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Zahraa Dbouk, Nesrine Belhadj, Maxence Lailliau, Roland Benoit, Philippe Dagaut. On the autoxidation of terpenes: Detection of oxygenated and aromatic products. *Fuel*, 2024, 358 (Part B), pp.130306. 10.1016/j.fuel.2023.130306 . hal-04296922

HAL Id: hal-04296922

<https://hal.science/hal-04296922v1>

Submitted on 21 Nov 2023

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On the autoxidation of terpenes: detection of oxygenated and aromatic products.

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Keywords: terpene, limonene, α -pinene, oxidation, cool flame, jet-stirred reactor, Orbitrap

Highlights:

- Stable products of oxidation measured by FTIR
- Ketohydroperoxides were detected by Orbitrap
- Highly oxidized products were detected by Orbitrap
- Highly unsaturated products were detected by Orbitrap
- Products of Korcek and Waddington mechanisms detected

Abstract

Limonene-O₂-N₂ and α -pinene-O₂-N₂ mixtures were oxidized in a jet-stirred reactor at atmospheric pressure, in the cool flame regime, and fuel-lean conditions. Samples of the reacting mixtures were analyzed by on-line Fourier transform infrared (FTIR) and collected, dissolved in acetonitrile for analysis by flow injection or chromatographic separation by ultra-high performance liquid chromatography and Orbitrap mass spectrometry. OH/OD exchange using D₂O and reaction with 2,4-dinitrophenylhydrazine were carried out for probing the existence of hydroxyl or hydroperoxyl, and carbonyl functions in the products, respectively. A large number of oxidation products, including highly oxygenated organic products with more than ten oxygen atoms, were observed. Unexpectedly, aromatic and polyunsaturated products with a contribution of 8-10% were detected for both terpenes over the range of temperatures studied. Van Krevelen plots, computed oxidation state of carbon, aromaticity index, and aromaticity equivalent index in products were used to rationalize the results.

1. Introduction

The terpenes are naturally released by vegetation. They constitute a large fraction of volatile organic chemicals detected in the troposphere [1]. Besides, because of their high-energy-density, they could be used as biojet fuels [2, 3]. With their high octane numbers (e.g., 88-89 for limonene [4, 5] and 84 for α -pinene [5]), one could also use them as drop-in fuels to reduce the carbon footprint in transportation.

35 However, the use of terpenes as biofuel or drop-in fuel would certainly contribute to increasing their
36 concentration in the troposphere through unburnt fuel emissions and evaporation during transport and
37 refueling. While the terpenes kinetics of oxidation under atmosphere-relevant conditions has been the
38 topic of many works, a good understanding of the multiple oxidation routes has not been attained yet
39 [6]. The chemical kinetics of combustion of such chemicals have not received much attention to date.
40 Indeed, only burning velocity in air, impact on ignition, and flame structures have been reported [7-9].
41 This is not enough to characterize terpenes oxidation chemistry which involves many reaction pathways,
42 particularly under cool flame conditions. In hydrocarbons (RH) cool flames, we consider the production
43 of oxygenates such as ketohydroperoxides (KHPs) which lead to chain branching via decomposition
44 [10]: $\text{RH} + \cdot\text{OH} \rightarrow \text{R}\cdot + \text{H}_2\text{O}$ (1), $\text{R}\cdot + \text{O}_2 \rightleftharpoons \text{RO}_2\cdot$ (2), $\text{RO}_2\cdot + \text{HO}_2\cdot \rightleftharpoons \text{RO}_2\text{H} + \text{O}_2$ (3), $\text{RO}_2\cdot + \text{RH} \rightleftharpoons$
45 $\text{RO}_2\text{H} + \text{R}\cdot$ (4), $\text{RO}_2\cdot \rightleftharpoons \cdot\text{QO}_2\text{H}$ (5), $\text{RO}_2\cdot \rightleftharpoons \text{Q}$ (unsaturated product) + $\text{HO}_2\cdot$ (6), $\cdot\text{QO}_2\text{H} \rightleftharpoons \cdot\text{OH} + \text{QO}$
46 (cyclic ether) (7), $\cdot\text{QO}_2\text{H} + \text{O}_2 \rightleftharpoons \cdot\text{OOQO}_2\text{H}$ (8), $\cdot\text{O}_2\text{QO}_2\text{H} \rightleftharpoons \text{HO}_2\cdot\text{PO}_2\text{H}$ (9), $\text{HO}_2\cdot\text{PO}_2\text{H} \rightleftharpoons \cdot\text{OH} +$
47 $\text{HO}_2\text{P}=\text{O}$ (KHPs) (10), $\text{HO}_2\text{P}=\text{O} \rightleftharpoons \cdot\text{OH} + \text{OP}\cdot\text{O}$ (11). But, products of cool flame oxidation must be
48 better characterized. Indeed, recent studies [11, 12] have demonstrated the formation of more
49 oxygenated products in cool flames of a large set of fuels including *n*- and *iso*-alkanes, cycloalkanes,
50 alcohols, aldehydes, esters, and ethers. There, alternative oxidation pathways proceed via an internal H-
51 atom transfer in the $\cdot\text{O}_2\text{QO}_2\text{H}$ intermediate, involving a H-C group other than the H-COOH group which
52 is responsible for KHPs formation (Reactions 9 and 10). It opens new oxidation paths such as a third O_2
53 addition to $\text{HO}_2\cdot\text{PO}_2\text{H}$ yielding $\cdot\text{O}_2\text{P}(\text{O}_2\text{H})_2$. Such sequence of H-transfer and O_2 addition can repeat
54 several times, yielding highly oxidized products. Besides, $\cdot\text{QO}_2\text{H}$ decomposition yields stable products
55 and radicals via Reaction (7), $\cdot\text{QO}_2\text{H} \rightarrow \text{olefin} + \text{carbonyl} + \cdot\text{OH}$ (12), and $\cdot\text{QO}_2\text{H} \rightarrow \text{HO}_2\cdot + \text{olefin}$ (13).
56 In the case of unsaturated reactants, such as terpenes, in addition to these reaction pathways, the
57 Waddington mechanism [13] can proceed. It starts via an $\cdot\text{OH}$ addition on a C=C double bond and
58 continues with an O_2 addition and H-atom internal transfer from the hydroxyl group formed in Reaction
59 (14), to the peroxy group via Reaction (16), followed by decomposition (Reaction 17): $\text{R}^1-\text{C}=\text{C}-\text{R}^2 +$
60 $\cdot\text{OH} \rightleftharpoons \text{R}^1-\cdot\text{C}-\text{C}(\text{R}^2)-\text{OH}$ (14), $\cdot\text{C}(\text{R}^1)-\text{C}(\text{R}^2)-\text{OH} + \text{O}_2 \rightleftharpoons \cdot\text{OO}-\text{C}(\text{R}^1)-\text{C}(\text{R}^2)-\text{OH}$ (15), $\cdot\text{OO}-\text{C}(\text{R}^1)-$
61 $\text{C}(\text{R}^2)-\text{OH} \rightleftharpoons \text{HOO}-\text{C}(\text{R}^1)-\text{C}(\text{R}^2)-\text{O}\cdot$ (16), $\text{HOO}-\text{C}(\text{R}^1)-\text{C}(\text{R}^2)-\text{O}\cdot \rightarrow \text{R}^1-\text{C}=\text{O} + \text{R}^2-\text{C}=\text{O} +$
62 $\cdot\text{OH}$ (17). Via this sequence of reactions, the hydroxyl radical initially consumed in Reaction (14) is
63 finally regenerated in Reaction (17).

64 The Korcek mechanism [13] can also occur. This reaction pathway transforms γ -ketohydroperoxides
65 into a carbonyl product and a carboxylic acid. The Korcek mechanism has been considered in recent
66 combustion modeling [14-16]. Besides, the potential formation of highly unsaturated or aromatic
67 products from the oxidation of monoterpenes has not received attention, but needs to be investigated.

68 In this work, our goal is to provide a better characterization of the products of autoxidation of two
69 terpenes, namely limonene and α -pinene, under cool-flame conditions, and to investigate the formation

70 of highly unsaturated or aromatic products there. To this end, we carried out oxidation experiments in a
71 jet-stirred reactor at 1 bar, and oxidation products were characterized using high-resolution mass
72 spectrometry (Orbitrap HRMS). The complexity and size of datasets generated by HRMS require the
73 use of visualization tools to interpret the data. Here, Van Krevelen plots [17], oxidation state of carbon
74 [18], aromaticity index [19], and aromaticity equivalent index [20] were used.

75

76 **2. Experiment**

77

78 *2.1 Oxidation experiments*

79

80 Experiments were conducted in a 42 mL fused silica jet-stirred-reactor (JSR) introduced earlier [21,
81 22]. As previously [23, 24] for the injection of the fuels (98 % pure), we utilized a HPLC pump with an
82 online degasser. The fuels were sent to an in-house atomizer-vaporizer assembly fed with a nitrogen
83 flow. Fuel-N₂ (99.95 % pure) and N₂-O₂ (99.995 % pure) were carried separately to the reactor to avoid
84 premature oxidation before reaching the JSR entrance. Mass flow meters were used to deliver the
85 nitrogen and oxygen flows. A fused silica protected thermocouple (0.1 mm Pt-Pt/Rh-10% wires) was
86 moved along the vertical axis of the JSR to check thermal homogeneity. Typical gradients of < 1 K/cm
87 were measured. To study the oxidation of the fuels in the cool-flame regime (520-680 K), we used 1%
88 of fuel and operated at 1 bar, in fuel-lean conditions ($\phi = 0.5$), and at 1.5 s mean residence time.

89

90 *2.2 Chemical analyses*

91

92 Low-temperature oxidation products were dissolved into 20 mL of ≥ 99.9 pure acetonitrile,
93 maintained at 273 K, through 60 min bubbling. They were stored in a freezer at 258 K for the next
94 chemical analyses. Flow injection analyses/heated electrospray ionization (FIA/HESI) were done. The
95 samples were analyzed by Orbitrap Q-Exactive. Several m/z ranges were used for data acquisition in
96 order to improve C-trap transmission sensitivity [25]: 50-750, 150-750, and 300-750. Only signal ≥ 5000
97 counts were considered here. We performed mass calibrations in positive and negative ionization modes
98 using +/- HESI calibration mixtures. Reverse-phase ultra-high-performance liquid chromatography
99 (RP-UHPLC) analyses were performed using a C18 chromatographic column (1.6 μ m, 100 Å, 100x2.1
100 mm, Phenomenex Luna). 3 μ L of samples were eluted by a water-acetonitrile (ACN) mix at a flow rate
101 of 250 μ L/min (gradient 5% to 90% ACN, during 33 min). Also, atmospheric pressure chemical
102 ionization (APCI) was operated in positive and negative modes. Presently, with the techniques used in
103 this work, no quantification could be made whereas, recent work addressed this issue using other
104 experimental methods [26].

105 For determining the chemical structure of oxidation products after RP-UHPLC separation, MS/MS
106 analyses were performed using the lowest collision cell energy (10 eV). As in preceding works [23, 24],
107 2,4-dinitrophenylhydrazine (2,4-DNPH) addition to samples was also used to assess the presence of
108 carbonyl compounds. As before [11, 23, 24, 27], to evaluate the existence of hydroxyl (-OH) or
109 hydroperoxyl (-OOH) groups in oxidation products, we performed H/D exchange by adding D₂O to the
110 samples. We analyzed these solutions using FIA-HESI-HRMS and RP-UHPLC-APCI-HRMS. For
111 HRMS data, an uncertainty of $\leq 40\%$ was estimated [23]. Besides, we performed online Fourier
112 Transform Infrared spectroscopy (FTIR) analyses according to a procedure described in previous reports
113 [16, 28]. FTIR measurements were made in the T-range 520-800 K and HRMS measurements in the T-
114 range 540-680 K. Because gas samples have a complex composition, the infrared measurements of
115 carbon dioxide mole fractions present uncertainties larger than usual. The validity of the measurement
116 was checked carefully using the OMNIC and QuantPad softwares (ThermoScientific) and only reliable
117 data are reported. Table S1 presents a summary of the analytical methods.

118

119 **3. Results and discussion**

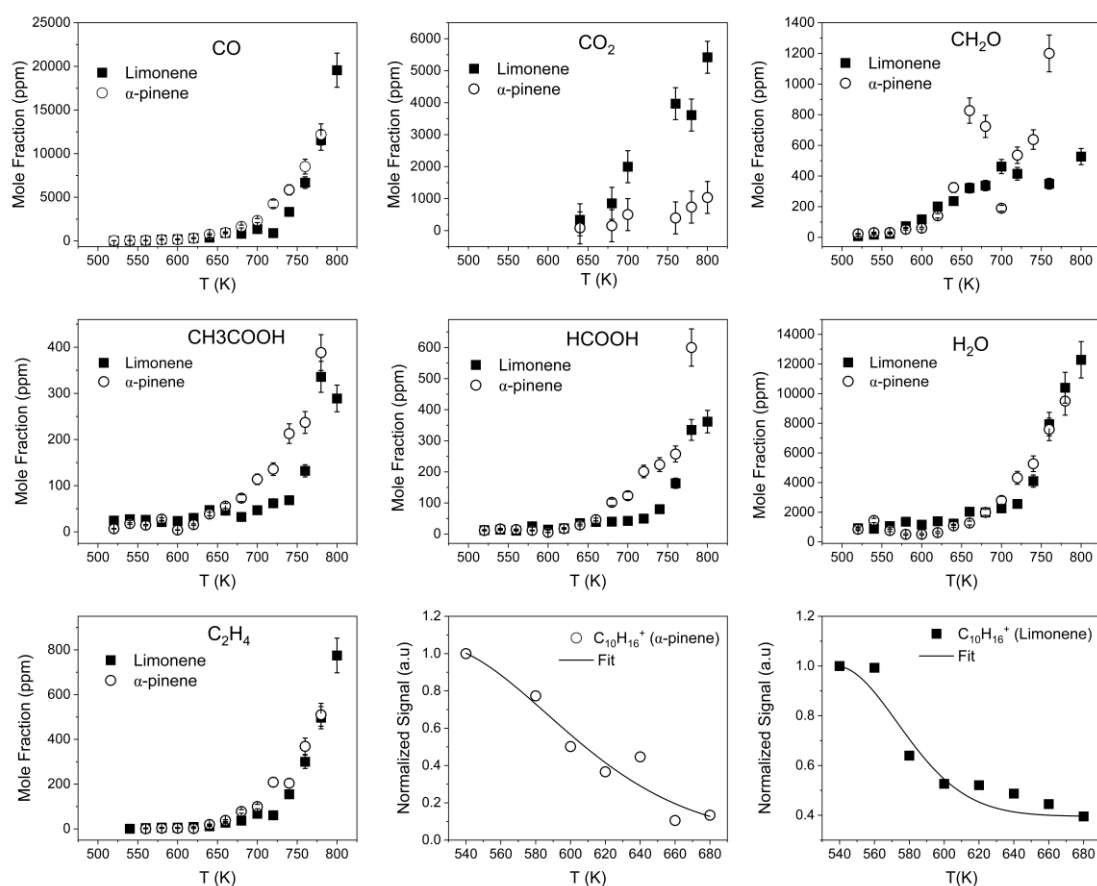
120

121 *3.1 Simple oxidation products and oxygenates*

122

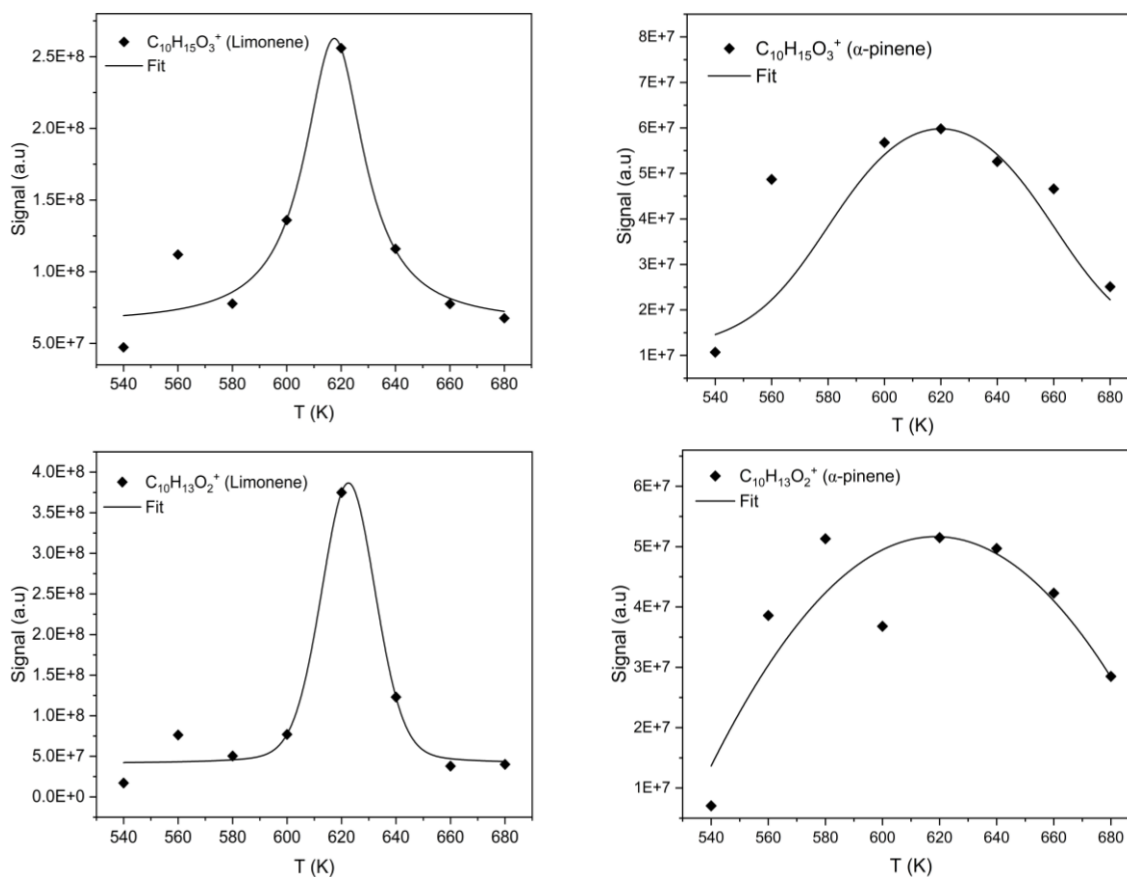
123 Many oxidation products were detected during the oxidation of the two terpenes. Among them,
124 simple products (not directly detectable by Orbitrap if they have a molecular weight <50) were measured
125 by FTIR (Fig. 1). As can be seen from that figure, products mole fractions are similar for the two fuels.
126 Formic acid was detected in FTIR analyses at small concentrations below 580 K for both fuels. We
127 measured a maximum of 16 ± 10 ppm and 14 ± 10 ppm for α -pinene and limonene, respectively.

128



129
 130 **Fig. 1.** Products measured during the oxidation of 1 % limonene and 1 % α -pinene in a JSR at 1 bar,
 131 equivalence ratio of 0.5 and residence time of 1.5 s, by FTIR and FIA-HESI(+)-HRMS (fuels).

132
 133 A large set of chemical formulas was observed via HRMS analyses. The exact structures of chemical
 134 formulas cannot be determined precisely because of limitations in chromatographic separation of the
 135 very large set of chemicals. However, several tools (oxidation state of carbon, aromaticity index, and
 136 aromaticity equivalent index in products) were used to show the presence of several chemical classes in
 137 the products, as presented in the next paragraphs. Oxidation products containing O-atoms were detected
 138 in limonene oxidation products: $C_7H_{10}O_4$ and 5, $C_8H_{12}O_2$ and 4, $C_8H_{14}O_2$ and 4, $C_9H_{12}O$, $C_9H_{14}O_1$ and 3 to 5,
 139 $C_{10}H_{12}O_2$, $C_{10}H_{14}O_1$ to 9, $C_{10}H_{16}O_2$ to 5, and $C_{10}H_{18}O_6$. For α -pinene oxidized under the same conditions,
 140 one could detect the following oxygenates: $C_7H_{10}O_4$ and 5, $C_{10}H_{12}O_2$ and 4, $C_{10}H_{14}O_3$ and 5, $C_{10}H_{12}O_2$,
 141 $C_{10}H_{14}O_1$ to 9, and $C_{10}H_{16}O_2$ to 6. Figure 2 shows results obtained for KHPs and isomers and for diketones
 142 which result from KHPs decomposition. H/D exchange using D_2O and reaction with 2,4-
 143 dinitrophenylhydrazine were performed to confirm the presence of hydroperoxyl, and carbonyl groups
 144 in the products, respectively. As can be seen from Figure 2, both products peak in the same range of
 145 temperature.



147

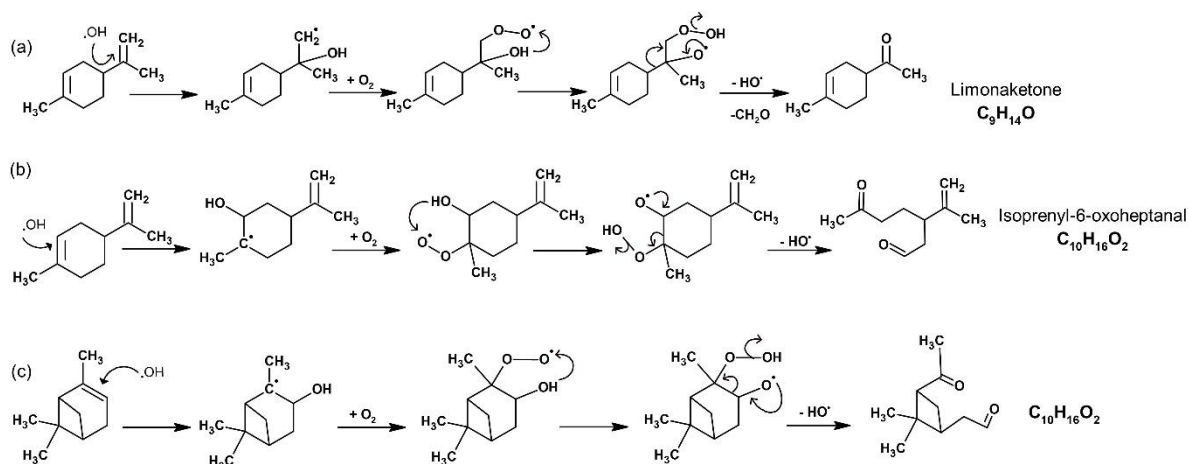
148 **Fig. 2.** Products of oxidation of limonene (left) and α -pinene (right) obtained by HRMS (symbols). The
 149 data for KHPs and isomers (top, $C_{10}H_{14}O_3$) and diketones and isomers (bottom, $C_{10}H_{12}O_2$) were obtained
 150 by FIA and HESI (+), i.e., $C_{10}H_{15}O_3^+$ m/z 183.1015 and $C_{10}H_{13}O_2^+$ m/z 165.0910, respectively. Errors
 151 estimated to be $\pm 40\%$.

152

153 Carbonyl oxidation products formed through the Waddington mechanism on *exo*- and *endo*-double
 154 bonds ($C=C$) of limonene were observed ($C_9H_{14}O$, $C_{10}H_{16}O_2$) as well as products of their oxidation. In
 155 our previous study on the analysis of limonene oxidation products at atmospheric pressure [28],
 156 isoprenyl-6-oxoheptanal ($C_{10}H_{16}O_2$) was identified through the injection of a standard. While the
 157 characterization of limonaketone ($C_9H_{14}O$), produced via route (a) in Scheme 1, was based on the
 158 fragmentation spectrum in addition to the 2,4-DNPH derivatization. The RP-UHPLC-HRMS enabled
 159 the detection of several $C_9H_{14}O$ isomers ($C_9H_{15}O^+$, m/z 139.1117), as seen in Fig. S1. Almost all of these
 160 isomers react with 2,4-DNPH. A fragmentation mechanism was proposed for the limonaketone and is
 161 presented in Fig. S2. The resulting fragments were found in the MS/MS spectrum of the isomer eluted
 162 at a retention time of 15.83 min (Fig. S2). Consequently, we considered that limonaketone was eluted at
 163 this time.

164 Products of oxidation via the Waddington mechanism (Scheme 1, route c) were also detected for α -
165 pinene ($C_{10}H_{16}O_2$).

166



167

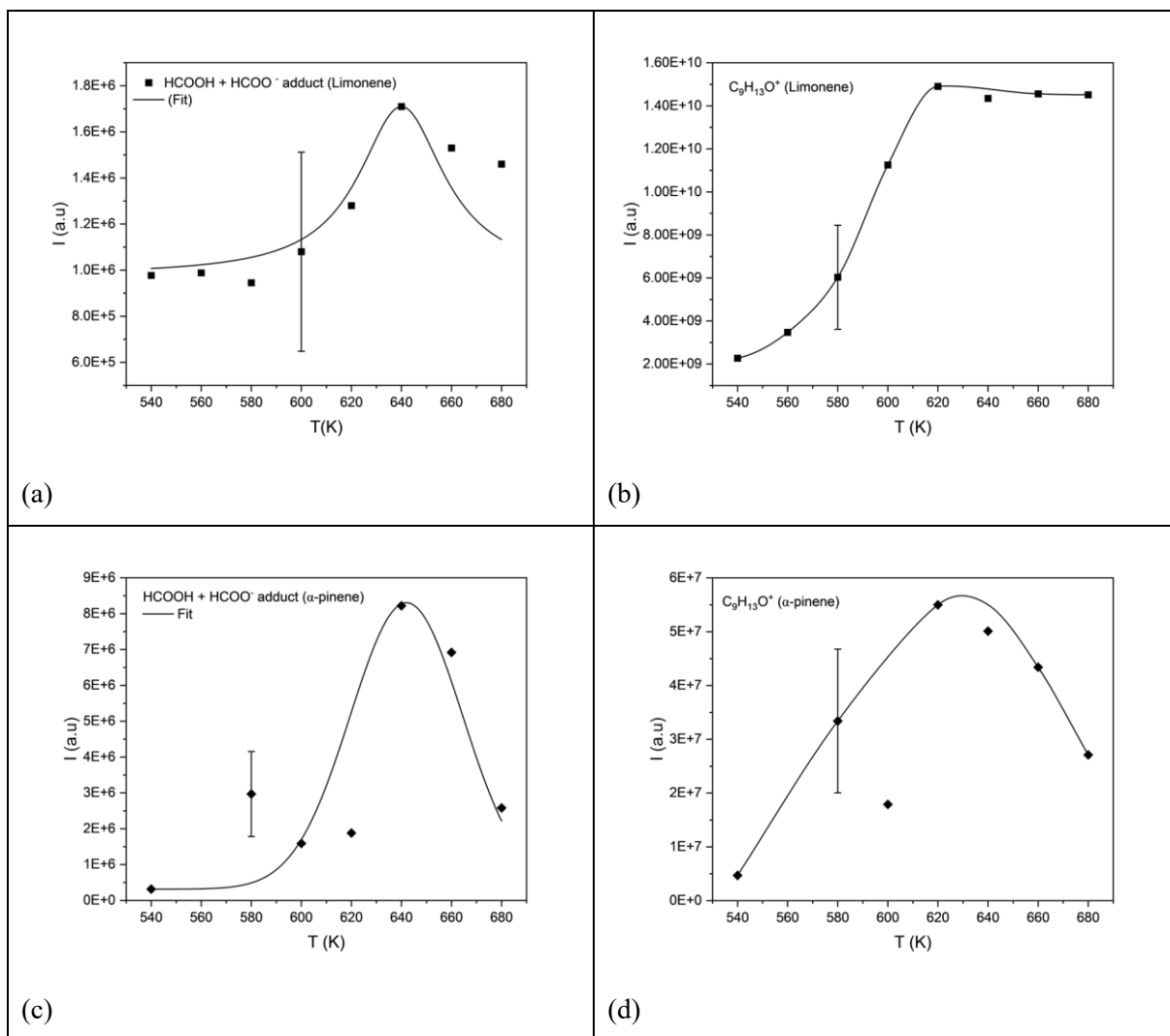
168

169 **Scheme 1.** Mechanism of oxidation of limonene (a) *exo*- and (b) *endo*-cyclic double bonds, and (c) α -
170 pinene through the Waddington mechanism.

171

172 Earlier, it was reported [29] a higher reactivity of the *endo* double bond vs. the *exo* double bond.
173 Estimated C-H bond dissociation energies, using a NREL software [30, 31], revealed a difference of 1.9
174 kcal/mol (the lower value found for the C-H in the *endo* double bond). Then, if H-atom abstraction on
175 these C-H groups is of importance, that could partially explain the difference in reactivity of the two C-
176 H groups. In line with the results presented earlier [29], higher ion signal was recorded for isoprenyl-6-
177 oxoheptanal ($C_{10}H_{17}O_2^+$) than for limonaketone ($C_9H_{15}O^+$), which result from oxidation of *endo* and *exo*
178 double bonds, respectively.

179 Oxidation products (carboxylic acids and carbonyls) formed via the Korcek mechanism were also
180 detected (Fig. 3). For the two terpenes, the signal obtained for both formic acid and $C_9H_{12}O$ reach a
181 maximum ~ 20 K higher than their parent ketohydroperoxides (see Fig. 2) which seems consistent with
182 a formation of formic acid and $C_9H_{12}O$ via the Korcek mechanism.



183 **Fig. 3.** Products of the Korcek mechanism during the oxidation of limonene and α -pinene. (a) and (b):
 184 data obtained by UHPLC-APCI(-) and UHPLC-APCI(+), respectively. (c) and (d): data obtained by
 185 FIA-HESI (-) and FIA-HESI(+), respectively. Errors estimated to be $\pm 40\%$.

186 Among the 18 KHPs derived from limonene oxidation, four isomers could decompose via the Korcek
 187 mechanism. But, only one isomer can possibly yield a cyclic intermediate peroxide linking the carbonyl
 188 and OOH groups, which yields a carbonyl compound, C₉H₁₂O, and formic acid, CH₂O₂, by
 189 decomposition (Scheme 2). Both products were detected by UHPLC-HRMS in this study (Fig. 3). The
 190 three other KHPs isomers generated C₁₀H₁₄O₃ isomers.

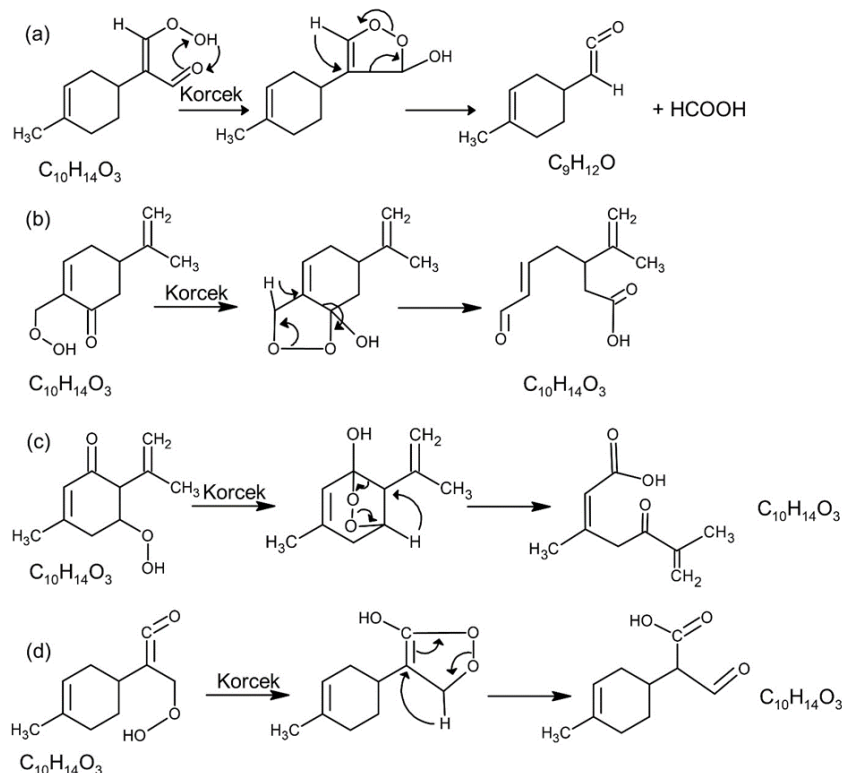
191 As can be seen from Fig. S3 in the supplementary information, RP-UHPLC-HRMS enabled us to
 192 identify several C₁₀H₁₄O₃ isomers (C₁₀H₁₅O₃⁺, m/z 183.1015).

193 After adding D₂O to our sample, an intense H/D exchange (C₁₀H₁₄D₁O₃⁺, m/z 184.1068, $I = 1.25E+8$)
 194 was detected indicating the presence of hydroperoxyl (OOH) or hydroxyl (OH) groups. At the same
 195 time, a signal corresponding to a second H/D exchange was detected (C₁₀H₁₃D₂O₃⁺, m/z 185.1139, $I =$

196 5.22E+7) suggesting the presence of hydroxy-hydroperoxide isomers. Furthermore, confirmation of the
 197 presence of the C=O functional group was obtained through 2,4-DNPH derivatization. It should be noted
 198 that all C₁₀H₁₅O₃⁺ isomers reacted with 2,4-DNPH, except that eluted at approximately 8.55 minutes, as
 199 shown in Fig. S4. This last product could be a hydroxy-hydroperoxide isomer.

200 In order to assess the presence of the products of the Korcek mechanism, the positive and negative
 201 modes of ionization / fragmentation spectra (MS/MS) of those isomers were used. It was confirmed that
 202 the specie produced by the decomposition of the KHPs isomer via route (b) in Scheme 2 was present in
 203 our sample.

204 One should note that in the fragmentation cell, the loss of CO₂ in negative mode from the parent ion
 205 [M-H]⁻, as well as the loss of CO from the same ion, confirm the presence of an acidic function and an
 206 aldehyde group in the molecule, respectively [32, 33]. At a retention time of 6.9 min (Fig. S3), in addition
 207 to the fragments observed in positive mode and shown in Fig. S5, perfectly matching the structure of
 208 the suggested isomer, fragments corresponding to [M-H-CO₂]⁻ (C₉H₁₃O⁻, *m/z* 137.0961) and [M-H-CO]⁻
 209 (C₉H₁₃O₂⁻, *m/z* 153.0909) were also detected in negative ionization mode (Fig. S6). These observations
 210 show that the isomer eluted at a retention time of 6.9 min contains acidic and aldehyde functions. The
 211 other products from the Korcek mechanism couldn't be identified.

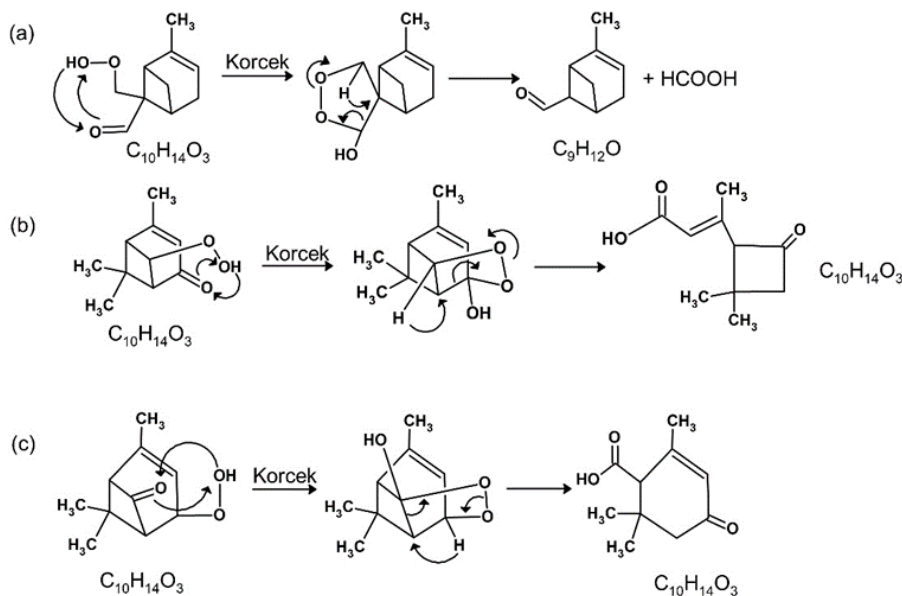


212

213 **Scheme 2.** Korcek mechanism during limonene oxidation.

214 For α -pinene, among the 22 KHPs derived from its oxidation, three isomers could decompose via the
 215 Korcek mechanism. Several products can be produced from these three γ -KHPs (Scheme 3). We tested

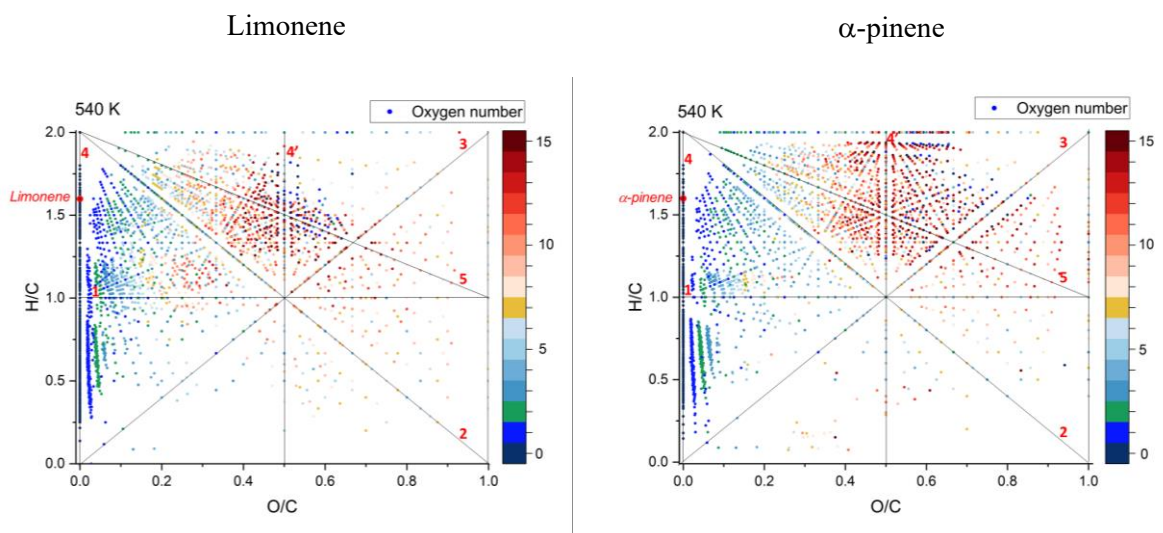
216 their presence in the products via FIA-HRMS. The products $C_9H_{12}O$ and $C_{10}H_{14}O_3$ (see Scheme 3) were
 217 detected by FIA-HRMS and UHPLC-HRMS. Unfortunately, MS/MS spectra did not allow us to identify
 218 the structure of the various oxidation products.

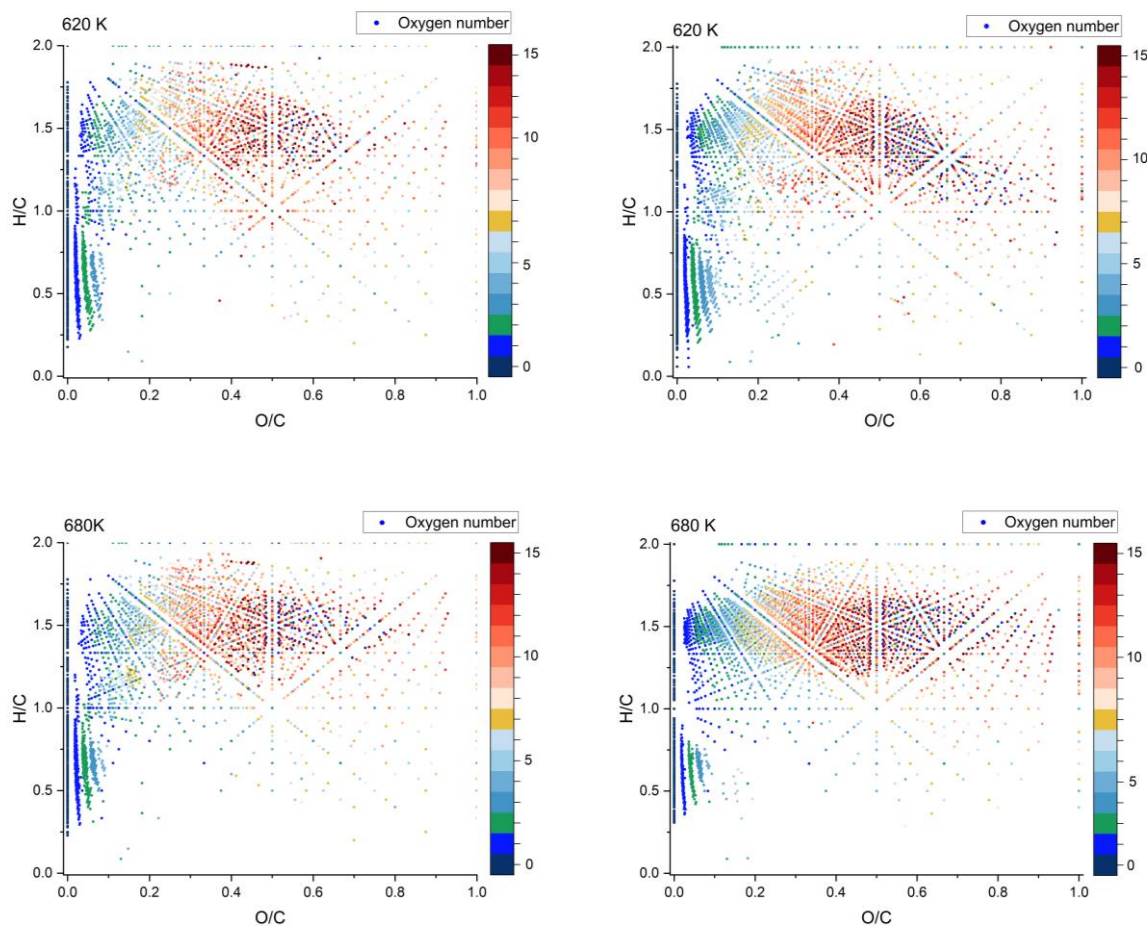


219

220 **Scheme 3.** Korcek mechanism during α -pinene oxidation.

221 Van Krevelen (VK) plots served to characterize the diversity of products of oxidation of limonene
 222 and α -pinene (Figs 4 and 5). As can be seen from these figures, similar products distribution was
 223 observed, although some differences could be noticed, as presented in the next Section. Also, one can
 224 see from these figures that many highly oxygenated species were formed, whereas products with no or
 225 little oxygen content were also detected ($O/C = 0-0.1$); see Section 3.2.

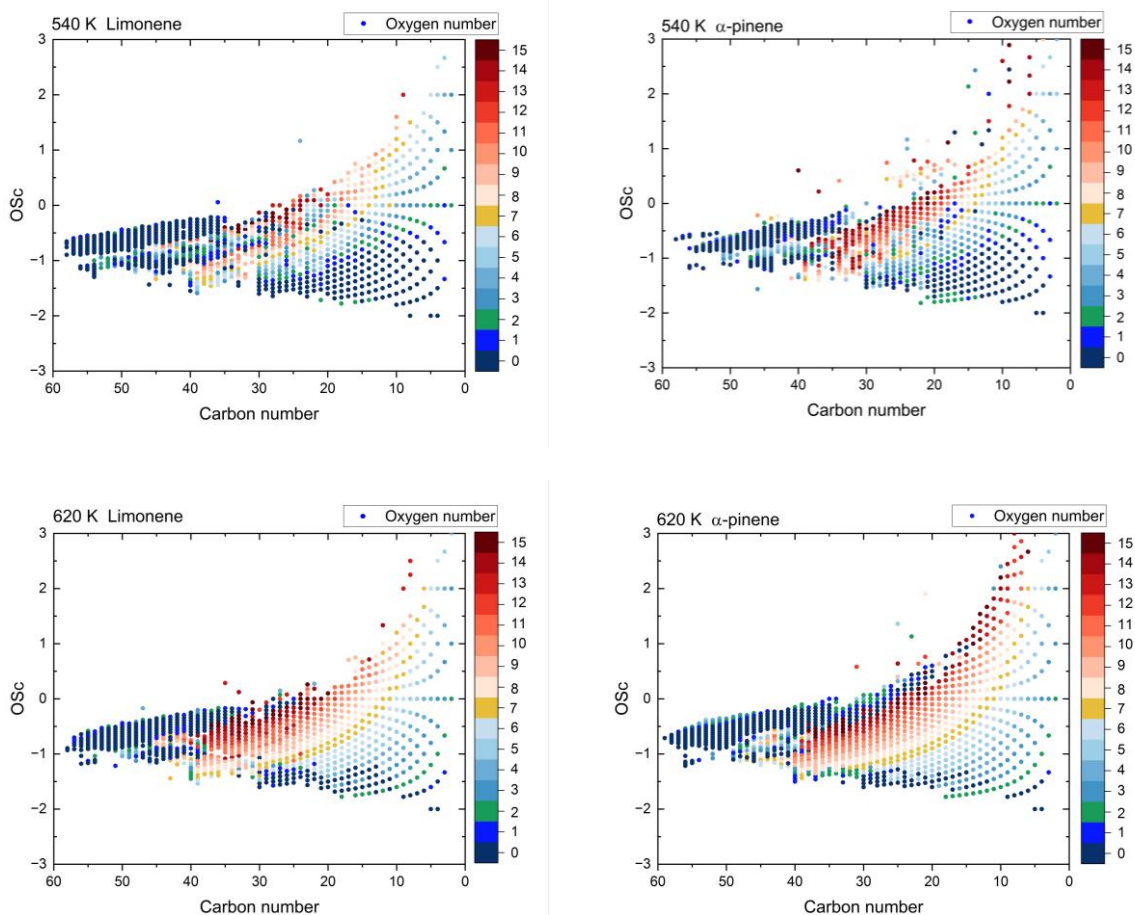


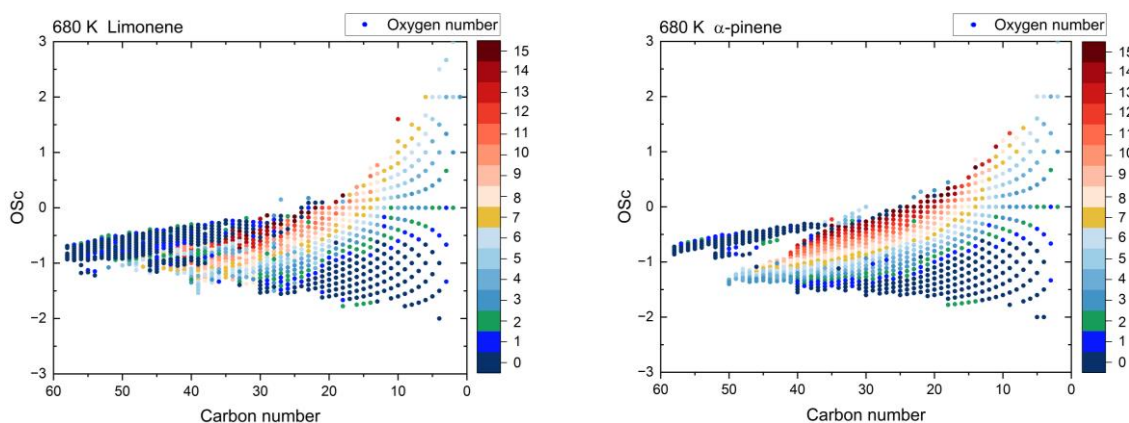


226 **Fig. 4.** Van Krevelen plot for limonene oxidation products (left) at three different temperatures (3025,
 227 3199, and 3954 chemical formulas were detected at 540 K, 620 K, and 680 K, respectively). Van
 228 Krevelen plot for α -pinene oxidation products (right) at three different temperatures (2974, 4141, and
 229 3361 chemical formulas were detected at 540 K, 620 K, and 680 K, respectively). ‘Oxygen number’
 230 stands for number of oxygen atoms in chemical formulas.

231 HESI+/-, FIA-HRMS data were used to draw Fig. 4. The lines indicate different reaction paths, i.e.,
 232 1: oxidation, 2: carbonylation, 3: hydration, 4: dehydrogenation, 5: carboxylation, or reverse processes
 233 [34, 35]. Three temperatures (540, 620, and 680 K), among those studied, were chosen to characterize
 234 the oxidation of these two terpenes. They are visualized using Van Krevelen plots and OSc vs. number
 235 of carbon atoms graphs (Fig. 4 and Fig. 5, respectively). Here, $OSc \approx 2 O/C - H/C$ [16, 31] where H, C,
 236 and O represent the number of hydrogen, carbon, and oxygen atoms, respectively. Generally speaking,
 237 in the Van Krevelen graphs (Fig. 4), on line 5, around the point $O/C=0.5$ and $H/C=1.5$, we observe an
 238 increase in the number of chemical formulas associated with an increase in the number of O-atoms. Also,
 239 on line 1 (Fig. 4), we observe the formation of unsaturation ($O/C=0$, $H/C<1$) and the addition of oxygen
 240 to these unsaturated products ($0<O/C<0.15$ and $H/C<1$). Although these oxidation phenomena occur

241 for both terpenes, the oxidation of α -pinene, in this temperature range, seems more advanced. The
242 oxidation state of carbon, OSc was computed for the products of oxidation of the two fuels. The OSc
243 versus the number of carbon atoms graphs (Fig. 5) confirm this observation and clarify the difference
244 between these two terpenes. In the space defined by $10 < \text{C-atoms} < 40$ and $-2 < \text{OSc} < 3$, the oxidation of
245 α -pinene is more advanced in terms of H/C-O/C space size and level of oxidation (number of O-atoms
246 in chemical formulas). By increasing temperature from 620 to 680 K, for α -pinene, chemical compounds
247 with a number of C-atoms greater than 40 decreased by almost 50%, unlike in the case of limonene
248 which was less affected (Fig. 5). This disappearance of chemical compounds belonging to the class of
249 unsaturated or polyunsaturated compounds is concomitant with the development of the space $10 <$
250 $\text{number of C-atoms} < 40$ and $-2 < \text{OSc} < 3$ (Fig. 5). Different hypotheses, such as the opening of the ring
251 and/or the presence of a double bond external to this ring in the case of limonene, will have to be further
252 explored in order to understand the kinetics of oxidation specific to the two terpenes.





253 **Fig. 5.** Overview of the distribution of limonene (left) and α -pinene (right) oxidation products observed.
 254 HESI+/-, FIA-HRMS data were used.

255 As can be seen from Fig. 5, similar trends were observed for both fuels. If we consider $OSc \geq 0$ for
 256 α -pinene, one can observe an increase of the number of chemical formulas between 540 and 620 K and
 257 a decrease of that number at 680 K. Also, one can see that the content of oxygen in chemical formulas
 258 is higher for α -pinene products at 620 K. This difference increases at 680 K, especially for chemical
 259 compounds with carbon numbers between 20 and 30. The formation of dimers and trimers is probably
 260 more developed in the case of limonene with carbon numbers close to 60 (see Fig. S9). The absence of
 261 oxygen for $OSc < 0$ and $C > 40$ confirms the presence of unsaturated or aromatic chemical compounds, as
 262 proposed elsewhere [36].

263

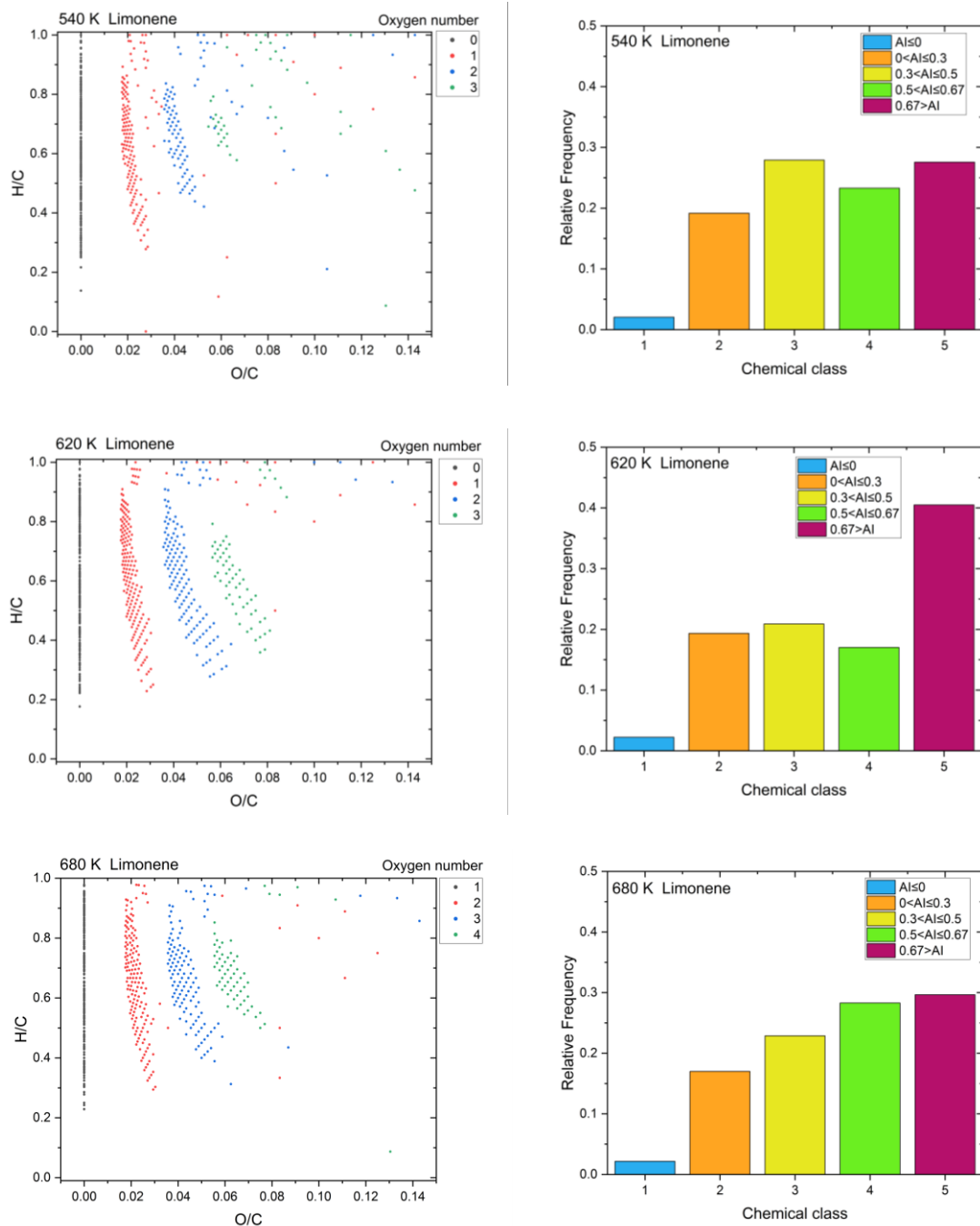
264 3.2 Polyunsaturated or aromatic products of oxidation

265

266 The formation of C_nH_4 ($n=5-6$), and C_nH_6 ($n=6-9$) isomers was observed for both terpene fuels on
 267 the vertical line with $O/C = 0$ (line 4) in Van Krevelen plots using HESI+/- FIA-HRMS data (in Fig. 4;
 268 the location of the fuels is shown as a circle). These plots indicated the formation of aromatics ($H/C <$
 269 0.7 and $O/C = 0$) and polyunsaturated products. In the space defined by $0 < O/C < 0.2$, we observed
 270 products of oxidation (line 1) and dehydrogenation (line 4). For $H/C < 1$, the degree of oxidation of
 271 products decreases with the H/C ratio.

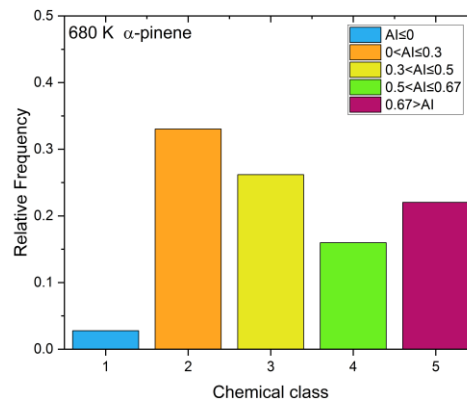
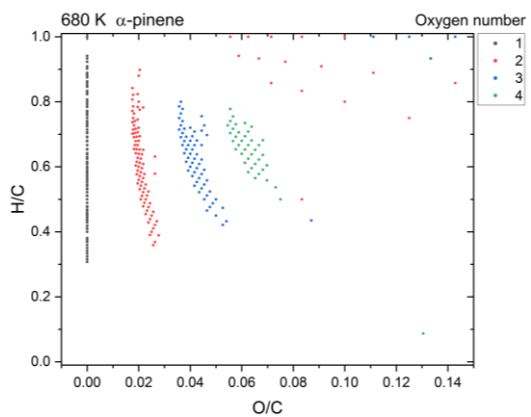
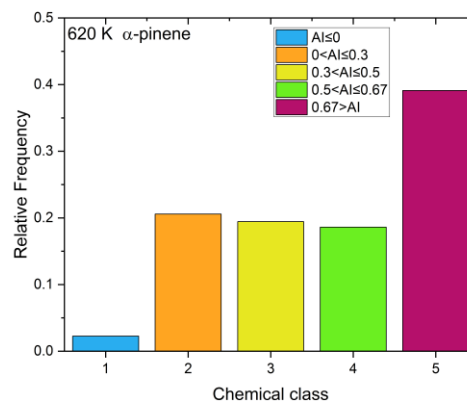
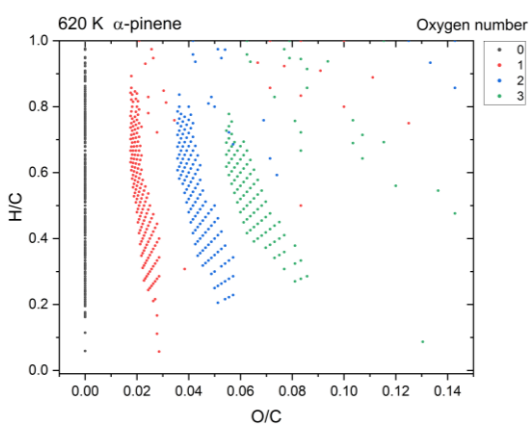
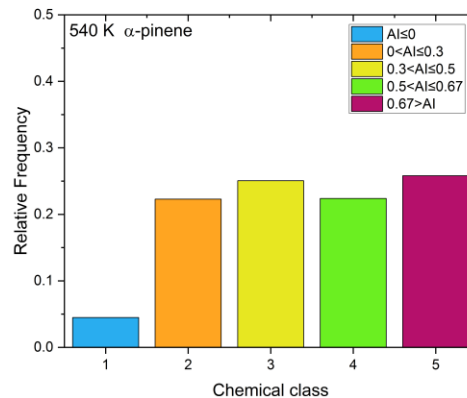
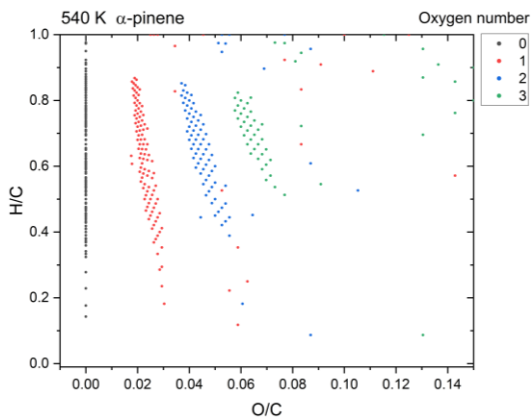
272 Plotting Van Krevelen diagram at different temperatures indicated some variations in several regions.
 273 Indeed, when the temperature increases, for $H/C < 1$ and $O/C < 0.1$, many more chemical formulas were
 274 detected. In particular, one could observe three subsets with 1 to 3 oxygen atoms which grow with
 275 temperature up to 620 K (Figs. 6 and 7). At 680 K, we observed a clear decrease of the population of

276 chemical compounds containing 0, 1, 2 or 3 O-atom in the case of α -pinene. In this space of the VK
 277 diagram, these oxygen additions are not random, since more than 50% of the chemical formulas remain
 278 with the same number of carbon and hydrogen atoms. If we associate these observations with reaction
 279 paths, one could propose that the oxidation products contain OH groups or ether functions.



280 **Fig. 6.** Van Krevelen plot for limonene oxidation products at three different temperatures (left) and
 281 frequency of occurrence of chemical classes (right). HESI+/-, FIA-HRMS data were used.

282

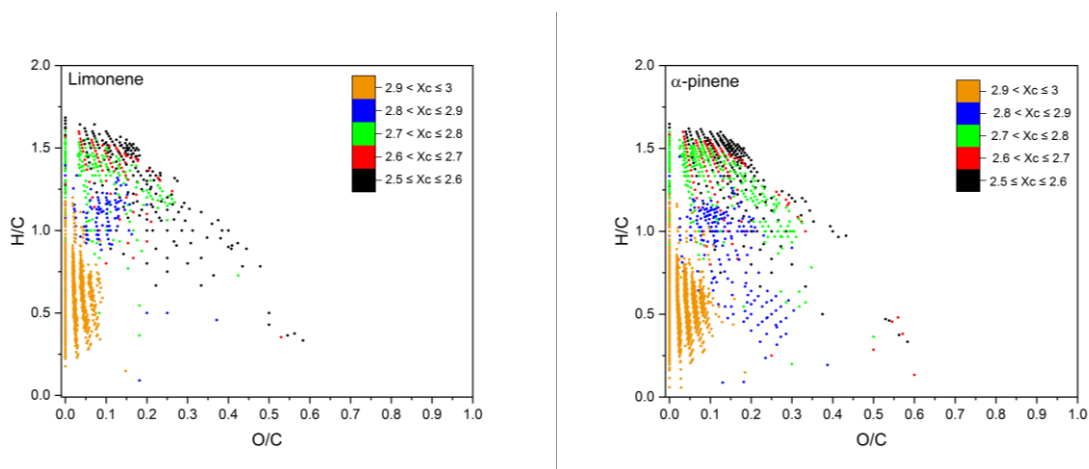


283 **Fig. 7.** Van Krevelen plot for α -pinene oxidation products at three different temperatures (left) and
 284 frequency of occurrence of chemical classes (right). HESI+/-, FIA-HRMS.

285 In order to further assess the presence of different chemical classes in the products of oxidation of
 286 the fuels, we computed the aromaticity index (AI_{mod}) and defined chemical families based on literature
 287 [37]: (1) aliphatics ($AI_{mod} \leq 0$), (2) olefinics and naphtenics ($0 < AI_{mod} \leq 0.3$), (3) highly unsaturated

288 compounds ($0.3 < AI_{\text{mod}} \leq 0.5$), (4) aromatics ($0.5 < AI_{\text{mod}} \leq 0.67$), and (5) polyaromatics ($0.67 < AI_{\text{mod}}$).
 289 One should note that the fuels have an AI_{mod} of 0.3; then, they are included in class (2). Here, the AI was
 290 computed according to the equation: $AI_{\text{mod}} = (1 + C - 0.5 \times O - 0.5 \times H) / (C - 0.5 \times O)$, where C, H, and O
 291 represent the number of carbon, hydrogen, and oxygen atoms, respectively, in the chemical formulas
 292 [19, 38]; see Figs. S7 and S8 for full dataset analysis. The differentiation of chemical classes of products
 293 arising from the oxidation of the two terpenes is particularly important at the early stages of oxidation.
 294 The histograms presented in Figs. 6 and 7 represent more than 1,000 chemical formulas detected in the
 295 subset $O/C \leq 0.1$ (1 to 3 additions of O) and $H/C \leq 1$. As can be seen from Figs. 6 and 7, for limonene
 296 and α -pinene, respectively, the aromatic fraction (4) decreases and the polyaromatic fraction (5)
 297 increases at 620 K. That could indicate an increased production of polyaromatic from aromatic products.
 298 However, at 680 K, these last two chemical classes decrease significantly in the case of α -pinene. In the
 299 case of limonene, for $AI > 0.67$ we observe chemical formulas with 40 to 60 carbon atoms which, given
 300 the unsaturation level, could correspond to chemicals with structural units composed of 3 to 4 aromatic
 301 rings. Beyond these hypotheses, we observed that for limonene (Fig. 6), chemical compounds with AI
 302 > 0.67 dominate at higher temperature (i.e., 680 K) which could be due to higher thermal stability, lower
 303 oxidation rates or higher production rates.

304 Whereas the computation of AI_{mod} is useful for probing the presence of aromatics in oxidation
 305 products, computing the aromaticity equivalent index (X_c) is of greater value, according to previous
 306 works [20]. Therefore, X_c were computed for the oxidation products of limonene and α -pinene. X_c was
 307 defined as: $[3(\text{DBE} - m \times O) - 2] / (\text{DBE} - m \times O)$, with $m=1$, as in previous works [20]. In that paper, the
 308 authors classified the chemical formulas according to X_c ($X_c \geq 2.5$ for aromatics; $X_c \geq 2.7143$ for
 309 condensed aromatics). Figure 8 shows the present results. One can see that the formation of
 310 polyaromatics ($2.9 \leq X_c \leq 3$) is confirmed. One can also note that more aromatics were detected in α -
 311 pinene oxidation products.



312 **Fig. 8.** Van Krevelen- X_c plot for limonene (left) and α -pinene (right) oxidation products. HESI+/-, FIA-

313 HRMS (samples taken at 620 K). The color-coding indicates the computed Xc values.

314

315 For $2.9 \leq X_c \leq 3$, we observed a carbon number distribution centered mainly on $\sim C_{50}$, which is not
316 the case for the multimodal distributions ($\sim 10, 20, 30, 40, 50, \dots$ carbon atoms) observed during the
317 formation of dimers, trimers or the initiation of oligomerization (Fig. S9). Finally, in the space $H/C \leq 1$
318 and $0 \leq O/C \leq 0.15$, where X_c is in the range 2.9 to 3, we detected 82-85 % of the total chemical formulas
319 with HESI (-). Then considering that aromatics are easily ionized with HESI (-) [39, 40], one can
320 conclude that aromatic products dominate in that space. Table S2 summarizes the detected formulas with
321 $O/C = 0$ and $H/C < 0.7$. To date, no reaction mechanism is available to describe their formation, although
322 one can speculate that they are formed via recombination reactions involving e.g., hydrocarbon radicals
323 and hydrocarbons.

324 Whereas the presently observed formation of aromatics or polyunsaturated products under cool-
325 flame conditions was rather unexpected, it should be investigated further since the oxidation of
326 aromatics could significantly contribute to the formation of secondary organic aerosols in the
327 troposphere [41].

328

329 **4. Conclusions**

330

331 In this study, we detected a large set of complex products of oxidation formed from cool flames of
332 two monoterpenes, limonene and α -pinene, at atmospheric pressure and fuel-lean conditions. Oxidation
333 pathways including autoxidation, the Waddington mechanism involving *exo*- and *endo*-double bonds
334 ($C=C$), autoxidation of its products, and the Korcek mechanism. The formation of aromatic and
335 polyunsaturated products was observed during the autoxidation of the two fuels through the use of
336 HRMS combined with graphic tools (Van Krevelen plots, oxidation state of carbon, aromaticity index,
337 and aromaticity equivalent index). The presence of unsaturated or polyunsaturated chemical compounds
338 at these temperatures needs to be investigated further. This work demonstrates that oxidation pathways
339 are numerous and complex, and many complex chemical products can be formed whereas reaction
340 pathways need to be delineated. The oxidation products detected in this work can be emitted to the
341 troposphere, which would increase the concentration of VOCs contributing to the formation of
342 particulates. The present results could be useful to improve existing atmospheric models.

343

344 **Acknowledgements**

345 Support from the CAPRYSES project (ANR- 11-LABX-006-01) and the VOLTAIRE project (ANR-

346 10-LABX-100-01) funded by ANR through the PIA (Programme d'Investissement d'Avenir) is
347 gratefully acknowledged.

348

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