Anonymous Reviewer #1

General comments

This manuscript describes environmental chamber experiments aimed at investigating the potential reactive uptake of isoprene-derived epoxides (IEPOX) onto a number of non-acidic aerosol seed particles under conditions of varying pH and relative humidity (RH). The main finding of the work is that IEPOX undergoes reactive uptake onto wet aerosol seeds comprised on ammonium salts, while no reactive uptake is observed when the aerosol seeds are dry or when non-ammonium salts (such as sodium) are present. These results are important in that they suggest an atmospheric mechanism by which IEPOX may undergo reactive uptake in a manner which is only weakly correlated to particle pH, a somewhat baffling conclusion reached from previous field studies. The ammonium-catalyzed mechanism proposed here is also novel for epoxide chemistry, and the work also raises the intriguing possibility of amine reactivity with IEPOX. The findings are relevant to the construction of accurate chemical mechanisms for the formation of isoprene-derived SOA. The work has been carefully planned and executed, and the manuscript is clearly written. For these reasons, this study is quite appropriate for Atmospheric Chemistry and Physics.

We thank the reviewer for the insightful feedback that has been helpful in improving the clarity of the manuscript. We've responded to the specific comments below and made the suggested revisions to the text.

Specific comments

p. 27684, line 24: Are the experimentally determined MS response factors (1.8) identical to the calculated dipole-polarizability MS response factors (1.4) to within the uncertainty of the measurement?

The definition of MS response ratio between species a and b were calculated in Paulot et al (2009b) as $R = S_a / [S_a + S_b]$, where S is the sensitivity of the species in CIMS. Our response ratio is calculated as $R = S_a / S_b$. If we calculate R from the theoretical dipole-polarizability approach described in Paulot et al. using the second definition, the response ratio is 1.6 (as quoted in Bates et al, JPCA 2014). This brings the theoretical response ratio within the uncertainty of the measurement of the experimentally-determined 1.8 ratio. We have corrected our error in describing the Paulot et al (2009b) number in the text so that it is directly comparable and added the following text after the response factor is mentioned in Section 2.2.1:

> *"The difference between the two ratios is within the error of the sensitivity determination."*

Figure 2: Why is the OA/IEPOX coefficient plotted on a log scale vs. LWC?

The log scale showed the 100%/-50% error bars as symmetric, so the data is easier to visualize than on a linear scale. We have reduced the range of the y-axis to eliminate most of the blank space.

Equation 1 suggests that there should be an inverse relationship.

We do observe an inverse relationship of $\Phi_{OA/IEPOX}$ with P_{LWC}. Equation 1 {$\Phi_{OA/IEPOX} = (C_{OA}/C_{IEPOX})/[10^{-6} \cdot R \cdot T \cdot P_{LWC}]$} suggests that if C_{OA}/C_{IEPOX} is constant, higher P_{LWC} will cause a decrease in $\Phi_{OA/IEPOX}$. If this were an equilibrium case (which is it not), C_{OA}/C_{IEPOX} would be proportional to P_{LWC}, thus keeping $\Phi_{OA/IEPOX}$ constant (then $\Phi=K_H$). However, in this non-equilibrium process, C_{OA}/C_{IEPOX} is dependent on both the amount of water available (Henry's partitioning) and the reaction kinetics which are dependent on the activities of the inorganic ions. The activities of the ions control the extent of Reactions 2 – 4 (i.e., inverse relationship with P_{LWC}) and the physical partitioning of the IEPOX controls Reaction 1 (direct relationship with P_{LWC}), so the overall effect is difficult to predict *a priori*.

p. 27691, line 12: I assume that the pH for the hydrated AS is somewhat acidic due to the bisulfate/sulfate acid dissociation process. This should be explicitly stated.

We have added the following underlined text under Section 3.1.2, "Particle Acidity," to explicitly mention this point that was previously implied (new text is bolded):

> *"Solutions of AS without additives had pH ~ 5.5 before atomization because, although no strong acid was present, H^+ is expected to be present in small quantities based on the dissociation equilibria of inorganics, **such as the bisulfate/sulfate dissociation**, and dissolution of CO_2."*

p. 27693, line 2: The actual kH+ value (0.036 M-1 s-1) for IEPOX-4 has been experimentally determined by Cole-Filipiak et al. (ES&T, 44, 6718-6723, 2010).

Thank you for pointing to this omission. We added the citation to Cole-Filipiak et al (2010) and the following text (new text is bolded):

> *"Eddingsaas et al. (2010) estimated k_{H+} ~ 5 x 10^{-2} M^{-1} s^{-1} **and Cole-Filipiak et al. (2010) determined k_{H+} = 3.6 x 10^{-2} M^{-1} s^{-1}** for IEPOX."*

p. 27693, line 5: Since this work identifies NH4+ as the catalyst for IEPOX uptake, I wonder why the authors did not carry out experiments at different NH4+ concentrations in order to ascertain whether the kinetics of the IEPOX uptake was catalyst-limited or nucleophile-limited. The subsequent discussion of differences in reactivity observed for different nucleophiles implies the latter, but this issue is not specifically discussed.

We are in the process of doing kinetic studies on IEPOX + NH_4^+ via NMR, similar to the experiments discussed in Eddingsaas et al (2010). These measurements are non-trivial due to the high salt content of the solutions, the long timescales of the measurements (because NH_4^+ is a weaker catalyst than H^+, as discussed on Page 27682, lines 27-28), and the advanced techniques involved (water suppression NMR). As such, the results are ongoing and will be discussed in an upcoming manuscript.

We are fairly certain we are in a nucleophile-limited regime because different nucleophiles affect the reactivity (as the reviewer pointed out) and because pH does not significantly impact the reaction (i.e., removing some of the catalyst activity, in this case H^+, does not make too much of a difference.) We added the following text in the Summary section:

"The weak dependence on pH and the strong dependence on nucleophile activity and particle liquid water suggest that the IEPOX reactions in hydrated ammonium salts are nucleophile-limited, rather than catalyst-limited"

p. 27694, line 14: It is interesting that the results seem to show that Cl- is a relatively poor nucleophile under the experimental conditions. While it is certainly possible that SO42- is a better nucleophile than Cl- under these conditions, Cl- is well known to be a better nucleophile than H2O. Since it is reported that no organochloride products were detected, it makes me wonder how much tetrol was produced under these conditions. I realize that the authors did not detect and quantify tetrol products in this study, but it might be useful to add a brief discussion of this issue.

We agree that this is worth discussing in more detail. Regarding the formation of tetrols, they are the thermodynamically-favored product (Darer et al, 2011) and so it should not necessarily follow that if H_2O is the poorest nucleophile that tetrols would be the least abundant compound in solution. Over time, even at moderate pH, compounds like organosulfates, organonitrates, and perhaps organochlorides will be converted to tetrols through hydrolysis.

Regarding why organochlorides were not observed, and whether it has implications on the nucleophilicity of Cl⁻ in this system, we have considered the following possibilities:

(1) <u>Are the organochlorides produced, but we are not measured well using AMS?</u> The EI source of the AMS should be able to ionize all the organic compounds, so the issue would lie in whether we can tell organic chlorine peaks from inorganic chlorine. The C-Cl bond is stronger than C-N bonds (~80 kcal/mol vs. ~70 kcal/mol, respectively), and we see organonitrates in the AMS as $C_cH_hN_{1-2}O_o^+$ and $C_cH_hN_{1-2}^+$ fragments. So it should be possible to witness the same fragments with Cl instead of N in the AMS ($C_cH_hCl^+$ for example), if they exist. For the NH_4Cl + IEPOX experiments, we have tried to look for the C-Cl containing fragment, suggested by Hayes et al (2013) to be CCl^+, C_2HCl^+, CCl_2^+, $C_2Cl_2^+$, $C_2HCl_2^+$, $CHOCl_2^+$, but did not find any evidence of these peaks.

(2) <u>Are the organochlorides produced, but they evaporate in the diffusion drier prior to being sampled with the AMS?</u> Organochlorides may be more volatile than the equivalent alcohol because the Cl group does not form hydrogen bonds with the solvent. For example, 2-chloro-2methylbutane (T_{boil} ~ 85 C) has a lower boiling point compared to 2-hydroxy-2methylbutane (T_{boil} ~ 102 C). If this is the case, we may be underestimating the total organic mass from the NH_4Cl experiments compared to the $(NH_4)_2SO_4$ experiments.

(3) <u>Are the organochlorides produced, but they are not stable in the aerosol water?</u> Darer et al (2011) demonstrated that tertiary organosulfates and polyols were stable in water, even at low pH. However, tertiary organonitrates get converted to polyols (hydrolysis) and organosulfates (nucleophilic substitution) in a relatively short time, and the hydrolysis is seemingly pH-independent. There is no such data on organochlorides, but it may be possible that they are hydrolyzed or are involved in other nucleophilic substitution reactions because the chloride anion is a relatively good leaving group. If this is the case, we might slightly underestimate the

total organic mass from the NH_4Cl experiments compared to the $(NH_4)_2SO_4$ experiments because Cl^- (35 g/mol) is heavier than OH^- (19 g/mol).

We have added the citation to Darer et al (2011) in the text, and the following discussion at the end of Section 3.2.1. "Cation and anion substitutions":

> *"Further, gas-phase organochlorides were not observed by the CIMS. It is possible that organochlorides are produced but are easily hydrolyzed in the aerosol liquid water due to the relatively-good leaving group ability of Cl^-, i.e., the hydrolysis behavior of organochlorides is more similar to that of tertiary organonitrates than that of organosulfates (Darer et al., 2011). It is also possible that organochlorides are preferentially evaporated in the diffusion drier because they might be more volatile than organosulfates or polyols. In both situations, but more so the latter, the total organic mass from the NH_4Cl experiments would be underestimated by ToF-AMS. Although we did not quantify tetrols and other polyols in this work, it is expected that they are present in substantial quantities because they are the thermodynamically-preferred products in the epoxide ring-opening reactions.*

p. 27695, line 16: With the Henry's Law coefficient in hand, it would be useful to provide a quick estimate of the extent of IEPOX physical partitioning under typical atmospheric conditions. Is it important at all?

If one assumes 2 ppb (2×10^{-9} atm) as an average IEPOX mixing ratio (which is realistic for the BEARPEX 2009 campaign), particle liquid water ~ 10 µg m^{-3}, and $K_H = 3 \times 10^7$ M atm^{-1} (+ 100%, - 50%), we obtain **0.04 – 0.14 µg m^{-3} IEPOX$_{(aq)}$.**

Given that the average organic aerosol mass at BEARPEX 2009 was 3.7 µg m^{-3} (Zhang et al, 2010), the condensed-phase IEPOX from physical partitioning alone can contribute up to 4% to the OA mass for this assumed liquid water content. The physical partitioning becomes more important in areas like the Southeast US where there is high liquid water content coupled to high isoprene emissions.

References:

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