Atmospheric
Chemistry
and Physics

Discussions

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

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Response to Anonymous Referee #2

**We thank Referee #2 for their comments and address each below. Our author responses are denoted after each referee comment with **.

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

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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.

**Gas diffusion may play a slight limiting role given the γ, and we have neglected any such effects in the results presented here. The effects of gas-phase diffusion would be most pronounced at large γ and particle sizes. Gaston et al. (2014) found only a slight effect (<10%) for this gas-aerosol system, and other systems with similar γ and aerosol sizes have reported minor effects (<3.5%) as well (Thornton et al., 2003). We have added the following statement to address this and reference the 1D models mentioned by the referee: "This approach neglects gas-phase diffusion – the effects of which are expected to be minor for the γ and particles sizes involved here (Gaston et al., 2014; Thornton et al., 2003). Aerosol-phase diffusion, adsorption/desorption of aerosol components, and other potential limitations that, while uncertain, have been explored in 1-D model studies for other systems are also not considered (Roldin et al.,

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2014; Shiraiwa et al., 2013; Wilson et al., 2012)."

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 kHet in this paper) over time. Would this change the predicted aerosol mass loading as shown in Fig. 1?

**We state that, "Aerosol surface area was held constant at initial seed aerosol levels over the course of a model run, and thus khet is insensitive to additional surface area resulting from IEPOX-derived SOA." The complete lack of studies regarding the effects of significant aerosol fractions of IEPOX-SOA on γ (or in other words khet) makes determining these effects prohibitively difficult, which we acknowledge unreservedly in the manuscript. Whether or not the particle growth does affect the uptake rate will depend on the nature of the SOA. Water soluble SOA may form homogenously mixed aerosols and enhance or perhaps not appreciably alter khet, whereas a more hydrophobic constituent may limit the uptake through core-shell coating effects such as those discussed by Gaston et al., (2014), which we reference in the manuscript.

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?

**As stated in the manuscript, "other SOA" was arbitrarily assumed to come exclusively from IEPOX-OS, even though the formation from tetrols and other reactions is plausible. This was a necessary simplification considering that we are unable to conclusively identify or quantify the individual species that make up the "other SOA".

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.

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**[H+] is held constant in the model. Presumably, this is not an oversimplification considering that H+ is a catalyst and should not be consumed by tracer formation. The following statement has been added to the manuscript: "[H+] and [H2O] are held constant over the course of a model run." We are unable to assess whether or not the production IEPOX-SOA could affect [H+] in other ways such as dilution.

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?

**The measured tracers are assumed to be essentially nonvolatile with any semi-volatile losses captured in Reactions R8 and the absence of these species on the collected filters. Given the lack of gas-phase tracer measurements and the uncertainty of parameters like effective Henry's Law constants for the tracers, such processes have not been considered. As stated in the manuscript, Reaction R8 is treated as a generic first-order loss and carries no pH dependence. We did not presume to know the formation mechanism of these volatile species and as a result, tried to keep the reaction as general as possible.

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?

**For each loop iteration, the rate constants were adjusted (k's for the first run were an initial guess), the model run, and the sum of the squares of the differences between the model and the measurements was calculated for minimization. MATLAB's Optimization Toolbox functions were used to perform the minimization. The optimization was ended when the sum of the squares of the differences was suitably low – all modeled tracers differed from the measured tracers by <5%. By requiring the rate constants to be

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positive there were no other values that led to the same model solution. We have included additional details in the manuscript.

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?

**The referee is correct in stating that kinetic rate constants should not, in theory, vary between the experiments. Averaging model outputs for a single initial experimental condition (seed loading and IEPOX injection amounts) would result in the smaller stated uncertainties, but we chose to represent the formation reactions as conservatively as possible by using different initial experimental conditions while insuring that there was reproducibility for a single initial condition. Requiring the rate constants to be positive ensured that the extracted rate constants were physical. While the standard deviation of the rate constants for the THFdiols and "other SOA" does exceed the mean, in reporting the standard deviation we err on the conservative side for the reported uncertainty. Admittedly, a Monte Carlo type simulation suggested by the referee may serve to reduce the uncertainty in the rate constants. However, the approach presented here is intended to be as unambiguous and straightforward as possible.

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.

**The rate constant obtained by Pye et al. (2013) which is derived from Eddingsaas et al. (2010) is directly comparable to the rate constant that we report. The same reaction, Reaction R1, is being described in both. While the aqueous-phase reaction mechanism to form the 2-methyltetrols is multistep, it is generally represented as an overall 3-body reaction by neglecting the formation of short-lived intermediates – a common practice. We have added text to this paragraph to communicate this is for the overall reaction.

Comment 9 Could the authors elaborate how much of the deviation of φSOA 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 φSOA (in their model / in general)?

**The IEPOX wall-loss and the aerosol wall-loss will both have similar effects on φSOA: as wall-losses increase, φSOA decreases. In this regard the following statement describing the factors that influence φSOA has also been added: "As described by Matsunaga and Ziemann (2010) and Zhang et al., (2014), wall-losses of VOC and SOA material can effectively decrease calculated φSOA for chamber studies. Considering the IEPOX and aerosol wall-loss rate constants provided above, the corrections for these experiments are minor (<2% change to φSOA). In general, φSOA should mainly be a function of the availability of nucleophiles, provided there is ample time for uptake and tracer formation (Riedel et al., 2015)." The referee raises an excellent point regarding the inclusion of φSOA for the atmospheric model case. We have added the following to the manuscript: "With the lack of wall-losses and the minor contribution of "other SOA", which lowers φSOA as described above, φSOA will be larger (φSOA = 0.125) for this atmospheric case compared to the chamber simulations."

Minor Comments: p. 28293, l. 9 – Please mention here why the growth ceases and

that the amount of injected IEPOX will decrease over time.

**We have edited the sentence to read as "The majority of the SOA mass growth occurred within the first hour of the injection period, and after 2h, significant SOA growth had ceased after the majority of IEPOX was injected and reacted."

p. 28301, l. 4 – Please repeat here what is meant with φSOA for better readability.

**This change has been made.

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Wilson, K. R., Smith, J. D., Kessler, S. H., and Kroll, J. H.: The statistical evolution of multiple generations of oxidation products in the photochemical aging of chemically reduced organic aerosol, Phys. Chem. Chem. Phys., 14, 1468-1479,

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 28289, 2015.

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