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1 **Autoxidation of terpenes, a common pathway in tropospheric**  
2 **and low temperature combustion conditions: the case of**  
3 **limonene and  $\alpha$ -pinene.**

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9

10 **Abstract.**

11 The oxidation of monoterpenes under atmospheric conditions has been the subject of numerous studies. They were  
12 motivated by the formation of oxidized organic molecules (OOM) which, due to their low vapor pressure,  
13 contribute to the formation of secondary organic aerosols (SOA). Among the different reaction mechanisms  
14 proposed for the formation of these oxidized chemical compounds, it appears that the autoxidation mechanism,  
15 involving successive events of H-migration and O<sub>2</sub> addition, common to both low-temperature combustion and  
16 atmospheric conditions, is leading to the formation of highly oxidized molecules (HOM). In atmospheric  
17 chemistry, the importance of autoxidation compared to other oxidation pathways has been the topic of numerous  
18 studies. Conversely, in combustion, autoxidation under cool flame conditions is the main oxidation process  
19 commonly taken into account. An analysis of oxidation products detected in both conditions was performed, using  
20 the present combustion data and literature data from tropospheric oxidation studies, to investigate possible  
21 similarities in terms of observed chemical formulae of products. To carry out this study, we chose two terpenes,  
22  $\alpha$ -pinene and limonene (C<sub>10</sub>H<sub>16</sub>), among the most abundant biogenic components in the atmosphere, and  
23 considered in many previous studies. Also, these two isomers were selected for the diversity of their reaction sites  
24 (exo- and endo- carbon-carbon double bonds). We built an experimental database consisting of literature  
25 atmospheric oxidation data and presently obtained combustion data for the oxidation of the two selected terpenes.  
26 In order to probe the effects of the type of ionization used in mass spectrometry analyses on the detection of  
27 oxidation products, we used heated electrospray ionization (HESI) and atmospheric pressure chemical ionization  
28 (APCI), in positive and negative modes. The oxidation of limonene-oxygen-nitrogen and  $\alpha$ -pinene-oxygen-  
29 nitrogen mixtures was performed using a jet-stirred reactor at elevated temperature (590 K), a residence time of 2  
30 s, and atmospheric pressure. Samples of the reacting mixtures were collected in acetonitrile and analyzed by high-  
31 resolution mass spectrometry (Orbitrap Q-Exactive) after direct injection and soft ionization, i.e. (+/-) HESI and  
32 (+/-) APCI. This work shows a surprisingly similar set of chemical formulae of products, including oligomers,  
33 formed in cool flames and under simulated atmospheric conditions. Data analysis showed that a non-negligible  
34 subset of chemical formulae is common to all experiments independently of experimental parameters. Finally, this  
35 study indicates that more than 40% of the detected chemical formulae in this full dataset can be ascribed to an  
36 autoxidation mechanism.

37



2

## 38 1 Introduction

39 The links between atmospheric and combustion chemistry have often been studied from the point of view of  
40 tropospheric reactions of combustion effluents or pollutants, e.g., oxidation of volatile organic compounds,  
41 nitrogen oxides reactions, sulfur chemistry (Barsanti et al., 2017; Shrivastava et al., 2017; Zhao et al., 2018; Bianchi  
42 et al., 2019). Climate change and the increase of large wildfire events have profoundly modified the relationship  
43 between atmospheric chemistry and combustion at large. When studying the oxidation of chemicals and the  
44 formation of SOA in the atmosphere, it becomes necessary to determine the contribution of different oxidation  
45 pathways pertaining to atmospheric chemistry, combustion chemistry, or both.

46 In low-temperature combustion (cool flame) the formation of oxidized organic molecules (OOM) is mainly  
47 attributed to autoxidation reactions (Belhadj et al., 2021; Benoit et al., 2021), whereas in atmospheric chemistry, it  
48 is only relatively recently that this pathway has been considered (Vereecken et al., 2007; Crouse et al.,  
49 2013; Jokinen et al., 2014a; Berndt et al., 2015; Jokinen et al., 2015a; Berndt et al., 2016; Iyer et al., 2021). Also, it  
50 has been identified that highly oxygenated molecules (HOMs), a source of secondary organic aerosols (SOA), can  
51 result from autoxidation processes (Wang et al., 2021; Tomaz et al., 2021; Bianchi et al., 2019). Modeling studies  
52 complemented by laboratory experiments showed that autoxidation mechanisms proceed simultaneously on  
53 different  $\text{RO}_2^\cdot$  radicals and leads to, through isomerization and addition of  $\text{O}_2$ , the production of a wide range of  
54 oxidized compounds in a few hundredths of a second (Jokinen et al., 2014a; Berndt et al., 2016; Bianchi et al.,  
55 2019). Autoxidation is based on an H-shift and oxygen addition which starts with the initial production of  $\text{RO}_2^\cdot$   
56 radicals. This mechanism can repeat itself several times and lead to recurrent oxygen additions to form HOMs:  $\text{R} +$   
57  $\text{O}_2 \rightleftharpoons \text{ROO}^\cdot$  (first  $\text{O}_2$ -addition);  $\text{ROO}^\cdot \rightleftharpoons \text{QOOH}$  (H-shift);  $\text{QOOH} + \text{O}_2 \rightleftharpoons \text{OOQOOH}$  (second  $\text{O}_2$ -addition);  
58  $\text{OOQOOH} \rightleftharpoons \text{HOOQOOH}$  (H-shift);  $\text{HOOQOOH} + \text{O}_2 \rightleftharpoons (\text{HOO})_2\text{QOO}^\cdot$  (third  $\text{O}_2$ -addition);  $(\text{HOO})_2\text{QOO}^\cdot$   
59  $\rightleftharpoons (\text{HOO})_2\text{QOOH}$  (H-shift);  $(\text{HOO})_2\text{QOOH} + \text{O}_2 \rightleftharpoons (\text{HOO})_3\text{QOO}^\cdot$  (fourth  $\text{O}_2$ -addition) etc. Recent works  
60 have shown that, under certain atmospheric conditions, this autoxidation mechanism could be competitive with  
61 other reaction pathways involving  $\text{RO}_2^\cdot$  radicals (Bianchi et al., 2019), e.g., the carbonyl channel ( $\text{ROO}^\cdot \rightarrow \text{R}_\text{H}\text{O}$   
62  $+ \text{OH}$ ), the hydroperoxide channel ( $\text{ROO}^\cdot + \text{HOO}^\cdot \rightarrow \text{ROOH} + \text{O}_2$  and  $\text{RO}^\cdot + \text{OH} + \text{O}_2$ ), disproportionation  
63 reactions ( $\text{ROO}^\cdot + \text{R}'\text{OO}^\cdot \rightarrow \text{RO}^\cdot + \text{R}'\text{O}^\cdot + \text{O}_2$  and  $\text{R}_\text{H}\text{O} + \text{R}'\text{OH} + \text{O}_2$ ), accretion reactions ( $\text{ROO}^\cdot + \text{R}'\text{OO}^\cdot \rightarrow$   
64  $\text{ROOR}' + \text{O}_2$ ). A study published in 2021 showed that the oxidation of alkanes follows this autoxidation  
65 mechanism under both atmospheric and combustion conditions (Wang et al., 2021). Also, that work confirmed  
66 that internal H-shifts in autoxidation can be promoted by the presence of functional groups, as predicted earlier  
67 (Otkjær et al., 2018) for  $\text{RO}_2^\cdot$  radicals containing OOH, OH,  $\text{OCH}_3$ ,  $\text{CH}_3$ ,  $\text{C}=\text{O}$ , or  $\text{C}=\text{C}$  groups. To further assess  
68 the importance of these pathways, available data must be compared along with their experimental specificities. In  
69 laboratory studies under simulated atmospheric conditions, oxidation occurs at near-ambient temperatures (250-  
70 300 K), at atmospheric pressure, in the presence of ozone and/or  $\text{OH}^\cdot$  radicals, and with low initial terpene  
71 concentrations. In combustion, the  $\text{OH}^\cdot$  radical, temperature, and pressure are driving autoxidation. Initial reactant  
72 concentrations are generally higher compared to atmospheric conditions, so as to compensate for the absence of  
73 ozone and get oxidation to proceed, since terpenes, as other hydrocarbons, react very slowly with  $\text{O}_2$ . Rising  
74 temperature increases isomerization rates and favors autoxidation, at the expense of other possible reactions of  
75  $\text{RO}_2^\cdot$  radicals. In atmospheric chemistry, at near room temperature, autoxidation can be initiated via two reaction  
76 mechanisms: reactions with ozone or with the  $\text{OH}^\cdot$  radical. Suppression of one of these pathways by scavengers



3

77 generally changes the amount of products formed (sometimes a drastic decrease >90% was observed (Kenseth et  
78 al., 2018;Meusinger et al., 2017;Pospisilova et al., 2020)), but does not affect the diversity of observed chemical  
79 formulae (Zhao et al., 2018;Pospisilova et al., 2020). It has been reported earlier that a temperature rise from 250  
80 to 273K does not affect the distribution of HOMs (Quéléver et al., 2019) whereas Trostl et al. suggested that the  
81 distribution of HOMs is affected by temperature,  $\alpha$ -pinene or particle concentration (Tröstl et al., 2016). Similarly,  
82 the experiments of Huang et al. performed at different temperatures (223 K and 296 K) and precursor concentration  
83 ( $\alpha$ -pinene 0.714 and 2.2 ppm) suggested that the physicochemical properties, such as the composition of the  
84 oligomers, can be affected by a variation of temperature (Huang et al., 2018). Both in combustion and atmospheric  
85 chemistry, autoxidation can yield highly oxygenated molecules (HOMs), e.g., compounds containing more than 7  
86 oxygen atoms (Benoit et al., 2021;Bianchi et al., 2019). The term ‘HOM’ is generally associated with atmospheric  
87 chemistry (Bianchi et al., 2019), but this nomenclature does not specify the chemical properties of a compound.  
88 In other words, in combustion we can also observe highly oxidized chemical compounds similar to those relevant  
89 to atmospheric chemistry. The broad range of chemical molecules formed and the impact of the experimental  
90 conditions on their character remain a subject for atmospheric chemistry as well as combustion chemistry studies.  
91 Moreover, whatever the mechanism of aerosol formation, i.e., oligomerization, addition, or accretion, their  
92 composition will be linked to that of the initial radical pool (Tomaz et al., 2021).

93 In low-temperature combustion, when the temperature is increased, autoxidation rate goes through a maximum  
94 between 500 and 670 K, depending on the nature of the fuel (Belhadj et al., 2020;Belhadj et al., 2021), and the rate  
95 of formation of HOM also increases (Bianchi et al., 2019). Therefore, temperature has a measurable effect on the  
96 amount of HOMs formed (Wang et al., 2021). In low-temperature combustion chemistry as in atmospheric  
97 chemistry, the oxidation of a chemical compound leads to the formation of several thousands of chemical products  
98 which result from successive additions of oxygen, isomerization, accretion, fragmentation, and oligomerization  
99 (Benoit et al., 2021). The exhaustive analysis of chemical species remains, in the current state of instrumental  
100 limitations, impossible. This would consist in analyzing several thousands of molecules in MS<sup>2</sup> mode using  
101 separative techniques such as ultra-high pressure liquid chromatography (UHPLC) or ion mobility spectrometry  
102 (IMS) (Krechmer et al., 2016;Kristensen et al., 2016). Nevertheless, it is possible to classify these molecular  
103 species, considering only C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> compounds, according to various criteria accessible via graphic tools  
104 representation such as van Krevelen diagrams, double bond equivalent number (DBE), and average carbon  
105 oxidation state (OSc) versus the number of carbon atoms (Kourtchev et al., 2015;Nozière et al., 2015). Such  
106 postprocessing of large datasets has the advantage of immediately highlighting families of compounds or  
107 physicochemical properties such as the condensation of molecules (vapor pressure), the large variety of oxygenated  
108 products (C<sub>x</sub>H<sub>y</sub>O<sub>1-15</sub> in the present experiments) and the formation of oligomers (Kroll et al., 2011;Xie et al., 2020).

109 In addition to the recent studies focusing on the first steps of autoxidation, a more global approach, based on the  
110 comparison of possible chemical transformations related to autoxidation in low temperature combustion and  
111 atmospheric chemistry, is needed for evaluating the importance of autoxidation under tropospheric and low-  
112 temperature combustion conditions. In order to study the effects of ozonolysis and combustion on the diversity of  
113 chemical molecules formed by autoxidation, we have selected  $\alpha$ -pinene and limonene, two terpene isomers among  
114 the most abundant in the troposphere. Limonene has a single ring structure and two double bonds, one of which is  
115 exocyclic.  $\alpha$ -Pinene has a bicyclic structure and a single endo-cyclic double bond. These two isomers with their  
116 distinctive characters are good candidates for studying autoxidation versus initial chemical structure and



4

117 temperature. For  $\alpha$ -pinene, in addition to the reactivity of its endo-cyclic double bond, products of ring opening of  
118 the cyclobutyl group have been detected, which could explain the diversity of observed oxidation products (Kurtén  
119 et al., 2015; Iyer et al., 2021). This large pool of products is increased in the case of limonene by the presence of  
120 two double bonds (Hammes et al., 2019; Jokinen et al., 2015a). Nevertheless, the diversity of oxidation products  
121 can be compensated by similarities in terms of reaction mechanisms and intermediates formed through  
122 autoxidation (Savee et al., 2015).

123 In the present work, which is a prolongation of that published earlier for the oxidation of limonene alone (Benoit  
124 et al., 2021), we oxidized  $\alpha$ -pinene and limonene in a jet-stirred reactor at atmospheric pressure, excess of oxygen,  
125 and elevated temperature. Then, we characterized the impact of using different ionization techniques (HESI and  
126 APCI) in positive and negative modes on the pool of detected chemical formulae. The particularities of each  
127 ionization mode were analyzed to identify the most suitable ionization technique for exploring the formation of  
128 autoxidation products under low temperature combustion. Chemical formulae detected here and in atmospheric  
129 chemistry studies were compiled and tentatively used to evaluate the importance of autoxidation under both  
130 conditions.

## 131 2 Experiments

### 132 2.1 Oxidation experiments

133 The present experiments were carried out in a fused silica jet-stirred reactor (JSR) setup presented earlier (Dagaut  
134 et al., 1986; Dagaut et al., 1988) and used in previous studies (Dagaut et al., 1987; Benoit et al., 2021; Belhadj et al.,  
135 2021). The two isomers  $\alpha$ -pinene and limonene were studied separately. As in earlier works (Benoit et al.,  
136 2021; Belhadj et al., 2021),  $\alpha$ -pinene (+), 98% pure from Aldrich and limonene (R)-(+), >97% pure from Sigma,  
137 were pumped by an HPLC pump (Shimadzu LC10 AD VP) with an online degasser (Shimadzu DGU-20 A3) and  
138 sent to a vaporizer assembly where it was diluted by a nitrogen flow. Each terpene isomer and oxygen, both diluted  
139 by  $N_2$ , were sent separately to a 42 mL JSR to avoid oxidation before reaching 4 injectors (nozzles of 1 mm I.D.)  
140 providing stirring. The flow rates of nitrogen and oxygen were controlled by mass flow meters. Good thermal  
141 homogeneity along the vertical axis of the JSR was recorded (gradients of  $< 1$  K/cm) by thermocouple  
142 measurements (0.1 mm Pt-Pt/Rh-10% wires located inside a thin-wall silica tube). In order to observe the oxidation  
143 of these isomers, which are not prone to strong self-ignition, the oxidation of 1% of these chemical compounds  
144 ( $C_{10}H_{16}$ ) under lean fuel conditions (equivalence ratio 0.25, 56%  $O_2$ , 43%  $N_2$ ), experiments were carried out at 590  
145 K, atmospheric pressure, and a residence time of 2 s. Under these conditions, the oxidation of the two isomers is  
146 initiated by slow H-atom abstraction by molecular oxygen. The fuel radicals react rapidly with  $O_2$  to form peroxy  
147 radicals which undergo further oxidation, characteristic of autoxidation. The absence of ozone, and no need for  
148 the addition of a scavenger, allow probing reaction mechanisms and observing chemical species potentially  
149 specific to autoxidation initiated by OH radicals. A 2 mm I.D. probe was used to collect samples. To measure low-  
150 temperature oxidation products ranging from early oxidation steps to highly oxidized molecules, the sonic probe  
151 samples were bubbled in cooled acetonitrile (UHPLC grade  $\geq 99.9$ ,  $T = 0^\circ C$ , 250 mL) for 90 min. The resulting  
152 solution was stored in a freezer at  $-15^\circ C$ .

153



5

## 154 2.2 Chemical analyses

155 Analyses of samples collected in acetonitrile were performed by direct sample instillation (rate: 3 μL/min and  
156 recorded for 1 min for data averaging) in the ionization chamber of a high-resolution mass spectrometer (Thermo  
157 Scientific Orbitrap® Q-Exactive, mass resolution 140,000 and mass accuracy <0.5 ppm RMS). Both heated  
158 electrospray ionization (HESI) and atmospheric chemical ionization (APCI) were used in positive and negative  
159 modes for the ionization of products. HESI settings were: spray voltage 3.8 kV, T vaporizer of 150°C, T capillary  
160 200°C, sheath gas flow of 8 arbitrary units (a.u.), auxiliary gas flow of 1 a.u., sweep gas flow of 0 a.u.. In APCI,  
161 settings were: spray voltage 3.8 kV, vaporizer temperature of 150°C, capillary temperature of 200°C, sheath gas  
162 flow of 8 a.u., auxiliary gas flow of 1 a.u., sweep gas flow of 0 a.u., corona current of 3 μA. In order to avoid  
163 transmission and detection effects of ions depending on their mass inside the C-Trap (Hecht et al., 2019),  
164 acquisitions with three mass ranges were performed (m/z 50-750; m/z 150-750; m/z 300-750). The upper limit of  
165 m/z 750 was chosen because of the absence of signal beyond this value. We verified that no significant oxidation  
166 occurred in the HESI and APCI ion sources by injecting a limonene-ACN mixture. The optimization of the  
167 Orbitrap ionization parameters in HESI and APCI did not show any clustering phenomenon for these two isomers.  
168 The parameters evaluated were: injection source - capillary distance, vaporization and capillary temperatures,  
169 applied difference of potential, injected volume, flow rate of nitrogen in the ionization source. Positive and  
170 negative HESI mass calibrations were performed using Pierce™ calibration mixtures (Thermo Scientific).  
171 Chemical compounds with relative intensity less than 1 ppm to the highest mass peak in the mass spectrum were  
172 not considered. Nevertheless, it should be considered that some of the molecules presented in this study could  
173 result from our experimental conditions (continuous flow reactor, reagent concentration, temperature, reaction  
174 time) and to some extent from our acquisition conditions, different from those of the previous studies (Deng et al.,  
175 2021; Quéléver et al., 2019; Meusinger et al., 2017; Krechmer et al., 2016; Tomaz et al., 2021; Fang et al.,  
176 2017; Witkowski and Gierczak, 2017; Jokinen et al., 2015b; Nørgaard et al., 2013; Bateman et al., 2009; Walser et  
177 al., 2008; Warscheid and Hoffmann, 2001; Hammes et al., 2019; Kundu et al., 2012). Indeed, the use of a continuous  
178 flow reactor operating at elevated temperature, as well as a high initial concentration of reagents can induce the  
179 formation of combustion-specific products, which does not exclude their possible formation under atmospheric  
180 conditions.

## 181 3 Data Processing

182 High resolution mass spectrometry (HR-MS) generates a large amount of data that is difficult to fully analyze by  
183 sequential methods. When the study requires the processing of several thousands of molecules, the use of statistical  
184 tools and graphical representation means becomes necessary. In this study, we have chosen to use the van Krevelen  
185 diagram (Van Krevelen, 1950) by adding an additional dimension, the double bond equivalent (DBE). The DBE  
186 number represents the sum of unsaturation and rings present in a chemical compound (Melendez-Perez et al.,  
187 2016).

$$188 \quad \text{DBE} = 1 + C - \text{H}/2 - \text{O}$$

189 This number is independent of the number of oxygen atoms, but changes with the number of hydrogen atoms.  
190 Decimal values of this number, which correspond to an odd number of hydrogen atoms, were not considered in  
191 this study. Then, duplications of chemical formulae in the O/C vs. H/C space are eliminated. The oxidation state



6

192 of carbon (OSc) provides a measure of the degree of oxidation of chemical compounds (alcohols, aldehydes,  
193 carboxylic acids, esters, ethers and ketones, but not peroxides) (Kroll et al., 2011). This provides a framework for  
194 describing the chemistry of organic species. It is defined by the following equation:

$$195 \quad \text{OSc} \approx 2 \text{O/C} - \text{H/C}$$

## 196 **4 Results and discussion**

197 The oxidation of the two isomers,  $\alpha$ -pinene and limonene ( $\text{C}_{10}\text{H}_{16}$ ), was studied at 590 K, under atmospheric  
198 pressure, with a residence time of 2 s and a fuel concentration of 1%. Under these conditions, the formation of  
199 peroxides by autoxidation at low temperature should be optimal (Belhadj et al., 2021), even if the conversion of  
200 the fuels remains moderate.

### 201 **4.1 Characterization of ionization sources**

202 First, we have studied the impact of APCI and HESI sources, in positive and negative modes, on the chemical  
203 formulae detected. The HESI and APCI sources in positive and negative mode were used and their operating  
204 parameters were varied, i.e., temperature, gas flow and accelerating voltage (see Section 2). For each polarity, only  
205 ions composed of carbon, hydrogen (even numbers) and oxygen were considered. Molecular duplicates inherent  
206 to mass range overlaps were excluded. Chemical formulae with relative intensity less than 1 ppm with respect to  
207 the highest mass peak of the mass spectrum were not considered. By following these rules, we obtained a different  
208 number of ions depending on the ionization source and the polarity used. Table 1 shows the number of ions  
209 according to the experimental conditions and the discrimination rules.

210 **Table 1.** Number of ions detected for each source in positive and negative modes.

Ionization source	$\alpha$ -Pinene		Limonene	
APCI	646 (+)	503(-)	1321(+)	1346(-)
HESI	594(+)	693(-)	1017(+)	1864(-)

211

212 Each combination of ionization sources and polarity generated a set of chemical formulae. To make a meaningful  
213 comparison between the positive and negative ions data, the chemical formulae used were the precursors of the  
214 ions identified in the mass spectra. These sets have common data, but also specific chemical formulae. For a given  
215 ionization source, less than 50% of the chemical formulae are common to both polarities. In other words, between  
216 30 and 50% of molecular species are ignored when using a single polarity. It is therefore essential to use both  
217 polarities in order to better describe all the species present. The HESI source data were compared to the APCI data  
218 (Tables 2 and 3), showing an increase of the number of chemical formulae detected by 20 to 30%. This increase  
219 is characterized by a better detection of negatively ionized species and those with a higher unsaturation number  
220 (DBE). In order to evaluate further the interest for using these ionization sources, we compiled these data in Venn  
221 diagrams and proposed a visualization of these sets with a van Krevelen representation; we added the number of  
222 DBE in the third dimension. These results are presented in Tables 2 and 3.



7

223 In positive ionization mode, independently of the ionization source and in addition to the common molecular  
224 formulae, we detected products with an O/C ratio  $< 0.2$  whereas in the negative ionization mode, we detected  
225 molecular formulae with an O/C ratio  $> 0.5$ . In addition to these observations, we noted that HESI is more  
226 appropriate for studying products with a large number of unsaturation (DBE  $> 5$ ). Finally, for an optimal detection  
227 of the oxidation products, it is necessary to consider the transmission limits of the C-Trap. Here, we could increase  
228 by more than 60% the number of molecular formulae detected using several mass ranges for data acquisition. The  
229 most appropriate ionization polarity to be used is tight to chemical functions present in products to be detected.  
230 We could increase by 30 to 100% the number of chemical formulae detected by using both positive and negative  
231 ionization modes. The ionization source used is also important. We could increase the number of detected chemical  
232 formulae by 20 to 30% using HESI. We believe that this approach to data validation and these results, although  
233 specific to this study, are applicable to any characterization by Orbitrap.

234





8

235 **Table 2.** Representation of the mass spectrometry data characterizing the oxidation of  $\alpha$ -pinene and  
 236 limonene (ionization source: APCI positive and negative mode, JSR experiments).

	$\alpha$ -Pinene			Limonene		
Source and mode	APCI <sup>+</sup>		APCI <sup>-</sup>	APCI <sup>+</sup>		APCI <sup>-</sup>
Number of compounds	646		503	1321		1346
Distribution	specific to positive mode 327	common 319	specific to negative mode 174	specific to positive mode 516	common 805	specific to negative mode 542
Venn graph	<p>Total : 820</p>			<p>Total : 1863</p>		
VK vs DBE						
	<p>Total : 1920</p>					

237

238



9

239 **Table 3.** Representation of the mass spectrometry data characterizing the oxidation of  $\alpha$ -pinene and  
 240 limonene (ionization source: HESI positive and negative modes, JSR experiments).

Source and mode	$\alpha$ -Pinene			Limonene		
	HESI <sup>+</sup>		HESI <sup>-</sup>	HESI <sup>+</sup>		HESI <sup>-</sup>
Number of compounds	594		603	1017		1864
Distribution	specific to positive mode 282	common 312	specific to negative mode 381	specific to positive mode 353	common 482	specific to negative mode 1342
Venn Graph	<p>Mieux ???</p> <p>Total : 975</p>			<p>Total : 2399</p>		
VK vs DBE						
	<p>Total : 2482</p>					

241

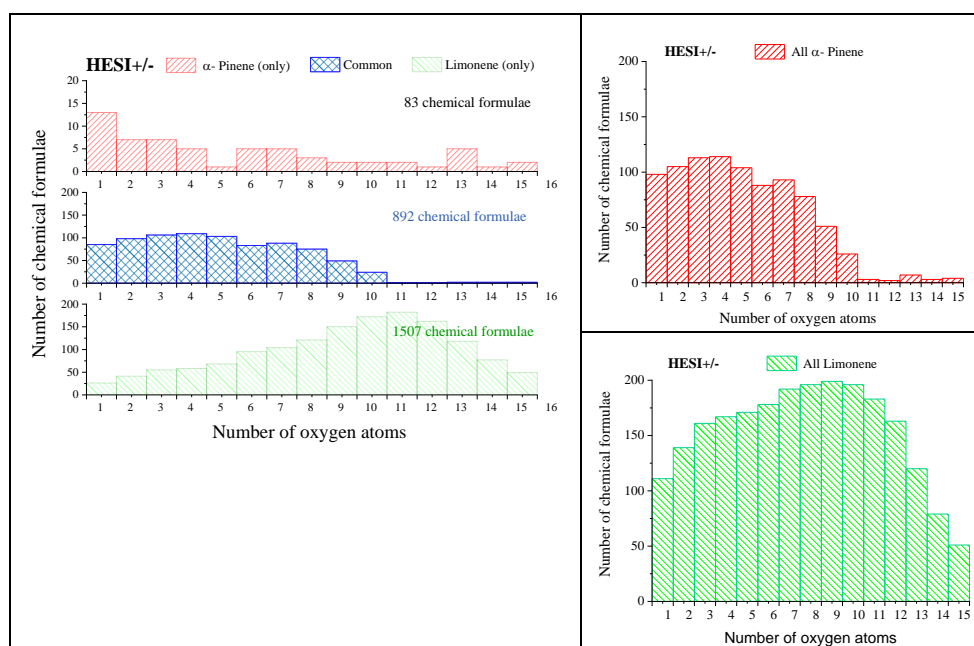
242 *4.2 Autoxidation products detected in a JSR*

243 In order to compare the oxidation of  $\alpha$ -pinene and limonene, we compiled the positive and negative ionization data  
 244 obtained with APCI (Table 2) and HESI (Table 3) ionization sources to obtain a more exhaustive database. For  
 245 the APCI and HESI sources, we distinguished three datasets, two of which are specific to the oxidation of  $\alpha$ -pinene



10

246 and limonene and one which is common to both isomers. In the following, the name "only" will be used to describe  
247 the molecules specific to the oxidation of one of the terpene isomers. This common dataset represents more than  
248 90% of the chemical formulae identified in  $\alpha$ -pinene oxidation samples, detected with both APCI and HESI. For  
249 limonene, where the number of identified chemical formulae is greater, this common dataset ranges between 68%  
250 in APCI and 37% in HESI. In these two cases, the relatively low residence time (2 seconds) and the diversity of  
251 the chemical formulae obtained show that the oxidation of these two terpene isomers leads to the opening of the  
252 ring, a phenomenon also observed in atmospheric chemistry (Berndt et al., 2016; Zhao et al., 2018; Iyer et al., 2021).  
253 Concerning the products' molecular formulae common to both isomers, figure 1 shows that they are limited to 10  
254 oxygen atoms. This limit is linked to  $\alpha$ -pinene whose oxidation beyond 10 oxygen atoms remains weak (less than  
255 2% of the totality of the identified molecules for this isomer). The autoxidation will allow keeping this similarity  
256 in the different steps of the oxidation by simple addition of two atoms of oxygen. In the case of limonene, the  
257 presence of an exocyclic double bond will increase, in a similar way to atmospheric chemistry (Kundu et al., 2012),  
258 the possibilities of oxidation and accretion. It remains however impossible, considering the size of the whole and  
259 the diversity of the isomers, to formalize all the reaction mechanisms. Nevertheless, the formation of oxidized  
260 species can be described with the help of graphical tools. The dispersion of the number of oxygen atoms per  
261 molecule shows for example that limonene oxidizes more than  $\alpha$ -pinene (Tables 2 and 3). In the case of limonene,  
262 with a HESI source, an oxygen number of up to 15 is measured, with maximum counts recorded for 10 O-atoms  
263 (Fig. 1), whereas it remains mostly less than or equal to 10 for  $\alpha$ -pinene (Fig. 1). Moreover, this graph shows, for  
264 the products specific of limonene oxidation, a distribution centered on 11 oxygen atoms with carbon skeletons  
265 probably resulting from accretion.

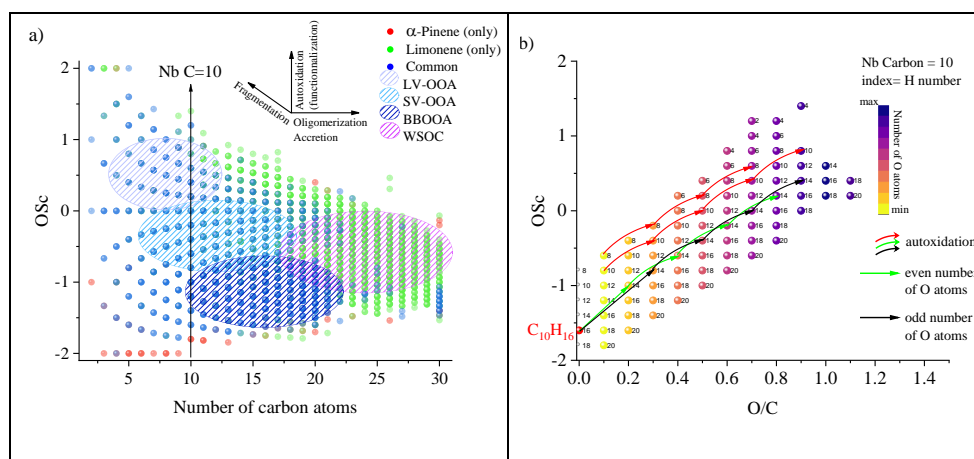


266  
267 **Figure 1:** Distribution of  $\alpha$ -pinene and limonene autoxidation products as a function of their oxygen content  
268 (ionization source: HESI, combined positive and negative modes data).



11

269 To verify this accretion hypothesis, we can plot the  $OSc$  as a function of the number of carbon atoms or the O/C  
270 ratio at fixed number of C-atoms (Fig. 2). One can visualize the evolution of the molecular oxidation for each  
271 carbon skeleton and the formation of oligomers. Species that are unique to one of the isomers, or common to both  
272 are differentiated using different colors. In addition to the autoxidation represented by the vertical axes for a given  
273 number of carbon atoms (Fig. 2a), we observe mechanisms of fragmentation, accretion and oligomerization  
274 between the carbon skeleton. These reaction mechanisms contribute to forming families according to the rate of  
275 oxidation and the size of their carbon skeleton. The increase in the number of oxygen atoms, but also of carbon  
276 atoms will decrease products volatility. We distinguish four families: low volatile oxygenated organic aerosols  
277 (LV-OOA), semi-volatile oxygenated organic aerosols (SV-OOA), biomass burning organic aerosols (BBOA) and  
278 water-soluble organic carbons (WSOC) following a classification proposed in the literature (Kroll et al., 2011). If  
279 we analyze the two sets of molecules from the APCI and HESI sources, positive and negative ionization modes  
280 combined, we find that nearly 73% of the molecules are linked to each other by a single difference of 2 oxygen  
281 atoms which reflects an autoxidation mechanism (Fig. 3).

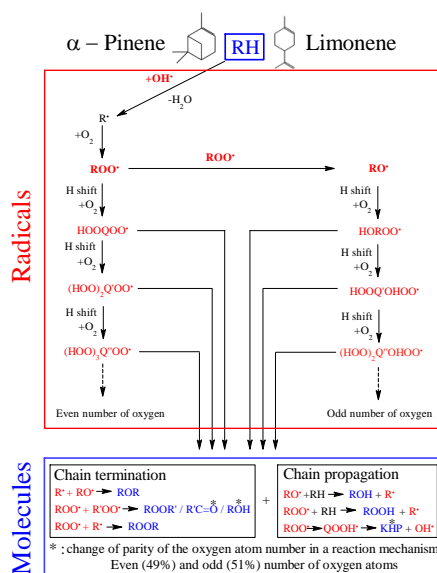


282 **Figure 2:** Overview of the distribution of limonene and  $\alpha$ -pinene oxidation products observed in a JSR: (a)  $OSc$   
283 versus carbon number in detected chemical formulae from APCI and HESI data. (b)  $OSc$  versus O/C atomic ratio  
284 for a carbon number of 10; index of the products: number of hydrogen atoms. Arrows indicate autoxidation from  
285 a  $C_6H_{16}$  isomer, according to the oxygen parity in products.

286 We can measure the amplitude of autoxidation for each carbon skeleton from the  $OSc$  vs. O/C space. For the two  
287 isomers, for which the initial carbon number (C) is equal to 10, one can observe (Fig. 2b) two autoxidation routes  
288 with an even and odd number of oxygen atoms. This parity distinction is initially present for the two main radicals,  
289  $ROO^{\cdot}$  and  $RO^{\cdot}$ , responsible for autoxidation. However, the termination and propagation reactions will change the  
290 oxygen parity to form a new distribution where the parity links between radicals and molecules are lost, making  
291 any interpretation of radical oxidation route impossible (Fig. 3). The autoxidation mechanisms indicated by arrows  
292 in Figure 2b characterize systematic hydroperoxy chain terminations which do not change oxygen parity. HESI  
293 data showed an equivalent distribution of the two oxygen parities in molecular products (odd: 51%; even 49%)  
294 therefore confirming a lack of selectivity of the reaction mechanisms with respect to the parity of the radicals.



12



295

296 **Figure 3:** Autoxidation reaction mechanisms in combustion (left) and in the atmosphere (left and right). \* indicates  
 297 a change in number of oxygen atoms.

### 298 4.3 Combustion versus atmospheric oxidation

299 We have explored potential chemical pathways related to autoxidation in the previous section. For this purpose,  
 300 we have performed experiments under cool flame conditions (590 K). This autoxidation mechanism is also present  
 301 in atmospheric chemistry, but it is only recently that it has been found that this mechanism could be one of the  
 302 main formation pathways for SOA (Savee et al., 2015). Studies have described this mechanism in the case of  
 303 atmospheric chemistry with the identification of radicals and molecular species (Tomaz et al., 2021). However,  
 304 previous studies of the propagation of this reaction mechanism are mainly focused on the initial skeletons of the  
 305 10-carbon isomers, whereas the other carbon skeletons are also concerned by autoxidation. It is therefore useful to  
 306 evaluate the proportion of products of autoxidation among the total species formed.

307 We propose a new approach which consists in assessing a set of molecules mainly resulting from autoxidation  
 308 against different sets of experimental studies related to atmospheric chemistry. The objective is to compare the  
 309 similarity between these conditions on the basis of autoxidation by considering different experimental parameters  
 310 chosen for their diversity. For this purpose, we selected, a HESI ionization source, better adapted to the  
 311 electronegativity of the oxidized molecules, as well as to higher *m/z*. Moreover, we have already shown in this  
 312 paper that the HESI (+/-) ionization source is better suited for detecting autoxidation products (detection of 96%  
 313 of the total chemical formulae observed in autoxidation).

314 Among published atmospheric chemistry studies of terpenes oxidation, we have selected 15 studies, 4 for  $\alpha$ -pinene  
 315 and 11 for limonene. The data were acquired using different experimental procedures (methods of oxidation,  
 316 techniques of characterization). Table 4 summarizes all the experimental parameters related to the selected studies.

317



13

318 **Table 4.** Experimental settings of 15 oxidation studies of two terpenes under atmospheric conditions and cool  
 319 flames.

Reference	Oxidation mode	Sampling	Experimental setup	Concentrations of reactants	Ionization /source	Instrument	Chemical formulae
<b><math>\alpha</math>-Pinene</b>							
Y. Deng et al. (2021)	Dark ozonolysis seed particles OH scavenger	online	Teflon bag; 0.7m <sup>3</sup>	3.3±0.6 ncps ppbv <sup>-1</sup> $\alpha$ -Pinene	ESI	ToF-MS	351
Quéléver et al. (2019)	Ozonolysis	online	Teflon bag 5 m <sup>3</sup>	10 & 50 ppb $\alpha$ -Pinene	NO <sub>3</sub> <sup>-</sup> (CI)	CI-API-TOF	68
Meusinger et al. (2017)	Dark Ozonolysis OH scavenger no seed particles	offline	Teflon bag 4.5 m <sup>3</sup>	60 ppb $\alpha$ -Pinene	Proton transfer	PTR-MS-ToF	153
Krechmer et al. (2016)	Ozonolysis	offline	PAM Oxidation reactor	Field measurement	ESI (-) and NO <sub>3</sub> <sup>-</sup> (CI)	CI-IMS-ToF	43
This work	Cool-flame autoxidation	offline	jet-stirred reactor	1%, $\alpha$ -Pinene No ozone	APCI(3kV) HESI (3kV)	Orbitrap® Q-Exactive	820 (APCI) 975 (HESI)
<b>Limonene</b>							
Krechmer et al. (2016)	Ozonolysis	offline	PAM Oxidation reactor	not specified	ESI (-) and NO <sub>3</sub> <sup>-</sup> (CI)	CI-IMS-ToF	63
Tomaz et al. (2021)	Ozonolysis	online	flow tube reactor (18 L)	45-227 ppb limonene	NO <sub>3</sub> <sup>-</sup> (CI) - Neg	Orbitrap® Q-Exactive	282
Fang et al. (2017)	OH-initiated photooxidation dark ozonolysis	online	smog chamber	900–1500 ppb limonene	UV; 10 eV	Time-of-Flight (ToF)	17
Witkowski and Gierczak (2017)	Dark ozonolysis	offline	flow reactor	2 ppm, limonene	ESI, 4.5 kV	Triple quadrupole	12
(Jokinen et al., 2015a)	Ozonolysis	online	flow glass tube	1–10000 x10 <sup>9</sup> molec.cm <sup>-3</sup> , limonene	chemical ionization	Time-of-Flight (ToF)	11
Nørgaard et al. (2013)	Ozone (plasma)	online	direct on the support	850 ppb ozone 15-150 ppb limonene	plasma	Quadrupole time-of-flight (QToF)	29
Bateman et al. (2009)	Dark and UV radiations ozonolysis	offline	Teflon FEP reaction chamber	1 ppm ozone 1 ppm limonene	modified ESI (+/-)	LTQ-Orbitrap Hybrid Mass (ESI)	924
Walser et al. (2008)	Dark ozonolysis	offline	Teflon FEP reaction chamber	1-10 ppm ozone 10 ppm limonene	ESI (+/-); 4.5 kV	LTQ-Orbitrap Hybrid Mass (ESI)	465
Warscheid and Hoffmann (2001)	Ozonolysis	online	Smog chamber	300-500 ppb limonene	APCI; 3kV	Quadrupole ion trap mass	21
Hammes et al., (2019)	Dark ozonolysis	online	flow reactor	15, 40, 150 ppb limonene	<sup>210</sup> Po $\alpha$ -	HR-ToF-CIMS	20
Kundu et al. (2012)	Dark ozonolysis	offline	Teflon reaction chamber	250 ppb ozone 500 ppb limonene	ESI; 3.7 and 4 kV	LTQ FT Ultra, Thermo Sct (ESI)	1199
This work	Cool-flame autoxidation	offline	jet-stirred reactor	1%, limonene No ozone	APCI(3kV) HESI (3kV)	Orbitrap® Q-Exactive	1863(APCI) 2399(HESI)

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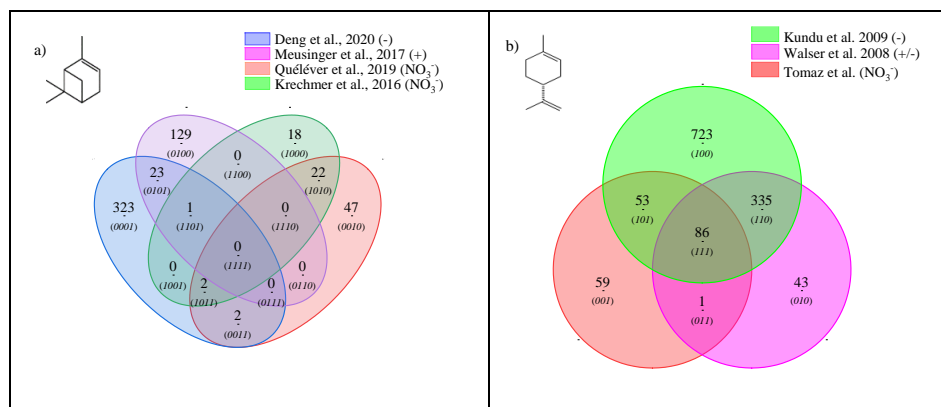
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321 The data are from the articles or files provided in the supporting information S2. In these studies, oxidation was  
322 performed only by ozonolysis with different experimental conditions that gather the main methods described in  
323 the literature: ozonolysis, dark ozonolysis, ozonolysis with OH scavenger, ozonolysis with or without seed  
324 particles. We considered that the methods of analysis by mass spectrometry did not modify the nature of the  
325 chemical species but only their relative importance, because of the type of ionization and the sensitivity of the  
326 instruments. The combination of data obtained using (+/-) HESI gives a rather complete picture of the autoxidation  
327 products.

328 First, we compared the data from ozonolysis studies of each terpene and identified similarities through the Venn  
329 diagram. For studies with two ionization sources, duplicate chemical formulae were removed. We selected the  
330 three most representative studies, by the number of the chemical formulae detected. Then, we compared the set of  
331 chemical formulae identified after ozonolysis to those produced in low-temperature combustion, the objective  
332 being (i) to highlight similarities in terms of products generated by the two oxidation modes and (ii) to identify  
333 data resulting from autoxidation.

334 For  $\alpha$ -pinene oxidation, the four studies identified 566 chemical formulae, all polarities combined. Only the study  
335 by (Meusinger et al., 2017) was performed in positive mode and none of the studies reported data obtained with two  
336 ionization modes (+/-). For limonene oxidation, the three studies identified 1862 chemical formulae. Only the  
337 studies by (Walser et al., 2008; Bateman et al., 2009) used (+) and (-) ionization modes. In the case of limonene,  
338 oxidation for which accretion is more important than for  $\alpha$ -pinene, and for which a greater number of chemical  
339 formulae were identified, the similarities is more important. These results are presented in Figure 4 where the  
340 ionization polarity used in each study is specified.

341



342 **Figure 4:** Venn diagrams for comparing the oxidation results from ozonolysis of (a)  $\alpha$ -pinene and (b) limonene  
343 (see conditions in Table 1). Each digit of the binary numbers in parentheses identifies the datasets being  
344 compared.

345 For  $\alpha$ -pinene, no global similarity is observed for the detected chemical formulae. Different hypotheses can be  
346 offered to explain this result. Among them, the number of chemical formulae identified per study remains limited  
347 (a few dozen to several hundred) and these small datasets are sometimes restricted to specific mass ranges (e.g.



15

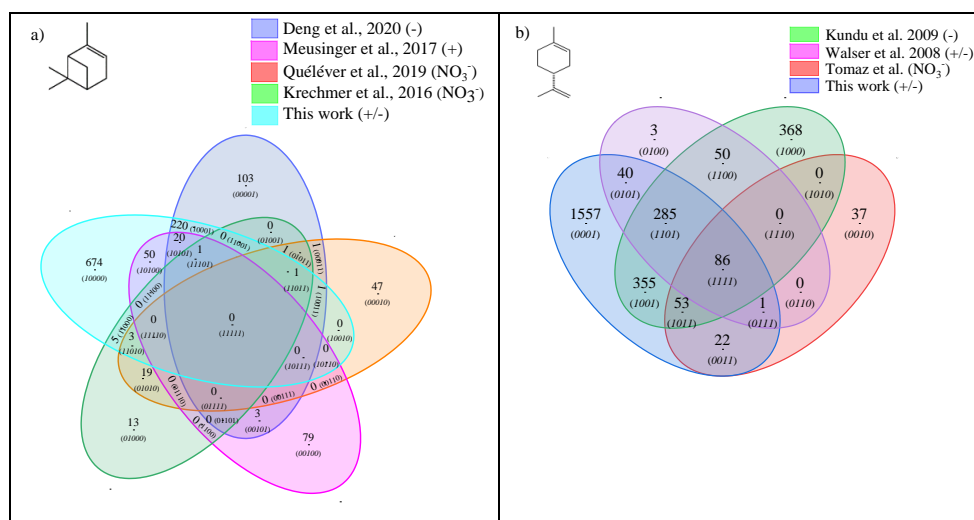
348 (Quéléver et al., 2019): C<sub>10</sub> to C<sub>20</sub>). In the case of studies carried out with an NO<sub>3</sub><sup>-</sup> source, sensitive to HOMS,  
349 produced preferentially by autoxidation, we note that nearly 50% of the chemical formulae (10/22) are linked by  
350 a simple difference of 2 oxygen atoms.

351 For limonene, 86 chemical formulae are common to the three studies considered here. In this dataset, nearly 43%  
352 of the chemical formulae present a relation similar to that of autoxidation (simple difference of two oxygen atoms)  
353 with less than 5% of fragments (Nb C<10). This result seems to indicate that autoxidation dominates.

354 One can then ask if reaction mechanisms common to atmospheric and combustion chemistry can generate, despite  
355 radically different experimental conditions, a set of common chemical formulae and if in this common dataset, a  
356 common link, characteristic of autoxidation, is observable?

357 To address that question, we compared all the previous results, for each of these terpenes to those obtained under  
358 the present combustion study. The comparisons were made using the HESI. One should remember that the  
359 oxidation conditions in a JSR were chosen in order to maximize low-temperature autoxidation. Again, we used  
360 Venn diagrams to analyze these datasets composed of 1590 chemical formulae in the case of  $\alpha$ -pinene and 2857  
361 chemical formulae in the case of limonene. The results of these analyses are presented in Figure 5.

362 It turned out that 301 chemical formulae were identified for  $\alpha$ -pinene and 735 chemical formulae for limonene to  
363 be common to oxidation by ozonolysis and combustion. This represents 31% of the chemical formulae for the  
364 ozonolysis of  $\alpha$ -pinene and 31% for those of limonene ozonolysis. For  $\alpha$ -pinene, the similarities compared to  
365 combustion are specific to each study: (Deng et al., 2021) 69% (Meusinger et al., 2017) 46% (Quéléver et al.,  
366 2019) 7% (Krechmer et al., 2016) 23%. Chemical formulae common to all studies were not identified. This lack of  
367 similarity may be due to a partial characterization of the chemical formulae, a weaker oxidation of  $\alpha$ -pinene with  
368 an ionization mode less favorable to low molecular weights.



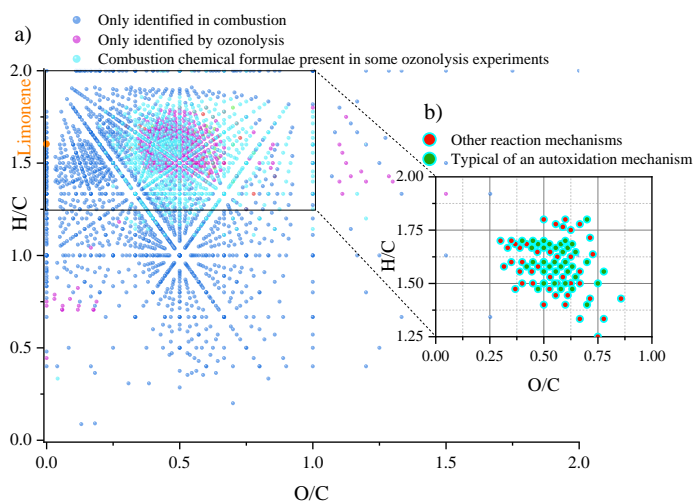
369 **Figure 5:** Venn diagrams comparing the oxidation results from ozonolysis and combustion of (a)  $\alpha$ -pinene and  
370 (b) limonene (see conditions in Table 1).





16

371 For limonene, the similarities with combustion are more important and less spread out. They represent for the  
372 different studies: (Kundu et al., 2012) 65% (Walser et al., 2008) 88% (Tomaz et al., 2021) 81%. Moreover, there  
373 is a common dataset of 86 chemical formulae which can derive from autoxidation mechanisms. It is necessary to  
374 specify again that different reaction mechanisms can cause the observed similarities. However, the preponderance  
375 of autoxidation in so-called cold flame combustion is obvious, and in atmospheric chemistry, this reaction  
376 mechanism remains competitive or dominates (Crouse et al., 2013; Jokinen et al., 2014b). If we search for an  
377 autoxidation link between these 86 chemical formulae, we observe that 43% of these chemical formulae meet this  
378 condition: difference of two oxygen atoms, at constant number of carbon and hydrogen atoms. More precisely,  
379 these molecules are centered in a van Krevelen diagram on the ratios  $O/C=0.6$  and  $H/C=1.6$ , in the range  $0.25 <$   
380  $O/C < 0.8$  and  $1.25 < H/C < 1.85$ . All oxidized molecules associated with this dataset are presented in Figure 6.  
381 The dispersion of the chemical formulae, far from being random, remains consistent with an autoxidation  
382 mechanism where the number of carbon atoms is constant.



383

384 **Figure 6:** Van Krevelen diagram showing specific and common chemical formulae detected after to oxidation of  
385 limonene by ozonolysis and combustion.

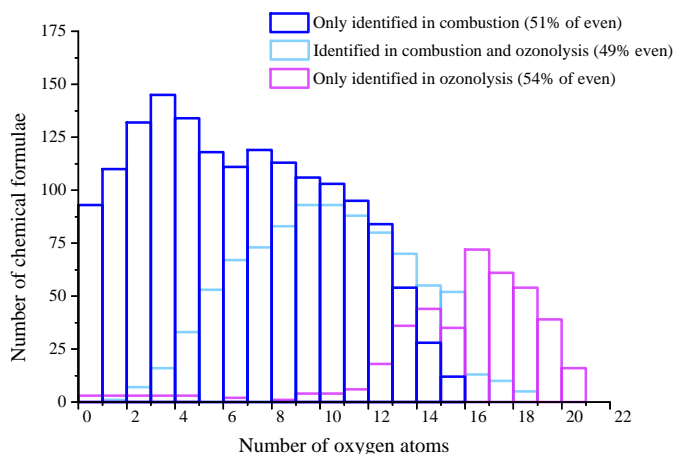
386 A 3-D representation of all limonene oxidation data is given in Fig. S1 (Supplement) where DBE is used as third  
387 dimension. From that figure, one can note that products with higher DBE are preferably formed under JSR  
388 conditions, i.e. at elevated temperature. The corresponding chemical formulae could correspond to carbonyls and  
389 / or cyclic ethers ( $^{\bullet}QOOH \rightarrow$  carbonyl + alkene + OH and / or cyclic ether + OH).

390



17

391 Specificities and similarities of these two oxidation modes were further investigated by plotting the distribution of  
392 the number of oxygen atoms in detected chemical formulae (Fig. 7). Indeed, the distribution of the number of  
393 oxygen atoms allows, in addition to the Van Krevelen diagram, to provide some additional details on these two  
394 modes of oxidation. It is in ozonolysis that we observe the chemical formulae having the largest number of oxygen  
395 atoms. There, oxidation proceeds over a long reaction time where the phenomenon of aging appears by promoting  
396 accretion or oligomerization. One should keep in mind that a short residence time (2 s) was used in JSR  
397 experiments. A short residence time should limit accretion which is favored under simulated atmospheric oxidation  
398 experiments performed over long reaction times. In combustion, the number of oxygen atoms remains limited to  
399 18, with a lower number of detected chemical formulae compared to the case of ozonolysis. However, it is in  
400 combustion that we observe the highest O/C ratios, indicating the formation of the most oxidized products. This  
401 difference, however, does not affect the similarities between the chemical formulae detected in the two modes of  
402 oxidation. Finally, the analysis of the parities in oxygen atoms, very similar to the three datasets, confirms that the  
403 reaction mechanisms presented in Figure 3 do not allow a simple link to be established between the parity of  
404 radicals and that of molecular products.



405  
406 **Figure 7:** Oxygen number distribution for all the molecules identified for the oxidation of limonene: only in  
407 combustion, only in ozonolysis and common to both processes. For each of these distributions, the parity in  
408 oxygen number is specified

## 409 5 Conclusion

410 We have analyzed and compared, thanks to different mathematical and visualization tools, the oxidation of  $\alpha$ -  
411 pinene and limonene under simulated tropospheric and low-temperature oxidation conditions. We have restricted  
412 the field of this study to organic compounds ( $C_nH_yO_z$ ) in order to study specifically autoxidation. This work is in  
413 the continuity of recently published studies which established the importance of autoxidation under tropospheric  
414 oxidation and low-temperature combustion conditions. Faced with the analytical limits of the chemical speciation  
415 of thousands of molecules, and in order to complete the work carried out on the reaction mechanisms of the first  
416 steps of oxidation, we have developed a global approach based on the study of families of chemical compounds  
417 present in these large sets (van Krevelen diagram, oxygen number distribution, oxidation state of carbon -OSc,



18

418 chemical relationship between molecules). We selected existing databases on ozonolysis with a purposive diversity  
419 of experimental conditions and compared these data to those obtained in low-temperature combustion conditions  
420 where autoxidation is important (cool flame combustion at 590 K). We showed that a significant portion of the  
421 chemical formulae were common to both atmospheric and combustion products. Surprisingly, the numerous  
422 oxidation mechanisms and the isomerization of chemical species proceeding under these two conditions did not  
423 lead to diverging data, but, on the contrary, to similarities. More than 35% of the chemical formulae detected in  
424 combustion chemistry experiments using a JSR have been detected in the studies carried out under atmospheric  
425 conditions. Finally, we have outlined the existence of a substantial common dataset of autoxidation products. This  
426 result tends to show that autoxidation is indeed inducing similarity between atmospheric and combustion products.

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431

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