Dear Dr Kourtchev,

Thank you for your comments and suggestions. We have taken them into account in the revised manuscript (April 2).
In the second part of this document, you will find the previous changes since October 14, 2020.

Best regards,

Roland BENOIT

Comments : I think you unintentionally combined responses on two comments into one. The way it can be read now that RF voltages will impact on observation of atmospherically unrealistic compounds. I assume this is not what you wanted to say. It is highly unlikely that RF voltages can lead to atmospherically unrealistic compounds. Although some MS conditions have shown to lead to formation of atmospherically irrelevant compounds (e.g. formation of non-covalent artifacts), these would not be related to RF voltages (please see my second comment below).

Here are the changes we have made

Line 171-180, page 6 (Experiments)

Nevertheless, it should be considered that some of the molecules presented in this study could result from our experimental conditions (continuous-flow tank reactor, concentration of reagents, temperature, reaction time,...) and to some extent to our acquisition conditions, different from those in the cited studies (Table 1). Indeed, the use of a continuous-flow tank reactor operating at elevated temperature , as well as a high initial concentration of reactants can induce the formation of unrealistic atmospheric compounds. About the acquisition conditions, the selected mass range has an influence on the transmission factor, especially at the higher mass range. Figure 9s, in the supplementary material, compares two spectra of oxidized limonene with different acquisition mass ranges. A decrease in trapping efficiency at higher masses is clearly visible when changing the mass range from m/z 150-750 to 50-750. It is also necessary to consider the possible formation of non-covalent artifacts, without excluding an incidence on the DBE number. A more detailed description of these technical aspects is available in a recent review (Hecht et al., 2019).

Dr Kourchev

Comments : Atmospherically unrealistic compounds would mainly arise from the experimental conditions, e.g. use of high concentrations of hydrocarbons in the flow tube vs more atmospherically relevant concentrations used in the chamber experiments (as stated by two reviewers). This needs to be clearly stated in your manuscript and in the right place (e.g. in introductory and conclusion sessions) to address the comment of the two reviewers. I would also add a statement of caution when you compare/consider the molecular composition or chemical evolution from different experiments in your Table 1 (chamber vs flow tube, and different MS instruments).

Here are the changes we have made

Line 24—25, page 1 (Abstract)

Unexpectedly, because of diversity of experimental conditions in terms of continuous-flow tank reactor, concentration of reactants, temperature, reaction time, mass spectrometry techniques and analyses conditions, 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.

Line 531-534, page 24 (Conclusion and perspectives)

Although diverse experimental conditions were used here, in terms of concentration of reactants, temperature, reaction time, analysis conditions, we observed strong similitude in terms of molecular formulae detected in atmospheric and 'combustion' chemistry experiments.

Line 555-559, page 25 (Conclusion and perspectives)

Among the chemical formulas observed in this work, some had not been reported in the 9 atmosphere-oriented studies considered here for comparison. It would be interesting to perform additional experiments under conditions relevant to the atmosphere to verify that these chemical formulas are absent. Additional experiments in a JSR at lower initial temperatures and concentrations could also be undertaken to clarify the variation in product formation as temperature and reactant concentration change.

Dr Kourchev

Comments : The use of MS acquisition scan ranges, on the other hand, can affect transmission of ions, especially at the higher mass range (as you clearly demonstrated in your additional experiments that were requested upon review) and thus impacting on presence/observation of e.g. molecular clusters observed e.g. on VK and DBE plots. Therefore this needs to be taken into account when comparing your data with that of literature (as they used different MS detectors, e.g. FTICRMS and/or acquisition parameters). Therefore, the statement in the line 174 'Thus, we cannot exclude that some new compounds are associated with unrealistic compounds with respect to the atmosphere' needs to be replaced with an appropriate statement reflecting the observed phenomenon. It is also worth adding such statement (based on your figure 9S) to the results and discussion section, e.g. ether after the line 237 or 248 indicating the caveat when comparing your results with the literature data or using their data for your interpretation.

Here are the changes we have made

Line 243-246, page 9 (Results and discussion)

It should be noted that this second set of data is generated from different experimental conditions than the previous one, i.e. with a continuous flow reactor, a high concentration of reactants, a high temperature and a reaction time of 2s. As previously mentioned, the mass range studied and some parts of the instrumentation also present differences (table 1) and can affect the inventory of this second set.

Previous changes : (since October 14, 2020)

Line 13-20, page 1

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.

Line 30-39, page 1-2

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 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).

Line 62-76, page 3

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.

Line 114-125, page 4

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).

Line 141-147, page 5

In order to be able to observe the oxidation of limonene, which is not prompt to strong autoignition (cetane number of 20, similar to that of iso-octane), the oxidation of 1% limonene ($C_{10}H_{16}$) under fuel lean conditions (equivalence ratio of 0.25, 56 %O_2, 43 %N_2) was performed at 590 K, atmospheric pressure, and at a residence time of 2 s. Under these conditions, the oxidation of limonene is initiated by H-atom abstraction by molecular oxygen. The radicals of the fuel rapidly react with O_2 to form peroxy radicals which undergo further oxidation, as presented in the introduction. The absence of ozone, and no need for the addition of a scavenger, allows probing reaction mechanisms and observing chemical species potentially specific to the oxidation by OH radical.

Line 166-180, page 6

The optimization of the orbitrap ionization parameters in HESI and APCI did not show any clustering phenomenon on pure limonene. The parameters evaluated were: injection source - capillary distance, vaporization and capillary temperatures, potential difference, injected volume, flow rate of nitrogen in the ionization source.). The APCI source, more versatile on polarities and adapted to low masses, was used to identify, in a second phase, KHPs and HOMs. This source, used in positive mode (minimization of salt adducts) has improved the response of low masses necessary for fragmentation. Nevertheless, it should be considered that some of the molecules presented in this study could result from our experimental conditions (continuous-flow tank reactor, concentration of reagents, temperature, reaction time,...) and to some extent to our acquisition conditions, different from those in the cited studies (Table 1). Indeed, the use of a continuous-flow tank reactor operating at elevated temperature , as well as a high initial concentration of reactants can induce the formation of unrealistic atmospheric compounds. About the acquisition conditions, the selected mass range has an influence on the transmission factor, especially at the higher mass range. Figure 9s, in the supplementary material, compares two spectra of oxidized limonene with different acquisition mass ranges. A decrease in trapping efficiency at higher masses is clearly visible when changing the mass range from m/z 150-750 to 50-750. A more detailed description of these technical aspects is available in a recent review (Hecht et al., 2019).

Line 446-475, page 20-22

4.2 Characterization of HOMs

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. $2\ RO_2^{\bullet} \rightarrow ROOOOR \rightarrow 2\ RO^{\bullet} + O_2$, $RO_2^{\bullet} + HO_2^{\bullet} \rightarrow RO^{\bullet} + {}^{\bullet}OH + O_2$, and $RO_2^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2$ followed by alkoxy H-shift (Baldwin and Golden, 1978; Atkinson and Carter, 1991) and peroxidation, $RO^{\bullet} \rightarrow {}^{\bullet}R_{-H}OH$; ${}^{\bullet}R_{-H}OH + O_2 \rightarrow {}^{\bullet}OOR'OH$. The reaction can continue with sequential H-shift and oxygen addition, yielding HOMs via up to six O_2 addition in the present study.

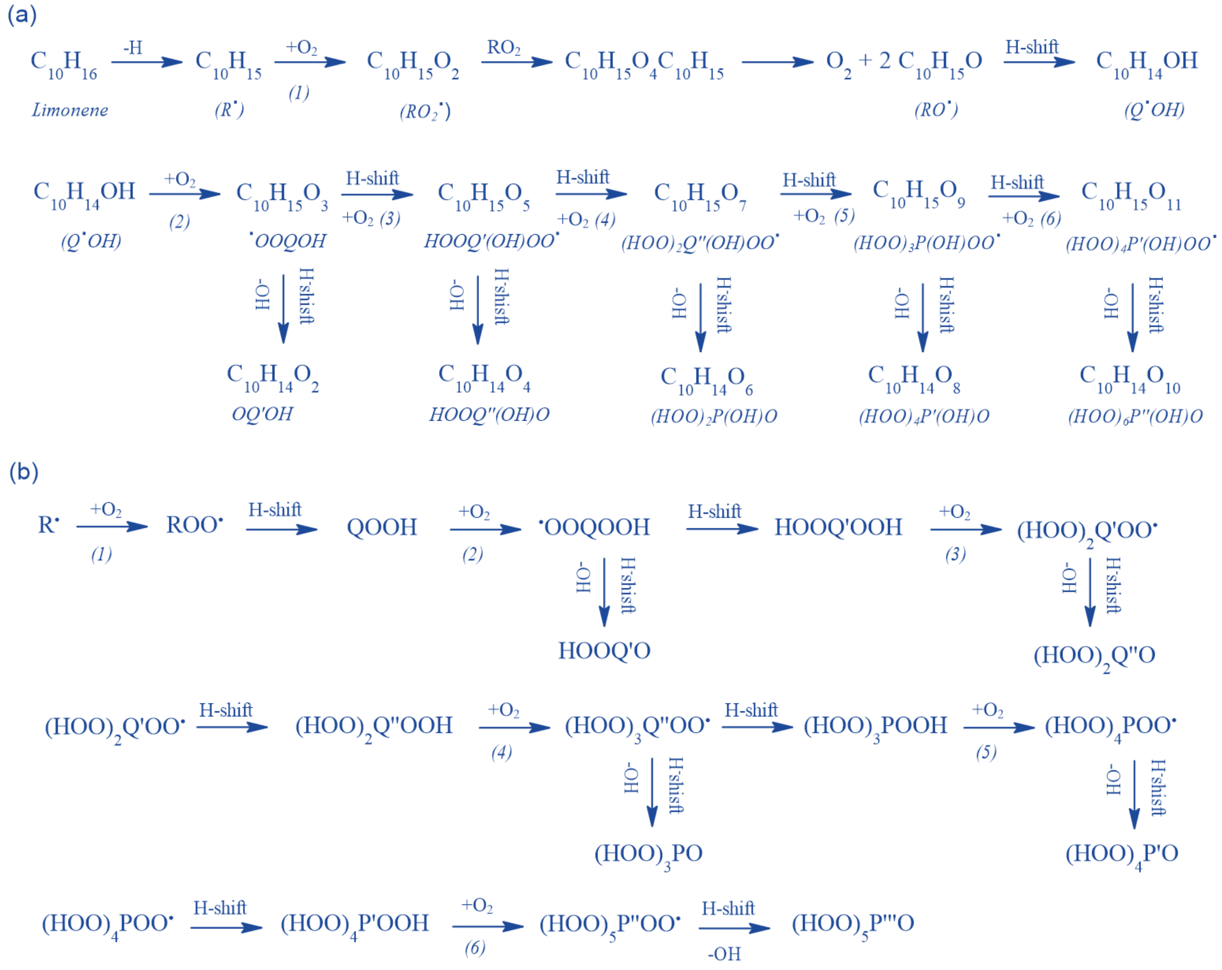

Figure 7. Reaction pathways to highly oxygenated products considered in atmospheric chemistry (a) and (b) (Bianchi et al., 2019). Recently extended reaction pathways in combustion (b) (Wang et al., 2017)

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 ($O/C \geq 0.6$ and $OS_c \geq 0$) consists of highly oxygenated and highly oxidized compounds (acids and carbonyls), Region 2 ($O / C \geq 0.6$ and $OS_c < 0$), consists of highly oxygenated and moderately oxidized compounds (alcohols, esters and peroxides), finally, Region 3 ($OS_c \geq 0$ and $H/C \leq 1.2$) 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 $C_{25}H_{32}O_{17}$.

Line 516-541, page 24

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.

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., $RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOOOR \rightarrow 2\ RO^{\bullet} + O_2$. 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). Although diverse experimental conditions were used here, in terms of concentration of reactants, temperature, reaction time, analysis conditions, we observed strong similitude in terms of molecular formulae detected in atmospheric and 'combustion' chemistry experiments. Besides, these two routes can produce a pool of OH radicals via decomposition of intermediates, e.g., $^{\bullet}OOQOOH \rightarrow {}^{\bullet}OH + HOOQ'O$ (KHP) and $(HOO)_2Q'OO^{\bullet} \rightarrow {}^{\bullet}OH + (HOO)_2Q''O$ (keto dihydroperoxide) for the 'combustion' route and $^{\bullet}OOQOH \rightarrow {}^{\bullet}OH + OQ'OH$ (keto alcool) and $HOOQ'(OH)OO^{\bullet} \rightarrow {}^{\bullet}OH + HOOQ''(OH)O$ (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.