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Atmospheric
Chemistry
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Discussions

Interactive comment on “Heterogeneous conversion of NO_2 and NO on HNO_3 treated soot surfaces” *by* J. Kleffmann and P. Wiesen

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Reply to Anonymous Referee #2

We would like to thank referee #2 for his comments, which are addressed below.

General remarks:

Insight to the mechanism:

The referee raised the objection that the present study does not give any new insight to the mechanism especially of the heterogeneous reaction (2), since the experiments were performed only for one soot substrate at room temperature without kinetic information.

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However, we would like to draw the attention of the referee to the fact that the present study is the first of reaction (2) in which HONO could have been specifically identified with a high sensitivity (DL 0.2 ppbv for typical HNO3 concentrations of a few hundred ppbv) at atmospheric conditions, i.e. humidity and pressure. Up to now only two studies of reaction (2) exist, which focused on the formation of HONO on soot substrates (Aubin and Abbatt, Salgado Muñoz and Rossi), however with controversial results. Accordingly, this study was aimed at answering the question whether or not HONO is formed in reaction (2) under atmospheric conditions. At least for reaction (1), the soot used has the ability to form HONO with a yield similar to that found for the fuel rich soot (Salgado Muñoz and Rossi) and fresh diesel soot (Arens et al.). The flame soot is well characterised and has never been used until now for the study of reaction (2). The study thus adds another type of soot for which no formation of gas phase products was observed, in good agreement with almost all studies at low concentration. In addition, since this study was performed under atmospheric conditions, i.e. 50 % r.h., in contrast to most other studies, we conclude that our results can be better extrapolated to the atmosphere compared to studies under completely dry conditions.

Analysis of the literature data:

We agree with the referee comment that one might get the impression that irreversible reaction of HNO3 was only observed in one study, which might not be correct. However, since the focus of our manuscript was the formation of gas phase products, i.e. answer the question whether reaction (2) could be of importance for a possible “renoxification” of the atmosphere, this statement is still true. Neither in the study of Seisel et al. nor in the study of Kirchner et al. gas phase products were observed. In addition, since it is well known that HNO3 sticks very strongly on surfaces, the desorption of HNO3 might not be observable e.g. on the time scale of the experiments of Seisel et al. Even for our conditions, for which the soot sample was continuously flushed with synthetic air, we were able to desorb only ca. 80 % of the adsorbed HNO3 after one day. In contrast, the time scale of Knudsen cell experiments is typically only a few tens of minutes. In

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addition, active flushing by humid synthetic air will lead to a faster desorption of HNO3 compared to simple effusion, as in the study of Seisel et al.

We will clarify this in the revised manuscript by using “formation of gas phase products” instead of “irreversible reaction”.

Minor comments and questions:

Page 6753, line 15-16:

The adsorption of HNO3 on the filter holder was typically more than a factor of 20 smaller compared to the adsorption on the soot substrate. In addition, the surface was saturated much faster with HNO3 compared to the soot experiments. Thus, errors caused by the adsorption on the filter holder are small. We will add this information to the revised manuscript.

Results and discussion, Figure 2:

We only wanted to show that reaction (2) is not of importance for the atmosphere. Thus, we did not put too much effort into the high concentration experiments. The reported experiment is only meant to confirm the conclusions given by Choi and Leu to explain different results of different studies performed at different HNO3 concentrations. For the mechanism of reaction (2) at high concentration we refer to the study of Choi and Leu. This was not the focus of our study.

Page 6754, line 11-15:

If a molecule has a long residence time on the surface after a collision, it will slowly diffuse into the pores of the soot. Thus, much smaller measured uptake coefficients (using the BET or “accessible” surface, see Kirchner et al.) will be determined compared to aerosol flow tube experiments, in which pore diffusion is no problem. To overcome this problem a pore diffusion correction has to be applied which includes the residence time of a molecule on the surface. The pore diffusion correction will increase with increasing residence time of a molecule on a surface. Since for the experiments

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of Kirchner et al. no pore diffusion correction was applied, the measured uptake coefficients are most probably too small, especially for HNO3.

Page 6755, line 1:

We thank the referee for this comment. We used this number for the HNO3 uptake, since this was assumed also by Kirchner et al. (see page 8914 of their paper, first paragraph). However, we will correct this in the revised manuscript.

Page 6756, line 23-26:

We only used humid conditions in order to be as close to atmospheric conditions as possible. Since we did not observe any reaction for these conditions, the humidity dependence was not further investigated.

Page 6757, Section 3.3:

The deactivation of active sites for reaction (1) by NO2 formed by reaction (2) was not studied. However, the deactivation by NO2 is well documented in the literature. And again, we did not want to study the mechanism of a reaction, which will only take place at unrealistically high HNO3 concentrations. The aim of this paper was to find out whether these reactions are of importance under atmospheric conditions. The simultaneous introduction of NO2 and HNO3 was not studied. However, for low concentrations of HNO3 the NO2 reaction will not be affected by HNO3, since HNO3 desorbing from the soot was still present in the NO2 experiments with the treated soot samples, i.e. HNO3 and NO2 came into contact for all these experiments.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6747, 2004.