

Atmos. Chem. Phys. Discuss., referee comment RC1  
<https://doi.org/10.5194/acp-2021-964-RC1>, 2021  
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## Comment on acp-2021-964

Anonymous Referee #1

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Referee comment on "Autoxidation of terpenes, a common pathway in tropospheric and low temperature combustion conditions: the case of limonene and  $\alpha$ -pinene" by Roland Benoit et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-964-RC1>, 2021

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The manuscript entitled "Autoxidation of terpenes, a common pathway in tropospheric and low-temperature combustion conditions: the case of limonene and  $\alpha$ -pinene" presents new findings of atmospherically-relevant chemical reactions of BVOCs. Connecting combustion-related chemistry with the processing of BVOCs and the formation of SOAs is also timely due to more and more common vegetation fires and recently observed similarities between reactions in the atmosphere and low-temperature combustion-driven chemistry. The results presented in the manuscript as well as in the supplement will be of benefit to the members of the ACP community that are interested in combustion and oxidation of the monoterpenes in the atmosphere.

The paper is scientifically sound, methods and experimental details are adequately presented. The article achieves an ambitious goal of combining experimental data with an extensive review of the literature data that is firstly compiled and analyzed and then evaluated against the acquired results. It is important to note that such an evaluation likely required a significant amount of time and diligent work.

At the same time, the article would benefit from some revisions. Generally, the use of the English language should be improved because it is frequently awkward, even from the point of view of a non-native speaker. Moreover, in a number of paragraphs, the sentences are too long and the entire manuscript should be generally more focused. This can be accomplished by removing unnecessary details and repetition that are present in the entire text.

Also, in its current form, the article is too focused on the methodology and initially appears to be a method paper. It almost seems like two articles (one methodology paper and the second, focused on the atmospheric implications of the acquired results) were at some point combined into one, lengthy manuscript. From the context of the title and

introduction, I would expect the discussion to be more focused on the atmospheric implications of the acquired results and less on methodology.

Specific comments:

**Abstract:** The entire abstract should be shortened and re-written. It contains too many elements that belong in the introduction and too many details (for instance discussing the literature data but without citing the appropriate references, e.g. lines 16-18). Such statements do not belong in the abstract, I recommend focusing on the most important findings.

**Lines 14-16 and others** This sentence is correct but can be separated into two shorter ones to improve the readability.

**Lines 21-22** After giving the elemental formula for monoterpenes once it is rather obvious that they are structural isomers.

Likewise, the **introduction** can be shortened and the discussion can be more compact to improve the readability. Currently, it contains too many details and repetitions that are not critical for summing up the current state of knowledge and introducing the reader to the work presented in the manuscript.

Also, the connection between the atmospheric chemistry and autoxidation of VOCs could be better outlined. Wildfires are briefly mentioned, is there an argument to be made that open vegetation burning is expected to contribute to the formation of HOM/SOA from monoterpenes (biogenic VOCs) via low-temperature combustion? Or does the low-temperature combustion is only used to mimic (mechanistically) analogous reactions in the atmosphere, occurring at ambient temperatures? Perhaps both statements are true? Either way, this may not be obvious for all readers.

**Lines 39-45** This discussion can be strengthened by adding review article(s) underlying the scale and global impacts of the wildfires/biomass burning emissions.

**Lines 46-47 and 123-125** Under the experimental conditions used, how well can the autoxidation pathway be separated, while effectively eliminating/suppressing the other reaction pathways for RO<sub>2</sub>? Was this previously discussed, if so please state that with the

appropriate reference. Again, this may not be obvious for some readers.

**Line 60** What conditions specifically?

**Lines 52-67** I recommend including a figure/scheme containing these reactions (numbering them perhaps) to improve the readability. Also, symbols/abbreviations such as  $\text{RO}_2\cdot$  should be defined first - peroxy radical(s) - before using them in that form.

**Lines 70-71** What is low is relative, defining the range of said concentrations would be more precise.

**Lines 67 and 71** Radical or radicals? Please check if the names are uniform throughout the manuscript. Defining the symbol once (OH stands for hydroxyl radicals) and skipping the radical term all together would even further improve the readability.

**Lines 73-75** Is this statement based on the literature data (missing reference) or the findings in the work presented?

**Lines 85-86** Autooxidation of monoterpenes? To what carbon backbone these 7 oxygen atoms can be attached?

**Lines 96-99** Terms like chemical compound and chemical product, chemical species are not commonly used, awkward, and should be avoided. In the context of atmospheric chemistry, what other compounds are there aside from chemical compounds?

**Lines 99-100** I recommend making such statements less definitive, analytical chemistry tools and methods are continuously evolving. Coupling UHPLC with Orbitrap mass analyzer would still significantly enhance the selectivity of analytical protocol, even if obtaining a baseline separation for such a large number of analytes is indeed highly unlikely. Perhaps leading with the statement in line 102 would be more appropriate for this paragraph.

**Lines 114-115** I propose incorporating the molecular structures of the compounds under investigation into the figure discussing the autooxidation mechanism or into a separate figure. Discussing the molecular structures in the text feels unnecessary.

**Section 2.1.** This section also contains some unnecessary details (like for instance line

135 – as in earlier work – or continuously underlying that limonene and alpha-pinene are structural isomers in line 138. These can be avoided to further improve the readability. I would also consider abbreviating limonene and alpha-pinene.

**Line 144** It is unnecessary to provide the elemental formula of monoterpenes over and over again.

**Line 151** missing % symbol from the acetonitrile (ACN) purity grade.

**Line 155** Direct sample injection/infusion into the ion source?

**Line 158** APCI is not heated? Usually, ESI is enough to state what ion source what used

**Line 159** Please remove the “for the ionization of products”

**Line 162** a.u. stands for arbitrary units?

**Line 166** Was this also verified for any oxygenated molecules to mimic the HOM under investigation?

**Line 166-167** Likewise, was the clustering phenomenon investigated for model oxygenated molecules? The formation of non-covalently bonded ion clusters in ESI is very common and difficult to avoid. Studying this phenomenon with precursors alone (hydrocarbons in this case) is not adequate. Different phenomena can occur inside the ion source, aside from oxidation of the precursors under investigation. These include clusters formation and in-source fragmentation. Were these investigated in any way?

**Section 3** I recommend numbering the equations used.

**Lines 197-200, 202-209** These details were already stated in the experimental section.

**Lines 212-214** I don't understand this explanation of the data processing scheme.

**Lines 217-218** Due to the way this sentence is structured, I did not understand at first which ionization method showed an increase in the number of molecular formulas detected, ESI and APCI.

**Tables**– the 3D graphs in this table are difficult to read in this format, please consider including them in separate figures in the main text or in the ESI, converting them into a larger format.

**Lines 254-255** “remains low”? I recommend re-writing this sentence.

**Table 4** Searching for specific molecular markers, as stated in **lines 305-306**, among studies with different experimental conditions (oxidation) and different analysis conditions (offline and online and ion sources) should be done carefully. In other words, in such data set(s) the results are best described as fluid since even one parameter can have a significant impact on the results (molecular formulas identified).

**Lines 362-368** The argument can be made that the authors are simply detecting more products because the performance of their instrument (state-of-the-art HR Orbitrap MS) is superior, including wider mass range (as stated) and sensitivity. A much more accurate (but impossible to carry out) comparison would be achieved by injecting samples from all of these studies into the same analytical instrument. Or carrying out chamber ozonolysis and analyzing such an SOA via the instrument used in the work presented. Moreover, common elemental composition (formula) may or may not correspond to the same molecular structure(s). I feel like this fact is somewhat lost in the otherwise very well presented discussion in section 4.3.

**Line 371** Similarities between oxidation/ozonolysis and combustion?

**Line 372** Is the number 86 referring to the discussion in line 351? The entire paragraph (lines 373-381) that contain a discussion about limonene is difficult to understand.