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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "The ozonolysis of primary aliphatic amines in single and multicomponent fine particles" *by* J. Zahardis et al.

**J. Zahardis et al.**

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We wish to thank Referee 1 for these well thought out comments and suggestions.

We provide our responses below:

Comment 1) The response to this question should be read in conjunction to the response to comment 4 by Referee # 2. We do not imply in the submitted text that we thought $NO_2/NO_3$ was being generated in the gas phase and being transported as a gas into the mass spectrometer. The $NO_2$ is most likely formed by progressive oxidation of the amine (please see our reply to Comment 1 by Referee 2) to the corresponding nitroalkanes. The thermal degradation of aliphatic nitro compounds, even at room temperature, has been reported [1] and can lead to the formation of $NO_2$, (although we have found no reports reagrding high molecular weight amines like hexadecylamine

and octadecylamine doing the same). The $NO_3^-$ and $NO_3^-HNO_3$ ion signals we report likely arise from nitric acid formed at or near the surface of the particle by the scheme presented on page 14612 of the submitted document and transported into the mass spectrometer on the particle. The text will be revised to make clearer (in R3a, page 14612) that we mean the *particle surface*, not the surface of the flow reactor. We also provide additional references in the Experimental Methods section attesting to the efficacy of the aerodynamic lens to selectively deliver particles to the collection probe in vacuum (e.g., [2-4]). In any case, this comment along with comment 4 by Referee #2 prompted us to check to effectiveness of our specific aerodynamic lens in separating gas and particle phases. We flowed varying concentrations of ozone (up to ~ $10^{-3}$ atm) and $NO_2$ (from $NO_2/N_2$) through the flow reactor while sampling with the particle inlet open. We saw no ion signals (including no signal at 46 m/z for $NO_2^-$ or 62 m/z of $NO_3^-$). In regards to Referee # 2 Comment 4, we also did this with increasing RH and saw no ion signals.

Comment 2) We agree with the referee that we need to consider the possible role of $N_2O_5$ as a source of $HNO_3$ and subsequently $NO_3^-(HNO_3)$ and will include that in section 3.1. The $N_2O_5$ could build up on or near the particle surface and result in nitric acid formation by a process such as:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \overset{particle\ surface}{\rightleftharpoons} N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$



ACPD
7, S7221–S7225, 2007





EGU

The nitric acid could then proceed to react by R3b and R3c (page 14612) to give the $NO_3^-(HNO_3)$ cluster. We believe that this process may be significant at the particle surface and have modified the text to discuss this possibility; however, we do not consider the series of events 1) evaporation of $NO_2$ from the particle surface, 2) condensation of the $NO_2$ on the tube wall, 3) further oxidation of $NO_2$ on the wall, 4) desorption of the $HNO_3$ from the wall and, finally 5) condensation of the $HNO_3$ back onto the particles to be significant.

Comment 3) We will minimize the use of acronyms by deleting those that we only use several times. To save space we shall retain the use of the acronyms for the two main amines discussed (octadecylamine, ODA; and hexadecylamine, HDA) and the other two main components of the particles (oleic acid, OL; dioctyl sebacate, DOS).

Comment 4) We agree with the referee that Figure 8 should be modified. We have done so to emphasize the decay of OL with the concomitant increase in the 438 m/z secondary amide and the overall integrated amide/imine ion intensity. What is lost in this overly crowded figure is that oleic acid is retained in the particles at very high ozone exposures and this likely corresponds with the formation of these high molecular weight products. However, we feel that Figure 7 is highly instructive in that it shows both the retention of oleic acid at very high ozone exposure (compared to pure oleic acid) as well as indicting that this is probably specific to certain surfactant species, since we see this effect for amides and possible imines formed in the ozonolysis of particles composed of octadecylamine + oleic acid but not in the ozonolysis of hexadecylamine + oleic acid. We will state this more clearly in the text. We feel that reiterating this point, along with modification of Figure 8 (which further clarifies the relation between the high molecular weight products and the oleic acid retention) merit Figure 7 to be presented in its current depiction.

Comment 5) We would like to point out that we discussed both binary and ternary mixtures (i.e. azelaic acid + octadecylamine + dioctyl sebacate). The ternary particles were helpful in the elucidation of the mechanism of the amide formation and were im-



ACPD
7, S7221–S7225, 2007





EGU

portant in showing that the amide forms from the reaction of the amine with stabilized Criegee intermediates as opposed to the “classic acylation” reaction, namely the reaction of amines with organic acids. Although this is an important conceptual feature to this paper we did not dedicate a lot of space to discussing ternary systems. In light of this we will change the title to “The ozonolysis of primary aliphatic amines in fine particles”.

Comment 6) Prior to passing the particles through the flow reactor (where the particles are exposed to ozone), we pass the aerosol through a ˜ 1 m drying column packed with silica and activated charcoal. The activated charcoal removes the majority of ethanol from the particles [5]. This methodology has been clarified in the Experimental Method section with the appropriate reference. However, the particles may contain a residual amount of ethanol when ozonized. We were aware that the ethanol was a possible isobaric interference for nitrogen dioxide, so we have directly deposited and vaporized ethanol on the Nichrome filament that we used in these studies and noted that no 46 m/z ion formed (i.e. no significant associative electron attachment ion formation from ethanol was observed). We repeated this experiment with an ethanolic solution of pure oleic acid, with the same result (i.e., no ion signal was measured at 46 m/z). It should be noted that we observed no lower m/z signals indicative of dissociate electron attachment for ethanol (i.e. 45 m/z, via loss of H; or 29 m/z via loss of OH). In light of this, we opted not to use any thermal methods to dry the particles prior to ozonolysis, since this could induce unwanted reactions such as ester formation between the acid and the ethanol.

**Works Cited**

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ACPD

7, S7221–S7225, 2007

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4. Petrucci, G.A., et al., *A differentially pumped particle inlet for sampling of atmospheric aerosols into a time-of-flight mass spectrometer: Optical characterization of the particle beam.* Aerosol Sci. Technol., 2000. **33**: p. 105-121.

5. Hrvaèiæ, B., et al., *Applicability of an ultrasonic nebulization system for the airways delivery of beclomethasone dipropionate in a murine model of asthma.* Pharm. Res., 2006. **23**: p. 1765-1775.



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7, S7221–S7225, 2007