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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 #4

Received and published: 10 April 2007

This paper describes laboratory experiments to assess the potential for conversion of NO2 to HONO on submicron humic acid aerosol particles in the presence of visible and near-UV radiation. This topic is of great importance to atmospheric chemists as until recently sources of HONO were a mystery, and small concentrations of HONO can greatly alter the HOx budget.

I find the paper to be well written, the experiments carefully described, and the conclusions in concert with the reported results. The paper should be published as is or after a few issues are addressed.

Major Comments:

1. Are the nebulizing solutions colloidal or homogeneous, i.e., is there an insoluble

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component in the Aldrich humic acid? If so, the nebulization of the humic acid solutions likely enhances water soluble component in the particles, correct? Would this component exhibit the same photoreactivity as the whole mixture? This issue might also apply to the interpretation of work by Gysel, et al and Badger et al on humic acid humidograms if the aerosols were generated from an aqueous colloidal solution.

2. In noting that their extrapolations to HONO production on aerosols in the atmosphere yield upper limits, the authors could include, again, that the Alrich humic acid used to derive the production rates may have a factor of 10 greater photoreactivity towards NO2 than typical humic substances in ambient aerosols. This difference in photoreactivity is at least implied on page 4038, although the photoreactivity of humic acid like substances in ambient particles to NO2 has not yet been tested.

Minor Comments

1. The model predictions are referred to as "dashed-lines" in Figures 2-5 in the text (line 18, pg 4047). I don't see a model fit in Figure 2, and the line in Figure 4 does not appear dashed in my printout.

2. Does the ozone/OH (Xox) concentration scale linearly with the NO2-initial? What's a typical ozone concentration in the flow tube during illumination, can this estimate be used to assess either the lifetime of Ared or the potential for competitive absorption by O3?

3. Are the values of the Langmuir-Hinshelwood fit parameters reasonable (i.e. are they similar to those determined for NO2 on similar surfaces?) I'm wondering if you can make a stronger conclusion as to the mechanism driving this process.

4. The opening sentence of the paragraph starting on line 20 of pg 4047 is confusing. The paragraph is not so much about the model as it is about the dependence of HONO production rate on wavelength. I would delete this sentence.

Other miscellaneous typos:

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pg 4044, line 5, change "...on the humic acid aerosol increases not linearly" to "...on the humic acid aerosol does not increase linearly".

pg 4049, line 29, change "efflorescence" to "effloresce".

pg 4052, line 22, change "...in the ground near atmosphere" to "...in the near-ground atmosphere"

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