Review of Caudillo et al.
Anonymous Referee #2

Referee comment on "Chemical composition of nanoparticles from α-pinene nucleation and the influence of isoprene and relative humidity at low temperature" by Lucía Caudillo et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-512-RC2, 2021

General comments

Caudillo et al. present chamber measurements of new-particle formation from α-pinene (AP) oxidation products at low temperatures, and study the effects of added isoprene (IP) and increased relative humidity (RH). The main focus is on the chemical composition of gas-phase species and (non-size-resolved) ultrafine particles, determined with a nitrate chemical ionization mass spectrometer and a thermal desorption-differential mobility analyzer, and in addition also nucleation rates are reported. Isoprene is observed to affect the chemical composition through an increase in e.g. C_5 and C_{15} compounds, and to suppress new-particle formation as also reported in other studies.

Simultaneous measurements of gas- and particle-phase composition are essential for improving the understanding of biogenic secondary aerosol formation. The manuscript is generally well written and the results are clearly presented. I can recommend the work to be published in ACP after the authors have addressed the following comments:

Specific comments

1. Regarding the discussion on the effects of isoprene on the elemental composition, especially C_5 and C_{15} compounds are stated to be increased in intensity. This seems clearer in the case of gas phase, whereas for particle phase the effects seem more diverse and e.g. Figure 3 shows similar increases in the signal intensity for various compounds with carbon content of up to ca. C_{18}, C_{19}. I cannot clearly distinguish a stronger increase specifically at C_{15} in Figs. 3 or S1; can this be further clarified?

2. It may not be obvious that higher particle growth rates (GR) at larger particle sizes are due to isoprene (Section 3.2.1, last paragraph: "Reaching the same mass with a lower
number of particles for the experiment with isoprene (αIP-30,20) compared to α-30,20, means that the growth rates at larger sizes (> 15 nm) are higher in the presence of isoprene”.

Particle GRs can generally be higher at lower particle number concentrations, as the amount of available condensable vapor per particle is higher. Can it be concluded that the enhanced growth at larger sizes is specifically related to isoprene, and not to such dynamic effects?

3. Effect of RH (Section 3.2.2): the particle mass concentration is observed to increase at elevated RH at otherwise similar conditions. However, Fig. S3 shows that the α-pinene level is somewhat higher for the experiments with higher RH. Can the higher AP level contribute to the increased particle mass?

Also, the RH range of 60-100% for the high-RH experiments is rather broad. What is the reasoning for lumping together these different RH values, and is it possible that the RH effects vary within this 60-100% range?

4. Similarly to the RH experiments, it seems that the AP level during the particle formation event and sample collection of the isoprene experiment is not exactly similar to the experiments without IP; it seems to be lower for the AP-IP set-up (Figure 1, third row). Can this affect the AP vs. AP-IP comparison?

5. Section 3.3: It would be helpful to list the actual fractions of the different VBS bins instead of only stating that the particle-phase species are mainly LVOC, ELVOC and ULVOC (it also seems that ULVOC is only a minor fraction). This could be a table with the bin fractions given for the different experiments.

6. The O₃ level of 100 ppbv seems rather high. How does it compare with typical tropospheric values? This is relevant considering the discussion on the effects of mixing ratios on the composition and nucleation of HOM (Section 3.4.1).

7. On P5L149-150, it is stated that particle evaporation before analysis should not be substantial; can this be assessed in a quantitative manner? Are there other uncertainty sources such as different charging efficiencies or transmission of the compounds?

I also agree with Referee #1 that an assessment of the relative contributions of the smallest and the larger particles to the particle-phase mass samples would be very useful.

8. P11L350: The meaning of “GCR conditions” is not explained; please clarify.
Technical corrections

P6L174: The particle formation rate is said to be defined as the flux of particles of a certain size as a function of time, but presumably the reported rates are not actually time-dependent; “as a function of time” should thus be removed, for clarity.

P6L202: It may be more appropriate to write “this is in line with the results of Kiendler-Scharr et al....” instead of “this confirms the results of ...”

P7L226-227: Please reformulate the expression “the gas and particle of α-pinene” and similar occurrences.

P8L245: Please change “nSEMS” to “nSMPS” (?)..

P8L254: Change “growth at higher sizes” to “growth at larger sizes”.

P9L268: The term “mass distribution” (here referring to particle mass size distribution?) may be a bit misleading as it might be confused with elemental composition or volatility distribution; please reformulate.

Figure 2 and similar plots: also the particle-phase fractions should preferably be written as positive instead of negative numbers (even if they are presented on the “negative” axis).

Caption of Figure 2: For clarity, “each system” could be changed to “each system and phase”.

Caption of Figure 3 and similar occurrences: the expression “mass defect plots of gas and particle phase and the intensity difference between them” is misleading; this sounds like the intensity difference between the gas and particle phases instead of the difference between the experiments. Please reformulate.

Legend of Figure 6 and similar occurrences: Please change “GRC” to “GCR”.

Caption of Figure 8 and similar occurrences: Please change “galactic comic rays” to
“galactic cosmic rays”. :-) 

Caption of Figure S4: Please state that this is Figure 5 in linear scale.

Figure S5: Why are the orange shades triangle-shaped?

Caption of Figure S6: Please explain the meaning of “overflow bin” and why the values of the first bin are both negative and positive.