayson-Pitts,* 2000b] the formation of HONO was observed when water vapor was added to a mixture of NO and NO_2 (again at high NO and NO_2 concentrations). The initial rate of HONO formation without the porous glass present was measured to be 6.9×10^{14} molecule cm^{-3} s^{-1} at initial concentrations of NO, NO_2 and H_2O of 11, 1.6 and 6.6×10^{17} molecule cm^{-3}, respectively. Scaling this rate of HONO generation to the air column (S = 5 cm^2) with NO and NO_2 concentrations of 100 ppb, and a water concentration equivalent to 50% relative humidity, the rate of HONO generation is estimated to be 2 molecules cm^{-3} s^{-1}. Over 8 hours, this gives a HONO concentration of only $\sim 10^{-6}$ ppb, a value much smaller than the one obtained from the heterogeneous HNO_3 + NO reaction. Thus, it seems more likely that the dependence of HONO on NO concentrations in air originates from the heterogeneous HNO_3 reaction with NO, rather than NO + NO_2 with water at surfaces.

Reaction (1) of NO_2 with Water on Surfaces: Svensson and coworkers [*Svensson et al.,* 1987] found that the rate of reaction (1) in their laboratory system could be expressed by:

$$\frac{-d[NO_2]}{dt} = \frac{2d[HONO]}{dt} = \left[5.6 \times 10^{-9}\frac{S}{V} + 2.3 \times 10^{-9} \right][NO_2][H_2O] \quad (I)$$

S/V is the surface-to-volume ratio (m^{-1}), the concentrations are in ppm and the rates in ppm min^{-1}. Using the conditions assumed above, S/V in the air column is 0.05 m^{-1}. At 100 ppb NO_2 and 50% RH, the rate of HONO formation is 0.12 ppb hr^{-1}, giving 0.9 ppb of HONO over 8 hours, a value similar to that from the heterogeneous reaction of HNO_3 with NO.

Reaction of NO_2 with Soot: The importance of the NO_2 reaction with soot as a HONO source in polluted areas is uncertain. If no surface deactivation occurs, this reaction could generate as much as 15 ppb overnight [*Aumont et al.,* 1999]; however, given the likelihood of some surface deactivation, this appears to be an upper limit [*Aumont et al.,* 1999; *Kalberer et al.,* 1999; *Longfellow et al.,* 1999].

5. Conclusions

These studies suggest that the heterogeneous reaction of NO with HNO_3 adsorbed on surfaces could be a significant source of HONO in polluted urban areas. The NO reaction with surface HNO_3 adsorbed on ice may also play a role in generation of HONO and NO_x in the snowpack [*Honrath et al.,* 1999; *Jones et al.,* 2000]. In more remote locations, the reaction will be most important during the day when NO levels are higher due to NO_2 photolysis. Finally, such a reaction which converts HNO_3 to NO_x may help to reconcile the discrepancy between the measured and modeled ratios of HNO_3 to NO_x in the troposphere [*Chatfield,* 1994; *Hauglustaine et al.,* 1996].

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