

# Experimental investigation of the low temperature oxidation of the five isomers of hexane

Zhandong WANG<sup>1,2</sup>, Olivier HERBINET<sup>1</sup>, Zhanjun Cheng<sup>2</sup>, Benoit HUSSON<sup>1</sup>, René Fournet<sup>1</sup>, Fei QI<sup>2</sup>, Frédérique BATTIN-LECLERC<sup>1</sup>

<sup>1</sup>Laboratoire Réactions et Génie des Procédés, Nancy Université, CNRS UPR 3349,  
BP 20451, 1 rue Grandville, 54000 Nancy, France

<sup>2</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China,  
Hefei, Anhui 230029, P. R. China.

## Supplemental data

- I. Comparison of GC and SVUV PIMS data for *n*-hexane, 2-methyl-pentane and 2,2-dimethyl-butane.
- II. Mass spectra of cyclic ethers which were not in databases.
- III. Structures of the parent cations obtained from the ionization of ketohydroperoxydes and diones.

# I. Comparison of GC and SVUV PIMS data for *n*-hexane, 2-methyl-pentane and 2,2-dimethyl-butane.

## 1. Comparison for *n*-hexane

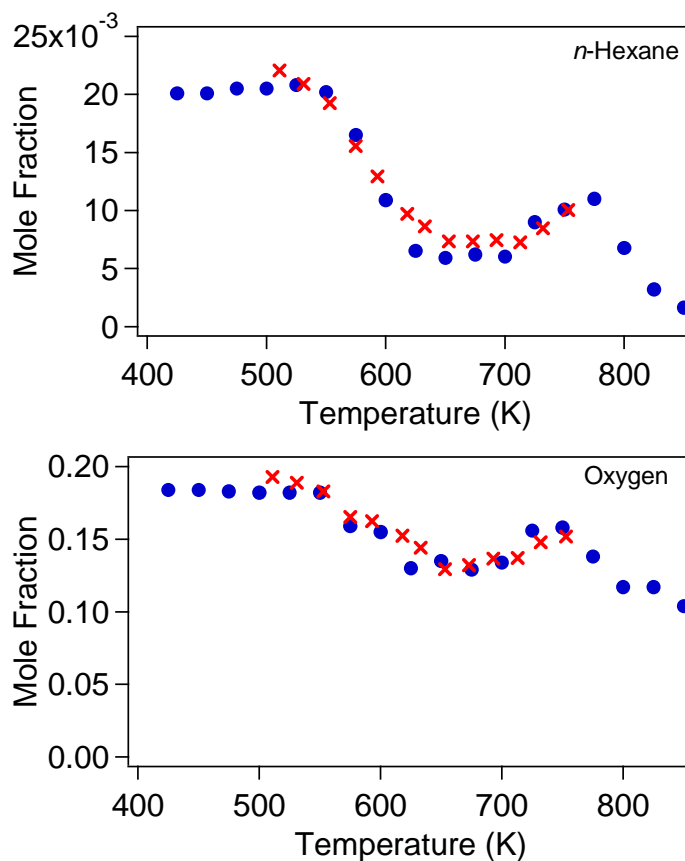


Figure S1: Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (×) for *n*-hexane and oxygen (fuel inlet mole fraction of 0.02). The signals recorded at 11 eV for  $m/z$  86 and at 16.6 eV for  $m/z$  32 were used for the quantification of *n*-hexane and oxygen, respectively.

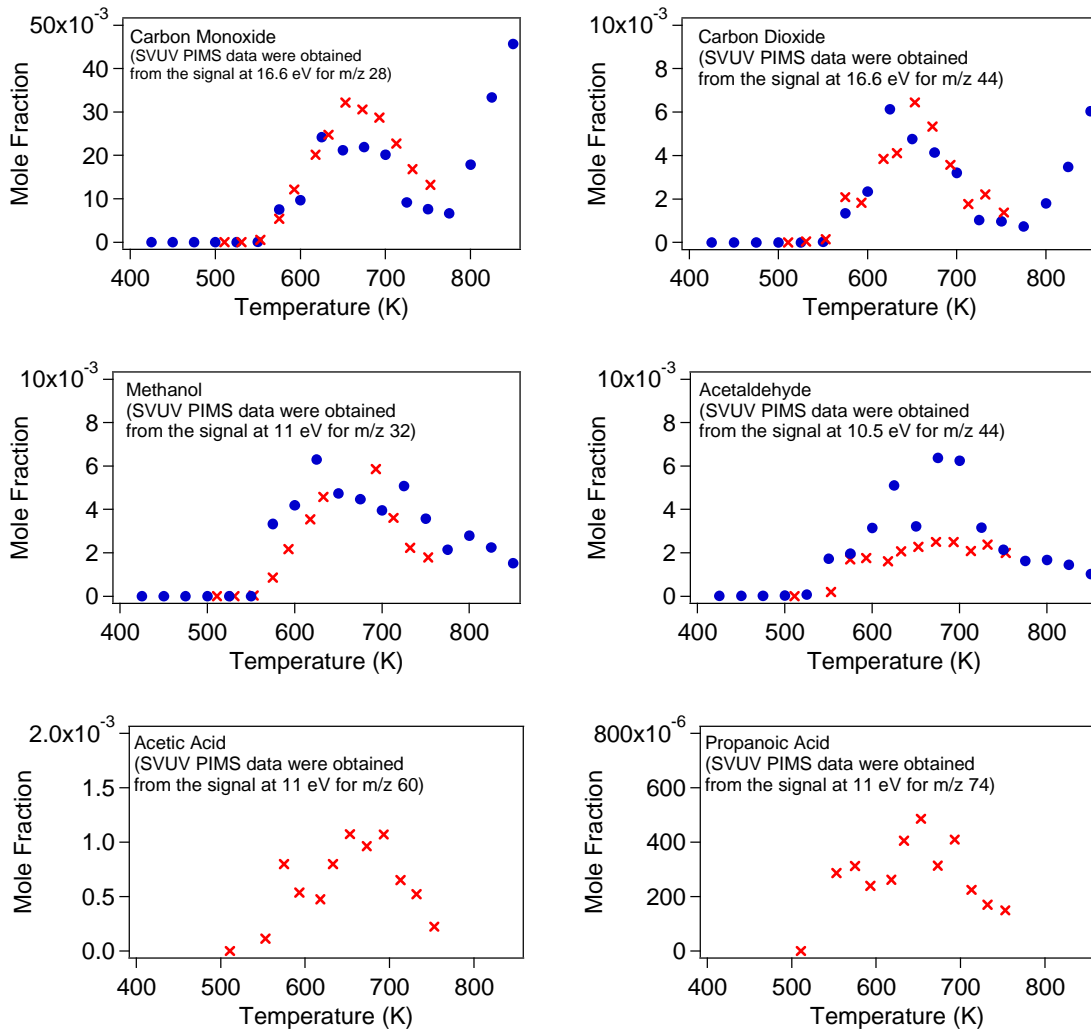


Figure S2: Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (×) for oxygenated reaction products (fuel inlet mole fraction of 0.02).

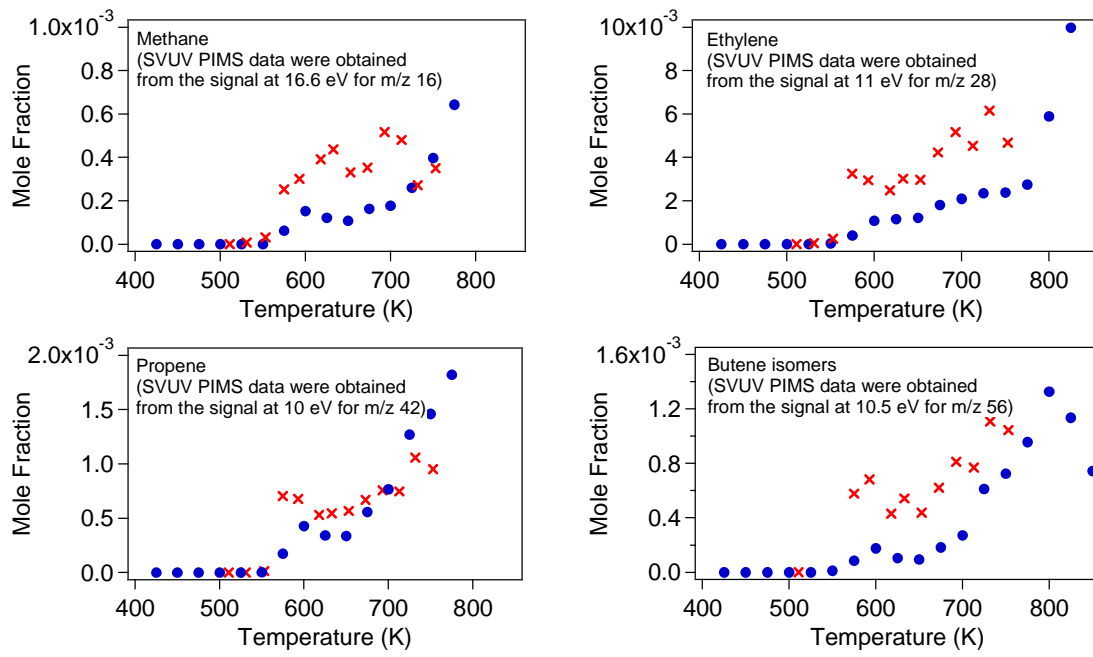


Figure S3: Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (x) for small hydrocarbon reaction products (fuel inlet mole fraction of 0.02).

## 2. Comparison for 2-methyl-pentane

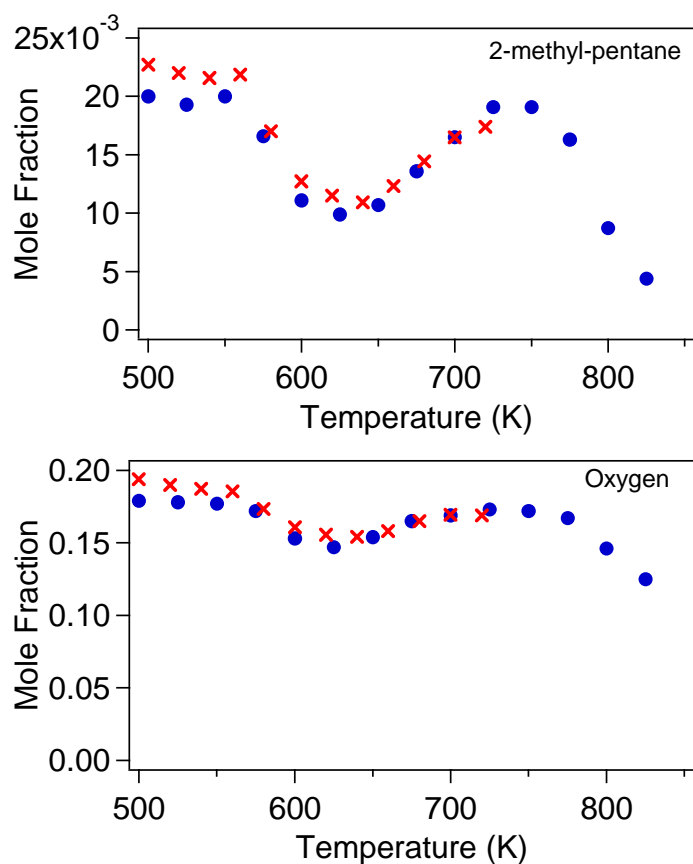


Figure S4: Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (×) for 3-methyl-pentane and oxygen (fuel inlet mole fraction of 0.02). The signals recorded at 11 eV for  $m/z$  86 and at 16.6 eV for  $m/z$  32 were used for the quantification of 2-methyl-pentane and oxygen, respectively.

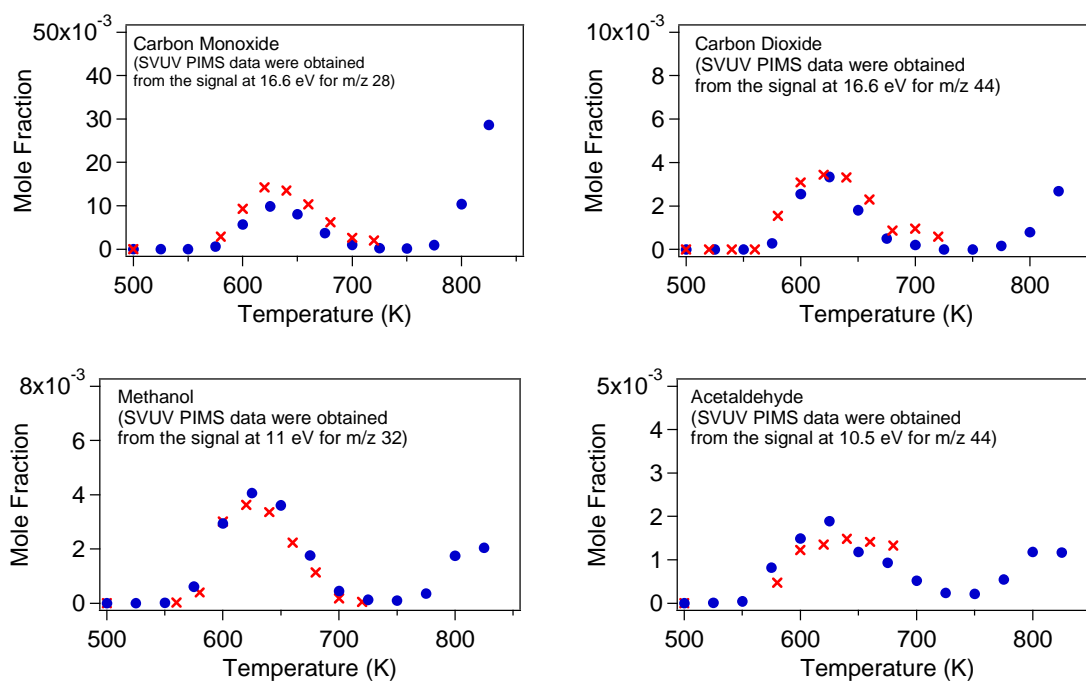


Figure S5: Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (×) for oxygenated reaction products (2-methyl-pentane inlet mole fraction of 0.02).

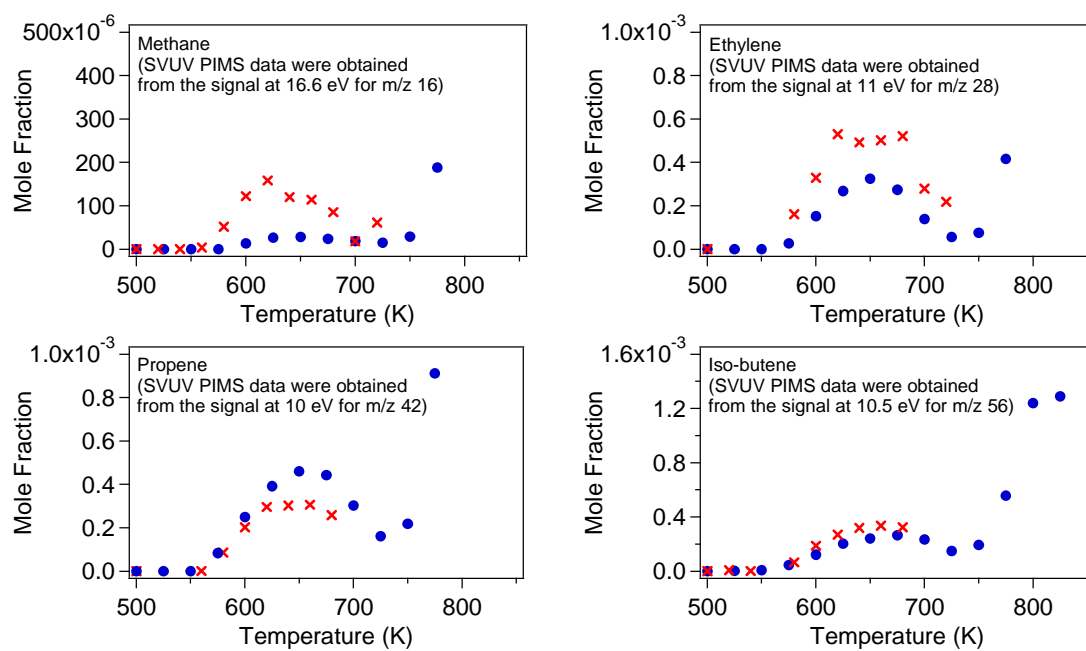
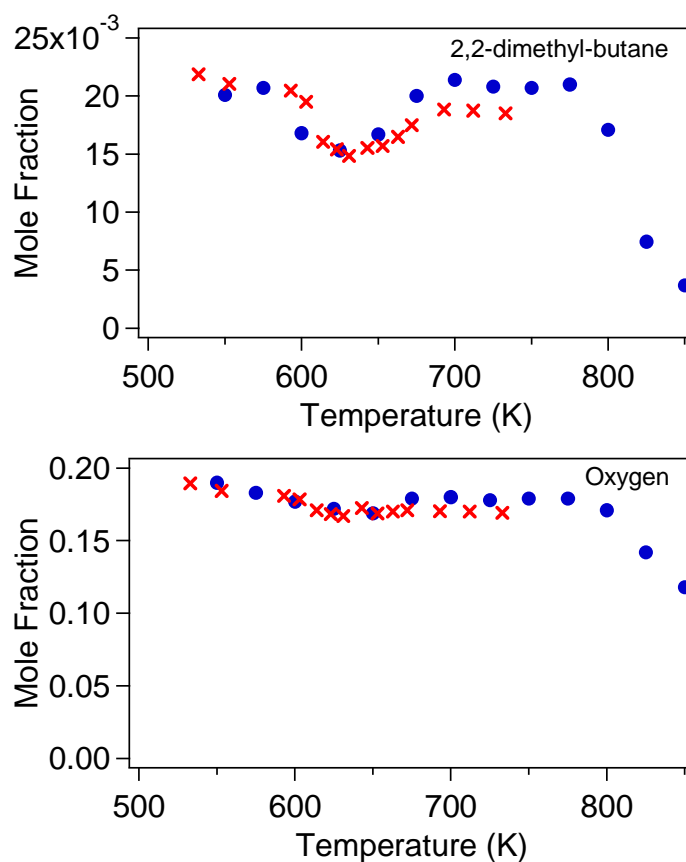


Figure S6: Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (×) for small hydrocarbon reaction products (2-methyl-pentane inlet mole fraction of 0.02).

### 3. Comparison for 2,2-dimethyl-butane



**Figure S7:** Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (×) for 2,2-dimethyl-butane and oxygen (fuel inlet mole fraction of 0.02). The signals recorded at 11 eV for  $m/z$  86 and at 16.6 eV for  $m/z$  32 were used for the quantification of 2,2-dimethyl-butane and oxygen, respectively.



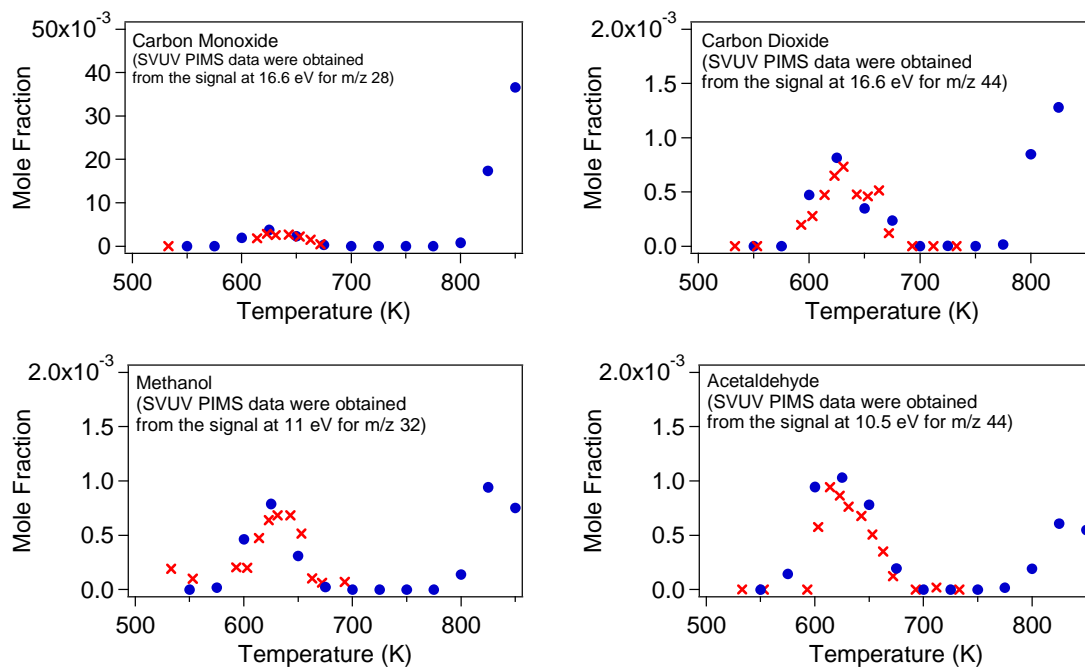


Figure S8: Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (×) for oxygenated reaction products (2,2-dimethyl-butane inlet mole fraction of 0.02).

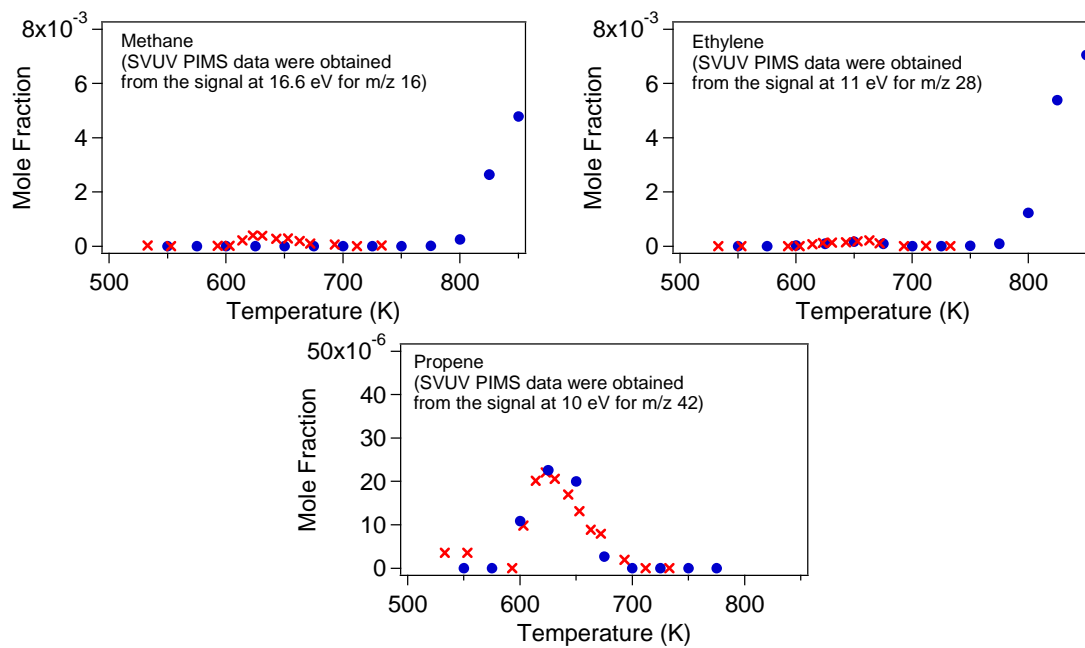


Figure S9: Comparison of mole fraction profiles obtained using gas chromatography (●) and SVUV-PIMS (×) for small hydrocarbon reaction products (2,2-dimethyl-butane inlet mole fraction of 0.02).

It was not possible to quantify *iso*-butene from the SVUV-PIMS data because the signal of *iso*-butene is masked by the large signal of the fragment at  $m/z$  56 coming from the decomposition of the fuel molecular ion.

## II. Mass spectra of cyclic ethers which were not in databases.

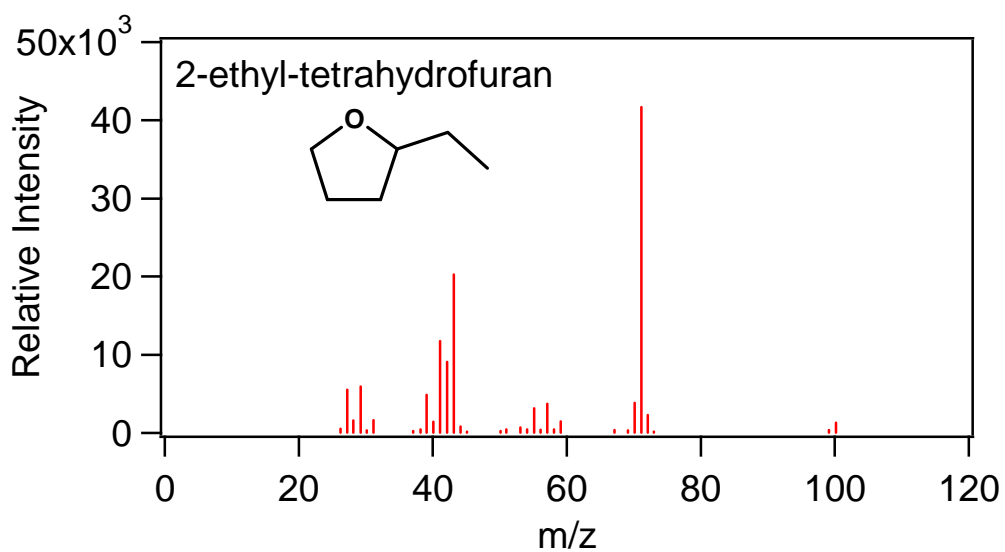


Figure S10: Mass spectrum of 2-ethyl-tetrahydrofuran (detected in the oxidation of *n*-hexane).

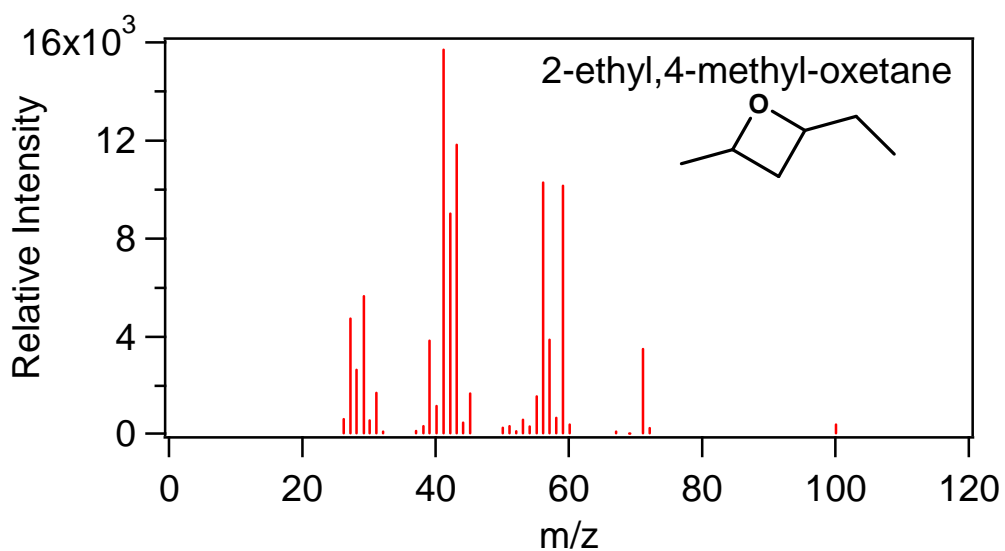


Figure S11: Mass spectrum of 2-ethyl,4-methyl-oxetane (detected in the oxidation of *n*-hexane).

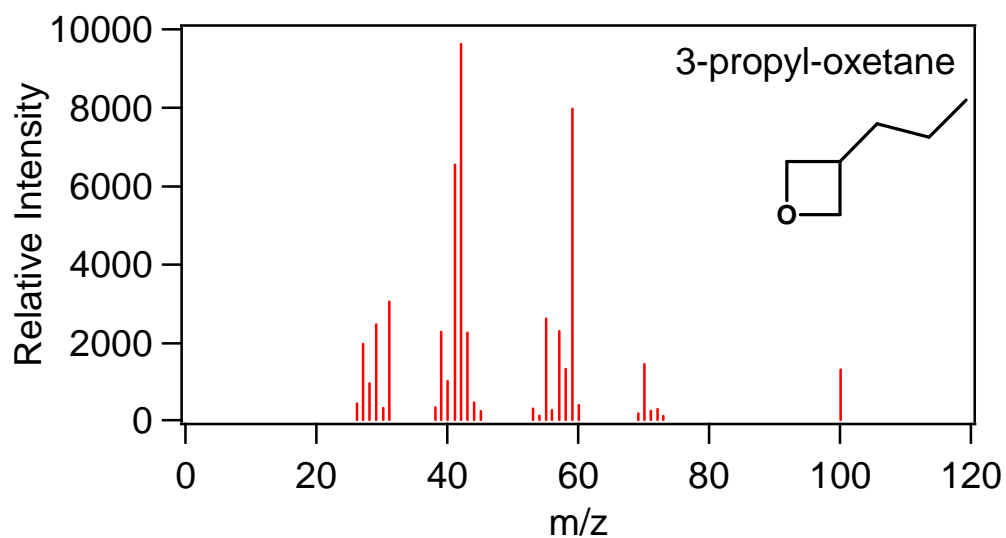


Figure S12: Mass spectrum of 3-propyl-oxetane (detected in the oxidation of 2-methyl-pentane).

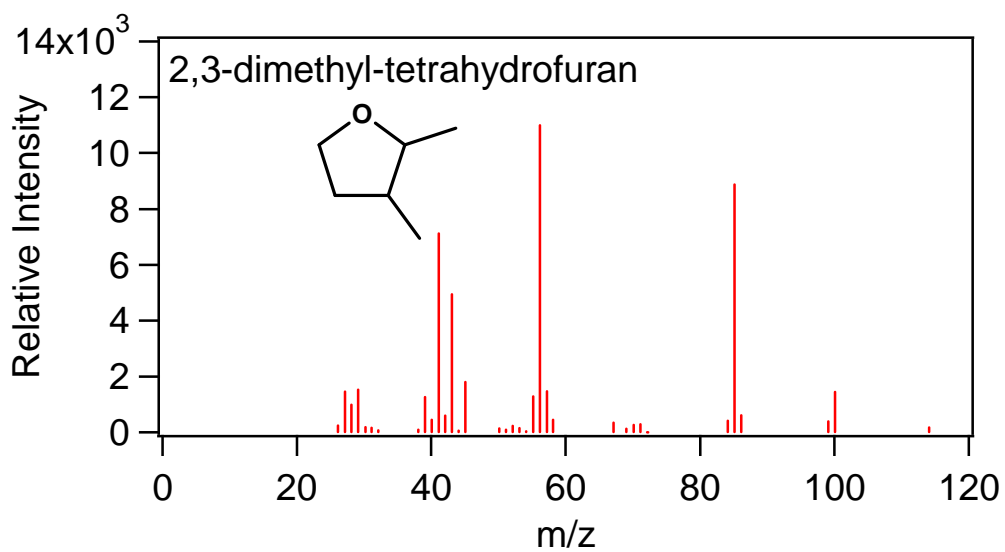


Figure S13: Mass spectrum of 2,3-dimethyl-tetrahydrofuran (detected in the oxidation of 3-methyl-pentane).

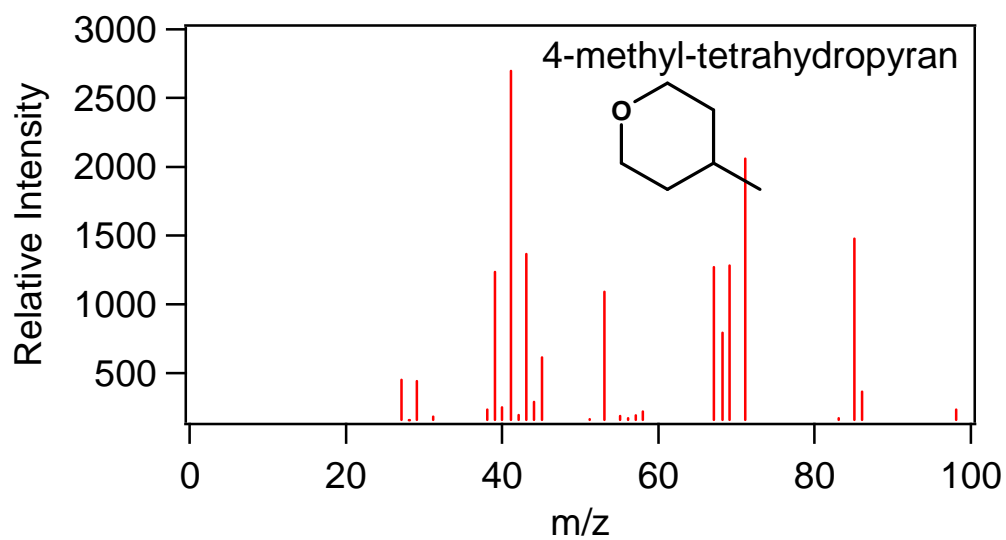


Figure S14: Mass spectrum of 4-methyl-tetrahydrofuran (detected in the oxidation of 3-methyl-pentane).

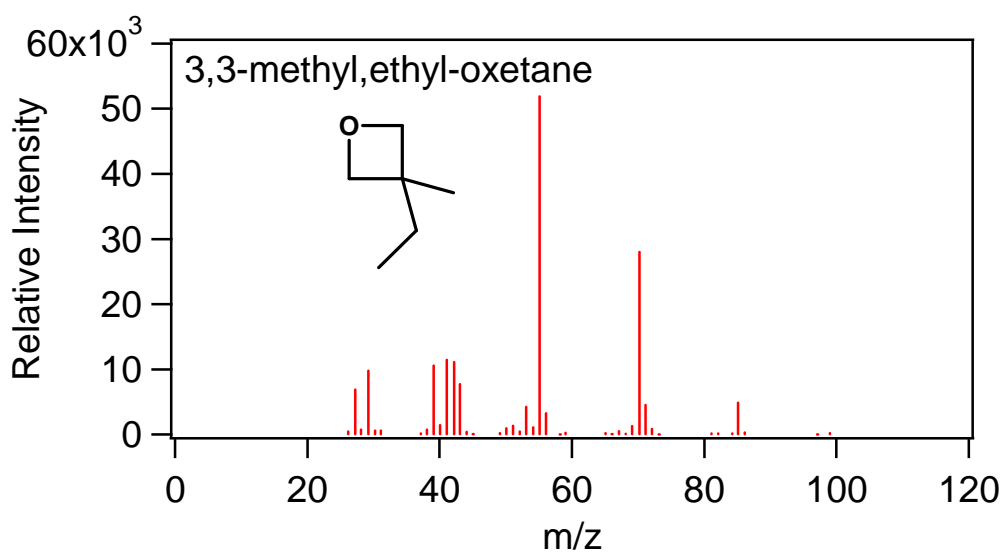


Figure S15: Mass spectrum of 3,3-methyl,ethyl-oxetane (detected in the oxidation of 2,2-dimethyl-butane).

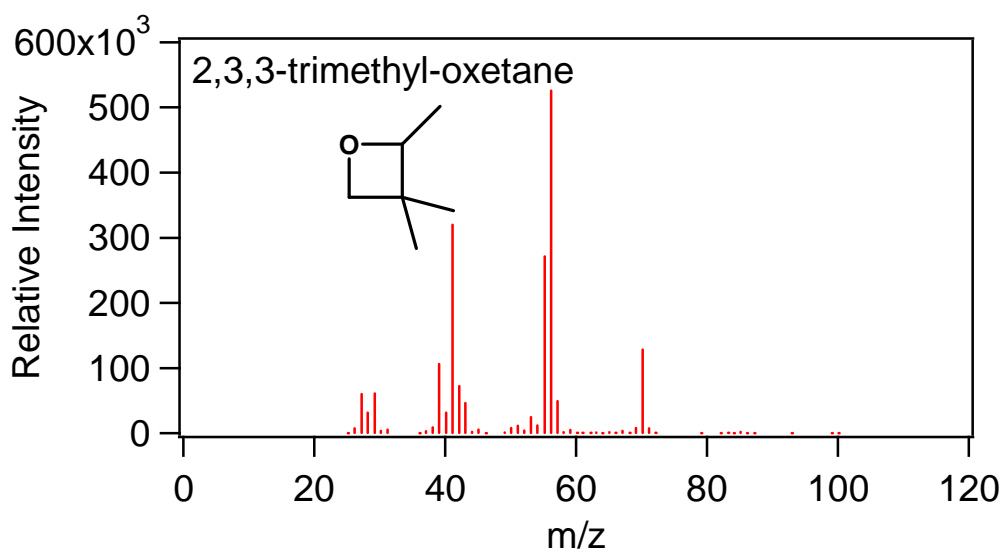


Figure S16: Mass spectrum of 2,3,3-trimethyl-oxetane (detected in the oxidation of 2,2-dimethyl-butane).

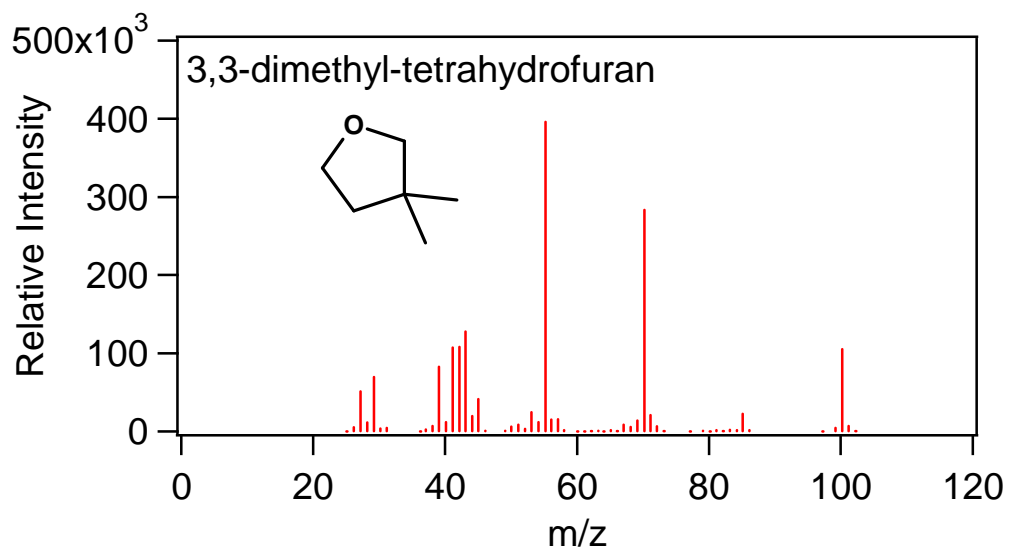

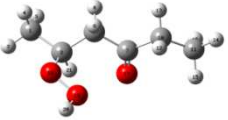








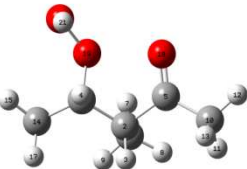

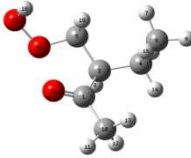
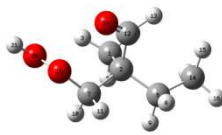




Figure S17: Mass spectrum of 3,3-dimethyl-tetrahydrofuran (detected in the oxidation of 2,2-dimethyl-butane).

### III. Structures of the parent cations obtained from the ionization of ketohydroperoxydes and diones.

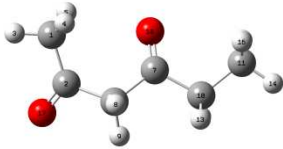
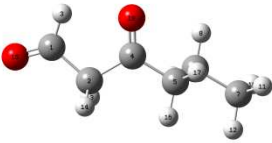

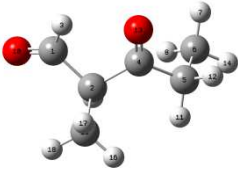


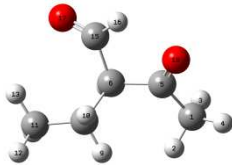

Table S1: Structures of the parent cation and calculated ionization energies of ketohydroperoxides detected during the oxidation of hexane isomers.

Name	Structure of the parent cation	Calculated ionization energy (eV)
<b>From <i>n</i>-hexane</b>		
4-hydroperoxyhexan-2-one		9.20
5-hydroperoxyhexan-3-one		9.50
1-hydroperoxyhexan-3-one		9.53
3-hydroperoxyhexanal		9.49
<b>From 2-methyl-pentane</b>		
4-methyl- 4-hydroperoxypentan-2-one		8.87
4-methyl- 3-hydroperoxypentanal		9.53
4-methyl- 1-hydroperoxypentan-3-one		8.95
2-methyl-3-hydroperoxypentanal		9.10

2-methyl-1-hydroperoxy pentan-3-one		9.36
<b>From 3-methyl-pentane</b>		
3-methyl-3-hydroperoxy –pentanal		9.21
3-methyl-4-hydroperoxy –pentan-2-one		9.18
2-ethyl-3-hydroperoxybutanal		9.04
3-(hydroperoxymethyl)pentan-2-one		9.26
<b>From 2,2-dimethyl-butane</b>		
2-(hydroperoxymethyl)-2-methylbutanal		9.12
2,2-dimethyl-3-hydroperoxybutanal		9.53
3,3-dimethyl-4-hydroperoxybutanone		9.33



**Table S2:** Structures and calculated ionization energies of diones detected during the oxidation of hexane isomers.

Name	Structure of the parent cation	Calculated ionization energy (eV)
<b>From <i>n</i>-hexane</b>		
2,4-hexadione		9.31
3-oxo-hexanal		9.37
<b>From 2-methyl-pentane</b>		
4-methyl-3-oxo-pentanal		9.26
2-methyl-3-oxo-pentanal		9.26
<b>From 3-methyl-pentane</b>		
3-methyl-2,4-pentadione		9.16
2-ethyl-3-oxobutanal		9.23
<b>From 2,2-dimethyl-butane</b>		
2-ethyl-2methylpropanedial		9.31
2,2-dimethyl-3-oxobutanal		9.13

