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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.

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Response to Anonymous Referee #1

**We thank Referee #1 for their comments and address each below. Our author responses are denoted after each referee comment with **.

Combining a box model and chamber experiments, the authors of this work provide constraints to the condensed-phase IEPOX reaction kinetics which lack experimental determination. The rate constants of a series of reactions are estimated by finding the best match to the measured tracer concentrations from filters collected in cham-

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ber experiments. Based on the rate constants, SOAformation under atmospherically relevant conditions is simulated, and the authors demonstrate that the results show consistency with a recent field measurement. Given that isoprene is by far the most emitted volatile organic compound species in the global scale, and that the reactions and uptake of IEPOX represent the most important steps of isoprene SOA formation, the current work is valuable and relevant to the scope of ACP. Before the paper is published, the following points should be addressed.

Comment 1 A major weakness of the current work lies in the fact that the rate constants are determined based on a countable number of chamber experiments whose conditions are not fully representative of the ambient atmosphere. A clearer link between the chamber and the ambient conditions should be presented. In particular:

1.1) Are the chamber conditions represent certain ambient conditions? If yes, the authors should mention what types of environment the chamber conditions are intended to simulate. If no, the authors should discuss potential problem of extrapolating the chamber experiments to the ambient.

**The main difference between the chamber and the atmosphere is the low RH and the lack of gas-phase IEPOX reactions. Given that we are investigating this as an isolated SOA production system, the latter are appropriately not considered. Indeed it is rare for ambient RH to be below 5%. The low RH means that the chamber aerosols have a comparatively small amount of liquid water, and the aerosol constituents are therefore more concentrated. Certainly the rates will change with aerosol liquid water, but, as we state in the manuscript, the rate constants themselves are independent of such RH effects. The vast majority of published chamber studies are performed at low RH. We agree with the referee's implication that higher RH experiments would be preferable, but, as discussed in the manuscript, performing these experiments at higher RH resulted in tracer inconsistencies that prevented such studies. Relatedly, at higher RH, the formation of hydrolysis products (i.e., 2-methyltetrols) may be too heavily favored, making it more difficult to obtain detectable quantities of the other tracers on the filters.

1.2) The authors can probably consider putting the ambient condition used in the simulation in Sect. 3.3 into Table 1 to make a clearer comparison with the conditions employed in the chamber experiments.

**Table 1 shows initial experimental conditions only. Including initial model conditions for the ambient simulation might cause confusion. Therefore, we chose not to add this information to Table 1.

1.3) Specifically, the chamber experiments are performed under dry conditions (i.e. RH < 5%), but this seems to be too low to represent the ambient condition. Can rate constants determined from dry chamber experiment be extrapolate to make implication for the ambient conditions? The authors should justify this in the paper.

**The formation rate constants for the tracers should be independent of RH. Please see the response to Comment 1.1 above regarding the RH of the chamber experiments.

1.4) In the simulation for ambient condition (Sect. 3.3.), RH is set at 50 %. Is this why 2-methyltetrol is the major SOA constituents in the ambient simulation, but “Other SOA” is the major constituent measured from the chamber? No explanations are provided to discuss the differences.

**The referee is correct that at the higher RH, the hydrolysis product loadings are enhanced. We allude to this Eq. 4 which shows the direct water dependence of the 2-methyltetrols formation rate. We have also added the following statement: “At the increased RH and associated increase in aerosol liquid water, the 2-methyltetrols represent the majority of the formed tracers (see Eq. 4).”

1.5) The authors mention that the ambient simulation is in “close correspondence to recent [field] measurements” (page 28302, line 3), but they do not seem very close to the reviewer. Why the major SOA constituents in the chamber and the simulation are different (also see the previous comment). Why sulfate titration is significant in

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the chamber but not under the ambient conditions? The authors should enrich the discussion to explain these differences.

**We did not intend to perfectly simulate the ambient observations. Our intent was to show that for a very general case, we are able to obtain tracer loadings on the same order as observations. We have changed the sentence indicate that the total tracer loading, rather than the distribution of tracers, is in “relatively close correspondence” to recent field studies. We have also added the following qualification: “Keeping in mind that we cannot hope to capture two field studies perfectly for such a general model case,” Sulfate titration is significant in the chamber because of the large amount of IEPOX used compared to the ambient simulation. At the comparatively small IEPOX mixing ratios used in the ambient simulation, there is simply not enough IEPOX to appreciably titrate aerosol sulfate. We have edited the sentence to communicate this: “Additionally, this simulation predicted no appreciable titration of total aqueous inorganic sulfate, suggesting that titration is unlikely to occur in atmospheric sulfate-containing aerosols given expected IEPOX mixing ratios on the order of 1 ppbv.”

Comment 2 Although the approach employed in the current work is robust in constraining rate constants that have not been measured experimentally, discussions about the limitations of this approach seems to be lacking from the current manuscript.

2.1) What are the potential danger of fitting multi-variables to match a countable number of chamber experiments? The authors briefly discuss the experimental limitations of the current work in Sect. 4 (Concluding Remark). Instead of mentioning these in the conclusion, the authors are encouraged to make a new section to summarize the potential shortcomings of the method.

**In requiring all of the rate constants to be positive, all nonphysical solutions to the minimization are not considered, so there is only one solution for each experiment. Any potential shortcomings or limitations stem mainly from method assumptions which are detailed throughout the manuscript in the appropriate sections. Examples include:

the lack of authentic standards for tracer quantification in the SOA tracer quantification section, the ability of the AIM model to correctly predict seed aerosol composition in the Model setup and evaluation section, the identity of the “other SOA” in the Model setup and evaluation section and now revisited in the Model-predicted tracer formation kinetics section, the assumption of 100% filter collection/extraction efficiency in the Model setup and evaluation section.

2.2) The uncertainties associated with the determined rate constants are currently listed as the standard deviation from the five chamber experiments (Table 3), but the uncertainties should be assessed more statistically. When each rate constant is fitted for the best match to the chamber experiment, can a statistical uncertainty be determined for each constant, instead of the standard deviation of the five experiments?

**As we state in the manuscript, the percent difference between the measured tracers and the model is quite small (<5%), so any statistical uncertainty calculated for the individual experiments would be much smaller than the standard deviation calculated across all of the experiments. Therefore, use of the standard deviations places a more conservative bound on the potential uncertainties than any statistics from the individual experiments.

2.3) Related to the previous comment, some of the uncertainties (Table 3) are so large that the rate constant can potentially be negative. Explanation should be added to address this issue. In particular, the large uncertainty associated with “Other SOA” formation should be discussed, given that “Other SOA” is the major fraction observed in the chamber experiment (Fig. 3).

**Indeed the uncertainties in the predicted rate constants for the THFdiols and the “other SOA” are larger than the rate constants. That said, none of the rate constants for any individual experiments were negative, a requirement that we state in the manuscript. This is certainly one of the drawbacks to this approach compared to a more traditional bulk-phase investigation of rate constants such as those described in

Eddingsaas et al., (2010) and Cole-Filipiak et al., (2010), where uncertainties are often just the error associated with a curve fit for the kinetic experiment. As we state in our response to Comment 2.2 above, the uncertainties are intended to be as conservative as possible. Please also see our response to Comment 7 from Anonymous Referee #2

Comment 3 The assumption of “other SOA” being IEPOX-OS should be better justified, or a sensitivity test should be performed. When “Other SOA” is assumed to be a compound with a larger or a smaller molecular weight, would the prediction of the rate constants be altered significantly?

**To clarify, we do not assume the “other SOA” is IEPOX-OS, only that it is formed from IEPOX-OS. The actual identity of the “other SOA” remains to be determined but, as we state in the manuscript, is likely a combination of both hydroxylated and sulfated products considering results from Lin et al., (2014). As suggested by the referee we have performed additional model runs assuming both a larger (600 g/mole) and smaller (100 g/mole) molecular weight for the “other SOA”. These tests are summarized in the added paragraph: “As a sensitivity test to the choice of 334 g mole-1 for the molecular weight of the “other SOA”, individual model runs were also performed assuming a molecular weight of 100 and 600 g mole-1. As expected, these tests had the most pronounced effect on the rate constants extracted from simulations with the largest “other SOA” loadings, Exp. No. 1 and 2 (see Table 2). For the 100 g mole-1 case, the resulting adjustment to the rate constants presented in Table 3 was at most a factor of 2.4 increase for IEPOX-OS and a 23% decrease, on average, across the remaining rate constants. For the 600 g mole-1 case, all of the rate constants were decreased by 25% on average. Apart from the IEPOX-OS rate constant under the 100 g mole-1 case, which was within 2sigma, all of the rate constants resulting from these sensitivity tests fell within the stated 1sigma uncertainties given in Table 3.”

Comment 4 I found that the information provided in Table 2 repetitive, making this table less informative. The authors are encouraged to find a better way to present the

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agreement between the actual measurement and modeled results.

**While we tend to agree with the referee that Table 2 is somewhat repetitive, the main reason we chose to display it as is was to provide readers with tracer loadings from each of the individual experiments. This information could be potentially valuable for other studies investigating IEPOX SOA components. Given the reviewer's comment and considering it is obvious from other figures and the text that the model reproduces the measurements well, we have removed the "model" rows from Table 2.

Technical comment: Page 28296 Line 3: "mostly likely" should be "most likely".

**This change has been made.

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