Introduction
With the growing interest for biomass-derived fuels the understanding of the combustion chemistry of terpenes becomes of major scientific importance. We studied the low-temperature oxidation of a series of terpenes (α- and β-pinene and limonene) in a jet-stirred reactor at atmospheric pressure. The formation of ketohydroperoxides and highly oxygenated molecules (HOMs) was observed.

Experimental conditions
Analyses were performed on solubilized products of terpenes oxidation in cooled acetonitrile. The samples were analyzed using HESI electrospray ionization (+/-) and an Orbitrap mass spectrometer (resolution: 140,000, mass accuracy <0.5 ppm RMS).
Experimental conditions selected based on the kinetic of oxidation of cyclic paraffins in a JSR to favor the production of ketohydroperoxides: and HOMs
1 bar, T = 590 K, ϕ = 0.5, τ = 1 s

Results
Ketohydroperoxides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Mass (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10H14O3</td>
<td>M</td>
<td>183.10167</td>
</tr>
<tr>
<td></td>
<td>MH⁺</td>
<td>184.10785</td>
</tr>
<tr>
<td></td>
<td>M(-H)⁻</td>
<td>181.08715</td>
</tr>
</tbody>
</table>

H/D exchange using D₂O: -OH → -OD to confirm the presence of -OOH

HOMs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Mass (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10H14O5</td>
<td>M</td>
<td>213.07688</td>
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<tr>
<td></td>
<td>M(-H)⁻</td>
<td>214.10566</td>
</tr>
</tbody>
</table>

Terpenes oxidation

Reaction pathways to ketohydroperoxides

R + O₂ ⇌ RO₂ ⇌ QOOH
2nd O₂ addition:

QOOH + O₂ ⇌ OOQOOH
OOQOOH ⇌ HOOQ’OOH
HOOQ’OOH → OH + HOOQ’O (KHP)

HOMs formation mechanism

OOQOOH ⇌ HOOP’O (alternative H-transfer, i.e., not from H-C-OOH)

3rd O₂ addition:

HOOP’O + O₂ ⇌ (HOO)₂P’OO ⇌ (HOO)₂P”OOH
(HOO)₂P”OOH → OH + (HOO)₂P”=O (C₁₀H₁₄O₂)

4th O₂ addition:

(HOO)₂P”OOH + O₂ ⇌ (HOO)₃P’OO ⇌ (HOO)₃P”OOH
(HOO)₃P”OOH → OH + (HOO)₃P”=O (C₁₀H₁₄O₃)

5th O₂ addition:

(HOO)₃P”OOH + O₂ ⇌ (HOO)₄P’OOH ⇌ (HOO)₄P”OOH
(HOO)₄P”OOH → OH + (HOO)₄P”=O (C₁₀H₁₄O₄)

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