

Atmos. Chem. Phys. Discuss., community comment CC1
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Reply on RC1

Roland Benoit

Community 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-CC1>, 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 autooxidation 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 autooxidation. 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 autooxidation.

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

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2021-964/acp-2021-964-CC1-supplement.pdf>