

## ***Interactive comment on “Secondary organic aerosol formation from primary aliphatic amines with NO<sub>3</sub> radical” by Q. G. J. Malloy et al.***

**Anonymous Referee #1**

Received and published: 8 August 2008

### General Comment:

This work details the experimental results of secondary organic aerosol (SOA) formation by the oxidation of gas phase primary amines. The results and implications of this paper, which show potentially environmentally impacting routes to organic nitrogen in particulate matter are well within the scope of ACP; however, the level of interpretation of the data presented is very limited and much more analysis and improvements in the clarity of the writing are necessary before I would consider it worthy of publishing.

### Specific comments:

According to the title, the manuscript deals with SOA formation from reaction of amines with NO<sub>3</sub>; however, the authors immediately set out to introduce reaction of aliphatic

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



amines with OH (Page 12696 Line 26) without any further mention of NO<sub>3</sub>; a theme which continues throughout!

I assume that this is based on the assumption that NO<sub>3</sub> is expected to be the nighttime equivalent of OH radicals and are thought to proceed by the same reaction pathways. If this is the case and the author is using these interchangeably, a clear and definite statement needs to be made to this effect. Otherwise this whole paper really appears to be about OH oxidation in the presence of NO.

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.

From Section 3.2 in Malloy et al.:

ex. "... tentatively been identified as a hydroxyl containing imine (C<sub>4</sub>H<sub>10</sub>NO<sup>+</sup>)". As written, it is not clear that this is a hydroxyl compound – this looks like a nitrosoalkane. The author needs to present a clearer representation of this ion, and ideally a mechanism of its formation.

ex. "... and the stable carbinolamine (C<sub>4</sub>H<sub>12</sub>NO<sup>+</sup>)". Again, as depicted, this ion looks like a nitrosoalkane not a carbinolamine. Also, many readers may not know what this class of compounds is, or that they are reaction products between amine and carbonyl compounds. This should be noted or discussed. It would be beneficial for the authors to make their own adaptation of Figure 1 (Schade et al. **1995**, J. Atmos. Chem. **22**, 319-346), using some of the reactants from their studies. They could, for example, show the formation of carbinolamines from aldehydes generated from imines that are formed *in situ*.

P 12698: 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.

P 12698: Filter extractions for HPLC-MS analysis were performed with water only. Is

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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?”

P 12699, line 16: (Suggestion) Would it be more accurate to say that particles are accelerated by the aerodynamic lens into a time-of-flight chamber.

P 12699, line 14: 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.

P 12700, 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. If the authors feel strongly that this section should be kept in the manuscript, some justification should be given. Also, they report that they cannot detect the parent amines by proton transfer reaction mass spectrometer (PTRMS), despite the proton affinity of primary aliphatic amines being greater than water. In light of this, some details on the conditions of the PTRMS should be provided especially in regards to the pressure of the drift tube. Can this pressure be changed? The recent work by Tanimoto et al. (International Journal of Mass Spectrometry 263 (2007) 1–11) shows how the optimization of the PTRMS instrumental configuration, with a drift tube pressure of ~5 Torr can increase hydronium ions intensities; suppress NO<sup>+</sup> interference facilitating the observation of volatile organic compounds, including amines (c.f. Figure 7 in Tanimoto et al).

P 12700, lines 17-19: 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? Also, the authors state that there are “few higher mass fragments”

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

but there clearly *are* higher mass fragments present and these appear to be consistent with the other spectra (although at different intensities).

P 12700, Section 3.1: This section is poorly written and should be made clearer. Particle formation immediately after injection into  $\text{NO}_x$ ? 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).

P 12701, lines 20-23: Is it an obvious conclusion that absence of  $\text{NO}$  and  $\text{NO}_2$  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.

P 12701, line 12: 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.

P 12703, lines 13-14: 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.

P 12712, Figure 4, lines 22-23: The authors state that  $\text{O}_3$  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.

P 12720, Figure 12 does not correspond with the text: "... a reaction sequence (Fig. 12) similar to that of formation of a Schiff base. In this reaction, a carbonyl group generated from loss of an alkyl group from the primary amine or belonging to an amide is protonated and subsequently reacts with the parent amine forming a stable carbinolamine intermediate." The authors' could show a nucleophilic attack on a protonated

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

carbonyl by the amine, forming the hydroxyl containing compound. The amine would probably be protonated before the carbonyl group, forming  $R_1NH_3^+$ , which is not nucleophilic.

Technical comments:

P 12696, line 14: should read "... when significant levels OF  $NO_3$  exist."

P12697, line1: Figure 1 only shows two possible routes (contrary to text). Move "(Fig. 1)" to after "The predominant route (Fig. 1)..." as these are shown in the Figure.

P 12697, line1: Delete "most"

P 12697, line 6: Insert "formation OF aldehyde products"

P 12699, line 13: should read "Details of this instrument and data analysis methods HAVE BEEN explained in detail..."

P 12699, line 15: Should this read "50-700 nm"?

P 12699, line 19: Should read "... lenses to the orthogonal extractor, where they are pulsed..." Note that orthogonal is misspelled in the manuscript.

P 12700, line 16: should read "... observed at the beginning OF THE experiment."

P 12701, lines 7-8: should read "... the appearance of high mass... 100.06, WHICH can be... respectively AND which..."

P 12702, line 26: should read "... obtained from a filter sample. AGAIN, many of the same..."

P 12703, line 16: I suggest changing "verified" to "supported"

P 12703, line 17: should read "high resolution HPLC-TOF..."

P 12704, line 16: insert space between "may" and "be"

P 12720, Figure 12: Should read "... only possible with primary and secondary

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



amines.”

## ACPD

8, S5736–S5741, 2008

---

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

S5741

