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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous conversion of NO_2 on secondary organic aerosol surfaces: A possible source of nitrous acid (HONO) in the atmosphere?" *by* R. Bröske et al.

R. Bröske et al.

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Reply to anonymous referee #2

We would like to thank referee #2 for his interest in our paper and his suggestions. The concerns he raised are addressed below:

Introduction:

Response to: "I recommend inserting "potential" before "importance". To my knowledge nobody has claimed that HONO formation from the NO2/soot interaction actually IS important!"

The sentence will be changed accordingly in the revised manuscript.

Response to: "At the end of the section change "decomposition" (of volatile organic) to "reaction" or "oxidation" by the action of O3 and/or OH". (page 599, line 17)

Instead of "decomposition" "reaction" will be used in the revised manuscript.

Response to: "The authors should clarify the sentence "Since the organic fraction of the atmospheric aerosol" to make sure there is no misunderstanding. The authors surely refer either to external mixtures of aerosols or coagulated atmospheric particles. SOA usually does not contain black carbon in its core and occurs as a liquid."

"Aerosol" is a general term for a mixture of solid and/or liquid particles in air, independent whether the different particles are internal, external or coagulated mixtures. Our intention was not to specify this.

Chapter 2.1:

Response to: "Did the authors check for the effect of the charcoal denuder on the particle density? Is there a blank experiment to report? Were there any insertion losses?"

As already written in the manuscript (page 600, line 19), the charcoal denuder did not change the particle size distribution. We think that an example of this statement in form of a figure is not necessary, since particle formation is not the objective of this paper.

Chapter 2.2:

Response to: "Did the authors perform blank experiments with the PenRay lamp and hydrocarbon alone? How good was the separation between photolysis of H2O and potential UV photolysis of the source hydrocarbons? Hard UV radiation ($<$ 200nm) in air generates ozone such that the separation between the OH and ozone reaction becomes problematic. Would the authors please provide experimental evidence for the absence of ozone or the absence of any photolytic effects on the hydrocarbons?"

As already written in the text, experiments with dry synthetic air (N2) and the hydro-

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carbons show no particle formation (s. page 601, line 1). However, a typing error was found in this sentence, since for these blank experiments dry nitrogen and not synthetic air was used similar to the aerosol generation (s. page 600, line 23 and also Figure 1). This will be changed in the revised manuscript. For the generation of the aerosols by OH reactions we exclude significant concentrations of ozone, (a) since nitrogen was used with the penray lamp and (b) since no particle formation was observed for dry nitrogen and e.g. limonene. In the case of significant ozone concentrations, we would have observed particle formation in this mixture. However, the separation between OH and O3 reactions is more problematic during the aerosol production by O3 reactions (chapter 2.1), since significant OH production is well known for O3 reactions. But again, the objective of this paper is not a detailed study of the aerosol formation. From the absence of particle formation for dry mixtures, we also exclude particle formation by photolysis products of the hydrocarbons.

Chapter 3.2:

Response to: "Filter experiments. What were the flow characteristics of the slow flow experiments? Flow rate? Gas phase residence time?"

The flow rates in the filter experiments were in the range 300-500 ml min-1 This information will be added to the revised manuscript. However, the residence time of a gas molecule at the particle sample in a filter is not well defined. For the calculation of the uptake coefficients (1) we assumed that the complete geometric surface of the filter came into contact with the gas phase molecules, which is reasonable for the low flow rates.

Chapter 3.3:

Response to: "Aerosol flow tube experiment. Why was the LOPAP instrument not protected by an aerosol filter? Any specific reason?"

In the case that the LOPAP instrument was protected by an aerosol filter, we would

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have measured the sum of HONO formation on particles in the gas phase and on the filter. In this case the aerosol surface area and the surface properties would not have been well defined. In addition, the instrument needs not to be "protected", since "in separate experiments it was shown that particles in the size range investigated are not taken up by the LOPAP instrument" (s. page 603, line 14).

Response to: "What were the flow characteristics of the flow tube? Laminar or turbulent (Reynolds number)?"

The flow characteristics of the flow tube were: length 80 cm, i.d. 5 cm, conic entrance and exit junctions, flow rate ca. 1 l/min, laminar flow (Reynolds number ca. 15). Details will be given in the revised manuscript.

Figure 4:

Response to: "Figure 4 conveys an uncertainty in the HONO concentration of 100 ppt rather than 10 ppt as stated in the text. The precision of the LOPAP instrument is less important than the experimental overall uncertainty given in an experiment and stated by the authors. I recommend using 100 ppt for DHONO in equation (2) in order to obtain a limiting value for gamma."

The uncertainty shown in figure 4 reflect the accuracy of the instrument including all possible errors, however the precision of the instrument is much better (ca. 1 %). In contrast to the statement of the referee, for the determination of the minimum change in the HONO concentration by possible formation on the aerosol, the precision of the instrument has to be used, since the precision is defined by a minimum detectable concentration change.

Figure 1:

Response to: "In Figure 1 the connections between elements 1 and 2 are not clear."

Elements 1 and 2 are separate flow tubes for the generation of aerosols by O3 (1) and OH (2) reactions (see chapters 2.1 and 2.2). They are used alternatively and not

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connected. However, the referee probably refers to the missing connection between the humidified organic gas mixture and the aerosol flow tube (1) which is covered by the grey shaded area. This will be changed in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 597, 2003.