Heterogeneous Reaction of Nitric Acid with Nitric Oxide on Glass Surfaces under Simulated Atmospheric Conditions

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Received: February 27, 2004; In Final Form: April 26, 2004

The heterogeneous reaction of nitric acid (HNO_3) with nitric oxide (NO) on borosilicate glass surfaces was studied in a flow system at relative humidity levels in the range 21−86%. Reactant concentrations were kept closer to ambient atmospheric levels as compared to all previous studies of this reaction. Within experimental error, no formation of the proposed reaction products nitrous acid (HONO) and nitrogen dioxide (NO_2) was observed. Upper limits of the reactive uptake coefficients of NO on borosilicate glass surfaces, covered with ~1 monolayer of HNO_3, were determined: $\gamma(NO \rightarrow HONO) < 4.0 \times 10^{-11}$ and $\gamma(NO \rightarrow NO_2) < 2.5 \times 10^{-9}$. These values are significantly lower than previously reported values, which were determined at higher reactant concentrations. Results obtained upon investigation of the secondary heterogeneous reaction of the proposed product HONO with HNO_3 under identical experimental conditions show that HONO should be observed in the study of the reaction $HNO_3 + NO$, if it is formed. Thus, the obtained upper limit $\gamma(NO \rightarrow HONO)$ is representative for the reaction $HNO_3 + NO \rightarrow HONO + NO_2$. Under the assumption that the glass surfaces, typically used in laboratory studies of this reaction, are representative for environmental surfaces, the latter reaction is unimportant for atmospheric HONO formation and for a “renoxification” of the atmosphere.

1. Introduction

Heterogeneous reactions of nitrogen oxides play an important role in atmospheric chemistry. For example, the heterogeneous hydrolysis of N_2O_5 is a significant sink of NO_x in both the stratosphere[1] and troposphere,[2] strongly affecting ozone concentration and acid rain formation, respectively. Another example is the heterogeneous reaction of NO_2 on humid surfaces

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \qquad (1)$$

which is proposed to be an important source of nitrous acid (HONO), in both laboratory systems and the atmosphere.[3−9] In several recent studies it was demonstrated that the photolysis of HONO can contribute significantly to OH radical formation during daytime.[10−13]

The sources of nitrous acid in the atmosphere are still not completely understood. In addition to direct emission,[8,14] heterogeneous pathways are most probably responsible for HONO formation in the atmosphere. Besides HONO formation by reaction 1, other heterogeneous pathways have been proposed. For example, it has been suggested that HONO is formed by the heterogeneous conversion of NO_2 on soot surfaces.[15,16] However, recent studies demonstrated that this noncatalytic reaction cannot explain current HONO levels in the atmosphere.[17,18] On the basis of correlation studies, it was proposed that the heterogeneous reaction of NO and NO_2 (or N_2O_3) on humid surfaces explains atmospheric HONO formation.[19] However, field studies[20,21] and a laboratory investigation in which the reaction was studied under humidity levels and NO_x concentrations prevailing in the atmosphere,[7] indicate that this reaction is unimportant.

From recent laboratory studies, the heterogeneous reaction of HNO_3 with NO

$$HNO_3(ads) + NO(g) \rightarrow HONO + NO_2 \qquad (2)$$

was proposed as a source of HONO in the atmosphere.[22,23] In addition, it was suggested that reaction 2 followed by reaction 3

$$HNO_3(ads) + HONO(ads) \rightarrow H_2O + 2NO_2 \qquad (3)$$

is of importance for a “renoxification” of the boundary layer.[24,25] Reaction 2 has been the subject of several other studies.[26−30] It was reported that the reaction rate is proportional to the HNO_3 and NO concentration and to the surface-to-volume ratio, demonstrating the heterogeneous nature of the reaction. However, it was also shown that the kinetics of reaction 2 is more complicated than the stoichiometry implies. For example, in the detailed study of Smith[26] the author concluded that the reaction is autocatalytic in NO_2. In addition, a positive water vapor dependence and a negative temperature dependence in the range 273−303 K was observed. A water vapor dependence of reaction 2 was also recently reported by Saliba et al.[24] who concluded that the reaction rate reached a maximum at intermediate humidity levels corresponding to a surface water coverage of approximately three monolayers.

In all studies reported up to now, reaction 2 was investigated at NO_y concentrations, which were orders of magnitude higher than those prevailing in the atmosphere. In addition, most studies on reaction 2 were carried out at low relative humidity (RH). Due to the complex reaction kinetics, an extrapolation of these results to atmospheric conditions is highly uncertain.

In the present study, reaction 2 was investigated in a flow system in the presence of atmospheric relative humidity levels and NO_y concentrations that were much lower compared to all

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10.1021/jp040184u CCC: $27.50

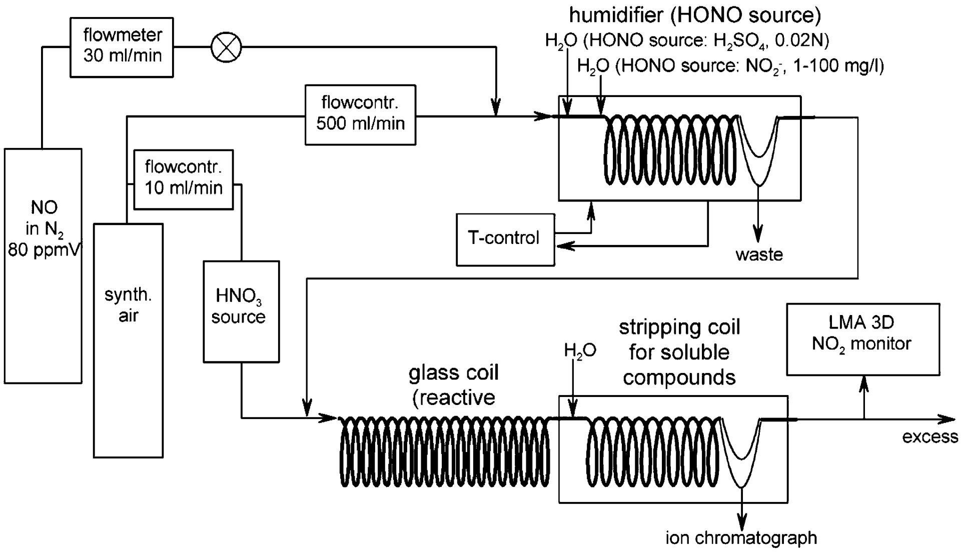

Figure 1. Experimental setup for investigation of reactions 2 and 3 and the adsorption of HNO_3 on glass surfaces.

studies reported so far. In addition, reaction 3 was studied using the same experimental setup to determine whether HONO, one of the products of reaction 2, can be observed under the experimental conditions or is rapidly converted to NO_2.

2. Experimental Section

Reaction 2 was investigated in a flow system, which is schematically shown in Figure 1. A calibrated mixture of NO in N_2 (Messer Griesheim, 80 ppm; flow meter: Tylan 0−30 mL/min) was diluted with synthetic air (flow controller: Brooks 0−500 mL/min) to achieve mixing ratios in the range 0.5−10 ppmV. The mixture was humidified (21−86% RH) with ultrapure water (Milli Pore) in a temperature controlled stripping coil, which also removed impurities of nitrous acid (HONO) from the NO mixture. The humidity was calculated under the assumption that the gas phase was saturated at the temperature of the stripping coil. Errors of the relative humidity were estimated from the accuracy of the temperature measurement to be <2%. Nitric acid (HNO_3) was generated by bubbling a small flow of synthetic air (flow controller: Brooks 0−10 mL/min) through a mixture containing 1% vol HNO_3 (65%) in H_2SO_4 (70%). The impurities NO_2 and HONO were found to be <0.1% after the HNO_3 source was allowed to run for a day. NO and HNO_3 were mixed in a PFA T-piece leading to a final HNO_3 mixing ratio of ∼600 ppbV at a total standard gas flow rate of 400−450 mL/min ($T = 298$ K, $p = 760$ Torr).

The PFA T-piece was directly attached to a glass coil (borosilicate glass, $l = 160$ cm, 0.2 cm i.d., $S/V = 19.6$ cm^{-1}), which was used as the reactive surface. It was cleaned prior to each experiment. The glass coil was connected to a second stripping coil in which soluble compounds, e.g., HONO and HNO_3, were removed by ultrapure water. The sampling efficiencies of the stripping coil for HONO and HNO_3, measured by an additional stripping coil, were found to be >97% and >99.9%, respectively, under the experimental conditions applied. For the investigation of reaction 3 also a different borosilicate glass coil ($l = 58$ cm, 0.2 cm i.d., $S/V = 20.0$ cm^{-1}) and a borosilicate glass flow tube ($l_{rxn} = 65$ cm, 1.7 cm i.d.) with a much lower surface-to-volume ratio of 0.72 cm^{-1}, including the transfer line to the second stripping coil, were employed. For the generation of HONO, a source similar to that reported by Taira and Kanda[31] was used. The HONO source of Taira and Kanda[31] was modified by mixing diluted solutions of sodium nitrite and H_2SO_4 in the temperature controlled stripping coil (see Figure 1). The HONO purity was higher compared to that from a bubbler system similar to that reported by Taira and Kanda,[31] which was also used earlier in our laboratory. In addition, with the modified setup, the HONO concentration could be varied much faster with a response time (10−90%) of about ∼2 min, as a result of the higher liquid-phase exchange rate of the HONO source. All liquid flows within the two stripping coils were adjusted by peristaltic pumps (Ismatec, Reglo 4).

The nitrite and nitrate concentrations in the effluent of the second stripping coil were measured by ion chromatography (Shimadzu, Model 6a) using UV detection at $\lambda = 209$ nm after preconcentration on a Dionex TAC LP1 column. The concentrations of HONO and HNO_3 were calculated using the measured nitrite and nitrate concentrations and the measured liquid and gas flow rates. The errors of the HONO and HNO_3 concentrations were calculated from the accuracy of the nitrite and nitrate measurements and the errors of the liquid and gas flow rate determination.

In contrast to HONO and HNO_3, the concentrations of NO and NO_2 were found to be almost unaffected by the stripping coils, due to the much lower solubilities and low reactivities of these compounds. Accordingly, the NO_2 concentration was measured downstream of the second stripping coil by a Luminol NO_x monitor (Unisearch, LMA-3D). The instrument was calibrated at NO_2 mixing ratios of 0−20 ppbV during blank experiments under the same conditions, i.e., [NO] and RH, as in the experiments with HNO_3 + NO. NO_2 was obtained from Messer Griesheim as a 2.09 ppmV premix-gas balanced with N_2. The error of the NO_2 concentration was calculated from the accuracy of the NO_2 calibration mixture, specified by Messer Griesheim, and the statistical errors of the calibration curve.

For studying reaction 2 the glass coil was first flushed with HNO_3 mixtures overnight. After determining the concentrations of HNO_3 and the upper limits for the impurities of HONO and NO_2 in the HNO_3 mixtures, different amounts of NO were added. Because the NO contained about 0.5% NO_2 small amounts of HONO were formed by reaction 1 in the flow system behind the humidifier and in the second stripping coil. Accordingly, the signals for HONO and NO_2 were also measured for

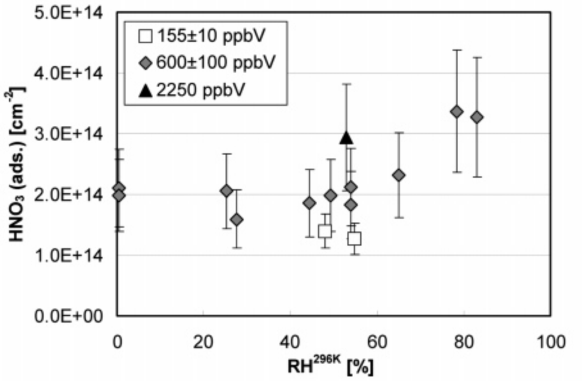

Figure 2. Adsorption of HNO_3 on the glass coil surface as a function of relative humidity ($T = 296 \pm 1$ K).

pure humidified NO mixtures at the same NO mixing ratios as in the experiments with HNO_3, for which the PFA T-piece with the HNO_3 source and the glass coil were removed from the flow system. The amount of HONO and NO_2 formed by reaction 2 was calculated after subtraction of the signals of the pure NO mixtures. The errors of the formed HONO and NO_2 were calculated from the errors of the HONO and NO_2 concentrations of both the reaction mixture and the pure NO mixture.

In separate experiments, reaction 3 was also studied using the setup shown in Figure 1 with HONO and HNO_3 mixing ratios in the range 30−770 and 150−2400 ppbV, respectively. In addition, the relative humidity was varied between 25 and 78%. The rate constant of reaction 3 was calculated from the NO_2 formed after subtraction of the blank signal, when the glass coil was removed from the system. The error of the rate constant was calculated from the accuracy of the concentrations of HONO, HNO_3 and NO_2 and the errors of t_{rxn} and S/V; see eq I. To demonstrate that reaction 3 is a heterogeneous process, the surface-to-volume ratio of the reactive surface was changed by a factor of ∼30 by using a flow tube with a larger inner diameter made of the same type of glass as used before.

In additional experiments, the amount of HNO_3 adsorbed on the glass coil was measured by ion chromatography at different humidities (0.5−83% RH) and different HNO_3 mixing ratios (145−2250 ppbV) by flushing the coil several times with ultrapure water.

3. Results and Discussion

3.1. HNO_3 Adsorption on the Glass Coil. Because reactions 2 and 3 are proposed to be heterogeneous processes, the amount of HNO_3 adsorbed on the surface is of potential importance for a mechanistic interpretation of the reactions. For this reason, the adsorption of HNO_3 was studied for the same glass coil, which was used for studying reactions 2 and 3 for different humidities and HNO_3 concentrations.

With ∼600 ppbV HNO_3 present at relative humidity levels of 0.5−78% a surface coverage of $\sim(2-3) \times 10^{14}$ cm^{-2} was determined, which corresponds to approximately one monolayer of HNO_3 on the surface.[25] Under these conditions the amount of HNO_3 adsorbed on the surface does not significantly depend on the relative humidity in the range 0.5−60% (cf. Figure 2). Only for higher relative humidities was an increase of the surface coverage observed, which is readily explained using the results reported by Saliba et al.[24] The authors demonstrated that below ∼50% RH HNO_3 remains undissociated on the surface and ionizes at higher relative humidity levels, leading to the observed higher adsorption.

TABLE 1: Summary of Experimental Conditions and Results for the Investigation of Reaction 3[a]

RH (%)	HNO_3 (ppbV)	HONO (ppbV)	ΔNO_2 (ppbV)	$10^{17}k(3)_{het}$ (cm^3 s^{-1} cm)
25.3	700	50	3.1	15.0 ± 3.3
25.3	690	170	10.2	15.1 ± 2.8
25.3	650	315	17.9	15.0 ± 2.7
33.9	1000	20	1.3	10.9 ± 3.3
33.9	1020	58	4.1	11.7 ± 2.4
33.9	1020	195	13.8	11.8 ± 2.1
33.9	1045	385	25.2	10.7 ± 1.8
49.3	735	87	2.5	6.7 ± 1.7
49.3	740	290	10.0	7.8 ± 1.6
49.3	750	570	15.3	6.1 ± 1.2
52.8*	2360	270	9.7	7.1 ± 1.2
52.8	2410	270	27.2	7.2 ± 1.0
52.8	2330	28	2.6	7.0 ± 1.4
53.9	630	595	13.5	6.0 ± 1.3
53.9	615	91	1.9	5.7 ± 1.7
53.9	620	300	6.6	5.9 ± 1.4
54.9	150	97	0.5	6.1 ± 3.7
54.9	160	315	1.6	5.3 ± 2.2
54.9	160	620	3.3	5.4 ± 2.0
57.2**	285	28	1.1	6.5 ± 2.1
57.2**	290	84	3.0	5.8 ± 1.1
57.2**	295	280	10.1	5.8 ± 0.9
57.2**	305	550	19.7	5.6 ± 0.8
78.4	715	120	1.5	2.9 ± 1.0
78.4	720	390	4.8	2.9 ± 0.7
78.4	730	770	7.6	2.3 ± 0.6

[a] Relative humidity (RH), initial HNO_3 and HONO mixing ratios, amount of NO_2 formed, and heterogeneous rate constant for reaction 3 in a borosilicate glass coil ($l = 160$ cm, S/V = 19.6 cm^{-1}, $t_{rxn} = 0.62$ s, $T = 296 \pm 1$ K). (*): length of the glass coil: 58 cm (S/V = 20.0 cm^{-1}, $t_{rxn} = 0.22$ s, $T = 296 \pm 1$ K); (**): flow tube ($l_{rxn} = 65$ cm, S/V = 0.72 cm^{-1}, $t_{rxn} = 61$ s, $T = 295 \pm 1$ K).

The adsorption was also studied for different HNO_3 mixing ratios at ∼50% RH. Upon increasing the HNO_3 mixing ratio from 145 to 2250 ppbV, the amount of adsorbed HNO_3 increased only by a factor of 2 (cf. Figure 2).

In summary, for the experimental conditions applied in the study of reactions 2 and 3 a surface coverage of HNO_3 of ∼1 monolayer was determined.

3.2. Investigation of Reaction 3. In several previous studies it was concluded that only small steady-state concentrations of HONO were observed for reaction 2 due to the much faster secondary reaction 3 leading to NO_2 as the final product.[22−25,30] To examine whether the small upper limit for HONO formation by reaction 2 (see section 3.3) was influenced by secondary chemistry, reaction 3 was also investigated. Because reaction 3 was found to be heterogeneous and thus dependent on the surface properties,[27] the same experimental setup as for the study of reaction 2 was used.

During the experiments significant amounts of NO_2 were formed (see Table 1). The rate of NO_2 formation increased linearly with the HONO and the HNO_3 concentration as well as with the surface-to-volume ratio (S/V), which is in good agreement with the study of Kaiser and Wu.[27] Thus, for the data evaluation, reaction 3 was treated as a second-order surface reaction. The rate constant $k(3)_{het}$ was calculated using eq I

$$k(3)_{het} = \frac{1}{[HNO_3]_0 - [HONO]_0} \ln \frac{[HNO_3]_t [HONO]_0}{[HNO_3]_0 [HONO]_t} \frac{1}{t_{rxn}} \frac{1}{S/V} \tag{I}$$

The measured concentrations $[HNO_3]_0$ and $[HONO]_0$, which were determined during the blank experiments when the glass coil was removed, were not used here, because the changes

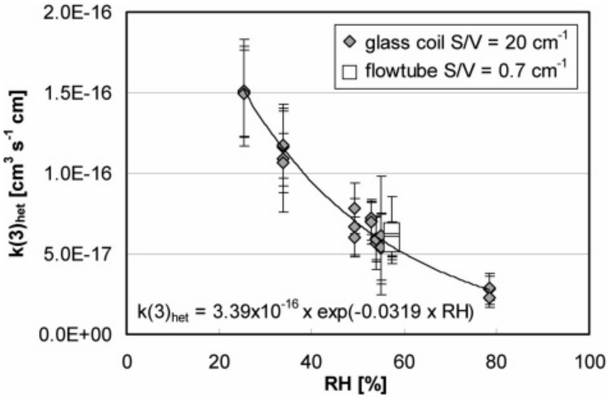

Figure 3. Humidity dependence of the heterogeneous rate constant $k(3)_{het}$ ($T = 296 \pm 1$ K).

caused by reaction 3 were smaller than the precision of the HNO_3 and HONO measurements. The values of the initial concentrations $[HNO_3]_0$ and $[HONO]_0$ were calculated from the measured concentrations $[HNO_3]_t$ and $[HONO]_t$, after reaction time t_{rxn} in the glass coil, and from the amount of NO_2 formed at t_{rxn}, taking into account the stoichiometry of reaction 3. In Table 1, all experimental results for reaction 3 are summarized. Within experimental error the rate constant of reaction 3 is independent of the concentrations of HONO and HNO_3 and of the surface-to-volume ratio at constant humidity. In contrast, for increasing relative humidity a significant decrease of the rate constant $k(3)_{het}$ was observed (cf. Figure 3). An exponential fit of the data points yields eq II for $k(3)$het

$$k(3)_{het}^{296\pm1K} = 3.39 \times 10^{-16} \exp(-3.19 \times 10^{-2}RH) \quad (cm^3\ s^{-1}\ cm) \quad (II)$$

Under the experimental conditions applied when studying reaction 2, i.e., the reaction surface, relative humidity, $[HNO_3]$, and reaction time, the rate constant of reaction 3 is determined to be in the range $k(3)_{het} = (2-15) \times 10^{-17}$ $cm^3\ s^{-1}$ cm (85−21% RH). For comparison, the second-order gas-phase rate constants reported earlier in the studies of Kaiser and Wu,[27] Streit et al.,[28] England and Cocoran,[32] and Wallington and Japar[33] were converted to heterogeneous rate constants using the corresponding surface-to-volume ratio. Values of $k(3)_{het}$ of $(2.5-8.6) \times 10^{-17}$,[27] 4.8×10^{-17},[28] 2.7×10^{-17},[32] and 5.0×10^{-18},[33] $cm^3\ s^{-1}$ cm were determined. Kaiser and Wu[27] reported that the rate of reaction 3 depended on the surface properties. For example, a 3.5 times higher rate constant was observed when a new untreated reactor was used.[27] With the exception of the study of Wallington and Japar,[33] all literature values are in excellent agreement within the range of rate constants obtained in the present study, which confirms that reaction 3 is indeed a heterogeneous process. Wallington and Japar[33] determined the rate constant from the observed decay of HONO. However, the authors reported a much faster decay of HNO_3, which could not be explained by the HNO_3 wall loss. Because possible HONO formation processes, for example, by reaction 1, were not taken into consideration, the value determined in this study appears to be too low.

It is concluded that only a minor fraction of the HONO formed by reaction 2 is converted into NO_2 by reaction 3 using identical experimental conditions as applied in the study of reaction 2; see below for details.

3.3. Investigation of Reaction 2. Reaction 2 was investigated in different experiments at relative humidities in the range 21−86%. In each set of experiments, NO at mixing ratios between 0.5 and 10 ppmV was added to HNO_3 mixtures of 350−750 ppbV at constant relative humidity. In addition, blank experiments with NO present but in the absence of HNO_3 were performed at the same humidity and NO mixing ratios. As an example, the HONO formation for an experiment at 30% relative humidity is shown in Figure 4. The HONO concentration increases linearly with the NO concentration for both pure NO and the HNO_3 + NO mixture.

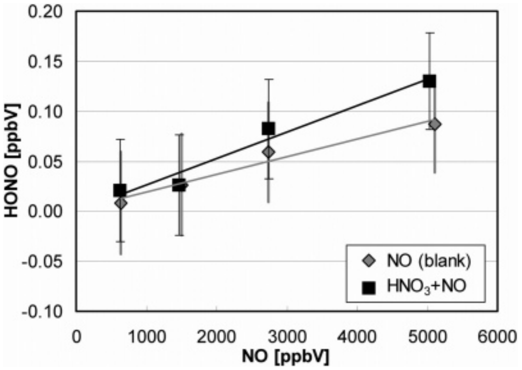

Figure 4. Typical plot of the HONO mixing ratio as a function of the NO mixing ratio for pure NO (blank) and for reacting HNO_3 + NO mixtures. ($[HNO_3]$ = 750 ppbV, RH = 30%, $T = 298 \pm 1$ K).

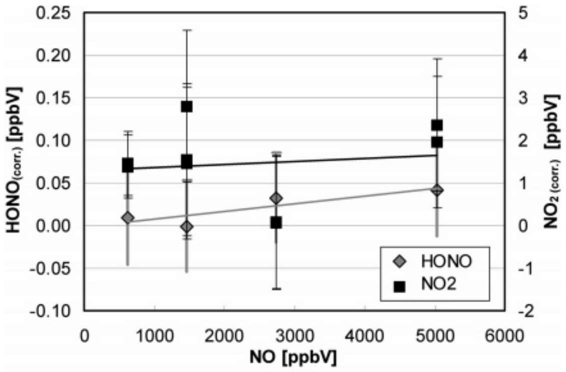

Figure 5. HONO and NO_2 mixing ratios in the reaction HNO_3 + NO corrected for the blank signals of pure NO as a function of the NO mixing ratio. ($[HNO_3]$ = 750 ppbV, RH = 30%, $T = 298 \pm 1$ K).

After subtraction of the blank signals, i.e., HONO and NO_2 in pure NO mixtures, from signals obtained with the reacting HNO_3 + NO mixtures, mixing ratios in the range ±0.15 ppbV for HONO and ±4 ppbV for NO_2 were determined. Figure 5 shows the results from an experiment conducted at 30% RH. The experimental uncertainty was significantly larger than the detection limits of the instruments of ∼0.05 and 0.2−0.6 ppbV for HONO and NO_2, respectively. This was caused by the subtraction of relatively large signals obtained for HONO and NO_2 from the pure NO mixtures. Within the experimental accuracy the corrected HONO and NO_2 levels were almost independent of the NO concentration present (cf. Figure 5).

From the data shown in Figure 5 reactive uptake coefficients γ_{rxn} can be calculated. The reactive uptake coefficient is the ratio between the reactive collisions of NO (ω_{rxn}) divided by the total number of wall collisions of NO ($\omega_{gaskinetic}$) per unit surface and time

$$\gamma_{rxn} = \frac{\omega_{rxn}}{\omega_{gaskinetic}} = \left(\frac{[NO]_{rxn}V_{coil}}{S_{coil}\Delta t_{rxn}}\right)\left(\frac{4}{[NO]_{ini}\bar{v}_{NO}}\right) \quad (III)$$

V_{coil} and S_{coil} denote the volume and surface of the glass coil, respectively, Δt_{rxn} is the reaction time of a gas molecule in the glass coil and $\bar{v}_{NO}$ is the mean velocity of NO molecules. Due

TABLE 2: Summary of Experimental Conditions and Results for the Investigation of Reaction 2[a]

RH (%)	*T* (K)	HNO_3 (ppbV)	range NO (ppbV)	$10^{11}\gamma$(NO→ HONO)	$10^{10}\gamma$(NO→ NO_2)
21.3	303	710	1250−9600	−5.1 ± 7.7	0.4 ± 5.0
30.3	298	760	620−5050	5.7 ± 4.5	4 ± 26
43.3	303	615	1450−9500	3.4 ± 4.5	−10.5 ± 8.6
49.5	299	550	640−5100	−2.9 ± 3.8	−11 ± 43
54.1	297	350	510−4350	1.9 ± 6.0	
61.3	297	550	630−5100	−1.5 ± 3.5	−34 ± 17
78.9	301	550	1400−9200	0.2 ± 8.3	2.1 ± 6.7
85.9	299	560	620−5000	−3.1 ± 12.8	42 ± 57

[a] Relative humidity (RH), temperature, HNO_3 mixing ratio, range of NO mixing ratios, and reactive uptake coefficients of NO for reaction 2 in a borosilicate glass coil (l = 160 cm, S/V = 19.6 cm^{-1}, t_{rxn} = 0.5−0.7 s). The error limits for the uptake coefficients represent the statistical precision (2σ) of the linear least-squares fits as shown in Figure 5.

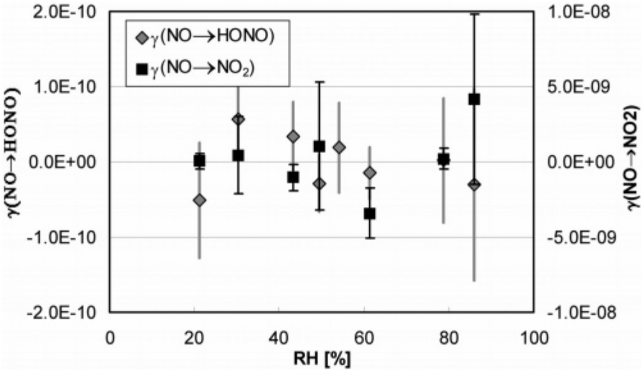

Figure 6. Reactive uptake coefficients γ(NO→HONO) and γ(NO→NO_2) as a function of relative humidity. The errors bars represent the statistical precision (2σ) of the linear least-squares fits as shown in Figure 5. (HNO_3 mixing ratio = 350−750 ppbV, T = 300 ± 3 K).

to the small uptake coefficients (see below), limitation by gas-phase diffusion to the walls was not considered here. Reactive uptake coefficients γ(NO→HONO) and γ(NO→NO_2) were determined corresponding to the stoichiometry of reaction 2, i.e., formation of one molecule of HONO and NO_2 per reacted NO molecule. To obtain a higher accuracy, γ(NO→HONO) and γ(NO→NO_2) on saturated glass surfaces at $[HNO_3] \approx 600$ ppbV were calculated from the slopes ($m_{HONO} = \Delta[HONO]/\Delta[NO]$ and $m_{NO_2} = \Delta[NO_2]/\Delta[NO]$) of the least-squares fits shown as an example in Figure 5

$$\gamma(\mathrm{NO}\rightarrow\mathrm{HONO}(\mathrm{NO_2})) = \frac{m_{\mathrm{HONO}}(m_{\mathrm{NO_2}})4V_{\mathrm{coil}}}{\Delta t_{\mathrm{reac}}\bar{v}_{\mathrm{NO}}S_{\mathrm{coil}}} \qquad \text{(IV)}$$

Equation IV is applicable under the assumption that reaction 2 is first order in NO, which has been observed in most previous studies of this reaction. The obtained reactive uptake coefficients for all experiments are listed in Table 2 and plotted in Figure 6 as a function of the relative humidity.

Mean values of the uptake coefficients of

$$\gamma(\mathrm{NO}\rightarrow\mathrm{HONO}) = (-0.2 \pm 3.7) \times 10^{-11} \quad \text{and} \quad \gamma(\mathrm{NO}\rightarrow\mathrm{NO_2}) = (0.2 \pm 2.3) \times 10^{-9}$$

(error limit 1σ) are determined, leading to upper limits of γ(NO→HONO) < 4 × 10^{-11} and γ(NO→NO_2) < 2.5 × 10^{-9} for the experimental conditions applied. Both coefficients are independent of the relative humidity. The much higher value for NO_2 formation is caused by the lower sensitivity of the NO_2 instrument and the higher blank values for NO_2.

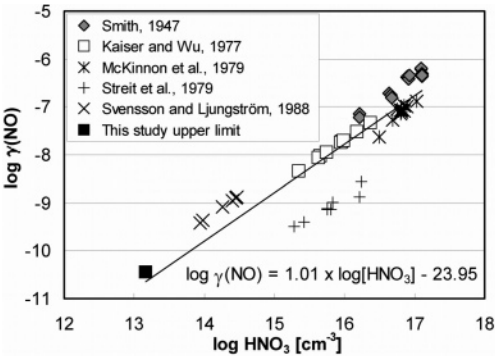

Figure 7. Comparison of literature data for uptake coefficients of NO on surfaces saturated with HNO_3 as function of the HNO_3 concentration with the upper limit obtained in the present study.

From the values of the rate constant of reaction 3 (see section 3.2) it is calculated that only 0.5−4% of the HONO (86−21% RH) possibly formed in reaction 2 is converted into NO_2 by reaction 3. Thus, the much lower value of γ(NO → HONO) < 4 × 10^{-11} is representative for reaction 2 and not significantly influenced by secondary chemistry.

Reaction 2 was investigated in several other studies.[22−30] The rate of the reaction was found to be proportional to $[HNO_3]$ and [NO][26−30] and to the surface-to-volume ratio.[26,27] In addition, the reaction was reported to be dependent on the relative humidity[24,26] and on the NO_2 concentration.[26] Due to the complex reaction kinetics any extrapolation of laboratory results to atmospheric conditions[22−25,30] is highly uncertain. In the present work, much lower NO_y concentrations as compared to all other studies were used at atmospheric relative humidity levels. An upper limit of the reactive uptake coefficient of γ(NO→HONO) < 4 × 10^{-11} is derived for reaction 2. For comparison with literature data, the available rate constants were converted to reactive uptake coefficients using the corresponding surface-to-volume ratios and under the assumption of a first-order NO dependence of reaction 2. With the exception of the experiments of Saliba et al.[24] and Rivera-Figueroa et al.[25] in which the gas phase concentrations of nitric acid were not explicitly specified, most studies were performed under equilibrium conditions;[26−30] i.e., high gas-phase concentrations of HNO_3 were in equilibrium with the adsorbed HNO_3. In the two former studies,[24,25] a different approach was used: First, the reaction surfaces were dosed with HNO_3 at very high gas-phase concentrations of about 10^{17} molecules cm^{-3}, and then some of the adsorbed HNO_3 was removed by evacuating the reactors. Because the gas-phase concentrations of HNO_3 were not specified, both studies could not be included in the comparison.

In Figure 7, the reactive uptake coefficients from previous studies are plotted in double logarithmic format as functions of the HNO_3 concentration. In addition, the upper limit determined in the present study is given. Clearly, the reactive uptake coefficient of NO is decreasing with decreasing HNO_3 concentration in accordance with the first-order HNO_3 dependence of reaction 2, as observed in most studies. All data are reasonably well described by a linear fit yielding a slope of 1.01 ± 0.07 (cf. Figure 7). In the study of Streit et al.,[28] significantly smaller uptake coefficients compared to all other values are calculated. This discrepancy was already discussed in the paper of Svensson and Ljungström[30] and remains to be resolved. However, because the reaction was reported to be dependent on the relative humidity,[24,26] autocatalytic in $[NO_2]$[26] and heterogeneous,[26,27] deviations from the fit shown in Figure 7 may be explained by the experimental conditions applied in the Streit et al.[28] study, e.g., different surface properties and relative humidities.

4. Atmospheric Implication

4.1. Reaction 2. Due to the dependence of the reactive uptake coefficient of NO for reaction 2 on the HNO_3 concentration as shown in Figure 7, it is concluded that the upper limit of γ(NO→HONO) < 4×10^{-11}, determined in this study at the lowest NO_y concentrations reported so far, is representative for reaction 2 under atmospheric conditions. The value should be strictly considered as an upper limit, because even in the present study, the NO_y concentrations used were still much higher than values typically observed in the urban atmosphere.[34] It follows that reaction 2 is insignificant for both heterogeneous HONO formation and possible "renoxification" processes in the atmosphere, in good agreement with the conclusion of Svensson an Ljungström.[30] However, this conclusion is only valid under the assumption that the glass surfaces, which were used in most studies are representative for environmental surfaces, as has been proposed, e.g., in the studies of Finlayson-Pitts et al.[9] and Rivera-Figueroa et al.[25]

In contrast hereto, reaction 2 was recently proposed to be of potential importance for atmospheric HONO formation[22,23] and for a "renoxification" of the atmosphere.[24,25] In the studies of Saliba et al.[24] and Rivera-Figueroa et al.,[25] reactive uptake coefficients of NO in the range 10^{-8} to 10^{-9} were obtained at higher reactant concentrations. However, even these values are 1 order of magnitude lower than the reactive uptake coefficients of NO_2 of 10^{-8} to 10^{-6} for reaction 1 as obtained in the laboratory for atmospheric humidity levels.[4,5,6,7] In the study of Rivera-Figueroa et al.,[25] it was speculated that uptake coefficients of 10^{-9} to 10^{-8} for reaction 2 could be of importance, due to a high BET surface of the ground. However, this argument would also hold for reaction 1, turning the latter into a much stronger HONO source. This argument is supported by field measurements in which significant HONO formation was observed in the atmosphere in the absence of NO.[20,21] In addition, in a study by Kleffmann et al.,[7] heterogeneous HONO formation by reaction 1 was not affected when high concentrations of NO were added to NO_2 mixtures in a quartz glass reactor under relative humidity and NO_2 concentration levels prevailing in the atmosphere. Because it can be expected that high amounts of HNO_3 formed by reaction 1 from several prior experiments were adsorbed on this reactor surface, as observed by other groups,[6,9] it is concluded that reaction 2 represents a much smaller atmospheric HONO source as compared to reaction 1.

In the study of Rivera-Figueroa et al.,[25] reaction 2 was postulated to be also of importance for a "renoxification" of the atmosphere. However, uptake coefficients of $<10^{-8}$ will result in insignificant NO_x formation in the atmosphere. For example from the measured HONO formation in the atmospheric boundary layer an upper limit of the NO_2 conversion by the heterogeneous reaction 1 on the ground of ~0.5−1%/h is calculated.[35,36] Even if the uptake coefficient of NO for reaction 2 is assumed to reach one-tenth of the value of the uptake coefficient of NO_2 for reaction 1, only less than 0.1%/h of NO will be converted by reaction 2 in the atmospheric boundary layer. In this estimation the possible enhancement of the surface area by a high BET surface of the ground and variations in the height of the atmospheric boundary layer are already taken into account. The estimated conversion rate for NO of <0.1%/h by reaction 2 is insignificant as compared to the lifetime of NO_x in the atmospheric boundary layer. It is thus concluded that reaction 2 is not of importance for a "renoxification" of the atmosphere.

4.2. Reaction 3. For the heterogeneous reaction 3 rate constants in the range $k(3)_{het} = (2-15) \times 10^{-17}$ cm^3 s^{-1} cm have been determined in the humidity range 85−21% RH for HONO and HNO_3 mixing ratios in the range 30−770 and 150−2400 ppbV, respectively. It follows that reaction 3 is an unimportant HONO sink in the atmosphere under the assumption that borosilicate glass is a representative proxy for environmental surfaces. Even for an upper limit of $k(3)_{het} = 15 \times 10^{-17}$ cm^3 s^{-1} cm, a boundary layer height of 100 m, and a maximum HNO_3 mixing ratio of 50 ppbV,[34] only 0.05% of the HONO present will be converted by reaction 3 during an 8 h night.

5. Conclusion

The heterogeneous reaction of HNO_3 with NO was studied on borosilicate glass surfaces in a flow system at various relative humidities (21−86% RH) and concentrations closer to atmospheric levels as compared to all previous studies reported in the literature. An upper limit of the reactive uptake coefficient of NO on glass surfaces, covered with ~1 monolayer of HNO_3, of γ(NO→HONO) < 4.0×10^{-11} is determined for reaction 2. This value is significantly lower compared to studies performed at higher nitrogen oxide concentrations. In the present study also the heterogeneous reaction of HONO with HNO_3, reaction 3, was studied under identical experimental conditions. The second-order rate constant is decreasing with increasing humidity and is found to be in good agreement with literature values. From the measured rate constants of reaction 3 it is concluded that the upper limit for HONO formation of $<4.0 \times 10^{-11}$ is representative for reaction 2 and that this value is not significantly influenced by secondary chemistry, i.e., reaction 3. In the case that the reaction kinetics observed for glass surfaces is similar to that on environmental surfaces, reaction 2 appears to be not of importance for atmospheric HONO formation and for a "renoxification" of the atmosphere.

Acknowledgment. The financial support by the European Commission in the framework V program, Contract No. EVK2-CT-1999-00025 (NITROCAT) is gratefully acknowledged.

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