Atmos. Chem. Phys. Discuss., 7, S2774–S2777, 2007
www.atmos-chem-phys-discuss.net/7/S2774/2007/

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.

Received and published: 29 June 2007

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)Properties of HA aerosol

The microchemistry of the HA aerosol as used in our experiments was not well known. It certainly contained the cations and anions present in the nebulized solution. However, we do not know the microstructure and precise phase and internal mixing state of the particles, but consider them as representative of the organic fraction of soil dust.

2)Protonation degree of HA

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The degree of protonation of the HA surfaces (bulk and particles) are unknown and may certainly differ from that inferred from the pH of the solutions, from which they were generated. However, the differences in the pH dependence between bulk and the aerosol studies cannot be explained by a complete buffering by the HA, since then we should have observed the same low pH dependence also in the bulk experiments (pH was changed in a similar way and the surfaces are produced in a similar way: drying of a parent solution and conditioning at constant humidity). However, as already stated in the manuscript (see page 4050, lines 6 ff), the low pH dependence in the aerosol study is caused by the much lower HA volume compared to the film experiments and, thus, the lower partitioning of HONO into the HA phase, even if the effective Henry's law constant is high for high pH values. We will change the first sentence on page 4051 to emphasize this.

Minor comments:

1)Will be changed in the revised manuscript.

2)We will add additional closing parentheses for the citation.

3)Interference in HONO measurement by particles

First of all the uptake of particles in the sub-micron range in the HONO instrument was found to be less than 0.01. Thus, in our two channel system particles would be still present in the second stripping coil, which is used to correct for interferences (for example by particles) to almost the same quantity (0.99). Thus, even if particles would interfere ("chemical properties...", see below), this interference could be corrected for by the instrument (for details, see instrument papers).

In addition, although "chemical properties" affect the interferences (however, corrected for by the instrument...), we do not expect significant amount of nitrite/HONO/other interferences forming HONO in the instrument in or on the particles since (a) the Henry's law constant of HONO in aqueous solutions (water, salt, acids) are low (see above) and (b) the partitioning of HONO to an organic surface is very low. In an earlier study, we were not able to detect adsorbed HONO on anthracenetriol (which could be considered as a proxy for HA) (Arens et al., 2002). This latter aspect will be added in the revised manuscript.

4)Surface area measurement

This sentence refers to a measurement of the total particle charge of one polarity after establishing charge equilibrium in a bipolar ion source. This method is used in addition to the SMPS, but provides high time resolution. From comparing the two signals, we know that this charge is proportional the aerosol surface area obtained by the SMPS within the range of aerosol concentrations used in such experiments. We will add a sentence to state this more explicitly.

5)Overall reaction

In the revised manuscript we will mention more explicitly that reaction (R1) is not representing the hydrolysis of NO_2 on humid surfaces, in which HNO_3 is formed. In contrast, R1 is a redox-reaction of NO_2 with organics, in which no HNO_3 is formed but a HONO yield near 100

6)Effect of photolysis

NO_2 was measured before the aerosol reactor, and HONO was measured behind the aerosol flow reactor (the second chemiluminescence detector at the reactor exit was only used for quality assurance purposes in these experiments; the change in NO_2 concentration due to photolysis was too small to be detectable). This will be described more clearly in the revised experimental section. Thus, photolysis of HONO will lead to higher production of HONO in the flow reactor than measured, while photolysis of NO_2 will lead to lower mean concentrations than measured. This leads indeed to an underestimation of k due the loss of both NO_2 and HONO, as correctly mentioned in the text.

7)Deactivation by OH

Possible deactivation of the surface reactivity by heterogeneous OH reactions will be mentioned in the revised manuscript.

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.

George, C., Strekowski, R.S., Kleffmann, J., Stemmler, K., and Ammann, M.: Photoenhanced uptake of gaseous NO_2 on solid organic compounds: A photochemical source of HONO?, Faraday Discuss., 130, 195-210, 2005.

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.