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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Light induced conversion of nitrogen dioxide into nitrous acid on submicron humic acid aerosol" *by* K. Stemmler et al.

Anonymous Referee #1

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Evaluation of the overall quality

The paper presents experimental investigation of the feasibility of heterogeneous chemistry for the conversion of NO2 to HONO on the surface of sub-micrometer humic-acid aerosols under UV-Vis radiation. This work expands and better relates the results to real atmospheric conditions by using aerosols rather than films. The paper is well written and arranged and the work is carefully done. However, some clarifications are required before accepting the paper.

Comments

1) It is possible that some of the below comments/questions would be unnecessary if the paper had included a schematic presentation of the system setup. Please consider

adding this illustration.

2) Since this work aims to improve the understanding of heterogeneous chemistry processes occurring in the troposphere. Why have you chosen to use less atmospheric related organic polymers such as Humic-acids for which you indicated that they are "tenfold higher photoreactivity towards NO2" instead of commercially available and intensively studied Fulvic-acid samples? If the reason is the availability of large quantities of the material that raises the question why you needed such high quantities (20 gL-) and what was the aerosol load in the flow tube during the experiments?

3) Page 4039 line 5. Using high concentrated (20 gL-1) humic-salt solutions enables the dissolution of the anionic humic. Still, at the concentration ranges used in these experiments (and especially for non water soluble matter such as humic-acid) aggregates and micelles can be formed. Did you make sure that no such particle structures have been formed? If such structures are formed they will change the surface chemistry in both cases (aggregates and micelles) and also the mobility diameter for aggregates. Moreover, by adjusting the pH to lower values you formed humic-acid which is not soluble by definition at pH $<$ 8, therefore, aggregates must have been formed.

4) Page 4039 line 9. After neutralizing the particles you have removed all charged particles from the flow stream. How did you perform the SMPS measurements using this setup? And for what purpose did you need to remove the charged particles?

5) Page 4039 line 13. You indicate that all measurements where preformed under the same size distribution with a "log-normal size distribution with a mean diameter of 100 nm and a geometric mean standard deviation of 1.85" but you did not mention the particles' concentrations. In addition, the only way to know particles concentration and thereby the particles' surface area and the particle volume inside the reactor flow tube is by assuming the same size distribution for neutral, positively charged and negatively charged particles and normalizing the above size distribution to a direct particle counting by a CPC in the entrance and/or exit of the reaction flow tube. If not done

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this can greatly affect the interpretation of the results. Moreover, it may allow you to estimate the fraction of losses in the flow tube and recalculate the base line for HONO production (Fig 2.) after the removal of the particles from the system.

6) Page 4049 line 2. You suggest that the presence of water molecules promotes the reaction. Could you provide a statement relating the water promotion to the reaction mechanism or to structural changes in the particles' surface area after the absorption of water (chemistry vs. structural changes)?

7) Page 4049 line 9. For polydisperse samples like humic substances there is no evidence for phase transition and in addition it is hard to see how polydisperse species find the way to selfassemble into crystalline form. Moreover, even humidograms of binary mixed well-defined species (such as a deliquescent salt and a non deliquescent organic acid) do not show a combination of hygroscopic patterns (meaning slight growth followed by deliquescence with increasing RH). The restructuring observed by Gysel et al. (2004) is another indication that the particles were not in a crystalline form and can be related to the post atomizing procedure. It is also suggested that at 90% RH dilution of the dry aerosol due to water absorption can lead to reduction in reactivity. However, the growth factor for humic acids (which are poorly soluble species) should be very low (GF $<$ 1.1) not enough to dilute the aerosol but may mask the dry particle by a layer of solution. I would suggest rewriting this paragraph or provide some more accurate into the gas-surface interface processes under humid conditions.

Technical corrections

8) Page 4047 line19 and Figs 2 and 4. "Figs 2-5 this model description is depicted by the dashed line". I can see a dashed line in Figs 3 and 5 I can not see any such line in Figs 2 and 4 (correct also in the legends of both Figs).

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4035, 2007.

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