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Interactive comment on "Constraining condensed-phase formation kinetics of secondary organic aerosol components from isoprene epoxydiols" *by* T. P. Riedel et al.

Anonymous Referee #2

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The authors show chamber measurements on the formation of secondary organic aerosol (SOA) from isoprene epoxydiols (IEPOX) which they analyze using a kinetic box model in order to determine the elusive bulk reaction rate constants / branching ratios of the acid-catalyzed reactions at work. These reactions are assumed to have high relevance for SOA formation in the troposphere and the topic hence fits nicely within the scope of ACP. I highly appreciate this first attempt to obtain the kinetic rate constants necessary for understanding the chemical system. The paper is well written and the authors discuss their results in the light of previous laboratory experiments and a recent field study. Besides a few minor general comments, I have comments and open questions regarding the modelling part of this study. This paper should be easily

publishable in ACP when these last issues are resolved.

Comment 1

The authors decided to use a zero-dimensional model and to prescribe the uptake coefficient γ. Recent modelling studies use 1D models and include adsorption/desorption of trace components explicitly, yielding time-dependent uptake coefficients (e.g. Wilson et al. (2012), Shiraiwa et al. (2013), Roldin et al. (2014)). Also gas diffusion might be a relevant factor at these values of γ. The authors correctly point out in the text that γ may change over time as organics accumulate in the particle phase. Since a more in-depth analysis might be out of the scope of the paper and could be dealt with in a follow-up study, I would suggest mentioning the difficulties that arise when using these models generally used in similar applications that led to their choice of a rather simple box model.

Comment 2

Do the authors consider changes in the total surface area of the aerosol phase due to particle growth and wall losses? It seems particle growth is strong enough to affect the uptake rates (in the form of k_{het} in this paper) over time. Would this change the predicted aerosol mass loading as shown in Fig. 1?

Comment 3

The authors mention two pathways for formation of "other SOA". What are the reasons for only considering the pathway via IEPOX-OS and not via coupling of tetrols?

Comment 4

Does the H^+ concentration ($[H^+]$) change over time in the particle phase due to accumulation of organic material or is it kept constant? I don't see a differential equation taking this into account. Since $[H^+]$ factors into every rate constant, it seems like a necessary inclusion.

Comment 5

Have the authors considered partitioning of semi-volatile products (such as tetrols) between gas and particle phase? This might skew the final product distribution considerably and not captured by reaction R8. On another note: Is reaction R8 not also acid-catalyzed?

Comment 6

The authors mention that reaction rates were "systematically varied" while the model "run in a continuous loop". Could they provide some additional information on how the parameters were obtained? Was it possible to find other sets of kinetic parameter leading to the same modelling result?

Comment 7

The reaction rate constants were obtained through averaging and errors in the determined reaction rate constants were obtained by taking the standard deviation of results returned from different experiments. I find this procedure of obtaining rate constants highly questionable since an average rate constant from a very limited number of experiments might not be physical at all, especially if the spread between these rate constants is very large (which seems to be the case as indicated by the negative lower bounds of reaction rate coefficients). Why should the kinetic rate constants vary between the experiments at all? Is it possible to find a "global fit" to all experimental data (cf. discussion in Berkemeier et al. (2013)), leading to a unique solution?

Comment 8

I am confused by the comparison of the obtained rate constants to literature values (p. 28300) and maybe I am misunderstanding this paragraph. If Pye et al. (2013) use a water concentration of 55 M to obtain a third–order rate constant, how does this compare to the third-order rate constant in this paper, which include H^+ as third body in the reaction? Is this 3-body reaction rate itself expected to be dependent on pH?

How much would it change in the atmospheric case? I would suggest revising this paragraph for better readability.

Comment 9

Could the authors elaborate how much of the deviation of φ_{SOA} from unity can be attributed to wall losses of (i) IEPOX and (ii) products? How strongly does this affect the wall-free atmospheric case? Can the authors give a clearer picture of all factors governing φ_{SOA} (in their model / in general)?

Minor Comments:

p. 28293, l. 9 – Please mention here why the growth ceases and that the amount of injected IEPOX will decrease over time. p. 28301, l. 4 – Please repeat here what is meant with φ_{SOA} for better readability.

References

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