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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.

K. Stemmler et al.

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We would like to thank this reviewer for thoroughly reading this manuscript and the constructive comments. In our response, we directly refer to the numbered comments raised by the referee.

Major comments:

1)Nature of humic acid aerosol

As noted in the reply to the other referees, we admit that the humic acid microstructure is not well known under the conditions of our experiments. We also assume that at the pH of 4.6 a fraction may have precipitated in colloidal form. That implicates that the internal mixing and phase state of the individual particles was not well defined. However, we believe that overall the aerosol was certainly a reasonable proxy of the

organic content of soil dust. As long as the nebulized solution (or rather suspension) remained homogeneous, the average composition of the particles remained the same.

2)Comparison of humic acid with real organic aerosol

In the revised manuscript in the “Discussion” and “Conclusions and atmospheric implications” section we will add a statement, in which we will point out that the estimated upper limit is based on the comparatively high reactivity of the used HA material, which further confirms our conclusion for more atmospheric relevant aerosol surfaces. We still keep ‘a door open’ by mentioning that the photoreactivity of ambient organic particles have not been measured so far. Because fulvic acids with respect to several aspects resemble HULIS in atmospheric aerosols, we cannot derive any conclusions about the photoreactivity of ambient organic particles.

Minor comments:

1)The sentence should read: “In Figs 3-5 this model description is depicted by the dashed lines”. The full line in Fig. 4 will be modified accordingly.

2)Formation of ozone by photolysis of NO_2

The ozone concentration will not scale linearly with the initial NO_2 caused by the nonlinear Leighton equilibrium. Although ozone was not measured during the experiments the ozone concentration can be estimated by the measured J(NO_2), known rate constants and the initial NO_2 concentration. The range of concentrations (up to a few ppb for the experiments under visible light) will be specified in the revised manuscript. The ozone level reached for the experiment with UV-A light (49ppb) is already mentioned in the text on p4048, line 23. Any further interpretation (lifetime of Ared etc.) could only be done if the experiments with the bulk surfaces (Stemmler et al., 2006) would be absolutely comparable to these aerosol experiments, which was found to be not the case.

3)Suggested mechanism

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We used a mechanism, in which the photo-produced reduced species reacts either with NO_2 or with an also photo-produced competing oxidant, as mentioned in the text (reactions (R2) to (R4)). Numerically, this can almost not be distinguished from a Langmuir-Hinshelwood (LH) surface reaction model that has been used to describe surface chemistry of NO_2 on different organics in the dark. Driven by the successful modelling of the light intensity dependence along with the dependence of NO_2 concentration, we believe that reactions (R2) to (R4) are the more likely processes limiting reactive uptake in this case. We will change the text on top of page 4047 accordingly to make clear that the following analysis is based on reactions (R2) to (R4), and not on a LH model. More detailed experiments into the short-lived transients would be necessary to pin down the details of this photochemical process.

4)Wavelength dependence

The sentence will be amended to express that the parameterisation given in equations (4) and (5) is only valid for the specific spectrum of the lamps used in the experiment. This then introduces the discussion about the wavelength dependence.

Other typos: pg 4044, line 5: will be changed in the revised manuscript.

pg 4049, line 29: will be changed in the revised manuscript

pg 4052, line 22: will be changed in the revised manuscript.

References

Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., and George, C.: Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, Nature, 440, 195-198, 2006.

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