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Amines enhance neutral and ion-induced sulfuric acid nucleation more than ammonia

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Laboratory and field measurements indicate that short-chain alipathic amines are likely to be involved in atmospheric new-particle formation, and that their role in enhancing sulfuric acid – water nucleation may possibly be greater than that of ammonia.

We have investigated the possible role of small alipathic amines in neutral and ion-induced sulfuric acid - related nucleation processes by computing quantum chemical reaction free energies for the addition of sulfuric acid to small neutral and charged clusters containing either ammonia or dimethylamine. The results indicate that dimethylamine enhances the addition of sulfuric acid to the clusters considerably more effectively than ammonia, with the difference in standard free energies being approximately 5 kcal/mol for the neutral clusters and 7 kcal/mol for the charged clusters. These differences are large enough to overcome the mass-balance effects associated with the fact that the atmospheric concentrations of amines are likely to be 2-3 orders of magnitude lower than those of ammonia, and possibly even lower far from the emission sources. For the charged clusters, the results are especially relevant given the recent prediction that ammonia is unlikely to play a role in ion-induced sulfuric acid nucleation.

The hydration of dimethylamine – sulfuric acid clusters has further been studied using a combination of molecular dynamics (with custom – made force fields) and quantum chemical methods. The results indicate that while hydration somewhat decreases the differences between ammonia – and amine – containing clusters (due to the greater water affinity of ammonia), it does not invalidate the qualitative conclusion that amines enhance sulfuric acid nucleation much more effectively.