We thank all the reviewers for their constructive comments and suggestions which allowed us to improve our article.
We have provided detailed responses (in blue) to each of the comments below. The modifications of the original text are identified in red.

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General Comments:
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 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

Answer:
The Abstract, Introduction and the Conclusion were revised and the link of this work to atmospheric chemistry is better presented in the revision. A focus on the comparison of these two chemistries, highlighting the common points and the differences, was carried out in the result section.
We would like to point out that under our experimental conditions, which are different from those found in the troposphere, we observe strong similitude in terms of detected molecular formulae of products. We clarified in the revision that both (i) autoxidation (generally considered as a combustion process) and (ii) reaction pathways (successive H-shift and molecular oxygen addition) following the initial formation of alkoxy radicals via the accepted mechanism of oxidation of VOCs in the troposphere, i.e., ROO + ROO → ROOOOR → 2 RO + O_2 (ROO + NO → RO + NO_2 is not relevant in our conditions where no nitric oxide is present) occur in our JSR, based on detected molecular formulae. Our findings are rather unexpected. The fact that these oxidation routes occur under very different conditions need to be brought to the attention of physical chemist involved in atmospheric and combustion related works.

The corrected section reads as follows:

Abstract. ~~Whereas the kinetics of oxidation of limonene has been extensively studied and mechanisms for its oxidation by OH and/or ozone have been proposed, more studies are required for better understanding its oxidation pathways.~~

Atmospheric oxidation chemistry, and more specifically, photooxidation, show that long-term oxidation of Organic Aerosol (OA) progressively erases the initial signature of the chemical compounds and can lead to a relatively uniform character of Oxygenated Organic Aerosol (OOA). This uniformity character observed after long reaction time seems to contrast with the great diversity of reaction mechanisms observed in the early stages of oxidation. The numerous studies carried out on the oxidation of terpenes, and more particularly on limonene for its diversity of reaction sites (endo and oxo cyclic), allow to study this evolution. We have selected for their diversity of experimental conditions, nine studies of limonene oxidation at room temperature over long reaction times to be compared to the present data set obtained at elevated temperature and short reaction time in order to investigate the similarities in terms of reaction mechanisms and chemical species formed. Here, the oxidation of limonene-oxygen-nitrogen mixtures was studied using a jet-stirred reactor at elevated temperature and atmospheric

pressure. Samples of the reacting mixtures were collected and analyzed by high resolution mass spectrometry (Orbitrap) after direct injection or after separation by reverse-phase ultra-high-pressure liquid chromatography and soft ionization, i.e., (+/-) HESI and (+/-) APCI. The results indicate that among the 1138 presently detected products, many oxygenates found in earlier studies of limonene oxidation by OH and/or ozone are also produced under the present conditions. Among these products, highly oxygenated ~~products~~molecules and oligomers were detected in the present work. The results are discussed in terms of reaction pathways involving the initial formation of peroxy radicals (RO$_2$), isomerization reactions yielding keto-hydroperoxides and other oxygenated intermediates and products up to $C_{25}H_{32}O_{17}$. Products which could derive from RO$_2$ autoxidation via sequential H-shift and O$_2$ addition ($C_{10}H_{14}O_{3,5,7,9,11}$) and products deriving from the oxidation of alkoxy radicals (produced by RO$_2$ self reaction or reaction with HO$_2$) through multiple H-shifts and O$_2$ additions ($C_{10}H_{14}O_{2,4,6,8,10}$). The oxidation of RO$_2$, with possible occurrence of the Waddington mechanism and of the Korcek mechanism, involving H-shifts are also discussed. The present work demonstrates similitude between the oxidation products and oxidation pathways of limonene under simulated atmospheric conditions and in those encountered during the self-ignition of hydrocarbons at ~~low temperatures, which should stimulate future interactions between communities of atmospheric chemistry and combustion chemistry to improve current chemical models.~~elevated temperatures. These results complement those recently reported by Vereecken and Nozière and confirms for limonene the existence of an oxidative chemistry of the alkylperoxy radical beyond 450 K based on the H-shift (Vereecken et Nozière, 2019, 2020).

Introduction (page 2, line 39)

Air particulates are responsible for increasing death rates and deseases worldwide (Lim et al., 2012~~) and~~). Furthermore, they 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 a large fraction of the volatile organic compounds (VOCs) present in the troposphere (Seinfeld and Pandis, 2006;Llusia` and Penuelas, 2000). In addition, one should note that these cyclic hydrocarbons are also considered as potential high-density biojet fuels (Pourbafrani et al., 2010;Meylemans et al., 2012;Harvey et al., 2010;Harvey et al., 2015). Their use as drop-in ground transportation fuel could also be of interest, considering their cetane number around 20 (Yanowitz et al., 2017). Their use as fuel would likely increase their emission into the troposphere. The atmospheric oxidation kinetics of terpenes has been extensively studied, although we are far from a detailed understanding of the many processes involved (Berndt et al., 2015).

Monoterpenes such as α-Pinene, β-pinene, and limonene are among the most abundant terpenes in the troposphere (Witkowski and Gierczak, 2017;Zhang et al., 2018). Their oxidation can yield a large variety of oxygenated organic compounds such as highly oxygenated molecules (HOMs) which are considered to play an important role in secondary organic aerosols (SOA) formation (Bianchi et al., 2019).

Recently, Kourtchev et al. have shown that the concentration of SOA (directly related to that of VOC) mainly influences the apparition of oligomers whereas environmental or experimental conditions (RH, ozonolysis vs. OH-oxidation/photolysis, long-term atmospheric aging) preferentially influences the evolution of these oligomers (Kourtchev et al., 2016). This initial concentration is presented as one of the determining factors of the chemical nature of SOAs and their evolution into oligomers. ~~The so-called cool flame combustion makes it possible to study the formation of SOA and oligomers under conditions of high VOC concentration and elevated temperature (T=520K here). Moreover, the absence of ozone, and no need for the addition of a scavenger, allows probing reaction mechanisms and observing chemical species potentially specific to this mode of oxidation.~~It was also shown that, under different conditions of oxidative aging, most of the chemical evolution of SOA was due to the reaction of the OH radical (Kourtchev et al., 2015).

Evolution of these primary compounds during atmospheric oxidation have been widely studied in atmospheric chambers, in Potential Aerosol Mass (PAM), but also in field measurements in order to understand the oxidation processes. In the case of limonene, although the fundamental aspects of the oxidation processes are mostly known, there is a real difficulty to observe and characterize these chemical species in the initial phase of oxidation

Whereas in atmospheric chemistry peroxy radicals self- and cross-reactions are very important (Wallington et al., 1992), in combustion (Bailey et Norrish, 1952;Benson et al., 1981;Cox and Cole, 1985;Morley et al., 1987), it is commonly accepted that the low-temperature oxidation of hydrocarbons (RH), also named cool-flame, can lead to the formation of oxygenated intermediates, but generally, it is assumed that the ~~auto-oxidation~~autoxidation proceeds through the formation of keto-hydroperoxides (KHPs) which provide chain branching by decomposition: RH + OH ⇆ R + H_2O, R+ O_2 ⇆ ROO, ROO ⇆ QOOH, QOOH + O_2 ⇆ OOQOOH, OOQOOH ⇆ HOOQ'OOH ⇆ HOOQ'O + OH, HOOQ'O ⇆ OQ'O + OH. However, recent studies reported the formation of HOMs during the so-called low-temperature oxidation (500–600 K) of hydrocarbons and other organics ~~(, e.g.,~~ alcohols, aldehydes, ethers, esters~~)~~ (Wang et al., 2018;Wang et al., 2017b;Belhadj et al., 2020). There, the H-atom transfer in the OOQOOH intermediate does not involve the H-C-OOH group but another H-C group, opening new oxidation pathways. Such alternative pathways do not yield ketohydroperoxides, and a third O_2 addition to HOOQ'OOH yielding OOQ'(OOH)$_2$ can occur. This sequence of reactions can proceed again, yielding highly oxygenated products (Wang et al., 2017b;Belhadj et al., 2020;Belhadj et al., 2021). Also, QOOH can decompose via: QOOH → OH + cyclic ether, QOOH → OH + carbonyl + olefin, and QOOH → HO_2 + olefin. In few studies devoted to the understanding of atmospheric oxidation mechanism of hydrocarbons yielding highly oxidized products, ~~auto-oxidation~~autoxidation was proposed as a pathway to organic aerosols, e.g. (Jokinen et al., 2014a;Jokinen et al., 2015;Mutzel et al., 2015;Berndt et al., 2016;Crounse et al., 2013;Ehn et al., 2014). The early H-shift, ROO ⇆ QOOH, is favored by increased temperature, which explains its importance in autoignition, but the presence of substituents such as OH, C=O, and C=C in the ROO radical can significantly increase the rate of H-shift making it of significance at atmospheric temperatures (Bianchi et al., 2019).

~~Besides~~Beside these processes, the Waddington mechanism (Ray et al., 1973), involving OH and O_2 successive additions on a C=C double bond, followed by H-atom transfer from –OH to –OO, can occur, yielding carbonyl compounds: R-C=C-R' + OH ⇆ R-C-C(-R')-OH, R-C-C(-R')-OH + O_2 ⇆ OO-C(-R)-C(-R')-OH ⇆ HOO-C(-R)-C(R')-O ⇆ OH + R-C=O + R'-C=O. The Korcek mechanism (Jensen et al., 1981) through which γ-ketohydroperoxides are transformed into a carboxylic acid and a carbonyl compound can occur too. The formation of carboxylic acids and carbonyl products via the Korcek mechanism has already been postulated by Mutzel et al. (Mutzel et al., 2015) whereas it is frequently considered in recent kinetic combustion modeling (Ranzi et al., 2015).

Then, questions arise: what are the similarities and differences between the products of oxidation of hydrocarbons under simulated atmospheric conditions and cool-flames? Do oxidation routes observed in ~~auto-oxidation~~autoxidation (cool flames) play a significant role under atmospheric conditions? Can atmospheric chemistry benefit from combustion chemistry studies and vice versa?

~~Litterature seems to indicate that cool flame combustion presents oxidation mechanisms similar to those observed in biomass burning . 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.~~

This work aims at characterizing the oxidation products of limonene, which has higher tendency to form HOMs by simulated atmospheric oxidation than more abundant monoterpenes (e.g., α-pinene and β-pinene) and compare the results with literature data obtained under atmospheric oxidation.

The aim of this work is to characterize the oxidation products of limonene and more particularly those resulting from chain branching. The identification of the isomers resulting from the oxidation of RO_2 will be carried out thanks to a UHPLC-Orbitrap coupling in tandem mode. The initial oxidation concentrations of hydrocarbons used in the laboratory, of the order of a few ppm, only allow the detection of the presence of HOMs without being able to exploit their fragmentation and their chemical speciation within a mixture of isomers. The confirmation of the reaction mechanisms remains difficult.

To overcome this limitation, and to form these compounds in gas-phase oxidation processes with a concentration compatible with the UHPLC separation, the ionization mode, the transfer function, the fragmentation and low residence time, we chose to increase the initial concentration of limonene. Given these conditions, the study focused only on the mechanistic reaction and qualitative aspects of chemical speciation.

The impact of this initial concentration and the experimental conditions on the range of chemical formulae was investigated by comparing our results to other limonene oxidation studies chosen for their experimental diversity (i.e. oxidation mode, concentration, type of characterization, aging time)

To this end, we studied the oxidation of limonene-oxygen-nitrogen mixtures in a jet-stirred reactor (JSR) at atmospheric pressure, large excess of oxygen, and elevated temperature. Our results are compared to literature data obtained under tropospheric relevant conditions where terpenes are oxidized by OH and/or ozone. Inventory and chemical speciation of oxidation products, as well as the comparison with products of other modes of oxidation (ozonolysis, OH˙ and photolysis) should yieldlead to a better characterizationcomprehension of the specificities of each mode of oxidation mode and provide new targetsdatatarget data for field experiments. For sake of clarity, the present oxidation experiments will be called "auto-oxidationautoxidation" in the following sections.

Charaterization of HOMs (page 20, line 393)
Different strategies were considered for tracking the production of HOMs. Because of higher sensitivity and difficulty in separating isomers, FIA was preferred. Besides KHPs ($C_{10}H_{14}O_3$), the compounds $C_{10}H_{14}O_5$, $C_{10}H_{14}O_7$, $C_{10}H_{14}O_9$, $C_{10}H_{14}O_{11}$ (Fig. 3, area (d)) were detected by FIA (APCI +, vaporizer temperature =120°C, sheath gas flow of 12 a.u., auxiliary gaz flow of 0 a.u.; sweep gas flow of 0 a.u., capillary temperature of 300°C, corona discharge current of 3 μA, flow of 8 μl/min). We also detected $C_{10}H_{14}O_2$ (keto-hydroxide), $C_{10}H_{14}O_4$, $C_{10}H_{14}O_6$, $C_{10}H_{14}O_8$, and $C_{10}H_{14}O_{10}$ (figure 7a).Whereas the products with odd numbers of oxygen atoms can derive from 'combustion' oxidation pathways (figure 7b), as presented in the introduction, those with pair numbers of oxygen atoms can be formed via the classical atmospheric oxidation pathway yielding alkoxy radicals, i.e. $2 RO_2˙ \rightarrow ROOOOR \rightarrow 2 RO˙ + O_2$, $RO_2˙ + HO_2˙ \rightarrow RO˙ + ˙OH + O_2$, and $RO_2˙ + NO \rightarrow RO˙ + NO_2$ followed by alkoxy H-shift (Baldwin and Golden, 1978; Atkinson and Carter, 1991) and peroxidation, $RO˙ \rightarrow ˙R_{-H}OH$; $˙R_{-H}OH + O_2 \rightarrow ˙OOR'OH$. The reaction can continue with sequential H-shift and oxygen addition, yielding HOMs via up to six O_2 addition in the present study.

(a)

$C_{10}H_{16}$ $\xrightarrow{-H}$ $C_{10}H_{15}$ $\xrightarrow[(1)]{+O_2}$ $C_{10}H_{15}O_2$ $\xrightarrow{RO_2}$ $C_{10}H_{15}O_4C_{10}H_{15}$ $\longrightarrow$ $O_2 + 2\,C_{10}H_{15}O$ $\xrightarrow{H\text{-shift}}$ $C_{10}H_{14}OH$

Limonene   (R˙)   (RO₂˙)   (RO˙)   (Q˙OH)

$C_{10}H_{14}OH$ $\xrightarrow[(2)]{+O_2}$ $C_{10}H_{15}O_3$ $\xrightarrow[+O_2\ (3)]{H\text{-shift}}$ $C_{10}H_{15}O_5$ $\xrightarrow[+O_2\ (4)]{H\text{-shift}}$ $C_{10}H_{15}O_7$ $\xrightarrow[+O_2\ (5)]{H\text{-shift}}$ $C_{10}H_{15}O_9$ $\xrightarrow[+O_2\ (6)]{H\text{-shift}}$ $C_{10}H_{15}O_{11}$

(Q˙OH)   ˙OOQOH   HOOQ'(OH)OO˙   (HOO)₂Q''(OH)OO˙   (HOO)₃P(OH)OO˙   (HOO)₄P'(OH)OO˙

(each via -OH / H-shift)

$C_{10}H_{14}O_2$ $C_{10}H_{14}O_4$ $C_{10}H_{14}O_6$ $C_{10}H_{14}O_8$ $C_{10}H_{14}O_{10}$

OQ'OH   HOOQ''(OH)O   (HOO)₂P(OH)O   (HOO)₄P'(OH)O   (HOO)₆P''(OH)O

(b)

R˙ $\xrightarrow[(1)]{+O_2}$ ROO˙ $\xrightarrow{H\text{-shift}}$ QOOH $\xrightarrow[(2)]{+O_2}$ ˙OOQOOH $\xrightarrow{H\text{-shift}}$ HOOQ'OOH $\xrightarrow[(3)]{+O_2}$ (HOO)₂Q'OO˙

(via -OH / H-shift) → HOOQ'O

(via -OH / H-shift) → (HOO)₂Q''O

(HOO)₂Q'OO˙ $\xrightarrow{H\text{-shift}}$ (HOO)₂Q''OOH $\xrightarrow[(4)]{+O_2}$ (HOO)₃Q''OO˙ $\xrightarrow{H\text{-shift}}$ (HOO)₃POOH $\xrightarrow[(5)]{+O_2}$ (HOO)₄POO˙

(via -OH / H-shift) → (HOO)₃PO

(via -OH / H-shift) → (HOO)₄P'O

(HOO)₄POO˙ $\xrightarrow{H\text{-shift}}$ (HOO)₄P'OOH $\xrightarrow[(6)]{+O_2}$ (HOO)₅P''OO˙ $\xrightarrow[-OH]{H\text{-shift}}$ (HOO)₅P'''O
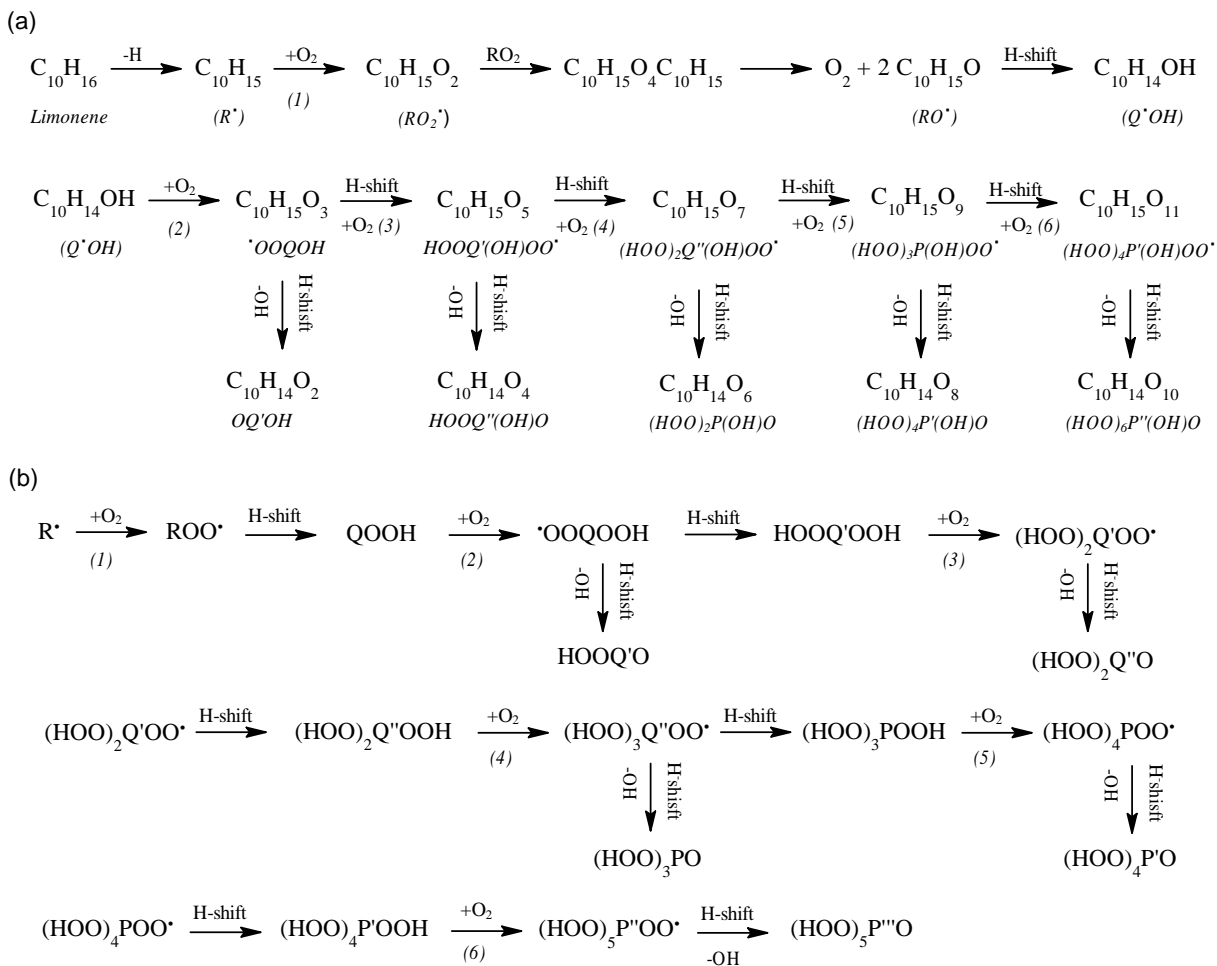
Figure 7. Reaction pathways to highly oxygenated products considered in atmospheric chemistry (a) and (b) (Bianchi et al., 2019). Recently extended reaction pathways in combustion (b) (Wang et al., 2017)

The intensity of ions signal decreases with increasing number of O atoms in the $C_{10}H_{14}O_{2,4,6,8,10}$ (by 5 orders of magnitude) and $C_{10}H_{14}O_{3,5,7,9,11}$ (by 6 orders of magnitude) products. Nevertheless, the diversity of reaction pathways, associated with the increasing number of chemical compounds, makes it difficult within a population of several hundred chemical compounds to identify all HOMs. Therefore, we have used again the van Krevelen diagram, which allows following the evolution of the oxidation of the first HOMs and to identify them according to definitions that seem to be consensus (Walser et al., 2008;Tu et al., 2016;Nozière et al., 2015;Wang et al., 2017a). To this end, we used the average carbon oxidation state OS_c which allows distinguishing three regions according to the nature of the functional groups: Region 1 (O/C ≥ 0.6 and OS_c ≥ 0) consists of highly oxygenated and highly oxidized compounds (acids and carbonyls), Region 2 (O / C ≥ 0.6 and OS_c <0), consists of highly oxygenated and moderately oxidized compounds (alcohols, esters and peroxides), finally, Region 3 (OS_c ≥ 0 and H/C ≤ 1.2) includes compounds with a moderate level of oxygen, but strongly oxidized (Tu et al., 2016).

It can be seen from Figure 3 that autoxidation enhances the development of HOMs, compared to ozonolysis/photooxidation, and that the majority of these new products are found in Regions 1 and 3 of the inset of Figure 3. Thus, further oxidation can go on. We observed products of addition of up to 17 oxygen atoms yielding $C_{25}H_{32}O_{17}$.

Conclusion and perspectives

Numerous studies on the ozonolysis of limonene have allowed characterizing the reaction mechanisms of its oxidation by describing a large fraction of chemical products. In these mechanisms, the formation of a Criegee intermediate has often been described as the major pathway ~~for the formation of~~to oxidized compounds, associated with the more restricted formation of the OH˙ radical.

Among these studies, some have shown that despite ~~these~~different oxidation conditions were used, implying differences in oxidation mechanisms ~~of~~in ozonolysis and OH-oxidation/photolysis, many of the products were similar~~. Moreover, it appears that these similarities are extended to photooxidation~~.

We noticed 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~~These results are in agreement with the previous study by Kourtchev et al. which shows that the evolution of chemical species is mainly dominated by the concentration of OH radical (Kourtchev et al., 2015). The present study has allowed us to highlight autoxidation 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.

Extensive oxidation of peroxy radicals yielding HOMs has been considered in atmospheric chemistry, but only recently a third-O_2 addition was added to combustion models, showing some influence on ignition modeling (Wang and Sarathy, 2016). Here, limonene oxidation was initiated by reaction with molecular oxygen yielding alkyl radicals which form peroxy radicals by reaction with O_2. The oxidation proceeds further by sequential H-shift and O_2 addition yielding a wide range of products with odd numbers of O atoms ($C_{10}H_{14}O_{5,7,9,11}$). Besides, products with even numbers of O atoms were measured in this work ($C_{10}H_{14}O_{4,6,8,10}$). They are expected to come from the oxidation of limonene via the commonly accepted tropospheric oxidation mechanism forming alkoxy radicals, i.e., RO_2˙ + RO_2˙ → ROOOOR → 2 RO˙ + O_2. The following sequential H-shift and O_2 addition on the alkoxy radicals yielded products of up to six O_2 addition in the present work ($C_{10}H_{14}O_{10}$). Such products have been reported in the previous ~~former~~ atmospheric chemistry studies considered here for comparison (Table 1) which demonstrates the strong similitude in terms of molecular formulae detected in atmospheric and 'combustion' chemistry. Besides, these two routes can produce a pool of OH radicals via decomposition of intermediates, e.g., ˙OOQOOH → ˙OH + HOOQ'O (KHP) and (HOO)$_2$Q'OO˙ → ˙OH + (HOO)$_2$Q''O (keto dihydroperoxide) for the 'combustion' route and ˙OOQOH → ˙OH + OQ'OH (keto alcool) and HOOQ'(OH)OO˙ → ˙OH + HOOQ''(OH)O (keto hydroxy hydroperoxide) for the 'tropospheric' oxidation route. Furthermore, similarly to what has been reported in atmospheric chemistry studies (Witkowski and Gierczak, 2017;Jokinen et al., 2015;Walser et al., 2008;Kundu et al., 2012;Fang et al., 2017;Nørgaard et al., 2013;Bateman et al., 2009;Warscheid and Hoffmann, 2001;Hammes et al., 2019)., a wide range of highly oxygenated products were detected, with molecular formula up to $C_{25}H_{32}O_7$ in the present work.

Analysis at the molecular level was complemented by observation at chemical family scale using Kendrick and van Krevelen visualization tools, necessary to compare and identify features in large data sets. Indeed, the formation of new HOMs and the development of combustion-related autoxidation are perfectly perceptible using these tools. The same is true for the oligomerization, which is not very important in autoxidation, in favor of addition and/or condensation reactions on limonene that are prompt to increase the DBE. As it stands, the meshing within these chemical families according to reaction, thermodynamic, or kinetic criteria remains sketchy, but will certainly develop in the light of all the available experimental and theoretical inputs. The observed similarity in terms of chemical ~~compounds~~formulae 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. Indeed, lower similarity for the production of the lighter species, mostly observed in low-temperature combustion, was noticed. Further studies

are needed to 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. Further studies involving others terpenes are underway. They should confirm the results presented here.

Additional Comments:

- In section 2, "a.u." are used as units in multiple location. I am not familiar with these units. Please clarify.
Line 89, please spell out FIA HESI/APCI for the reader who is unfamiliar with these acronyms.

Answer: "a.u." is spelled out in the revision: "arbitrary units (a.u.)" Line 89

Line 89, we spell out FIA HESI/APCI in the revision: "flow injection analyses heated electrospray ionization/atmospheric pressure chemical ionization (FIA HESI/APCI)"

Line 112, Cite Kendrick (1963).
Answer: 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

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?).

Answer: One should read "Chemical formula with relative intensity less than 1 ppm (relative to the highest magnitude peak) were not considered."

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.

Corrected

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?

Answer: 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.

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.

Answer: There is an inversion on the legends b and c of figure 3. The correct legend is (b) unsaturated hydrocarbons; (c) aromatics hydrocarbons; this is corrected in the revision.

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 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.

Answer: The notion of novelty has been removed. It is only a question of improvements.

Thanks to all the tools used in this work, especially the last one, the screening of selected classes of compounds is considerably simplified, and the mesh constituted by the reaction vectors ~~becomes a new method for~~<u>represents an efficient method</u> <u>for</u> evaluating the nature of a mixture of oxidation products.

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acp-2020-1070-RC2-ANSWERS

Comment : Even though the experiments are done carefully and the results are illustrated detaily, I am sceptical about the suitability and subsequent implications of the comparison of limonene oxidation under aforementioned conditions.

It is significantly unclear about how relevant/representative of the applied/selected fuel lean condition to the real ambient conditions and whether the composition of the oxidation products in JCR largely dependent on the temperatures and limonene/O2 concentration ratios.

Answer:

The oxidation conditions were adapted to the observation of ketohydroperoxides and HOMs. These chemical species present in atmospheric chemistry as well as in combustion remain difficult to observe and even more difficult to characterize. In order to overcome this limitation and to identify these species by fragmentation, we adjusted the initial concentration of limonene and used the short residence time specific to JSR (which is continuous-flow tank reactor). A JSR is a homogeneous system, very useful for studying chemical kinetics of oxidation processes. Regarding the products we focused on, such as ketohydroperoxides, one must keep in mind these are key-intermediates in both combustion (cool-flames) and tropospheric chemistry. The review of Bianchi (Chem. Rev. 119 (2019) 3472; see section 4.1) emphasizes the importance of that chemistry in the atmosphere. Due to the relative simplicity of ketohydroperoxides compare to HOMs, we devoted more attention on their characterization. They represent the early steps of oxidation of fuels or VOCs. We went beyond the measurement of ketohydroperoxides. The products of alkoxy radicals oxidation (ROO + ROO $\rightarrow$ ROOOOR $\rightarrow$ 2 RO + O$_2$ followed by multiple H-shits and molecular oxygen addition forming highly oxygenated products) were also measured showing the occurrence of this reaction pathway under our experimental conditions, although somewhat unexpected.

The abstract, the introduction and conclusion were modified to address the reviewer's comments.

The framework of the study has been justified with respect to atmospheric chemistry and the objective clarified.

The corrected section reads as follows:

Abstract. ~~Whereas the kinetics of oxidation of limonene has been extensively studied and mechanisms for its oxidation by OH and/or ozone have been proposed, more studies are required for better understanding its oxidation pathways.~~

Atmospheric oxidation chemistry, and more specifically, photooxidation, show that long-term oxidation of Organic Aerosol (OA) progressively erases the initial signature of the chemical compounds and can lead to a relatively uniform character of Oxygenated Organic Aerosol (OOA). This uniformity character observed after long reaction time seems to contrast with the great diversity of reaction mechanisms observed in the early stages of oxidation. The numerous studies carried out on the oxidation of terpenes, and more particularly on limonene for its diversity of reaction sites (endo and oxo cyclic), allow to study this evolution. We have selected for their diversity of experimental conditions, nine studies of limonene oxidation at room temperature over long reaction times to be compared to the present data set obtained at elevated temperature and short reaction time in order to investigate the similarities in terms of reaction mechanisms and chemical species formed. Here, the oxidation of limonene-oxygen-nitrogen mixtures was studied using a jet-stirred reactor at elevated temperature and atmospheric pressure. Samples of the reacting mixtures were collected and analyzed by high resolution mass spectrometry (Orbitrap) after direct injection or after separation by reverse-phase ultra-high-pressure liquid chromatography and soft ionization, i.e., (+/-) HESI and (+/-) APCI. The results indicate that among the 1138 presently detected products, many oxygenates found in earlier studies of limonene oxidation by OH and/or ozone are also produced under the present conditions. Among these products, highly oxygenated products molecules and oligomers were detected in the present work. The results are discussed in terms of reaction pathways involving the initial formation of peroxy radicals (RO$_2$), isomerization reactions yielding keto-hydroperoxides and other oxygenated intermediates and products up to C$_{25}$H$_{32}$O$_{17}$. Products which could derive from RO$_2$ autoxidation via sequential H-shift and O$_2$ addition (C$_{10}$H$_{14}$O$_{3,5,7,9,11}$) and products deriving from the oxidation of alkoxy radicals (produced by RO$_2$ self reaction or reaction with HO$_2$) through multiple H-shifts and O$_2$ additions (C$_{10}$H$_{14}$O$_{2,4,6,8,10}$). The oxidation of RO$_2$, with possible occurrence of the Waddington mechanism and of the Korcek mechanism, involving H-shifts are also discussed. The present work demonstrates similitude between the oxidation products and oxidation pathways of limonene under simulated atmospheric conditions and in those encountered during the self-ignition of hydrocarbons at low temperatures, which should stimulate future interactions between communities of atmospheric chemistry and combustion chemistry to improve current chemical models. elevated temperatures. These results complement those recently reported by Vereecken and Nozière and confirms for limonene the existence of an oxidative chemistry of the alkylperoxy radical beyond 450 K based on the H-shift (Vereecken et Nozière, 2019, 2020).

Introduction (page 2, line 39)
Air particulates are responsible for increasing death rates and deseases worldwide (Lim et al., 2012). Furthermore they 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 terpenes emitted by vegetation represent a large fraction of the volatile organic compounds (VOCs) present in the troposphere (Seinfeld and Pandis, 2006;Llusia` and Penuelas, 2000). In addition, one should note that these cyclic hydrocarbons are also considered as potential high-density biojet fuels (Pourbafrani et al., 2010;Meylemans et al., 2012;Harvey et al., 2010;Harvey et al., 2015). Their use as drop-in ground transportation fuel could also be of interest, considering their cetane number around 20 (Yanowitz et al., 2017). Their use as fuel would likely increase their emission into the troposphere. The atmospheric oxidation kinetics of terpenes has been extensively studied, although we are far from a detailed understanding of the many processes involved (Berndt et al., 2015).

Monoterpenes such as α-Pinene, β-pinene, and limonene are among the most abundant terpenes in the troposphere (Witkowski and Gierczak, 2017;Zhang et al., 2018). Their oxidation can yield a large variety of oxygenated organic compounds such as highly oxygenated molecules (HOMs) which are considered to play an important role in secondary organic aerosols (SOA) formation (Bianchi et al., 2019).

Recently, Kourtchev et al. have shown that the concentration of SOA (directly related to that of VOC) mainly influences the apparition of oligomers whereas environmental or experimental conditions (RH, ozonolysis vs. OH-oxidation/photolysis, long-term atmospheric aging) preferentially influences the evolution of these oligomers (Kourtchev et al., 2016). This initial concentration is presented as one of the determining factors of the chemical

nature of SOAs and their evolution into oligomers. ~~The so-called cool flame combustion makes it possible to study the formation of SOA and oligomers under conditions of high VOC concentration and elevated temperature (T=520K here). Moreover, the absence of ozone, and no need for the addition of a scavenger, allows probing reaction mechanisms and observing chemical species potentially specific to this mode of oxidation.~~It was also shown that, under different conditions of oxidative aging, most of the chemical evolution of SOA was due to the reaction of the OH radical (Kourtchev et al., 2015).

Evolution of these primary compounds during atmospheric oxidation have been widely studied in atmospheric chambers, in Potential Aerosol Mass (PAM), but also in field measurements in order to understand the oxidation processes. In the case of limonene, although the fundamental aspects of the oxidation processes are mostly known, there is a real difficulty to observe and characterize these chemical species in the initial phase of oxidation under the above conditions. This difficulty is notably reinforced, in the first steps, by the isomerization phenomena present during the oxidation of alkylperoxy radicals, RO_2 and the instability of these chemical species. These reaction mechanisms are mainly related to the H-shift whose rate constant varies with temperature, but may also be dependent on the presence of double bonds (Nozière et Vereecken, 2019). In atmospheric chemistry, hydrogen migration on carbon chains is a critical step in the formation of highly oxygenated molecules. It has been recently shown that this mechanism, which is also responsible for the formation of OH radicals, increases with temperature and requires further modelling over a temperature range between 200 and 450 K (Vereecken et Nozière, 2020). Studies show that this H-shift and autoxidation mechanism continues beyond 450 K and increases to 600K depending on the chemical nature of the compound (Belhadj et al., 2021). Among the numerous studies available in the literature on the oxidation of terpenes, limonene has the particularity of having endocyclic and exocyclic bonds which favor the formation of SOA.

Whereas in atmospheric chemistry peroxy radicals self- and cross-reactions are very important (Wallington et al., 1992), in combustion (Bailey et Norrish, 1952;Benson et al., 1981;Cox and Cole, 1985;Morley et al., 1987), it is commonly accepted that the low-temperature oxidation of hydrocarbons (RH), also named cool-flame, can lead to the formation of oxygenated intermediates, but generally, it is assumed that the autoxidation proceeds through the formation of keto-hydroperoxides (KHPs) which provide chain branching by decomposition: RH + OH $\leftrightarrows$ R + H_2O, R+ O_2 $\leftrightarrows$ ROO, ROO $\leftrightarrows$ QOOH, QOOH + O_2 $\leftrightarrows$ OOQOOH, OOQOOH $\leftrightarrows$ HOOQ'OOH $\leftrightarrows$ HOOQ'O + OH, HOOQ'O $\leftrightarrows$ OQ'O + OH. However, recent studies reported the formation of HOMs during the so-called low-temperature oxidation (500–600 K) of hydrocarbons and other organics, e.g., alcohols, aldehydes, ethers, esters (Wang et al., 2018;Wang et al., 2017b;Belhadj et al., 2020). There, the H-atom transfer in the OOQOOH intermediate does not involve the H-C-OOH group but another H-C group, opening new oxidation pathways. Such alternative pathways do not yield ketohydroperoxides, and a third O_2 addition to HOOQ'OOH yielding OOQ'$(OOH)_2$ can occur. This sequence of reactions can proceed again, yielding highly oxygenated products (Wang et al., 2017b;Belhadj et al., 2020;Belhadj et al., 2021). Also, QOOH can decompose via: QOOH $\rightarrow$ OH + cyclic ether, QOOH $\rightarrow$ OH + carbonyl + olefin, and QOOH $\rightarrow$ HO_2 + olefin. In few studies devoted to the understanding of atmospheric oxidation mechanism of hydrocarbons yielding highly oxidized products, autoxidation was proposed as a pathway to organic aerosols, e.g. (Jokinen et al., 2014a;Jokinen et al., 2015;Mutzel et al., 2015;Berndt et al., 2016;Crounse et al., 2013;Ehn et al., 2014). The early H-shift, ROO $\leftrightarrows$ QOOH, is favored by increased temperature, which explains its importance in autoignition, but the presence of substituents such as OH, C=O, and C=C in the ROO radical can significantly increase the rate of H-shift making it of significance at atmospheric temperatures (Bianchi et al., 2019).

Beside these processes, the Waddington mechanism (Ray et al., 1973), involving OH and O_2 successive additions on a C=C double bond, followed by H-atom transfer from –OH to –OO, can occur, yielding carbonyl compounds: R-C=C-R' + OH $\leftrightarrows$ R-C-C(-R')-OH, R-C-C(-R')-OH + O_2 $\leftrightarrows$ OO-C(-R)-C(-R')-OH $\leftrightarrows$ HOO-C(-R)-C(R')-O $\leftrightarrows$ OH + R-C=O + R'-C=O. The Korcek mechanism (Jensen et al., 1981) through which γ-ketohydroperoxides are transformed into a carboxylic acid and a carbonyl compound can occur too. The formation of carboxylic acids and carbonyl products via the Korcek mechanism has already been postulated by Mutzel et al. (Mutzel et al., 2015) whereas it is frequently considered in recent kinetic combustion modeling (Ranzi et al., 2015).

Then, questions arise: what are the similarities and differences between the products of oxidation of hydrocarbons under simulated atmospheric conditions and cool-flames? Do oxidation routes observed in autoxidation (cool flames) play a significant role under atmospheric conditions? Can atmospheric chemistry benefit from combustion chemistry studies and vice versa?

~~Litterature seems to indicate that cool flame combustion presents oxidation mechanisms similar to those observed in biomass burning . 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.~~

~~This work aims at characterizing the oxidation products of limonene, which has higher tendency to form HOMs by simulated atmospheric oxidation than more abundant monoterpenes (e.g., α-pinene and β-pinene) and compare the results with literature data obtained under atmospheric oxidation.~~

The aim of this work is to characterize the oxidation products of limonene and more particularly those resulting from chain branching. The identification of the isomers resulting from the oxidation of RO_2 will be carried out thanks to a UHPLC-Orbitrap coupling in tandem mode. The initial oxidation concentrations of hydrocarbons used in the laboratory, of the order of a few ppm, only allow the detection of the presence of HOMs without being able to exploit their fragmentation and their chemical speciation within a mixture of isomers. The confirmation of the reaction mechanisms remains difficult.

To overcome this limitation, and to form these compounds in gas-phase oxidation processes with a concentration compatible with the UHPLC separation, the ionization mode, the transfer function, the fragmentation and low residence time, we chose to increase the initial concentration of limonene. Given these conditions, the study focused only on the mechanistic reaction and qualitative aspects of chemical speciation.

The impact of this initial concentration and the experimental conditions on the range of chemical formulae was investigated by comparing our results to other limonene oxidation studies chosen for their experimental diversity (i.e. oxidation mode, concentration, type of characterization, aging time)

To this end, we studied the oxidation of limonene-oxygen-nitrogen mixtures in a jet-stirred reactor (JSR) at atmospheric pressure, large excess of oxygen, and elevated temperature. Our results are compared to literature data obtained under tropospheric relevant conditions where terpenes are oxidized by OH and/or ozone. Inventory and chemical speciation of oxidation products, as well as the comparison with products of other modes of oxidation (ozonolysis, OH˙ and photolysis) should lead to a better ~~characterization~~comprehension of the specificities of each oxidation mode and provide new target data for field experiments. For sake of clarity, the present oxidation experiments will be called "autoxidation" in the following sections.

Charaterization of HOMs (page 20, line 393)

Different strategies were considered for tracking the production of HOMs. Because of higher sensitivity and difficulty in separating isomers, FIA was preferred. Besides KHPs ($C_{10}H_{14}O_3$), the compounds $C_{10}H_{14}O_5$, $C_{10}H_{14}O_7$, $C_{10}H_{14}O_9$, $C_{10}H_{14}O_{11}$ (Fig. 3, area (d)) were detected by FIA (APCI +, vaporizer temperature =120°C, sheath gas flow of 12 a.u., auxiliary gaz flow of 0 a.u.; sweep gas flow of 0 a.u., capillary temperature of 300°C, corona discharge current of 3 μA, flow of 8 μl/min). We also detected $C_{10}H_{14}O_2$ (keto-hydroxide), $C_{10}H_{14}O_4$, $C_{10}H_{14}O_6$, $C_{10}H_{14}O_8$, and $C_{10}H_{14}O_{10}$ (figure 7a).Whereas the products with odd numbers of oxygen atoms can derive from 'combustion' oxidation pathways (figure 7b), as presented in the introduction, those with pair numbers of oxygen atoms can be formed via the classical atmospheric oxidation pathway yielding alkoxy radicals, i.e. 2 RO_2˙ → ROOOOR →2 RO˙ + O_2, RO_2˙ + HO_2˙ → RO˙ + ˙OH + O_2, and RO_2˙ + NO → RO˙ + NO_2 followed by alkoxy H-shift (Baldwin and Golden, 1978; Atkinson and Carter, 1991) and peroxidation, RO˙ → ˙R-$_H$OH; ˙R-$_H$OH + O_2 → ˙OOR'OH. The reaction can continue with sequential H-shift and oxygen addition, yielding HOMs via up to six O_2 addition in the present study.

(a)

$$C_{10}H_{16} \xrightarrow{-H} C_{10}H_{15} \xrightarrow[(1)]{+O_2} C_{10}H_{15}O_2 \xrightarrow{RO_2} C_{10}H_{15}O_4C_{10}H_{15} \longrightarrow O_2 + 2\, C_{10}H_{15}O \xrightarrow{\text{H-shift}} C_{10}H_{14}OH$$

Limonene   (R˙)   (RO₂˙)   (RO˙)   (Q˙OH)

$$C_{10}H_{14}OH \xrightarrow[(2)]{+O_2} C_{10}H_{15}O_3 \xrightarrow[+O_2\,(3)]{\text{H-shift}} C_{10}H_{15}O_5 \xrightarrow[+O_2\,(4)]{\text{H-shift}} C_{10}H_{15}O_7 \xrightarrow[+O_2\,(5)]{\text{H-shift}} C_{10}H_{15}O_9 \xrightarrow[+O_2\,(6)]{\text{H-shift}} C_{10}H_{15}O_{11}$$

(Q˙OH)   ˙OOQOH   HOOQ'(OH)OO˙   (HOO)₂Q''(OH)OO˙   (HOO)₃P(OH)OO˙   (HOO)₄P'(OH)OO˙

(each with ↓ -OH / H-shift)

$$C_{10}H_{14}O_2 \qquad C_{10}H_{14}O_4 \qquad C_{10}H_{14}O_6 \qquad C_{10}H_{14}O_8 \qquad C_{10}H_{14}O_{10}$$

OQ'OH   HOOQ''(OH)O   (HOO)₂P(OH)O   (HOO)₄P'(OH)O   (HOO)₆P''(OH)O

(b)

$$R˙ \xrightarrow[(1)]{+O_2} ROO˙ \xrightarrow{\text{H-shift}} QOOH \xrightarrow[(2)]{+O_2} ˙OOQOOH \xrightarrow{\text{H-shift}} HOOQ'OOH \xrightarrow[(3)]{+O_2} (HOO)_2Q'OO˙$$

↓ -OH / H-shift → HOOQ'O

↓ -OH / H-shift → (HOO)₂Q''O

$$(HOO)_2Q'OO˙ \xrightarrow{\text{H-shift}} (HOO)_2Q''OOH \xrightarrow[(4)]{+O_2} (HOO)_3Q''OO˙ \xrightarrow{\text{H-shift}} (HOO)_3POOH \xrightarrow[(5)]{+O_2} (HOO)_4POO˙$$

↓ -OH / H-shift → (HOO)₃PO

↓ -OH / H-shift → (HOO)₄P'O

$$(HOO)_4POO˙ \xrightarrow{\text{H-shift}} (HOO)_4P'OOH \xrightarrow[(6)]{+O_2} (HOO)_5P''OO˙ \xrightarrow[-OH]{\text{H-shift}} (HOO)_5P'''O$$
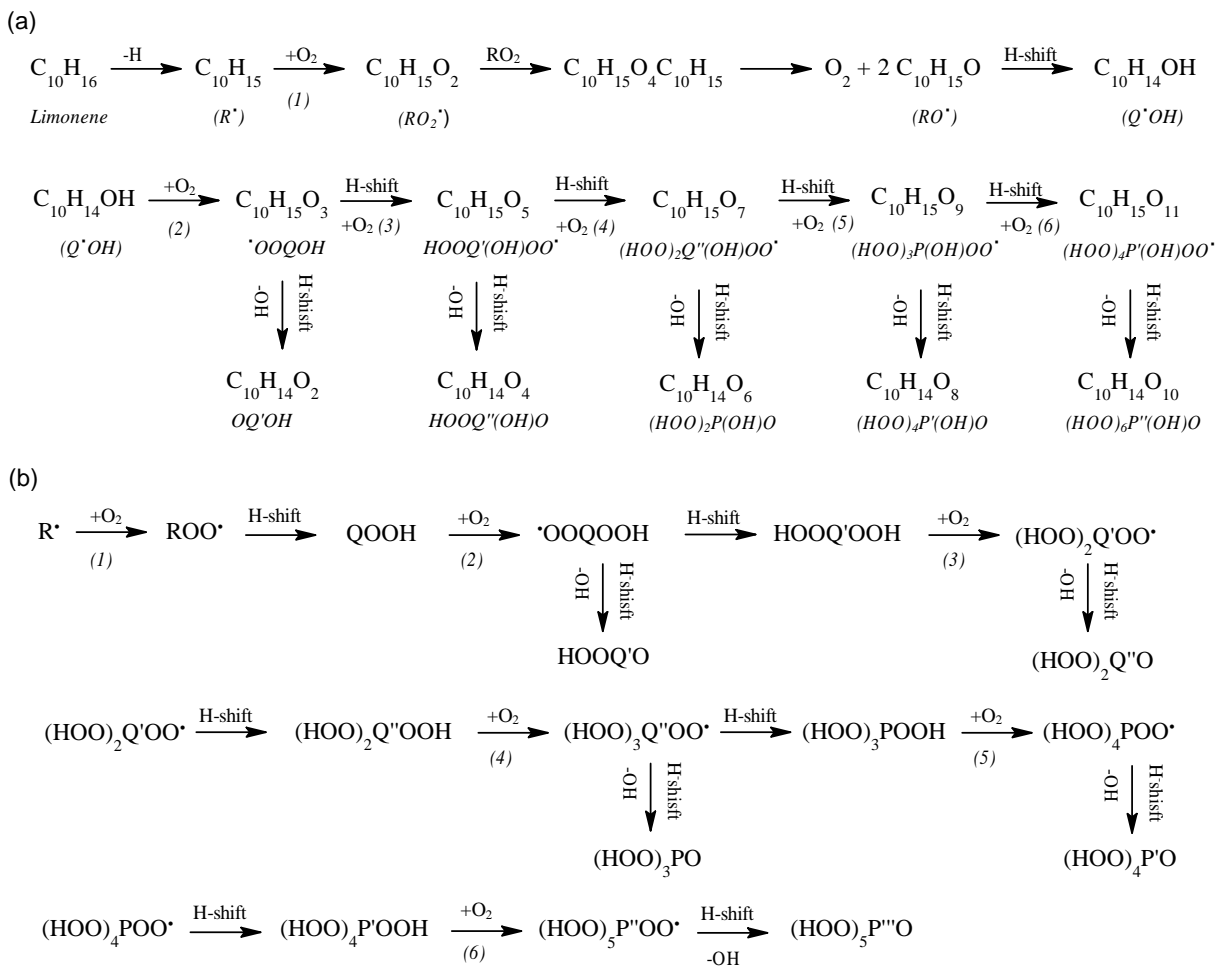
Figure 7. Reaction pathways to highly oxygenated products considered in atmospheric chemistry (a) and (b) (Bianchi et al., 2019). Recently extended reaction pathways in combustion (b) (Wang et al., 2017)

The intensity of ions signal decreases with increasing number of O atoms in the $C_{10}H_{14}O_{2,4,6,8,10}$ (by 5 orders of magnitude) and $C_{10}H_{14}O_{3,5,7,9,11}$ (by 6 orders of magnitude) products. Nevertheless, the diversity of reaction pathways, associated with the increasing number of chemical compounds, makes it difficult within a population of several hundred chemical compounds to identify all HOMs. Therefore, we have used again the van Krevelen diagram, which allows following the evolution of the oxidation of the first HOMs and to identify them according to definitions that seem to be consensus (Walser et al., 2008;Tu et al., 2016;Nozière et al., 2015;Wang et al., 2017a). To this end, we used the average carbon oxidation state OS_c which allows distinguishing three regions according to the nature of the functional groups: Region 1 (O/C ≥ 0.6 and OS_c ≥ 0) consists of highly oxygenated and highly oxidized compounds (acids and carbonyls), Region 2 (O / C ≥ 0.6 and OS_c <0), consists of highly oxygenated and moderately oxidized compounds (alcohols, esters and peroxides), finally, Region 3 (OS_c ≥ 0 and H/C ≤ 1.2) includes compounds with a moderate level of oxygen, but strongly oxidized (Tu et al., 2016).

It can be seen from Figure 3 that autoxidation enhances the development of HOMs, compared to ozonolysis/photooxidation, and that the majority of these new products are found in Regions 1 and 3 of the inset of Figure 3. Thus, further oxidation can go on. We observed products of addition of up to 17 oxygen atoms yielding $C_{25}H_{32}O_{17}$.

Conclusion and perspectives

Numerous studies on the ozonolysis of limonene have allowed characterizing the reaction mechanisms of its oxidation by describing a large fraction of chemical products. In these mechanisms, the formation of a Criegee intermediate has often been described as the major pathway ~~for the formation of~~to oxidized compounds, associated with the more restricted formation of the OH˙ radical.

Among these studies, some have shown that despite ~~these~~different oxidation conditions were used, implying differences in oxidation mechanisms ~~of~~in ozonolysis and OH-oxidation/photolysis, many of the products were similar~~. Moreover, it appears that these similarities are extended to photooxidation~~.

We noticed 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~~These results are in agreement with the previous study by Kourtchev et al. which shows that the evolution of chemical species is mainly dominated by the concentration of OH radical (Kourtchev et al., 2015). The present study has allowed us to highlight autoxidation 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.

Extensive oxidation of peroxy radicals yielding HOMs has been considered in atmospheric chemistry, but only recently a third-O_2 addition was added to combustion models, showing some influence on ignition modeling (Wang and Sarathy, 2016). Here, limonene oxidation was initiated by reaction with molecular oxygen yielding alkyl radicals which form peroxy radicals by reaction with O_2. The oxidation proceeds further by sequential H-shift and O_2 addition yielding a wide range of products with odd numbers of O atoms ($C_{10}H_{14}O_{5,7,9,11}$). Besides, products with even numbers of O atoms were measured in this work ($C_{10}H_{14}O_{4,6,8,10}$). They are expected to come from the oxidation of limonene via the commonly accepted tropospheric oxidation mechanism forming alkoxy radicals, i.e., $RO_2˙ + RO_2˙ \rightarrow ROOOOR \rightarrow 2\,RO˙ + O_2$. The following sequential H-shift and O_2 addition on the alkoxy radicals yielded products of up to six O_2 addition in the present work ($C_{10}H_{14}O_{10}$). Such products have been reported in the previous former atmospheric chemistry studies considered here for comparison (Table 1) which demonstrates the strong similitude in terms of molecular formulae detected in atmospheric and 'combustion' chemistry. Besides, these two routes can produce a pool of OH radicals via decomposition of intermediates, e.g., ˙OOQOOH → ˙OH + HOOQ'O (KHP) and (HOO)$_2$Q'OO˙ → ˙OH + (HOO)$_2$Q"O (keto dihydroperoxide) for the 'combustion' route and ˙OOQOH → ˙OH + OQ'OH (keto alcool) and HOOQ'(OH)OO˙ → ˙OH + HOOQ"(OH)O (keto hydroxy hydroperoxide) for the 'tropospheric' oxidation route. Furthermore, similarly to what has been reported in atmospheric chemistry studies (Witkowski and Gierczak, 2017;Jokinen et al., 2015;Walser et al., 2008;Kundu et al., 2012;Fang et al., 2017;Nørgaard et al., 2013;Bateman et al., 2009;Warscheid and Hoffmann, 2001;Hammes et al., 2019)., a wide range of highly oxygenated products were detected, with molecular formula up to $C_{25}H_{32}O_7$ in the present work.

Analysis at the molecular level was complemented by observation at chemical family scale using Kendrick and van Krevelen visualization tools, necessary to compare and identify features in large data sets. Indeed, the formation of new HOMs and the development of combustion-related autoxidation are perfectly perceptible using these tools. The same is true for the oligomerization, which is not very important in autoxidation, in favor of addition and/or condensation reactions on limonene that are prompt to increase the DBE. As it stands, the meshing within these chemical families according to reaction, thermodynamic, or kinetic criteria remains sketchy, but will certainly develop in the light of all the available experimental and theoretical inputs. The observed similarity in terms of chemical ~~compounds~~formulae 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. Indeed, lower similarity for the production of the lighter species, mostly observed in low-temperature combustion, was noticed. Further studies

are needed to 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. Further studies involving others terpenes are underway. They should confirm the results presented here.

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acp-2020-1070-RC3-ANSWERS

Specific comments :

In the reviewed manuscript ("On the similarities and differences between the products of oxidation of hydrocarbons under simulated atmospheric conditions and cool flames", acp-2020-1070), the authors use ultrahigh-resolution mass spectrometry to compare the auto-oxidation products of limonene in a jet-stirred reactor with molecular formulae found in the literature for reactions with ozone and OH-radicals under more atmospherically relevant conditions. The study is technically sound, the manuscript is well written and it would be good to see the results published somewhere. However, the authors don't do a very good job arguing why this manuscript is appropriate for publiC1 ACPD Interactive comment Printer-friendly version Discussion paper cation in ACP specifically. Maybe one could make the argument that if one has a very good understanding of the difference between the chemistry under the two very different conditions, one could use JSR experiments to predict atmospheric chemistry. . .but why would that be beneficial compared to just directly doing flow reactor or simulation chamber experiments? related).

Answer:
The Introduction and the Conclusion were revised and the link of this work to atmospheric chemistry is better presented in the revision. A focus on the comparison of these two chemistries, highlighting the common points and the differences, was carried out in the result section.
We do not claim using a JSR (which is continuous-flow tank reactor) can replace smog chambers or flow-tube reactors. All of these systems can bring useful information. What we claim is that under our experimental conditions, which are different from those found in the troposphere, we observe strong similitude in terms of detected molecular formulae of products. We clarified in the revision that both (i) autoxidation (generally considered as a combustion process) and (ii) reaction pathways (successive H-shift and molecular oxygen addition) following the initial formation of alkoxy radicals via the accepted mechanism of oxidation of VOCs in the troposphere, i.e., $ROO + ROO \rightarrow ROOOOR \rightarrow 2 RO + O_2$ ($ROO + NO \rightarrow RO + NO_2$ is not relevant in our conditions where no nitric oxide is present) occur in our JSR, based on detected molecular formulae. Our findings are rather unexpected. The fact that these oxidation routes occur under very different conditions need to be brought to the attention of physical chemist involved in atmospheric and combustion related works.

Given the strong focus on the compounds which aren't atmospherically relevant and the fact that only one set of conditions was tested for the JSR (so we have no idea about the breadth of variation in composition for JSR reactions), I wonder if this article wouldn't be better suited for a different journal (i.e. something combustion) ".

Answer:
We agree that all the parameters which can be varied in a JSR were not. One could argue this is the same in many studies performed at room temperature in flow tube reactor or a smog chamber. At least, a JSR is a

homogeneous system, very useful for studying chemical kinetics of oxidation processes. Regarding the products we focused on, such as ketohydroperoxides, one must keep in mind these are key-intermediates in both combustion (cool-flames) and tropospheric chemistry. The review of Bianchi (Chem. Rev. 119 (2019) 3472; see section 4.1) emphasizes the importance of that chemistry in the atmosphere. Due to the relative simplicity of ketohydroperoxides compare to HOMs, we devoted more attention on their characterization. They represent the early steps of oxidation of fuels or VOCs. We went beyond the measurement of ketohydroperoxides. The products of alkoxy radicals oxidation (ROO + ROO → ROOOOR → 2 RO + O_2 followed by multiple H-shits and molecular oxygen addition forming highly oxygenated products) were also measured showing the occurrence of this reaction pathway under our experimental conditions, although somewhat unexpected.

Regarding the choice of the journal, ACP (or another atmosphere-oriented journal) looks to be a good place for publishing our results. A combustion journal would most likely not be interested because the processes yielding highly oxygenated products would be viewed as marginal and worth publishing in an atmosphere-oriented journal.

The corrected section reads as follows:

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Atmospheric oxidation chemistry, and more specifically, photooxidation, show that long-term oxidation of Organic Aerosol (OA) progressively erases the initial signature of the chemical compounds and can lead to a relatively uniform character of Oxygenated Organic Aerosol (OOA). This uniformity character observed after long reaction time seems to contrast with the great diversity of reaction mechanisms observed in the early stages of oxidation. The numerous studies carried out on the oxidation of terpenes, and more particularly on limonene for its diversity of reaction sites (endo and oxo cyclic), allow to study this evolution. We have selected for their diversity of experimental conditions, nine studies of limonene oxidation at room temperature over long reaction times to be compared to the present data set obtained at elevated temperature and short reaction time in order to investigate the similarities in terms of reaction mechanisms and chemical species formed. Here, the oxidation of limonene-oxygen-nitrogen mixtures was studied using a jet-stirred reactor at elevated temperature and atmospheric pressure. Samples of the reacting mixtures were collected and analyzed by high resolution mass spectrometry (Orbitrap) after direct injection or after separation by reverse-phase ultra-high-pressure liquid chromatography and soft ionization, i.e., (+/-) HESI and (+/-) APCI. The results indicate that among the 1138 presently detected products, many oxygenates found in earlier studies of limonene oxidation by OH and/or ozone are also produced under the present conditions. Among these products, highly oxygenated ~~products~~molecules and oligomers were detected in the present work. The results are discussed in terms of reaction pathways involving the initial formation of peroxy radicals (RO$_2$), isomerization reactions yielding keto-hydroperoxides and other oxygenated intermediates and products up to $C_{25}H_{32}O_{17}$. Products which could derive from RO$_2$ autoxidation via sequential H-shift and O$_2$ addition ($C_{10}H_{14}O_{3,5,7,9,11}$) and products deriving from the oxidation of alkoxy radicals (produced by RO$_2$ self reaction or reaction with HO$_2$) through multiple H-shifts and O$_2$ additions ($C_{10}H_{14}O_{2,4,6,8,10}$). The oxidation of RO$_2$, with possible occurrence of the Waddington mechanism and of the Korcek mechanism, involving H-shifts are also discussed. The present work demonstrates similitude between the oxidation products and oxidation pathways of limonene under simulated atmospheric conditions and in those encountered during the self-ignition of hydrocarbons at ~~low temperatures, which should stimulate future interactions between communities of atmospheric chemistry and combustion chemistry to improve current chemical models.~~elevated temperatures. These results complement those recently reported by Vereecken and Nozière and confirms for limonene the existence of an oxidative chemistry of the alkylperoxy radical beyond 450 K based on the H-shift (Vereecken et Nozière, 2019, 2020).

Introduction (page 2, line 39)

Air particulates are responsible for increasing death rates and deseases worldwide (Lim et al., 2012). Furthermore they 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 terpenes emitted by vegetation represent a large fraction of the volatile organic compounds (VOCs) present in the troposphere (Seinfeld and Pandis, 2006;Llusia` and Penuelas, 2000). In addition, one should note that these cyclic hydrocarbons are also considered as potential high-density biojet fuels (Pourbafrani et al., 2010;Meylemans et al., 2012;Harvey et al., 2010;Harvey et al., 2015). Their use as drop-in ground transportation fuel could also be of interest, considering their cetane number around 20 (Yanowitz et al., 2017). Their use as fuel would likely increase their emission into the troposphere. The atmospheric oxidation kinetics of terpenes has been extensively studied, although we are far from a detailed understanding of the many processes involved (Berndt et al., 2015).

Monoterpenes such as α-Pinene, β-pinene, and limonene are among the most abundant terpenes in the troposphere (Witkowski and Gierczak, 2017;Zhang et al., 2018). Their oxidation can yield a large variety of oxygenated organic compounds such as highly oxygenated molecules (HOMs) which are considered to play an important role in secondary organic aerosols (SOA) formation (Bianchi et al., 2019).

Recently, Kourtchev et al. have shown that the concentration of SOA (directly related to that of VOC) mainly influences the apparition of oligomers whereas environmental or experimental conditions (RH, ozonolysis vs. OH-oxidation/photolysis, long-term atmospheric aging) preferentially influences the evolution of these oligomers (Kourtchev et al., 2016). This initial concentration is presented as one of the determining factors of the chemical nature of SOAs and their evolution into oligomers. The so-called cool flame combustion makes it possible to study the formation of SOA and oligomers under conditions of high VOC concentration and elevated temperature (T=520K here). Moreover, the absence of ozone, and no need for the addition of a scavenger, allows probing reaction mechanisms and observing chemical species potentially specific to this mode of oxidation.It was also shown that, under different conditions of oxidative aging, most of the chemical evolution of SOA was due to the reaction of the OH radical (Kourtchev et al., 2015).

Evolution of these primary compounds during atmospheric oxidation have been widely studied in atmospheric chambers, in Potential Aerosol Mass (PAM), but also in field measurements in order to understand the oxidation processes. In the case of limonene, although the fundamental aspects of the oxidation processes are mostly known, there is a real difficulty to observe and characterize these chemical species in the initial phase of oxidation under the above conditions. This difficulty is notably reinforced, in the first steps, by the isomerization phenomena present during the oxidation of alkylperoxy radicals, RO_2 and the instability of these chemical species. These reaction mechanisms are mainly related to the H-shift whose rate constant varies with temperature, but may also be dependent on the presence of double bonds (Nozière et Vereecken, 2019). In atmospheric chemistry, hydrogen migration on carbon chains is a critical step in the formation of highly oxygenated molecules. It has been recently shown that this mechanism, which is also responsible for the formation of OH radicals, increases with temperature and requires further modelling over a temperature range between 200 and 450 K (Vereecken et Nozière, 2020). Studies show that this H-shift and autoxidation mechanism continues beyond 450 K and increases to 600K depending on the chemical nature of the compound (Belhadj et al., 2021). Among the numerous studies available in the literature on the oxidation of terpenes, limonene has the particularity of having endocyclic and exocyclic bonds which favor the formation of SOA.

Whereas in atmospheric chemistry peroxy radicals self- and cross-reactions are very important (Wallington et al., 1992), in combustion (Bailey et Norrish, 1952;Benson et al., 1981;Cox and Cole, 1985;Morley et al., 1987), it is commonly accepted that the low-temperature oxidation of hydrocarbons (RH), also named cool-flame, can lead to the formation of oxygenated intermediates, but generally, it is assumed that the autoxidation proceeds through the formation of keto-hydroperoxides (KHPs) which provide chain branching by decomposition: RH + OH ⇆ R + H_2O, R+ O_2 ⇆ ROO, ROO ⇆ QOOH, QOOH + O_2 ⇆ OOQOOH, OOQOOH ⇆ HOOQ'OOH ⇆ HOOQ'O + OH, HOOQ'O ⇆ OQ'O + OH. However, recent studies reported the formation of HOMs during the so-called low-temperature oxidation (500–600 K) of hydrocarbons and other organics, e.g., alcohols, aldehydes, ethers, esters (Wang et al., 2018;Wang et al., 2017b;Belhadj et al., 2020). There, the H-atom transfer in the

OOQOOH intermediate does not involve the H-C-OOH group but another H-C group, opening new oxidation pathways. Such alternative pathways do not yield ketohydroperoxides, and a third O_2 addition to HOOQ'OOH yielding OOQ'(OOH)$_2$ can occur. This sequence of reactions can proceed again, yielding highly oxygenated products (Wang et al., 2017b;Belhadj et al., 2020;Belhadj et al., 2021). Also, QOOH can decompose via: QOOH → OH + cyclic ether, QOOH → OH + carbonyl + olefin, and QOOH → HO$_2$ + olefin. In few studies devoted to the understanding of atmospheric oxidation mechanism of hydrocarbons yielding highly oxidized products, autoxidation was proposed as a pathway to organic aerosols, e.g. (Jokinen et al., 2014a;Jokinen et al., 2015;Mutzel et al., 2015;Berndt et al., 2016;Crounse et al., 2013;Ehn et al., 2014). The early H-shift, ROO ⇄ QOOH, is favored by increased temperature, which explains its importance in autoignition, but the presence of substituents such as OH, C=O, and C=C in the ROO radical can significantly increase the rate of H-shift making it of significance at atmospheric temperatures (Bianchi et al., 2019).

Beside these processes, the Waddington mechanism (Ray et al., 1973), involving OH and O_2 successive additions on a C=C double bond, followed by H-atom transfer from –OH to –OO, can occur, yielding carbonyl compounds: R-C=C-R' + OH ⇄ R-C-C(-R')-OH, R-C-C(-R')-OH + O$_2$ ⇄ OO-C(-R)-C(-R')-OH ⇄ HOO-C(-R)-C(R')-O ⇄ OH + R-C=O + R'-C=O. The Korcek mechanism (Jensen et al., 1981) through which γ-ketohydroperoxides are transformed into a carboxylic acid and a carbonyl compound can occur too. The formation of carboxylic acids and carbonyl products via the Korcek mechanism has already been postulated by Mutzel et al. (Mutzel et al., 2015) whereas it is frequently considered in recent kinetic combustion modeling (Ranzi et al., 2015).

Then, questions arise: what are the similarities and differences between the products of oxidation of hydrocarbons under simulated atmospheric conditions and cool-flames? Do oxidation routes observed in autoxidation (cool flames) play a significant role under atmospheric conditions? Can atmospheric chemistry benefit from combustion chemistry studies and vice versa?

~~Litterature seems to indicate that cool flame combustion presents oxidation mechanisms similar to those observed in biomass burning . 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.~~

~~This work aims at characterizing the oxidation products of limonene, which has higher tendency to form HOMs by simulated atmospheric oxidation than more abundant monoterpenes (e.g., α-pinene and β-pinene) and compare the results with literature data obtained under atmospheric oxidation.~~

The aim of this work is to characterize the oxidation products of limonene and more particularly those resulting from chain branching. The identification of the isomers resulting from the oxidation of RO$_2$ will be carried out thanks to a UHPLC-Orbitrap coupling in tandem mode. The initial oxidation concentrations of hydrocarbons used in the laboratory, of the order of a few ppm, only allow the detection of the presence of HOMs without being able to exploit their fragmentation and their chemical speciation within a mixture of isomers. The confirmation of the reaction mechanisms remains difficult.

To overcome this limitation, and to form these compounds in gas-phase oxidation processes with a concentration compatible with the UHPLC separation, the ionization mode, the transfer function, the fragmentation and low residence time, we chose to increase the initial concentration of limonene. Given these conditions, the study focused only on the mechanistic reaction and qualitative aspects of chemical speciation.

The impact of this initial concentration and the experimental conditions on the range of chemical formulae was investigated by comparing our results to other limonene oxidation studies chosen for their experimental diversity (i.e. oxidation mode, concentration, type of characterization, aging time)

To this end, we studied the oxidation of limonene-oxygen-nitrogen mixtures in a jet-stirred reactor (JSR) at atmospheric pressure, large excess of oxygen, and elevated temperature. Our results are compared to literature data obtained under tropospheric relevant conditions where terpenes are oxidized by OH and/or ozone. Inventory

and chemical speciation of oxidation products, as well as the comparison with products of other modes of oxidation (ozonolysis, OH· and photolysis) should lead to a better ~~characterization~~comprehension of the specificities of each oxidation mode and provide new target data for field experiments. For sake of clarity, the present oxidation experiments will be called "autoxidation" in the following sections.

Charaterization of HOMs (page 20, line 393)

Different strategies were considered for tracking the production of HOMs. Because of higher sensitivity and difficulty in separating isomers, FIA was preferred. Besides KHPs ($C_{10}H_{14}O_3$), the compounds $C_{10}H_{14}O_5$, $C_{10}H_{14}O_7$, $C_{10}H_{14}O_9$, $C_{10}H_{14}O_{11}$ (Fig. 3, area (d)) were detected by FIA (APCI +, vaporizer temperature =120°C, sheath gas flow of 12 a.u., auxiliary gaz flow of 0 a.u.; sweep gas flow of 0 a.u., capillary temperature of 300°C, corona discharge current of 3 µA, flow of 8 µl/min). We also detected $C_{10}H_{14}O_2$ (keto-hydroxide), $C_{10}H_{14}O_4$, $C_{10}H_{14}O_6$, $C_{10}H_{14}O_8$, and $C_{10}H_{14}O_{10}$ (figure 7a).Whereas the products with odd numbers of oxygen atoms can derive from 'combustion' oxidation pathways (figure 7b), as presented in the introduction, those with pair numbers of oxygen atoms can be formed via the classical atmospheric oxidation pathway yielding alkoxy radicals, i.e. $2 RO_2· \rightarrow ROOOOR \rightarrow 2 RO· + O_2$, $RO_2· + HO_2· \rightarrow RO· + ·OH + O_2$, and $RO_2· + NO \rightarrow RO· + NO_2$ followed by alkoxy H-shift (Baldwin and Golden, 1978; Atkinson and Carter, 1991) and peroxidation, $RO· \rightarrow ·R_{-H}OH$; $·R_{-H}OH + O_2 \rightarrow ·OOR'OH$. The reaction can continue with sequential H-shift and oxygen addition, yielding HOMs via up to six O_2 addition in the present study.
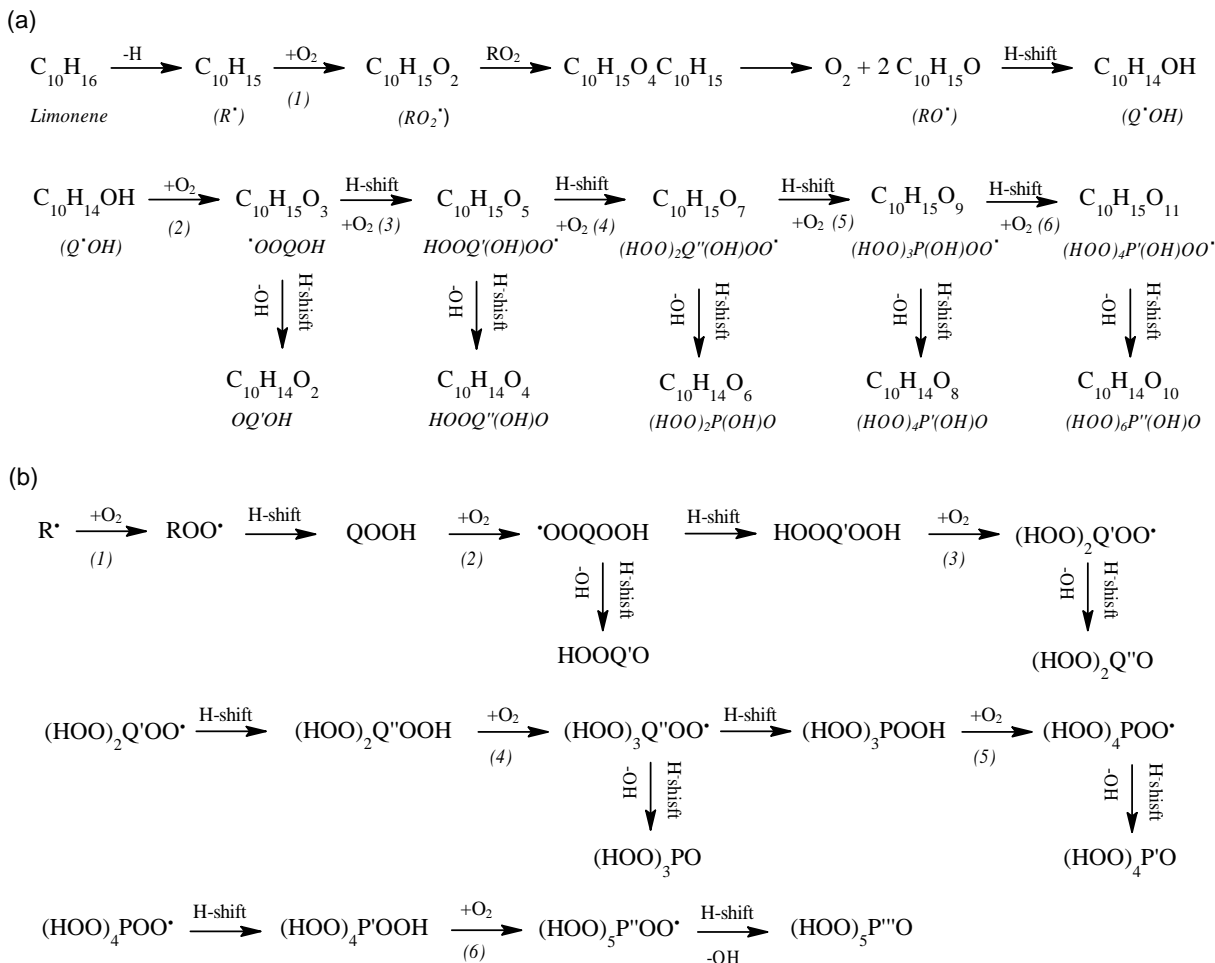
(a)

(b)

Figure 7. Reaction pathways to highly oxygenated products considered in atmospheric chemistry (a) and (b) (Bianchi et al., 2019). Recently extended reaction pathways in combustion (b) (Wang et al., 2017)

The intensity of ions signal decreases with increasing number of O atoms in the $C_{10}H_{14}O_{2,4,6,8,10}$ (by 5 orders of magnitude) and $C_{10}H_{14}O_{3,5,7,9,11}$ (by 6 orders of magnitude) products. Nevertheless, the diversity of reaction pathways, associated with the increasing number of chemical compounds, makes it difficult within a population of several hundred chemical compounds to identify all HOMs. Therefore, we have used again the van Krevelen diagram, which allows following the evolution of the oxidation of the first HOMs and to identify them according to definitions that seem to be consensus (Walser et al., 2008;Tu et al., 2016;Nozière et al., 2015;Wang et al., 2017a). To this end, we used the average carbon oxidation state OS_c which allows distinguishing three regions according to the nature of the functional groups: Region 1 (O/C ≥ 0.6 and OS_c ≥ 0) consists of highly oxygenated and highly oxidized compounds (acids and carbonyls), Region 2 (O / C ≥ 0.6 and OS_c <0), consists of highly oxygenated and moderately oxidized compounds (alcohols, esters and peroxides), finally, Region 3 (OS_c ≥ 0 and H/C ≤ 1.2) includes compounds with a moderate level of oxygen, but strongly oxidized (Tu et al., 2016).

It can be seen from Figure 3 that autoxidation enhances the development of HOMs, compared to ozonolysis/photooxidation, and that the majority of these new products are found in Regions 1 and 3 of the inset of Figure 3. Thus, further oxidation can go on. We observed products of addition of up to 17 oxygen atoms yielding $C_{25}H_{32}O_{17}$.

Conclusion and perspectives

Numerous studies on the ozonolysis of limonene have allowed characterizing the reaction mechanisms of its oxidation by describing a large fraction of chemical products. In these mechanisms, the formation of a Criegee intermediate has often been described as the major pathway ~~for the formation of~~to oxidized compounds, associated with the more restricted formation of the OH˙ radical.

Among these studies, some have shown that despite ~~these~~different oxidation conditions were used, implying differences in oxidation mechanisms ~~of~~in ozonolysis and OH-oxidation/photolysis, many of the products were similar~~. Moreover, it appears that these similarities are extended to photooxidation~~.

We noticed 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~~These results are in agreement with the previous study by Kourtchev et al. which shows that the evolution of chemical species is mainly dominated by the concentration of OH radical (Kourtchev et al., 2015). The present study has allowed us to highlight autoxidation 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.

Extensive oxidation of peroxy radicals yielding HOMs has been considered in atmospheric chemistry, but only recently a third-O_2 addition was added to combustion models, showing some influence on ignition modeling (Wang and Sarathy, 2016). Here, limonene oxidation was initiated by reaction with molecular oxygen yielding alkyl radicals which form peroxy radicals by reaction with O_2. The oxidation proceeds further by sequential H-shift and O_2 addition yielding a wide range of products with odd numbers of O atoms ($C_{10}H_{14}O_{5,7,9,11}$). Besides, products with even numbers of O atoms were measured in this work ($C_{10}H_{14}O_{4,6,8,10}$). They are expected to come from the oxidation of limonene via the commonly accepted tropospheric oxidation mechanism forming alkoxy radicals, i.e., $RO_2^{•} + RO_2^{•} \rightarrow ROOOOR \rightarrow 2\ RO^{•} + O_2$. The following sequential H-shift and O_2 addition on the alkoxy radicals yielded products of up to six O_2 addition in the present work ($C_{10}H_{14}O_{10}$). Such products have been reported in the previous former atmospheric chemistry studies considered here for comparison (Table 1) which demonstrates the strong similitude in terms of molecular formulae detected in atmospheric and 'combustion' chemistry. Besides, these two routes can produce a pool of OH radicals via decomposition of intermediates, e.g., $^{•}OOQOOH \rightarrow {}^{•}OH + HOOQ'O$ (KHP) and $(HOO)_2Q'OO^{•} \rightarrow {}^{•}OH + (HOO)_2Q''O$ (keto dihydroperoxide) for the 'combustion' route and $^{•}OOQOH \rightarrow {}^{•}OH + OQ'OH$ (keto alcool) and $HOOQ'(OH)OO^{•} \rightarrow {}^{•}OH + HOOQ''(OH)O$ (keto

Analysis at the molecular level was complemented by observation at chemical family scale using Kendrick and van Krevelen visualization tools, necessary to compare and identify features in large data sets. Indeed, the formation of new HOMs and the development of combustion-related autoxidation are perfectly perceptible using these tools. The same is true for the oligomerization, which is not very important in autoxidation, in favor of addition and/or condensation reactions on limonene that are prompt to increase the DBE. As it stands, the meshing within these chemical families according to reaction, thermodynamic, or kinetic criteria remains sketchy, but will certainly develop in the light of all the available experimental and theoretical inputs. The observed similarity in terms of chemical ~~compounds~~formulae 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. Indeed, lower similarity for the production of the lighter species, mostly observed in low-temperature combustion, was noticed. Further studies are needed to 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. Further studies involving others terpenes are underway. They should confirm the results presented here.

Comment: Page 6, line 160: are these 1233 molecules or 1233 molecular formulae? For a fair comparison with your acquired data, it should be the latter.

Answer: One should read '1233 molecular formulae'; this is corrected in the revision

Comment: In addition, it is not completely clear from the text whether the list of 1233 compounds/molecular formulae only contains formulae that were common to all of the "atmospheric" studies or every formula found in any of the studies. If it is the latter, I think some caveats regarding chemical diversity should be added since precursor concentration can affect the product composition and many of the listed studies are quite far away from atmospheric concentrations in this regard.

Answer: The list of 1233 compounds/molecular formulae corresponds to a set of every formula found in any of the studies found in the literature. This is corrected in the revision.
To address the second point, we revised the statement in question: "These nine experimental studies performed under diverse initial conditions, as shown in Table 1, yielded a first set of 1233 molecular formulae for an inventory which, although incomplete, gives a broad representativeness of the chemical products which can result from limonene ozonolysis and OH-initiated photooxidation.

Comment: Page 7. Line 169: relative to what? I'm assuming it is supposed to be relative to the peak maximum of the highest mass peak in the spectrum, but this should be stated explicitly.

Answer: It was stated "*Chemical formula with relative intensity was less than 1 ppm were not considered*". To address this point, the revised sentence reads: "Chemical formula with relative intensity to the peak maximum of the highest mass peak in the spectrum less than 1 ppm were not considered."

Comment: Page 10, line 249: could you elaborate a bit more about how you arrived at your compound family classification here? Especially since the limits you are setting seem to differ from the cited Bianco et a. regarding e.g. the aromatic structures.

Answer: There is an inversion on the legends b and c of figure 3. The correct legend is (b) unsaturated hydrocarbons; (c) aromatics hydrocarbons; this is corrected in the revision.