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Atmospheric
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Discussions

Interactive comment on "Secondary aerosol formation from atmospheric reactions of aliphatic amines" *by* S. M. Murphy et al.

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General comments:

The present paper by Murphy et al. is a good and conclusive presentation of the state of the art of secondary organic aerosol formed from amines. It further elucidates several possible production pathways by a number of smog chamber studies with a change in conditions, i.e. photooxidation, ozonolysis and nitric acid reactions. The authors have investigated several amines and the aerosol composition by two instruments: (a) a PILS-ion chromatograph and (b) a c time of flight-aerosol mass spectrometer.
The study is well done and points out the high complexity of a smog chamber sys-

tem, with some of the compounds measured and others derived by indirect methods (e.g. OH). The latter applies especially for parameters such as the 'effective density'. Therefore, some of the results rely on the method of interpretation and might change in the future with further available tools to confirm or disprove some of the assumptions made. This is a common feature for all the secondary organic aerosol studies conducted so far. All of the experimental results shown are of great interest and provide more details on the previously neglected formation of secondary organic aerosols close to the sources of aliphatic amines (animal husbandry for example).
Because of this I like to congratulate the authors for their conclusive study. If the smog chamber results can be applied to ambient conditions, will depend on the ability of the results to be 'downscaled' to ambient concentrations and the prevailing aerosol composition (acidic or not). Again this is a common feature of all smog chamber studies.
However there are some minor topics, which require correction, and some issues, which I failed to understand in detail and hope for assistance by the authors to clarify them.

Specific comments:

1) At several locations in the paper it is being mentioned that gaseous aliphatic amines are oxidised by acids (nitric acid, sulphuric acid), ozone and OH, which are all investigated within this study. However, it is said once (p. 299, l. 4-6) that oxidation occurs by the nitrate radical as well, as I would have expected. This would act complementarily to OH, one oxidizing during night time (NO_3) and the other one during day time. The participation of NO_3 in the atmospheric oxidation should be mentioned already in the introduction section, in which a more general overview is given. However the reactions investigated can certainly be high lightened.
2) In the experimental section the supply of H_2O_2 solution is explained. Therefore, the

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Discussion Paper

air has been bubbled through a H_2O_2 solution and afterwards any present solution droplets remaining in the gas-phase have been extracted by a particle filter (Kroll et al., 2006) to avoid liquid phase reactions of amines. How does this filtration affect the H_2O_2 gas-phase concentration, i.e. how much H_2O_2 was removed from the air stream by that and how did the liquid film on the filter (extraction of droplets) affect the gaseous H_2O_2, which might get dissolved into the extracted droplets on the filter surface? Did the authors check the H_2O_2 concentrations within the chamber by other methods to confirm the estimated OH concentration for SOA production? This could significantly impact on the conclusions of OH derived aerosol yield.

3) Moreover propene was introduced in some experiments as an alternative OH source, which results in some side products (radicals etc). Is it possible that these influence the results? This kind of behaviour of different OH sources is known for alkene oxidation smog chamber studies for a long time (e.g. Seinfeld and Pandis, 1998).

4) A very interesting topic is the wall deposition rate, which depends not only on the gas but also on the particle size. Did the authors use any unreactive tracer to be able to estimate the gas-phase losses?

5) p. 301, l. 3: "...the voltages of the cToF-AMS are tuned towards the vaporizer". If I get it correctly the voltage of the AMS was adjusted in that way so that it became nearly identical to the voltages of the vaporizer (PILS-IC instrument). Please reformulate to make this clear.

6) p. 320p: It is stated that the effective density of the aerosols produced during ozone reactions was larger than the one during photooxidation. I am somewhat afraid of using this technique to conclude about the density. Could it be that some products get destroyed during analysis (depending on the instrument technique) and the obtained effective density is more a detection efficiency? I am aware that my statement is rather speculative.

7) p. 306, l. 28: It is being hypothesized that salts are probably 'trapped' inside an external layer of oxidised aerosol. However, if the aerosol phase is rather liquid like

and the products have various functionalities, I would assume a reasonably well mixed solution. Would it be possible to have a heterogeneous reaction of gases on the aerosol surface forming products re-evaporating later on, which is prevented by a thin layer of organic products only (less soluble) and thus no salts?

8) Table 3 (p.331): There is a big 'jump' between dimethyl and trimethyl ammonium nitrate by 5 orders of magnitude (values taken from Cottrell and Gills (1951)). Does this reflect problems with high uncertainty in some older publications or is this only due to the different functionality?

9) Figure 6 (p. 339): There is always mixture of ozone and OH in the experiments due to presence of NO_x. How did you cope with, when distinguishing between aerosol yield by each of them? Have you added e.g. ethene in one of the experiments to suppress the influence of ozone?

10) (9 continued) Table 4 (p. 332): It is shown that OH derived aerosol production is larger than the ozone derived one. This is in contrast to the observations for alkenes, which are certainly different in chemical properties. Nevertheless, in Figures 9-11 it is apparent that at the same time as ozone rises the aerosol volume increases remarkably. Wether this is due to OH or due to ozone reactions remains speculative, when we have no detailed information about the processes leading to condensable compounds. Is the OH yield of ozone + amines known?

Technical corrections:

The specific comments are mainly caused by typos.

p. 291, l. 27: insert: "... found a significant increase **in** the rate of..."

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p. 293, l. 4: delete ‘from’ and insert ‘light range’ after ‘the ultraviolet’.

p. 293, l. 5-8: Change ‘Coupled’ to ‘coupled’.

p. 294: Don’t explain PILS-IC twice within 9 lines.

p. 308, l. 14: There is a missing bracket - “**(**Angelino et al., 2001....”

p. 314, l. 7: typo - 5.4 Methylamine (MA) photooxid**ai**ton

p. 324: reference Chase, M.W. Please check the year and remove one of the two given .

references: several locations: Please check for capitals within the publication titles.

Several places in Tables : ‘NA’ is used but not explained. Is this a reference to nitric acid (NA - nitric acid)?

Table 2 : Experiments 28 and 29 - Only NO/NO$_2 ratioofNO_2wasgivenwithoutanymixingratio.Ifnotavailablepleaseindicat$

Figure 2 (p. 335): ‘550$^\circ C'insteadof‘550C'$.

Figure 5 (p. 338p): Where does the OH group in the lower right (below amide) come from? Is there a further oxidation process? If it is an intramolecular rearrangement, rename for example R1 to R’1. There are several locations in A and B, where this

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might apply.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 289, 2007.