

Interactive comment on “Kinetic study of esterification of sulfuric acid with alcohols in aerosol bulk phase” by J. Li and M. Jang

Anonymous Referee #1

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General Comments

This manuscript describes a study of the formation of organosulfates of 1-heptanol, glyoxal, glycerol, and sucrose on concentrated sulfuric acid aerosols that are postulated to form via an alcohol sulfate esterification mechanism. The goal of the work is to determine whether the bulk aerosol phase can present a different reaction medium than bulk solution. Previously, bulk solution measurements have shown that these alcohol sulfate esterification reactions are probably too slow to be relevant to atmospheric aerosol processing.

My main criticism of the experimental design is that I am not totally convinced that the authors have actually observed the formation of organosulfates on aerosols. In-

C7238

deed, it is only for the 1-heptanol system that the organic compound and the sulfuric acid aerosol component must interact via gas-particle partitioning and then followed (potentially) by a bulk aerosol phase reaction. For the other organic species, the organic compounds are premixed with the sulfuric acid solution before they are atomized into particles. How does one actually know whether any observed chemical reaction occurred in the solution phase before atomization or during the chemical system's time as an aerosol particle?

The 1-heptanol system is the more straightforward one to consider. Unfortunately, the arguments that attempt to prove that organosulfates have formed on the aerosol particles are not totally convincing. Figure 2 shows the growth of particle phase compounds with C-H stretching vibrations as proof for organosulfate formation. However, the simple partitioning of 1-heptanol to the particle phase would presumably give the same C-H stretching region absorption (on the other hand, the supporting information has more convincing infrared spectra, O-S ester stretching, for the presence of organosulfates for the premixed systems). On p 23226, line 6, the authors attempt to rule out this alternative explanation with a MgSO₄ control experiment. However, why would one expect that 1-heptanol would have similar partitioning to solid MgSO₄ particles as to liquid sulfuric acid particles?

The discussion of the kinetics results is not convincing. The authors find that the organosulfate reactions are observed to occur faster at higher relative humidities. This is quite a surprising result, since it is well known that alcohol sulfate esterification reactions are acid-catalyzed (Deno and Newman). The authors rationalize this effect as being due to a viscosity effect for a diffusion-limited process. However, later on in the manuscript, they calculate a molecular diffusion time in a 0.1 μm particle of 3×10^{-5} seconds, which is much, much faster than the organosulfate processes that they believe that they are measuring (for example at a sulfuric acid concentration of 8.6 M, the k_1 value for the 1-heptanol system indicates a reaction lifetime of 40 minutes). The authors never directly address the question of why a process that is most definitely

C7239

acid-catalyzed in the solution bulk phase would somehow not be acid-catalyzed in their aerosol experiments.

The authors' main claim supporting their hypothesis that the aerosol bulk phase can be quite different than the solution bulk phase concerns the formation of hydrophobic organosulfates, which can then accelerate the evaporation of water from the particles, thus altering the composition of the reaction medium. This is an interesting hypothesis, but I wonder if the conditions that would allow it to occur are common in the atmosphere. The authors claim to identify dialkyl sulfates as the key hydrophobic species via a NMR analysis of a bulk solution experiment. However, I'm not totally convinced of this assignment, either, since there is no discussion of how the NMR spectrum provides definitive proof for the presence of these species. The authors go on to use the formation of dialkyl sulfates as a way to rationalize the loss of particle acidity. However, is there evidence that dialkyl sulfate formation occurs in the ambient atmosphere? To the best of my knowledge, the field measurement literature has reported only monoalkyl sulfate species in ambient aerosol (despite the criticism of the HPLC-MS methods given in the introduction to the manuscript, one strength of the TMS-derivatization HPLC-MS method is that it can determine the number of free hydroxyl groups).

In any case, it seems pretty clear that the particle organic concentration ratio in these systems must be pretty high (although there are some partitioning calculations described in the manuscript, I couldn't find any actual values given for the particle concentrations of the parent organic compounds). Therefore, even though I'm not convinced of the dialkyl sulfate identification, it's perhaps not an unreasonable result that if the significant organic content underwent extensive chemical conversion to a more hydrophobic species, the bulk solution properties could change enough such that water loss could occur. Nonetheless, even if you accept that the authors have created a system that rapidly produces hydrophobic species that lead to dynamic water loss, it's still not clear that it's an atmospherically relevant one. This is why the broad claim

C7240

that sulfate esterification processes will happen faster in the aerosol bulk phase than the solution bulk phase is potentially misleading. While it is possible to compare solution and aerosol bulk phase experiments that had similar sulfuric acid concentrations, the present experiments apparently had much, much higher organic content which ultimately leads to the dynamic water loss effect. Rather, the claim should be that the bulk phase composition rapidly changes in these particular aerosol phase experiments (as opposed to the previous bulk solution phase experiments), and that somehow this leads to a faster rate of sulfate esterification. I would have guessed that this could be due to a rise in particle acidity as water is lost, but the present measurements show the acidity trend is in the opposite direction, so it's not clear what the kinetic mechanism is here. Finally, there isn't any argument given in the manuscript that this situation is more likely in ambient aerosols than the situation modeled by the solution bulk phase experiments. If ambient aerosol bulk phase properties change slowly due to particle phase processing (relative to gas-particle equilibria dynamics), then it would seem that the solution bulk phase experiments are more atmospherically relevant than the present experiments.

Specific Comments

None of the fundamental data that are used to determine the rate constants are given in the manuscript. It is important to see explicitly how the fundamental data, in conjunction with equations 7 and 8, leads to the derived rate constants (perhaps presented in one or more plots).

What are the actual values used to calculate K_{in} in equation 8?

p. 23232 line 15: Looking at Minerath et al. Figure 1, it's unclear how the authors came up with organosulfate yield of 17.5%. It looks like the majority of the ethylene glycol converted to organosulfate. Therefore, there doesn't really seem to be yield difference between the solution bulk phase experiments and the present aerosol bulk phase ones.