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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 #2

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Review of manuscript “Self-limited uptake of alpha-pinene-oxide to acidic aerosol . . .” by Drozd et al.

The authors studied uptake of alpha-pinene-oxide to acidic aerosols using bulk solutions and submicrometer particles. In these studies, they showed that the reactive uptake results in products that phase separate, and they provide evidence that suggests the phase separation impacts the reactive uptake coefficients and loss of water upon drying. The paper is well structured and clear. The paper also addresses an im-

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portant new topic in atmospheric chemistry: liquid-liquid phase separation. The topic is well suited for Atmospheric Chemistry and Physics. Although the paper is very interesting, it needs to be improved before it meets the high quality expected for Atmospheric Chemistry and Physics. Specially, the authors have made assumptions in some of their analysis that need to be discussed further and better justified. More details are given below.

Page 7155. Lines 5-9. Smith et al. 2012 provided evidence of liquid-liquid phase separation, but I don't think they provided information on the morphology after phase separation. Papers that have considered morphologies after phase separation include the following: [Ciobanu et al., 2009; Kwamena et al., 2010; Reid et al., 2011; Song et al., 2012]. Other papers that may be relevant for this manuscript include the following: [Anttila et al., 2007; Prisle et al., 2010].

Page 7155. Line 18-20. "A DMA was used to size-select 150 nm particles." I assume this refers to particles with a single charge. Do particles with a double charge play a role in these experiments and contribute to uncertainty in the results? Please discuss.

Page 7156, line 11-13. How do the concentrations of sulfuric acid and pH used in the bulk studies compare with the concentrations and pH in the aerosol studies?

Page 7158, Section 3.2, line 8. The units are not written correctly.

Page 7158, Section 3.2. lines 7-10. On lines 7-10, the authors compared their measured effective partitioning coefficient with the effective partitioning coefficient reported in linuma et al. It would be useful to mention the growth factor in the experiments by linuma et al. since the current study shows that the effective partitioning coefficient depends strongly on this value. Without knowing the growth factor in the work by linuma et al. it is hard to compare the results directly.

Page 7158, Section 3.2 line 13. The authors state "this is good agreement given measurement uncertainty and the observed increase in uptake coefficient with lower alpha-

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PO concentrations". Please add a reference to previous measurements of uptake coefficients or refer to Section 2.5 for further information.

Page 7159, Section 3.3. The authors used Fick's law to estimate a diffusion coefficient. In addition, they assumed that the rate limiting step for the change in the thickness of the red layer over time is molecular diffusion. First it is not clear exactly what the authors used for distance, x , and time, t in their calculation. Second, for the liquid-liquid phase separation process I wonder if molecular diffusion is the rate limiting step for the change in thickness of the red layer over time. The authors should give some justification for the assumption of molecular diffusion controlling the change in the thickness of the red layer.

Is it possible that the reaction studied by the authors lead to a colloidal dispersion of organic-rich particles immersed in an aqueous-rich phase? This would appear as a cloudy suspension. If this is the case, then could the rate limiting step for the change in thickness of the red layer be due to coagulation of these organic-rich particles and transport of these organic-rich particles (not the molecules) by buoyancy forces. Please discuss why coagulation and transport of the organic-rich particles by buoyancy forces is not important.

Page 7160, Section 3.4. Here the authors are measuring the fraction of water lost, which is the change in water content from drying normalized to the predicted change in water content assuming only sulfuric acid and ammonium sulfate. The authors observed that the fraction of water lost is less than unity for a large amount of organic on the particles, and from the observations they conclude that the organic component of the particle inhibited evaporation. First, more information on the drying experiments are needed. For example, what was the residence time in the dryer and what were the starting and final RH values in the drying experiment? Also, how was drying achieved and were the particles dried below the efflorescence point of the particles? Second, I wonder if there is a possible thermodynamic explanation for the author's observations rather than a kinetic explanation. For example could a large fraction of the sulfate be

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converted into organosulfates, which would have different hygroscopic properties compared to sulfuric acid and ammonium sulfate? As another example, could some of the organic still mix with the sulfuric acid and ammonium sulfate even though there is phase separation? This would change hygroscopic properties, such as efflorescence relative humidities. These possible thermodynamic explanations need to be discussed and some justification for why they are not important needs to be given.

Page 7160, Page 3.4, line 24-25. This sentence could be improved for clarity. Maybe change to “the observed trend in water loss highlights the importance of phase separation in predicting water uptake/loss”?

Page 7161, Section 3.5. The authors use equation 4 to estimate an uptake coefficient from their experiments. The duration of condensation (Δt) used in the equation was taken from Inuma et al. 2009. Inuma used a different sized chamber (19 m^3 vs 3.5 m^3) and likely different experimental conditions. Why use the duration of condensation from Inuma et al.? The authors should also discuss how the uncertainty in Δt translate to an uncertainty in the experimental uptake coefficient (i.e. what is the uncertainty in the experimental uptake coefficient due to the uncertainty in the duration of condensation).

Page 7157. Line 18-20. “Inuma et al. ran experiments with acidic and neutral aerosol, but only observe uptake at $\text{pH}=0$ (Lai et al. 2012).” I assume that “Lai et al. 2012” should be replaced with “Inuma et al. 2009”.

Figure 3. In Figure 3a the red layer appears to be the less dense phase (i.e. the red layer is the top layer). In Figure 3b, however, the dark/red layer appears to be the more dense phase (i.e. the red/dark layer is the bottom layer). Why the change in the location of the red layer? Also in Figure 3b, at first glance there appears to be three layers – a top red layer, a middle clear layer, and a bottom red layer. I assume the top red layer is just a reflection/optical effect? Please explain what is shown in Figure 3b. Some annotation in the figure may help, or perhaps improved images may help.

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