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

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Response to Comments

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Title: Kinetic study of esterification of sulfuric acid with alcohols in aerosol bulk phase

Response to Referee 1:

We deeply thank referee 1 for the thoughtful comments. The manuscript has been significantly improved due to valuable comments from Referee 1.

General Comments

1. 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. Indeed, 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 systems time as an aerosol particle?

Response: The reactions between sulfuric acid and organic compounds (e.g., sucrose, glyoxal, and glycerol) in the solution phase before atomization are negligible because the concentrations of both sulfuric acid and organic compounds are very low (0.01 mol/L). Even when organic compounds in high concentrations ([organic compounds] >0.8 mol/L) were mixed with high concentrations of sulfuric acid solution (7.06 mol/L) in the NMR tube, no organosulfate product was observed for the first 3 hours after mixing. The NMR data indicates the slow organosulfate formation in the solution phase. In our chamber study, the low concentration (0.01 mol/L) sulfuric acid aqueous solution, and the organic compound aqueous solution (e.g., sucrose, glyoxal, or glycerol, 0.01 mol/L) were mixed just before nebulizing the particles into the chamber. In total, the mixing and atomization process took about 2–3 minutes. During this process the production of organosulfates was not substantial based on our acidity data shown in Figure 4.

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2. 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 MgSO_4 control experiment. However, why would one expect that 1-heptanol would have similar partitioning to solid MgSO_4 particles as to liquid sulfuric acid particles?

Response:

The FTIR absorbance of organosulfates functional groups (-COS-) appears at 876 cm^{-1} (Maria et al. 2003). For sulfuric acid aerosol, the first step dissociation of sulfuric acid into bisulfate is complete, thus, the FTIR absorbance of sulfuric acid particle has three peaks (bisulfate peaks) in the range of $800\text{--}1200\text{ cm}^{-1}$ (as shown in the spectra labeled as 0 min 0 second in the Figure R1), one of which overlaps with -COS- peak at 876 cm^{-1} .

Figure R1. The FTIR spectra of H_2SO_4 particle after introducing gaseous 1-heptanol into the FTIR flow chamber.

For sulfuric acid particle, the FTIR absorbance at 876 cm^{-1} is relatively weaker than that at 1050 cm^{-1} (as shown by the spectra labeled 0 minute 0 second in Figure R1). However, after exposing to gaseous 1-heptanol, the intensity of FTIR absorbance at 876 cm^{-1} becomes relatively higher than that at 1050 cm^{-1} , indicating the transformation of sulfuric acid into organosulfate.

MgSO_4 particle is hygroscopic, and the "predeliquescence" of fine MgSO_4 particles with 500 nm diameter is reported to occur before $\text{RH}=15\%$ (Wang et al. 2008). Thus,

the MgSO_4 particle phase (at $\text{RH}=50\%$) in this study is liquid. We have also seen the strong water peak in the FTIR spectrum of MgSO_4 particle under our experimental humidity.

The partitioning coefficient (K_{in}) of 1-heptanol into inorganic particle can be determined by the Pankow's absorptive partitioning equation (Pankow 1994).

$$K_{in} = \frac{f_{in}760RT}{MW_{in}\gamma p_{l,i}^0 10^6} \quad (1)$$

where f_{in} is the weight fraction of the absorbing inorganic phase ($f_{in}=1$), R is the gas constant, T is the temperature (K), and MW_{in} is the mean molecular weight of the absorbing inorganic medium. $p_{l,i}^0$ is the vapor pressure of i at the temperature of interest. It is 15 Pa for 1-heptanol at 293 K. γ is the activity coefficient of a compound (i) in an inorganic medium and can be estimated using the thermodynamic model (e.g., AIOMFAC) (Zuend 2011), presupposing that the activity of 1-heptanol in gas phase equals that of 1-heptanol in aerosol phase under the given 1-heptanol concentration in the gas phase. The estimated γ value is reported in Table 1. The estimated aerosol-phase concentration of 1-heptanol based on gas-particle partitioning is insignificant (0.00013 mol/L), and the mass fraction of 1-heptanol in the particle is $1.46 \times 10^{-8}\%$ which cannot be detected using FTIR. In general to be seen in FTIR spectra, the mass fraction of an analyte should be higher than several percent (2-3%).

3. 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 um particle of 3×10^{-5}

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

Response: Thanks for the reviewer's comments. We have found that there was a mistake in estimating the activity coefficient (γ) of 1-heptanol in sulfuric acid aerosol. In the previous manuscript, incorrect activity coefficients were applied to gas-aerosol partitioning coefficients. It has been corrected in the revised manuscript. After this correction, the higher reaction rate constant was observed in the 1-heptanol- H_2SO_4 esterification under lower RHs. This result agrees with the typical trend in acid-catalyzed reactions. Table 1 has been updated for rate constants with units in $\text{L mol}^{-1} \text{s}^{-1}$ (see specific comment 7 from Referee 2) in the revised manuscript and reads now.

As shown in Table 1, the rate constant at 20% RH is three orders of magnitude higher than that at 60% RH.

However, for the multi-alcohol (very hygroscopic), the sulfate esterification reaction rate constant is slightly higher under higher RHs, which is different from the observation for mono-alcohol (e.g., 1-heptanol). This might be associated with the differences in their partitioning into aerosol aqueous phase. For mono-alcohols, their gas-aerosol partitioning coefficient dramatically increases as RH increases (e.g., for 1-heptanol, $K_{in}=3.6 \times 10^{-13} \text{ m}^3 \mu\text{g}^{-1}$ at RH=20%, $K_{in}=2.0 \times 10^{-11} \text{ m}^3 \mu\text{g}^{-1}$ at RH=60%) while the partitioning coefficient of multi-alcohols slightly decreases as RH increases (e.g., for glycerol $K_{in}=1.0 \times 10^{-2} \text{ m}^3 \mu\text{g}^{-1}$ at RH=32% and $K_{in}=3.8 \times 10^{-3} \text{ m}^3 \mu\text{g}^{-1}$ at RH=60%). Compared to the effect of RH on esterification rate constants of 1-heptanol-sulfuric acid, RH dependency of the rate constant of organosulfate formation in multi-alcohol-sulfuric acid is insignificant (less than one order difference between RH=20% and RH=60%). We also noticed that within 40-minute reaction time, all reaction com-

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pleted with high organosulfate yields (Figure 4). For multi-alcohols, no difference appeared in organosulfate yields at different RHs within error bars (Figure 5 in the revised manuscript).

This has been discussed in Section 3.3. Impact of RH on reaction rate constants of sulfate esterification in the revised manuscript.

4. 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 am 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).

Response: As shown in the Figure S1, compared to the ^1H -NMR spectra of glyoxal in D_2O , the NMR spectra of glyoxal in D_2O - D_2SO_4 solution move to upward due to the change in pH of the solution. For the chemical shift lower than 6.0, the shape of the spectra keeps the same (Figure S1), however, a strong new peak at chemical shift=6.2 ppm appears in the NMR spectra of glyoxal in D_2O - D_2SO_4 solution, indicating the formation of new products in the solution. The chemical shift of the new peak subjective to organosulfate formation is higher than that of glyoxal, suggesting the proton in the

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product was affected by a neighboring electron-withdrawing group, which should be sulfate in this case. NMR spectra also show how many hydrogen neighbors exist for a particular hydrogen or group of equivalent hydrogens. In general, an NMR resonance will be split into $N+1$ peaks where N is the number of hydrogens on the adjacent atom or atoms. In Figure S1, the new peak has a single peak without splitting, indicating the protons associated with organosulfate are equivalent (symmetric in molecular structure) without neighbored protons. The structure of the new product was proved by the Chem Draw simulation.

Figure S1. ^1H -NMR spectra of glyoxal in D_2O , and glyoxal in D_2O - D_2SO_4 (glyoxal: $\text{D}_2\text{SO}_4 = 1:5.67$ in mole ratio). The D_2O - D_2SO_4 solution was made by 1:1 mass ratio, which is equivalent to the D_2SO_4 aerosol composition at relative humidity = 35.5% at 298 K.

The stability of dialkyl sulfate has been tested by mixing 5 μL of a dialkylsulfate–diethyl sulfate (98%, Sigma Aldrich) with 50 mL of high-purity water and sonicated for 5 minutes at 363 K. The resulting diethyl sulfate aqueous solutions stand at the room temperature (293–295 K) to cool down and analyzed by the IC for measuring inorganic sulfate concentrations ($c_{\text{SO}_4^{2-}, \text{IC}}$). The reversibility of dialkylsulfates (R_{OS}) in hot water extraction can be estimated as follows:

$$R_{\text{OS}} = \frac{c_{\text{SO}_4^{2-}, \text{IC}}}{c_{\text{OS}}} \times 100\% \quad (2)$$

where c_{OS} is the initial concentration of dialkylsulfates in the solution. The resulting R_{OS} of dimethyl sulfate that is mixed with water is $98.5\% \pm 3.2\%$ at 363 K, suggesting that dialkylsulfates are not stable when they are extracted with solvent, particularly in hot water. Thus, for the ambient aerosol analyzed using mass spectrometers, most organosulfates manifest as separate organic and sulfate components due to the low thermal stability, with little difference in fragmentation from inorganic sulfate (Farmer et

al. 2010). But it does not mean dialkyl sulfates are not forming in the ambient aerosol.

We have measured the ambient dialkyl sulfates concentrations using the C-RUV method at sampling site located at the UF campus at Gainesville, FL. The results showed that dialkyl sulfate concentrations are 0.66 ± 1.09 to 3.49 ± 2.78 nmol/m³ in the ambient air, which account 0.3%–4.5% mole fraction of the total sulfate.

5. (a) 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 could not find any actual values given for the particle concentrations of the parent organic compounds). Therefore, even though I am 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 is still not clear that it is an atmospherically relevant one. This is why the broad claim 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. (b) 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 is not clear what the kinetic mechanism is here. (c) Finally, there is not 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

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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.

Response: (a) The concentration of organic compounds in the internally mixed organic- H_2SO_4 aerosol dynamically changed as the reaction process (eq. 12). At the beginning of reactions, the concentration of organic compounds (e.g., glyoxal, glycerol, and sucrose) in the organic- H_2SO_4 aerosol ranges from 1.08 to 4.91 mol/L, and the mole ratio of organic to sulfuric acid ranges from 0.11 to 0.7 at given experimental conditions. According to the study of Zhang et al. (2007), organic aerosol comprises a major fraction (18–70%; average = 45%) of the non-refractory submicron particle mass in the 37 field campaigns, while sulfate accounts for 10–67% (avg = 32%) of the particle mass. Thus, the organic to sulfate ratio in this study is reasonable and can happen in the ambient aerosol. However, the acidity of aerosol is higher than ambient aerosol because sulfuric acid is quickly neutralized by ammonia in the ambient air.

(b) Particle acidity is determined by RH and inorganic composition. The aerosol acidity of remained sulfuric acid cannot be high because water produced via organosulfate is evaporated. If the amount of proton is normalized with inorganic portion only excluding organosulfate, the particle acidity will be the same as the sulfuric acid without reactions.

(c) The outcome of this study is the estimation of time scale of organosulfate formation in aerosol phase. The organosulfate formation in aerosol is much faster than that in solution. For example, the estimated half-life of sucrose under our experimental condition is about 10 minutes. This result suggests that organosulfate can be efficiently produced in the ambient aerosol when the aerosol contains sufficient acidic sulfates and the multifunctional organic compounds that have alcohols and aldehydes. The aerosol suspended in the air allows water to evaporate as organosulfate forms while solution chemistry keeps the same amount of water. The recent study by Tolocka and Turpin has reported that OS could comprise as much as 5?–10% of the organic mass in IMPROVE PM_{2.5} field data suggesting that the amount of organosulfate is not

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negligible. In a recent field study by Stone et al. (2012), organosulfate mass in four Asian locations was estimated to account for 2.3% of total organic carbon mass and 3.8% of total sulfates using a semi-quantitative analysis.

In addition to the fast reaction rate of organosulfate formation, high yields (>50%) of organosulfate were observed in aerosol while low organosulfate yields (17.5% with even higher acidity) appear in solution chemistry. In order to respond to the reviewer, the Conclusion Section of the manuscript has been revised and reads now (3rd paragraph of the Conclusion Section):

Based on our observation of this study, the organosulfate formation in aerosol is much faster than that in solution. The insignificant effect of RH on k_2 for multi-alcohols was also observed as shown in Table 3. The estimated half-life of sulfuric acid mixed with sucrose (sucrose:H₂SO₄ = 1:2) at RH = 26.1% is about 18 minutes. This result suggests that the ambient aerosol can also significantly produce organosulfate when the aerosol contains sufficient acidic sulfates and reactive multifunctional organic compounds.

Specific comments:

1. 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).

Response: All information related to equations 7 and 8 has been included in Table 1 (as shown in the respond to the question 3 of the general comments above). Sentence, 'All information to estimate equations 7 and 8 has been reported in Table 1.', has been added into the revised manuscript.

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

Response: To calculate the K_{in} of 1-heptanol using equation 8, f_{in} is the weight fraction

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of the absorbing inorganic phase, which equals 1; R is the gas constant, which equals $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, T is the temperature (K), MW_{in} is the mean molecular weight of the absorbing inorganic medium, which is estimated using the molecular weight of water and sulfuric acid times their mole fraction, respectively; γ is the activity coefficient of a compound (i) in the inorganic medium, which is estimated using the thermodynamic model (e.g., AIOMFAC) (Zuend 2011) by presupposing that the activity of 1-heptanol in gas phase equals that of 1-heptanol in aerosol phase under the given 1-heptanol concentration in the gas phase and reported in Table 1, $p_{l,i}^0$ is the vapor pressure of i at the temperature of interest. It is 15 Pa for 1-heptanol at 293K. The estimated K_{in} for 1-heptanol onto H_2SO_4 particle at $\text{RH}=20\%$ is $3.6 \times 10^{-13} \text{ m}^3 \mu\text{g}^{-1}$.

3. p. 23232 line 15: Looking at Minerath et al. Figure 1, it is 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.

Response: The yield of dialkyl sulfate from the reaction of ethylene glycol and sulfuric acid was estimated using the data reported by Minerath et al. (2008). Under their experimental condition (ethylene glycol: $\text{D}_2\text{SO}_4=1:95$ in 75 wt% D_2SO_4 - D_2O solution, equivalent equivalent $\text{RH}=2\%$ at 298K),

$$K_{eq,1} = \frac{[ROSO_3H]}{[ROH]} = 2.43 \quad (3)$$

$$K_{eq,2} = \frac{[ROSO_3OR]}{[ROSO_3H]} = 0.30 \quad (4)$$

Thus,

$$Y_{di-OS} = \frac{[ROSO_3OR]}{[ROH] + [ROSO_3H] + [ROSO_3OR]} = 0.175 \quad (5)$$

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Table S1. Experimental conditions for studies of kinetics of the formation of organosulfate *via* the reaction of sulfuric acid particle with 1-heptanol using a flow reactor integrated with FTIR.

Set	[1-heptanol] _g ^a 10 ⁻⁵ mol/m ³	RH %	Particle	M _p ^b μg	[H ₂ SO ₄] _p ^c mol/L	[H ₂ O] ^d mol/L	γ ^e 10 ⁵	M _{OS} ^f μg	k ₁ 10 ⁻⁵ L mol ⁻¹ s ⁻¹	k ₋₁ 10 ⁻⁵ L mol ⁻¹ s ⁻¹
1	0.35	20	H ₂ SO ₄	65	8.6	11.4	135	9.5	40.5	14.2
2	0.72	20	H ₂ SO ₄	72	8.6	11.4	135	14.7	40.5	14.2
3	1.21	20	H ₂ SO ₄	54	8.6	11.4	135	18.2	40.5	14.2
4	0.35	40	H ₂ SO ₄	53	6.7	39.7	15.9	4.4	6.5	6.6
5	0.72	40	H ₂ SO ₄	56	6.7	39.7	15.9	8.4	6.5	6.6
6	0.35	60	H ₂ SO ₄	50	5.0	44.0	3.1	3.3	0.05	0.26
7	0.72	60	H ₂ SO ₄	51	5.0	44.0	3.1	6.0	0.05	0.26
8	0.36	50	MgSO ₄	75	n.a. ^g	48.9 ^h	7.1	0	n.a.	n.a.

^aConcentrations of 1-heptanol in the gas phase ([1-heptanol]_g) was measured using GC-MS. The error associated with 1-heptanol concentration is 15%.

^bThe mass of particle (M_p) was obtained by weighing the silicon disk mass before and after sampling. The error associated with the particle mass is ±1 μg.

^cConcentration of sulfuric acid ([H₂SO₄]_p) in the particle was estimated using E-AIM model II (Clegg 1998).

^dConcentration of water ([H₂O]_p) in the sulfuric acid particle was estimated using E-AIM model II (Clegg 1998).

^eActivity coefficient of 1-heptanol in sulfuric acid aerosol was estimated using AIOMFAC (Zuend 2011).

^fThe mass (M_{OS}) of organosulfate when the reaction of 1-heptanol and sulfuric acid reach equilibrium.

^gnot applicable.

^hConcentration of water in the magnesium sulfate particle was estimated using data reported by Zhao et al. (2006).

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