

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.

Received and published: 6 November 2008

The author would like to thank both reviewers for their helpful and insightful comments overall. Since we have previously addressed the first reviewer comments and any short comments arising therefrom, we will only address the concerns given by the second reviewer here. The major trend in comments from reviewer number 2 are in giving further evidence that NO₃ is the actual oxidant in this system. They rightfully point out that the OH reaction is faster than the NO₃ reactions in general. While not shown, we have completed experiments utilizing only the parent amine and N₂O₅ in the dark. These experiments indicate that no particle formation is observed until addition of N₂O₅. Furthermore, the particle formation rate follows the same fast trend as shown in the experiments in the manuscript. A paragraph stating this has been added to the paper in order to give the reader further evidence for the case of NO₃ as the oxidant.

With respect to ozone acting as the primary oxidant in this system, no new particle formation was seen after addition of ozone to the chamber. Time traces of ozone concentrations remain constant during the time period when only ozone and the parent amine are present. The lack of new particle formation and the absence of any change in ozone concentrations indicate that ozone is not the major oxidant in this system. This has already been mentioned by the reviewer in stating that the reaction of ozone with primary amines has been observed to be slow (Tuazon et al), and is known to be slower than tertiary amines by three orders of magnitude (Finlayson-Pitts and Pitts). There is no obvious source of OH in our experiments, which were performed under completely dark conditions, ruling out hydroxyl as the major oxidant.

Other concerns raised by the second reviewer were addressed in response to the first reviewer. Namely revision of both figures depicting the reaction mechanisms of amines, information about the C-H versus N-H bond strength, and the issue of particle formation observed after injection into the chamber with no other oxidants present.

The issue of HONO presence in chambers is well known and can certainly confound results from these types of reactions. However, if nitrous acid (HONO) were reacting directly with the amine one would expect the formation of the diazonium salt. Since we have already addressed the lack of observed salt signal in the mass spectra, we feel confident that this route can be ruled out. In addition to this, if large amounts of HONO were present, it would be observed in our analyzers as NO_x . Our chamber facility has an extremely low NO_x background ($\ll 1$ ppb), for more information about our chamber construction see the paper of Carter et al. 2005.

I am glad to see the reviewer mention reproducibility of our results as this is a major concern in the chamber community. Experiments were conducted in duplicate but were not shown for clarity. Mass spectra and aerosol formation as determined by the AMS and SMPS respectively were similar in all cases.

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

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