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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.

S. M. Murphy et al.

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We want to express our appreciation to Dr. Bonn for writing an in-depth review that raises many interesting questions and has enabled us to clarify several important issues within the paper. Answers to the specific issues raised by Dr. Bonn are given below.

1.) Mention of the possible role of the nitrate radical in amine oxidation has been added to the introduction and in the discussion. The discussion is rather limited given that, to our knowledge, there are no publications addressing the rates of reaction, or products for reactions between amines and the nitrate radical.

2.) The concentration of H2O2 that is introduced into the chamber using these methods was calculated during the Kroll et al. (2006) study using the following method:

“The concentration of H2O2 is not measured directly, but from the rate of isoprene decay during irradiation, and literature values of sigma_H2O2, K_OH+isoprene,and K_OH+H2O2,[H2O2] is estimated to be ˜3-5 ppm; this may decrease somewhat over the course of the experiment due to wall loss, photolysis, and reaction with OH.”

We have never attempted to measure the concentration of H2O2 in the supply air stream before the particle filter and it is likely that the concentration of H2O2 changes when it passes through the particle filter. Measurements of the OH concentrations created in the chamber by H2O2 injected in this way have been repeated recently using hydrocarbons other than isoprene. These recent measurements indicate that the concentration of OH is approximately constant from one experiment to the next and that the concentration of OH produced is relatively insensitive to the exact amount of time that H2O2 is bubbled into the chamber (a result of the OH + H2O2 reaction limiting the maximum possible OH level). Because we were unable to measure gas-phase amine concentrations, we were unable to directly calculate the concentrations of OH and H2O2 in the current experiments, but we feel confident that they are similar to those found in Kroll et al. (2006).

It is also important to note that if reaction with OH was the only route by which amines could form aerosol, and if wall losses of gas-phase species were negligible, the exact concentration of OH would be unimportant because the final equilibrium yield should be constant regardless of how fast the amine is oxidized. Clearly, in these studies, there are many competing reactions, including reaction with nitric acid, ozone and loss of intermediate oxidation products to the walls. Because of these competing reactions, the relative concentrations of OH, NOx and ozone may be important in determining the yields for specific experiments. We emphasize that the yields given in this paper should be viewed more in the context of which amines have the potential to form aerosol than exact measures of the aerosol yield for specific amines.

3.) For the high NOx experiments, we used three different systems to oxidize the amines: H2O2, NOx with Propene, and NOx alone. We did not measure significant

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differences in the aerosol composition generated by these three different systems with either the ToF-AMS or the PILS. We did find that the yields were higher when H2O2 was used which we attribute to the formation of higher concentrations of OH resulting in faster reactions and less time for wall-loss of gas-phase compounds. It is possible that introducing propene causes different gas-phase chemistry and there may also be different gas-phase reactions occurring in the H2O2 experiments than in the experiments with NOx alone, but if there is different gas-phase chemistry, it does not appear to significantly affect the products formed in the aerosol phase. To be complete, it is always possible that the ToF-AMS is unable to differentiate compounds that are structurally different but have similar chemical compositions.

4.) We agree that the topic of gas-phase wall loses is very interesting and relevant to all chamber studies. We did not use an unreactive tracer gas to estimate gas-phase losses. It is unclear which, if any, unreactive tracers might accurately represent the physical characteristics (vapor pressure, etc.) of amines and amine oxidation products. Also, if such a tracer was found, it would probably possess the same properties which make measurement of gas-phase amines difficult.

5.) We have rewritten this section of the paper to clarify it. We also give a brief explanation here. The last paragraph of section 4.1 discusses the observation that amines are ionized on the high temperature vaporizer of the ToF-AMS. Signals from the ToF-AMS are only quantifiable if detected ions are created by electron impact of molecules in the gas phase after particles are vaporized. If ions formed on the vaporizer (as opposed to by electron impact) are detected, the calibrated ionization efficiency will be incorrect and there will appear to be more mass than there actually is. This problem can be avoided if the voltages that extract ions into the flight chamber of the mass spectrometer are set to only allow ions that are far from the surface of the vaporizer to be extracted. These ions that are far from the surface of the vaporizer are created exclusively by electron impact. On the other hand, if the voltages are set to allow extraction of ions that are near the vaporizer surface, ions created on the vaporizer will be extracted in addition to ions created by electron impact and incorrect mass loadings will be calculated.

This effect relates to the PILS-IC measurements only to the extent that we try to compare loadings measured by the ToF-AMS with those measured by the PILS-IC throughout the paper. The loadings of aminium nitrate salts measured by the ToF-AMS will only agree with the loadings measured by the PILS if the extraction voltages on the ToF-AMS are set to only extract ions far from the vaporizer.

6.) The referenced paragraphs on effective density focus on triemethylamine (TMA) and triethylamine (TEA) because these are the only two amines that formed significant non-salt aerosol when oxidized by OH or ozone. To be clear, the statement made in the paper concerning effective densities is that the aerosol formed during ozonolysis of TEA and TMA is of a higher effective density than the effective density of the nitrate salts of these compounds (TEAN and TMAN). During photooxidation, the density of the aerosol increases as the nitrate salt revolatilizes and more oxidized aerosol condenses. The effective density of the non-salt aerosol formed during photooxidation is similar to the effective density of the aerosol formed during ozonolysis, and both types of oxidized aerosol have higher effective densities than the nitrate salts.

The way in which the effective density is calculated using the ToF-AMS and DMA distributions, makes it highly improbably that this effective density would be incorrect because some of the aerosol was destroyed during analysis. To calculate an effective density, all that is required is that some fragment ions of the aerosol components are detected, which allows for the calculation of the mass of the parent molecules (Jimenez et al 2003). Even if a very large molecule is severely fragmented, either thermally or by electron impact, this will not change the calculated effective density. One potential way that the effective density could be compromised is if particle size or compositions affected bounce on the vaporizer. If this occurred, the mass distribution from the ToF-AMS would not have the same shape as the volume distribution from the DMA and it would be difficult to calculate an effective density at all. We observe that the mass and volume distributions agree closely with one another.

It is important to remember that these are effective densities and not material densities. It is very possible, in fact probable, that the nitrate salts have non-unity shape factors, similar to the non-unity shape factor observed for ammonium nitrate (Jayne et al., 2000). If this is the case, the observation that the effective density of the oxidized aerosol is greater than the effective density of the salt may not mean that the material density is greater, but that the shape factor is different. The main use of the effective density in this paper is to show that there are physical changes occurring within the aerosol. These physical changes could be the filling in of void spaces, condensed material making the particles more spherical, or an actual change in material density.

7.) At the low RH of these experiments, the aminium nitrate salts are probably solid particles with a defined crystal structure. We proposed that as oxidized organic material condenses onto these solid salt particles, it might form a layer that prevents the salt from equilibrating with gas-phase amine and nitric acid. This is merely a hypothesis and as reviewer number 2 has pointed out, it is relatively improbable that the organic layer would be organized enough or thick enough to prevent diffusion on long time scales. Thus it may simply be different dissociation constants and gas-phase concentrations of amine and nitric acid that are causing the different amines to show different behaviors with respect to salt re-volatilization. The manuscript has been revised to reflect this.

8.) This is probably caused by the uncertainty in the heat of formation data from Cottrell and Gill. The dissociation constant for trimethylammonium nitrate based on the Cottrell and Gill data is probably incorrect because it is dramatically different than all other calculated dissociation constants, though we will not know conclusively until more accurate thermodynamic data are obtained.

9.) We have not used ethene or any other ozone scavenger in our experiments. It would be interesting to do this and to observe the change in yield that result, though this is beyond of the scope of this paper which is intended to be a first look at aerosol forming potential of amines. We did not attempt to differentiate between aerosol formation from reaction with OH and reaction with ozone in the photooxidation experiments, though it is clear from the mass spectra shown in Figure 14 that the aerosol phase products generated during photooxidation are distinct from those formed during ozonolysis.

10.) We agree completely that the contribution of ozone to the photolysis yield remains ambiguous. To out knowledge, the OH yield of ozone + amines has not been reported in the literature.

Technical Corrections: All of the corrections given by the reviewer have been implemented in the revised manuscript, including a more detailed description of the reactions in Figure 5. The OH group in the lower right (below amide) is from further oxidation of the amide.

References

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