

Multiphase composition and reactive oxygen species formation during limonene oxidation in the new Cambridge Atmospheric Simulation Chamber (CASC) by Gallimore et al.

Reviewer comments

This is an interesting paper highlighting the capabilities of a new simulation chamber in Cambridge. A variety of online measurement techniques were used to characterise the gas and particles formed during limonene ozonolysis. Of particular interest are the online reactive oxygen species measurements, showing potential difference in the times scale for ROS formation. I do have a number of concerns that need to be clarified before publication in ACP.

General comments

Experimental

Firstly there is too little experimental detail given in this paper. The authors direct the reader to other papers for basic details on the mass spectrometers. For instance the flow rate and mass analyser (and indeed the mass resolution) used for EESI is not given. Since this is a unique instrument, the reader should be given much more extensive details of the instrumentation and its capabilities without needing to read another paper alongside this one. There are lots of cases where the reader is directed to a paper that has been submitted and so I cannot judge the links inferred.

Again, since this is the first chamber paper I need more details. The chamber is apparently collapsible but I couldn't work out if this was what was happening or was a dilution flow being used? What was the final volume of the chamber and does that impact wall losses? There are lots of details of the lamps and then the NO_x chemistry, but then I assume these are not actually used in the one experiment that is shown? There seems to be a disconnect- is this a chamber characterisation paper (which is limited) or a SOA characterisation paper? Most of the chamber characterisation is in the SI.

Diffusion versus ozone uptake

Firstly more details are needed about the model. Is partitioning based solely on equilibrium partitioning and if so how were the vapour pressures of the products determined? How was the reaction rate coefficient of ozone with the products determined? I would have thought a C₁₀ species with only 4 oxygens would be a semi-volatile species and so its profile could be impacted by its gas phase reactivity as well, with subsequent re-volatilisation. However, I cannot tell from the data presented how the model deals with this.

Clearly *m/z* 199 shows a different profile than the other species shown. However, this is not the only ion shown with a double bond. *m/z* 185 is most likely limonic acid (C₉H₁₃O₄). This also has an intact double bond but clearly does not show the same effect. Have you looked for any other species with an intact double bond? Can you predict what the product of *m/z* 199 might be and look for the trend in that? I realise it may be complicated by isobaric species.

ROS quantification

I have a concern here about the method used to correct the data. Was the ROS and/or the SOA mass corrected for particle loss? On reading it seems like you use the ROS measured in the chamber and divide this by the loss corrected particle mass (I have assumed this is what you have done). If this is the case, I disagree with his approach. The ROS you have measured is based on what is actually in the chamber when you measure. The amount of SOA mass is much lower than the corrected number. Thus you are normalising to particle mass that is not present. If you used the actual measured particle mass the trend would look very different, increasing at longer reaction times. This needs to be clarified and the approach justified.

Specific points

In general the text is well written and easy to follow.

Page 1: not sure you need “new” in the title

Page 3, line 3: Give estimate of limonene emission

Page 3: There is very little given here about previous studies of limonene. I would expect some more background.

Page 4, line 1: Change to “was studied”

Page 4, line 3: FEP given before explained

Page 5, Fig 2: Collapsible spelt wrong. Im assuming there is no dilution here. What is the mechanism that allows the chamber to collapse?

Page 6, line 5: How clean is the zero air? Any peaks in PTR-MS above detection limit?

Page 6, line 9: Im surprised you don't see any OVOC from the water. How often is it changed?

Page 7: As described above there is far too little experimental detail included here, especially for the ROS and EESI-MS. How many OVOC standards have you investigated to ensure there is no in-source dimers formed or in-source fragmentation? Ive looked at the Gallimore and Kalberer paper, but there is very limited information on using the signal as a pseudo-quantification. Do you think the changing mix of organics will lead to any matrix effects?

Page 8, lines 3-4: Need spaces between units

Page 8, line 11: change to “can be associated”

Page 8, line 21: I assume this should be “Stainless steel’. Was a filter used in the PTR-MS sample line?

Page 10, line 1: a-pinene is a rather volatile species to use to account for wall losses. Please justify its use here.

Page 10, line 16: This section lacks details rather than relying on a different paper.

Page 11: I was rather surprised after the characterisation section that only 1 experiment was included. How representative are the results here of other ozone – limonene experiments? Why not show a OH reaction as well?

Page 11, line 14: give $\pm 1\sigma$ on diameter

Page 12, line 6: You use the term “characteristic” but I don't know what this applies to? It sounds like a description of more than one experiment but that is not presented here. Page 12, line 6: insert “the PTR”

Page 12, line 14: Which of these structures is most likely based on mechanisms.

Page 12, Fig 4: The purple and blue lines are very similar. Can an ozone profile be included for comparison.

Page 12, line 8: Limonaldehyde appears to form slightly later than the limonaketone. How do these compare to the ROS short profile?

Page 13, line 12: Can these species be seen in previous studies using PTR-MS. I don't know but I'm surprised you don't see them at all.

Page 13, line 26: Do you think that dimers are present based on the masses observed? I would think even if both double bonds are oxidised you would still see species up to C18, say from reaction of the stabilised Criegee intermediate with other products.

Page 14, line 12: can you estimate the elemental composition of these ions?

Page 14, line 19: I got a bit confused as to how small carbonyls were related? Do you mean heterogeneous or in-particle chemistry of two smaller OVOC is forming a C10 compound rather than the first stages of limonene oxidation?

Page 19, line 2: I don't like the use of the word decomposed – suggests some chemistry. Perhaps use “split”

Page 20, fig 7: Can you predict possible elemental formulae for the small ions? How efficient is gas phase removal of OVOC products in the ROS injection system?

Page 23, line 13: I don't understand what is meant by “collected in an offline manner”. Needs some more details.

SI

Table legends need to be above the tables.

Page 3, Table S1: can you add what kind of lamps are in the other chambers for comparison.

Page 5, line 7: Were the particles dried or not for the wall loss experiments?

Page 6, line 13: How does this yield compare to previous studies?