NEW PARTICLE FORMATION FROM SULFURIC ACID AND AMINES: SIMILARITIES AND DIFFERENCES BETWEEN MONO-, DI-, AND TRIMETHYLAMINES

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INTRODUCTION

New particle formation (NPF) from sulfuric acid and bases, including ammonia and amines, is likely to contribute significantly to present-day atmospheric aerosol concentrations (Dunne *et al*., 2016). Amines are organic base species that are emitted to the atmosphere from both anthropogenic and natural sources. While the concentrations of amines are significantly lower than that of ammonia, amines are stronger bases and thus expected to be capable of more efficiently enhancing the initial steps of sulfuric acid-driven aerosol formation. Both theoretical (Kurtén *et al*., 2008) and laboratory (Jen *et al*., 2014) studies suggest that mono-, di-, and trimethylamines (MMA, DMA, and TMA, respectively) are able to form small, strongly bound molecular clusters with sulfuric acid.

Despite the potential importance for atmospheric aerosol formation, quantitative estimates on the emissions and thermochemical properties of different types of amines remain relatively uncertain. Because of this and also due to computational reasons, recent large-scale modeling studies have implemented sulfuric acid–amine nucleation via 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). However, the quantitative efficiency of these three amines to enhance NPF may be different (Jen *et al*., 2014), which causes uncertainties to the lumping approach. Systematic comparisons are needed to assess how to treat these complex species in atmospheric models and what level of simplification is justifiable.

In this work, we model nanoparticle formation from sulfuric acid, water, and either MMA, DMA or TMA to study the differences and similarities between the three amines. We apply quantum chemical methods to study the thermochemistry of H_2SO_4–amine–H_2O molecular cluster formation, and simulate cluster concentrations and formation rates at boundary layer conditions with a cluster population dynamics model using cluster evaporation rates calculated from the quantum chemical formation free energies (Olenius *et al*., 2013). We study the dependence of particle formation rate on precursor vapor concentrations, temperature and relative humidity, and assess how to represent the process in climate and air quality models.

PARTICLE FORMATION EFFICIENCY AND DEPENDENCE ON AMBIENT CONDITIONS

Figure 1 shows the concentration of clusters containing two acids ("dimers", $\sum[(H_2SO_4)_2]$) and the formation rate of ~1–1.5 nm nanoparticles (J) at different precursor vapor concentrations for MMA, DMA and TMA. Simulations for H_2SO_4–NH_3 clustering are included for a comparison. The results agree with previous laboratory observations on the relative particle formation strength: DMA ≥ TMA > MMA > NH_3 (Jen *et al*., 2014). The clustering mechanisms depend on the base: For all amines, the first growth step is the formation of the H_2SO_4•amine complex, while for NH_3, it is the base-free H_2SO_4 dimer. For NH_3 and

MMA, the growth occurs through the addition of single molecules, but for DMA and TMA, cluster self-coagulation has a significant role. Simulations performed at different temperatures and relative humidities (not shown here) suggest that while particle formation involving MMA is enhanced with increasing relative humidity and decreasing temperature, clustering for DMA and TMA is rather insensitive to these quantities.
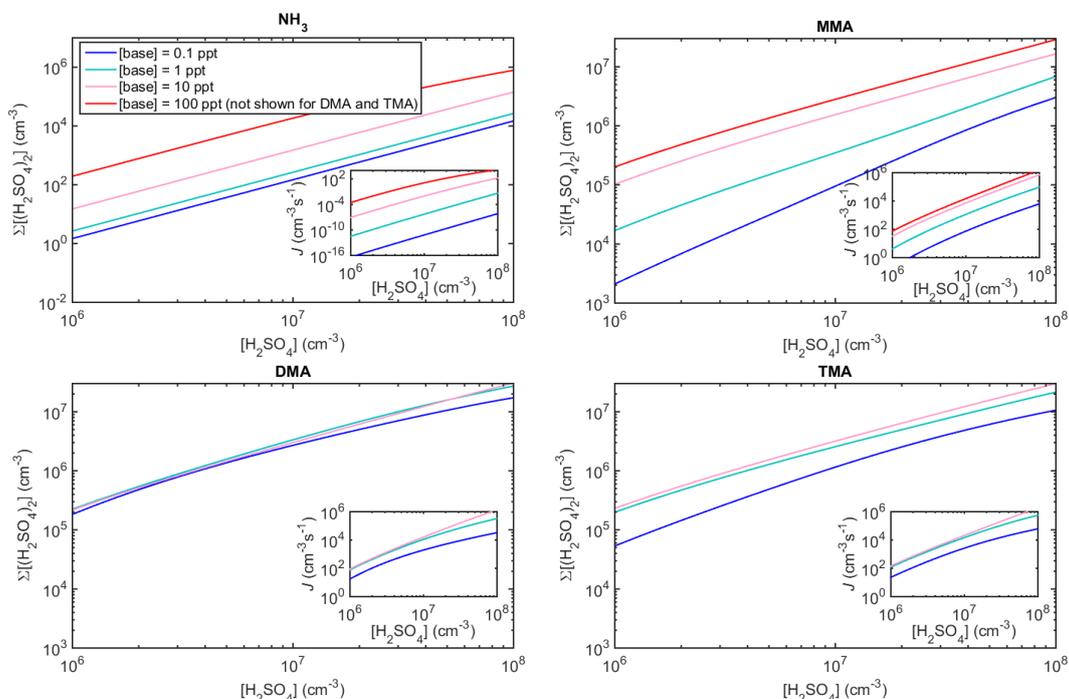

Figure 1. Simulated concentration of stabilized sulfuric acid dimers $\sum[(H_2SO_4)_2]$ and particle formation rate J at ~1–1.5 nm as a function of H_2SO_4 and base concentrations at 278 K, RH = 38 %, and a cluster scavenging sink corresponding to average boundary layer conditions.

CONCLUSIONS

The modeling results on nanocluster formation suggest that DMA and TMA can be approximated as a lumped species in a H_2SO_4–amine particle formation scheme. Merging MMA together with DMA and TMA, on the other hand, is likely to introduce inaccuracies, as for MMA, clustering is somewhat weaker and more sensitive to vapor concentrations and temperature compared to the two other amines. Therefore, including MMA emissions in a surrogate amine scheme which assumes that the amine has the clustering properties of DMA or TMA may result in an over-prediction of particle formation rate. On the other hand, MMA still enhances H_2SO_4-based NPF much more strongly than ammonia. Finally, as cluster self-coagulation is likely to be an important growth mechanism for strongly-bound amine clusters, clustering models neglecting this process are not applicable for these systems.

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