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The ozonolysis of primary aliphatic amines in fine particles

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Abstract. The oxidative processing by ozone of the particulate amines octadecylamine (ODA) and hexadecylamine (HDA) is reported. Ozonolysis of these amines resulted in strong NO_2^- and NO_3^- ion signals that increased with ozone exposure as monitored by photoelectron resonance capture ionization aerosol mass spectrometry. These products suggest a mechanism of progressive oxidation of the particulate amines to nitroalkanes. Additionally, a strong ion signal at 125 m/z is assigned to the ion NO_3^- (HNO_3). For ozonized mixed particles containing ODA or HDA + oleic acid (OL), with $p_{\text{O}_3} \geq 3 \times 10^{-7}$ atm, imine, secondary amide, and tertiary amide products were measured. These products most likely arise from reactions of amines with aldehydes (for imines) and stabilized Criegee intermediates (SCI) or secondary ozonides (for amides) from the fatty acid. The routes to amides via SCI and/or secondary ozonides were shown to be more important than comparable amide forming reactions between amines and organic acids, using azelaic acid as a test compound. Finally, direct evidence is provided for the formation of a surface barrier in the ODA + OL reaction system that resulted in the retention of OL at high ozone exposures (up to 10^{-3} atm for 17 s). This effect was not observed in HDA + OL or single component OL particles, suggesting that it may be a species-specific surfactant effect from an in situ generated amide or imine. Implications to tropospheric chemistry, including particle bound amines as sources of oxidized gas phase nitrogen species (e.g. $-\text{NO}_2$, NO_3), formation of nitrogen enriched HULIS via ozonolysis of amines and source apportionment are discussed.

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