

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

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1) This reviewer (and the other) bring up the valid point that the tertiary amines are reacting upon interaction with ozone and thus the reaction of NO₃ when NO is introduced may be with an amine-O₃ reaction product and not the amine itself. This was something overlooked in the original version of the paper. We do have incontrovertible evidence that the NO₃-amine reaction forms significant aerosol as we have reacted the tertiary amines directly with NO₃ (via the introduction and thermal decomposition of N₂O₅). We have new figures prepared showing the reaction PTR-MS trace and the SMPS data for a reaction of the tertiary amines with NO₃. However, the reviewers' point that the tertiary amines also react with ozone is valid and under the ozone/NO_x reaction sequence originally described, it is likely that NO₃ is reacting with one (or more) of

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the 1st generation reaction products identified in our original reaction sequence (figure 8). The most likely candidate is the amide, which does show a decrease after the introduction of NO_x (Product 1G from original figure 8) So, to summarize, NO₃ reacts with both the tertiary amines and with the reaction products of the amine-ozone gas-phase reaction to form significant amounts of aerosol. The particulate mass concentrations (and aerosol mass yields) observed from the direct reaction with NO₃ is significantly larger than that of the ozone/NO_x sequence. The fundamental claims of the original paper that NO₃ reacts with tertiary amines are correct, even though the original figures did not make the case adequately. It is still our contention that NO₃ is the key to leading to large amounts of aerosol. However, the mass spectra from the ozone-NO_x-amine reaction and the NO₃-amine reaction look mostly similar in terms of higher mass fragments. There are some differences in terms of lower mass fragments that we think are due to more prevalent RO₂-RO₂ interactions in the direct reaction with NO₃. The greater aerosol yield from NO₃ vs. O₃/NO_x results from a higher proportion of radicals in the case of the h-abstraction by NO₃. From the initiation of the radical chain, we stand by the original reaction sequence to produce aerosol through a hydrogen-shift and production of hydroxyl amides. We note that there were no negative comments about this specific reaction sequence in the original reviews. This proposed sequence explains the spectral similarity in our experiments and the experiments reported by Murphy et. al (2007) for the reaction of trimethylamine with OH and also has an empirical formula consistent with the building block of oligomer formation we saw in our previous work with trimethylamine (Silva et. al, 2008). Effectively NO₃ and OH both lead to the same aerosol products via a hydrogen shift in the alkyl radical chain

2) The reviewer would like more information on the NO⁺ and NO₂⁺ ions to validate the assertion that formation of ammonium salt with nitric acid was minimal. A figure that shows the fraction of total aerosol signal accounted for by NO⁺ and NO₂⁺ (using a high resolution AMS) for each tertiary amine is in the revised manuscript. In all three cases, the signal from NO⁺ and NO₂⁺ is less than 10% of the total aerosol signal. Assuming that all of that signal is due to a nitrate salt of the relevant tertiary amine (as opposed

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to organic molecules that have gained a nitro or nitroso functional group which is also possible), the maximum mass that can be accounted for by nitrate salt in the aerosol sample is less than 20% of the total aerosol mass for tributylamine and even less for the two smaller amines. (b) The high resolution AMS data show that most of the m/z 30 signal is not due to NO^+ , though it is significant. Approximately 2/3 of the signal at m/z 30 is due to the amine fragment, CH_4N^+ , while $\sim 1/3$ is due to NO^+ . We have new figures made to show the time trends of these peaks as well; essentially the amine peak shows up after introduction of O_3 while both peaks grow in after introduction of NO_x . The amine peak is still $\sim 2x$ higher than the nitrate peak after introduction of the NO . this difference. The time trend of the $\text{NO}^+/\text{NO}_2^+$ peaks does change during the experiments to an extent: Obviously neither peak is present after the addition of ozone while both show up after the introduction of NO_x .

3) The reviewer wants to know why the mass yields for TBA is smaller than TEA which is smaller than TMA. For TMA, as stated in the original paper, this amine shows evidence for oligomer formation, both in the AMS spectra and in analysis of filter extracts using LC-MS. This indicates a further reaction step that can take place for TMA and thus create greater amounts of aerosol mass relative to the other two larger compounds. For TBA, the mass yield does appear to be less than TEA but we have no specific explanation for why that may be the case. Both compounds appear to be producing the same type of products in the gas-phase and particulate phase. A specific mechanistic reason for the lower yield for TBA versus TEA is unknown with a variety of factors possible including steric hinderances or the formation of stable intermediates.

4) Minor points (a) We have calculated equivalent densities for the aerosol produced from each amine using the AMS and SMPS data and will include that in a revised manuscript. (b) Air peaks have been removed in all new mass spectra for a potential revised manuscript. (c) The reaction converting $\text{NO} \rightarrow \text{NO}_2$ is included in the revised manuscript. (d) The reviewer is correct that the parent ion of compounds is often not the best for detecting specific compounds in mass spectrometry using EI ionization. How-

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ever, trimethylamine-n-oxide has been atomized previously (See Silva, ES&T, 2008, supplemental information). Only two ions are potentially useful to identify TMAO from TMA salt, m/z 76 (the parent) and m/z 60. Both are low intensity ions and since m/z 60 can come from other hypothesized amine compounds besides TMAO and TMA, we have chosen to use the parent to identify the presence of TMAO. We agree it is not ideal, and have tried to also utilize ion chromatography to quantify TMAO in the aerosol products. (Erupe et. al, 2010, J. of Chrom. A.) (e) AMS masses in exact numbers are provided in the revised manuscript. (f) We agree with the reviewer's comment that the degree of unsaturation of a fragment ion does not necessarily translate to degree of unsaturation of parent organic. Fragment ions can show more unsaturation than the parent as in the cited example of alkanes. However, we are using the fragment ion to put a maximum limit on unsaturation, not the reverse. Since in EI mass spectrometry (even with the elevated temperatures in the AMS) ions do not pick up hydrogen atoms (protonate) during the ionization event (as they would in LDI or other soft ionization methods), the fragment having only one degree of unsaturation tells us that two of the oxygen atoms in the fragment (thus in the parent molecule) have only single bonds. This puts a limit on the number of carbonyl moieties in the molecule and indicates the presence of alcohols, ethers, or esters. Our inclination is that the bonds are most likely alcohols since the hydrogen shift proposed in our reaction sequence is a plausible mechanism resulting in them rapidly and alcohol functionality is known in the secondary aerosol formation community to lead to significant drops in vapor pressure on molecules. We would welcome suggested structures incorporating ether or ester functionality that would be consistent with the mass spectra as well as the rapid formation times observed. (g) The amine profile drops quickly because of gas-phase reactions of the amine with ozone forming compounds such as the amide. There is only a small amount of particle formation and no salt formation at all according to the AMS data for the amine-ozone reaction. (h) Resonance structure for TMAO has been corrected to the zwitterion form. (i) We do not have any NO^+RO_2 reactions in the mechanism. The reviewer is correct that in an NO_3 environment, NO cannot be

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present. For the amine-ozone-NO_x system, we listed an O₃ + RO₂ reaction which has been observed by Carter and others at the UCR smog chamber before, but with the direct reaction of the amine with NO₃, the reviewer is correct that the most plausible mechanism for conversion of the peroxy radical to the alkoxy radical is an RO₂-RO₂ interaction. This is reflected in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16585, 2008.

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