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

P. DAGAUT, N. BELHADJ, R. BENOIT, G. DAYMA, M. LAILLIAU, Z. SERINYEL
CNRS–INSIS, ICARE, 1C avenue de la Recherche Scientifique, Orléans, France
Université d’Orléans, Collegium Sciences et Techniques, 1 rue de Chartres, Orléans, France

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, \( \varphi = 0.5 \), \( \tau = 1 \) s.

Results

Ketohydroperoxides

\[ \text{C}_6\text{H}_{12}\text{O}_4: \text{M} \]
- \( \text{MH}^+ \) m/z = 149.08084
- \( \text{MNa}^+ \) m/z = 171.06278

H/D exchange using \( \text{D}_2\text{O} \): -OH \( \rightarrow \) -OD to confirm the presence of -OOH

- \( \text{MH}^+ \) m/z = 149.08084 (59%)
- \( \text{MD}^+ \) m/z = 150.08711 (41%)
- \( \text{MNa}^+ \) m/z = 171.06278 (37%)
- \( \text{MdNa}^+ \) m/z = 172.06906 (63%)

HOMs

\[ \text{C}_6\text{H}_{12}\text{O}_4: \text{M} \]
- \( \text{MH}^+ \) m/z = 181.07066
- \( \text{MNa}^+ \) m/z = 203.05261 (77%)
- \( \text{MdNa}^+ \) m/z = 204.05889 (23%)

\[ \text{C}_6\text{H}_{12}\text{O}_4: \text{M} \]
- \( \text{M}(-\text{H})^- \) m/z = 211.04594
- \( \text{M}(-\text{H})\text{HO}^- \) m/z = 229.05651
- \( \text{M}(-\text{H})\text{HCOO}^- \) m/z = 257.05142

Korcek products

\[ \text{C}_6\text{H}_{12}\text{O}_4: \text{M} \]
- \( \text{MH}^+ \) m/z = 75.04406 (77%)
- \( \text{MD}^+ \) m/z = 76.05033 (23%)

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