

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 reviewer #2 for an insightful review that has improved the manuscript. Answers to the specific issues raised by the reviewer are given below.

REFeree: In the experimental section (section 2, page 293), it is stated that the concentration of the amine is estimated through the volume of amine injected. This assumes that the volume of the chamber is always 28 m³. How accurate is this? Is this uncertainty taken into account when calculating SOA yields? Or is this uncertainty small compared to all others?

AUTHORS: In numerous previous studies conducted by our group, the reactant concentration measured by gas chromatography with flame ionization detection (GC-FID) is

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consistently within approximately 10 percent of the concentration calculated assuming a chamber volume of 28 cubic meters. The measured concentrations are nearly always lower than the predicted which is assumed to be the result of reactant loss to the walls of the chamber and tubing, but could also be the result of the chamber volume being incorrect. The uncertainty of the chamber volume was not addressed when calculating SOA yields given that the yields presented are acknowledged to be approximate and presented solely to show which amines have potential for oxidative yield.

REFEREE: In equation (1), d (delta) is defined as being the internal void fraction. It is then stated the effective density is that of the material (I assume this is ρ_m ? This needs to be defined.) if this parameter has a value of zero. However, based on equation (1), if $d = 0$, the effective density should be infinite. Should the term in the equation be $(1-d)$?

AUTHORS: The reviewer makes a good point that delta is poorly defined in the paper. The correct definition of delta is given in Decarlo et al. (2004) to be:

$$\delta = (\rho_m / \rho_p)^{1/3}$$

where ρ_m is the material density and ρ_p is the particle density. This definition of delta has been added to the manuscript. The reviewer correctly points out that delta must go to 1 as the void space approaches zero, which this properly defined delta does.

REFEREE: I would suggest moving the discussion of reaction pathways associated with Figure 5a-c to section 3 where the atmospheric reaction pathways of amines are discussed. This would clearly necessitate the renumbering of figures.

AUTHORS: Though we see the reviewer's point that Figure 5 and the associated discussion could fit well in section 3, after detailed consideration we have decided not to move the figure or the discussion. Our rationale is that section 3 is meant to be a brief overview of general reaction pathways of amines. We feel that moving Figure 5 and

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the associated discussion into section 3 would distract the reader with too many details and disrupt the general flow of this part of the paper. Also, we feel that it is beneficial for the reader to see figure 5 directly before the discussion of the chemical results, in which we reference the figure many times. We have added a note to section 3 letting the reader know that details of the oxidation pathway will be covered in more depth in section 5.

REFEREE: In section 4.2, should the statement ‘typically assumed to be the dominant atmospheric nitrate salt’ (referring to ammonium nitrate) be qualified? This is only true in areas with sufficient ammonia to neutralize sulfate. In areas where this is not the case, the dominant form of nitrate appears to be that associated with soil or sea salt. This could also be qualified by referring to the dominant FINE nitrate salt.

AUTHORS: We have added the term “fine” to the statement.

REFEREE: In section 4.4, would it be possible to derive a time-dependent collection efficiency so that the sulfate data from the PILS and the AMS match?

AUTHORS: First, it is important to note that the ToF-AMS mass loadings shown in Figure 4 have already been multiplied by a collection efficiency which causes the cToFAMS sulfate loadings to match the PILS-IC sulfate loadings at the beginning of the run when there was nothing in the particle phase other than ammonium sulfate. Deriving an additional, time-dependent, collection efficiency to force the sulfate loadings from the cToF-AMS to match the sulfate loadings from the PILS-IC throughout the experiment is rather straightforward and can be done by simple division of the cToF-AMS and PILS-IC results. The time-dependent collection efficiency curve for sulfate derived in this way is approximately a step function, increasing when the amine is injected. The problem with this approach is how to apply the derived time-dependent collection efficiency to species other than sulfate. The DMA data show that there are new methylammonium nitrate particles formed when the methylamine is injected, creating an external mixture of particles in the chamber (this is also confirmed by the mass distribution measured

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by cToF-AMS). The external mixture initially consists of methylammonium nitrate, ammonium sulfate and methylammonium sulfate. The collection efficiency derived using sulfate loadings clearly cannot be applied to the methylammonium nitrate and because the size distributions of the nitrate and sulfate particles overlap, one cannot use size to determine what fraction of the methylammonium is associated with nitrate versus sulfate. One could make assumptions about the molar ratios of sulfate and nitrate to methylammonium in the particles and proceed to apply the sulfate derived collection efficiency to the fraction of methylammonium believed to be associated with sulfate, but we feel that doing this only obfuscates the results. Thus, though possible, we have decided not to utilize a time dependent collection efficiency. In addition to minimizing the data manipulations, leaving the data in its current form places emphasis on the fact that the physical properties of the particles change when ammonium is replaced by methylammonium causing less bounce off the vaporizer surface of the cToF-AMS.

REFeree: In some cases, the authors see that the original salt continues to disappear after the formation of oxidation-induced SOA. In other cases, the original salt does not disappear. Wouldn't these results argue that the dissociation constant, not a coating, controls the dissociation? This is an important result that influences our understanding of heterogeneous processes and should be highlighted. Could this be explored a little more by investigating how thick an organic layer might be present to see if this is a relevant parameter?

AUTHORS: The reviewer is correct that the observation that some salts do not return rapidly to the gas phase may be the result of these salts having smaller dissociation constants than those which do re-volatilize. Because of the uncertainty in the thermodynamic calculations it is not currently possible to say if the thermodynamics are controlling the system or if some other factors, perhaps an organic coating or condensed organics mixing with the salt, are playing a role. We recognize that an organic coating might not present enough of a mass transfer barrier to prevent equilibration on the time scales of this experiment (hours). We have modified the discussion to empha-

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size that it is probably thermodynamics and not organic coatings that are causing the salt to remain in the particle phase. We have also added comments on the thickness of the organic layer formed. One final consideration is the concentration of nitric acid in the system. Though we attempted to have equivalent levels of NO_x and OH in all high NO_x experiments, we did not directly measure nitric acid and it is possible that slightly higher levels were formed in some experiments than others which may have affected how much salt remained in the particle phase.

REFeree: Could relevant effective densities be included in the summary results presented in Table 4?

AUTHORS: The relevant effective densities have been added to the revised manuscript.

REFeree: In Figure 5a, it could be included how the amide is converted to the relevant acid.

AUTHORS: The exact mechanism of conversion of aldehydes to acids in atmospheric systems is not well understood. The proposition of this step is a hypothesis which agrees with some of the fragment ions observed in the cToF-AMS not a definitive conclusion. Accordingly, a “?” has been added to the arrow showing this further oxidation of the aldehyde.

Technical Corrections: All of the corrections given by the reviewer have been implemented in the revised manuscript, including a more consistent use of the term SOA.

References

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, *Aerosol Sci. Technol.*, 38(12), 1185-1205, 2004.

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