

Dear Editor,

Thank you for your comments and suggestions. We have taken them into account in the revised manuscript.

In this document, you will find changes made in response to reviewer 2 comments

Best regards,

Roland BENOIT et al.

## **Reviewer 2**

### **Comments:**

The authors clarified few points raised by the reviewers. However, there are still some shortcomings on discussing the autoxidation and composition of observed compounds with HESI/APCI. There are still too many unclear points to justify acceptance for publication, some of which were brought up also by other reviewers.

I am still puzzled how authors came to the conclusions regarding autoxidation. It is unclear to me how the autoxidation products were selected and how other products were confirmed not to form in autoxidation. This makes also the arrows on Figure 2b confusing. Indeed, some studies before relied on the O<sub>2</sub> difference, but it was also supported by the relative abundance of the compounds (for instance, only even-oxygen compound were present) and quite often was only applied to products with larger oxygen number.

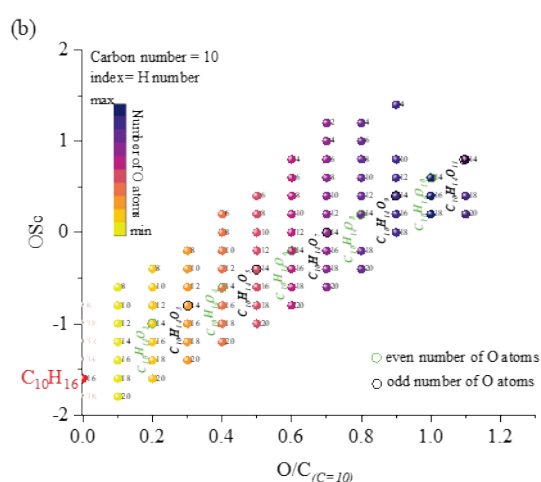
### **Answer:**

First, one should remember autoxidation was first described in ‘combustion studies’ performed at relatively low-temperature (<800K); see Introduction for references going back to 1952. What was not considered in most ‘combustion’ studies was the formation on highly oxidized products which have been described in publications relative to ‘atmospheric’ oxidation studies and named HOMs. In 2017, one of the authors of the present work published in PNAS a study demonstrating the formation of highly oxidized products through autoxidation (<https://doi.org/10.1073/pnas.1707564114>). Several other studies by ZD Wang et al. and Belhadj et al. followed (some references cited in the present paper). Thus, there is no clear reasons to be ‘puzzled when reading here we could form and detect autoxidation

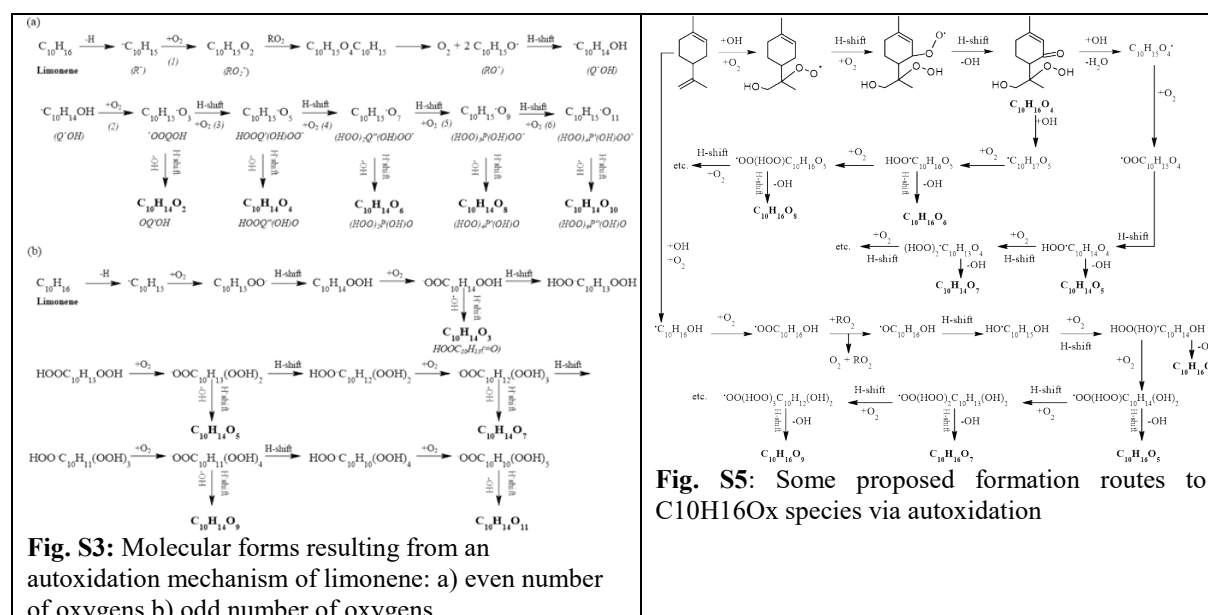
products. Our strength, compared to what was done with TOF MS (resolution ~4,000), is the use of a much better sensitive and precise MS instrument (Orbitrap with resolution of 120,000).

The products were selected based on the autoxidation scheme (Fig. S3) given in the supplementary. There, one can see the formation routes to  $C_{10}H_{14}O_{2-10}$  and  $C_{10}H_{14}O_{3-11}$ . These molecular formulas were detected in our experiments as show in fig. 2b. The others formulas presented in fig. 2b should result from others oxidation pathways. Indeed, products with chemical formulas with  $H \geq 16$  cannot derived from autoxidation pathways described in Fig S3. However, other pathways (Fig. S5) can yield such species, e.g., through the initial addition of OH on terpenes double bonds followed by  $O_2$  addition and autoxidation of products.

Fig. 2b as been revised: arrows connecting molecular formulas have been removed since these species are not directly connected (Fig. S3) whereas the radicals generated these stable species are connected by an autoxidation pathway (e.g.,  $C_{10}H_{15}O_3 \rightarrow C_{10}H_{15}O_5 \rightarrow C_{10}H_{15}O_7 \rightarrow C_{10}H_{15}O_9 \rightarrow \dots$ ,  $C_{10}H_{15}O_2 \rightarrow C_{10}H_{15}O_4 \rightarrow C_{10}H_{15}O_6 \rightarrow C_{10}H_{15}O_8 \rightarrow \dots$ )



Two new figures (Fig S3 and S5) have been added to describe the reaction pathways that can form the detected molecules.



The chemical formulas detected (for both oxygen parities) and their relative intensity were specified in Table 2. Chemical formulas are highlighted in red in the Supplementary database.

	<b>Limonene</b>	<b>Alpha-pinene</b>
<b>Even number of oxygen atom</b>		
<b>hydroxyketone</b>	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub> (1.61442E+7)	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub> (4.54785E+7)
<b>+O<sub>2</sub> (1<sup>st</sup>)</b>	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub> (3.34718E+7)	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub> (2.52885E+6)
<b>+O<sub>2</sub> (2<sup>nd</sup>)</b>	C <sub>10</sub> H <sub>14</sub> O <sub>6</sub> (9.58108E+6)	C <sub>10</sub> H <sub>14</sub> O <sub>6</sub> (7.56393E+4)
<b>+O<sub>2</sub> (3<sup>rd</sup>)</b>	C <sub>10</sub> H <sub>14</sub> O <sub>8</sub> (9.55306E+5)	C <sub>10</sub> H <sub>14</sub> O <sub>8</sub> (2.91182E+4)
<b>+O<sub>2</sub> (4<sup>th</sup>)</b>	C <sub>10</sub> H <sub>14</sub> O <sub>10</sub> (1.00597E+4)	C <sub>10</sub> H <sub>14</sub> O <sub>10</sub> (not detected)
	C <sub>10</sub> H <sub>14</sub> O <sub>12</sub> (not detected)	--
<b>Odd number of oxygen atom</b>		
<b>3hydroperoxyl carbonyl</b>	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub> (3.23297E+7)	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub> (9.3999E+6)
<b>+O<sub>2</sub> (1<sup>st</sup>)</b>	C <sub>10</sub> H <sub>14</sub> O <sub>5</sub> (2.27278E+7)	C <sub>10</sub> H <sub>14</sub> O <sub>5</sub> (1.17044E+5)
<b>+O<sub>2</sub> (2<sup>nd</sup>)</b>	C <sub>10</sub> H <sub>14</sub> O <sub>7</sub> (4.04207E+6)	C <sub>10</sub> H <sub>14</sub> O <sub>7</sub> (7.17307E+4)
<b>+O<sub>2</sub> (3<sup>rd</sup>)</b>	C <sub>10</sub> H <sub>14</sub> O <sub>9</sub> (1.92816E+5)	C <sub>10</sub> H <sub>14</sub> O <sub>9</sub> (not detected)
<b>+O<sub>2</sub> (4<sup>th</sup>)</b>	C <sub>10</sub> H <sub>14</sub> O <sub>11</sub> (6.34129E+3)	--
	C <sub>10</sub> H <sub>14</sub> O <sub>13</sub> (not detected)	--

The discussion has been reconsidered in the light of these clarifications (lines 315-332)

In addition, we have specified in the database, in the case of combustion, the chemical formulae consistent with an autoxidation mechanism and added a comment (lines 451-458):

JSR-FIA-HRMS data indicated many more sets of chemical formulas differing by two O-atoms in the range C<sub>10</sub>H<sub>x</sub>O<sub>2-10</sub> (C<sub>10</sub>H<sub>12</sub>O<sub>2-10</sub>, C<sub>10</sub>H<sub>12</sub>O<sub>3-9</sub>, C<sub>10</sub>H<sub>14</sub>O<sub>2-10</sub>, C<sub>10</sub>H<sub>14</sub>O<sub>3-9</sub>, C<sub>10</sub>H<sub>16</sub>O<sub>2-8</sub>, C<sub>10</sub>H<sub>16</sub>O<sub>3-9</sub>); see Supplementary database. Although at this stage one cannot prove these species were formed through autoxidation, their formulas are consistent with autoxidation products

#### Comments:

I disagree that if compounds, especially closed-shell species shown for instance in Table 3, are separated by two oxygens, they are directly connected by autoxidation. In other words, C<sub>10</sub>H<sub>16</sub>O<sub>6</sub> probably did not directly result in autoxidation of C<sub>10</sub>H<sub>16</sub>O<sub>4</sub> and so on.

#### Answer:

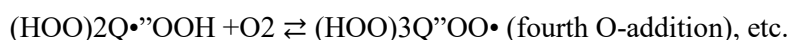
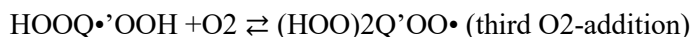
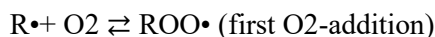
We agree with this comment. Indeed, only radicals are directly connected by addition O<sub>2</sub> through autoxidation (Fig S3). However, C<sub>10</sub>H<sub>16</sub>O<sub>x</sub> species can derive from addition of OH on terpenes double bonds followed by O<sub>2</sub> addition and autoxidation of products (Fig. S5).

#### Comments:

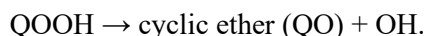
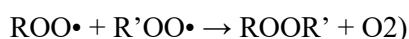
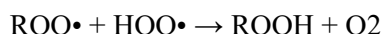
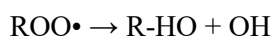
Nothing is mentioned about several oxidation steps (not autoxidation) or if those are expected in combustion (this was asked during review, but not expanded on by authors).

#### Answer:

The reactions presented in the introduction cover a set including autoxidation, but not limited to autoxidation:



The above reactions describe an autoxidation mechanism (cited in the Introduction). Those below are complementary and can occur under both 'atmospheric' and 'combustion' conditions (they are cited in the manuscript):



Mechanisms are presented in the literature; we cite the paper of Wang et al. (2017) in PNAS where many reaction pathways are described, including autoxidation.

### Comments:

The authors mentioned they added the database of detected molecules, but I did not find it in the revised Supplementary. It would have made a bit more clear, which compounds did not meet the criteria of "autoxidation" if we had a list of compounds with the marked selection.

### Answer:

A database was added with all detected molecules for limonene and  $\alpha$ -pinene (HESI, negative & positive modes). The molecules of interest cited in the article have been highlighted in red. The 78 molecules common to the four studies cited in the article and combustion experiments are present in the database.

### Comments:

Since authors make a comprehensive review of the detected products, I do not find some of the replies related to compounds with formulas  $C_xH_4O_y$  and  $C_{21}+H_xO_y$  sufficient. Also, I realized there are some  $C_xH_{20}O_y$  compounds. Since these formulas were identified in the authors' experiments, there should have been some explanation what those may be (are they artifacts or do they form in multiple oxidation steps, or there is another explanation?). Some of those species should not exist. Those are seen in Figure 2b, but also other figures and are actually discussed in terms of high DBE content, and something about their origin should have been mentioned.

**Answer:**

**Formulas  $C_xH_4O_y$ :** clarifications have been made in the text (lines 332-335).

Finally, some chemical formulas have no chemical relevance ( $C_xH_4O_y$ ). These are probably artefacts linked to the characterization method (ionization mode, ions transfer, ions isolation in the c-trap, incorrect masse identification). We chose to leave these data, knowing that they would be discarded in the various subsequent comparisons.

**Formulas  $C_{21}+H_xO_y$ :** We have specified line 294-297 that the combinations of fragmentations ( $C < 10$ ) and accretions, observed in Figure 2a, form a continuous incrementation of the carbon number. We have added the explanation of the  $C=30$  limit. This limit is probably due to the ionization or detection possibilities of the spectrometer.

The chemical formulas  $C_xH_{20}O_y$  cited and presented in figure 2b correspond to the  $C_{10}H_{20}O_y$  formulas (in figure 2B, the carbon number is 10)

**Comments:**

Lines 254-256: I am still not sure how observed compounds with high DBE is a result of 'hydroperoxide and carboxyl groups along with the fact that a heated ionization source favors vaporization of low volatility compounds. This is the revised sentence, but authors did not provide justification.

**Answer:**

The increase in DBE results from the decrease of 2 hydrogens atoms or the increase of 1 carbon atoms. In this case, without carbonyl formation (while the number of oxygens increases), the increase in DBE would only result from the formation of vinyl or unsaturation groups. These conditions seem unlikely when the DBE is greater than 5, 10 or 15 under oxidation conditions. For this reason, we have used the term probable.

The volatility of a chemical compound is always favored by the rise in temperature. The modification of ESI sources to HESI has greatly contributed to the improvement of the ionisation of low volatile chemical compounds.

**Comments:**

Line 467. Where this D2O experiment shown?

**Answer:**

The results obtained by H/D exchanges with D2O and derivatization of carbonyls with 2,4-DNPH were added to the Fig S7 (supplements).

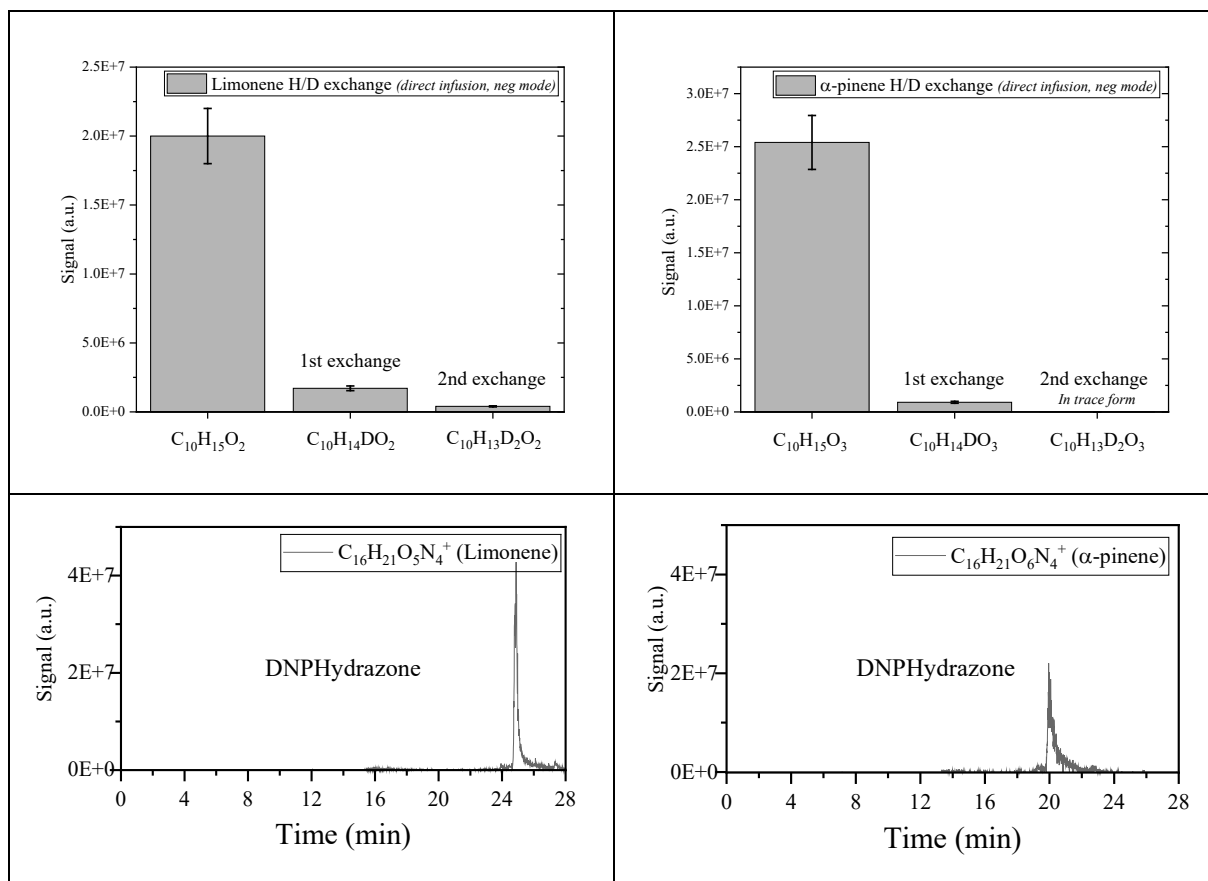


Fig. S7: D<sub>2</sub>O exchanges for limonene and  $\alpha$ -pinene (direct infusion, negative ionization mode) - top; and derivatization of carbonyls in limonene and  $\alpha$ -pinene oxidation samples using 2,4-DNPH (UHPLC, positive mode) – bottom.

### Comments:

Comparison of combustion to ozonolysis studies remains questionable as it should produce somewhat different autoxidation products. Some discussion if these compounds are expected to be the same in any circumstance would be useful.

### Answer:

Indeed, “The subject is challenging because the oxidation chemistry of monoterpenes is highly complex and far from fully understood, either under atmospheric or cold flame conditions. It is clear that covering both regimes in all details in one paper is difficult to achieve”.

We hope to have contributed some input to this question. It is clear that the database created will be a useful complement for those who want to continue this work.