

Interactive comment on “Secondary organic aerosol formation from primary aliphatic amines with NO₃ radical” by Q. G. J. Malloy et al.

Q. G. J. Malloy et al.

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Response to Reviewer 1 of "Secondary Organic Aerosol formation from primary aliphatic amines with NO₃ radical" By Q.G.J. Malloy

The authors would like to thank the reviewer for their helpful and insightful comments concerning the manuscript. The manuscript has been greatly reworded and references added to enhance its clarity and provide a more insightful analysis of the data presented. Particular attention was given to highlighting the role of NO₃ chemistry and clarifying the proposed ion structures as well as providing justification for the proposed reaction mechanism.

Referee Comment: "According to the title, the manuscript deals with SOA formation from reaction of amines with NO₃; however, the authors immediately set out

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to introduce reaction of aliphatic amines with OH (Page 12696 Line 26) without any further mention of NO₃; a theme which continues throughout!"

We have modified the introduction to reflect the lack of previous work with NO₃ and amines. We have also added a statement (page 2 line 14) indicating that NO₃ oxidation is thought to follow the same route as the hydroxyl radical.

"Little work has been done on the NO₃ initiated oxidation of amines, however, it is thought to follow that of OH and ..."

We have also revised Figure 1 to reflect the oxidant study in this paper.

Referee Comment: "The notation for many of the ions is vague and structurally uninformative: Here are a few examples. I stress that this is a pervasive problem in this document that will not be remediated by only correcting the few demonstrative examples presented below."

The author has added a table for each amine studied, reflecting the structure associated with the ions mentioned throughout the manuscript.

Also, as requested information and references concerning the formation and stability of carbinolamines have been added.

Referee Comment: "Were experiments in the chamber run under "true" dark conditions or in room light with the black lights off or . . . ? This should be stated explicitly in the manuscript."

We have added a comment to indicate that all experiments were performed under completely dark conditions.

Referee Comment: "Filter extractions for HPLC-MS analysis were performed with water only. Is there any efficiency data for the extraction process? Why was a non-polar solvent also not used to extract hydrophobic products? Could this be a reason for the "lack of certain peaks?"

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The authors acknowledge this could account for some of the missing peaks in the HPLC. Water was initially used as the extraction solvent for these experiments based on the assumption that salt formation was expected to dominate the particulate matter. Clearly this was not the case. We have added a statement to the paper reflecting that extraction by water alone would not extract the hydrophobic compounds formed in the chamber. (page 8 line 23-24).

"The absence of peaks corresponding to m/z 128 and m/z 146 in the AMS spectra could be due to the use of water as the only extraction solvent, causing hydrophobic compounds to remain on the filter."

Referee Comment: "Would it be more accurate to say that particles are accelerated by the aerodynamic lens into a time-of-flight chamber."

The manuscript has been reworded to reflect the acceleration of particles through the aerodynamic lens.

Referee Comment: "The authors cite DeCarlo et al (2006) in regards to the details on the High Resolution Time of Flight Aerosol Mass Spectrometer (AMS). There was no corresponding reference. The author's probably are referring to DeCarlo et al., Anal. Chem. 2006, 78, 8281-8289."

The reference has been added.

Referee Comment: "(Section 2.3) This section should be omitted because the method did not produce any usable results pertinent to the discussion. Perhaps mention could be made in the text that PTRMS was tried but did not produce measurable ion signals."

Section 2.3 has been removed. A mention in text to the fact that the PTRMS was unable to produce measurable ion signals was added (page 4 line 4-5)

"PTRMS measurements of the parent amine were also attempted; however no measurable ion signals were detected."

Referee Comment: "Is it possible that the nitramines and/or nitrosamines were in fact formed but decomposed in the measurement? Were standards run to demonstrate that these compound classes could be measured directly with the AMS? In other words, was any work done to investigate the stability of the nitrosamine/nitramine products with 70 eV electrons?"

Evidence for the formation of nitramines and /or nitrosamines was not present. We have added more information to section 3.1 to reflect this lack of evidence.

"This mass spectrum can also rule out formation of nitrosamines since there is no apparent ion at m/z 44 or strong molecular ion (m/z 60 $\text{CH}_4\text{N}_2\text{O}^+$) as would be expected (Rainey et al., 1978). The formation of nitramines are more difficult to identify due to the strong NO_2^+ signal associated with them could be attributed to the corresponding ammonium salt. In this case, the formation of nitramines would be accompanied by their relatively strong molecular ion peak as reported by Bulusu et al. (Bulusu et al., 1970). The expected molecular ion for methyl nitramine would be seen at m/z 76 ($\text{CH}_4\text{N}_2\text{O}^+$), as seen in figure 3, no such ion exists."

We feel this added information and the corresponding references are enough to rule out formation of nitramines and /or nitrosamines. This same information can be used to rule out formation of nitramines and /or nitrosamines for all the amines studied.

Referee Comment: "the authors state that there are "few higher mass fragments" but there clearly are higher mass fragments present and these appear to be consistent with the other spectra (although at different intensities)."

The author agrees with the referee and information such as empirical formula and structures proposed for the ions are given for methylamine (page 6 line 10 and Figure 4). The higher mass fragments for other amines are already mentioned and their structures were added to their respective table of proposed ion structures.

Referee Comment: "(Section 3.1) This section is poorly written and should be

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made clearer. Particle formation immediately after injection into NO_x ? into chamber? If the amine is injected into a clean chamber, how is methylammonium nitrate formed? What is the source of acid? (Same question for initial particle formation in reaction of other amines studied)."

Section 3.1 has been extensively rewritten to avoid confusion in the future. Formation of particles upon injection of the amine into the chamber has been proposed to be the ammonium salt of the parent amine. It is thought that trace amounts of NO_x exist in the chamber despite all efforts. It is this trace amount of NO_x that is thought to react with the amine directly forming the corresponding ammonium salt. The authors have added this to the paper and listed the detection limits of the NO/NO_x and ozone analyzers (page 4 line 3) to give the reader some idea what the highest limit of "trace amount" is.

Referee Comment: "Is it an obvious conclusion that absence of NO and NO_2 signals from the AMS spectra necessarily indicates organic aerosols? If so, a suitable reference should be provided for the readers that are not experts in AMS data interpretation."

A reference has been added and discussion is given to support the conclusion that large NO and NO_2 signals are associated with ammonium salts (page 10 line 19).

"Additionally, using the high resolution capabilities of the AMS, we can exclude the corresponding salts as a significant portion of the aerosol formed due to the small contribution of NO^+ and NO_2^+ to the total aerosol signal (Fig. 15), which are expected to be present during the presence of ammonium salts (Murphy et al 2007)."

Referee Comment: "This is the first instance where the authors discuss the carbinolamine intermediate. The carbinolamine ($\text{C}_4\text{H}_{12}\text{NO}^+$, in the authors' notation) is referred to as being stable several times in this document - is this a commonly observed product in mass spectrometry, how is it known to be stable? A few references on this carbinolamine and/or its corresponding ion are in order."

More discussion is given the presence of the carbinolamine compounds present since these are not commonly encountered products. (Page 7 line 13-19)

"The presence of carbinolamine compounds is not wholly unexpected as they are an intermediate compound to imine formation via reactions between carbonyl compounds and primary or secondary amines; a more in depth discussion of their formation is given later. These compounds have been observed as intermediates in other carbonyl-amine reactions and have been shown to have a slow reverse reaction, remaining stable in solution for up to 24 hrs. (Cheung et al., 2005, Cocivera et al., 1976, Pedersen et al., 1999)."

In addition, we have expanded the proposed reaction figure (figure 16) to include a more precise picture of carbinoalmine formation.

Referee Comment: "Some discussion should be provided as to why the amide peak is not expected in the methylamine system, yet is measured in the spectra of the other amines."

This information and appropriate references have been added to section 3.5 (page 9 line 6-11)

"This observation is partially supported by examination of bond dissociation enthalpies of hydrogen attached to the alpha carbon of aliphatic amines as reported by Lalevée, who noticed a slight decrease in energy as the alkyl chain increased in carbon number (Lalevée et al. 2002). However, this minor change cannot fully explain the tendency for only ethyl, propyl, and butylamine to form amides and further exploration into this issue is necessary."

Referee Comment: "The authors state that O₃ was added after particle formation had reached a steady-state. Are they referring to particle mass? Clearly this is not the case with particle numbers. This should be clarified."

The authors have revised the manuscript to clearly indicate that ozone was added after

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particle *mass* had reached a steady state (page 4 line 10)

"350-400 ppb of ozone was introduced by passing 20 psig of pure air through two UV ozone generators only after the mass concentration of particles formed from initial injection of the parent amine had reached a steady state (2 hrs)."

Referee Comment: "Figure 12 does not correspond with the text...."

This figure (figure 16) has been revised for clarity and to reflect the wording of the paper.

Technical comments: All comments in this section have been incorporated into the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12695, 2008.

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