



# Heterogeneous conversion of NO<sub>2</sub> and NO on HNO<sub>3</sub> treated soot surfaces

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# Heterogeneous conversion of NO<sub>2</sub> and NO on HNO<sub>3</sub> treated soot surfaces

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## Abstract

In the present study, the heterogeneous conversion of nitrogen oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) was studied at atmospheric humidity levels on flame soot surfaces, which were treated with gaseous nitric acid (HNO<sub>3</sub>). In addition, the heterogeneous reaction of HNO<sub>3</sub> on soot was investigated at atmospheric humidity.

For the treatment of soot by pure HNO<sub>3</sub> only reversible uptake with a surface coverage of  $\sim 1\text{--}2 \times 10^{14}$  HNO<sub>3</sub> cm<sup>-2</sup> was observed for HNO<sub>3</sub> mixing ratios in the range 250–800 ppbv. Only for higher HNO<sub>3</sub> mixing ratios of >800 ppbv the formation of NO and NO<sub>2</sub> was observed. The results were not affected by the addition of NO. In none of the experiments with HNO<sub>3</sub> the formation of nitrous acid (HONO) was observed. For HNO<sub>3</sub> mixing ratios <600 ppbv the upper limit yields for HONO, NO<sub>2</sub> and NO were found to be <0.2%, <0.5% and <1%, respectively. Compared to untreated soot, the product formation of the reaction of NO<sub>2</sub> with soot was not significantly affected when the soot surface was treated with gaseous HNO<sub>3</sub> prior to the experiment. Only for high surface coverage of HNO<sub>3</sub> the formation of HONO was suppressed in the initial phase of the reaction, probably caused by the blocking of active sites by adsorbed HNO<sub>3</sub>.

Under the assumption that the experimental findings for the used model flame soot can be extrapolated to atmospheric soot particles, the results show that the reactions of HNO<sub>3</sub> and HNO<sub>3</sub>+NO on soot surfaces are unimportant for a “renoxification” of the atmosphere and do not represent an atmospheric HONO source. In addition, the integrated HONO yield of ca.  $10^{14}$  cm<sup>-2</sup> in the reaction of NO<sub>2</sub> with soot is not significantly influenced by simulated atmospheric processing of the soot surface by HNO<sub>3</sub>, and is still too small to explain HONO formation in the atmosphere.

## 1. Introduction

Soot, which is formed during incomplete combustion processes, represents an ubiquitous material of the atmospheric aerosol and has a direct and indirect impact on the

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radiative balance of the Earth's atmosphere. In addition, caused by the fractal structure of soot and by the ability to act as a reducing agent, heterogeneous reactions on soot aerosols might be of importance for the transformation of atmospheric pollutants. In particular, heterogeneous reactions of nitrogen oxides on soot surfaces have attracted considerable attention during the last years since they may have an influence on the  $\text{NO}_x/\text{HNO}_3$  ratio and on the  $\text{HO}_x$  balance of the atmosphere (Bekki, 1997; Hauglustaine et al., 1996; Kotamarthi et al., 2001; Lary et al., 1997, 1999). Unfortunately, these model studies were based either on laboratory data determined under experimental conditions not prevailing in the atmosphere, i.e. very high reactant concentrations, or these studies did not take into consideration deactivation processes of the soot surface, which have been observed in laboratory studies, leading to unrealistic conclusions (Aumont et al., 1999).

The following three reactions of  $\text{NO}_y$  on soot were proposed to be of importance for the atmosphere (simplified reaction mechanisms):



Reaction (1) was first identified by Ammann et al. (1998) and Gerecke et al. (1998) and was proposed to be a significant source of HONO in the atmosphere. Since HONO is a very important OH radical precursor during the day (e.g. Alicke et al., 2002, 2003; Aumont et al., 2003; Ren et al., 2003; Vogel et al., 2003; Zhou et al., 2002, 2003) and since the formation mechanism of HONO in the atmosphere is not well established, formation by Reaction (1) would represent an attractive formation pathway. However, more recent laboratory studies (Arens et al., 2001; Kleffmann et al., 1999) demonstrated that the integrated HONO yield of the non-catalytic Reaction (1) of  $\sim 10^{14} \text{ cm}^{-2}$  is too small to explain HONO formation in the atmosphere. Furthermore, in all studies in which the ageing of soot in the atmosphere was simulated by processing of the soot

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surface with  $\text{H}_2\text{SO}_4$  (Kleffmann et al., 1999; Longfellow et al., 1999) or by  $\text{O}_3$  (Kalberer et al., 1999), even a decrease (Kalberer et al., 1999; Kleffmann et al., 1999) or at least no change (Longfellow et al., 1999) of the HONO yield was observed. However, the influence of adsorbed  $\text{HNO}_3$  on Reaction (1) is still unclear. The conclusion, that Reaction (1) cannot account for atmospheric HONO formation is in good agreement with a model study in which the deactivation of the soot surface was taken into consideration (Aumont et al., 1999). Only in the case that a fast reactivation of the soot surface was proposed (Aumont et al., 1999), yet not observed in the laboratory, or when the well documented deactivation was ignored (Kotamarthi et al., 2001; Lary et al., 1999) a significant influence on the atmosphere was calculated.

In model studies, Reaction (2) was considered to explain the unexpected high  $\text{NO}_x/\text{HNO}_3$  ratio observed in the atmosphere (Bekki, 1997; Hauglustaine et al., 1996; Lary et al., 1997). These calculations were based on the first study of Reaction (2) by Rogaski et al. (1997), who investigated the reaction at high concentrations of  $\text{HNO}_3$  and reported large uptake coefficients and the formation of NO and  $\text{NO}_2$ . However, in more recent studies, performed at reactant concentrations more closer to atmospheric conditions, only a reversible uptake of  $\text{HNO}_3$  (Aubin and Abbatt, 2003; Choi and Leu, 1998; Longfellow et al., 2000) or the absence of any product formation (Saathoff et al., 2001; Seisel et al., 2000) was observed. The difference was explained by a surface reaction which takes place only at high  $\text{HNO}_3$  concentrations for multilayer coverage of adsorbed  $\text{HNO}_3$  (Choi and Leu, 1998). This is in accordance with other studies of Reaction (2) in which the formation of  $\text{NO}_x$  was observed for very high  $\text{HNO}_3$  concentrations (Disselkamp et al., 2000; Prince et al., 2002; Rogaski et al., 1997). However, in a very recent study of Salgado Muñoz and Rossi (2002) an irreversible reaction of  $\text{HNO}_3$  with soot was observed also for low reactant concentrations. These authors observed the formation of HONO on flame soot produced in a fuel rich flame, whereas NO and  $\text{NO}_2$  were formed on soot generated in a lean flame. The formation of HONO in the reaction of  $\text{HNO}_3$  on soot surfaces was also proposed in a model study by Lary et al. (1999) and was observed in the reaction of soot with liquid  $\text{HNO}_3$  solutions (Louis-

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nard et al., 1995). However, in the more recent study of Aubin and Abbatt (2003) no formation of HONO was observed, although the authors could not determine the upper limit for the HONO yield, because of the missing calibration of their mass spectrometer. Although more recent studies point to the fact that the discrepancies of the modelled and measured  $\text{NO}_x/\text{HNO}_3$  ratio cannot be explained by Reaction (2) (e.g. Osterman et al., 1999) and most probably result from incorrect gas phase rate constants (e.g. Brown et al., 1999; Gao et al., 1999), it is still under discussion whether or not  $\text{HNO}_3$  irreversibly reacts with soot under atmospheric conditions. In addition, it is still an open question, whether the reaction might be a source of HONO in the atmosphere.

Based on laboratory studies on silica surfaces, the heterogeneous reaction of NO with adsorbed  $\text{HNO}_3$ , Reaction (3), was postulated to be a source of HONO and a “renoxification” process in the atmosphere (Mochida and Finlayson-Pitts, 2000; Rivera-Figueroa et al., 2003; Saliba et al., 2000, 2001). However, a very recent study indicates that the reaction is too slow to be of importance in the atmosphere (Kleffmann et al., 2004). On soot surfaces, Reaction (3) was only studied by Salgado Muñoz and Rossi (2002), who observed the formation of  $\text{NO}_2$ . However, it is still unclear to what extent Reaction (3) influences the  $\text{NO}_x/\text{HNO}_3$  ratio in the atmosphere.

Accordingly, in the present study the reactions of  $\text{HNO}_3$  and  $\text{HNO}_3 + \text{NO}$ , Reactions (2) and (3), were studied on soot surfaces at atmospheric humidity levels. In addition, the influence of treating the soot with gaseous  $\text{HNO}_3$  on the reaction of  $\text{NO}_2$  with soot, Reaction (1), was investigated.

## 2. Experimental

Reactions of nitrogen oxides with soot surfaces were studied in filter experiments similar to those explained in the study of Kleffmann et al. (1999). For the experiments only commercial flame soot (Degussa: Lamp Black 101, BET:  $20 \text{ m}^2 \text{ g}^{-1}$ ) was used. The chemical behaviour of Lamp Black 101 concerning Reaction (1), i.e. integrated HONO yield, was found to be similar compared to flame and diesel soot samples used in other

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studies (compare Kleffmann et al., 1999 with e.g. Arens et al., 2001 and Gerecke et al., 1998). It is worth mentioning that no experiments were performed with Degussa FW 2 soot, which has been often used in other studies, since this type of soot is already oxidised by the manufacturer. The soot samples (10–30 mg) were exposed to the reactants on Teflon membrane filters (Schleicher & Schuell TE 37, 1  $\mu\text{m}$ ) in a special filter holder made by pure PFA (see Fig. 1). Commercial filter holders were not used, caused by the strong adsorption of gaseous  $\text{HNO}_3$ , affecting the results of experiments with  $\text{HNO}_3$  and the soot. Wall effects in the transfer lines (PFA, 4 mm i.d.) and on the filter holder were corrected for by using a similar filter holder without the soot sample (see Fig. 1, “blank”).

$\text{NO}_2$  and NO mixtures (500–600 ppbv and 500 ppbv, respectively) were generated by dilution of calibrated mixtures of  $\text{NO}_2$  and NO (Messer Griesheim, 10 ppmv  $\text{NO}_2$  or 10 ppmv NO in  $\text{N}_2$ ) with synthetic air, which was humidified by bubbling through ultra pure water. The humidity ( $50 \pm 5\%$  r.h.) was calculated under the assumption that the gas phase was saturated at the measured water temperature. Nitric acid ( $\text{HNO}_3$ ) was generated by bubbling a small flow of synthetic air through a mixture containing 1%vol  $\text{HNO}_3$  (65%) in  $\text{H}_2\text{SO}_4$  (70%). The impurities  $\text{NO}_2$  and HONO were found to be  $<0.1\%$  after the  $\text{HNO}_3$  source was allowed to run for a day. The  $\text{HNO}_3$  was mixed with the other gases in a PFA T-piece directly in front of the filter holder to reduce the adsorption in the transfer lines, leading to final  $\text{HNO}_3$  mixing ratios of 200–1400 ppbv. All gas flows were adjusted by calibrated flow controllers (Brooks). The total standard gas flow rate was in the range  $350\text{--}400\text{ ml min}^{-1}$  (298.15 K, 1 atm).

The filter holders were connected with a short PFA line (4 mm i.d., 10 cm) to a stripping coil in which soluble compounds, i.e. HONO and  $\text{HNO}_3$ , were removed by ultra-pure water (see Fig. 1). The sampling efficiencies of the stripping coil for HONO and  $\text{HNO}_3$ , measured by an additional stripping coil, were found to be  $>98\%$  and  $>99.9\%$ , respectively, under the experimental conditions applied. All liquid flows within the stripping coil were adjusted by a peristaltic pump (Ismatec, Reglo 4). The nitrite and nitrate concentrations in the effluent of the stripping coil were measured by ion chromatog-

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raphy (Shimadzu, Model 6a) using UV detection at  $\lambda=209$  nm after pre-concentration on a Dionex TAC LP1 column. The mixing ratios of HONO and  $\text{HNO}_3$  were calculated from the measured nitrite and nitrate concentrations and the measured liquid and gas flow rates. The errors of the HONO and  $\text{HNO}_3$  mixing ratios of  $\pm(10\%+0.2$  ppbv) and  $\pm(10\%+1$  ppbv), respectively were determined 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  $\text{HNO}_3$ , the mixing ratios of NO and  $\text{NO}_2$  were found to be almost unaffected by the stripping coil, due to the much lower solubilities and low reactivities of these compounds. Accordingly, the NO and  $\text{NO}_2$  mixing ratios were measured downstream of the stripping coil by a Luminol  $\text{NO}_x$  monitor (Unisearch, LMA-4). The errors of the NO and  $\text{NO}_2$  mixing ratios of  $\pm(7\%+1$  ppbv) and  $\pm(10\%+0.5$  ppbv), respectively were calculated from the accuracy of the calibration mixtures, specified by Messer Griesheim, and the statistical errors of the calibration curves.

For studying the reactions of  $\text{HNO}_3$  and  $\text{HNO}_3$ +NO with soot, the gas mixtures were first flushed through the blank filter holder. After determining the uptake of  $\text{HNO}_3$  by reversible adsorption on the filter holder, the final reactant mixing ratio and the impurities of HONO and  $\text{NO}_x$ , the mixture was directed to the filter holder with the soot sample. After the soot sample was saturated with  $\text{HNO}_3$ , the  $\text{HNO}_3$  source was disconnected and the desorption of  $\text{HNO}_3$  was monitored.

For the study of the reaction of  $\text{NO}_2$  with  $\text{HNO}_3$  treated soot, the samples were first exposed over night to pure  $\text{HNO}_3$  at mixing ratios in the range 420–800 ppbv to completely saturate the surfaces. After isolating the soot from the gas flow and shutting down the  $\text{HNO}_3$  source,  $\text{NO}_2$  mixtures were flushed through the blank filter holder, to determine the initial  $\text{NO}_2$  mixing ratio and the impurities of HONO and NO. Finally, the  $\text{NO}_2$  mixture was directed to the soot sample and the product formation and the desorption of  $\text{HNO}_3$  was measured.

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### 3. Results and discussion

#### 3.1. Reaction of $\text{HNO}_3$ with soot surfaces

In the reaction of  $\text{HNO}_3$  with soot, Reaction (2), a strong initial uptake was monitored, which continuously decreased to non measurable values after several hours (see Fig. 2). No formation of HONO,  $\text{NO}_2$  and NO was observed for  $\text{HNO}_3$  mixing ratios <600 ppbv, even for reaction times of up to 2 days (cf. Fig. 2). The upper limits for the yields of HONO,  $\text{NO}_2$  and NO were calculated to be <0.2%, <0.5% and <1%, respectively. Only, for  $\text{HNO}_3$  mixing ratios >800 ppbv NO and  $\text{NO}_2$  were formed as products. However, even for these conditions no formation of HONO was detected (cf. Fig. 2).

In contrast to the filter experiments with  $\text{NO}_2$  and soot, described by Kleffmann et al. (1999), no uptake coefficients were determined for  $\text{HNO}_3$  on soot surfaces in the present paper, since the surface area is not defined for a “sticky” molecule such as  $\text{HNO}_3$ .  $\text{HNO}_3$  is initially only taken up by the upper surface of the soot and is diffusing into the pores of the soot later. Instead of the kinetic evaluation, only the integrated adsorbed amount of  $\text{HNO}_3$  was determined in different experiments. For  $\text{HNO}_3$  mixing ratios in the range 250–800 ppbv a surface coverage of  $0.8\text{--}2.4 \times 10^{14} \text{ HNO}_3 \text{ cm}^{-2}$  was derived (cf. Fig. 3) by using the BET surface of  $20 \text{ m}^2 \text{ g}^{-1}$ , given by the manufacturer. After the  $\text{HNO}_3$  source was stopped,  $\text{HNO}_3$  desorption was observed (cf. Fig. 4) leading to a  $\text{HNO}_3$  recover of  $\sim(80 \pm 10)\%$  within 24 h.

Based on the results of Choi and Leu (1998), who reported the formation of products only for multilayer adsorption, it is concluded that a monolayer coverage of  $\text{HNO}_3$  on Lamp Black 101 of  $\sim 2 \times 10^{14} \text{ HNO}_3 \text{ cm}^{-2}$  is reached for mixing ratios of  $\sim 800$  ppbv. This value is slightly lower than the value of  $3.8 \times 10^{14} \text{ cm}^{-2}$  determined for n-hexane flame soot by Choi and Leu (1998), but is in excellent agreement with the values of  $2 \times 10^{14} \text{ HNO}_3 \text{ cm}^{-2}$  reported by Aubin and Abbatt (2003) also for n-hexane flame soot. In addition, this value is also in excellent agreement with the maximum number of active

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sites of  $2.2 \times 10^{14} \text{ cm}^{-2}$  determined by Kirchner et al. (2000) for spark generator soot.

The observed product formation of Reaction (2), i.e. formation of NO and NO<sub>2</sub> only for high HNO<sub>3</sub> concentrations, is in excellent agreement with nearly all studies of this reaction. In these studies no product formation was observed for low reactant concentrations (Aubin and Abbatt, 2003; Choi and Leu, 1998; Longfellow et al., 2000; Saathoff et al., 2001; Seisel et al., 2000), whereas the formation of NO<sub>x</sub> was observed for high reactant concentrations (Choi and Leu, 1998; Disselkamp et al., 2000; Prince et al., 2002; Rogaski et al., 1996). In addition, the absence of any HONO formation for Reaction (2) is in good agreement with the study of Aubin and Abbatt (2003), although the authors could not determine the upper limit of the product yield. The missing HONO formation, even for high HNO<sub>3</sub> concentrations when the HONO precursor NO<sub>2</sub> is formed (cf. Fig. 2), can be explained by the blocking of active sites for Reaction (1) by adsorbed HNO<sub>3</sub> (see Sect. 3.3).

In contrast to other studies, the formation of products as NO, NO<sub>2</sub> and HONO was very recently observed for Reaction (2) by Salgado Muñoz and Rossi (2002) also for low HNO<sub>3</sub> concentrations. The authors observed the formation of HONO on flame soot produced in a fuel rich flame, whereas NO and NO<sub>2</sub> were formed on soot generated in a lean flame. The reason for this discrepancy to other studies is unclear. It could be speculated that different properties of the soot might be responsible for the differences. However, the authors reported a reaction for both types of soot investigated, which were produced under very different conditions. It should be pointed out that the use of very different types of soot, i.e. graphite (Choi and Leu, 1998), spark generator soot (Saathoff et al., 2001), Degussa FW2 (Choi and Leu, 1998), Degussa Lamp Black 101 (this study) and flame soot produced from the combustion of methane (Longfellow et al., 2000), propane (Longfellow et al., 2000), n-hexane (Aubin and Abbatt, 2003; Choi and Leu, 1998) and kerosene (Choi and Leu, 1998; Longfellow et al., 2000; Seisel et al., 2000), did not lead to the formation of products at low HNO<sub>3</sub> concentrations. Furthermore, the reactivity of the soot produced in a fuel rich flame by Salgado Muñoz and Rossi (2002) showed a very similar behaviour for Reaction (1) compared to Lamp

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Black 101 which was used in the present study (compare Stadler and Rossi, 2000 with Kleffmann et al., 1999). In agreement with the results of most studies, it is concluded that  $\text{HNO}_3$  is not reacting with soot under  $\text{HNO}_3$  concentrations prevailing in the atmosphere and hence is not a “renoxification” pathway or a source of HONO in the atmosphere.

### 3.2. Reaction of $\text{HNO}_3$ and NO with soot surfaces

When soot was exposed to a humid mixture of  $\text{HNO}_3$  and NO at mixing ratios of 280 and 500 ppbv, respectively, a similar behaviour was observed compared to pure  $\text{HNO}_3$  mixtures (see Sect. 3.1 and Figs. 2 and 4). Again, a  $\text{HNO}_3$  adsorption of  $\sim 10^{14} \text{ cm}^{-2}$ , a desorption of  $\text{HNO}_3$  after stopping the  $\text{HNO}_3$  source and no formation of  $\text{NO}_2$  and HONO was observed. In addition, no NO uptake on the soot was monitored. The upper limits for the HONO and  $\text{NO}_2$  yields, with respect to the uptake of  $\text{HNO}_3$ , were  $<0.1\%$  and  $<0.5\%$ , respectively. Under the assumption that the whole BET surface of the soot is exposed to NO, which was shown to be the case for the uptake of  $\text{NO}_2$  on the same type of soot and under similar experimental conditions (Kleffmann et al., 1999), upper limits for the reactive uptake coefficients of NO for HONO and  $\text{NO}_2$  formation of  $\gamma_{\text{NO} \rightarrow \text{HONO}} < 1 \times 10^{-10}$  and  $\gamma_{\text{NO} \rightarrow \text{NO}_2} < 5 \times 10^{-10}$  were calculated for  $\text{HNO}_3$  saturated soot surfaces.

The reaction of  $\text{HNO}_3 + \text{NO}$  on soot surfaces, Reaction (3), was investigated previously by Salgado Muñoz and Rossi (2002), who reported the formation of  $\text{NO}_2$ . The reason for the discrepancy between both studies is unclear. It could be speculated, similar to the discussion of the  $\text{HNO}_3 + \text{soot}$  reaction (see Sect. 3.1), that different surface properties might be responsible for the observed difference. Furthermore, in both studies the humidity was quite different. Whereas the humidity was extremely low in the Knudsen flow reactor of Salgado Muñoz and Rossi (2002), a relative humidity of  $\sim 50\%$  was used in the present study.

From the results of the present investigation it is concluded that the reaction of  $\text{HNO}_3$

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and NO on soot surfaces is unimportant for the atmosphere, in good agreement with a recent study on silica surfaces (Kleffmann et al., 2004).

### 3.3. Reaction of NO<sub>2</sub> with HNO<sub>3</sub> treated soot surfaces

For the simulated ageing of the soot surface by treatment with HNO<sub>3</sub>, mixing ratios of up to 800 ppbv were used, in order to exclude the formation of NO<sub>2</sub> (see Sect. 3.1), which would result immediately in a deactivation of active sites on the soot surface for the non-catalytic reaction of NO<sub>2</sub> and soot (Kleffmann et al., 1999). After the samples were saturated with HNO<sub>3</sub> over night, the soot was exposed to humid NO<sub>2</sub> mixtures at mixing ratios of 500–600 ppbv. A strong uptake of NO<sub>2</sub> and the formation of HONO and NO with yields of ~60% and 10–25%, respectively, was observed. For the initial phase of the reaction, the yield of HONO was affected by the amount of HNO<sub>3</sub> adsorbed. This means that the initial HONO yield decreased with increasing amount of adsorbed HNO<sub>3</sub>, however, get well back to the values for untreated soot somewhat later (see Fig. 5). The time period for the increase of the HONO yield up to the values for untreated soot was rising with increasing amount of adsorbed HNO<sub>3</sub>. This behaviour can be explained by the adsorption of HNO<sub>3</sub> and the blocking of active sites for Reaction (1). For HNO<sub>3</sub> concentrations of 800 ppbv a HNO<sub>3</sub> monolayer coverage of the soot surface was estimated, leading to very small initial yields of HONO (see Fig. 5). However, since HNO<sub>3</sub> desorbes from the soot when the HNO<sub>3</sub> source is stopped, the active sites become accessible for NO<sub>2</sub> later, leading to the observed rising HONO yields (see Fig. 5). However, since the decrease in the HONO yield was only pronounced for atmospheric non-relevant high HNO<sub>3</sub> concentrations, it is concluded that the ageing of the soot surface has no significant effect on the HONO formation by Reaction (1). For Reaction (1) an integrated HONO yield of  $(0.8 \pm 0.2) \times 10^{14} \text{ cm}^{-2}$  was observed for untreated soot, which is in excellent agreement with the study of Kleffmann et al. (1999). In the study of Kleffmann et al. (1999) it was concluded that this value is too small to explain HONO formation in the atmosphere.

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## 4. Conclusions

For the reaction of flame soot surfaces with  $\text{HNO}_3$  (Reaction 2) at atmospheric humidity levels only reversible adsorption was observed for  $\text{HNO}_3$  mixing ratios  $<600$  ppbv, in excellent agreement with almost all studies of this reaction at low reactant concentrations. The upper limits for the yields of HONO,  $\text{NO}_2$  and NO were calculated to be  $<0.2\%$ ,  $<0.5\%$  and  $<1\%$ , respectively. Only, for  $\text{HNO}_3$  mixing ratios  $>800$  ppbv NO and  $\text{NO}_2$  were formed as products. A monolayer coverage of  $\text{HNO}_3$  on soot of  $\sim 2 \times 10^{14} \text{ cm}^{-2}$  was estimated, in good agreement with previous studies. The behaviour of the  $\text{HNO}_3$ +soot system remained unaffected when 500 ppbv of NO were added. Upper limits for the reactive uptake coefficients of NO for HONO and  $\text{NO}_2$  formation of  $\gamma_{\text{NO} \rightarrow \text{HONO}} < 1 \times 10^{-10}$  and  $\gamma_{\text{NO} \rightarrow \text{NO}_2} < 5 \times 10^{-10}$  were calculated for  $\text{HNO}_3$  saturated soot surfaces. From the results of the present study it is concluded that heterogeneous reactions of  $\text{HNO}_3$  on soot surfaces are unimportant for the “renoxification” and for the formation of HONO in the atmosphere.

Treating the soot surfaces with gaseous  $\text{HNO}_3$  had no significant impact on the heterogeneous reaction of  $\text{NO}_2$  for atmospheric humidity levels. Only for high surface coverage of the soot with  $\text{HNO}_3$ , the HONO yield was reduced. The results show, that ageing of the soot surfaces by  $\text{HNO}_3$  had no significant influence on the integrated HONO yield of  $\sim 10^{14} \text{ cm}^{-2}$ , which is too small to explain atmospheric HONO concentrations.

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## References

Alicke, B., Platt, U., and Stutz, J.: Impact of Nitrous Acid Photolysis on the Total Hydroxy Radical Budget During the Limitation of Oxidant Production/Pianura Padana Produzione di

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- Ozono Study in Milan, J. Geophys. Res., 107, 8196, doi:10.1029/2000JD000075, 2002.
- Alicke, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Pätz, H. W., Schäfer, J., Stutz, J., Volz-Thomas, A., and Platt, U.: OH Formation by HONO Photolysis During the BERLIOZ Experiment, J. Geophys. Res., 108, 8247, doi:10.1029/2001JD000579, 2003.
- 5 Ammann, M., Kalberer, M., Jost, D. T., Tobler, L., Rössler, E., Piguet, D., Gägger, H. W., and Baltensperger, U.: Heterogeneous Production of Nitrous Acid on Soot in Polluted Air Masses, Nature, 395, 157–160, 1998.
- Arens, F., Gutzwiller, L., Baltensperger, U., Gägger, H. W., and Ammann, M.: Heterogeneous Reaction of NO<sub>2</sub> on Diesel Soot Particles, Environ. Sci. Technol., 35, 2191–2199, 2001.
- 10 Aubin, D. G., and Abbatt, J. P.: Adsorption of Gas-Phase Nitric Acid to *n*-Hexane Soot: Thermodynamics and Mechanism, J. Phys. Chem. A, 107, 11030–11037, doi: 10.1021/jp036105g, 2003.
- Aumont, B., Madronich, S., Ammann, M., Kalberer, M., Baltensperger, U., Hauglustaine, D., and Brocheton, F.: On the NO<sub>2</sub> + Soot Reaction in the Atmosphere, J. Geophys. Res., 104, 1729–1736, 1999.
- 15 Aumont, B., Chervier, F., and Laval, S.: Contribution of HONO Sources to the NO<sub>x</sub>/HO<sub>x</sub>/O<sub>3</sub> Chemistry in the Polluted Boundary Layer, Atmos. Environ., 37, 487–498, 2003.
- Bekki, S.: On the Possible Role of Aircraft-Generated Soot in the Middle Latitude Ozone Depletion, J. Geophys. Res., 102, 10751–10758, 1997.
- 20 Brown, S. S., Talukdar, R. K., and Ravishankara, A. R.: Reconsideration of the Rate Constant for the Reaction of Hydroxyl Radicals with Nitric Acid, J. Phys. Chem. A, 103, 3031–3037, 1999.
- Choi, W. and Leu, M.-T.: Nitric Acid Uptake and Decomposition on Black Carbon (Soot) Surfaces: Its Implications for the Upper Troposphere and Lower Stratosphere, J. Phys. Chem. A, 102, 7618–7630, 1998.
- 25 Disselkamp, R. S., Carpenter, M. A., and Cowin, J. P.: A Chamber Investigation of the Nitric Acid-Soot Aerosol Chemistry at 298 K, J. Atmos. Chem., 37, 113–123, 2000.
- Gao, R. S., Fahey, D. W., Del Negro, L. A., Donnelly, S. G., Keim, E. R., Neuman, J. A., Teverovskaia, E., Wennberg, P. O., Hanisco, T. F., Lanzendorf, E. J., Poffitt, M. H., Margitan, J. J., Wilson, J. C., Elkins, J. W., Stimpfle, R. M., Cohen, R. C., McElroy, C. T., Bui, T. P., Salawitch, R. J., Brown, S. S., Ravishankara, A. R., Portmann, R. W., Ko, M. K. W., Weisenstein, D. K., and Newman, P. A.: A Comparison of Observations and Model Simulations of NO<sub>x</sub>/NO<sub>y</sub> in the Lower Stratosphere, Geophys. Res. Lett., 26, 1153–1156, 1999.
- 30

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Gerecke, A., Thielmann, A., Gutzwiller, L., and Rossi, M. J.: The Chemical Kinetics of HONO Formation Resulting from Heterogeneous Interaction of NO<sub>2</sub> with Flame Soot, *Geophys. Res. Lett.*, 25, 2453–2456, 1998.

Hauglustaine, D. A., Ridley, B. A., Solomon, S., Hess, P. G., and Madronich, S.: HNO<sub>3</sub>/NO<sub>x</sub> Ratio in the Remote Troposphere during MLOPEX 2: Evidence for Nitric Acid Reduction on Carbonaceous Aerosols? *Geophys. Res. Lett.*, 23, 2609–2612, 1996.

Kalberer, M., Ammann, M., Arens, F., Gäggeler, H. W., and Baltensperger, U.: Heterogeneous Formation of Nitrous Acid (HONO) on Soot Aerosol Particles, *J. Geophys. Res.*, 104, 13 825–13 832, 1999.

10 Kirchner, U., Scheer, V., and Vogt, R.: FTIR Spectroscopic Investigation of the Mechanism and Kinetics of the Heterogeneous Reactions of NO<sub>2</sub> and HNO<sub>3</sub> with Soot, *J. Phys. Chem. A*, 104, 8908–8915, 2000.

Kleffmann, J., Becker, K. H., Lackhoff, M., and Wiesen, P.: Heterogeneous Conversion of NO<sub>2</sub> on Carbonaceous Surfaces, *Phys. Chem. Chem. Phys.*, 1, 5443–5450, 1999.

15 Kleffmann, J., Benter, T., and Wiesen, P.: The Heterogeneous Reaction of Nitric Acid with Nitric Oxide on Glass Surfaces under Simulated Atmospheric Conditions, *J. Phys. Chem. A*, 27, 5793–5799, 2004.

Kotamarthi, V. R., Gaffney, J. S., Marley, N. A., Doskey, P. V.: Heterogeneous NO<sub>x</sub> Chemistry in the Polluted PBL, *Atmos. Environ.*, 35, 4489–4498, 2001.

20 Lary, D. J., Lee, A. M., Toumi, R., Newchurch, M. J., Pirre, M., and Renard, J. B.: Carbon Aerosols and Atmospheric Photochemistry, *J. Geophys. Res.*, 102, 3671–3682, 1997.

Lary, D. J., Shallcross, D. E., and Toumi, R.: Carbonaceous Aerosols and their Potential Role in the Atmospheric Chemistry, *J. Geophys. Res.*, 104, 15 929–15 940, 1999.

Longfellow, C. A., Ravishankara, A. R., and Hanson, D. R.: Reactive Uptake on Hydrocarbon Soot: Focus on NO<sub>2</sub>, *J. Geophys. Res.*, 104, 13 833–13 840, 1999.

25 Longfellow, C. A., Ravishankara, A. R., and Hanson, D. R.: Reactive and Nonreactive Uptake on Hydrocarbon Soot: HNO<sub>3</sub>, O<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub>, *J. Geophys. Res.*, 105, 24 345–24 350, 2000.

Louisnard, M., Baudoin, C., Billet, G., Garnier, F., Hills, D., Mentel, T., Mirabel, P., Petit, J. C., Schultz, J. L., Taleb, D., Thlibi, J., Wahner, A., and Woods, P.: Physics and Chemistry in the Aircraft Wake, in: *AERONOX - The Impact of NO<sub>x</sub> Emissions from Aircraft Upon the Atmosphere at Flight Altitudes 8 - 15 km*, ed.: U. Schumann, Report EUR 16209 EN, ISBN-92-826-8281-1, 195–309, 1995.

30 Mochida, M., and Finlayson-Pitts, B. J.: FTIR Studies on the Reaction of Gaseous NO with

---

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- HNO<sub>3</sub> on Porous Glass: Implications for Conversion of HNO<sub>3</sub> to Photochemically Active NO<sub>x</sub> in the Atmosphere, *J. Phys. Chem. A*, 104, 9705–9711, 2000.
- Osterman, G. B., Sen, B., Toon, G. C., Salawitch, R. J., Margitan, J. J., Blavier, J.-F., Fahey, D. W., and Gao, R.S.: Partitioning of NO<sub>y</sub> Species in the Summer Arctic Stratosphere, *Geophys. Res. Lett.*, 26, 1157–1160, 1999.
- Prince, A. P., Wade, J. L., Grassian, V. H., Kleiber, P. D., and Young, M. A.: Heterogeneous Reactions of Soot Aerosols with Nitrogen Dioxide and Nitric Acid: Atmospheric Chamber and Knudsen Cell Studies, *Atmos. Environ.*, 36, 5729–5740, 2002.
- Ren, X., Harder, H., Martinez, M., Leshner, R. L., Oligier, A., Simpas, J. B., Brune, W. H., Schwab, J. J., Demerjian, K. L., He, Y., Zhou, X., and H. Gao: OH and HO<sub>2</sub> Chemistry in Urban Atmosphere of New York City, *Atmos. Environ.*, 37, 3639–3651, 2003.
- Rivera-Figueroa, A. M., Sumner, A. L., and Finlayson-Pitts, B. J.: Laboratory Studies of Potential Mechanisms of Renoxification of Tropospheric Nitric Acid, *Environ. Sci. Technol.*, 37, 548–554, 2003.
- Rogaski, C. A., Golden, D. M., and Williams, L. R.: Reactive Uptake and Hydration Experiments on Amorphous Carbon Treated with NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, *Geophys. Res. Lett.*, 24, 381–384, 1997.
- Saathoff, H., Naumann, K.-H., Riemer, N., Kamm, S., Möhler, O., Schurath, U., Vogel, H., and Vogel, B.: The Loss of NO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub>, and HO<sub>2</sub>/HOONO<sub>2</sub> on Soot Aerosol: A Chamber and Modeling Study, *Geophys. Res. Lett.*, 28, 1957–1960, 2001.
- Salgado Muñoz, M. S., and Rossi, M. J.: Heterogeneous Reactions of HNO<sub>3</sub> with Flame Soot Generated under Different Combustion Conditions. Reaction Mechanism and Kinetics, *Phys. Chem. Chem. Phys.*, 4, 5110–5118, doi:10.1039/b203912p, 2002.
- Saliba, N. A., Mochida, M., and Finlayson-Pitts, B. J.: Laboratory Studies of Sources of HONO in Polluted Urban Atmosphere, *Geophys. Res. Lett.*, 27, 3229–3232, 2000.
- Saliba, N. A., Yang, H., and Finlayson-Pitts, B. J.: Reaction of Gaseous Nitric Oxide with Nitric Acid on Silica Surfaces in the Presence of Water at Room Temperature, *J. Phys. Chem. A*, 105, 10 339–10 346, 2001.
- Seisel, S., Keil, Th., and Zellner, R.: Laboratory Studies of the Interaction of HNO<sub>3</sub> and H<sub>2</sub>O with Soot Surfaces, in: EC/EUROTRAC-2 Joint Workshop, EC Cluster 4: “Chemical Processes and Mechanisms”, EUROTRAC-2: „Chemical Mechanism Development (CMD)” (Proc.), edited by Rossi, M. J. and Rossi, E.-M., Lausanne, 229–232, 2000.
- Stadler, D., and Rossi, M. J.: The Reactivity of NO<sub>2</sub> and HONO on Flame Soot at Ambi-

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ent Temperatures: The Influence of Combustion Conditions, Phys. Chem. Chem. Phys., 2, 5420–5429, 2000.

Vogel, B., Vogel, H., Kleffmann, J., and Kurtenbach, R.: Measured and Simulated Vertical Profiles of Nitrous Acid, Part II – Model Simulations and Indications for a Photolytic Source, Atmos. Environ., 37, 2957–2966, 2003.

Zhou, X., Civerolo, K., Dai, H., Huang, G., Schwab, J., and Demerjian, K.: Summertime Nitrous Acid Chemistry in the Atmospheric Boundary Layer at a Rural Site in New York State, J. Geophys. Res., 107(D21), 4590, doi:10.1029/2001JD001539, 2002.

Zhou, X., Gao, H., He, Y., Huang, G., Bertman, S., Civerolo, K., and Schwab, J.: Nitric Acid Photolysis on Surfaces in Low-NO<sub>x</sub> Environments: Significant Atmospheric Implications, Geophys. Res. Lett., 30(23), 2217, doi:10.1029/2003GL018620, 2003.

ACPD

4, 6747–6767, 2004

---

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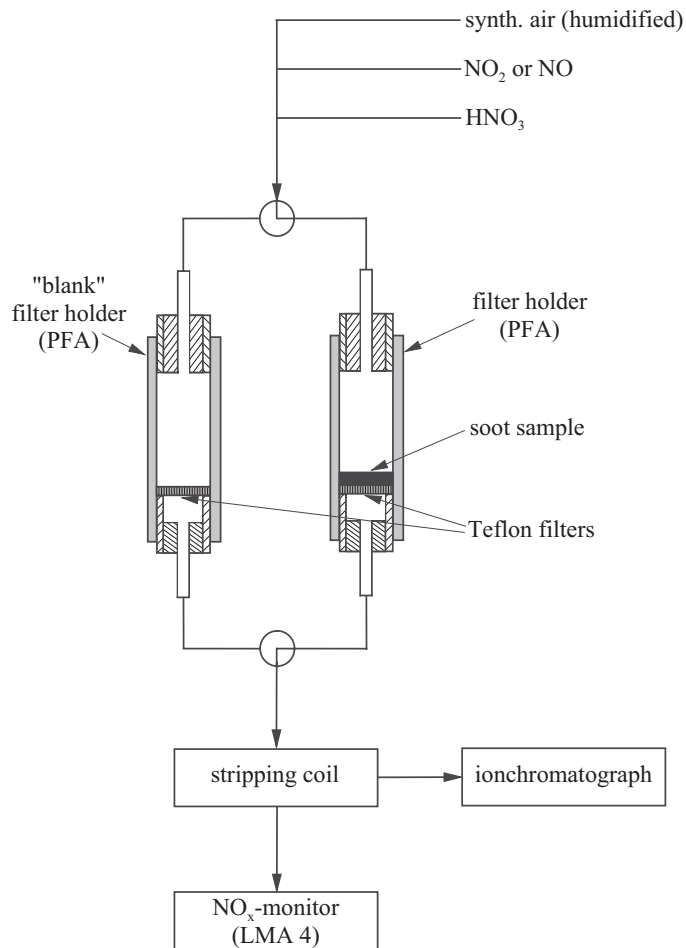
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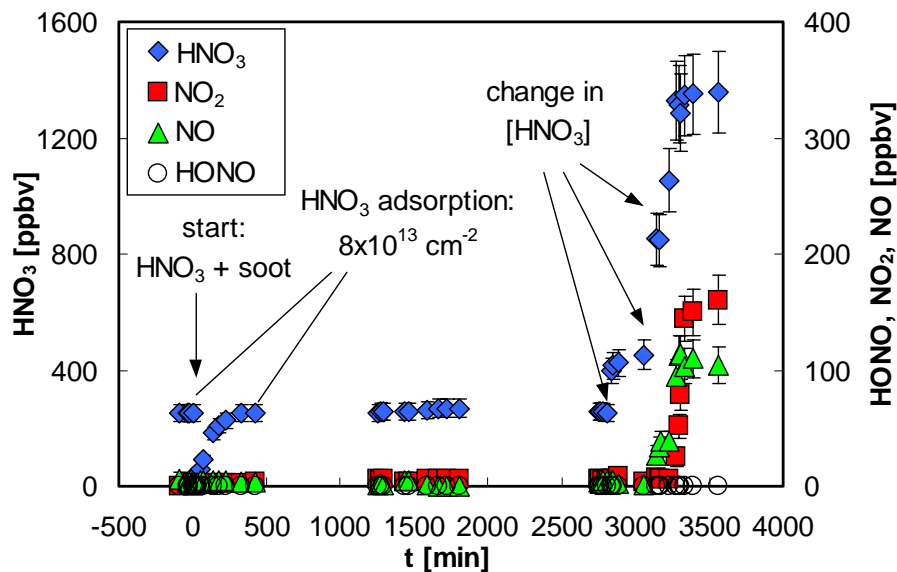
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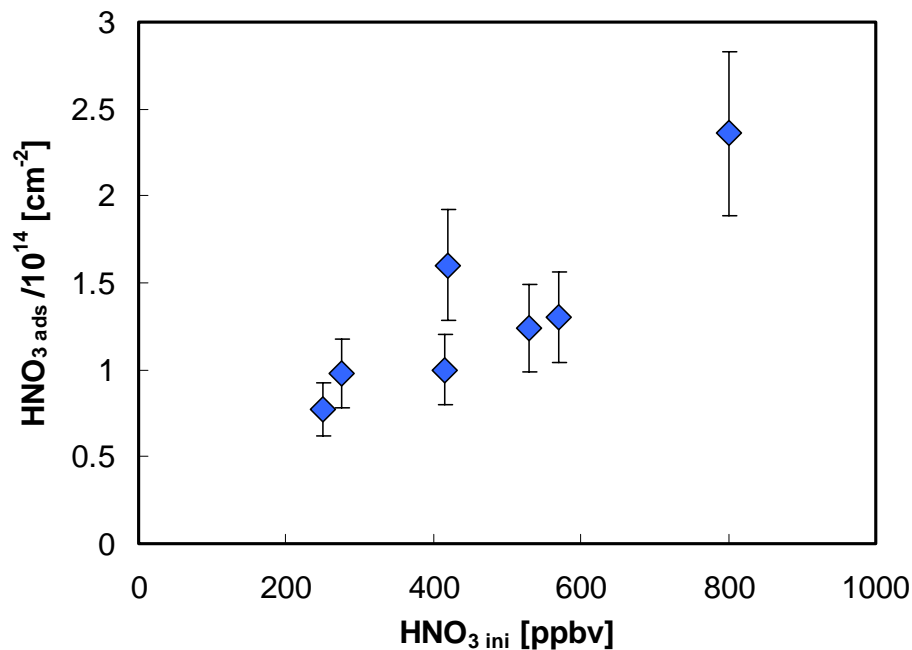
**Fig. 1.** Experimental set-up.

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**Fig. 2.** Reaction of pure gaseous  $\text{HNO}_3$  with Lamp Black 101 at different  $\text{HNO}_3$  mixing ratios (14 mg, 55% r.h.).

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**Fig. 3.** Adsorption of  $\text{HNO}_3$  on Lamp Black 101 as a function of the initial  $\text{HNO}_3$  mixing ratio (10–30 mg,  $50 \pm 5\%$  r.h.).

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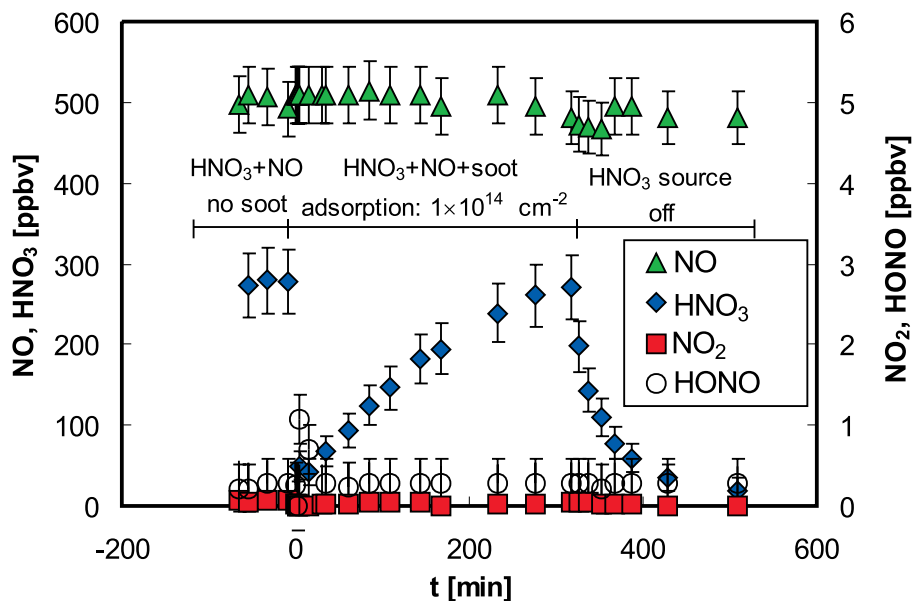
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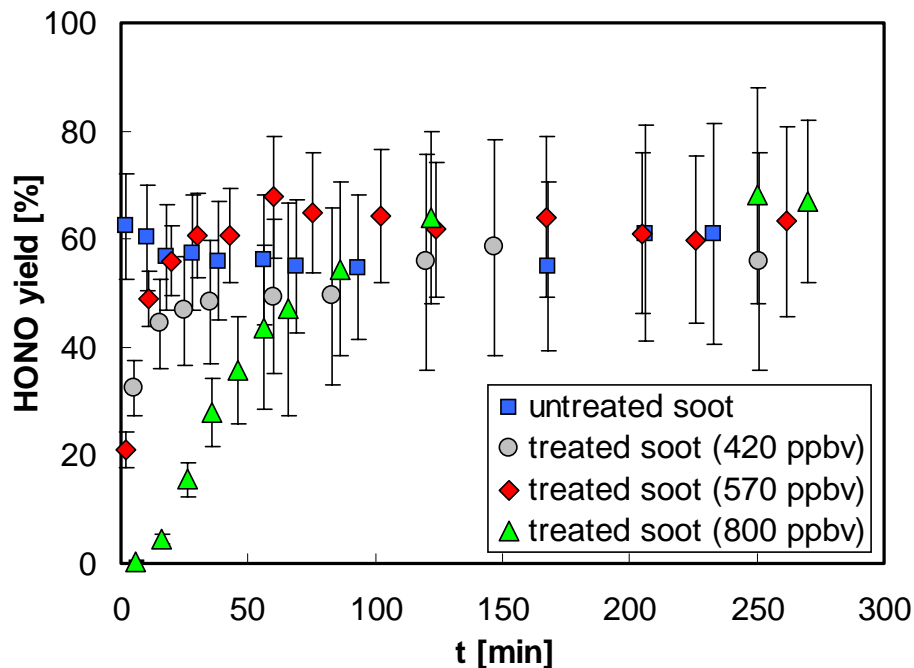


**Fig. 4.** Reaction of  $\text{HNO}_3 + \text{NO}$  with Degussa Lamp Black 101 (13 mg, 48% r.h.).

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**Fig. 5.** HONO yield in the reaction of  $\text{NO}_2$  with Degussa Lamp Black 101 treated with different amounts of gaseous  $\text{HNO}_3$  prior to the experiment ( $[\text{NO}_2]_0=500\text{--}600$  ppbv,  $\sim 50\%$  r.h.).

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