

Interactive comment on “Secondary organic aerosol formation from reaction of tertiary amines with nitrate radical” by M. E. Erupe et al.

Anonymous Referee #1

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This manuscript describes results from several laboratory experiments examining the dark oxidation of tertiary amines, trimethylamine (TMA), triethylamine (TEA), and tributylamine (TBA). This work is important in that amines represent an important class of organics in the troposphere, and appear to be important precursors of secondary organic aerosol (SOA). The experiments are carried out in a large, well-instrumented chamber, and reported results include those from a scanning mobility particle sizer (SMPS), high-resolution aerosol mass spectrometer (AMS), and proton transfer reaction mass spectrometer (PTRMS). The quality of data is quite high, and the experiments appear to be carefully done. However, the work suffers from a lack of analysis of results; the vast majority of the paper reports the experimental approach (including the operating principles of the individual instruments) and details of the results, mostly

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the key ions detected by the AMS and PTRMS. Only a few paragraphs are devoted to interpretation of results, involving a proposed mechanism that does not fully explain all the observed results (see below). Given the excellent dataset that has been compiled, I think the paper would be greatly improved by more detailed analysis of the evolving PTRMS, AMS, and SMPS data, particularly in conjunction with changing reaction conditions (ozone and NO_x concentrations). Some examples of how the analysis of the SOA formation mechanism could be improved are given below.

(1) The mechanism presented at the end does not seem to describe the observed chemistry very well. The mechanism begins with the reaction of NO₃ with the amine (as described on p. 16594, line 25, and shown in Fig 6). However this does not seem to be the case from the time traces of amine concentration. For both TMA and TEA (Figs 1a and 3a), the amine is rapidly lost when ozone is added, and aerosol is formed, strongly suggesting an ozone-amine reaction (which is also shown in Fig 6). (The OH radical generated will also react with some amine, possibly forming SOA.) When NO is added, amine loss continues, but at the same rate; this suggests that amine loss continues to be by ozone, and not by the nitrate radical (or else the NO₃ formed reacts with amine at the exact same rate). Showing the ozone and NO concentrations as a function of time would help address this.

The large increase in aerosol mass upon NO addition is very interesting. Either (1) the newly formed NO₃ is reacting with the products of the O₃ (or OH)+amine reaction, forming second-generation condensable products, (2) nitrate salt formation is promoted, or (3) the NO is changing the O₃+amine reaction pathway (possibly by affecting RO₂ chemistry). Further analysis and/or additional experiments are needed to distinguish these different possibilities.

(2) Very little information is given on two of the most important peaks in the AMS spectrum, NO⁺ and NO₂⁺ (the nitrate marker ions). Some data are shown for TEA (Figure 4), and it is stated that "Formation of aminium salt with nitric acid was minimal, based on the low intensities of nitrate ions" (p. 16594, line 7). More information is

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needed here, as the data raise several questions:

- It is hard to tell from the spectra (Figs 1b, 3b, 5b) but the m/z 30 peaks seem rather large. How much of this ion intensity is from NO^+ ? A quantitative look at charge balance would be very useful: assuming the NO^+ and NO_2^+ are from nitrate ions, how much mass is this? How much mass of the corresponding aminium ion is needed to balance the negative charge from the nitrate? This would allow for quantification of the importance (or unimportance) of the salts. Does this change with time?

- Figs 3a, 4a and 4c: nitrate aerosol is formed when ozone is introduced to the chamber with gas-phase amine. What causes this "sudden buildup of nitric acid"? Is it a NO_x (or HNO_3) impurity in the ozone?

- Figs 3a, 4b, and 4d: when NO is added to the chamber, the nitrate peaks grow further. Is this additional salt formation? (Or might they be organic nitrates?)

(3) Contrary to expectations, TMA forms more aerosol than TEA. More importantly, while TBA forms the most aerosol, mass yields are lower (due to MW differences). What causes these effects?

Minor points:

- aerosol mass concentrations are reported assuming a density of 1 g/mL. Given both AMS and SMPS data were taken, densities should be calculated. (This may give some insight into the possible importance of aminium salts.)

-AMS spectra seem to include air peaks (m/z 28, 32); these should be removed for reporting the spectra of the aerosol.

- P. 16590: the reaction converting NO to NO_2 should also be shown.

- P. 16592, lines 1-7: the parent ion of TMAO may not be the best one for identification. This can be addressed by atomizing TMAO (which is commercially available) into the AMS, to obtain a spectrum for comparison.

- Throughout the paper, the reported AMS masses are of peaks found, not the exact mass of the ion; this should be stated explicitly somewhere
- p. 16594, lines 14-15: degree of unsaturation of an ion doesn't necessarily equate to degree of unsaturation of the parent organic (particularly in the AMS, with its vaporizer at 600C). For example, branched alkanes have substantial ion signal at m/z 41, 55, 69, etc.
- Fig 3a: The complex amine profile (dropping almost to zero upon ozone addition then recovering) should be described in more detail. If this is from a burst of salt formation, shouldn't aerosol mass have spiked?
- Fig 6: the resonance structure of the TMA oxide should be removed, as it shows 10 electrons around the N; only one structure, with formal charges, is necessary (see Tuazon et al 1994). Also the product after the H-shift is not a radical; the formal charge has switched to the carbon atom.
- Fig 6: several $\text{NO} + \text{RO}_2$ reactions are proposed. Since they react with each other rapidly, NO_3 and NO cannot be co-present in high concentrations; so if NO_3 chemistry is occurring, the RO_2 radicals may be reacting with RO_2 , HO_2 , or NO_3 instead.

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