

On the formation of highly oxidized pollutants by autoxidation of terpenes under low temperature combustion conditions: the case of limonene and α -pinene.

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Fig. S1: Comparison of the mass spectra of pure (standard) and oxidated limonene

Tab. S1: APCI source +/–, α -Pinene, limonene and APCI source α -Pinene/limonene

Tab. S2: HESI source +/–, α -Pinene, limonene and HESI source α -Pinene/limonene

Fig. S2: AP and LM mass Spectra acquired with a HESI source in negative mode

Fig. S3: molecular forms resulting from an autoxidation mechanism of limonene: (a) even number of oxygens (b) odd number of oxygens.

Fig. S4: 3-D representation of all limonene oxidation data where DBE is used as third dimension and OSc vs DBE graph

Fig. S5: Some proposed formation routes to C₁₀H₁₆O_x species via autoxidation

Fig. S6: Superposition of chromatographs (UHPLC) of limonoaldehyde (left) and pinonic acid (right) standards and C₁₀H₁₆O₂ and C₁₀H₁₆O₃ isomers (positive ionization mode).

Fig. S7: D₂O exchanges for limonene and α -pinene (direct infusion, negative ionization mode) - top; and derivatization of carbonyls in limonene and α -pinene oxidation samples using 2,4-DNPH (UHPLC, positive mode) – bottom.

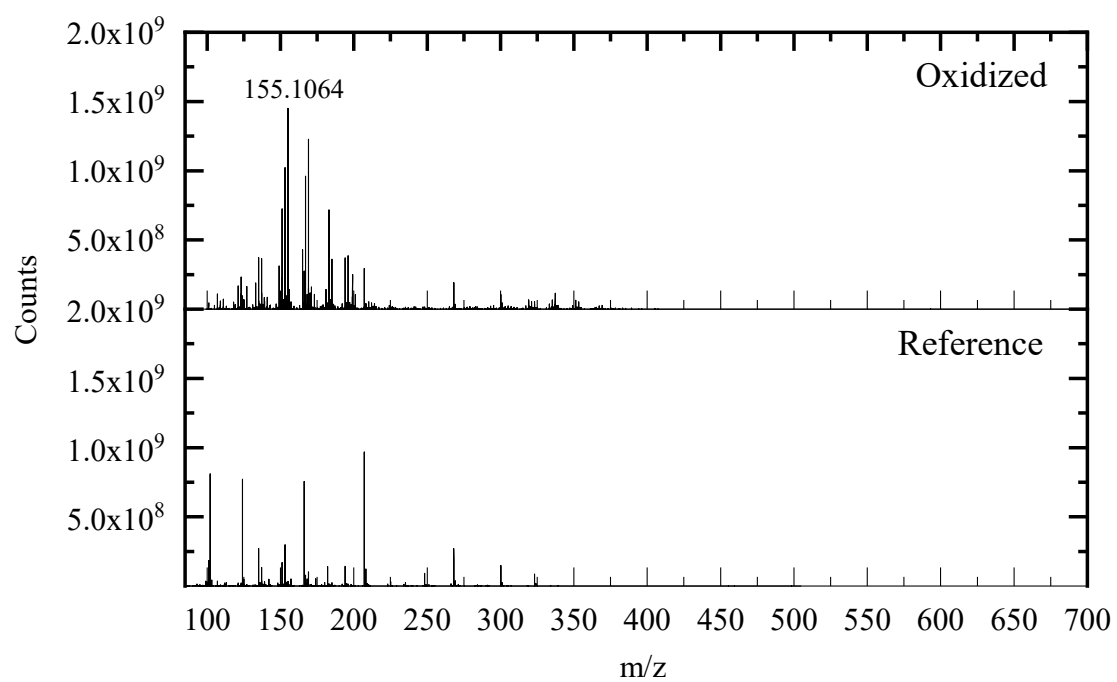


Fig. S1: Comparison of the mass spectra of pure (standard) and oxidated limonene

Table S1. Representation of the mass spectrometry data characterizing the oxidation of α -pinene and limonene (ionization source: APCI positive and negative mode, JSR experiments).

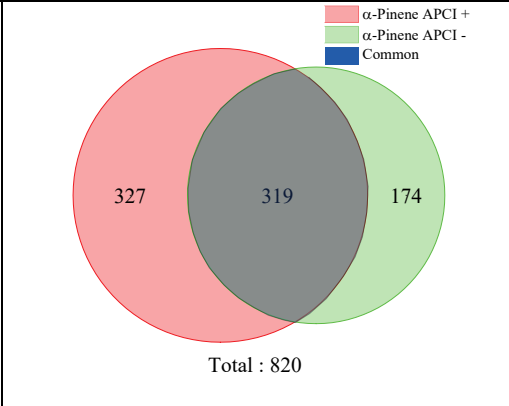
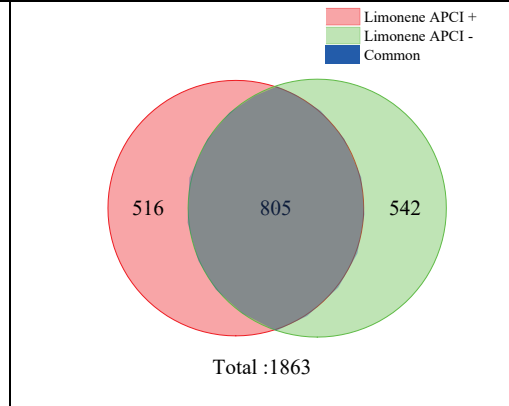
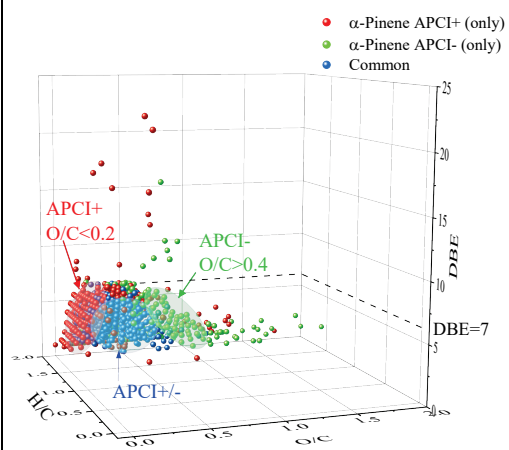
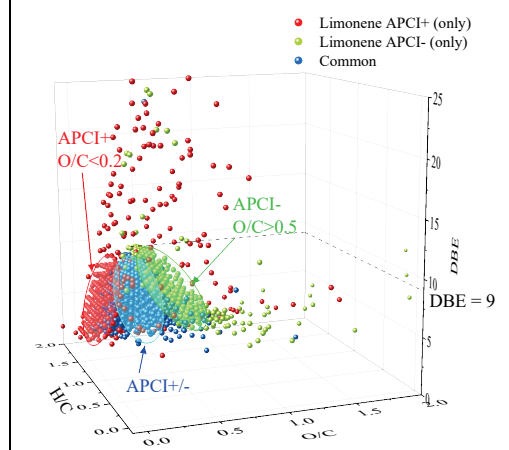
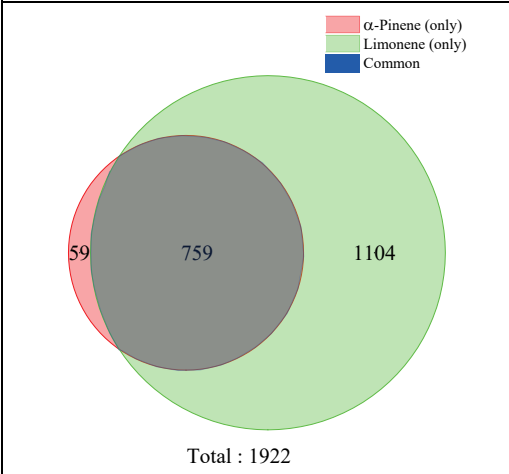
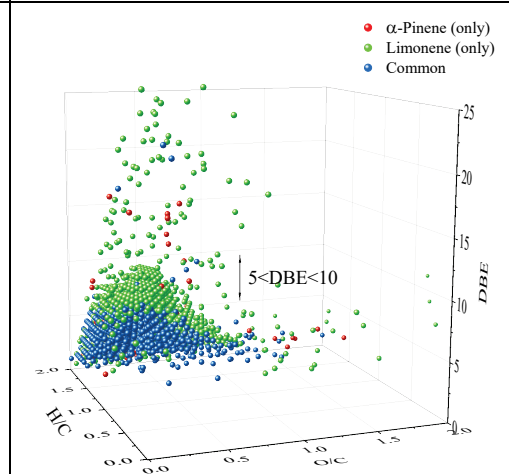

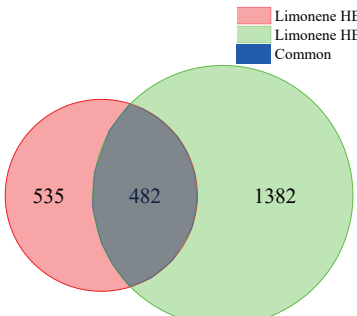
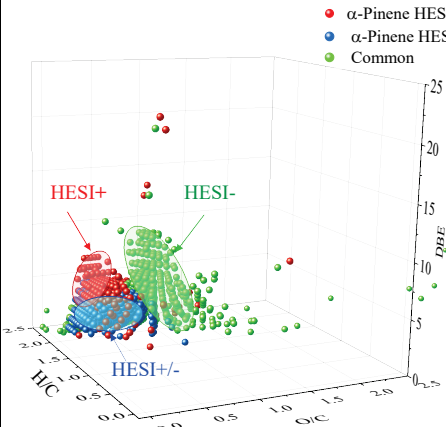
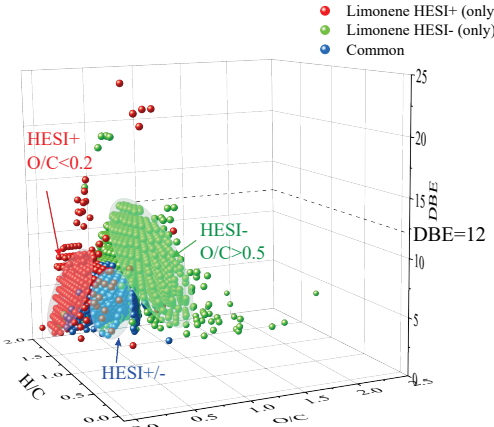
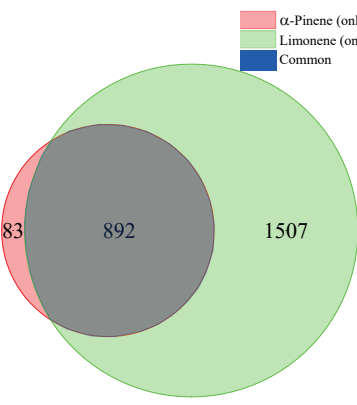
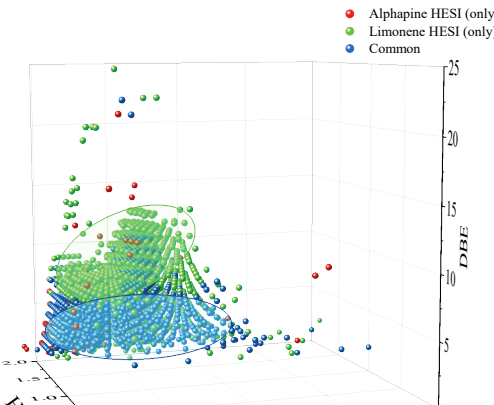
	α-Pinene			Limonene		
Source and mode	APCI⁺		APCI⁻	APCI⁺		APCI⁻
Number of compounds	646		503	1321		1346
Distribution	specific to positive mode 327	common 319	specific to negative mode 174	specific to positive mode 516	common 805	specific to negative mode 542
Venn graph						
VK vs DBE						
						

Table S2. Representation of the mass spectrometry data characterizing the oxidation of α -pinene and limonene (ionization source: HESI positive and negative modes, JSR experiments).

	α -Pinene			Limonene		
Source and mode	HESI ⁺		HESI ⁻	HESI ⁺		HESI ⁻
Number of compounds	594		693	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>Total : 975</p>			 <p>Total : 2399</p>		
VK vs DBE						
	 <p>Total : 2482</p>					

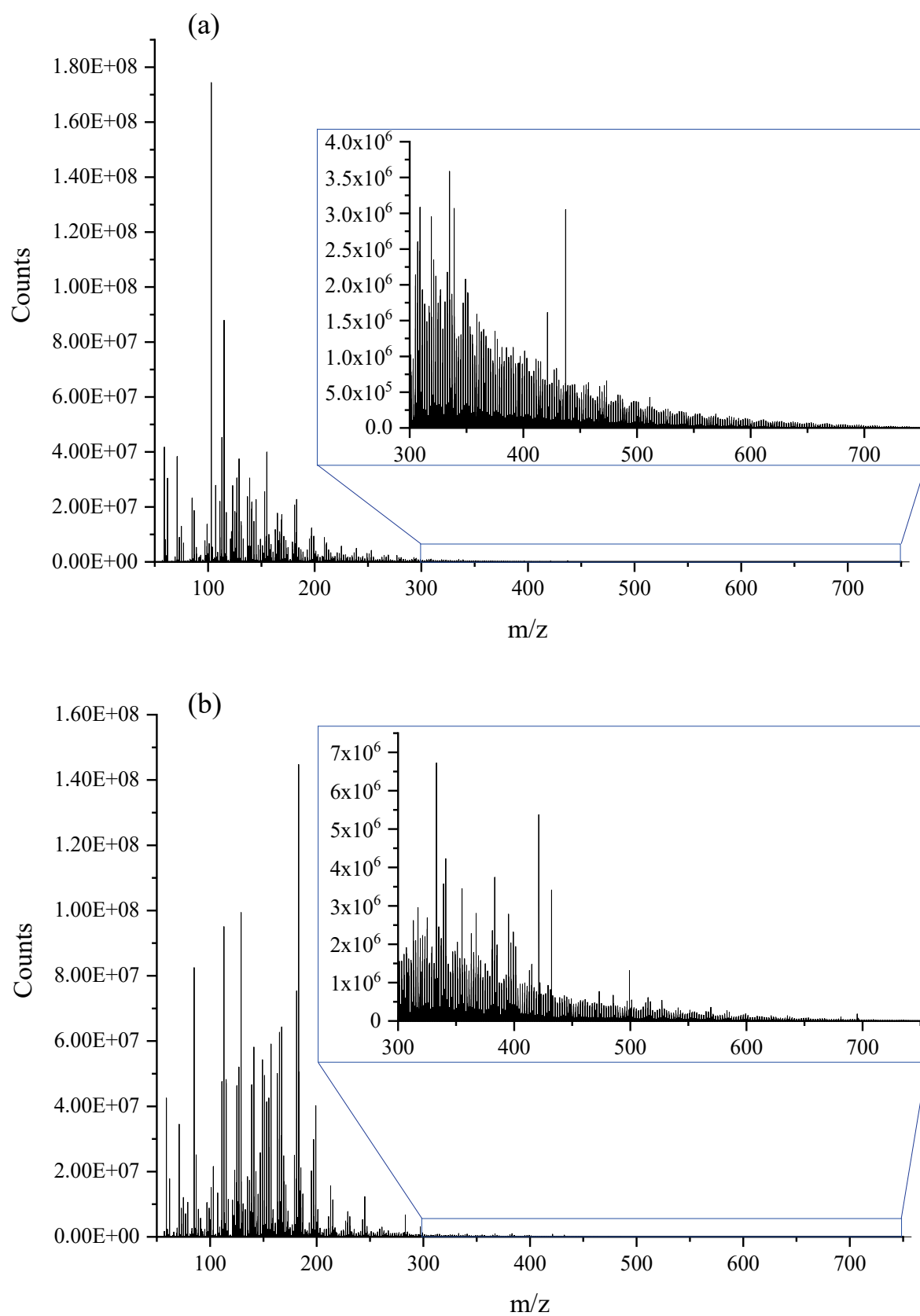
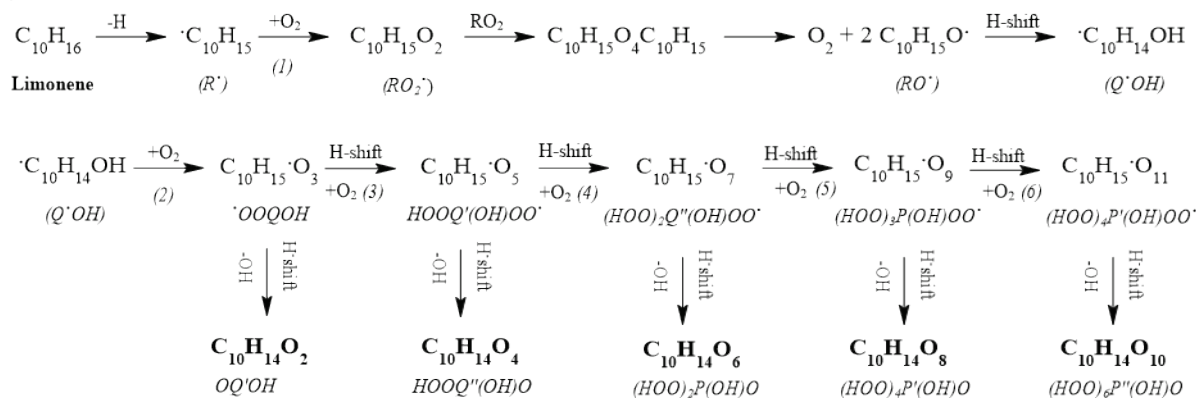


Fig. S2: α -pinene and limonene mass Spectra acquired with a HESI source in negative mode

(a)



(b)

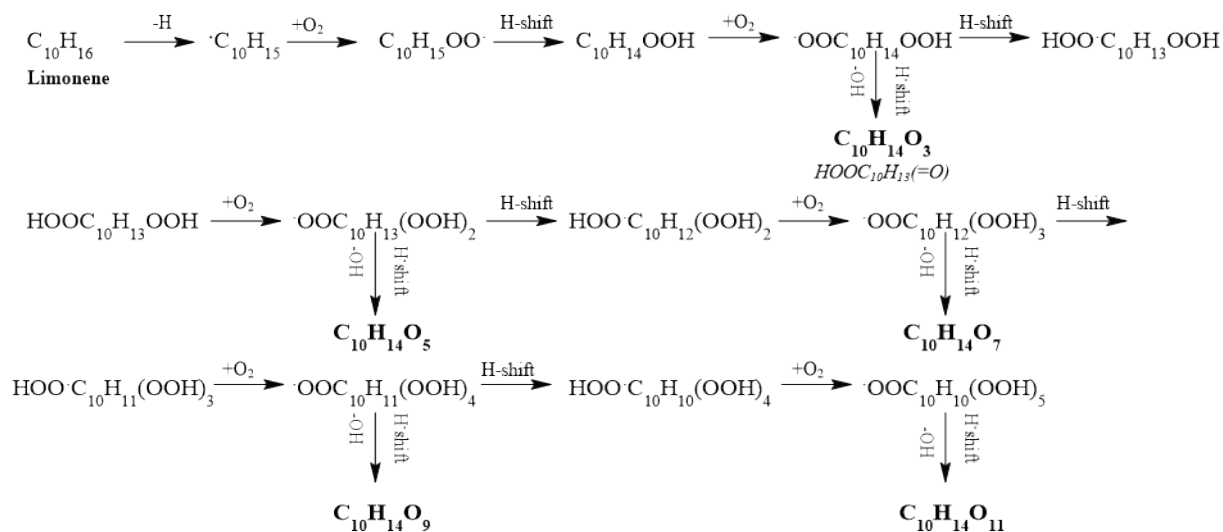


Fig. S3: Molecular forms resulting from an autoxidation mechanism of limonene: a) even number of oxygens b) odd number of oxygens.

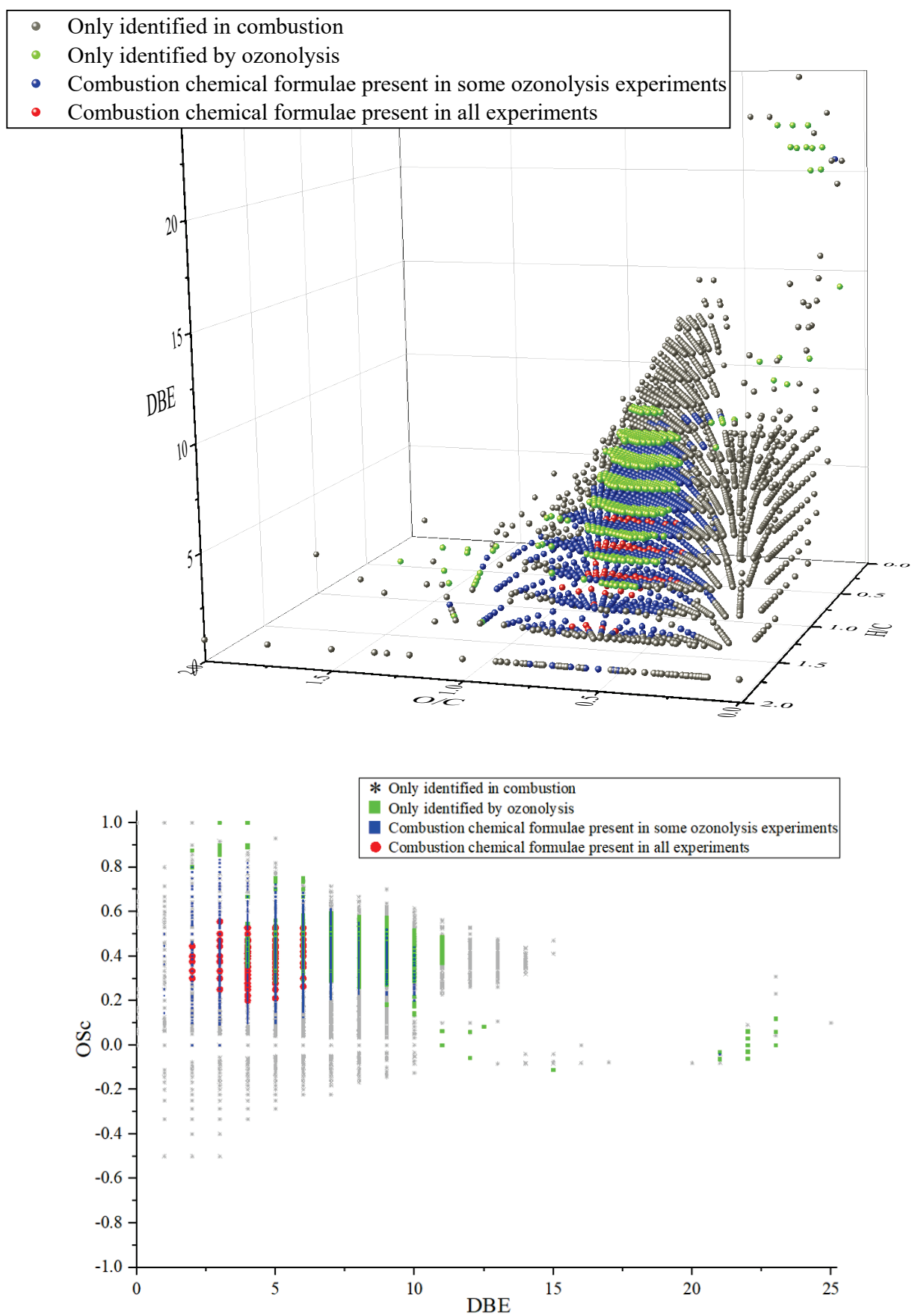


Fig. S4: a) 3-D representation of all limonene oxidation data where DBE is used as third dimension and b) Osc vs DBE graph

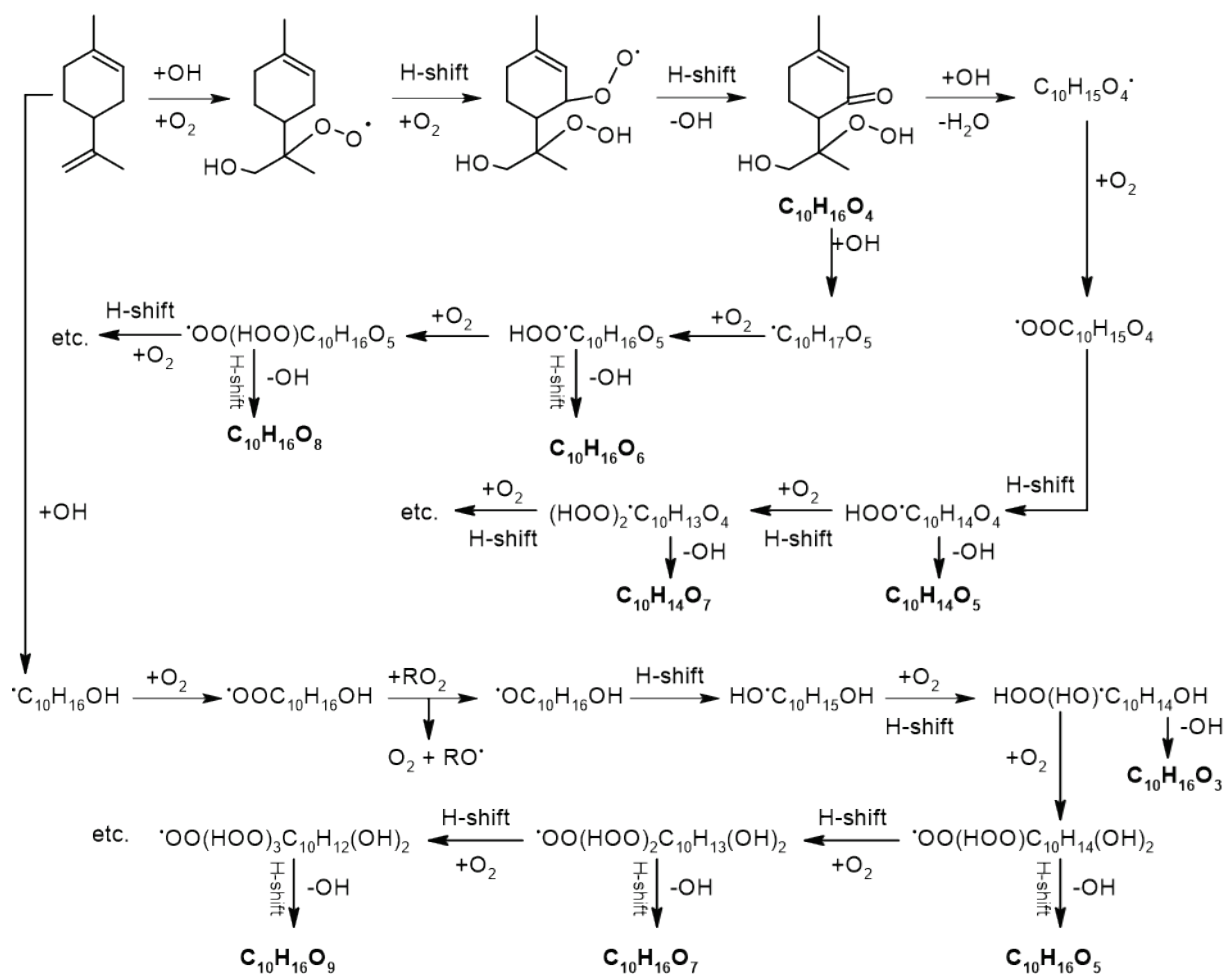


Fig. S5: Some proposed formation routes to $C_{10}H_{16}O_x$ species via autoxidation

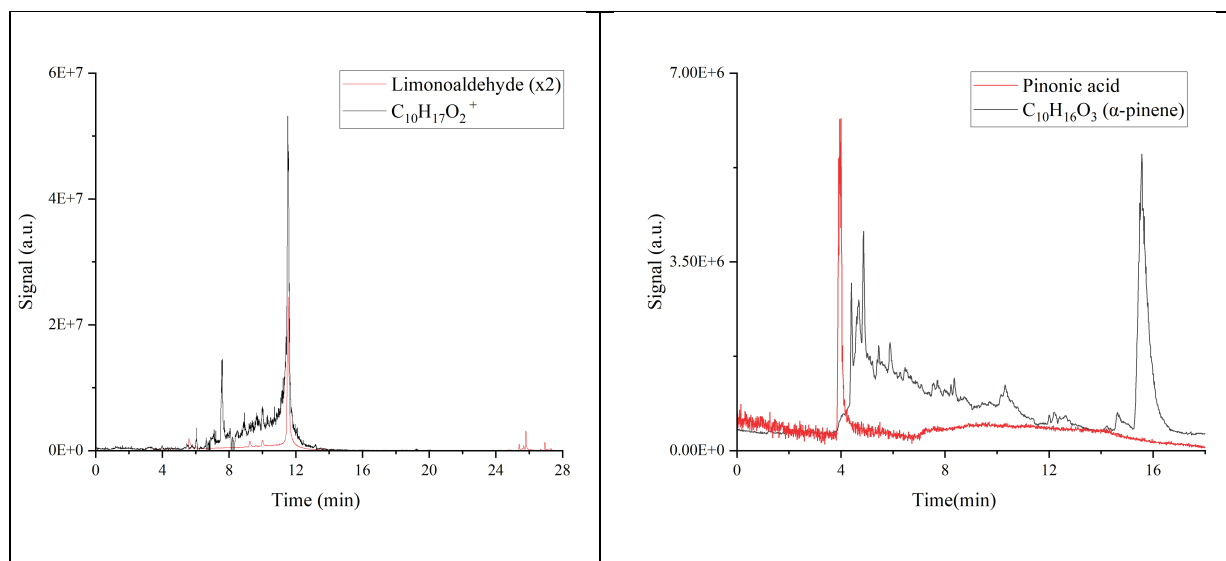


Fig. S6: Superposition of chromatographs (UHPLC) of limonoaldehyde (left) and pinonic acid (right) standards and $C_{10}H_{16}O_2$ and $C_{10}H_{16}O_3$ isomers (positive ionization mode).

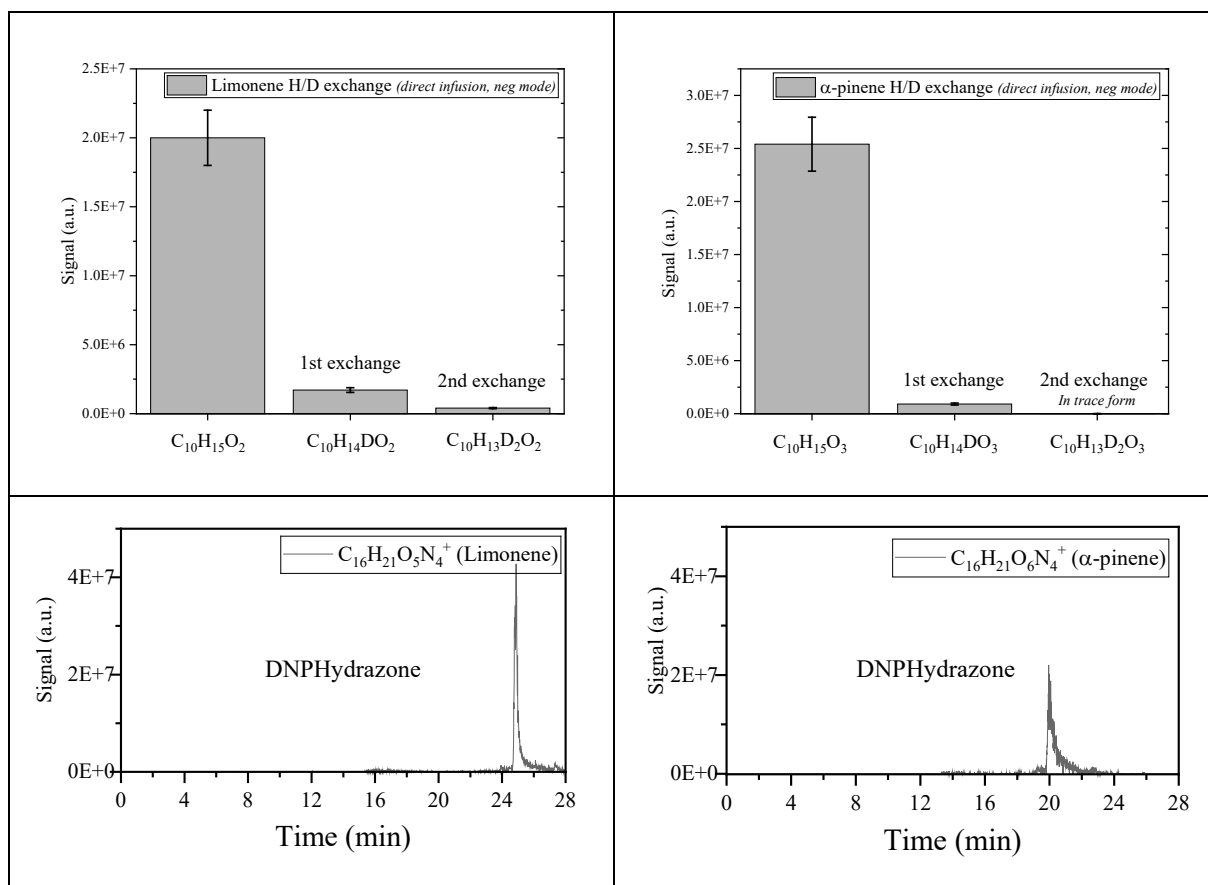


Fig. S7: D₂O exchanges for limonene and α -pinene (direct infusion, negative ionization mode) - top; and derivatization of carbonyls in limonene and α -pinene oxidation samples using 2,4-DNPH (UHPLC, positive mode) – bottom.