New particle formation from sulfuric acid and amines: Similarities and differences between mono-, di-, and trimethylamines

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Amines are organic base species that are emitted to the atmosphere from both anthropogenic and natural sources. Both theoretical and laboratory studies suggest that mono-, di-, and trimethylamines (MMA, DMA, and TMA, respectively) are capable of enhancing the initial steps of sulfuric acid-driven aerosol particle formation much more strongly than ammonia (Kurtén et al., 2008; Jen et al., 2014). Despite the potential importance for atmospheric new particle formation, quantitative estimates on the emissions and thermochemical properties of amines remain relatively uncertain. Because of this and also due to computational reasons, recent large-scale modeling studies have treated sulfuric acid–amine nucleation by introducing a single surrogate amine species, the total emissions of which combine together MMA, DMA and TMA but which resembles DMA or TMA in its various properties (e.g. Bergman et al., 2015). On the other hand, there are likely to be differences in the potentials of the three amines to enhance particle formation, causing uncertainties to the lumping approach. Systematic comparisons are needed to evaluate how to treat these species in atmospheric models and to assess what level of simplification is justifiable.
In this work, we study the differences and similarities of MMA, DMA and TMA by modeling nanoparticle formation from sulfuric acid, water, and each of the three amines. We simulate molecular cluster concentrations and formation rates at boundary layer conditions with a dynamic cluster population model using quantum chemistry-based cluster evaporation rates, and study the dependence of particle formation rate on precursor vapor concentrations, temperature and relative humidity.
The results suggest that for the three amines, there are differences in the nucleation mechanism and hygroscopicity of molecular clusters. However, for DMA and TMA, formation of nanometer-sized particles and its dependence on ambient conditions is roughly similar: both efficiently form molecular clusters with sulfuric acid, and cluster formation is rather insensitive to changes in temperature and relative humidity. For MMA, on the other hand, particle formation is weaker and more sensitive to ambient conditions. Therefore, the results indicate that DMA and TMA can be approximated as a lumped species, but merging MMA together with DMA and TMA introduces inaccuracies in sulfuric acid–amine particle formation schemes. Moreover, including MMA emissions in a surrogate amine approach which assumes that the amine has the thermochemical properties of DMA or TMA is likely to result in an overprediction of particle formation rate.

References
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