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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air" *by* M. Ehn et al.

Anonymous Referee #1

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This manuscript presents elemental composition data of highly oxidized compounds as clusters of nitrate ion, NO3-, and biogenic volatile organic compounds, especially a-pinene, oxidation products. The authors present a brief description of the APi-ToF instrument and mass calibration procedure for a large mass range, followed by comparison of mass spectra from Jülich chamber and the Hyytiälä field site along with a hypotheses for the formation mechanism of the highly oxidized compounds. Finally, the authors estimate the concentration of neutral molecules from the observed ion clusters. The data presented is very convincing and the manuscript is suitable for publication in ACP after the following comments are addressed.

General comments:

1. Methods: Can the authors provide a quick statement as to why the experiments

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were conducted at the specific conditions reported? Where these the conditions at Hyytiala when the field data was collected?

Last paragraph of the "Data analysis and APi-TOF mass calibration" section. This paragraph needs further improvement. In its present form, it will confuse the reader. I suggest deleting this paragraph and adding a sentence at the end of the previous paragraph stating that throughout the iterative process of adding new ions for mass calibration, the difference between the 3-parameter fit and the exact mass of each ion was within the 20 ppm instrumental accuracy.

2. Identification of elemental composition: Pg 4601/line 12. The authors use exact mass of the proposed ion and the 10 ppm mass accuracy to calculate the different elemental composition that are within this mass range. Rather, wouldn't it be more appropriate to use the measured mass of the ion at 340 Th and the mass accuracy to identify the compound that best fits this peak?

3. Possible formation mechanism: Where there any chamber experiment done at low RH, that can be compared to the experiments discussed here and provide an insight into how important gas-phase hydration is? Also, clearly stating that α-pinene oxidation products that have aldehydes and ketones, along with carboxylic acids, are possibly hydrated in gas-phase, thus producing products that have high O to C and H to C ratios would clarify the argument for a reader. Another hypothesis that is presented is hydroperoxide formation. Can the authors refer to any past studies that provide an indication to the yields of hydroperoxides from α-pinene ozonolysis? It would be helpful for the reader if the hypotheses are clearly stated at the start of the section followed by the reasoning for each one.

4. Estimation of neutral HOM concentrations: Can the authors provide a reference for the ion lifetimes used in the calculation of the HOM concentration. Although the HOM concentration is a lower bound estimate, have the authors considered ion transmission difference between NO3- ion and HOMâĂćNO3- clusters as a function of

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mass/charge? I would assume that this correction will be less than an order of magnitude but accounting for this difference would nevertheless be useful.

Specific comments (page/line)

4591/14 – remove “can”

4592/1-4 – These two sentences seem out of place. Also, absorptive partitioning theory was proposed by Pankow (1994) and not by Robinson et al.

4592/13 – Add Smith et al (2010) reference

4594/13 – Correct Thompson to Thomson (Th)

4594/23 – Change “running” to “operating”. Please change similar wording in other places, example 4594/28 change “run” to “operated”.

4595/2 – Add reference for the transmission numbers quoted here.

4595/6 – Remove “so”

4595/25-26. The authors quote the α- and β-pinene concentrations in the figure captions but please also mention them here.

4596/10-11 – Please remove the wording “it cannot be stressed enough” and I suggest the authors rather use “therefore”.

4597/12-14 – Please re-phrase the sentence. As worded, it does not provide any information.

4597/15 – Remove “the”.

4598/11 – Remove “practically”.

4598/11-12 – Please reword “under field conditions with frequently changing conditions”. I suggest, “However, with frequently changing ambient conditions . . .”.

4598/24 – Change “comes off” to either “desorbs” or “evaporates”.

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4599/29 – Change “look” to looks.

4600/17 – Remove “truly”.

4600/19 – Reword “still next to identical”. I suggest “largely consistent”.

4600/22 – Authors mention that 341 Th is different is chamber and field data, but Fig 2c does not show any difference. Please clarify?

4602/21 – Change “were” to “are”

4605/13 – Please add the reference for ester formation.

4606/12 – “water to the carbonyl groups”

4610/22 – Remove “at night”

Figures

Fig 1 and 2: Please offset the spectra from the origin slightly and add intermediate ticks. Also, increase the font size for the axes labels.

Figure 3: Increase the font size for the axes labels and legend.

Fig 4: Please label these as (a) and (b) rather than left and right so that it is easier to refer them in the main text (see pg 4603/ line 1). X-axis label missing. Also, increase the font size for the axes labels and legend.

Fig 5: Increase the font size for the axes labels and change E.g., to e.g. in the caption.

Pankow, J. F.: An Absorption-Model of the Gas Aerosol Partitioning Involved in the Formation of Secondary Organic Aerosol, Atmos. Environ., 28, 189–193, 1994.

Smith, J. N.: Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, PNAS, doi/10.1073/pnas.0912127107, 2010

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4589, 2012.