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Comment on acp-2022-312

Anonymous Referee #2

Referee comment on "The influence of the addition of isoprene on the volatility of particles formed from the photo-oxidation of anthropogenic–biogenic mixtures" by Aristeidis Voliotis et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-312-RC1>, 2022

In this manuscript the authors report on experiments where they investigated the volatility of SOA particles in chamber studies, using both single precursor and mixed precursor experiments. The precursors were chosen to present two important biogenic VOC (isoprene and α -pinene), and a VOC to represent anthropogenic emissions (cresol). Their findings show that simple interpolation from single precursor data does not always yield correct predicted values for the mixed systems compared to actual measured values, bringing into question the validity of using such an approach in many models.

The overall results presented in the manuscript are good and an important addition to our understanding of the complexity of atmospheric SOA formation and one of the relevant properties of SOA, its volatility. There are few minor revisions (detailed below) and technical comments that would need addressing, but after those have been successfully handled, the work can be accepted for publication.

General comments:

- More discussion on the atmospheric relevance of the results is in order. The used [VOC] concentrations and seed concentrations are quite high, and may impact the behaviour of the system both chemically and physically. The effect of this in the experiments is pointed out in the manuscript lines 294-295, but should be further discussed later in the manuscript as well. Similarly, the [OH] reported is quite low in comparison to the [VOC], and it is much closer to atmospherically relevant concentrations. How does this affect the interpretation and relevance of the results? The possible change of reaction pathways is mentioned ($\text{RO}_2 + \text{HO}_2$ to $\text{RO}_2 + \text{RO}_2$), but

the effect and implications for the results could be discussed further.

- It is mentioned that due to low organic mass produced in some experiments, the last FIGAERO sampling cycle has been chosen for each experiment for further analysis (lines 180-183). This is a good approach, however it would be better to include the OH exposure for different samples, and add discussion on the potential effect of (possibly) differing OH exposures.
- How were the FIGAERO-CIMS data calibrated? This should be made more clear, especially as C* can also be directly derived from measured FIGAERO-CIMS data, if there are proper T_{\max} calibrations done.

Detailed comments:

- lines 120-121 and 125: what is meant by additivity and predictions could be introduced here as well with a sentence.
- lines 136-138: it would be useful to provide background [VOC] concentration as well. Especially as in the isoprene case the "background" mass formation was mentioned to be $1\mu\text{g m}^{-3}$.
- line 145: "setting its walls in constant motion" has this noticeable effect on particle wall losses? The data used in the study is wall loss corrected at least regarding particles?
- line 153: "using aqueous solutions of ammonium sulfate of concentration 10 g L^{-1} ." How does the size distribution of the seed population look like? To condensing vapours, total surface area is more relevant than total mass, how does the seed surface area compare between experiments?
- lines 180-183: "Due to the particularly low organic concentrations in the first hours of the experiments with the o-cresol and o-cresol/isoprene systems as well as for comparison with the TD measurements, all the results shown here by the FIGAERO-CIMS correspond to the data obtained during the last FIGAERO-CIMS cycle of each experiment (i.e., > 5h after lights on)." how do the OH exposures between chosen samples compare with each other? Can they be directly compared in this manner? Depending on the results of the OH exposure calculation, this needs to be discussed further.
- lines 184-188: "As a result of a lack of calibration standards and the experimental limitations associated with the FIGAERO-CIMS operation, the quantification of the observed signals remains challenging (Riva et al., 2019). Consequently, in this study, uniform instrument sensitivity was assumed for all the detected products. Detailed description of the instrumentation and the experimental setup is provided in Voliotis et al. (2021)." What calibrations have been done? Gas phase and/or particle phase sensitivity calibrations? Voltage scanning? T_{\max} /temperature ramp calibration? Due to the relevance of the FIGAERO-CIMS data and method for the results and their interpretation, it is important to include this information here as well.
- lines 206-208: "During the gas phase sampling, the instrument was periodically flushed with high purity N_2 in order to establish a dynamic gas phase "instrument background" signal, which was subtracted from the measurements" Was the N_2 flow humidified? Was there a significant change in instrument response due to changing $[\text{H}_2\text{O}]$ in the IMR?
- lines 208-213: "A corresponding "instrument background" was assumed for the particle phase measurements to be the 60th-90th second of the desorption cycle as shown in Voliotis et al., (2021). In the second step, the data collected during the "chamber

stabilisation" phase (see Section 2.1) were subtracted from the gas-phase measurements to account for any potential background gas phase species in the MAC. Correspondingly, the data collected during the "dark unreactive" phase (see Section 2.1) were subtracted from the particle phase measurements to account for any potential chamber background and/or seed effects." This is mostly very nice and thorough. However, were there no filter blanks taken during the experiments? There can be a measurable effect of gas phase collecting on filter, leading to seemingly higher signal for certain ions, and this effect will not be captured by using the tail of the thermogram or samples taken before reactions start.

- line 236-238: "The resultant volatility of the identified compounds in each system was expressed in logarithmically spaced bins in the VBS framework as:..." Does this mean that the direct volatility information of SOA total bulk was not used or analysed? This could give a direct way to compare different experiments with each other, assuming proper instrument calibration.
- lines 328-329: "Although the SOA mass formed at the isoprene single-precursor experiments was found to be below our background ($\sim 1 \mu\text{g m}^{-3}$), in all isoprene-containing systems studied here we were able to attribute a small fraction of the total FIGAERO-CIMS signal ($\leq 6\%$) to isoprene-derived products" Here it is mentioned that isoprene-derived products were found in mixed systems. Were the isoprene-derived products identified only from these mixed experiments, or was the isoprene only experiment data analysed to identify the isoprene-derived products? How easy were they to distinguish from whatever was in the "background" particles produced in the chamber?
- lines 332-335: "In support of this, it can be seen from Figures 4 and 5 that the majority of the isoprene-derived products have $C^* \geq 100 \mu\text{g m}^{-3}$ which would cause these products to remain predominantly in the gas phase in the single-isoprene experiments where the total absorptive mass was $\leq 1 \mu\text{g m}^{-3}$." In Table 1 it can be seen that in high [isoprene] and [α -pin]+[isoprene] the seed is comparable. Is the idea here that the isoprene oxidation products would only condense towards the end of the mixed experiment? Is this supported by the data during the experiment? I.e. there is more isoprene-derived products that only appear at the end of the experiment(s)?
- line 342: "'Common" were classified as the products with common elemental formulae between the systems involved." Does this mean all three cases of systems? And not just the ones used in each experiment?
- line 361: relating Figure 4: there doesn't seem to be C_{15} compounds in α -pinene+isoprene mix, although one might expect C_{10} and C_5 compounds to form C_{15} . Is there a possible explanation for this?
- line 377-378: "The SOA volatility distribution measured in the o-cresol/isoprene showed high variability between the two experiments conducted (i.e., see error bars in Fig. 3 middle panels)..." For me all the error bars in each panel seem comparable in range (top and bottom, respectively). I see no real difference in the middle panels compared to the other two.
- line 371: "...TD showed three peaks,..." I'm not sure how you can say there are three peaks in the TD figures. With such large error bars, it could be as justifiable to include the signal at 0.1 as is to include the $100 \mu\text{g m}^{-3}$.
- lines 374-376: "The SOA concentration in these experiments was of the order of $10 \mu\text{g m}^{-3}$ so the presence of such high concentrations of IVOCs in the particulate phase can be explained either by very high corresponding IVOC concentrations in the gas phase or by a significant underestimation of the less volatile SOA components by the FIGAERO-CIMS technique." Has it been considered if the high IVOC contribution might be an effect from using FIGAERO-CIMS, and assigning false C^* to the smaller thermal decomposition compounds known to appear in FIGAERO-CIMS data?
- line 379: what does "appreciable" mean here? How much of the 46% was this largest fraction?
- lines 416-418: "Considering that in the binary systems, only half of the total initial reactivity of the system was attributed to each of the precursors, the experiments at

half initial reactivity were used to make such predictions." Here again bringing up if OH exposures were calculated/estimated for each system? This could help with understanding how the system developed, and present a possible additional source for observed differences.

- line 422: "...in the FIGAERO-CIMS measurements the LVOC, SVOC and IVOC content were about 0, 87 and 13%, respectively (Fig. S4)..." Relating also for the mentioned Fig. 4S: how much of the IVOC signal, present only in FIGAERO-CIMS data, is actually thermal decomposition? as this been considered and taken into account during data analysis? The total lack of LVOC in FIGAERO-CIMS data seems odd, as their presence is shown in TD data.
- lines 441-445: "Particularly, the FIGAERO-CIMS measurements showed that the o-cresol/isoprene system had a ~10% increased measured than predicted IVOC fraction with a corresponding decrease in the SVOC fraction. The TD measurements showed a similar LVOC/SVOC split between the measured and predicted volatilities, yet the measured volatility distributions exhibited significantly higher contributions in the $C^* \geq 100 \mu\text{g m}^{-3}\text{bin}$ (18% vs. 11% of the total mass; Fig. 3)." Why the discrepancy between FIGAERO-CIMS and TD?" Cresol-isoprene TD has larger variability compared to the other two systems, but much less than in FIGAERO-CIMS. Could this be related to formed products breaking more easily in the cresol-isoprene case than e.g. α -pinene-isoprene case? This would explain the large number of IVOCs present, as it has been suggested that compounds labelled as IVOC can sometimes be actually thermal decomposition products. This might go towards explaining some of the changes in predicted vs measured IVOC/SVOC.
- lines 489-490: "...were almost identical with those measured ($\leq 3\%$ of the total mass/signal; Fig. S5 and S6)." Figures S6b and Fig 3 tern.mix do not seem identical. Am I comparing the right ones? This is somewhat unclear.
- lines 493-494: "...a system that cannot also be predicted based on the additivity (see Fig. S5)." Should this say "a system that can also"? They seem relatively consistent with predicted to me.
- lines 500-503: "Interestingly, the measured volatility distributions are lower compared to those predicted in all cases and for both techniques, further confirming that the chemical interactions occurring in this system will lower the resultant SOA particle volatility." The measured and predicted values presented in S7 middle panels seem very similar in both methods. Is it really worse than what is shown in Figure 3 for ternary system? I cannot see a real difference.
- line 556: "Such an example might be clean environments where the RO₂:HO₂ has been found to be high..." Would such clean atmosphere have the quite high [VOC] used in these experiments?

Technical comments:

- line 17: "using" instead of "use of a"
- line 48: "in a chemically highly complex" instead of "in a highly chemically complex"
- line 177: "at the exhaust of the ion molecule region (IMR)" what does this mean? I do not quite understand where the mass flow controller was positioned.
- lines 179-180: "The reagent ions were produced by passing CH₃I and UHP N₂ over a 210 Po radioactive source introduced directly into the IMR." would be better to replace

- "introduced" with "connected".
- lines 329-330: "...is significant and/or this is could be attributed to a" please fix the grammar
 - lines 332: "...opposed to the single-precursor isoprene would have favoured the partitioning of the more volatile species..." grammar: add "which" between "isoprene" and "would"
 - line 338: " Figure 3: Measured and predicted based on the additivity SOA particle volatility distributions from the TD..." the "what" of the description should be at the start, after "predicted".
 - line 338: relating Figure 3: it is commendably to have the error bars in the figures, but they make reading the bottom row bar plots quite tricky. There are already many coloured segments in the plots, with the added error bars especially bottom left figure is almost unreadable in detail. One option could be to ,for this one figure, to leave the error bars out form the main figure, but then include them in additional Supplements figure.
 - line 348: add "were" after "6%"
 - line 350: "and our technique is unable to resolve" should this be "OR our technique is unable to resolve"? Add "that" before "our technique".
 - lines 392: relating Figure 5: the chosen colour scheme might be very challenging to readers with red-green colour blindness.
 - line 516: "to what extent" rather than "the extent that"
 - line 517: "combination of both" instead of "combination of the above".
 - line 526: "interactions still lead" not leads
 - Supplementary material:
 - Figure S2: Are the symbols presenting particle phase signal, or the square root of the signal, as in all other figures?
 - Figure S3: Is isoprene shown in the figure? I can't see it.
 - Figure S5: last sentence of the description should read: "...result that is consistent **with** the chemical information..."