

## ***Interactive comment on “Climate-relevant physical properties of molecular constituents relevant for isoprene-derived secondary organic aerosol material” by M. A. Upshur et al.***

**TB Nguyen (Referee)**

tbn@caltech.edu

Received and published: 23 July 2014

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 com-

C5207

ments have been thoroughly addressed.

Detailed comments:

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.
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?
3. It's not clear to me why cis and trans b-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?

C5208

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.

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).

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?

d) Pg 17209, line 23: cis-b-IEPOX makes up  $\sim 1/3$  of the isomer distribution so why would SFG spectra look exclusively like the trans-b-IEPOX ( $\sim 2/3$  the distribution) and not a weighted average of the two? Figs. 2-3 show that their surface tension depression properties are very different.

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.

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

---

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 17197, 2014.