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Atmospheric Chemistry and Physics
Discussions

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 2:

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

General Comments

The formation of organosulfates is important for understanding atmospheric particle phase C- and S- budget and the means of chemical transformations. M. Jang has taken part in the discovery of these compounds in an early stage and now examines a hypothesis: Namely, that the simple esterification reaction between alcohols and sulfuric esters (organosulfates are organic esters of sulfuric acid) does proceed more efficient than in bulk solution. The authors claim that the esterification reaction is 1000 times faster than found in bulk phase experiments. This finding would be very interesting but hard to understand ï£¡C is the rate constant changing or is that just an effect of higher concentrations. This does not become clear in the abstract and the whole manuscript. One possible explanation represents a thread for the manuscript: The authors might have studied a surface reaction but do analyze them in terms of particle bulk phase chemistry ï£¡C a more thorough investigation is hence needed. I am afraid that the authors confuse bulk chemical and surface processes. In the introduction only bulk processes are discussed and it is only in the experimental that in fact a surface process is followed (P 23222, line 15). This urgently needs to be clarified. Cleary, a surface reaction can occur totally different from a bulk reaction. The authors need to clarify this. The whole introduction does not fit to the performed work and needs to be re-written. Aerosol particle composition should be varied to isolate whether this has to do with the observed differences in rate constants. Further experimental work appears necessary before a revision might be undertaken. It must be made clear whether a surface or a bulk process has been studied. This can be characterized experimentally and, accordingly, should be done. I feel the paper as it stands cannot be published in its present form and suggest rejection. It might be possible to revise the manuscript but, in my view, this will require additional laboratory work and constitute a mayor effort.

Response: To confirm the reaction between gaseous 1-heptanol and sulfuric acid particle progressed in the aerosol bulk phase, the diffuso-reactive parameter, *q* is characterized using the equation shown below (Finlayson-Pitts and Pitts, 2000):

$$q = d\sqrt{\frac{k_r}{d_l}} \tag{1}$$

where *d* is the particle radius (here assuming 100 nm), k_r is the aqueous phase reaction rate constant and D_l is the diffusion coefficient. The kr of 1-heptanol-sulfuric acid reaction is adopted by the data reported in Minerath et al (2008) using NMR. In their study, the k_r for the reactions between an alcohol and sulfuric acid solution were 1.75 $\times$ 10^{-4} s^{-1} in 75 wt% sulfuric acid solution at 297 K. The D_l of an alcohol in water is about 1.1$\times$ 10^{-9} m^2 s^{-1} (Delgado, 2007). Thus, q is 4.0$\times$ 10^{-5}, which is much smaller than 1. In general, a high *q* value indicates that the reaction occurs on the surface. The *q* for alcohol-sulfuric acid reaction is less than 10^{-4}, suggesting that their reactions are much slow compared to diffusion so that reactions take place throughout the entire volume of the particle. Although the rate constants obtained in our study are higher than those reported in solution chemistry (e.g., 7.04 $\times$ 10^{-3} s^{-1} for glyoxal-sulfuric acid reaction at RH=70%), the estimated *q* value is still very small as 2.5$\times$ 10^{-4}. Thus, we concluded that orgnaosulfate production is controlled by the bulk phase reactions.

Specific comments: 1. P 23219, line 14: an organosulfates signal. ï£¡C Wording: Do not leave articles away.

Response: Thanks for the reviewer. The grammar has been corrected in the revised manuscript.

2. P.23220, l. 24: Please differentiate between rate constants and rate of reaction in this discussion. What is the text referring to? It is known that deliquescent aerosol particles have ionic strength, say, in the range 6–20 mol/l. Solute concentrations of, say, HSO4-, might also reach several mol/l. If organics are then taken up, the esterification might occur with quite a high rate of reaction but that does not mean that the reaction rate constant changes - just the reactant concentrations change and the rate of reaction increases even if the rate constant (a concentration-independent proportionality factor) does not change at all. Please urgently explain if this paper is about changing rate constants - then why should they change or if it is about changing rate of reactions - then this is not a surprise. All of this is misleading if in fact a surface reaction was studied.

Response: This study estimates the reaction rate constant for all the organic-sulfuric acid reactions. The reaction rate constants were defined and estimated using equation 6 and equation 11 in the manuscript.

3. P 23220, l24: Water evaporation could influence the flux from educts to products in both the equlibria (1) and (2) because of Le Chateliers principle but this would not change kf, kb or K.

Response: We agree with the reviewer that the evaporation of water from the aerosol should not change the equilibrium of the reaction. But according to the Le Chateliers principle, the reactions between sulfuric acid and organic reactants would go further and produce more organosulfate products due to the water evaporation. However, the reaction rate constant may be affected by the water evaporation. For example, Nguyen et al. (2012) observed that the formation of light absorbing products in the mixture of sulfuric acid and SOA aqueous extracts that were subject to evaporation is faster by at least three orders of magnitude than the same reaction in aqueous solution.

4. P 23220, l27: I think the sentence starting ï£¡ï£¡Both water evaporationï£¡ï£¡ is probably pain wrong but at least pure speculation and should be removed from the

manuscript.

Response: Thanks for the reviewer. We have revised the manuscript as shown below (5th paragraph of the Introduction Section of the revised manuscript):

ï£¡ï£¡However, it is disputable whether the reaction rate constants observed in solution chemistry are applicable to reactions in the aerosol bulk phase. The aerosol suspended in the air allows water, a by-product of sulfate esterification [Eqs. (1) and (2)], to evaporate from aerosol while solution chemistry retains water in the system. In addition to water evaporation, the hygroscopic property of the aerosol changes as organosulfate forms because organosulfates are relatively hydrophobic compare to reagents (sulfuric acid and hydrophilic organic compounds). To investigate how chemical and physical properties of aerosol (e.g., water evaporation and the formation of hydrophobic organosulfates) influence both reaction rate constants and yields of organosulfate, the characterization of the aerosol bulk phase calls for.ï£¡ï£¡

5. P 23221, l 4: I do not understand the last sentence of the first paragraph.

Response: Thanks for the comments. The sentence has been rewritten and shown in the response to question 4 above.

6. P23222, l 15: It is only here in this manuscript that the authors state that they are following a process on the surface of sulfuric acid particles. Hence, the whole introduction does not fit to the performed work and needs to be re-written.

Response: Thanks for the comments. The discussion of surface reaction vs. aerosol bulk phase reaction has been addressed as shown in the response to the ï£¡ï£¡General Commentsï£¡ï£¡ above, and the Introduction Section of the manuscript has been revised .

7. P23227, l 10: The last sentence of this paragraph is plain wrong. A chemical reaction with such a low absolute rate constant cannot be diffusion ï£¡Ccontrolled. NOTE: second order rate constant should always be given in mol / l * s and not mol/ l *

min.

Response: Thanks for the comments. We agree with the reviewer that the reactions between sulfuric acid and organic reactants (e.g., 1-heptanol, sucrose, glyoxal, and glycerol) are not diffusion controlled reactions. The discussions about the diffusion-controlled reactions have been removed from the revised manuscript, and the unit of the reaction rate constant has been changed into mol L^{-1} s^{-1}.

8. Section 3.1.3. May be the differences can be due to differences in matrix composition. Please check how the observed rate constants change when binary particle composition changes. Please thoroughly elucidate if you have studied a surface process but analyze it as a bulk process. The remaining results as well as the atmospheric implications suffer from the above unclarities identified up to here and, accordingly, need to be fully revised.

Response: The impact of aerosol composition on the reaction rate constant has been studied using the internally mixed sucrose-H_2SO_4 aerosol as shown in the Section 3.2.2 of the manuscript. The reaction rate constant is $1.51 \pm 0.11 \times 10^{-4}$ mol L^{-1} s^{-1} for the reaction between sucrose and sulfuric acid when the mole ratio of sucrose to sulfuric acid ranges from 0.11 to 0.50 at RH=25% (Table 3). This result proves that the high reaction rate constant in aerosol bulk phase is independent of the concentrations of the reactants or the matrix compositions.

9. The English of the manuscript needs to be revised throughout.

Response: The English of this manuscript has been revised by a native English speaker.

10. Figure 5: This figure is not helpful.

Response: Thanks for the suggestion. Figure 5 has been deleted in the revised manuscript.

References

Delgado, J. (2007). Molecular diffusion coefficients of organic compounds in water at different temperatures. Journal of Phase Equilibria and Diffusion 28:427-432.

Minerath, E., Casale, M. and Elrod, M. (2008). Kinetics feasibility study of alcohol sulfate esterification reactions in tropospheric aerosols. Environmental Science & Technology 42:4410-4415.

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