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Secondary aerosol formation from atmospheric reactions of aliphatic amines

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Abstract. Although aliphatic amines have been detected in both urban and rural atmospheric aerosols, little is known about the chemistry leading to particle formation or the potential aerosol yields from reactions of gas-phase amines. We present here the first systematic study of aerosol formation from the atmospheric reactions of amines. Based on laboratory chamber experiments and theoretical calculations, we evaluate aerosol formation from reaction of OH, ozone, and nitric acid with trimethylamine, methylamine, triethylamine, diethylamine, ethylamine, and ethanolamine. Entropies of formation for alkylammonium nitrate salts are estimated by molecular dynamics calculations enabling us to estimate equilibrium constants for the reactions of amines with nitric acid. Though subject to significant uncertainty, the calculated dissociation equilibrium constant for diethylammonium nitrate is found to be sufficiently small to allow for its atmospheric formation, even in the presence of ammonia which competes for available nitric acid. Experimental chamber studies indicate that the dissociation equilibrium constant for triethylammonium nitrate is of the same order of magnitude as that for ammonium nitrate. All amines studied form aerosol when photooxidized in the presence of NO_x with the majority of the aerosol mass present at the peak of aerosol growth consisting of aminium (R_3NH^+) nitrate salts, which repartition back to the gas phase as the parent amine is consumed. Only the two tertiary amines studied, trimethylamine and triethylamine, are found to form significant non-salt organic aerosol when oxidized by OH or ozone; calculated organic mass yields for the experiments conducted are similar for ozonolysis (15% and 5% respectively) and photooxidation (23% and 8% respectively). The non-salt organic aerosol formed appears to be more stable than the nitrate salts and does not quickly repartition back to the gas phase.

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