

Overall Comment and Recommendation:

Nguyen et al. conducts a series of new dark reactive uptake experiments in the Caltech smog chambers using synthetic *cis*- and *trans*- β -IEPOX. This study basically follows the experimental approach of the UNC group (Lin et al., 2012, ES&T; Zhang et al. 2012, ACP); specifically, the Caltech group adapts synthetic procedures outlined in Zhang et al. (2012, ACP) to make *cis*- and *trans*- β -IEPOX to conduct a series of dark reactive uptake experiments in the presence of seed aerosol. The biggest difference in this new study compared to the previous UNC group studies is that the authors explore the effect of seed composition and relative humidity, which hasn't been fully examined in prior studies. Importantly, the results of Nguyen et al. are consistent with dry experiments conducted by Lin et al. (2012, ES&T). For example, Nguyen et al. directly analyzes the IEPOX-derived SOA generated in their experiments using the HR-AMS instrument. Similarly to Lin et al. (2012) (where this prior study collected filters from their dark reactive uptake experiments of β - and *d*-IEPOX and then extracted and reaersolized these extracts into a HR-AMS), this study also found a strong ion signal at *m/z* 82 in the AMS dataset. Consistent with both Lin et al (2012, ES&T) and Budisulistiorini et al. (2013, ES&T), this ion has now been proposed to be directly linked to IEPOX reactive uptake chemistry and has been resolved from PMF analyses of OA collected from isoprene-rich regions (Budisulistiorini et al., 2013, ES&T; Slowik et al., 2011, ACP; Robinson et al., 2011, ACP). Furthermore, OA formation was not observed from IEPOX in the presence of seed aerosol under dry conditions, which is again consistent with previous work. The most notable finding from this new study is that OA formation from IEPOX is observed from both *cis*- and *trans*- β -IEPOX only on wet ammonium salt seed aerosols, where as no significant uptake is observed on seed aerosols that are dry or contain no ammonium salts. These new findings are important and warrant publication in *Atmospheric Chemistry and Physics*, especially since they show that OA formation from IEPOX depends on coupled relationship between inorganic composition and liquid water content of pre-existing aerosol. I want to stress here to the authors and the Editors that I fully concur with Reviewer 1's comments and I won't repeat these here, but they should be fully addressed before publication. In addition, I have a number of specific comments that should be addressed by the authors before publication of this manuscript.

Specific Comments:

1.) Importance of $[H^+]$:

The authors need to be extremely careful in concluding that $[H^+]$ doesn't seem to matter as much as $[NH_4^+]$ in the atmosphere. First, field measurements by Lin et al. (2013, ACP) and Budisulistiorini et al. (2013, ES&T) acknowledged the likely fact that the IEPOX-derived SOA products could form upwind and over the

course of transport to their respective field sites. Thus, the aerosol likely became more neutralized (based on charge balance estimated by either IC or AMS analyses) over transport time. Thus, there was likely a weak correlation of the IEPOX-derived SOA to model estimated $[H^+]$ for this reason. I bring this up since the neutralization issue from previous field studies seems to be a major motivation for this new study. In addition, in the study by Lin et al. (2013), high-volume PM_{2.5} samplers were used. As the authors know, high-volume samplers do not use denuders of any kind and also use quartz filter media. As a result, it is possible that gases (inorganic and organic) absorb on these filters over sampling time to make charge balance appear to be neutralized. Finally, I remind the authors of the Surratt et al. (2007, ES&T) study on organosulfate formation from isoprene under low-NO conditions. Please refer to Figure 2B. As the authors know from this study, IEPOX (although not known at the time in 2007) was RAPIDLY consuming the inorganic sulfate in the seed aerosol (as measured by PILS-IC) to create the IEPOX-derived organosulfates. In fact, more than 50% of the initial inorganic sulfate as measured for the seed aerosol was consumed in just a few hours (more than wall loss alone could explain)! Thus, if you are someone in the field making IC measurements from filters, what you will likely find is that $[NH_4^+]$ appears to be in high abundance compared to $[H^+]$, and thus, the aerosol appears to be fully neutralized. These issues are MAJOR caveats to what the authors are strongly proposing here, and I think more caution is warranted in the discussion and conclusions about the potentially important role of $[H^+]$. I still don't think there is enough data (yet) to discount the need of $[H^+]$. The point I'm trying to make here is that measuring the aerosol acidity that gaseous IEPOX encounters in the field is not as straightforward as it may seem. This is always estimated at the site at where the aerosol is collected, but the reality is that upwind of the site the IEPOX partitioning and acid-catalyzed reactions in the particle-phase are kinetically limited and are occurring over the entire transport time.

2.) Questions about estimation of aerosol pH:

The authors estimate a particle pH of "-10" for MgSO₄+H₂SO₄ under dry conditions (RH<5%) in Lin et al. (2012). I am not sure if they estimate this based on the properties of bulk aerosol solutions (0.06M MgSO₄+H₂SO₄). If so, this is likely not accurate. If one uses IC data collected from these aerosol experiments, the aerosol pH is around 1.10 (estimated by isorropia) under dry acidic conditions.

Related to all of this, I'm curious as to why the AMS was not used to measure aerosol acidity as $NH_4^+_{measured}/NH_4^+_{neutralized}$? This seems very straightforward to do for these experiments. How would these values relate to your OA formation? As the authors know, the $NH_4^+_{measured}/NH_4^+_{neutralized}$ is a measurement of degree of neutralization, which could be useful to determine more- or less-acidic periods.

Aerosol acidity is indicated by H^+ (nmol/m³) which is the difference between NH_4^+ measured in the particles and concentrations of SO_4^{2-} , NO_3^- , and Cl^- . Estimating those values from AMS measurements might give information on the evolution of acidity on the aerosol over the course of experiments.

Lastly, I know the Caltech group has a PILS-IC system. I'm curious as to why this was not utilized as well to directly measure inorganic ions. This would seem useful as inputs into your model estimations of aerosol acidity.

I would suggest the authors add a section in the experimental section to more clearly describe how the aerosol acidity was estimated in each experiment instead of burying this information in the discussion sections. Would they agree? I think directly measuring the inorganic ions over the course of the experiment should have been done in feeding the models. I'm not quite sure if this was done or if instead the initial composition of the atomization solution was used.

3.) Question about the number of experiments:

How many experiments were conducted from the NaCl and Na₂SO₄ seed aerosol experiments? This wasn't clear from Table 1. Furthermore, from Table 1, it appears that each condition of RH and seed aerosol type has been examined once by the authors. Have these conditions been repeated to confirm trends you have observed in the data? This was unclear from the main text.

4.) Drying aerosol from the wet chamber before AMS detection:

How might the drying process before AMS detection affect the type of composition and abundance observed by this technique? Do the authors foresee any reaction occurring during this process? What aerosol acidity do you estimate when comparing the DMA data to the AMS data??

5.) Need of charcoal denuder:

It isn't clear in the text exactly why the charcoal denuder was used in this study before filter collection. Was this really used to remove gaseous IEPOX from the air stream before filter collection? If so, why was this done? Please clarify in the experimental section.

6.) Potential formation of a N-containing IEPOX-derived SOA constituent:

Why was the ESI source not also operated in the positive ion mode to detect the "potential" amine-containing products? This seems like a straightforward experiment to do. I'm not convinced by the AMS data alone that these products even matter. Since ESI operated in the positive ion mode is sensitive to basic

species (such as the proposed product in Scheme 2), I would expect you to be able to observe the proposed amine-derived product. Until then, I think these are fairly tentative. Along with this, molecular identification of SOA products is one of the weakest aspects of this study and would provide further credibility to the tentatively proposed pathways.

7.) Abstract and elsewhere:

The authors must be careful in saying neutralized conditions. Even with ambient aerosols, the aerosol pH is likely not 7. Usually it is somewhere between 4-5. Related to this, should you really use "non-acidified" in your title? Maybe it is better to remove this word in order to prevent readers from thinking you are using non-acidic particles. In most cases, the pH is below 4 (as shown in Table 1).

8.) Addition of NaOH to seed aerosols:

I'm still confused by this experiment. The reason for this confusion is you say the pH of your atomizing solution was 7, but the model estimated aerosol pH is really 5.5. You likely saw substantial OA formation due to the aerosol really being slightly acidic in the chamber and the water content being high. Thus, can you really conclude that $[H^+]$ really doesn't matter as much as $[NH_4^+]$?

9.) Related to # 8 above, I don't quite understand why they did not observe uptake with Na_2SO_4 seed. As shown in Figure 4, they definitely did not see uptake with $NaCl$ and Na_2SO_4 seeds, but the difference between NH_4Cl and $(NH_4)_2SO_4$ seeds is significant as well. It looks to me that both NH_4^+ and SO_4^{2-} are necessary. They cannot really conclude only on the importance of NH_4^+ . There is likely some interaction between NH_4^+ and SO_4^{2-} to cause the huge OA formation, and also the H^+ also matters.

10.) Figure 3:

In Figure 3, I think the data point is not enough to conclude that the reactive partitioning coefficient is low at atmospheric relevant pH. First, the modeled pH was not fully examined. In addition, there is no data point between pH 4-5.5, which is more representative of the real atmosphere. I think the authors need to at least provide one more data point there to show the consistency.

Minor Comment:

1.) References: I noted there are references cited in the main text but the details of these references are missing in the reference section. For example, Surratt et al. (2007) was cited in the main text but not in the references section.