

Heterogeneous conversion of NO₂ and NO on HNO₃ treated soot surfaces: atmospheric implications

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Abstract. In the present study, the heterogeneous conversion of nitrogen oxide (NO) and nitrogen dioxide (NO₂) was studied at atmospheric humidity levels on flame soot surfaces treated with gaseous nitric acid (HNO₃). In addition, the heterogeneous reaction of HNO₃ on soot was investigated at atmospheric humidity.

For the treatment of soot by pure HNO₃ only reversible uptake with a surface coverage of $\sim 1\text{--}2 \times 10^{14}$ HNO₃ cm⁻² was observed for HNO₃ mixing ratios in the range 250–800 ppbv. Only for higher HNO₃ mixing ratios of >800 ppbv the formation of NO and NO₂ was observed. The results were not affected by the addition of NO. In none of the experiments with HNO₃ the formation of nitrous acid (HONO) was observed. For HNO₃ mixing ratios <600 ppbv the upper limit yields for HONO, NO₂ and NO were found to be <0.2%, <0.5% and <1%, respectively. Compared to untreated soot, the product formation of the reaction of NO₂ with soot was not significantly affected when the soot surface was treated with gaseous HNO₃ prior to the experiment. Only for high surface coverage of HNO₃ the formation of HONO was suppressed in the initial phase of the reaction, probably caused by the blocking of active sites by adsorbed HNO₃.

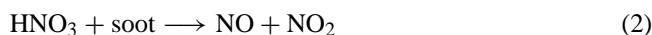
Under the assumption that the experimental findings for the used model flame soot can be extrapolated to atmospheric soot particles, the results show that the reactions of HNO₃ and HNO₃+NO on soot surfaces are unimportant for a “renoxification” of the atmosphere and do not represent an atmospheric HONO source. In addition, the integrated HONO yield of ca. 10¹⁴ cm⁻² in the reaction of NO₂ with soot is not significantly influenced by simulated atmospheric processing of the soot surface by HNO₃, and is still too small to explain HONO formation in the atmosphere.

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1 Introduction

Soot, which is formed during incomplete combustion processes, represents a ubiquitous material of the atmospheric aerosol and has a direct and indirect impact on the 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 NO_x/HNO₃ ratio and on the 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 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 $\sim 10^{14}$ 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 surface with H₂SO₄ (Kleffmann et al., 1999; Longfellow et al., 1999) or by O₃ (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 HNO₃ 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 NO_x/HNO₃ 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 HNO₃ and reported large uptake coefficients and the formation of NO and NO₂. However, in more recent studies, performed at reactant concentrations closer to atmospheric conditions, only a reversible uptake of HNO₃ (Aubin and Abbatt, 2003; Choi and Leu, 1998; Longfellow et al., 2000) or the absence of any gas phase products (Saathoff et al., 2001; Seisel et al., 2000) was observed. The difference was explained by a surface reaction which takes place only at high HNO₃ concentrations for multilayer coverage of adsorbed HNO₃ (Choi and Leu, 1998). This is in accordance with other studies of Reaction (2) in which the formation of NO_x was observed for very high HNO₃ 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 HNO₃ 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 NO₂ were formed on soot generated in a lean flame. The formation of HONO in the reaction of HNO₃ 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 HNO₃ solutions (Louisnard 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 NO_x/HNO₃ 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 HNO₃ is irreversibly reduced to NO_x on 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 HNO₃, 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 NO₂. However, it is still unclear to what extent Reaction (3) influences the NO_x/HNO₃ ratio in the atmosphere.

Accordingly, in the present study the reactions of HNO₃ and HNO₃+NO, Reactions (2) and (3), were studied on soot surfaces at atmospheric humidity levels. In addition, the influence of treating the soot with gaseous HNO₃ on the reaction of NO₂ 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 and well characterised flame soot (Degussa: Lamp Black 101, BET: 20 m² g⁻¹) was used as a proxy for atmospheric soot. It must be stressed that the chemical behaviour of soot can depend on the way of production, as demonstrated e.g. by Stadler and Rossi (2000). Accordingly, extrapolation of results from laboratory studies using proxies to the atmosphere might be uncertain. However, the chemical behaviour of Lamp Black 101 concerning reaction (1), i.e. integrated HONO yield, was found to be similar compared to fresh flame and diesel soot samples used in other 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 μm) in a special filter holder made by PFA (perfluoroalkoxy fluorocarbon) only (see Fig. 1). Commercial filter holders were not used, because of potential strong adsorption of HNO₃ that can interfere with the experiments. 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").

NO₂ and NO mixtures (500–600 ppbv and 500 ppbv, respectively) were generated by dilution of calibrated mixtures of NO₂ and NO (Messer Griesheim, 10 ppmv NO₂ or 10 ppmv NO in N₂) with synthetic air, which was humidified by bubbling through ultra pure water. The humidity (50±5% r.h.) was calculated under the assumption that the gas phase was saturated at the measured water temperature. Nitric acid (HNO₃) was generated by bubbling a small flow of synthetic air through a mixture containing 1% vol HNO₃ (65%) in H₂SO₄ (70%). The impurities NO₂ and HONO were found to be <0.1% after the HNO₃ source was allowed to run for a day. The HNO₃ 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 HNO₃ 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 350–400 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 HNO₃, were removed by ultra-pure water (see Fig. 1). The sampling efficiencies of the stripping coil for HONO and HNO₃, 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 chromatography (Shimadzu, Model 6a) using UV detection at λ=209 nm after pre-concentration on a Dionex TAC LP1 column. The mixing ratios of HONO and HNO₃ were calculated from the measured nitrite and nitrate concentrations and the measured liquid and gas flow rates. The errors of the HONO and HNO₃ mixing ratios of ±(10%+0.2 ppbv) and ±(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 HNO₃, the mixing ratios of NO and NO₂ 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 NO₂ mixing ratios were measured downstream of the stripping coil by a Luminol NO_x monitor (Unisearch, LMA-4). The errors of the NO and NO₂ mixing ratios of ±(7%+1 ppbv) and ±(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 HNO₃ and HNO₃+NO with soot, the gas mixtures were first flushed through the blank filter holder to determine the uptake of HNO₃ by reversible adsorption on the filter holder, the final reactant mixing ratio and the impurities of HONO and NO_x. Corrections, by the wall effects on the filter holder were found to be small.

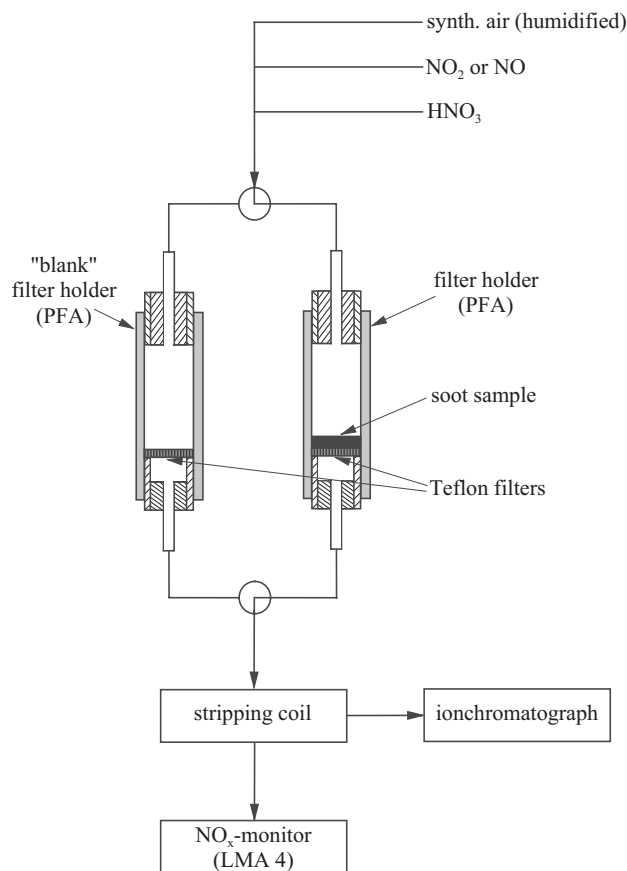


Fig. 1. Experimental set-up.

Thereafter, the mixture was directed to the filter holder with the soot sample. After the soot sample was saturated with HNO₃, the HNO₃ source was disconnected and the desorption of HNO₃ was monitored.

For the study of the reaction of NO₂ with HNO₃ treated soot, the samples were first exposed over night to pure HNO₃ 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 HNO₃ source, NO₂ mixtures were flushed through the blank filter holder, to determine the initial NO₂ mixing ratio and the impurities of HONO and NO. Finally, the NO₂ mixture was directed to the soot sample and the product formation and the desorption of HNO₃ was measured.

3 Results and Discussion

3.1 Reaction of HNO₃ with Soot Surfaces

In the reaction of HNO₃ 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, NO₂ and NO was observed for HNO₃

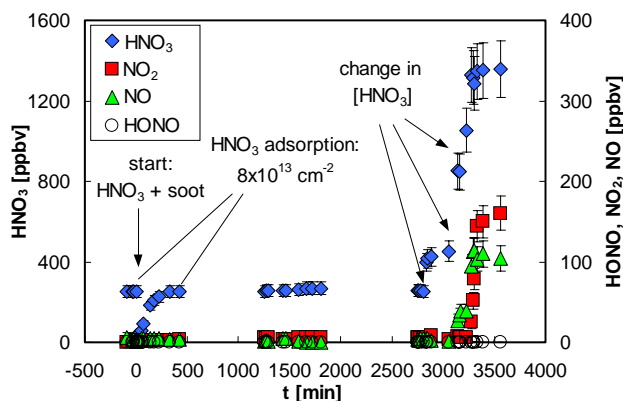


Fig. 2. Reaction of pure gaseous HNO₃ with Lamp Black 101 at different HNO₃ mixing ratios (14 mg, 55% r.h.).

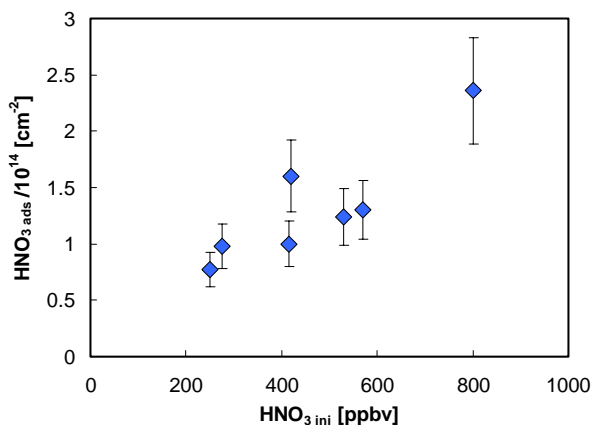


Fig. 3. Adsorption of HNO₃ on Lamp Black 101 as a function of the initial HNO₃ mixing ratio (10–30 mg, 50±5% r.h.).

mixing ratios <600 ppbv, even for reaction times of up to 2 days (cf. Fig. 2). The upper limits for the yields of HONO, NO₂ and NO were calculated to be <0.2%, <0.5% and <1%, respectively. NO and NO₂ were only formed for HNO₃ mixing ratios >800 ppbv. However, even for these conditions no formation of HONO was detected (cf. Fig. 2).

In contrast to the filter experiments with NO₂ and soot, described by Kleffmann et al. (1999), no uptake coefficients were determined for HNO₃ on soot surfaces in the present study, since the surface area is not defined for a “sticky” molecule such as HNO₃. HNO₃ is initially taken up by the upper surface of the soot and diffuses into the pores of the soot later. Instead of the kinetic evaluation, only the integrated adsorbed amount of HNO₃ was determined in different experiments. For HNO₃ mixing ratios in the range 250–800 ppbv a surface coverage of 0.8–2.4×10¹⁴ HNO₃ cm⁻² was derived (cf. Fig. 3) by using the BET surface of 20 m² g⁻¹, given by the manufacturer. After the HNO₃ source was stopped, HNO₃ desorption was observed (cf. Fig. 4) leading to a HNO₃ recovery of ∼(80±10)% within 24 h.

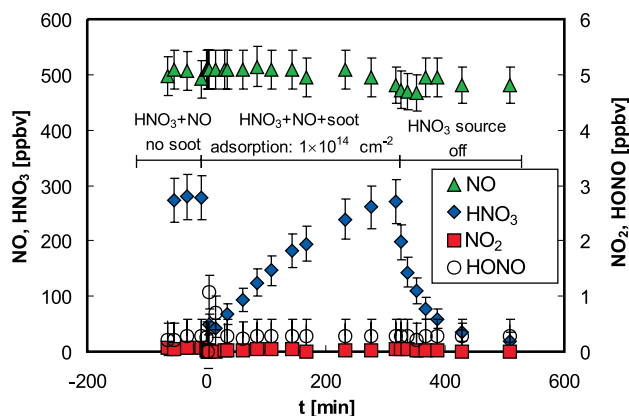


Fig. 4. Reaction of HNO₃+NO with Degussa Lamp Black 101 (13 mg, 48% r.h.).

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 HNO₃ on Lamp Black 101 of ∼2×10¹⁴ HNO₃ cm⁻² is reached for mixing ratios of ∼800 ppbv. This value is slightly lower than the value of 3.8×10¹⁴ cm⁻² determined for n-hexane flame soot by Choi and Leu (1998), but is in excellent agreement with the values of 2×10¹⁴ HNO₃ cm⁻² reported by Aubin and Abbatt (2003) also for n-hexane flame soot.

The observed product formation of Reaction (2), i.e. formation of NO and NO₂ only for high HNO₃ 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_x 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 HNO₃ concentrations when the HONO precursor NO₂ is formed (cf. Fig. 2), can be explained by the blocking of active sites for Reaction (1) by adsorbed HNO₃ (see Sect. 3.3).

In contrast to other studies, the formation of gas phase products as NO, NO₂ and HONO was very recently observed for Reaction (2) by Salgado Muñoz and Rossi (2002) also for low HNO₃ concentrations. The authors observed the formation of HONO on flame soot produced in a fuel rich flame, whereas NO and NO₂ 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 gas phase products at low HNO₃ concentrations. At least some of these soot substrates (e.g. Aubin and Abbatt, 2003; Longfellow et al., 2000; Seisel et al., 2000) were produced under very similar conditions compared to the study of Salgado Muñoz and Rossi (2002), i.e. deposition of fresh flame soot on a inert substrate. 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 Black 101 which was used in the present study (compare Stadler and Rossi, 2000 with Kleffmann et al., 1999), although the reactive sites for Reactions (1) and (2) might be different. The different time resolution of the experiments can also not explain the different results, since the first data point of the present study was typically a mean of the concentration for a reaction time of 2–4 min (sampling interval for the ion chromatograph). For this time interval HONO and NO_x were still observable in the experiments of Salgado Muñoz and Rossi (2002) in contrast to our results. In addition, the time resolution of most of the other studies, in which no reaction was observed (e.g. Aubin and Abbatt, 2003; Longfellow et al., 2000; Seisel et al., 2000) was comparable to that of the experiments of Salgado Muñoz and Rossi (2000).

In agreement with the results of most studies in which very different types of soot substrates were used, it is concluded that HNO₃ is not reacting with soot under HNO₃ concentrations prevailing in the atmosphere and hence is not a “renoxification” pathway or a source of HONO in the atmosphere.

3.2 Reaction of HNO₃ and NO with Soot Surfaces

When soot was exposed to a humid mixture of HNO₃ and NO at mixing ratios of 280 and 500 ppbv, respectively, a similar behaviour was observed compared to pure HNO₃ mixtures (see Sect. 3.1 and Figs. 2 and 4). Again, a HNO₃ adsorption of $\sim 10^{14}$ cm⁻², a desorption of HNO₃ after stopping the HNO₃ source and no formation of NO₂ and HONO was observed. In addition, no NO uptake on the soot was monitored. The upper limits for the HONO and NO₂ yields, with respect to the uptake of HNO₃, 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 NO₂ 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 NO₂ formation of $\gamma_{\text{NO} \rightarrow \text{HONO}} < 1 \times 10^{-10}$

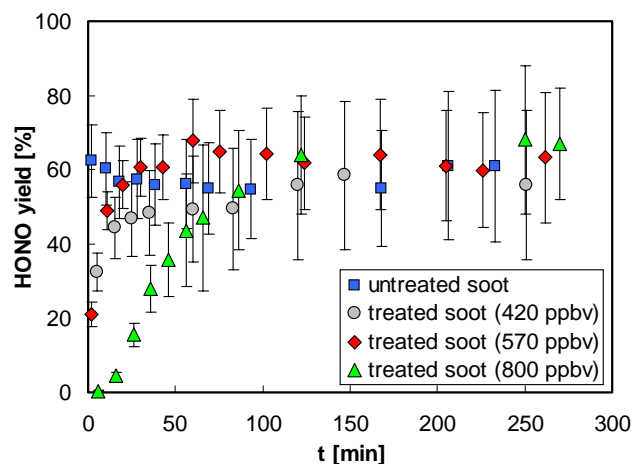


Fig. 5. HONO yield in the reaction of NO₂ with Degussa Lamp Black 101 treated with different amounts of gaseous HNO₃ prior to the experiment ([NO₂]₀=500–600 ppbv, ~50% r.h.).

and $\gamma_{\text{NO} \rightarrow \text{NO}_2} < 5 \times 10^{-10}$ were calculated for HNO₃ saturated soot surfaces.

The reaction of HNO₃+NO on soot surfaces, Reaction (3), was investigated previously by Salgado Muñoz and Rossi (2002), who reported the formation of NO₂. The reason for the discrepancy between both studies is unclear. It could be speculated, similar to the discussion of the HNO₃+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 ~50% was used in the present study.

From the results of the present investigation it is concluded that the reaction of HNO₃ 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 NO₂ with HNO₃ Treated Soot Surfaces

For the simulated ageing of the soot surface by treatment with HNO₃, mixing ratios of up to 800 ppbv were used, in order to exclude the formation of NO₂ (see Sect. 3.1), which would result immediately in a deactivation of active sites on the soot surface for the non-catalytic reaction of NO₂ and soot (Kleffmann et al., 1999). After the samples were saturated with HNO₃ over night, the soot was exposed to humid NO₂ mixtures at mixing ratios of 500–600 ppbv. A strong uptake of NO₂ 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 HNO₃ adsorbed. This means that the initial HONO yield decreased with increasing amount of adsorbed HNO₃, 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 HNO₃. This behaviour can be explained by the adsorption of HNO₃ and the blocking of active sites for Reaction (1). For HNO₃ concentrations of 800 ppbv a HNO₃ monolayer coverage of the soot surface was estimated, leading to very small initial yields of HONO (see Fig. 5). However, since HNO₃ desorbs from the soot when the HNO₃ source is stopped, the active sites become accessible for NO₂ 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 HNO₃ 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.

4 Summary

For the reaction of flame soot surfaces with HNO₃ (Reaction 2) at atmospheric humidity levels only reversible adsorption was observed for HNO₃ 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, NO₂ and NO were calculated to be <0.2%, <0.5% and <1%, respectively. Only, for HNO₃ mixing ratios >800 ppbv NO and NO₂ were formed as products. A monolayer coverage of HNO₃ on soot of $\sim 2 \times 10^{14} \text{ cm}^{-2}$ was estimated, in good agreement with previous studies. The behaviour of the HNO₃+soot system remained unaffected when 500 ppbv of NO were added. Upper limits for the reactive uptake coefficients of NO for HONO and NO₂ 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 HNO₃ saturated soot surfaces. From the results of the present study it is concluded that heterogeneous reactions of HNO₃ on soot surfaces are unimportant for the “renoxification” and for the formation of HONO in the atmosphere.

Treating the soot surfaces with gaseous HNO₃ had no significant impact on the heterogeneous reaction of NO₂ for atmospheric humidity levels. Only for high surface coverage of the soot with HNO₃, the HONO yield was reduced. The results show, that ageing of the soot surfaces by HNO₃ 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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