

Atmos. Chem. Phys. Discuss., author comment AC1
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Reply on RC1

Roland Benoit et al.

Author comment on "Autoxidation of terpenes, a common pathway in tropospheric and low temperature combustion conditions: the case of limonene and α -pinene" by Roland Benoit et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-964-AC1>, 2022

Dear Reviewer 1,
Thank you for your comments and suggestions. We have taken them into account in the revised manuscript.
In this document, you will find changes made in response to your comments
Best regards,
Roland BENOIT et al.

1/Reviewer 1

Comments: The manuscript entitled "Autoxidation of terpenes, a common pathway in tropospheric and low-temperature combustion conditions: the case of limonene and α -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.

Answer:

We thank the reviewer for his comments and suggestions which we tried to address in the revision.

2/Reviewer 1

Comment: 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.

Answer:

We polished the English in the revised manuscript and removed unnecessary details (details below).

3/Reviewer 1

Comment: 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.

Answer: Our goal was not to propose a new analytical procedure and apply it to terpenes oxidation. We wanted to probe the presence of autoxidation products under cool flame conditions and verify their presence under simulated atmospheric oxidation conditions. Before doing so, we first probed the impact on the results of the methods used, i.e., HESI versus APCI, positive versus negative ionization mode. Then we could focus on the interpretation of the data. The present results indicated strong similitude in terms of products' chemical formulae observed under the two different experimental conditions. We revised the discussion section to address this comment as detailed below.

4/Reviewer 1

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.

Answer:

The text was edited to address this comment:

Abstract: line 11-29, page 1. The abstract was shortened and the framework of the study was clarified.

The oxidation of monoterpenes under atmospheric conditions has been the subject of numerous studies. They were motivated by the formation of oxidized organic molecules (OOM) which, due to their low vapor pressure, contribute to the formation of secondary organic aerosols (SOA). Among the different reaction mechanisms proposed for the formation of these oxidized chemical compounds, it appears that the autoxidation mechanism, common to both low-temperature combustion and atmospheric conditions, is important. An analysis of OOM detected in both conditions was performed. We used the present combustion data and literature data from tropospheric oxidation studies to investigate possible similarities in terms of observed chemical formulae of OOM. Two terpenes, α -pinene and limonene, among the most abundant biogenic components in the atmosphere were considered. We built an experimental database consisting of literature atmospheric oxidation data and presently obtained combustion data. In order to probe the effects of the type of ionization used in mass spectrometry analyses on the detection of OOM, we used heated electrospray ionization (HESI) and atmospheric pressure chemical ionization (APCI), in positive and negative modes. The oxidation of limonene-oxygen-nitrogen and α -pinene-oxygen-nitrogen mixtures was performed using a jet-stirred reactor at elevated temperature (590 K), a residence time of 2 s, and atmospheric pressure. Samples of the reacting mixtures were collected in acetonitrile and analyzed by high-resolution mass spectrometry (Orbitrap Q-Exactive) after direct injection and soft ionization. This work shows a surprisingly similar set of chemical formulae of OOM, including oligomers, formed in cool flames and under simulated atmospheric conditions. Data analysis showed that a non-negligible subset of chemical formulae is common to all experiments, independently of experimental parameters. Finally, this study indicates that more than 40% of the detected chemical formulae in this full dataset can be ascribed to an autoxidation mechanism.

5/Reviewer 1

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

Answer:

The text was edited to address this comment: Lines 13-15, page 1 (Abstract)
Among the different reaction mechanisms proposed for the formation of these oxidized chemical compounds, it appears that the autoxidation mechanism, common to both low-temperature combustion and atmospheric conditions, is important.

6/Reviewer 1

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

Answer:

The text was edited to address this comment: Lines 20-21, page 1 (Abstract)

The word isomer has been removed.

7/Reviewer 1

Comments : introduction. 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.

Answer:

We thank the reviewer for this suggestion. The text was edited to address this comment: Lines 35-42, (Introduction) page 1

The background has been clarified and bibliographic references have been added:

Among the factors contributing to climate change, biomass burning is an important source of gases and aerosols in the atmosphere on a regional and global scale. These contributions, estimated at more than 90% for primary aerosols at the global level, have an impact on the chemical composition of the atmosphere (Chen et al., 2017;Andreae, 2019;Fawaz et al., 2021). Furthermore, Van Krevelen analyses of biomass burning samples indicated the presence of HOMs with O/C > 0.6 (Smith et al., 2009). When studying the oxidation of chemicals and the formation of SOA in the atmosphere, it becomes necessary to determine the contribution of different oxidation pathways pertaining to atmospheric chemistry, combustion chemistry, or both.

Chen, J., et al., A review of biomass burning: Emissions and impacts on air quality, health and climate in China. *Science of The Total Environment*, 2017. 579: p. 1000-1034.

Andreae, M.O., Emission of trace gases and aerosols from biomass burning – an updated assessment. *Atmos. Chem. Phys.*, 2019. 19(13): p. 8523-8546.

Fawaz, M., et al., Technical note: Pyrolysis principles explain time-resolved organic aerosol release from biomass burning. *Atmos. Chem. Phys.*, 2021. 21(20): p. 15605-15618.

Smith, J. S., Laskin, A., and Laskin, J.: Molecular Characterization of Biomass Burning Aerosols Using High-Resolution Mass Spectrometry, *Analytical Chemistry*, 81, 1512-1521, 10.1021/ac8020664, 2009.

8/Reviewer 1

Comments: 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 RO₂? Was this previously discussed, if so please state that with the appropriate reference. Again, this may not be obvious for some readers.

Answer:

The text was edited to address this comment:

In combustion, the rise in temperature will promote autoxidation. We have studied this oxidation at 590

K, temperature at which one can observe a maximum formation of hydroperoxides and HOMs under our experimental conditions. Nevertheless, other reaction mechanisms are probably present and this hypothesis is confirmed through the attribution of 40% of the molecules to autoxidation. References have been added: Lines 38-39, page 2
 A specification has been added: 119-129, page 4
 The present worked is a prolongation of that published earlier for the oxidation of LM alone (Benoit et al., 2021). We attempted to probe possible similitudes in terms of products' chemical formulae (product signals appearing with the same exact mass) observed under two different experimental conditions, i.e., (i) atmospheric oxidation and (ii) cool flame oxidation of terpenes and link them to common oxidation routes (Scheme 1). AP and LM were oxidized in a jet-stirred reactor at atmospheric pressure, excess of oxygen, and at a temperature of 590 K where the concentration of hydroperoxides and HOMs is maximal, under our experimental conditions.

9/Reviewer 1

Comments : Lines 60. What conditions specifically?

Answer:

Lines 53-56, page 2

The conditions have been clarified and a literature reference has been added to support this clarification.

This mechanism can repeat itself several times, leading HOMs. It can be competitive under atmospheric conditions, in pristine environments, with other reaction pathways involving RO₂·

radicals (Bianchi et al., 2019; Vereecken et al., 2020).

Vereecken, L., and Nozière, B.: H migration in peroxy radicals under atmospheric conditions, Atmos.

Chem. Phys., 20, 7429-7458, 10.5194/acp-20-7429-2020, 2020.

10/Reviewer 1

Comments : Lines 52-67 I recommend including a figure/scheme containing these reactions

(numbering them perhaps) to improve the readability. Also, symbols/abbreviations such as RO₂ should

be defined first -peroxy radical(s) - before using them in that form.

Answer:

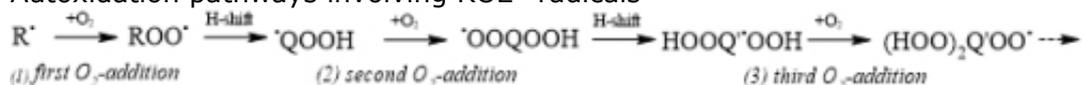
The text was edited to address this comment:

Lines 57, page 2

A scheme has been introduced to improve readability. The abbreviation RO₂ has been defined.

Scheme 1. Description of the autoxidation mechanism and complementary reaction pathways

Autoxidation pathways involving RO₂· radicals



Other reaction pathways involving RO₂· radicals

Carbonyl channel (ROO· ⇌ R-HO + OH)

Hydroperoxide channel (ROO· + HOO· ⇌ ROOH + O₂ and RO· + ·OH + O₂)

Disproportionation reactions (ROO· + R'OO· ⇌ RO· + R'O· + O₂ and R-HO + R'OH + O₂)

Accretion reactions ($\text{ROO}\bullet + \text{R}'\text{OO}\bullet \rightarrow \text{ROOR}' + \text{O}_2$).

11/Reviewer 1

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

Answer:

Lines 63-66, page 2

A clarification has been added: with low initial terpene concentrations (5-50 ppm)

12/Reviewer 1

Comments: 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.

Answer:

Symbols have been defined for $\text{RO}_2\bullet$ and $\text{OH}\bullet$. the word radical deleted.

13/Reviewer 1

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

Answer:

Lines 69-70, page 3

This statement is based on literature data: a bibliographic reference has been added Wang, Z., et al., Efficient alkane oxidation under combustion engine and atmospheric conditions. *Communications Chemistry*, 2021. 4(1): p. 18.

14/Reviewer 1

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

Answer:

The text was edited to address this comment:

Lines 80-82, page 3

Both in combustion and atmospheric chemistry, autooxidation of carbon skeleton mainly with more than 10 carbon atoms can yield highly oxygenated molecules (HOMs), e.g., compounds containing more than 7 oxygen atoms

15/Reviewer 1

Comments: 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?

Answer:

Corrections have been made: The term chemical compound is used throughout the paper.

16/Reviewer 1

Comments: 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.

Answer:

Corrections have been made, lines 95-96, page 3

The exhaustive analysis of chemical species remains difficult in the current state of instrumental limitations.

17/Reviewer 1

Comments: 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.

Answer:

Lines 111-118, page 4

This paragraph describes the oxidation processes specific to unsaturations. It shows for example, that for alpha-pinene that breaking of both rings is necessary to obtain the "ELVOC" products with the very high O:C ratios (Kurtén et al., 2015;Iyer et al., 2021). In addition, it shows that the similarities and differences observed in the oxidation compounds of the two monoterpenes may come from the exocyclic double bond of limonene (Hammes et al., 2019;Jokinen et al., 2015a).

This paragraph also introduces the basis of a similarity of the reaction mechanisms of the two environments (Savee et al., 2015).

The molecular structures of the two monoterpenes are shown in the figure describing the autoxidation mechanism.

18/Reviewer 1

Comments: 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.

Answer:

Here are the changes we have made:

The suggestions were followed to improve readability: limonene (LM), alpha-pinene (AP). The word isomer has been deleted when possible

(Here, the line numbers are those of the initial version) Line 144: Correction done

Line 151: Correction done

Line 155: Direct sample infusion (correction done)

Line 158: APCI source can be heated : Ion Source Temperature Range Probe temperature from 50–500 °C. For the ESI source, ThermoFisher has modified its model and now offers a heater, hence the term HESI is used to name this newer device. Line 159: Correction done

Line 162: Yes. This is how it is defined in the "Tune" software that controls the ionization sources.

Line 166: We verified that the ionization sources did not spontaneously oxidize the two monoterpenes used. The experimental conditions described in the article were chosen to limit oxidation there. Nevertheless, the question remains relevant and we paid much attention to that.

19/Reviewer 1

Comments: 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?

Answer:

Lines 158-159, page 5

The formation of clusters, or the occurrence of aggregation phenomena, through whatever physico-chemical mechanism is inevitable in a HESI ionization source. However, as far as this study is concerned, the very low concentration of the studied compounds and the solvent used (which favors the evaporation and the dispersion of the molecules), did not show such phenomena. Moreover, we did not observe on the spectral data a particular periodicity related to this type of phenomena.

Mass spectra of AP and LM have been added in the supplements (Fig.S1)

20/Reviewer 1

Comments: Section 3 I recommend numbering the equations used.

Answer: Correction done

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

Answer:

These lines were deleted

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

Answer:

Here are the changes we have made: Lines 207, page 6.

The set of chemical compounds obtained were compared (under their molecular form) thanks to Venn diagrams.

21/Reviewer 1

Comments: 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.

Answer:

Here are the changes we have made: Lines 211-212, page 6

In negative mode, the HESI data were compared to the APCI data (Tables 2 and 3), showing an increase of the number of chemical formulae detected by 20 to 30%.

22/Reviewer 1

Comments: 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.

Answer:

The online versions of the articles published by ACP allow for enlargement to A4 size for each figure, without loss of resolution. Nevertheless, enlarged formats have been added to the supplements (SI3 & SI4)

23/Reviewer 1

Comments : Lines 254-255 "remains low"? I recommend re-writing this sentence:

Answer: Correction done: line 255, page 10. remain low.

24/Reviewer 1

Comments: 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 dataset(s) the results are best described as fluid since even one parameter can have a significant impact on the results (molecular formulas identified).

Answer:

The objective of the study is to compare these experimental differences and to identify, despite these differences, common chemical compounds which, may have been produced by the same reaction mechanisms.

The interest of this study is therefore to identify a common set of chemical compounds (molecular formulae) observed under rather different oxidation conditions, different analytical conditions, different instruments used. Within such a dataset, one can link products through an autoxidation mechanism, i.e., $C_nH_mO_x$ to $C_nH_mO_{x+2}$

25/Reviewer 1

Comments: 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.

Answer:

Each instrument associated with an ionization mode will identify a part of the chemical compounds present in the studied environment. The orbitrap, also used in 5 works cited out of 12 (limonene oxidation) has the advantage of minimizing the problems of identification of chemical compounds thanks to a very good resolution in mass (140,000) compared to other mass spectrometers, except FT-ICR-MS. This study has the advantage of showing that whatever the imperfections and diversities of analytical methods, there is a large set of common data which could result from the same reaction mechanisms.

26/Reviewer 1

Comments: Line 371 Similarities between oxidation/ozonolysis and combustion?

Answer:

Here are the changes we have made. Line 370, page 15: For LM, the similarities between oxidation by ozonolysis and combustion are more important and less spread out.

27/Reviewer 1

Comments: Line 372 Is the number 86 referring to the discussion in line 351?

Answer: text edited for clarification: line 371, page 15

They represent for the different studies: 65% (Kundu et al., 2012), 88% (Walser et al., 2008), 81% (Tomaz et al., 2021).

28/Reviewer 1

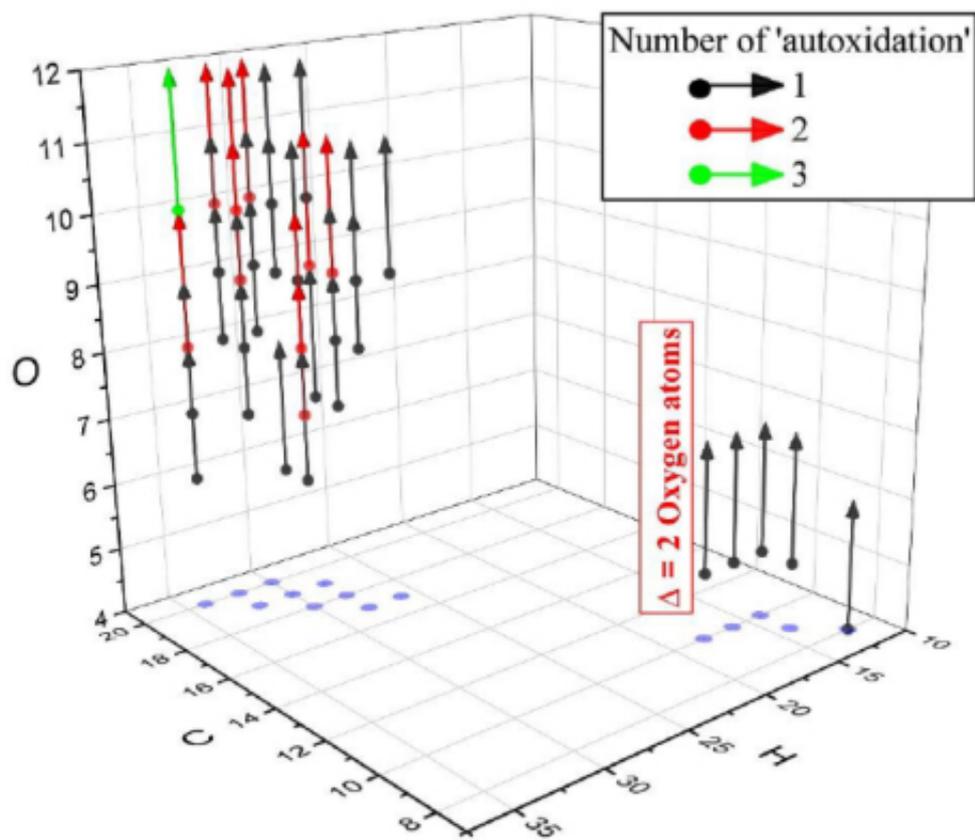
Comments: entire paragraph (lines 373-381) that contain a discussion about limonene is difficult to understand.

Answer:

The paragraph has been rewritten to clarify our points: line 372-383, page 16

Moreover, there is a common dataset of 86 chemical formulae which can derive from autoxidation mechanisms. Whereas different reaction mechanisms can cause the observed similarities, the preponderance of autoxidation in cool flame combustion is obvious (Affleck and Fish, 1967; Fish, 1968). In atmospheric chemistry, this reaction mechanism remains competitive or dominates (Crouse et al., 2013; Jokinen et al., 2014b). If we search for an autoxidation link between these 86 chemical formulae, i.e., $C_nH_mO_x$ to $C_nH_mO_{x+2}$, we observe that 40% of these chemical formulae meet this condition (Fig. 6b). Indeed, a difference of two oxygen atoms, at constant number of carbon and hydrogen atoms is observed. In order to visualize the 'autoxidation' links between these chemical compounds, a three dimensional graph is presented in the Supplements (Fig S5). More precisely, these molecules are centered in a van Krevelen diagram on the ratios $O/C=0.6$ and $H/C=1.6$, in the range $0.25 < O/C < 0.8$ and $1.25 < H/C < 1.85$. All oxidized molecules associated with this dataset are presented in Figure 6. The dispersion of the chemical formulae, far from being random, remains consistent with an autoxidation mechanism where the number of carbon atoms is constant.

Figure 6 was reviewed and a supplemental figure showing the autoxidation linkage within these 86 chemical molecules (in vector form) was added to the supplements (SI 5).



Please also note the supplement to this comment:
<https://acp.copernicus.org/preprints/acp-2021-964/acp-2021-964-AC1-supplement.pdf>