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Atmospheric Chemistry and Physics Discussions

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

J. Kleffmann and P. Wiesen

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Reply to Anonymous Referee #1

We would like to thank Referee #1 for his interest in our paper and his suggestions and comments. The concerns he raised are addressed below.

Reply to general comments:

Complexity of the soot substrate:

We completely agree with the comment of the referee that flame soot substrates are highly complex mixtures of organic and elementary carbon components and that the complexity depends on the way in which the substrates are produced. Accordingly, the results from laboratory studies, in which proxies for atmospheric soot are normally used, have always to be treated with caution when extrapolating to atmospheric conditions, even when, e.g. flame soot substrates are produced under very different condition (see Salgado Muñoz and Rossi). Only studies with real atmospheric soot samples, like e.g. fresh diesel soot, could lead to more reliable results, although they are much more difficult to perform. However, as already mentioned in the manuscript very different kinds of soot samples have been used in the different studies published in the literature and have led to almost the same results for reaction (2). Our intention was not to repeat all these experiments. Instead, we used the commercial flame soot Lamp Black 101, since:

a) it is well characterised,

b) it is not chemically treated, i.e. oxidised by treatment with NO2 or HNO3 like e.g. the often used FW2 soot,

c) it still has the ability to form HONO by the NO2 reaction (1) with a similar absolute yield compared to flame soot substrates freshly prepared in the laboratory (Gerecke et al.), or to fresh diesel soot samples (Arens et. al.),

d) it has not been used up to now in other studies of reaction (2), and therefore, adds another piece to the complex puzzle of the heterogeneous soot reactions (1-3). We will, however, add a statement to the revised manuscript concerning the general restrictions of the results obtained from studies with soot proxies.

Comparison with other studies:

We agree with the referee that very different kinds of soot substrates were used in the different studies making a direct comparison impossible. However, since almost the same results were obtained in most of these studies, i.e. no formation of gas phase products, we conclude that these results do not depend very much on the kind of soot substrate used. We will add this statement to the revised manuscript.

We still have no explanation for the different results of the present and most of the other studies with those of the study of Salgado Muñoz and Rossi, for the following reasons:

a) the way of production of the flame soot was very comparable with at least some of the other studies, i.e. deposition of fresh flame soot on an inert substrate (e.g. Aubin and Abbatt, Longfellow et al., Seisel et al.). In this context, we do not agree with the referee's comment that the "soot" was passivated by HNO3 before each experiment in the study of Aubin and Abbatt. These authors stated that the "system" was passivated with HNO3 when the "movable injector was positioned with its tip beyond the downstream end of the soot film".

b) As already mentioned in the manuscript, different flame conditions, i.e."lean" and "rich", when producing the soot, can also not explain the difference. For both types of soot formation of gas phase products was observed by Salgado Muñoz and Rossi at low HNO3 concentrations. This is in contradiction to all other studies performed at low HNO3 concentration using similarly produced soot samples (e.g. Aubin and Abbatt, Longfellow et al., Seisel et al.).

c) In addition, the different time resolution of the experiments is also not an explanation for the different results, since our first data point 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 NOx were still observable in the experiments of Salgado Muñoz and Rossi (see e.g. Figs. 1, 4, 9) in contrast to our results, i.e. we surely would not have missed this time period. In addition, the time resolution of most of the other studies with MS detection, in which no gas phase products were observed (e.g. Aubin and Abbatt, Longfellow et al., Seisel et al.) was very comparable to that of the experiments of Salgado Muñoz and Rossi. We will add information about the time resolution of the different experiments to the revised manuscript. A plausible but nonetheless speculative explanation for some of the different results has been given by reviewer #3, however, we have no experience with the detection of the different NOy species by MS using electron impact and would like to leave this as an open discussion among experts in this field.

Reply to specific comments:

Page 6752, line 23:

As already mentioned in the manuscript, we would not like to determine the kinetics of the HNO3 uptake, since the surface area is not well defined for a sticky molecule such as HNO3 in our filter experiments. Firstly, HNO3 will mainly absorb on the outer surface of the soot and once the surface is saturated, HNO3 will slowly diffuse more and more into the deeper pores of the soot. Accordingly, the uptake cannot be explained by a simple first order kinetic and the life time of HNO3 is not well defined. The kinetic of the reaction of HNO3 on soot can only be accurately determined by using aerosol flow tube experiments with e.g. air suspended diesel soot particles. Only in such experiments pore diffusion and the long residence time of HNO3 molecules on the surface will not be a problem for the determination of the uptake kinetics.

Page 6754, line 21:

The only products we were looking for were HONO, NO and NO2. Accordingly, we cannot confirm the absence of any other products for high HNO3 concentrations. However, from the mass balance, the yield of other products can be estimated to be small (see next point).

We only wanted to show that reaction (2) is unimportance 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.

Page 6755, line 2:

In Figure 2 the HNO3 concentration passing the filter sample was monitored after t=0, so the initial concentration can be only exactly quantified for the first part of the experiment, i.e. 250 +- 30 ppbv (data before t=0). Later, the HNO3 concentration was increased by increasing the flow through the HNO3 source. Since the concentration of the HNO3 is linearly dependent on the gas flow through the source, the initial HNO3 concentrations can be roughly estimated to be 250 +- 30 ppbv (0-2807 min), 500 +- 50 ppbv (2808-3053 min), 1000 +- 100 ppbv (3054-3169 min), and 1550 +- 160 ppbv (3170-3562 min) assuming that the source was running constant for this long time period. For the highest HNO3 concentration, 1350 +- 140 ppbv HNO3 and 250 +- 30 ppbv NOx were observed after the filter sample. Accordingly, the concentration of reacted HNO3 is equal to the concentration of NOx in between the experimental errors. This leads to a NOx yield of ca. 100 %, leaving no room for a significant fraction of other products at high concentrations. However, the formation of surface products, as observed, e.g. by Kirchner et al., cannot be excluded in this estimation, since the surface might have been saturated before, during the two days of HNO3 treatment at low concentration (see Fig. 2).

Page 6755 and 6756:

We agree with the comment of the referee and we will clarify this in the revised manuscript. We have given this information to demonstrate that the chemical behaviour of the soot used in this study (commercial) was not completely different to the flame soot used in the study of Salgado Muñoz and Rossi, at least for the NOy reaction (1).

Page 6757, lines 5-8:

The HNO3 concentrations of $<$800 ppbv were used to exclude NO2 formation in reaction (2), see results for high HNO3 concentration. If NO2 was formed by reaction (2), it would have deactivated the active sites for reaction (1), which is the topic of this section. We clearly do not think that the active sites for reaction (1), i.e. reduction of NO2, and reaction (2), i.e. only adsorption, are the same.

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Page 6756, line 17:

The upper limits for the uptake coefficient which we determined were given for the uptake of the non-sticky and non-reactive molecule NO on the soot surface, for which we assumed that it will come in contact with the same surface like e.g. N2 or Ar used for the determination of the BET surface. Even for the reaction of NO2 with the same experimental set-up, we observed that the whole BET surface of the soot was reacting for the time scale of our experiments (min to h), see Kleffmann et al (1999). Accordingly, we assume that the error in the upper limit of the uptake coefficient of the even less reactive NO molecule, is small. And even if our surface area was smaller by one order of magnitude, this would not change the conclusion that reaction (3) is completely unimportant for the atmosphere. The upper limits for the yields of HONO and NOx were determined from the concentration of HNO3 taken up and the detection limits for HONO and NOx. Accordingly, these upper limit yields are independent of the surface area.

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