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Ketohydroperoxides and Korcek mechanism identified during the oxidation of dipropyl ether in a JSR by high-resolution mass spectrometry



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Introduction

With the growing interest for biomass-derived fuels the understanding of the combustion chemistry of ethers becomes of major scientific importance.

We studied the low-temperature oxidation of dipropyl ether in a jet-stirred reactor at atmospheric pressure. The formation of ketohydroperoxides and highly oxygenated compound was observed as well as the products of the so-called Korcek mechanism yielding propanoic acid.

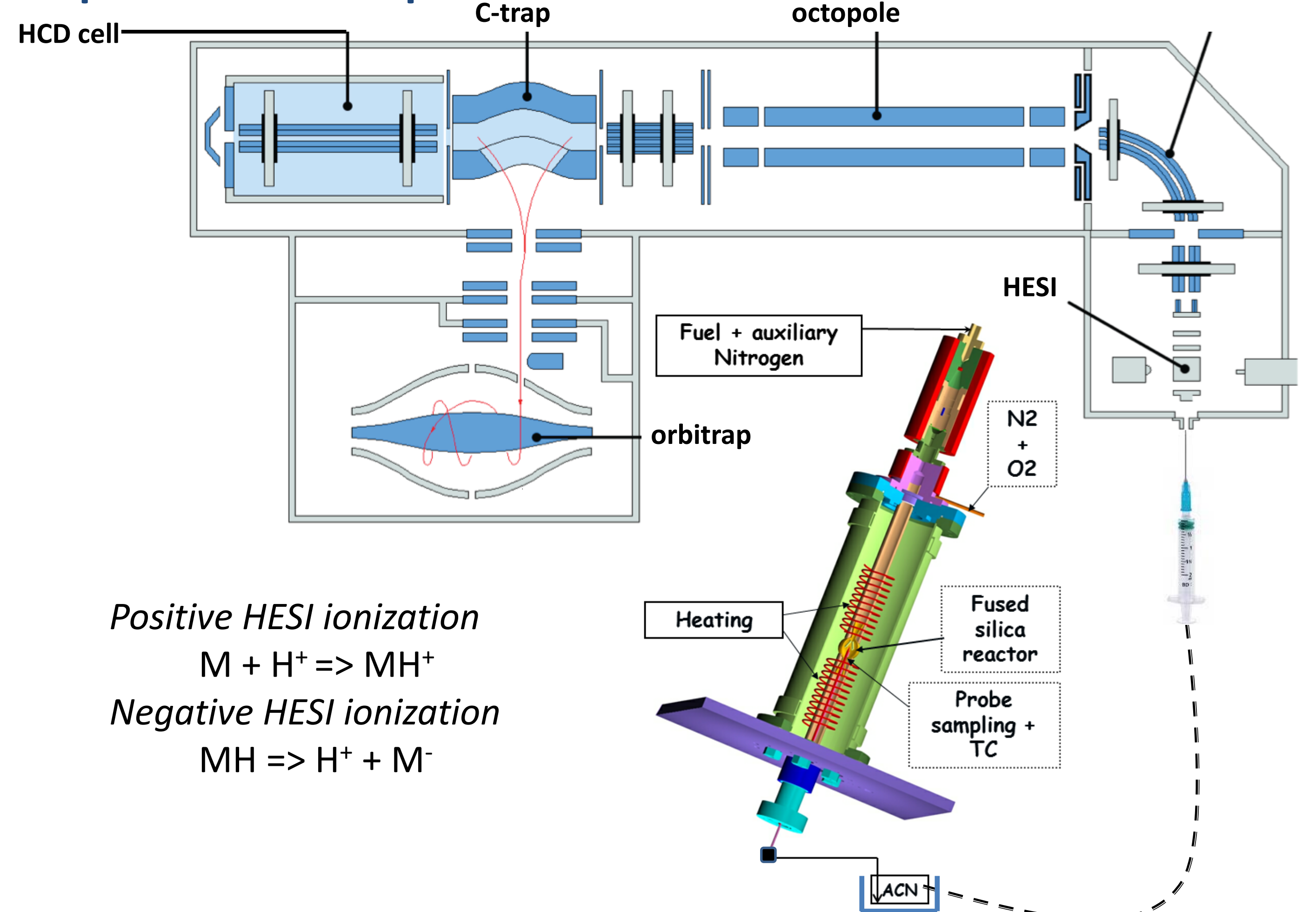
Experimental conditions

Analyses were performed on solubilized products of dipropyl ether 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 model of Serinyel et al. (2019) to maximize the production of ketohydroperoxides:

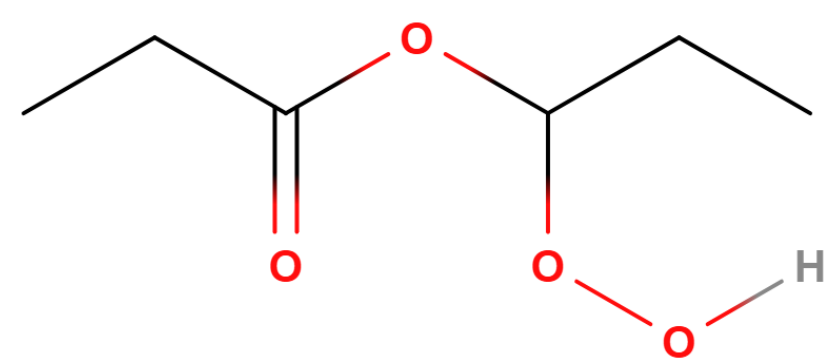
1 bar, T = 520-530 K, $\phi = 0.5$, $\tau = 1$ s

Experimental setup



Results

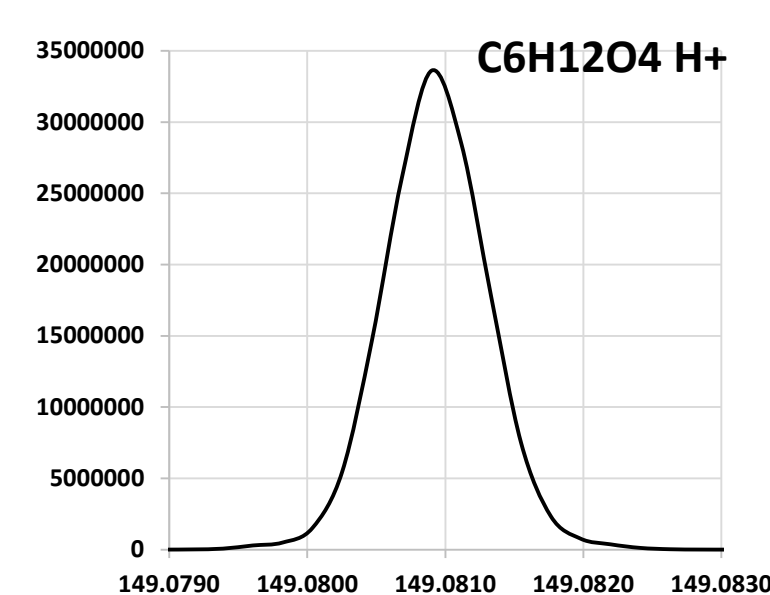
Ketohydroperoxides



$C_6H_{12}O_4 : M$

MH^+ $m/z = 149.08084$

MNa^+ $m/z = 171.06278$



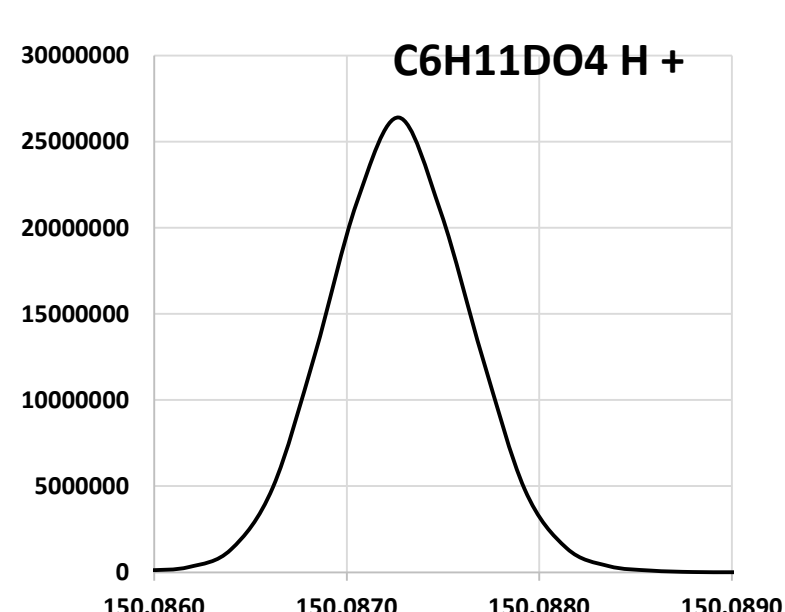
H/D exchange using D_2O : $-OH \rightarrow -OD$ to confirm the presence of $-OOH$

MH^+ $m/z = 149.08084$ (59%)

MD^+ $m/z = 150.08711$ (41%)

MNa^+ $m/z = 171.06278$ (37%)

$MdNa^+$ $m/z = 172.06906$ (63%)



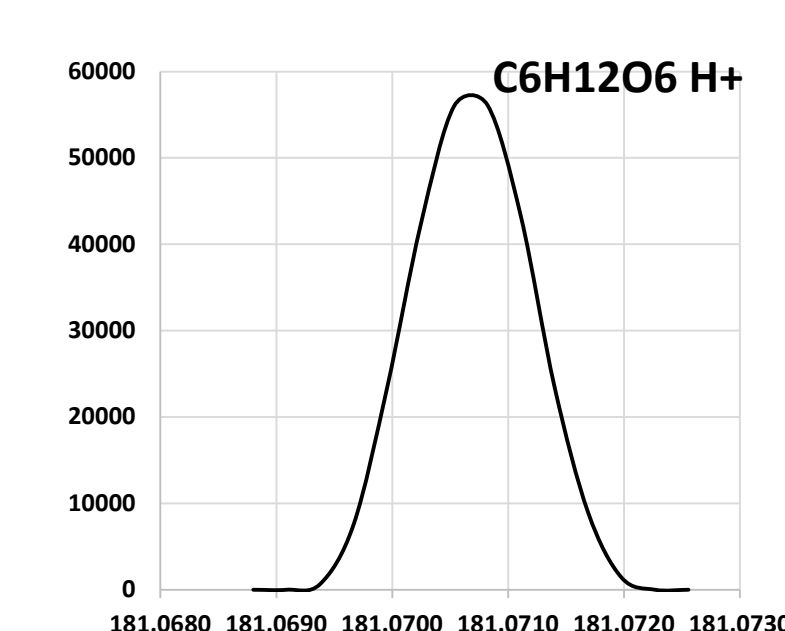
HOMs

$C_6H_{12}O_6 : M$

MH^+ $m/z = 181.07066$

MNa^+ $m/z = 203.05261$ (77%)

$MdNa^+$ $m/z = 204.05889$ (23%)

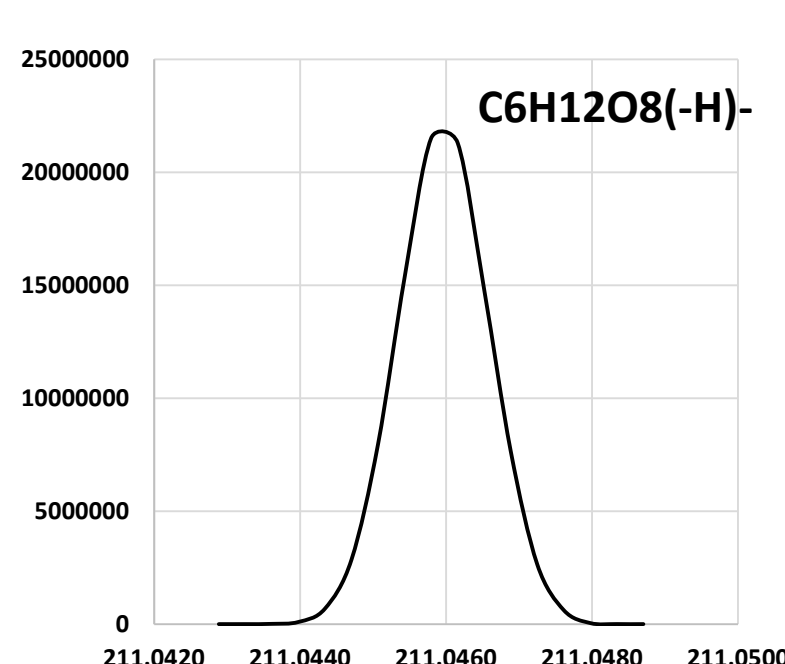


$C_6H_{12}O_8 : M$

$M(-H)^+$ $m/z = 211.04594$

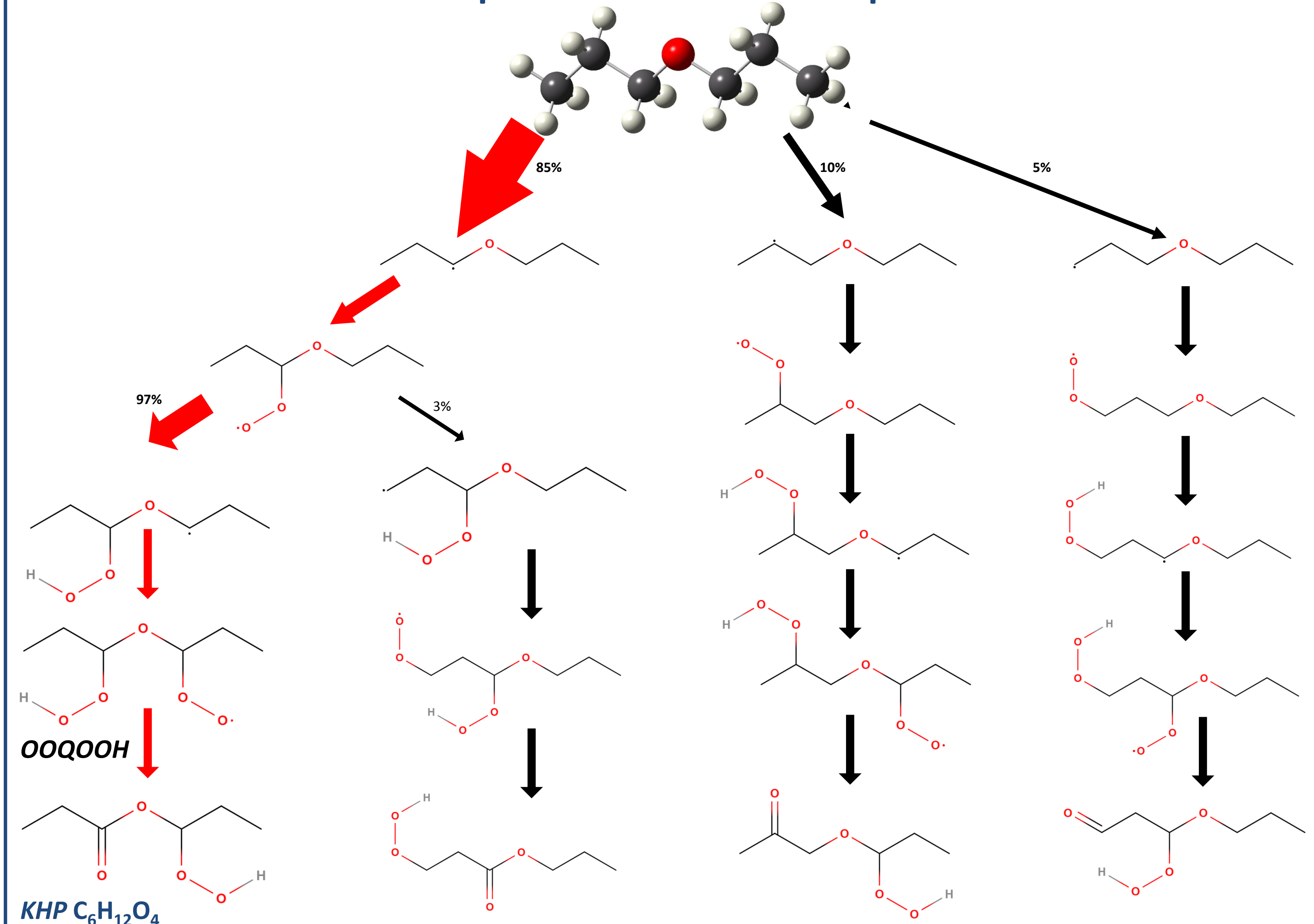
$M(-H)OH^+$ $m/z = 229.05651$

$M(-H)HCOO^+$ $m/z = 257.05142$



Dipropyl ether oxidation

Reaction pathways to ketohydroperoxides



HOMs formation mechanism

$OOQOOH \rightleftharpoons HOOPOOH$ (alternative H-transfer, not from HC-OOH)

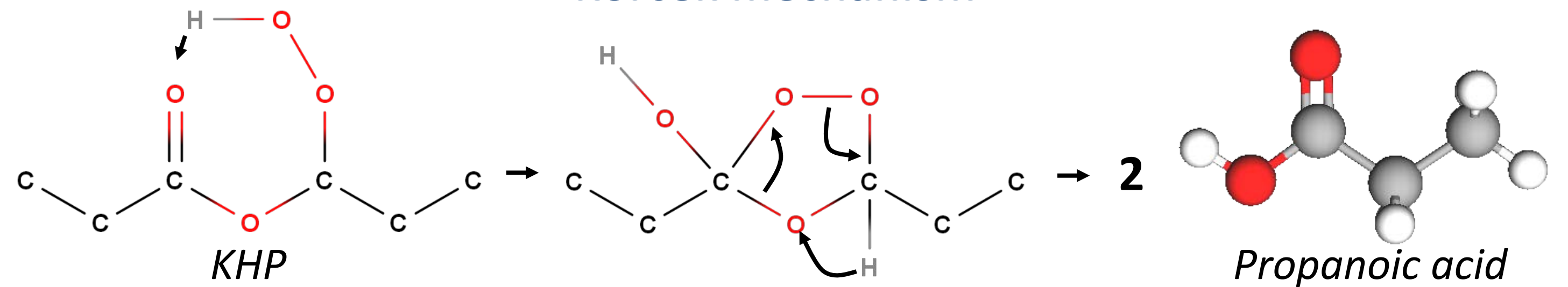
3rd O_2 addition:

$HOOPOOH + O_2 \rightleftharpoons (HOO)_2POO \rightleftharpoons (HOO)_2P'OOH \rightarrow OH + (HOO)_2P'=O (C_6H_{12}O_6)$

4th O_2 addition:

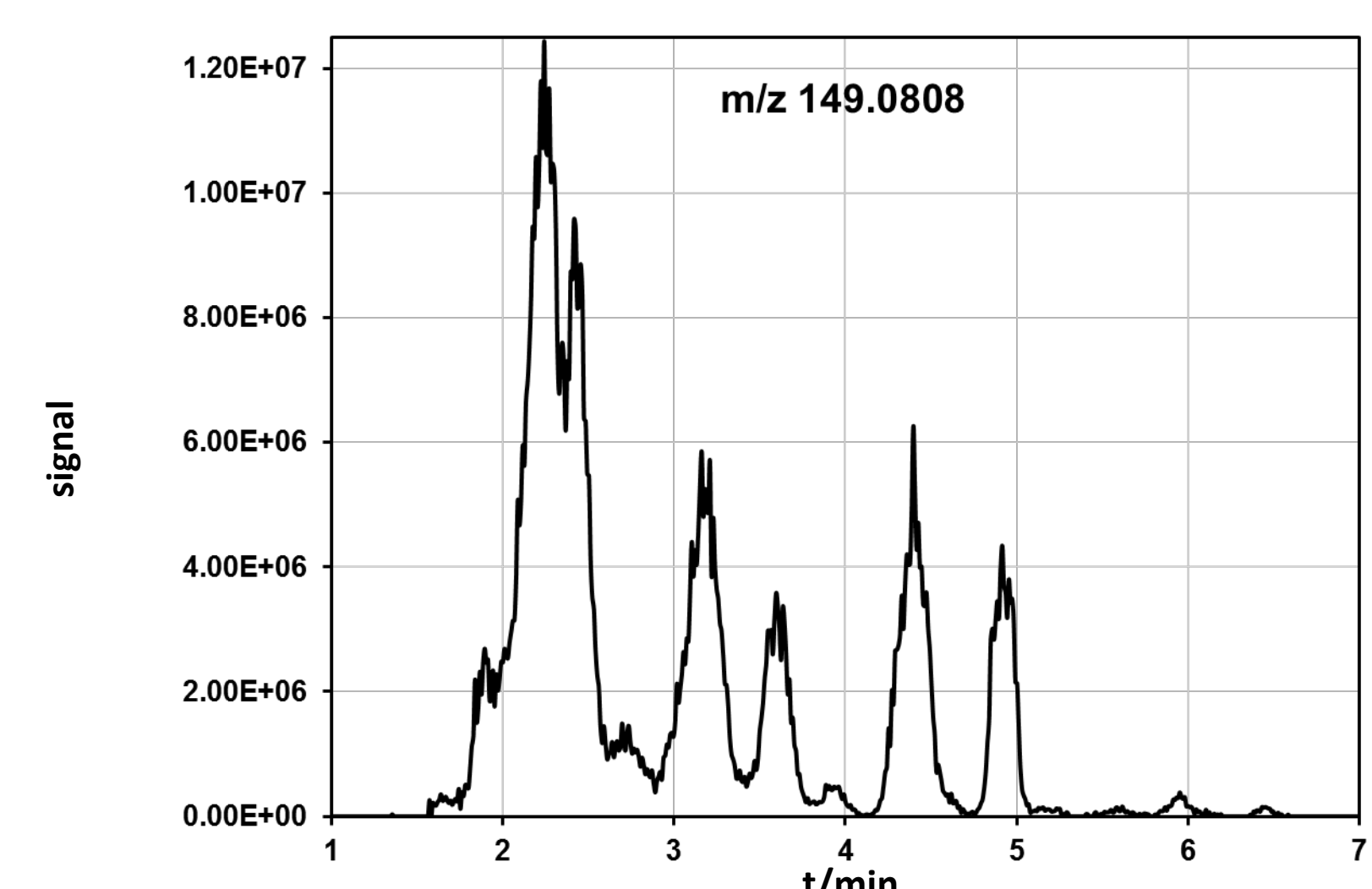
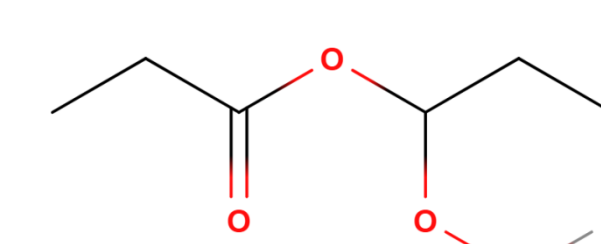
$(HOO)_2P'OOH + O_2 \rightleftharpoons (HOO)_3P''OO \rightleftharpoons (HOO)_3P''OOH \rightarrow OH + (HOO)_3P''=O (C_6H_{12}O_8)$

Korcek mechanism

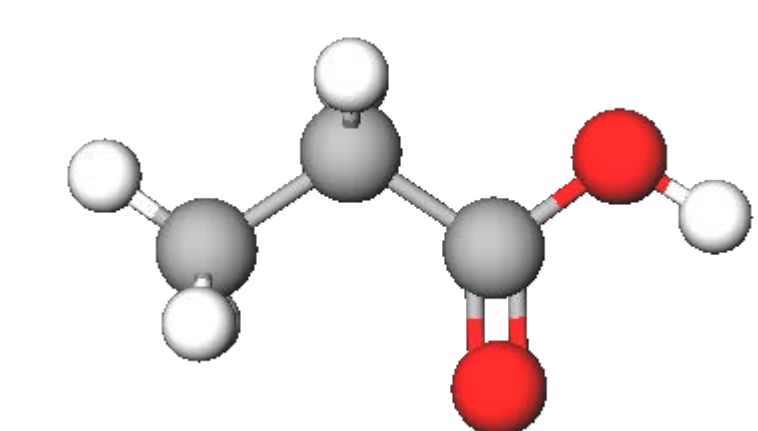


UHPLC analyses

Major KHP isomer:



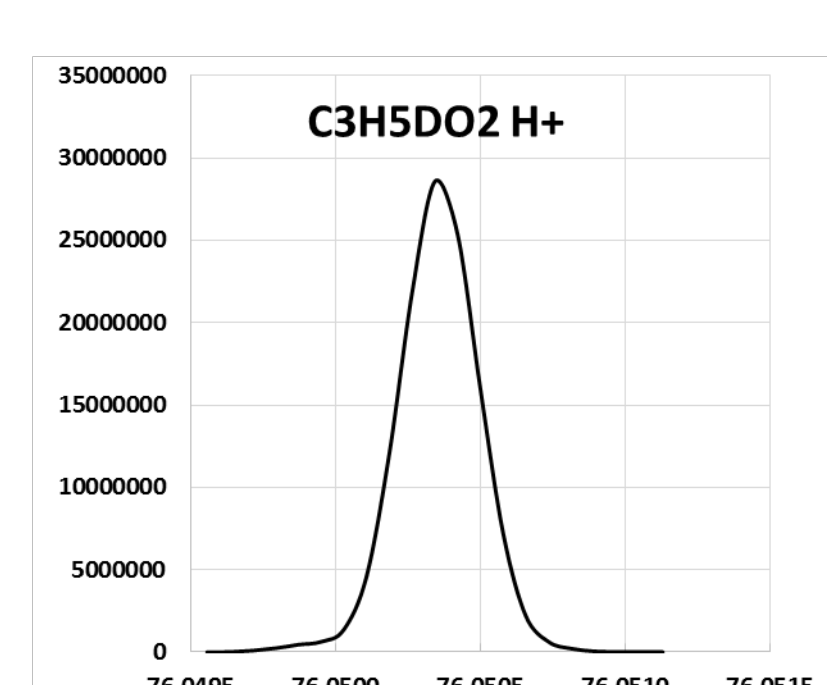
Korcek products



$C_3H_6O_2 : M$

MH^+ $m/z = 75.04406$ (77%)

MD^+ $m/z = 76.05033$ (23%)



Acknowledgements

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