

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

Anonymous Referee #2

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Review of 'Kinetic study of esterification of sulfuric acid with alcohols in aerosol bulk phase' by J. Li and M. Jang, submitted to ACPD

General: 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 – 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

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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 – 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. Clearly, 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. Details P 23219, line 14: '...an organosulfates signal...'. – Wording: Do not leave articles away. 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. P 23220, l24: Water evaporation could influence the flux from educts to products in both the equilibria (1) and (2) because of Le Chateliers principle but this would not change k_f , k_b or K . P 23220, l27: I think the sentence starting “Both

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water evaporation. . ." is probably plain wrong but at least pure speculation and should be removed from the manuscript. P 23221, l 4: I do not understand the last sentence of the first paragraph. 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. P 23227, l 10: The last sentence of this paragraph is plain wrong. A chemical reaction with such a low absolute rate constant cannot be diffusion –controlled. NOTE: second order rate constant should always be given in mol / l * s and not mol/ l * min. 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 analyse 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. The English of the manuscript needs to be revised throughout. Figure 5: This figure is not helpful.

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