Reply on RC2
Roland Benoît 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 Benoît et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-964-AC2, 2022

Dear Reviewer 2,
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 Benoît et al.

1/Reviewer 2
Comments: This work is dealing with a comparison of product formation from the oxidation of two monoterpenes carried out at room temperature or at 590 K, standing for low-temperature combustion conditions. The authors conducted the experiments at 590 K in a jet-stirred flow reactor with a residence time of 2 s. Products were trapped in acetonitrile and analyzed by mass spectrometric techniques. The fuel feed was about 1% and the oxidations was initiated by H abstraction via the reaction of O2 with the terpenes. The authors did not perform any experiments at room-temperature conditions. They used information from the literature for comparison taken from ozonolysis reactions of both terpenes conducted using different approaches. In their data analysis, the authors came to the conclusion that more than 40% of the detected "chemical formulae" are based on autoxidation processes.
Answer:
We thank the reviewer for his comments and suggestions which we tried to address in the revision

2/Reviewer 2
Comment: While a deeper mechanistic understanding of oxidation processes in cool flames and for atmospheric conditions is a very important topic, especially with respect to autoxidation, I have some doubts regarding significance of this work in this field.
Answer:
The present experiments were not designed to mimic atmospheric oxidation processes. One of our goals was to probe possible similitudes in terms of products’ chemical formulae (of 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.

Observed chemical formulae with odd and even numbers of oxygen atoms linked to two
oxidation routes ((i) RO2 => QOOH ... => ketohydroperoxides and HOMs a,d (ii) 2 RO2 => O2+ 2 RO => R-HOH ... => hydroketohydroperoxides and HOMs) were observed, confirming that these two pathways considered in atmospheric chemistry also proceed under different conditions, i.e., elevated temperature.

Paragraph 4.3, line 409-419, page 17, has been introduced
This is clarified in the revised paper.
Also, we expect that this work will stimulate interactions between physical chemists working in the fields of combustion and atmospheric chemistry.

3/Reviewer 2
Comment: Comparison of “chemical formulae”: I think the authors mean the comparison of product signals appearing with the same exact mass or the same chemical formula.
Answer:
Yes, what is meant is a comparison of product signals appearing with the same exact mass. This is clarified in the revised paper.

4/Reviewer 2
Comment: Why not performing own experiments on terpene oxidation for lower temperature than 590 K down to 300 K? I know it’s more challenging to run such experiments at reduced temperature without disturbing the unimolecular processes important in autoxidation. But, it would allow a more direct comparison of formed products, and likely of important reaction paths, depending on temperature using the same analytical technique.
Answer:
A noticeable oxidation of terpenes and other hydrocarbons cannot be observed below ca. 550 K in our JSR because the reaction with molecular oxygen is rather slow. Generation and injection of radicals (e.g. OH) or ozone can initiate the autoxidation process. This is what was done in the publications considered in our paper for comparing the formation of products with the same exact mass.
We agree with the reviewer that using the same experimental setup to probe the oxidation chemistry of terpenes under atmospheric and cool flame conditions would be interesting. Unfortunately, this is not practically possible.
This is included in the revised paper, line 144-147, page 5: “The experimental temperature was selected in order to be able to detect the formation of products of oxidation such as ketohydroperoxides and HOMs- Previous studies of ours showed a maximum formation of these chemical products at much a temperature (Belhadj et al., 2021)”. See also, what we already stated in the Introduction, line 89-91, page 3. “In low-temperature combustion, when the temperature is increased, autoxidation rate goes through a maximum between 500 and 670 K, depending on the nature of the fuel (Belhadj et al., 2020;Belhadj et al., 2021), and the rate of formation of HOM also increases (Bianchi et al., 2019)”.

5/Reviewer 2
Comment: Products were trapped in a solvent and stored in a freezer. Can we rule out any processing of products before analysis, especially for highly oxidized products?
Answer:
We cannot fully rule out that trapped products do not suffer degradation after trapping. In previous studies of ours involving other reactants (C4 to C8 ethers, C5-C8 alkanes), we observed a rather good stability of trapped products within several weeks after trapping (refs:
Belhadj, N., Benoit, R., Dagaut, P., and Lailliau, M.: Experimental characterization of n-
Belhadj, N., Lailliau, M., Benoit, R., and Dagaut, P.: Towards a Comprehensive Characterization of the Low-Temperature Autoxidation of Di-n-Butyl Ether, Molecules, 26, 7174, 2021g.
This would be important to evaluate stability of samples if quantitative measurements were done. Unfortunately, we are not able yet to quantify highly oxidized products because we cannot calibrate them due to the lack of standards. This is included in the revised paper.
The text was edited to address this comment, line 153.155, page 5: The stability of the chemical compounds collected in acetonitrile was verified and no detectable changes on a mass spectrum obtained on the orbitrap were observed after more than one month.

6/Reviewer 2
Comment: No mass spectra are shown. Would give the readership an impression what are the measured data used in the analysis.
Answer: We thank the reviewer for this suggestion. This is included in the revised supplements (SI Fig. S1)

7/Reviewer 2
Comment: Nothing is said regarding weighting of measured signals, i.e., stands a bigger signal for higher concentration?
Answer: Again, without standards, no calibration and not quantification can be made. However, a reduction of the MS signal with increasing MW must indicate a trend in the actual concentrations in the samples. Nevertheless, we cannot rule out a loss of heavy material by condensation before reaching the acetonitrile trap.
This is included in the revision. Line 161-162, page 5. Nevertheless, for products with the same exact mass, one can assume the signal increases with concentration.

8/Reviewer 2
Comment: Only the identification of a product with a certain formula (and without structural information) does not help to get out any information on the important pathways in a reaction system. So, what does it mean that 40% of the detected “chemical formulæ” can be ascribed to autoxidation processes? Do we learn anything about the chemical steps going on?
Answer:
We agree that it would be great to provide the structure of every product detected. However, it does not seem feasible due to technical limitations. Under JSR conditions, what we learn is that autoxidation proceeds much further than generally considered in the literature, i.e., up to a second addition of molecular oxygen on fuel's radicals most of the time, and more rarely up to a third addition. The highly oxidized molecular products observed here have the same chemical formulæ (same exact mass) as many of those reported in previous atmospheric chemistry studies in the literature.
Observed chemical formulæ with odd and even numbers of oxygen atoms linked to two oxidation routes ((i) RO2 => QOOH … => ketohydroperoxides and HOMs a,d (ii) 2 RO2 => O2+ 2 RO => R-HOH … => hydroketohydroperoxides and HOMs, see Figure 3 and the associated discussion) were observed, confirming that these two pathways considered in atmospheric chemistry also proceed under different conditions, i.e., elevated temperature. This is clarified in the revision.

9/Reviewer 2
Comment: I think, an analytical journal could be a better place for this manuscript.
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 probed the impact on the results of using HESI or APCI, and the ionization mode +/- . The present results indicated strong similitude in terms of products’ chemical formulæ observed under the two different experimental conditions. We believe this result is interesting for both the atmospheric chemistry and the combustion chemistry communities. Furthermore, this work should stimulate interactions between physical chemists working in the fields of combustion and atmospheric chemistry.

Please also note the supplement to this comment: https://acp.copernicus.org/preprints/acp-2021-964/acp-2021-964-AC2-supplement.pdf