

Reviewer's comments	Answers and modifications of the manuscript
<p>With “On the similarities and differences between the products of oxidation of hydrocarbons under simulated atmospheric conditions and cool-flames”, Benoit et al. Compare the molecular composition of limonene subjected to low temperature combustion conditions to literature data for limonene subjected to ozonolysis. The authors use the datasets to examine differences and similarities due to the reaction pathways and explore potential reaction mechanisms responsible for the observed composition. The dataset and interpretations are both very good quality, and the manuscript is technically sound. The justification for the study and its importance to understanding atmospheric chemistry are not well developed, however, and the manuscript requires revisions so readers can understand the importance of the work. These and other comments are discussed below.</p> <p>General Comments:</p> <p>At the end of the introduction (lines 67-75), the authors describe the study's aim as to compare the molecular composition of laboratory “cool flame” combustion of limonene to that of limonene subjected to atmospherically-relevant conditions. While this section describes the study aim/objective, what is needed is a justification/purpose for the study. How will comparing</p>	<p>The introduction was modified to address the reviewer's comments :</p> <p>« Introduction »</p> <p>Several corrections</p> <p>L 26-29 : <u>Air particulates are responsible for increasing death rates and diseases (Lim et al., 2012) and have a negative impact on climate (Myhre et al., 2013). With increasing temperatures, particularly in summer, biogenic emissions of volatile organic compounds are more important than anthropogenic (Lamarque et al., 2010). Among them, one finds terpenes emitted by vegetation. They represent ...</u></p> <p>L-46 : <u>Whereas in atmospheric chemistry peroxy radicals self- and cross-reactions are very important (Wallington et al., 1992), in ...</u></p>

these two datasets provide valuable new information for our understanding of atmospheric organics (or human health, pollution, climate, etc.)? Just how these comparisons will benefit atmospheric chemists needs to be clearly stated so the study can be placed in proper context.

Additionally, in the conclusions section (lines 391-407), the authors note that the composition of autoxidation processes are similar to those of ozonolysis and photooxidation, but they never make an argument for why the reader should care about these results. How this work enhances our understanding of atmospheric organic composition or processes in the atmosphere is never explained.

The authors need to revise the Introduction and Conclusions sections to very clearly state the justification for and implications of the study.

L 73-79 : Can atmospheric chemistry benefit from combustion chemistry studies and vice versa?

Literature seems to indicate that cool flame combustion presents oxidation mechanisms similar to those observed in biomass burning (Koppmann et al., 2005; Reid et al., 2004). Koppmann et al. study showed that the rise in the temperature of the biomass causes the evaporation of all the families of VOCs (0.2 to 15% by mass of the biomass) as well as their “combustion without flame”. This “combustion” consists in an oxidation of VOCs more or less pronounced, depending on the temperature and humidity of the environment, and contributes to the formation of a wide diversity of chemical compounds.

L 86-88 : Inventory and chemical speciation of oxidation products, as well as the comparison with products of other modes of oxidation (ozonolysis, OH° and photolysis) should yield a better characterization of the specificities of each mode of oxidation and provide new targets data for field experiments.

The conclusion was modified to address the reviewer's comments :

L 413-419 : We notified that in the absence of ozone, the oxidation by the OH° radical, common to ozonolysis, gives similar results. Nevertheless, this study has allowed us to highlight auto-oxidation specific processes, such as formation of KHPs and diketones, occurrence of the Korcek and Waddington reaction mechanisms.

Extensive oxidation of peroxy radicals yielding HOMs is considered in atmospheric chemistry only recently; it was added to combustion models, showing some influence on ignition modeling (Wang and Sarathy, 2016). The present results indicate that one should pay more attention to the Korcek and Waddington mechanisms yielding specific products observed here and in previous smog chamber experiments and field measurements.

L426-432 : The observed similarity in terms of chemical compounds obtained by different reaction mechanisms remains qualitative. It does not cover the aspects of quantification and chemical speciation, specific to a reaction mechanism. Nevertheless, we noticed that products similarity is predominant in ozonolysis and photolysis, whereas it is only close to 50% for limonene low-temperature combustion. Lower similarity for the production of the lighter species, mostly observed in low-temperature combustion, was noticed. Further studies are needed to

<p>Additional Comments:</p> <p>- In section 2, "a.u." are used as units in multiple location. I am not familiar with these units. Please clarify.</p> <p>Line 89, please spell out FIA HESI/APCI for the reader who is unfamiliar with these acronyms.</p> <p>Line 112, Cite Kendrick (1963).</p> <p>Line 169, "Chemical formula with relative intensity was less than 1 ppm were not considered." To what does 1 ppm refer? Please explain how this relative intensity is calculated (relative to what? the highest magnitude peak? the total spectral magnitude?).</p> <p>In the Figure 2 caption, the circle symbols are not color coded as they are in the figure. Please fix or describe the color coding with words.</p>	<p><u>clarify the reasons for this difference and assess the impact of residence time and/or ageing on the observed degree of similarity. In any case, it appears possible to differentiate, thanks to visualization tools, a signature of the compounds formed by low-temperature combustion.</u></p> <p>"a.u." is spelled out in the revision: "arbitrary units (a.u.)" Line 89</p> <p>Line 89, we spell out FIA HESI/APCI in the revision: "flow injection analyses heated electrospray ionization/atmospheric pressure chemical ionization (FIA HESI/APCI)"</p> <p>Reference cited." A Mass Scale Based on CH₂ = 14.0000 for High Resolution Mass Spectrometry of Organic Compounds. Edward. Kendrick Anal. Chem. 1963, 35, 13, 2146–2154. https://doi.org/10.1021/ac60206a048</p> <p>One should read "Chemical formula with relative intensity less than 1 ppm (relative to the highest magnitude peak) were not considered."</p> <p>Corrected</p>
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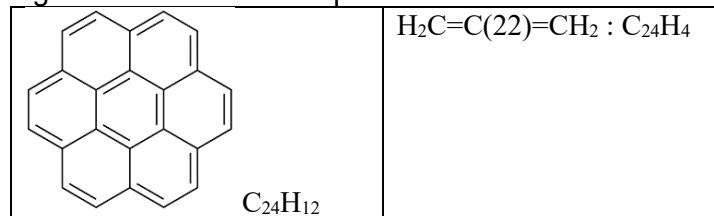
Line 204, why were the auto oxidation experiments restricted to 2 s residence times? Can the short residence times relative to the ozonolysis and photo oxidation experiments explain the differences in composition?

Figure 3 caption – the “aliphatics hydrocarbon,” “aromatic hydrocarbon,” and “unsaturated hydrocarbon” compound classes classified exactly? Intuitively, the unsaturated hydrocarbon classification would refer to compounds having at least one double bond and would extend to higher H/C ratios. Aromatic hydrocarbons would be likely to show lower H/C ratios than merely unsaturated hydrocarbons. Please clarify how these classifications are calculated and use classification names that represent the probably compound structural characteristics.

Figure 8 – the novelty and importance of these figures is overstated by the authors. Molecular formula exact mass datasets have been mathematically compared to identify reaction precursors and products in several previous studies (e.g., Gomez-Saez et al., 2016; Abdulla et al., 2020, and others). The same information can be visualized using Kendrick Mass defect analysis (using the expected difference(s) in elemental composition between

To operate our JSR under ideal ‘perfectly stirred reactor’ conditions, one must respect a range of residence time compatible with reactor geometry. Our reactor cannot operate at longer residence time at atmospheric pressure. This is a technical limitation. Observed differences could be ascribed to differences in residence times.

The border between unsaturated and aromatic compounds is narrow. These compounds have a lower H/C ratio than aliphatic compounds. The spaces cited in this work are from the literature (Bianco et al., 2018; Nozière et al., 2015). There is obviously an overlap of these two spaces which nevertheless can be positioned with respect to the chemistry studied. For an increasing number of carbon (with $C > 6$), the H/C ratio will be preferentially higher for aromatics compared to unsaturated chains.



The reviewer said that “The visualization and comparison are not as novel as stated by the authors.”

The notion of screening integrates here an algorithm allowing in this van Krevelen space to quantify the most probable chemical reactions. The exploratory field is more advanced and easier to interpret than many representations of Kendrick. It is also possible to specify in the algorithm restrictive conditions for the evolution of the DBE allowing a more accurate analysis than the one described in the literature.

precursor and product in place of CH₂), vK diagrams, or other visualization techniques. The comparisons made in this instance are robust and valuable. The visualization and comparison are not as novel as stated by the authors.

OTHER CORRECTIONS :

L.111: 'CAN' replaced by 'ACN'

L.127: reference added : Kendrick 1963

L.265: 'aliphatics' replaced by 'aliphatic'

L 279: New chemical reaction

L. 314 reference added : Mutzel et al. 2015 "Jensen et al. 1981"

L. 365 : corrected chemical formula indices

Figure 8 '+ Auto-Oxidation' corrected