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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.

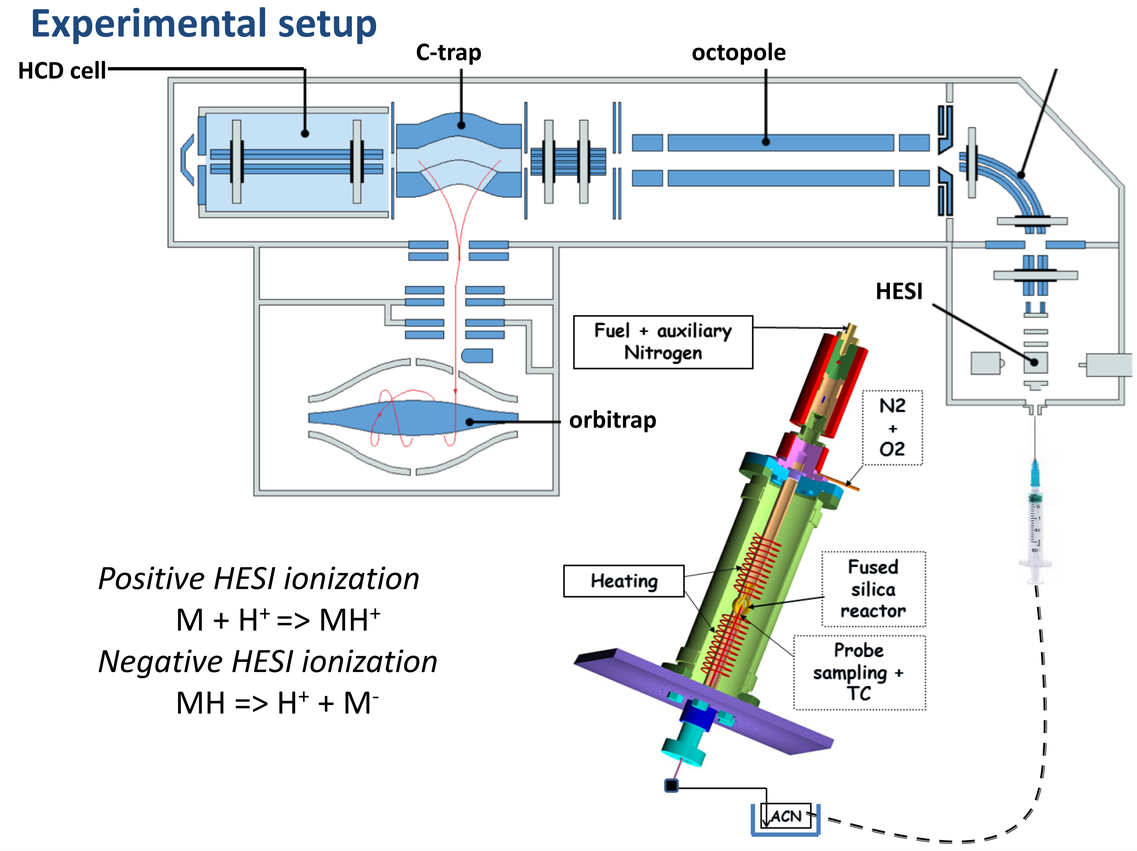
Experimental conditions

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, φ = 0.5, τ = 1 s

Experimental setup



Positive HESI ionization

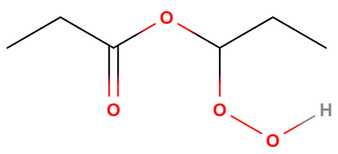
$M + H^+ \Rightarrow MH^+$

Negative HESI ionization

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

Results

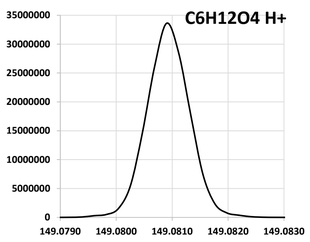
Ketohydroperoxides



$C_6H_{12}O_4$: M

MH^+ m/z= 149.08084

MNa^+ m/z= 171.06278



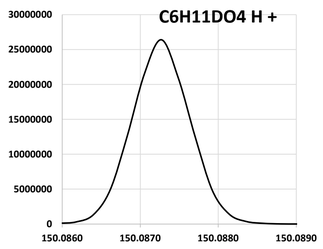
H/D exchange using D_2O: -OH ⟶ -OD to confirm the presence of -OOH

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

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

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

M*d*Na^+ m/z= 172.06906 (63%)



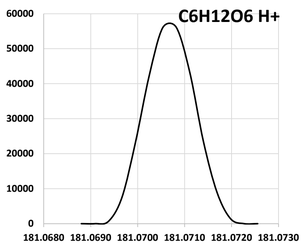
HOMs

$C_6H_{12}O_6$: M

MH^+ m/z= 181.07066

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

M*d*Na^+ m/z= 204.05889 (23%)

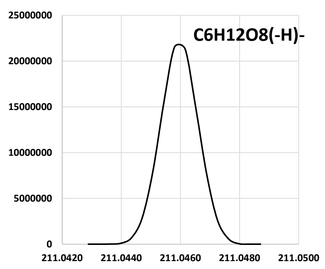


$C_6H_{12}O_8$: M

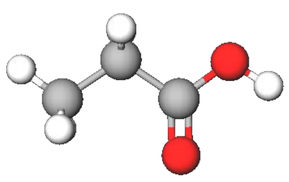
$M(-H)^-$ m/z= 211.04594

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

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



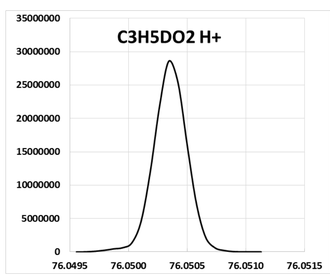
Korcek products



$C_3H_6O_2$: M

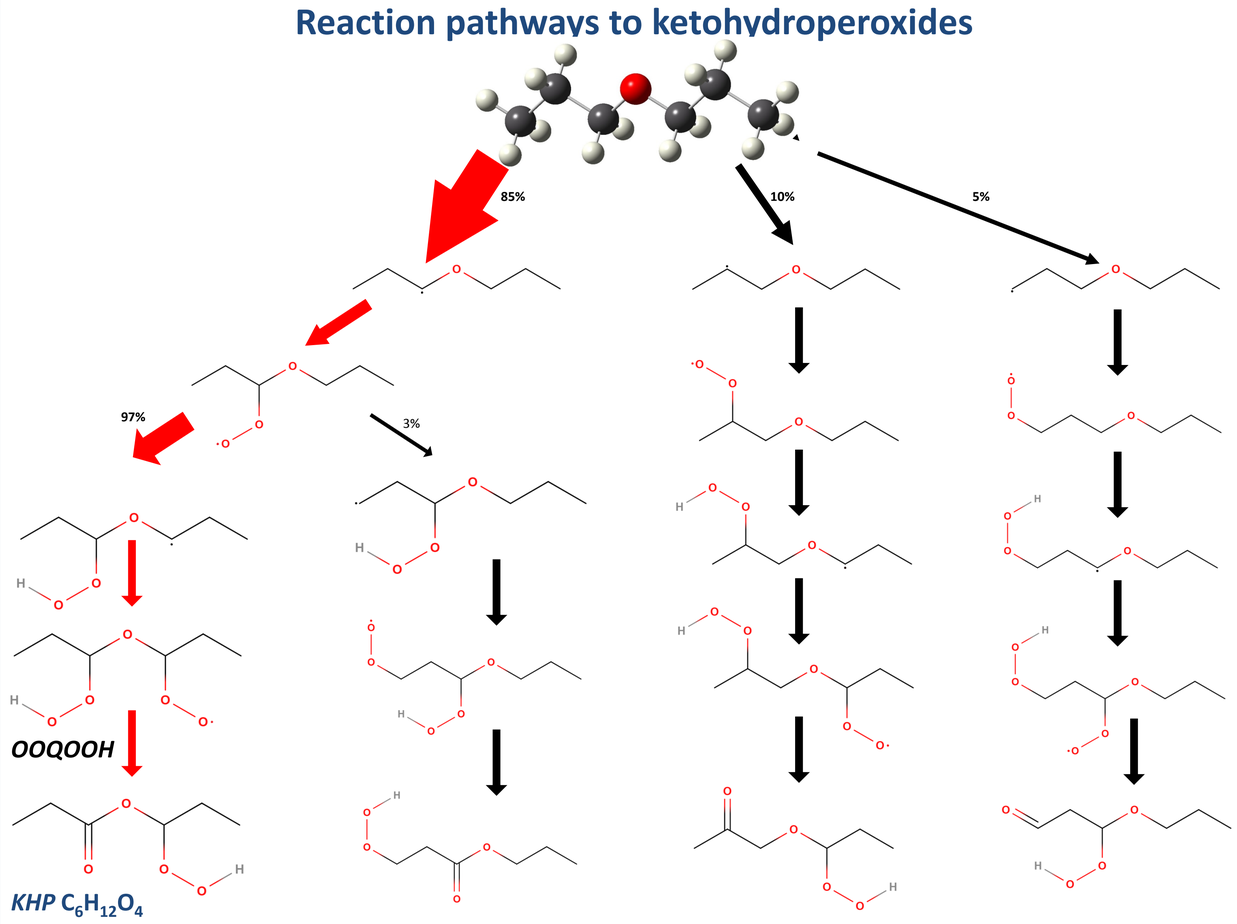
MH^+ m/z= 75.04406 (77%)

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



Dipropyl ether oxidation

Reaction pathways to ketohydroperoxides



HOMs formation mechanism

OOQOOH ⇆ HOOPOOH (alternative H-transfer, not from HC-OOH)

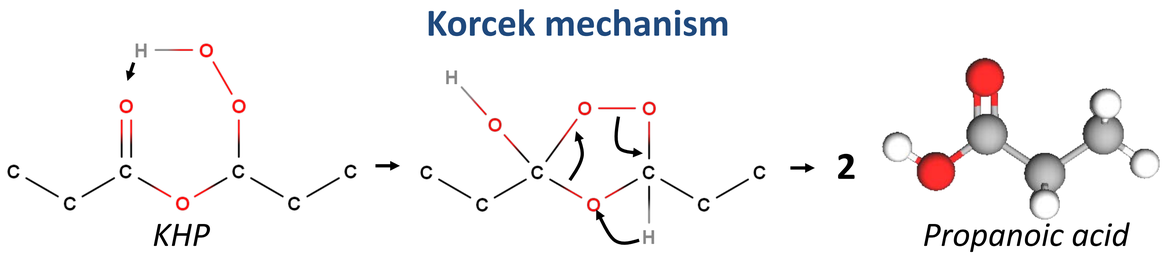
3rd O_2 addition:

$HOOPOOH + O_2$ ⇆ $(HOO)_2POO$ ⇆ $(HOO)_2P'OOH$ → $OH + (HOO)_2P'=O$ ($C_6H_{12}O_6$)

4th O_2 addition:

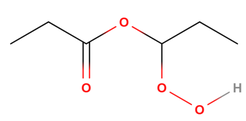
$(HOO)_2P'OOH + O_2$ ⇆ $(HOO)_3P''OO$ ⇆ $(HOO)_3P''OOH$ → $OH + (HOO)_3P''=O$ ($C_6H_{12}O_8$)

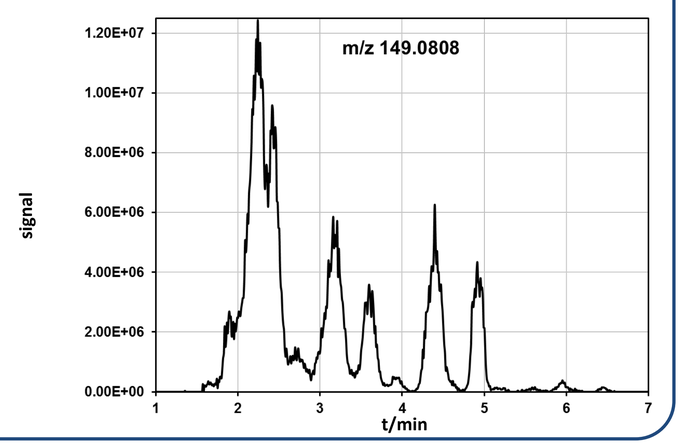
Korcek mechanism



UHPLC analyses

Major KHP isomer:





Acknowledgements

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