

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 2 for these well thought out comments and suggestions.

We provide our responses below:

Comment 1) The progressive oxidation of amines has precedence in the literature and was originally presented by Bailey et al. [1]. Keinan and Mazur [2] have reported an efficient conversion of aliphatic primary amines to nitro compounds (generally over 60% conversion) via the oxidation of amines by ozone on dry silica. Of course, the results from these ‘traditional’ studies of organic chemistry have to be regarded with caution in regards to their viability in understanding the atmospheric oxidative conversions of amines. For example, in the studies by Keinan and Mazur [2] the oxidation generally was carried out at $-78\text{ }^{\circ}\text{C}$ and with very high ozone concentrations (3%). Their mech-

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anism of progressive oxidation of amines is similar to the mechanism we present: the initial conversion of the amine to an alkylhydroxylamine, then further oxidation to the nitrosoalkane, and finally oxidation to nitroalkanes. The nitroalkanes can decompose yielding NO_2 [3]. We propose that the NO_2 formed at the surface of the particles can react by R3a–R3c (page 14612) to give HNO_3 and subsequently NO_3^- and the nitric acid based clusters.

In section 3.1 we address several pathways that lead to the formation of the observed NO_2^- ion. Nitrogen dioxide can arise from the thermal decomposition of nitroalkanes [3] as well as the fragmentation that occurs in the ionization process [4, 5]. As we discuss in the paper and as shown in Figure 3, we have shown that gas phase 1-nitrohexane gives a strong NO_2^- ion signal from the photoelectron attachment process. Since the submission of this paper we have performed PERCI MS experiments with a host of other volatile nitroalkanes (abnegating the need for any thermal ramping) and saw similar results, the NO_2^- signal is the base peak in all cases (e.g. nitrobutane, nitropropane, and 6-nitrocaproic acid), suggesting that the aliphatic nitroalkanes typically fragment by dissociative electron attachment at ~ 0 eV ionization energy to give NO_2^- . We will incorporate a brief summary of these results in the submitted document. We will also make a statement in the manuscript about the high electron affinity of NO_2 , NO_3 and nitric acid (referencing appropriate studies), which may translate into higher electron capture cross-sections; however, we cannot discount the possibility that there is a high conversion of the amine to the nitroalkanes at the particles surface upon ozone exposure.

Comment 2) We assume that Referee #2 meant the “kinetics of imine formation of an *aldehyde* and an amine” rather than “an acid and amine” since it is the aldehyde functional group of 9-oxononanoic acid, not the carboxyl group that it will lead to the imine when reacting with the amine. Hine et al. [6, 7] have studied the kinetics of imine formation from the reaction of aldehydes and ketones with primary amines. In their stopped-flow spectrophotometry studies of the reactions of primary aliphatic amines [7]

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(e.g. *n*-propylamine) with isobutyraldehyde they describe some key features to imine formation: a) imine formation is preceded by the formation of carbinolamine intermediate and b) the formation is second (overall) order. The formation of the carbinolamine intermediate was very rapid, in the authors' words was "too fast to follow." The subsequent formation of the imine appears to be strongly dependent on pH (their study was in an aqueous solution) and we estimated from their data (see Figure 1 in their work [7]) that the log of the second order rate constant was ~ 2 at pH = 5.5 while ~ 2.5 at pH of 11. These results seem to *suggest* that imine formation is sufficiently fast in slightly acidic media to react on the time scale that we perform our experiments. However we take caution in directly comparing the results of the aqueous phase studies of Hines et al. to our particle-based investigations. The particles investigated in our studies were initially anhydrous with only a small amount of water formed in situ (see Figure 2 in our submitted work) during ozonolysis. We will add a few brief comments with appropriate references about the established kinetics of the reaction of primary amines with aldehydes and ketones that give imines, noting the aforementioned precautions of drawing correlation between the results of studies performed in aqueous solution compared to (relatively) anhydrous particles.

Comment 3) We will take note of the formation of α -acyloxyalkyl hydroperoxides and other hydroperoxides under step 3.

Comment 4) The response to this question should be read in conjunction to the response to comment 1 by Referee #1. In response to both Referee #1 and 2, we introduced NO_2 (as NO_2/N_2) into the flow tube with varying concentrations of ozone (up to 10^{-3} atm) and with variable RH (up to 90%). We saw no ion signals in the PERCI mass spectrum, including for NO_2^- (46 m/z). This indicates that the aerodynamic lens system is still effectively separating gas from particle phases. As stated in the comments to Referee 1, this particle inlet and aerodynamic lens system is well-characterized [8-10] and we will make a concise statement about this, with appropriate references in the modified document. In regards to the formation of the $\text{NO}_3^- \text{HNO}_3$ ion: in light of

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seeing a strong ion signal for this species (125 m/z) both before and during the vaporization process, we believe one of the viable channels in its formation is a) formation of the nitroalkanes via the mechanism of progressive oxidation, b) thermal degradation of nitroalkanes [3] forming NO_2 and c) reaction sequence R3a – R3c on page 14612 that occurs at or near the surface of the particle. Although we do not know how well $\text{NO}_3^- \text{HNO}_3$ adsorbs to the surface of the particle, nitric acid is known to desorb only very slowly from surfaces [11] and suggests that $\text{NO}_3^- \text{HNO}_3$ may behave similarly on the surface of particles, allowing for transport into the ionization region of the mass spectrometer.

Comment 5) We are planning to perform some off-line studies employing LC-MS with ozonized solutions of amines and acids in conjunction with current studies of amine enriched meat-cooking aerosol proxies that we are investigating in our laboratory.

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