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HIGHLY OXYGENATES MOLECULES FORMED BY OXIDATION OF TERPENES IN A JET-STIRRED REACTOR

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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.

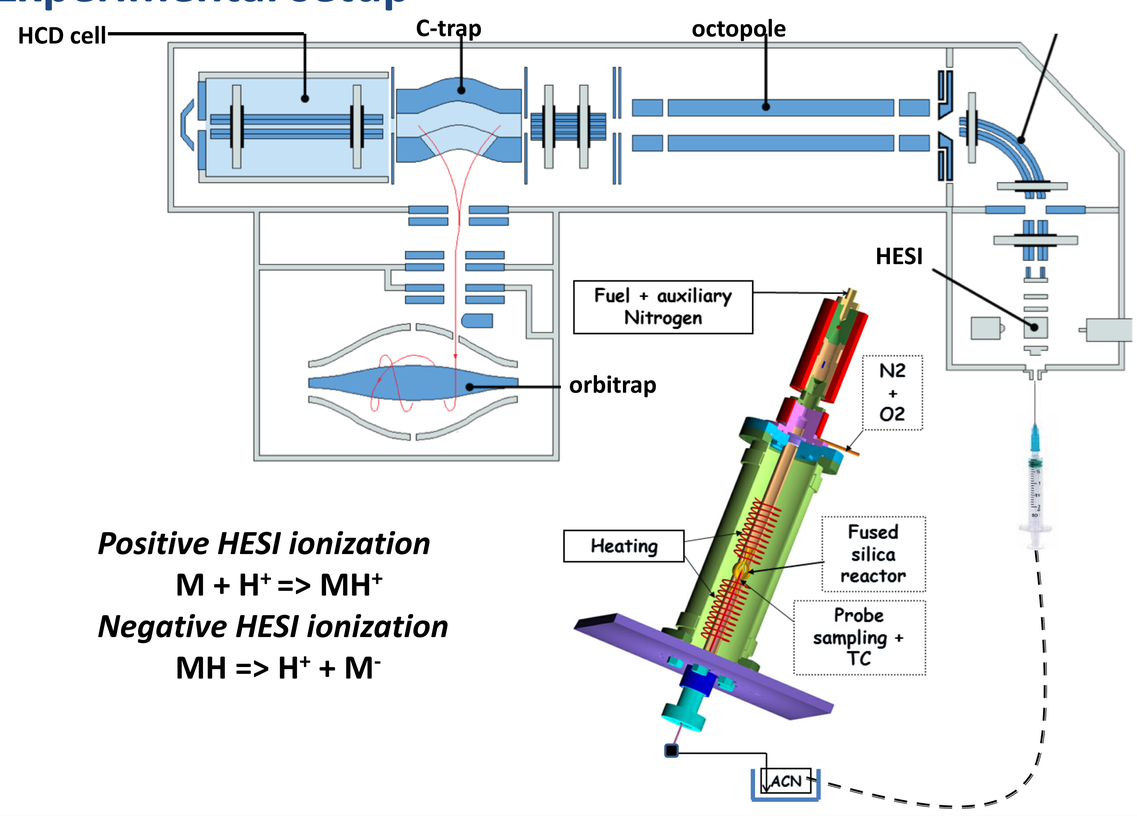
Experimental conditions

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, $\varphi = 0.5$, $\tau = 1$ s

Experimental setup



Positive HESI ionization

$M + H^+ \Rightarrow MH^+$

Negative HESI ionization

$MH \Rightarrow H^+ + M^-$

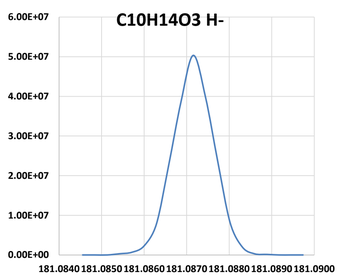
Results

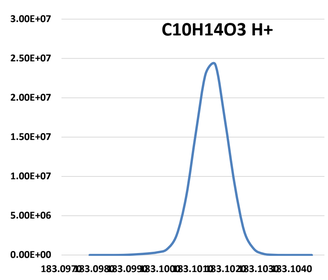
Ketohydroperoxides

$C_{10}H_{14}O_3$: M

MH^+ m/z= 183.10167

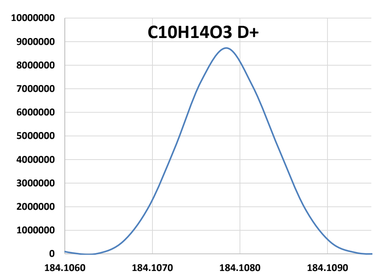
$M(-H)^-$ m/z= 181.08715





H/D exchange using D_2O: -OH ⟶ -OD to confirm the presence of -OOH

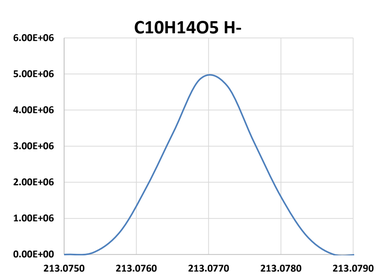
MD^+ m/z= 184.10785



HOMs

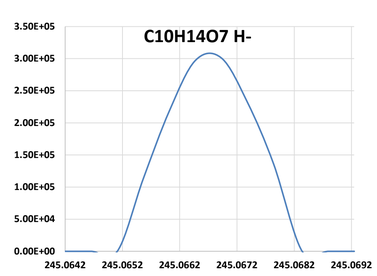
$C_{10}H_{14}O_5$: M

$M(-H)^-$ m/z= 213.07688



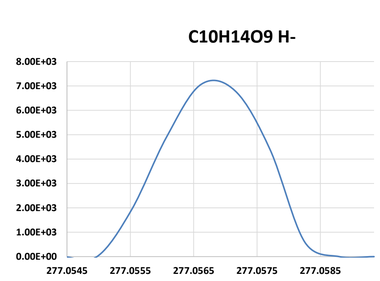
$C_{10}H_{14}O_7$: M

$M(-H)^-$ m/z= 245.06694

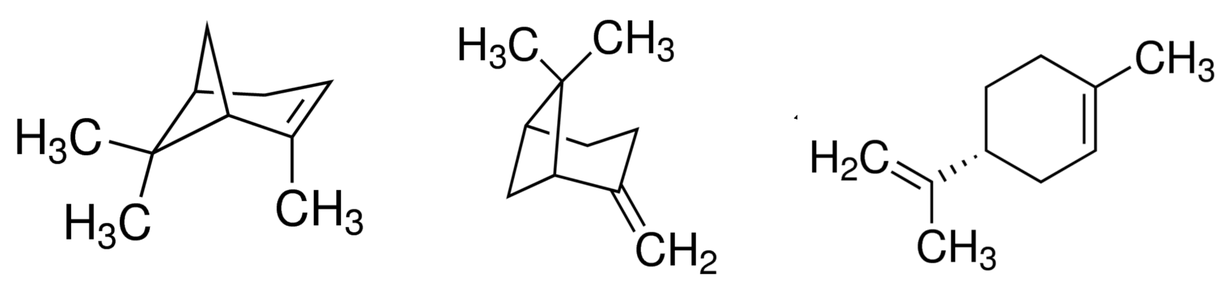


$C_{10}H_{14}O_9$: M

$M(-H)^-$ m/z= 277.05661



Terpenes oxidation



Reaction pathways to ketohydroperoxides

$R + O_2 \leftrightarrows RO_2 \leftrightarrows QOOH$

2nd O_2 addition:

$QOOH + O_2 \leftrightarrows OOQOOH$

$OOQOOH \leftrightarrows HOOQ'OOH$

$HOOQ'OOH \rightarrow OH + HOOQ'O$ (KHP)

HOMs formation mechanism

$OOQOOH \leftrightarrows HOOPOOH$ (alternative H-transfer, i.e., not from H-C-OOH)

3rd O_2 addition:

$HOOPOOH + O_2 \leftrightarrows (HOO)_2POO \leftrightarrows (HOO)_2P'OOH$

$(HOO)_2P'OOH \rightarrow OH + (HOO)_2P'=O$ ($C_{10}H_{14}O_5$)

4th O_2 addition:

$(HOO)_2P'OOH + O_2 \leftrightarrows (HOO)_3P'OO \leftrightarrows (HOO)_3P''OOH$

$(HOO)_3P''OOH \rightarrow OH + (HOO)_3P''=O$ ($C_{10}H_{14}O_7$)

5th O_2 addition:

$(HOO)_3P''OOH + O_2 \leftrightarrows (HOO)_4P'''OO \leftrightarrows (HOO)_4P'''OOH$

$(HOO)_4P'''OOH \rightarrow OH + (HOO)_4P'''=O$ ($C_{10}H_{14}O_9$)

Acknowledgements

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