Reply on RC1
Roland Benoit et al.

Author comment on "On the formation of highly oxidized pollutants by autoxidation of terpenes under 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-2022-635-AC1, 2022

Dear Reviewer,

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 “On the formation of highly oxidized pollutants by autoxidation of terpenes under low-temperature combustion conditions: the case of limonene and α-pinene” is the second submission of this work to ACP. The presents an investigation of the cool-flame autoxidation of the two atmospherically-abundant monoterpenes in connection with the formation of highly-oxidized molecules under the atmospherically-relevant conditions.

The author’s workload is excellent, and the manuscript is noticeably improved as compared with the previous submission. The authors clearly focused on addressing the previous reviewers' comments and, in connection with the previous criticism, carried out additional experiments. The presentation and the discussion of the results in the context of atmospheric chemistry is also noticeably better.

From the technical point of the article is scientifically sound, and methods and experimental details are presented well. The use of the English language is also significant. At the same time, their writing style is still very unfocused, providing too many experimental details, unnecessary sentences, and repetitions in a number of places. These should be addressed via further corrections.
Answer:

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

2/Reviewer 1

Comment: Line 363 Can the authors discuss the possible causes for such behavior, mechanistically wise? Are unsaturated molecules (first-generation products is the oxidation of limonene) more prone to undergo autooxidation?

Answer:

The presence of double bonds will indeed promote the formation of allylic radicals and the fixation of oxygens. We can cite this reference “Taking the comparison between n-pentane and 1-pentene, shown in Fig. 26 as an example, it can be seen that the bond dissociation energy for the secondary allylic C–H bond is about 13.0 kcal mol -1 lower than that for the normal secondary C–H bond, which makes the formation of allylic radicals in 1-pentene oxidation very competitive” Chong-WenZhou et al., DOI: 10.1016/j.pecs.2021.100983. We propose this modification line 372: Considering the very different experimental conditions, we must wonder about the impact of the double bonds in this similarity. In the case of limonene, we think their presence will indeed promote the formation of allylic radicals and then peroxide radicals (one of the motors of autooxidation).

3/Reviewer 1

Comment: Section 2.1. The authors seem to be discussing their results under the assumption that no (or almost no) other reaction pathways exist under the experimental conditions used (cool-flame oxidation), aside from autooxidation. Can such an assumption be properly justified? If, for instance, OH is generated in the flame, it will generate OH oxidation products, that will obviously overlap (formulas-wise) with the products generated via dark ozonolysis in the absence of scavengers.

Answer:

A clarification has been made line 143: Nevertheless, this autoxidation mechanism, although the predominant one, is not exclusive and other oxidation mechanisms are possible Belhadj et al. 10.3390/molecules26237174. In this case, there may be a random overlap of chemical formulas. The autoxidation criteria (two chemical formulas separated by two oxygen atoms) allows to limit or avoid these overlaps.

4/Reviewer 1

Comment: 409-410 I would be careful with such definitive statements; the presence of the same elemental composition does not necessarily mean that these are the same molecules, observed in the chamber of flow-tube experiments. The same reasoning should be applied to Table 3
A modification has been made line 418: Furthermore, we verified that the chemical formulas of the main isomers identified in atmospheric chemistry were present.

5/Reviewer 1

Comment: Table 3. The authors can state that they detected cis-pinonic acid and other compounds listed only after they obtain a sufficient separation of the isomers detected (which wasn’t possible) followed by a comparison of the retention time of the standard. This would only be possible for cis-pinonic acid (without resorting to synthesizing the other molecules listed) but from the discussion presented in section 4.3.2 it appears that the authors did not analyze CPA standard.

Answer:

We analyzed by UHPLC, with the same experimental conditions of our study, two standards (limononaldehyde and Pinonic acid). See section 4.3.2.

6/Reviewer 1

Comment: Section 4.3.2. I understand that the motivation behind carrying out LC/MS analyses was to unambiguously prove that the same molecules (?) are formed from combustion-initiated autoxidation and from ozonolysis/OH reaction of α-pinene and limonene? However, this goal was not accomplished, the authors found that compounds with -OH or -OOH and C=O functionalities are formed via the autooxidation mechanism but did not show which specific products present in the chamber and field samples are also formed in their cool-flame oxidation. The LC/MS section, in its current form, does not provide any more information than the above-discussed DI-MS measurements.

Answer:

We propose this modification line 420: We have analyzed by UHPLC, with the same experimental conditions as our study, two standards limononaldehyde and Pinonic acid. These two respective isomers of C\textsubscript{10}H\textsubscript{16}O\textsubscript{2} and C\textsubscript{10}H\textsubscript{16}O\textsubscript{3} are among the most studied isomers in atmospheric chemistry. Our study shows a superposition of the elution times of these standards with the isomers detected in combustion (Fig S4). This superposition is more evident for limonoaldehyde (11.5 min) than for acid Pinonic at 3.9 min. Unfortunately, coelution did not fully allow exploiting MS/MS fragmentation carried out on the two chemical formulas, and to formally identify the two compounds.

7/Reviewer 1

Comment: Technical comments: 74-75 Awkwardly phased

Answer:

We propose this modification line 74: To better understand the importance of these reaction pathways, the experimental conditions unique to these two chemistries must be considered.
8/Reviewer 1

**Comment:** 148-149 Please clarify what was measured with HPLC, it is also customary to provide more column parameters (length, ID, and particle size as well as the manufacturer) and a more detailed gradient elution program – 5% held for x min then linear gradient too.). Was eluent A pure water or did it contained any additive to adjust the pH? What instrument (liquid chromatograph) was used?

**Answer:**

We propose this modification line 152: UHPLC conditions were: A Vanquish UHPLC Thermo Fisher Scientific with a C18 column (Phenomenex Luna, 1.6µm, 110 Å, 100x2.1 mm). The column temperature was maintained at 40°C. 3µl of sample were eluted by mobile phase containing water-ACN mix (pure water, ACN HPLC grade) at a flow rate of 250 μL/min (gradient: 5% to 20% ACN -3 min, 20% to 65% ACN - 22 min, 65% to 75% ACN – 4 min, 75% to 90% ACN - 4 min, for a total of 33 min)

9/Reviewer 1

**Comment:** 151 “Direct infusion“; **Answer:** done

**Comment:** 203-204 Repeated information from lines 167-168; **Answer:** line 209-210 removed

10/Reviewer 1

**Comment:** Line 274 participating in autoxidation?

**Answer:**

We propose this modification line 280: This parity distinction is initially present for the two main radicals, ROO˙ and RO˙, involved in autoxidation mechanisms.

11/Reviewer 1

**Comment:** Line 355 In the absence of scavengers, ozonolysis also involves a reaction with the OH. Some authors use the term “ozone-initiated oxidation”.

**Answer:**

We propose this modification line 361: It turned out that for α-pinene, 301 chemical formulas and for limonene 871 chemical formulas were common to oxidation by ozonolysis (with or without scavenger) and combustion
Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2022-635/acp-2022-635-AC1-supplement.pdf