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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia" *by* T. Kurtén et al.

T. Kurtén et al.

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We thank the reviewer for his or her constructive comments. Answers to specific comments are given below. Changes to the manuscript also indicated.

1. In previous studies, it has been found that the effect of water molecules on the binding of e.g. sulfuric acid and ammonia molecules to each other is relatively minor (see e.g. the discussion in Kurtén et al., ACP 7, 2765 and references therein). However, all of these species are highly hydrophilic, so the same may not, as the reviewer points out, apply to acid-amine binding as the more highly substituted amines are indeed more hydrophilic. Some discussion on this topic has been added to the manuscript as requested by the reviewer. As a side note, we are currently working on modeling the

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hydration of amine-sulfuric acid clusters using a multilevel method, and hope to be able to provide some data on the issue in the future.

Changes to the manuscript: "While it is very unlikely that the addition of water molecules will change the central conclusion that amines are much more strongly bound to sulfuric acid than ammonia is, hydration may change the bonding patterns seen in Figures 1-3, and affect the relative stability of different amine-acid clusters. For example, the more highly substituted amines are less hydrophilic than ammonia or the less substituted amines. Thus, accounting for hydration of the clusters is likely to somewhat decrease the differences in stability observed in Tables 1 and 2."

"Quantitative determination of the effect of amines on sulfuric acid - water nucleation, and especially the relative effect of different amines, will require the explicit modeling of amine - sulfuric acid cluster hydration, which is beyond the scope of the present paper."

2. By "association reaction lifetime" the reviewer presumably means the average time it takes for one amine molecule to collide with a sulfuric acid molecule (or vice versa). Certainly there will not be enough amines in the air to contribute significantly to particle growth beyond the nanometer scale, our focus here is on the initial steps of nucleation. A sentence to this effect has been added to the manuscript. As pointed out by the reviewer, the real dimer formation rate will of course be somewhat lower than the hard-sphere collision rate, but the difference is not likely to be very large, as the activation energies for dimer formation are likely to be very close to zero. (We have not found any energy barrier for the proton transfer reaction from the acid to the amine). The only "kinetic" effects which could potentially reduce the dimer formation rate from the hard-sphere collision rate would thus be steric factors (which may be relevant for the more highly substituted and higher-molecular weight amines but probably not very important for e.g. dimethylamine) and energy non-accommodation, which is also not likely to be very important due to the large number of vibrational modes of the dimer (e.g. 45 for dimethylammonium bisulfate cluster, even before hydration is considered).

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Changes to the manuscript:

"Still, in these conditions each sulfuric acid molecule or small cluster collides with an amine molecule only every 100 seconds or so, implying that while amines are likely to play a significant role in the initial steps of nucleation, their role in subsequent particle growth is likely to be minor. This is in line with atmospheric observations which indicate that the vapors responsible for the formation of 1 nm scale particles are not the same as those responsible for the growth of particles (Kulmala et al., 2007)."

3. We have expressed the cluster concentrations as a function of hypothetical "steady-state" reactant concentrations because otherwise the ratio of cluster concentrations would depend not only on the ratio of the ammonia and amine concentrations but also on their absolute values (as well as that of sulfuric acid and the bisulfate ion). As there is very little measurement data on gas-phase amine concentrations, and as the free energy values given here are only qualitatively reliable (due to e.g. the harmonic approximation and the neglect of hydration), the values in Table 5 are only intended as a crude qualitative demonstration of the order of magnitude of the possible relative cluster concentrations. The advantage of the approach selected here is that it is easy to tabulate; a "dynamic" treatment would require presenting a large matrix with different absolute initial concentrations spanning the range of atmospheric measurements (or "guesstimates"). In any case, any values computed for a equilibrium situation with certain (absolute) initial reactant concentrations would not really reflect conditions in the atmosphere due to the rapid variations in condensable trace gas concentrations. We are currently working on modeling the hydration of amine-sulfuric acid clusters; once this data is available a kinetic treatment including dynamic cluster concentration simulations will be feasible. We have clarified the presentation of the results as requested by the reviewer.

Changes to the manuscript:

"Table 5. Ratio of the concentrations of dimethylamine-containing to ammonia-

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containing neutral and ionic trimer clusters, as a function of the gas-phase concentration ratio of dimethylamine to ammonia in a hypothetical steady-state situation, based on the free energies of complex formation given in Tables 2 and 4."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7455, 2008.

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