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# Formation of harmful oxygenated components during the oxidation of di-*n*-butyl ether as a potential biofuel candidate

2<sup>ème</sup> Journée Scientifique Climibio, 22.05.2019, Univ. Lille

## Introduction

- More than 80% of the world's primary energy supply is currently produced through combustion process. Fossil fuels still dominate energy supplies, ~90% worldwide, leading to large amounts of emissions of greenhouse gases CO<sub>2</sub>.
- The use of biofuels to substitute the fossil fuels has been identified as a sustainable solution for mitigating global CO<sub>2</sub> emissions and improving the energy security.
- Di-*n*-butyl ether (DBE) has been proposed as a promising biofuel for diesel engines [1] (e.g. a high cetane number and favorable heating value, Table 1). **However, emissions of harmful oxygenated components (e.g. aldehydes, acids, dions) from the oxidation of this fuel are still not well understood.**

	Diesel	DBE
Formula	C <sub>8</sub> -C <sub>25</sub>	C <sub>8</sub> H <sub>18</sub> O
Structure	C <sub>8</sub> -C <sub>25</sub> HC	
Boiling point (K)	443-633	414
Density (kg/m <sup>3</sup> )	833	770
Lower heating value LHV (MJ/kg)	42.9	38.4
Cetane number	54	~100

## Experimental methods

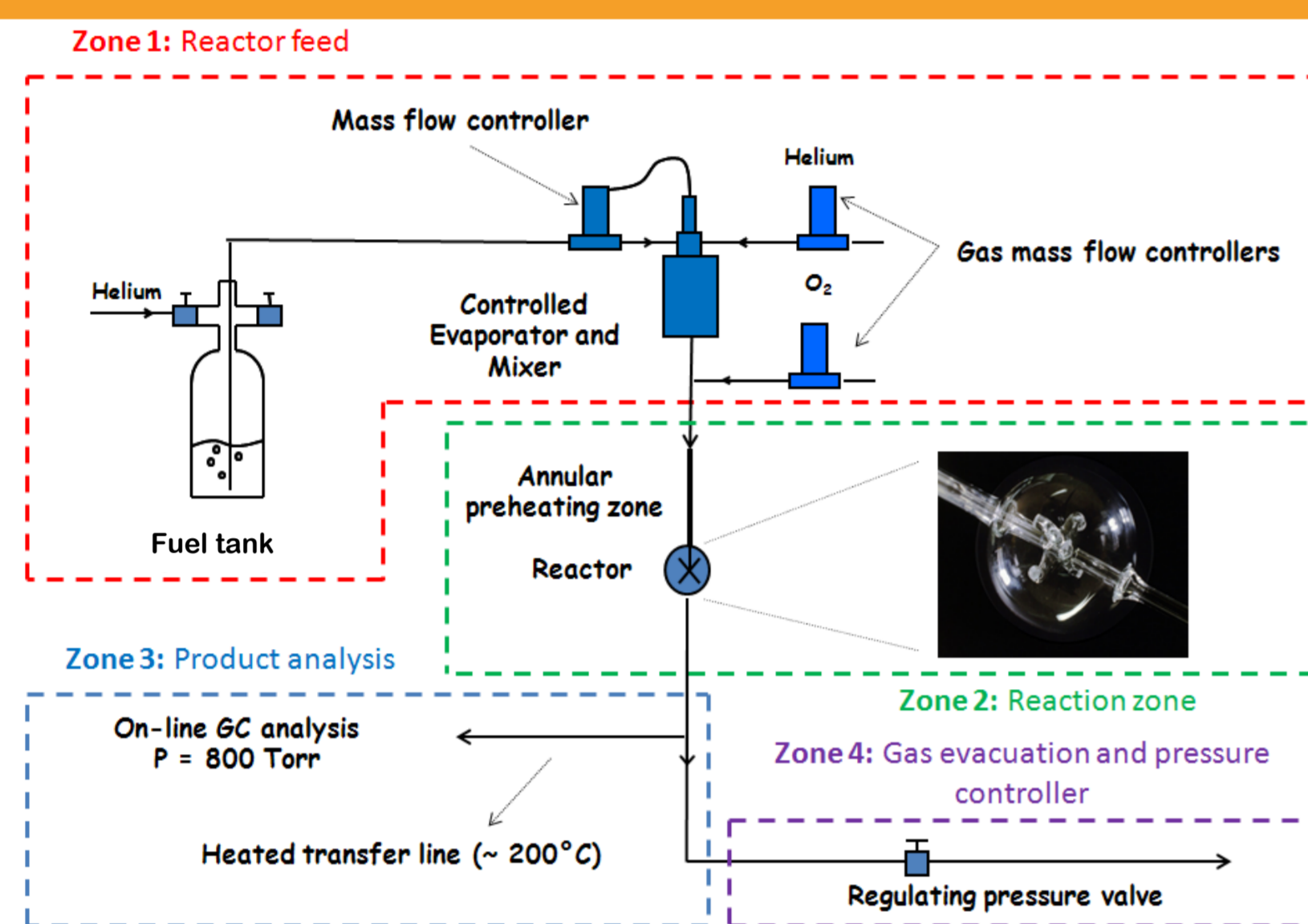


Fig. 1a JSR-GC system at LRGP-CNRS Nancy

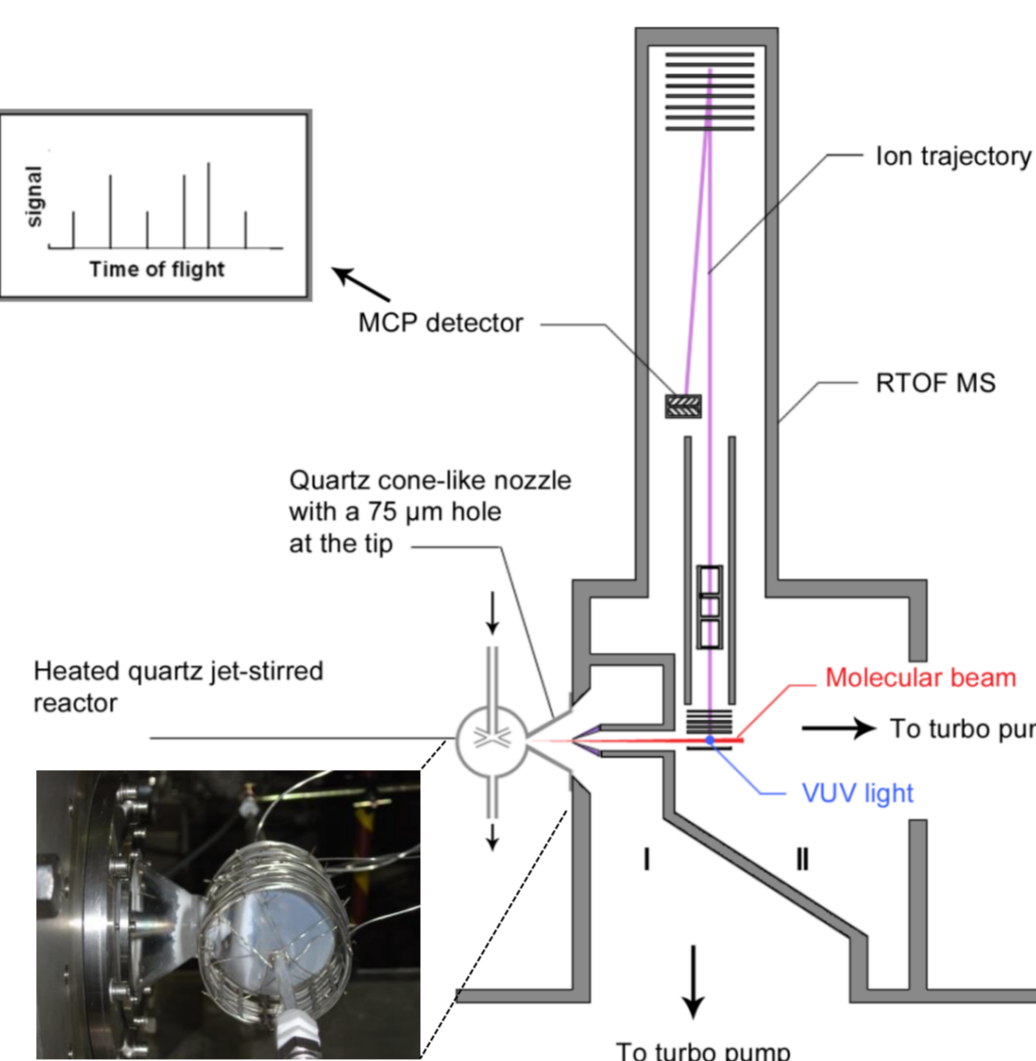


Fig. 1b JSR-PI-MBMS system at NSRL Hefei

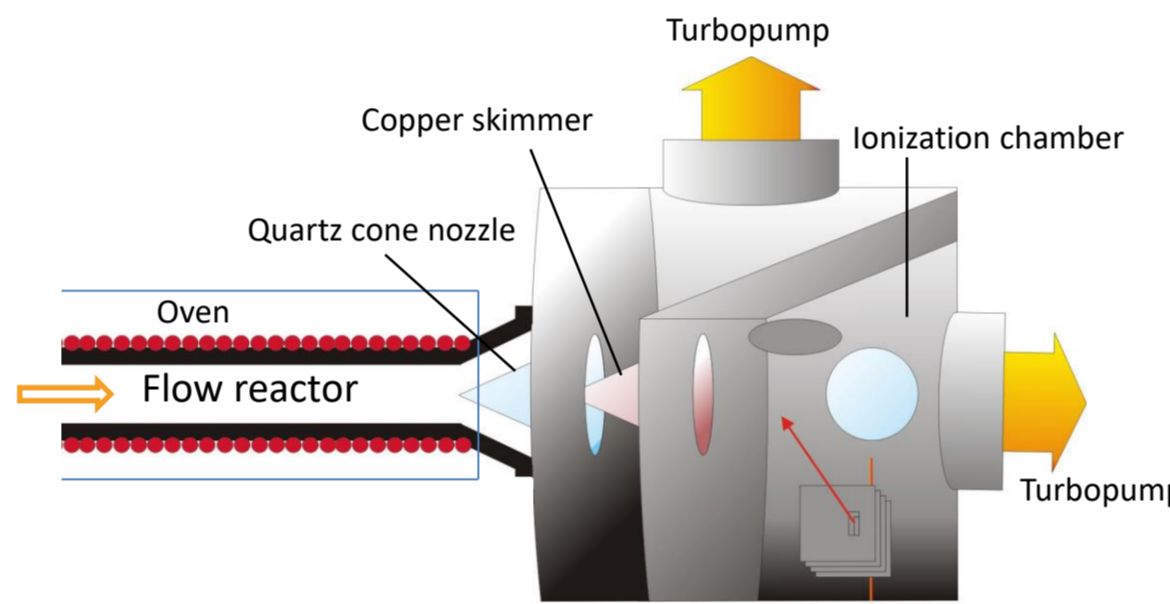


Fig. 1c PFR-EI-MBMS system at Bielefeld University

### Atmospheric jet-stirred reactor (JSR) experiments:

- Experimental conditions are given in Table 2.
- Analysis of chemical species:
  - gas chromatographs (GC) (Fig. 1a) with 3 columns, coupled to a thermal conductivity detector, a flame ionization detector/methanizer, and a mass spectrometric detector [2].
  - tunable synchrotron vacuum ultraviolet photoionization molecular-beam mass spectrometry (SVUV-PI-MBMS) (Fig. 1b) with energy resolution  $E/\Delta E \approx 4000$  and mass resolution  $m/\Delta m \approx 2500$  [3].

### Atmospheric plug-flow reactor (PFR) experiment:

- Experimental conditions are summarized in Table 2.
- Analysis of chemical species by electron ionization (EI)-MBMS at 17 eV with mass resolution  $m/\Delta m \approx 2200$  (Fig. 1c) [4].

Reactor	$\phi$	t (s)	T (K)	Initial gas mole fraction			GC
				He or Ar <sup>a</sup>	O <sub>2</sub>	DBE	
JSR	1	2	435-1100	0.870	0.12	0.01	GC
PFR	1	2 <sup>b</sup>	448-1015	0.935	0.06	0.005	EI-MBMS
	0.7	2 <sup>b</sup>	448-900	0.909	0.086	0.005	EI-MBMS

<sup>a</sup> He: GC experiments, Ar: MBMS experiments. <sup>b</sup> at ~1000 K

## Results

### Observation of an unusual oxidation behavior: two negative-temperature coefficient (NTC) zones

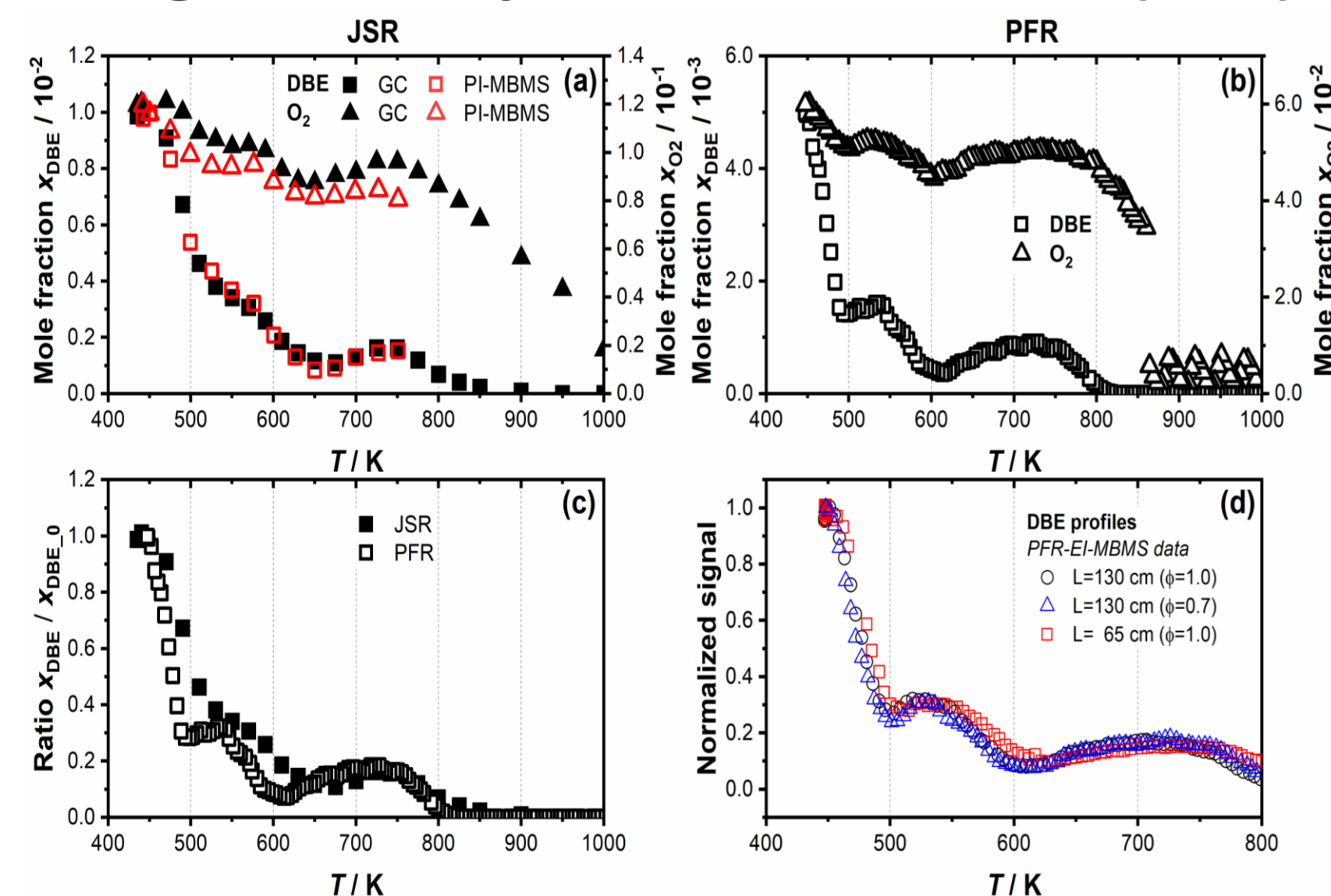


Fig. 2. Experimental mole fraction profiles of DBE and O<sub>2</sub>. (a) JSR ( $\phi=1.0$ , 1% DBE), (b) PFR ( $\phi=1.0$ , 0.5% DBE), (c) DBE profile in JSR-GC and PFR-EI-MBMS experiments, (d) DBE profiles for different  $\phi$  and PFR lengths  $L$ . Profiles in (c) and (d) are normalized by the respective inlet DBE mole fractions.

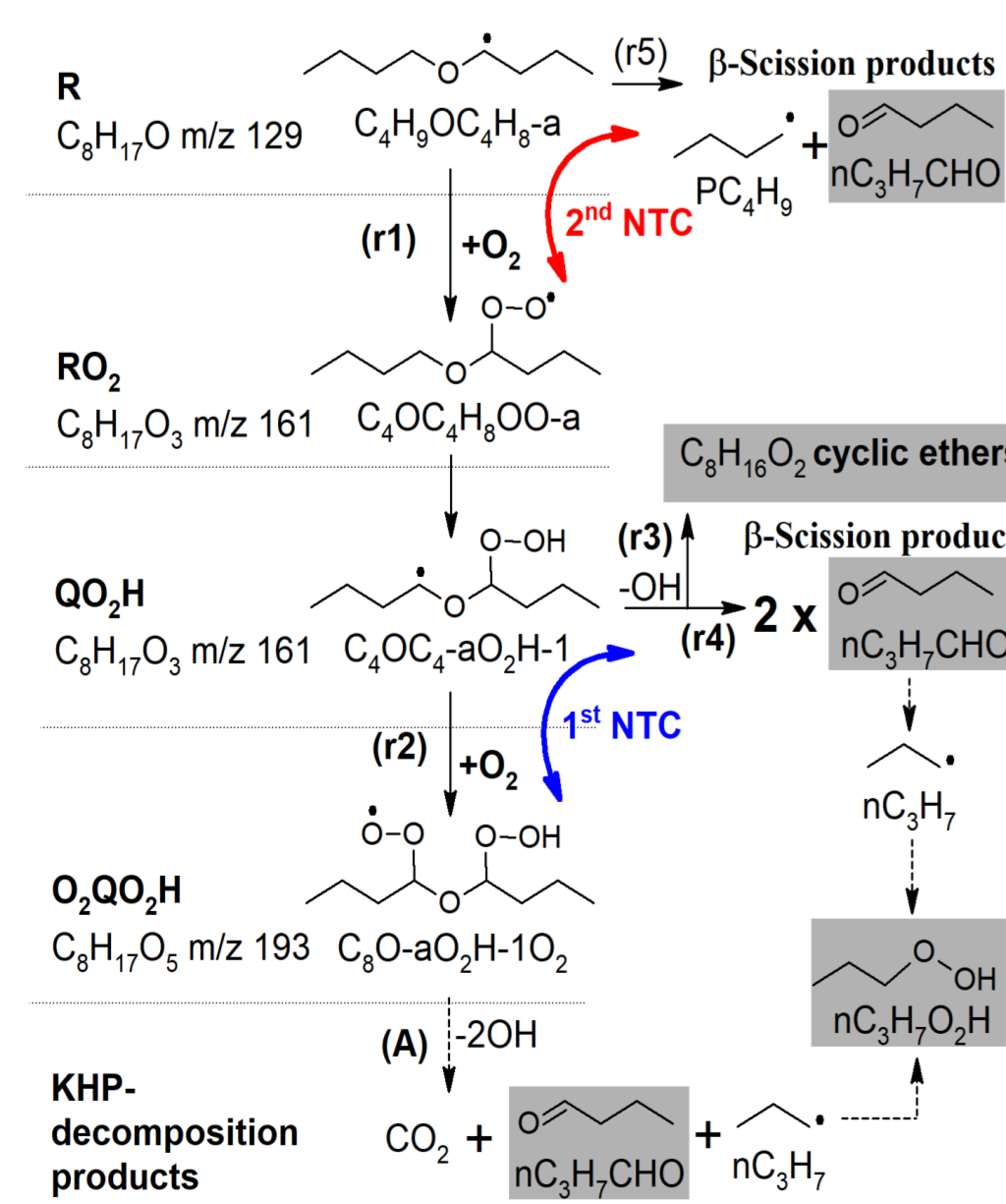


Fig. 3. Proposed mechanism of DBE oxidation resulting in two NTC zones. Dashed arrows represent series of reactions.

### Detection of previously unobserved oxygenated components

#### Acids

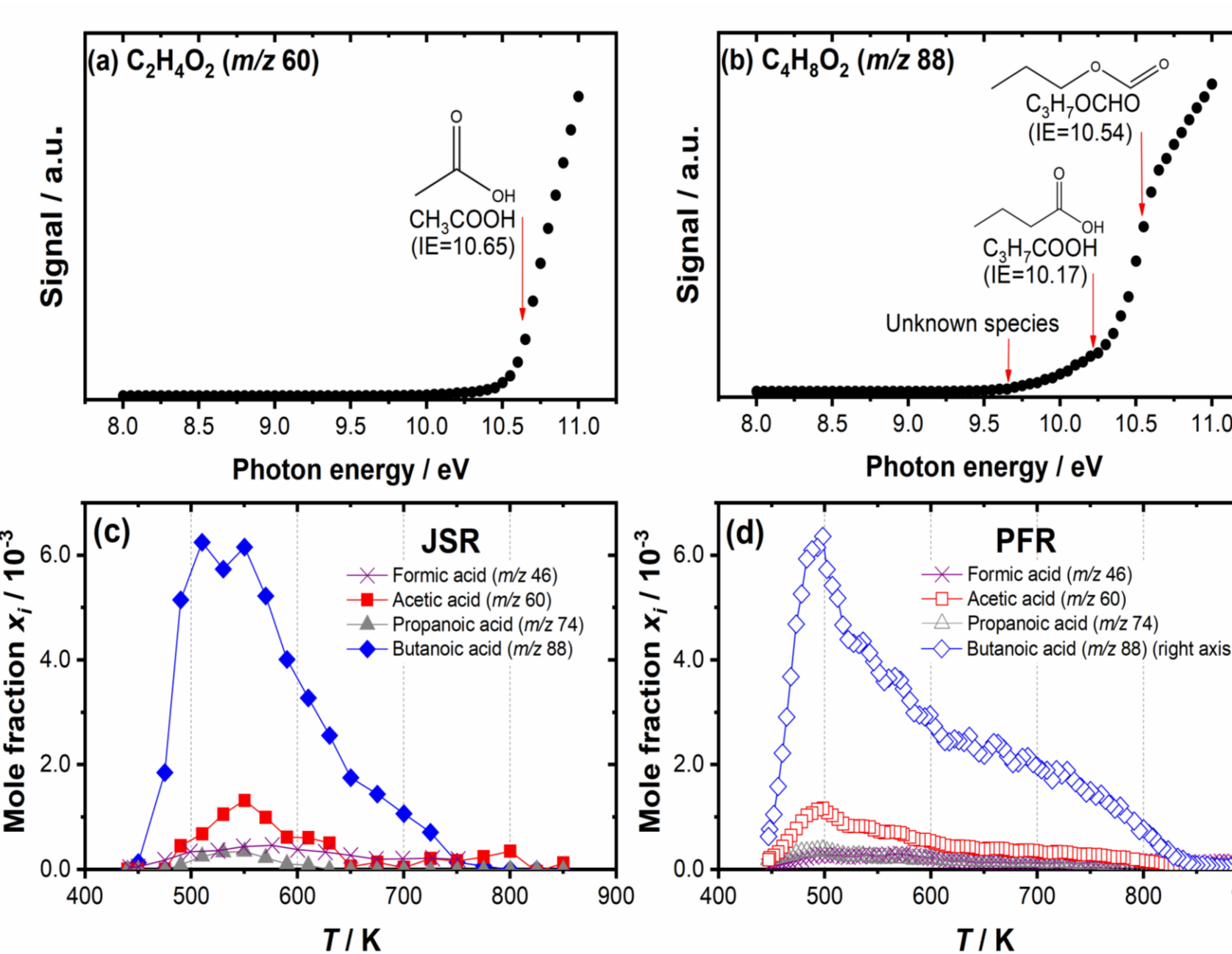


Fig. 4. Photoionization efficiency curves at 500 K from the JSR-PI-MBMS experiment for  $m/z$  60 (a) and 88 (b), corresponding to acetic acid (CH<sub>3</sub>COOH) and butanoic acid (C<sub>3</sub>H<sub>7</sub>COOH), respectively. Profiles of the detected acids: (c) JSR, (d) PFR.

#### C<sub>8</sub>H<sub>16</sub>O<sub>2</sub> cyclic ethers

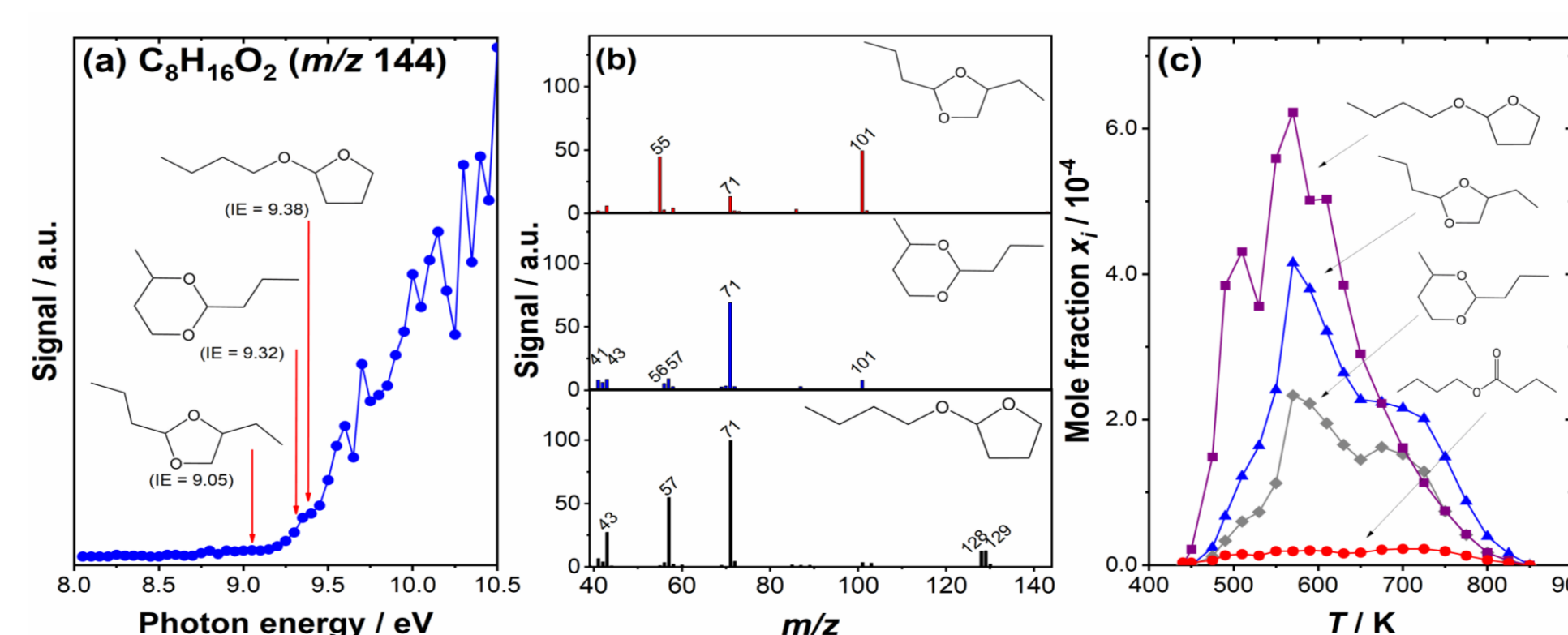


Fig. 5. (a) PIE curves for the C<sub>8</sub>H<sub>16</sub>O<sub>2</sub> cyclic ethers, (b) fragmentation mass spectra from GC-MS, (c) mole fraction profiles of the C<sub>8</sub>H<sub>16</sub>O<sub>2</sub> isomers identified by the JSR-GC experiments.

#### Diones (C<sub>8</sub>H<sub>14</sub>O<sub>3</sub>)

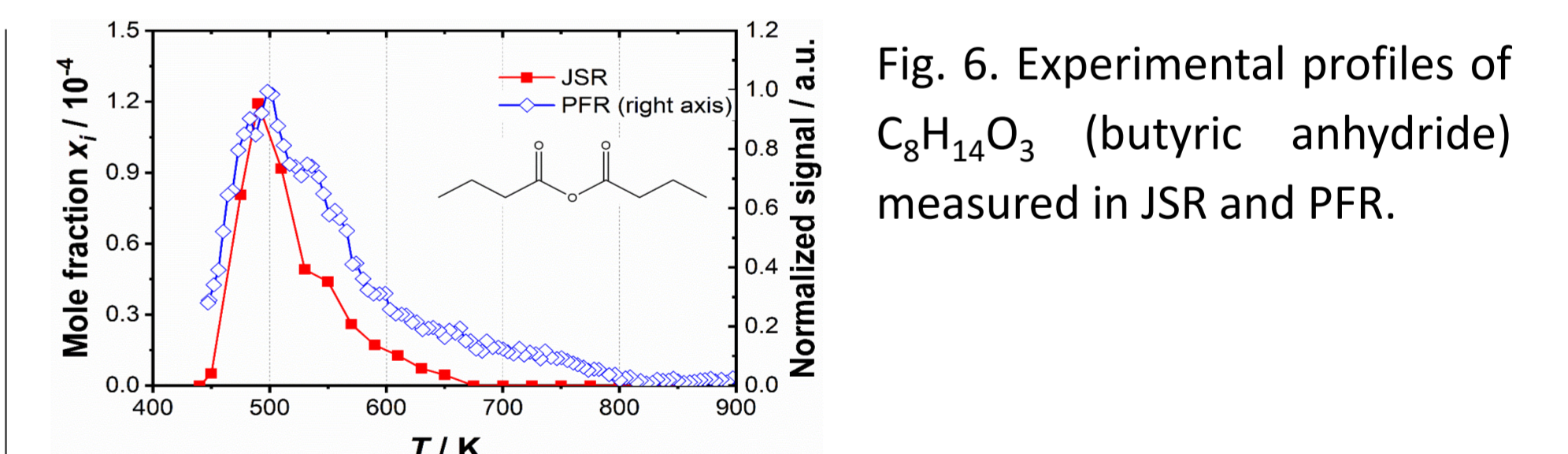


Fig. 6. Experimental profiles of C<sub>8</sub>H<sub>14</sub>O<sub>3</sub> (butyric anhydride) measured in JSR and PFR.

#### Highly-oxygenated reactive species

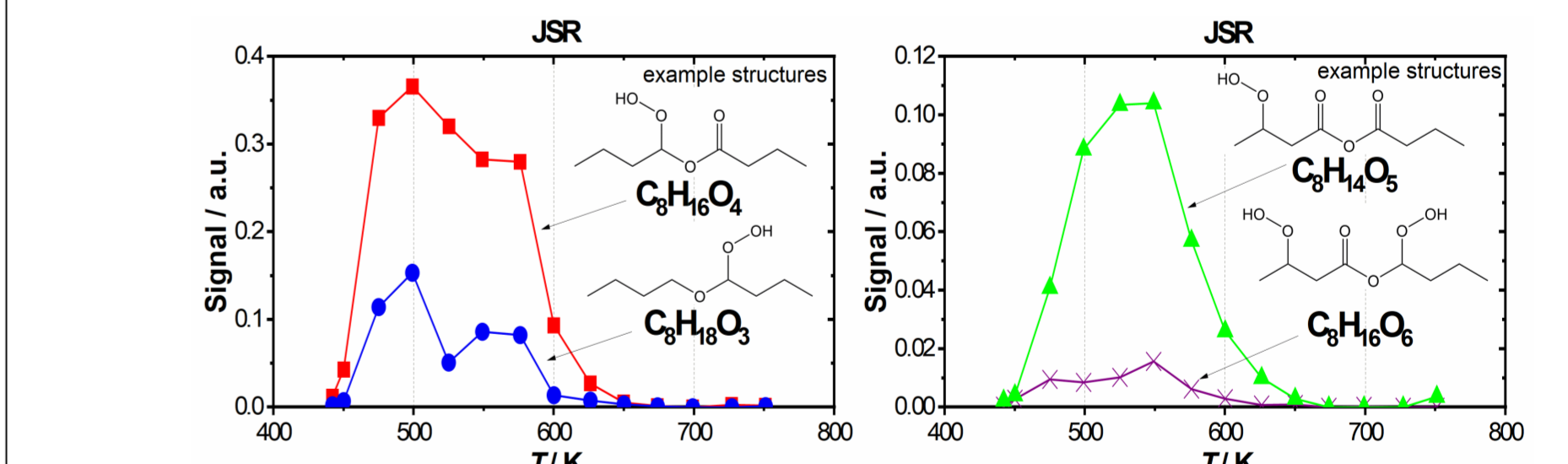


Fig. 7. Profiles of fuel-specific peroxides: hydroperoxides C<sub>8</sub>H<sub>18</sub>O<sub>3</sub> (products of the first O<sub>2</sub> addition), keto-hydroperoxides C<sub>8</sub>H<sub>16</sub>O<sub>4</sub> (products of the second O<sub>2</sub> addition), di-keto-hydroperoxides C<sub>8</sub>H<sub>14</sub>O<sub>5</sub> and keto-di-hydroperoxides C<sub>8</sub>H<sub>16</sub>O<sub>6</sub> (products of the third O<sub>2</sub> addition).

#### Examples of newly-proposed reaction pathways

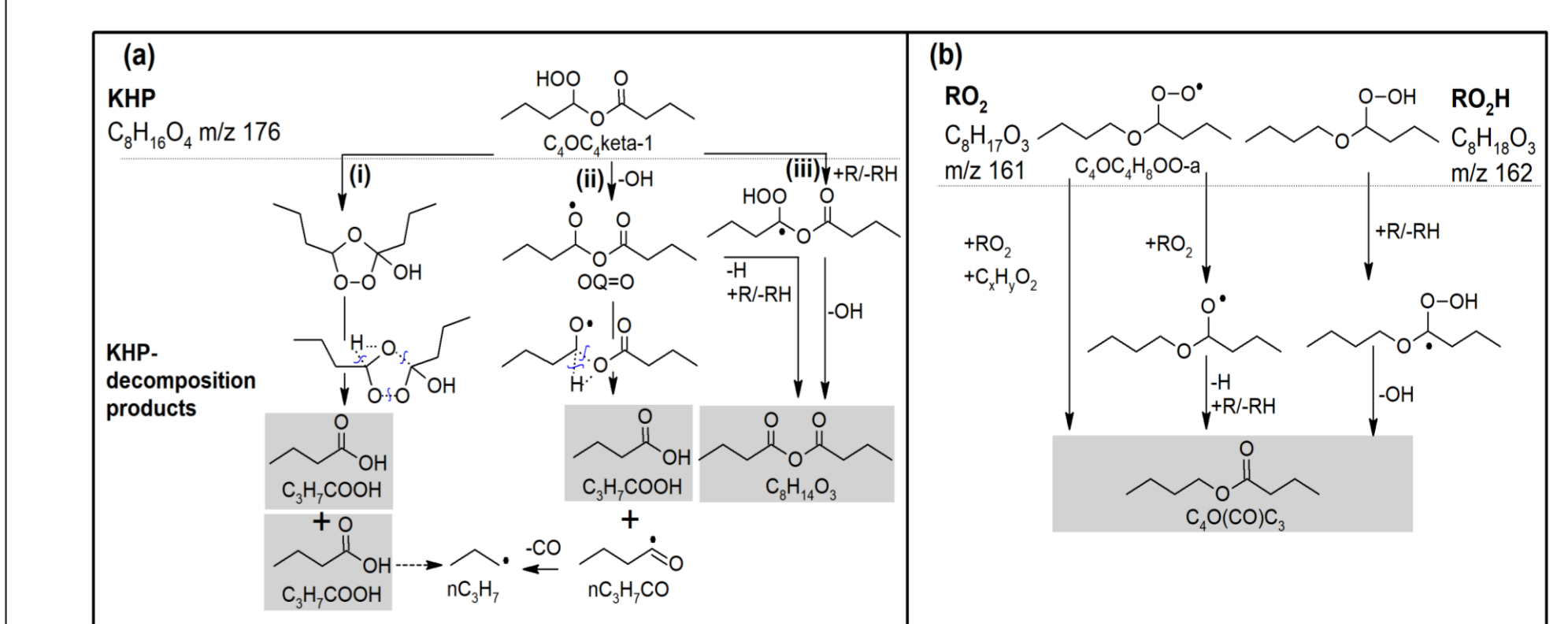


Fig. 8. Newly-proposed paths for DBE LT mechanism. (a) Formation of butanoic acid (C<sub>3</sub>H<sub>7</sub>COOH) and butyric anhydride (C<sub>8</sub>H<sub>14</sub>O<sub>3</sub>). (b) Formation of *n*-butyl butanoate (C<sub>4</sub>O(CO)C<sub>3</sub>).

## Acknowledgements

## References

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