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Atmospheric
Chemistry
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Discussions

Interactive comment on “Reversible and irreversible processing of biogenic olefins on acidic aerosols” *by* J. Liggio and S.-M. Li

Anonymous Referee #2

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Review of "Reversible and irreversible processing of biogenic olefins on acidic aerosols" by Liggio and Li.

General comments:

This paper presents new experimental data for the reactive uptake of selected monoterpenes, oxygenated monoterpenes and sesquiterpenes to sulfuric acid particles. The same authors have reported in their previous work that the reactive uptake of isoprene, alpha-pinene and their gas phase oxidation products to sulfuric acid particles can lead to the formation of high Mw compounds and this manuscript essentially presents similar results for other biogenic volatile organic compounds (BVOCs). While the presented information is interesting, the experimental approach used in this study is not satisfac-

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tory. In addition, I have serious concern about the way the authors have interpreted the data. Among my concerns, my biggest problem with this manuscript is the proposal of formation mechanisms for high Mw compounds based solely on the AMS data. In my opinion, the AMS data presented in the manuscript is not sufficient enough to draw reaction pathways and formation mechanisms. The authors must at least show evidence for the presence of proposed high Mw compounds from GC-MS or HPLC-MS analysis. Another point that I have a serious concern is the experimental conditions used in this study. The BVOC concentrations are unrealistically high and the pH values are unrealistically low compared to atmospheric conditions. The authors acknowledge this problem in the "Atmospheric Significance" section. However, the argument put forward by the authors in favor of the employed experimental conditions is not convincing mainly because no atmospheric evidence for such polymeric biogenic olefins is presented in the manuscript. Therefore, I feel that the manuscript requires more than a major revision and it is not suitable for publication in ACP at this stage.

Specific comments:
Page 11975, line 15-29
There are a number of papers that the authors have not cited here but should be cited here.

Table 1
It seems that the authors have used AIM2 calculated H+ concentrations to derive pH values shown in the 6th column. The pH values need to be calculated from H3O+ activities instead of H+ concentrations. Do the revised pH values still support authors' explanation for higher organic mass yields at lower RH? The presented initial seed particle composition indicates that the sulfuric acid concentrations for the lowest RH experiments were almost that of concentrated sulfuric acid (98

Page 11977, line 9-10
Why do you change aerosol composition and hydrocarbon concentrations within the same group of experiments? It makes more sense to run two separate sets of ex-

periments, one with acidic seed particles and the other with neutral particles at the same hydrocarbon concentration, so that the influence of acidity can be compared. The comparison experiment must be included if the manuscript to be considered for re-review.

Page 11977, line 10-11
What is the reason to choose such large seed particle diameter? I would expect highly acidic particles in freshly nucleating nano-particles rather than sub-micron particles. The authors need to give a rationalization for this size selection.

Page 11977, line 24
The PTR-MS results are unfortunately not shown in the manuscript. They should be included in the manuscript or Supplemental Information.

Page 11978, line 15
The AMS operating conditions such as the EI voltage and ion source temperature should be given. Have the authors considered utilizing lower EV and temperatures for better structural elucidation of high Mw compounds using the AMS?

Page 11979, line 3
The heading should be "Results and Discussion".

Page 11979, line 14
How do the time profiles of other experiments look like? Time dependent mass loading curves for other experiments should be included in Supplemental Information. In addition, there appears to be severe wall losses. How did the authors eliminate the contribution of wall reactions, especially for sesquiterpenes? Fig. 1 shows a dramatic decrease in available surface area as a function of time. How much does this influence the uptake and partitioning of the olefins to the particle phase?

Page 11980, line 20
"under atmospheric conditions" should be "under atmospheric RH conditions".

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Page 11980, line 22-23
Assuming that the pH values shown in Table 1 are correct, does the solubility greatly differ between pH -1.0 and -1.5?

Page 11981, line 25-26
Have the authors observed an increase in the gas phase hydrocarbon concentration when the RH is increased? Does the PTR-MS data support the authors' claim?

Page 11982, line 8-9
In my opinion, the evidence provided by the authors is not sufficient enough to support this sentence.

Page 11982, line 21-24
The authors state here that numerous ion fragments appear in the mass spectra and they are far greater than the Mw of the monoterpene and oxygenated monoterpene. I disagree. The highest m/z signals that I see in Fig. 4 and Fig. 2 of Supplemental Information are all smaller than m/z 280 regardless of starting biogenic olefins. There aren't even such signals for sesquiterpenes. Moreover, the intensities of such signals are very low.

Page 11982-11985, Section 3.2. and 3.3., Figure 5 and Figure 3 of Supplemental Information
In addition to the lack of evidence for proposed products, I have a serious concern about the proposed formation mechanisms.
- Why do the authors propose secondary carbocation pathways instead of tertiary carbocations in Figure 3 of Supplemental Information? A secondary carbocation is unstable unless it is adjacent to a conjugated system.
- In the same figure, the authors suggest a ring opening of cyclobutane as a first step. Why is it so?
- The proposed fragmentation patterns are not based on the single compound analysis and do not provide meaningful information to readers. Moreover, why do similar

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fragmentation patterns correspond to similar reaction mechanisms?
- In Figure 5A, the authors suggest the formation of a tertiary carbocation at the C(1) position where the endocyclic double bond is located. In general, a tertiary carbocation does not form when it cannot become planar.
- Sulfate is not a good nucleophile. The steps from A to E and G to K are very unlikely under the employed experimental conditions.
- Sulfuric acid is also a good dehydrating agent. How does this influence the uptake of hydroxy-monoterpenes at lower RH?
- Doesn't the position of a double bond (endo- or exocyclic) influence the formation of a carbocation, hence the reactivity?
- Why does the abundance of m/z 205 for beta-caryophyllene imply a carbocation polymerization mechanism? Have the authors compared the mass spectra for pure beta-caryophyllene particles (and monoterpenes) and experimental data using an AMS (not a NIST reference mass spectrum)?
- A decrease in an AMS sulfate signal is not reliable evidence for the formation or existence of organosulfates.
- By increasing RH, the authors state that the equilibrium shifts to the gas phase rather than the hydration due to the decrease in solubility. Do the authors have equilibrium constants to support this claim?
- Does the (Low RH-High RH) for 3-carene (Fig. 4c) mean the subtraction of Exp. 11 from Exp. 9 at the end of the experiments? This information should be included. How does the subtraction of Exp. 9 mass spectra at 200 min (high RH) from at 100 min (low RH) compare to Fig. 4c?

Page 11987, line 2
How do the AMS derived TSP masses compare to the DMPS or SMPS values?

Page 11991-11995, Atmospheric Significance
This section is unnecessarily long and confusing. The authors should focus on the

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most possible scenarios in which the proposed mechanisms may play a significant role rather than a list of all probable scenarios.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11973, 2007.