

Response to Reviewer Comments: Climate-Relevant Physical Properties of Molecular Constituents for Isoprene-Derived Secondary Organic Aerosol Material

Comments from T. B. Nguyen

This work by Upshur et al describes the viscosity, octanol-water partitioning coefficients, and surface tension depression characteristics of four IEPOX isomers and syn- and anti-2-methyltetraol compounds. The main goal of the work is to assess CCN activity of these biogenic compounds. Modeling (GAMMA) and field data comparisons were done to estimate relevant concentrations of IEPOX in the condensed phase (7- 12 mM in certain areas) and measurements covered the relevant range. This is a good physical chemistry study that offers novel information about important compounds in the atmosphere. The manuscript should be published in ACP, after the following comments have been thoroughly addressed.

Detailed Comment #1:

I have reservations about measuring IEPOX with a commercial GC. This is not typically employed for IEPOX measurements, and we are starting to realize the reasons. Now that IEPOX standards are more readily available for study, it has been demonstrated that they are quite labile to decomposition upon heating and especially when sampled through metals in the Agilent GC inlet and sample loop. One of the preliminary results from the recent FIXCIT laboratory campaign (forthcoming manuscripts) is that IEPOX decomposes into methyl vinyl ketone (amongst other products) in the heated sample loop (150 degC) and inlet (155 degC) of a commercial GC before elution through the column. The campaign experiments showed that changing the temperature of the sample loop and inlet changes the decomposition yield. Column choice may still matter in that one selects which decomposition products one can detect. I will be happy to share preliminary data with the authors if necessary. Based on the chromatograms shown in the SI of this work, it indeed appears that IEPOX has decomposed in the Agilent GC (inlet 260 degC), leading to a myriad of peaks in the chromatogram in contrast to the clean chromatogram of the methyltetraols. This does not diminish the importance of the measurement, only that it may change the interpretation. The authors should discuss in more detail about the peaks in the chromatogram, why they picked the peaks they did to represent IEPOX, and what does it mean for the k_{ow} measurements if the GC-MS peak was a decomposition product instead of IEPOX.

RESPONSE:

Overlap of octanol and IEPOX+octanol GC trace (Figures S3 and S4 below) has been added to supplementary information as evidence that we do not believe we observed significant IEPOX decomposition in our GC setup. Additional peaks in chromatogram are attributed to octanol. Also when we consider the case of δ -IEPOX (Figure S4), where there are two diastereomers present, the integration ratio of the two peaks in the chromatogram (appearing past the 12 minute mark) matches that calculated for the two δ -IEPOX diastereomers by NMR. Figure S5 is also added to supplementary information, showing that a common decomposition product of the IEPOX compounds, methyl vinyl ketone is not present at significant concentrations in the IEPOX chromatograms.

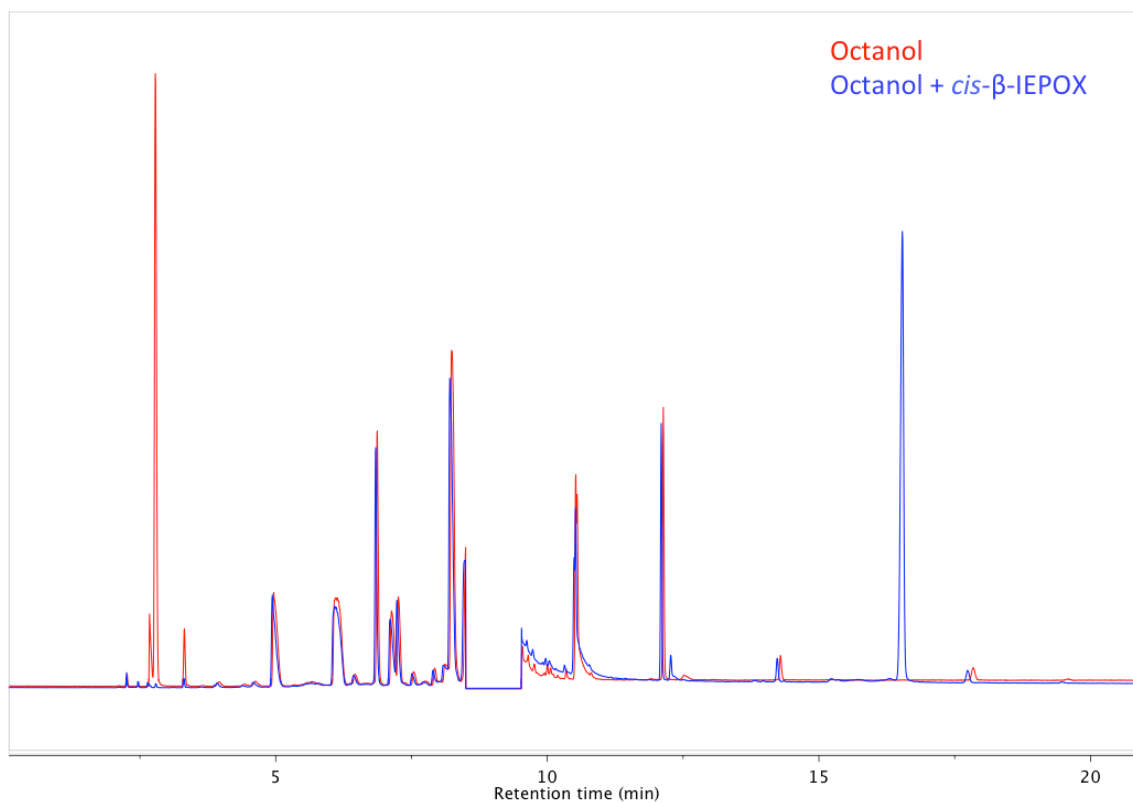


Figure S3. Overlap of GC chromatogram of octanol solvent and solution containing octanol and ~45 mM *cis*-β-IEPOX. Octanol peaks occurring around the 2-minute mark are attributed to contamination of other solvents while peak eluting around 16.5 minutes is attributed to the *cis*-β-IEPOX isomer.

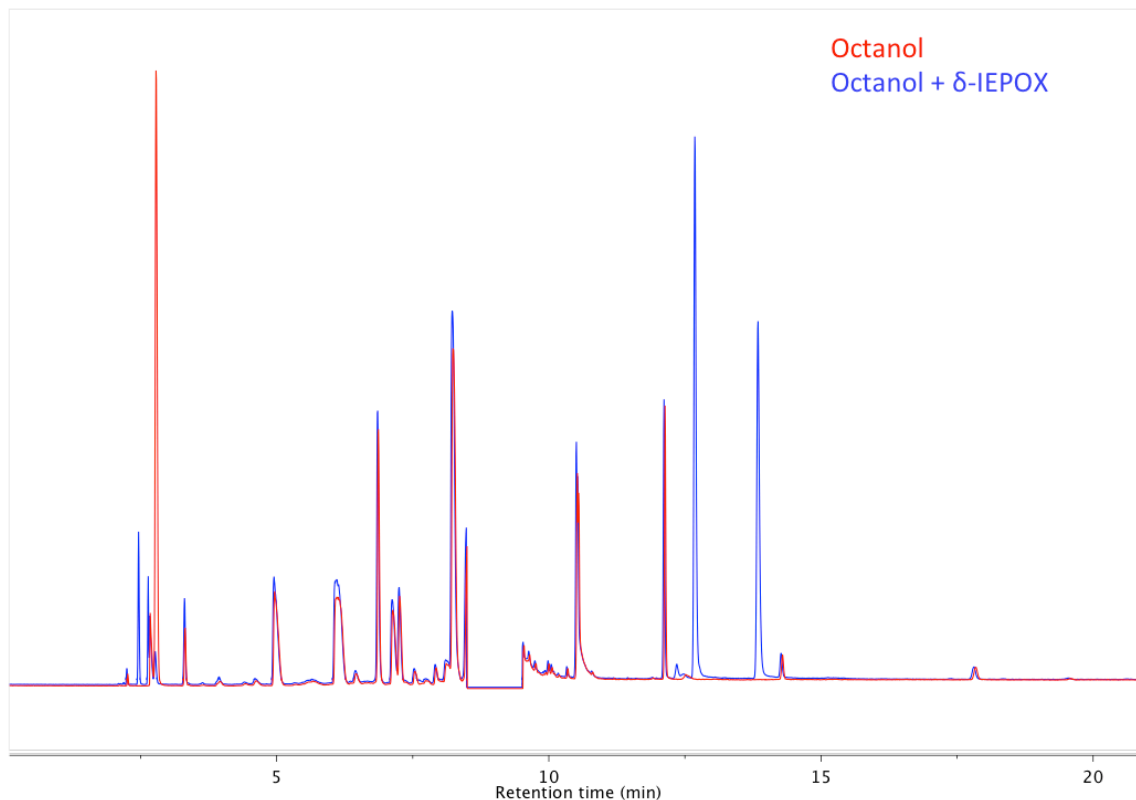


Figure S4. Overlap of GC chromatogram of octanol solvent and solution containing octanol and ~45 mM δ -IEPOX. Octanol peaks occurring around the 2-minute mark are attributed to contamination of other solvents while peaks eluting around 13.9 and 12.7 minutes are attributed to the two δ -IEPOX diastereomers. Integration ratios of the two peaks assigned to the two δ -IEPOX diastereomers on the GC chromatogram match integration ratios calculated by NMR.

Detailed Comment #2:

When the authors mixed IEPOX with ammonium sulfate, does some of the IEPOX convert to organosulfates and tetraols? This reaction may be slow, but I wonder if it is at all important in the timescale of the measurements done here?

RESPONSE:

Reaction of IEPOX with ammonium sulfate and conversion of IEPOX compounds to organosulfates and tetraols was determined to occur on too slow a timescale to be relevant for the measurements done here.

The sentence on page 17202 line 9: “Solutions were stored in glass vials at ~4 °C.” was deleted.

The following sentences was added in its place (page 17202 line 9):

“Solutions containing 100 mM IEPOX compounds in 1 M $(\text{NH}_4)_2\text{SO}_4$ were allowed to stir at room temperature for one week and monitored by NMR. No conversion into the organosulfate or tetraols was observed during this time. All solutions for surface tension experiments were measured within a week of their formation and were stored in glass

vials at ~4 °C in between measurements to further reduce the probability of conversion of IEPOX compounds into the organosulfate or tetraol products.”

Detailed Comment #3:

It’s not clear to me why *cis* and *trans* β -IEPOX would have similar hydrophobicities (k_{ow}) and similar reactive uptake (from Nguyen et al, ACP 2014) but different surface activity. Can the authors speculate on the reason for this?

RESPONSE:

We appreciate the reviewer’s comments. In order to add further speculation as to why *trans*- β -IEPOX (1) and *cis*- β -IEPOX (2) may have similar hydrophobicities but different surface activities the following sentences was added on page 17206 line 20:

“The difference in surface activity of *trans*- β -IEPOX (1) and *cis*- β -IEPOX (2) may be a reflection of the fact that the relative orientation of the two hydroxyl and the single epoxide groups in *cis*- and *trans*- β -IEPOX (1, 2) differ and so does their propensity to form hydrogen bonds with water molecules inside the water droplet. The greater surface tension depression of *trans*- β -IEPOX (1) may indicate that this compound forms fewer hydrogen bonds than *cis*- β -IEPOX (2), which could be verified through computational chemistry, such as molecular dynamics simulations.”

Technical Corrections

a) Introduction – I do not believe that Bates et al 2014 supports the idea that oxidation products have low volatility and condense or dissolve into cloud droplets to make SOA. Quite the opposite: that was a gas-phase study and showed that OH oxidation of IEPOX results in fragmentation, which increases volatility of the oxidation products in relation to the parent.

We agree with the reviewer that the Bates et al. 2014 is not an appropriate citation on page 17198 line 24 and was removed.

b) Section 2.1: The authors should mention the purity of the synthesized compounds and whether measurements performed in this work are sensitive to certain impurities at the 5% level (which is approximately the accuracy for most NMRs).

The following sentence was added to section 2.1, page 17200 end of line 18:

“Purity of synthesized compounds was determined based on NMR spectra. Measurements performed in this work are most likely insensitive to impurities below the detection limit of NMR spectroscopy due to the higher concentrations of IEPOX and tetraols used in this study (above micromolar amounts).”

c) Pg 17208, line 12: Nguyen QT, et al, 2013 appears to be unrelated to the aqueous IEPOX mechanism and GAMMA. That work studied the source apportionment of inorganics in particles in Greenland and does not discuss IEPOX. Could the authors have meant Nguyen TB, et al, 2014 instead?

Nguyen et al. 2013 citation was removed from page 17208, line 12 and replaced with the correct citation Nguyen et al. 2014.

d) Pg 17209, line 23: cis-b-IEPOX makes up \approx 1/3 of the isomer distribution so why would SFG spectra look exclusively like the trans-b-IEPOX (\approx 2/3 the distribution) and

not a weighted average of the two? Figs. 2-3 show that their surface tension depression properties are very different.

SFG spectroscopy is sensitive only to surface components of the aerosol material and is insensitive to compounds (such as *cis*- β -IEPOX) that may be present within the bulk of the aerosol material. Therefore the match between SOA material and the spectrum of *trans*- β -IEPOX (rather than a weighted average of the *cis*- β -IEPOX and *trans*- β -IEPOX) could be due to the increased surface activity of *trans*- β -IEPOX, indicating that *trans*- β -IEPOX is present at much higher concentrations at the surface of the aerosol. In addition, the increased stability of the *trans*- β -IEPOX may result in a longer lifetime within the aerosol, also contributing to the resemblance between *trans*- β -IEPOX and SFG aerosol surface spectrum.

“Surface specific” was added to page 17209 line 23 in order to emphasize this point: “This *surface-specific* study identified...”

e) Pg. 17210, line 5: Worton et al (2013) does not seem to fit here. The laboratory studies by Elrod and coworkers, e.g., Darer et al, EST 2011 which studied the formation and stability of organonitrates and organosulfates, would be more relevant. Also, I suggest to drop or modify “acid-catalyzed” because this is not the only way the epoxide ring can open. As mentioned in (1), heat + metals work and so does ammonium. We may yet find out more mechanisms besides acid.

References were edited so that Worton et al. 2013 is removed from page 17210 line 5 and Darer et al. 2011 was added in its place. The phrase “acid-catalyzed” was removed from page 17210 line 3 in order to reflect that there may be other mechanisms involved in epoxide ring opening.

f) References: a number of references appear to be missing titles.

References were submitted to ACPD in the correct form but the technical editors mishandled the document and introduced the errors. Nevertheless, the references have been edited to include titles/authors where missing:

Page 17210 line 20 (Bates et al. 2014)

Title missing: Gas Phase Production and Loss of Isoprene Epoxydiols

Page 17210 line 23 (Broekhuizen et al. 2004):

Title missing: Partially soluble organics as cloud condensation nuclei: Role of trace soluble and surface active species

Page 17211 line 4 (Chan et al. 2010):

Title missing: Characterization and Quantification of Isoprene-Derived Epoxydiols in Ambient Aerosol in the Southeastern United States

Page 17211 line 7 (Claeys et al. 2004a):

Title missing: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide

Page 17211 line 7 (Claeys et al. 2004b):

Title missing: Formation of secondary organic aerosols through photooxidation of isoprene

Page 17211 line 12 (Corrigan et al. 1999):

Title missing: Cloud condensation nucleus activity of organic compounds: a laboratory study

Page 17215 line 17 (Salma et al. 2006)

Authors missing: Salma, I., Ocskay, R., Varga, I., and Maenhaut, W.

Comments from Y. Rudich

In this study, Upshur et. al. synthesized isoprene oxidation products that may partition into secondary organic aerosol phase. It is hypothesized that under atmospherically relevant concentrations some of these compounds (trans- α -IEPOX (1) for example) could lead to substantial reduction in the surface tension which would translate into activation of cloud droplets at lower relative humidities than super-saturation conditions that would otherwise lead to cloud droplet activation. The authors measured also the octanol-water partition coefficient and showed that some of the products will tend to be dissolved in the organic phase rather than the water phase. However the results of this section of the study are not very well connected to the main focus of the paper and perhaps should be omitted, unless specifically discussed.

Overall this is a good laboratory study, which should be published as such. The synthesis of these compounds opens a nice avenue for interesting research and this is important by itself. I am questioning how robust and relevant are the conclusions about the atmospheric implications though. First, we do not really know if these products will indeed be in significant concentrations in the aerosol/droplet phase. There is no supporting evidence from the GAMMA runs, and no validation or comparison of the GAMMA conclusions with measurements. Adding such validation is essential for strengthening the paper. More information about the modeling should be provided. Also, if the uptake of these compounds is governed by reactive uptake, wouldn't these compounds be transformed to a different species that may not be surface active? Since these compounds would partition to the organic phase, how do you envision that they will partition from the aerosol phase to the aqueous phase? Some discussion about these issues is warranted. These issues need to be discussed in order to put the results in the atmospheric context. Finally, these references deserve to be included in the introduction and in the discussion: [listed].

Comment #1:

“Results of this section (octanol-water partition coefficients) are not very well connected to the main focus of the paper and perhaps should be omitted, unless specifically discussed.”

RESPONSE:

We appreciate the reviewer's comments but we believe that the octanol-water partitioning coefficients indicate the relative hydrophobicities of the compounds in this study and are therefore relevant when compared to the surface tension results. In particular, the partitioning coefficients indicated that *cis*- β -IEPOX and *trans*- β -IEPOX had nearly identical hydrophobicities but significantly different surface activity, demonstrating that orientation and potentials for hydrogen bonding within an aqueous droplet may differ for these two compounds. In the case of α -IEPOX, its increased hydrophobicity relative to the other IEPOX compounds may have also contributed to its higher observed surface activity (see page 17204, line 26) and potentially its increased instability relative to the other IEPOX compounds.

The following sentences were added on page 17206, line 20:

“The difference in surface activity of *trans*- β -IEPOX (1) and *cis*- β -IEPOX (2) may be a reflection of the fact that the relative orientation of the two hydroxyl and the single epoxide groups in *cis*- and *trans*- β -IEPOX (1, 2) differ and so does their propensity to form hydrogen bonds with water molecules inside the water droplet. The greater surface tension depression of *trans*- β -IEPOX (1) may indicate that this compound forms fewer hydrogen bonds than *cis*- β -IEPOX (2), which could be verified through computational chemistry, such as molecular dynamics simulations.”

Comment #2:

“We do not really know if these products will indeed be in significant concentrations in the aerosol/droplet phase. There is no supporting evidence from the GAMMA runs, and no validation or comparison of the GAMMA conclusions with measurements. Adding such validation is essential for strengthening the paper. More information about the modeling should be provided.”

RESPONSE:

Based on the Reviewer’s suggestion, we have created a Supplementary Information section describing GAMMA 1.4 and the details of the calculations.

Comment #3:

“If uptake of these compounds is governed by reactive uptake, wouldn’t these compounds be transformed to a different species that may not be surface active?”

RESPONSE:

Our revised materials and methods section now includes a statement referring to NMR data that show no hydrolysis of the epoxides in ammonium sulfate solution over the course of one week. While reactive uptake may be important in other systems, and is certainly important for SOA particles, it is not relevant for our aqueous model experiments. A sentence to that effect is now added on page 14, before the ‘Conclusions’ section.

Comment #4:

“Since these compounds would partition to the organic phase, how do you envision that they will partition from the aerosol phase to the aqueous phase?”

RESPONSE:

The epoxides will partition to cloud droplets or aerosol water in particles where there is no separate organic phase present. They will then partition further to the surface of the aqueous droplet given their differences in surface activity.

Comment #5:

Include listed references in the Introduction and/or Discussion

1. Djikaev and Tabazadeh, 2003 will be added to references cited on page 17199 line 5, as well as references cited on page 17206 line 24.

Full Reference: Djikaev, Y.S., and Tabazadeh, A.: Effect of adsorption on the uptake of organic trace gas by cloud droplets, *J. Geophys. Res.*, 108, 4689-4697, 2003

2. Aumann and Tabazadeh, 2008 will be added to references cited on page 17199 line 8.

Full Reference: Aumann, E., and Tabazadeh, A.: Rate of organic film formation and oxidation on aqueous drops, *J. Geophys Res.*, 113, D23205, 2008

3. Tabazadeh, 2005 will be added to references cited on page 17199 line 8, as well as references cited on page 17206 line 24

Full Reference: Tabazadeh, A.: Organic aggregate formation in aerosols and its impact on the physicochemical properties of atmospheric particles, *Atmos. Environ.*, 39, 5472-5480, 2005

4. Taraniuk et al., 2007 will be added to references cited on page 17199 line 8, as well as references cited on page 17206 line 24

Full Reference: Taraniuk, I., Graber, E.R., Kostinski, A., and Rudich, Y.: Surfactant properties of atmospheric and model humic-like substances (HULIS), *Geophys. Res. Lett.*, 34, L16807, 2007

5. Taraniuk et al. 2008 will be added to references cited on page 17199 line 8, as well as page 17206 line 24.

Full Reference: Taraniuk, I., Kostinski, A.B., and Rudich, Y.: Enrichment of surface-active compounds in coalescing cloud drops, *Geophys. Res. Lett.*, 35, L19810, 2008

RESPONSE:

These have been added, and we thank the reviewer for pointing them out.