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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 specific comments raised by the referee.

1)Figure of experimental setup

A detailed scheme of the setup would be very involved and would imply a complete description in the figure caption, as well as explanations in the text. We believe that the detailed description in the current text suits the needs of the reader better than a very complex figure. However, we will amend the text with regard to the issues raised below in the comments.

2)Choice of humic acid

Aldrich HA with relatively high photoreactivity was chosen to obtain measurable quantities of HONO in addition to the considerable background formation of HONO in the flow reactor in absence of aerosol. Moreover, HA films of the same material were already used in a previous study by Stemmler et al. (2006) allowing for a comparison of the results. As mentioned in the text, that study also provides a comparison between Aldrich HA and a number of authentic HAs, and we also mention in the introduction that the Aldrich HA has an about 10 times higher photoreactivity than a typical fulvic acid. Therefore, detecting HONO formation over a fulvic acid aerosol may have been too close to the precision of the measurments. The significant amounts needed to perform the experiment was therefore more a secondary issue, and mostly related to the relatively inefficient way of nebulization, in which a large fraction of nebulized solution is not contributing to the aerosol actually needed in the flow reactor (a few mg per m3). Nevertheless, and also driven by other comments in this direction, we will explicitly mention typical number, surface and mass concentrations in the reactor.

3)Structure of humic acid aerosol

We are aware that the microstructure of the HA was not well defined in these experiments. It is correct that the solution adjusted to a pH of 4.6 most likely contained non-dissolved material. We note that similar aerosol generation methods have been used in other studies, and we refer to those in the text, where we discuss the observed humidity dependence, as well as the uncertainty of the aerosol surface area determined by the SMPS system. Overall, we did the best possible to allow for reproducible results in the context of this study focussing on the reaction of NO_2. It was assured that solutions, from which the aerosol was generated, remained homogeneous during the experiments to avoid fractionation of some components. We will add a few sentences on this issue into the experimental section and the results section, where the kinetics is discussed first. We will also come back to these uncertainties in the conclusion / atmospheric implications section and make a proper caveat.

4)Particle Charge

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The charged particles were removed to ensure no significant losses of particles in the aerosol flow reactor and a constant aerosol surface area during the experiments. The SMPS system as well as the electrometer device both include a 85Kr-source to re-establish Boltzmann charge equilibrium after the aerosol reactor as in standard SMPS configuration, which includes all necessary charge corrections. The position of all 85Kr-sources and their purpose will be mentioned in the revised experimental section.

5)Total particle surface area

As mentioned above, only neutral aerosol entered the flow reactor. The total particle surface area was determined from the SMPS measurement performed after recharging the aerosol to charge equilibrium. The overall losses in the flow reactor are very small (<5

6,7)Effect of water on the reaction

This is a good point. In our discussion, we only concentrate on some of the physical issues (e.g., structural changes) that might affect the humidity dependence. Also, from reactions (R2) to (R4), the role of water does not become clear. In general, we note that the interaction of water with HA is not well understood. Therefore, even the physical aspects noted are highly hypothetical. Apart from the structural changes and the dilution effects already mentioned in the text, we may further think of whether the solubility of NO_2 in pure (dry) HA is higher than in deliquesced HA, and whether water competes with NO_2 for surface sites in the first adsorption step. Regarding chemical aspects, we note that the dark reaction of NO_2 with solid anthracenetriol showed a pronounced humidity dependence (Arens et al., 2002), indicating the role of water in hydrolysing the phenolic OH-group. In the case of the present HA, we thus expect that the electron donor properties of the phenolic moieties of HA might depend on water associated with the condensed phase. On the other hand, charge or energy transfer from the excited species (either a triplet or any reduced intermediate radical) is strongly depending on the medium, in which it occurs. Therefore, uptake of water into the HA structure might

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inhibit electron or energy transfer from the primary excited species. We will add these aspects to the revised version, where the humidity dependence is discussed. We note however, that more detailed information about the photochemical process itself cannot be obtained from the present data.

8)Technical comment (dashed line in Fig. 4)

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.

References

Arens, F., Gutzwiller, L., Gaggeler, H.W., and Ammann, M.: The reaction of NO_2 with solid anthrarobin (1,2,10-trihydroxy- anthracene), Phys. Chem. Chem. Phys., 4, 3684-3690, 2002.

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.

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