**Atmospheric
Chemistry
and Physics**
Discussions

Interactive comment on "Self-limited uptake of α-pinene-oxide to acidic aerosol: the effects of liquid-liquid phase separation and implications for the formation of secondary organic aerosol and organosulfates from epoxides" *by* G. T. Drozd et al.

Anonymous Referee #1

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Drozd et al. present findings from chamber experiments on the reactive uptake of α-pinene oxide (αPO) to acidic $(NH_4)_2SO_4/H_2SO_4$ liquid aerosol particles. Experiments with different levels of acidity and gas phase concentrations of αPO show that significant uptake is found only for highly acidic particles. This is also confirmed by bulk experiments of αPO uptake to concentrated aqueous sulfuric acid solutions. The authors report that effective uptake coefficients and effective partitioning coefficients correlate with initial acidity and the amount of organic aerosol material formed during reactive uptake. Reduced uptake is found for higher αPO gas phase concentrations.

It is suggested that an organic phase forms due to liquid-liquid phase separation on highly acidic particles, establishing an organic coating that limits further uptake.

The paper is well structured and the methods, results, and discussion are presented in a concise form. Some statements need to be revised for an unambiguous description. My main issue with this paper concerns the speculative nature of some of the assumptions and conclusions made. The procedures applied and data presented do not provide sufficient evidence for the conclusions drawn by the authors regarding the reasons for the self-limited uptake of αPO observed. The authors' explanation for the findings is plausible (on a certain timescale), yet with the current information only one possibility out of several. Additional information on the experiments and evaluation is necessary in order to clearly support or contradict the conclusions drawn. Alternative explanations of the experimental findings need to be discussed and major limitations of the assumptions made addressed adequately.

The topic of the paper and the new experimental data are certainly of interest for the community. However, this referee concludes that the manuscript needs to be improved substantially (see comments below) before publication in ACP can be recommended.

General Comments

1. Equilibration timescales of the experiments vs. physical and chemical steady-state and quasi-equilibrium assumptions.
   The authors state that the residence time in the continuous-flow chamber is ~ 4 h, which is in agreement with the physical dimensions and flows of the setup and the data of Fig. 2. In Section 2.1 it is stated that a a time of 3 to 4 hours to reach stable conditions is consistent with other studies using static chambers. How-

ever, the authors compare their steady-state timescale, i.e., the physical steady-state conditions due to their chamber volume and flows (residence time), with a reactive gas-particle partitioning "chemical" steady-state of static chamber experiments. Concluding from such a comparison anything about consistency and assuming that this means that chemical equilibrium is reached in the continuous-flow setup is speculative at best. In Section 3.5 it is correctly stated that the experiments do not directly yield the timescale to reach the final growth factor. The authors therefore use as an estimate a time of ~ 1.5 h from information on somewhat similar experiments by Iinuma et al. (2009), e.g. for estimating reactive uptake coefficients. However, Iinuma et al. (2009) did their experiments for a pH of zero and a concentration of 50 ppb αPO (i.e. at much lower concentrations than used in the study of Drozd et al.). It is possible that at acidities quite different from pH ~ 0 and higher precursor concentrations the timescale to reach "chemical" steady-state may be quite different (perhaps significantly longer than 4 h). The authors do not discuss this issue and no uncertainty analysis was made. It remains to be shown that the particles at high acidities actually reach (nearly) chemical equilibrium (uptake steady-state). Only if within this 4 h timescale all of the experiments reach chemical equilibrium, a comparison of effective partitioning coefficients and reactive uptake coefficients at different final growth factors is adequate. Otherwise the experimental findings may be interpreted as self-limited uptake, but instead it is possible that the uptake at higher αPO concentrations (higher growth factors) did not yet reach chemical steady-state and therefore equilibrium values of uptake and partitioning coefficients are compared to values during the process of ongoing particle growth.

Did the authors not attempt to address such issues by performing experiments at different chamber flow rates to obtain the chemical steady-state timescales for all experimental conditions used? Without this information, the interpretation of the experiments leaves a lot of room for speculations and assumptions that may be flawed.

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2. Definition and measurement / calculation of pH values.
   The effects of solution acidity are central to the current study and pH values given to characterize acidity. There are different ways to define pH values and different scales may be used, depending on whether units of concentration or actual chemical activity on a specific scale are used. The definition used in this work and the way pH values were measured and/or calculated should be described.

3. Diffusivity estimation vs. water loss measurements.
   In Section 3.4, the loss of particle water upon drying is discussed. It is stated that greater particle diameter growth was associated with a decreased water loss from particles. The authors suggest that the organic component (phase?) of the particles inhibited evaporation. However, the validity of such a conclusion depends on how the water loss data was obtained and on what timescale the water loss is inhibited. What was the residence time of the particles in the dryer? If the particles spent only seconds in the dryer, the larger particles with an organic coating may not have had enough time to evaporate on that timescale. It does not mean that they would not evaporate on a timescale of tens of seconds or minutes. So to conclude anything about the atmospheric relevance of the decreased evaporation, knowing the associated timescales is essential. Furthermore, if the organic diffusivity estimation of Section 3.3 is correct, the corresponding diffusivity of water molecules in the organic phase would likely be large enough to allow evaporation on the order of 0.01 s to a few seconds for submicron-sized particles. Hence, the conclusion that a liquid-liquid phase separation inhibits water loss and reactive uptake seems to be in contradiction with the estimated diffusivity value range. Again, a statement on the timescale for which such a limitation is considered important is missing – also with respect to atmospherically relevant timescales (typically greater than a few seconds) or concerns about timescales used in flow tube experiments and instruments.

Specific Comments

- Abstract (lines 16 to 18): Quantitative data for the effective uptake coefficient and the effective partitioning coefficient should be stated consistently and in a mathematically correct form, e.g., $(0.2 \text{ to } 1.6) \times 10^{-4} \text{ m}^3 \, \mu\text{g}^{-1}$ and not "$0.2 - 1.6 \times 10^{-4} \text{ m}^3 \, \mu\text{g}^{-1}$". Also on line 7 it should be: at 30 % or at 50 % RH.

- p. 7154, l. 6: In addition to the mentioned references, citation of Song et al. (2012) may be appropriate at this point.

- p. 7154, l. 14: (Smith et al., 2012): here also referring to Reid et al. (2011) and Krieger et al. (2012) is suggested.

- p. 7154, l. 25 and following page: "The chamber is run in steady-state operation with a constant gas flow of 13 Lpm for a chamber residence time of about 4 h, and in practice stable conditions were reached between 3 and 4 h. This is consistent with previous static chamber studies of epoxides and similar aerosol acidity, particle concentration, and αPO concentration that indicate reactive uptake reaches steady state after about 2 h (Lin et al., 2011; Iinuma et al., 2009)."
Comparing the steady-state timescale of the continuous flow chamber with 4 h residence time to the chemical steady-state timescales of other setups and stating that "This is consistent" seems rather misleading, as discussed above.

- p. 7155, l. 16: Statements require clarifications: "by atomizing a 0.2M (NH_4)2SO$_4$ with a nitrogen flow rate of 2 Lpm. Particle acidity was altered by adjusting the ratio of H$_2$SO$_4$: (NH_4)2SO$_4$ in the atomizing solution. In order to achieve precise growth measurements, the atomizer output was size-selected at 150nm using a DMA"
Consider: "by atomizing a 0.2 M aqueous solution of (NH_4)2SO$_4$" perhaps also adding "solution of (NH_4)2SO$_4$ and H$_2$SO$_4$ ", since the next statement mentions
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adjusting the sulfuric acid to ammonium sulfate ratio, without stating anything about a sulfuric acid content of the solution in the atomizer. It should be mentioned whether the DMA selects 150 nm particles by diameter or radius. Furthermore: how is the particle acidity measured / calculated / monitored? This should be stated.

- p. 7156, l. 12: The concentrations of the bulk solutions containing sulfuric acid are given. For a comparison with the acidity conditions of the chamber experiments, it would be good if corresponding pH values were stated as well.

- p. 7156, l. 21: "to monitor the depth of this colored layer with time and estimate the aqueous phase diffusion coefficient of αPO." Since apparently in the corresponding solution an organic phase forms on the top of the aqueous phase, should it not mainly be the diffusion coefficient of αPO through the organic-rich top phase combined with some diffusion into the aqueous phase? Furthermore, since the colored layer is formed as a result of acid-catalyzed reactive uptake coupled with liquid-liquid phase separation after the aqueous sulfuric acid phase is saturated, the growth of the organic layer may only allow a rough estimate of the bulk diffusion coefficient. The organic-rich phase may still contain a considerable amount of water, adding to the thickness of the layer. This may be worth some discussion.

- p. 7157, l. 9: What is the time after experiments started that is used for the volume-growth factors calculated? How can the authors be sure that until that chosen time, the particles did reach their near-equilibrium size for all different experimental conditions?

- p. 7158, Eq. (1): How well is the gas phase concentration known far from the chamber inlet? Is the C_g value assumed to remain nearly constant throughout the geometry and flows in the chamber? What is the estimated error for the

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evaluated $K_{p,eff}$? Please discuss.
Same page, l. 8 and 11: correct units.

- p. 7159, l. 7: The bulk diffusivity is calculated assuming that the colored top phase is consisting of organic reaction products only, but since water may also be present in that phase (concentration dependent, see comment above), this assumption may not be entirely valid. It seems possible, that the actual diffusivity would be lower than the current estimation, which would be more in line with the hypothesis of the authors concerning the self-limiting uptake effect of the organic phase. I suggest to add some discussion at this point, also regarding the diffusivity of αPO in the organic layer vs. the diffusivity of αPO in the aqueous phase. In addition, the estimated bulk diffusivity is compared to the diffusivity of glucose in water – but for what concentration of glucose and at what temperature (this information is essential for a meaningful comparison)?

- p. 7160, l. 9: It is stated: "The volumes of water can be predicted from the efflorescence and deliquescence curves for sulfuric acid and ammonium sulfate (Seinfeld and Pandis, 2006b)." This is a rather incomplete description of what was done and what is meant by "efflorescence and deliquescence curves". Efflorescence and deliquescence are phase transition events over narrow RH ranges when relative humidity is cycled. What curves were used from Seinfeld and Pandis (2006) and how were the acidities and phase transitions considered (reference should just be to year 2006, I do not see a 2006a anywhere)? Wouldn't it be better to calculate acidity and the water contents at the various sulfuric acid and ammonium sulfate compositions using a thermodynamic model (e.g., E-AIM, AIOMFAC, ISORROPIA), as it has been done by Iinuma et al. (2009)?

- p. 7160, l. 14: "This suggests that the organic component of the particle inhibited evaporation." As discussed above, the timescale over which the evaporation took place in the dryer is essential here.

- p. 7160, l. 17: "showed phase separation for particles of ammonium sulfate and organic compounds that have atomic O:C ratios of less than 0.7," A recent study by Song et al. (2012, GRL) has found a similar result as Bertram et al. (2011) using a wider range of organic components and compositions.

- p. 7161, l. 11,13: It should be called a "reactive" or "effective" uptake coefficient, because it combines effects of collision efficiency with subsequent chemical reaction (not purely physical uptake). Also, could the Authors give a reference for Eq. (4).
  On line 18 it should be written: we calculate reactive uptake coefficients between 1×10^{-6} and 50×10^{-6} for mathematical correctness.

- p. 7162, l. 5: Statement "We have demonstrated via bulk and aerosol chamber measurements that the reactive uptake of αPO to acidic aerosol is self-limiting due to liquid-liquid phase separation at high organic loadings." is too bold given the limited quantitative data and (lack of) associated uncertainty presented. A revision of this conclusion will be necessary alongside the changes in the revised article.

- Table 1: State what assumptions / model were used for the calculation of pH values (and what pH scale?). Also, state the temperature range and RH range of the experiments.

- Figure 6: Diameter growth units missing.

Technical Corrections

- At several places throughout the text: the proper citation style of ACP should be used. For example p. 7159, l. 18: "Lal et al. observed a change... (Lal et al.,

2012)." should be: "Lal et al. (2012) observed a change...". In these cases, there is no need to for citation at the end of the sentence.

- p. 7154, l. 9, 10: Zuend and Seinfeld are mentioned but Zuend et al. (2010) cited, do the authors actually refer to Zuend and Seinfeld (2012), Zuend et al. (2010) or both here?

- p. 7156, l. 14: wording and units: "to the room temperature vapor pressure of gas-phase αPO (0.819 torr, 25 C)." Maybe: "to the room temperature vapor of αPO (vapor pressure of ... Pa at 25 C)." (vapor is always in the gas phase) and pressure units should be SI units. Give a reference for the stated vapor pressure.

- p. 7157, l. 18: Iinuma et al. is mentioned (I guess Iinuma et al. (2009)?), but at the end of the sentence Lal et al., (2012) is cited.

- Figure 2, 3, 4, 5, 7: Sulfuric acid chemical formula should not be written with italic letter H.

- Figure 2: "time (hr)" should be time (h) to be consistent with the text. Stating in the caption the residence time of ~ 4 h in the chamber would be useful.

- Figure 3: First line of caption text needs some rewording.

- Figure 5: For consistency with Fig. 4 and 7, show blue symbols as triangles and show all three points for pH ~ 0 as in Fig. 7.

References

- Iinuma, Y., Boge, O., Kahnt, A., and Herrmann, H.: Laboratory chamber studies on the formation of organosulfates from reactive uptake of monoterpene oxides, Phys. Chem. Chem. Phys., 11, 7985-7997, doi:10.1039/B904025K, 2009.

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- Zuend, A., and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation, Atmos. Chem. Phys., 12, 3857-3882, doi:10.5194/acp-12-3857-2012, 2012.

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