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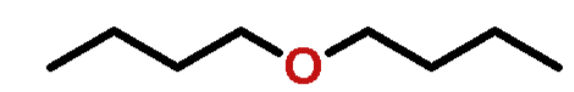
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Formation of harmful oxygenated components during the oxidation of di-*n*-butyl ether as a potential biofuel candidate

2^{ème} 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 CO₂.
- The use of biofuels to substitute the fossil fuels has been identified as a sustainable solution for mitigating global CO₂ 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 ₈ -C ₂₅	C ₈ H ₁₈ O
Structure	C ₈ -C ₂₅ HC	
Boiling point (K)	443-633	414
Density (kg/m ³)	833	770
Lower heating value LHV (MJ/kg)	42.9	38.4
Cetane number	54	~100

Experimental methods

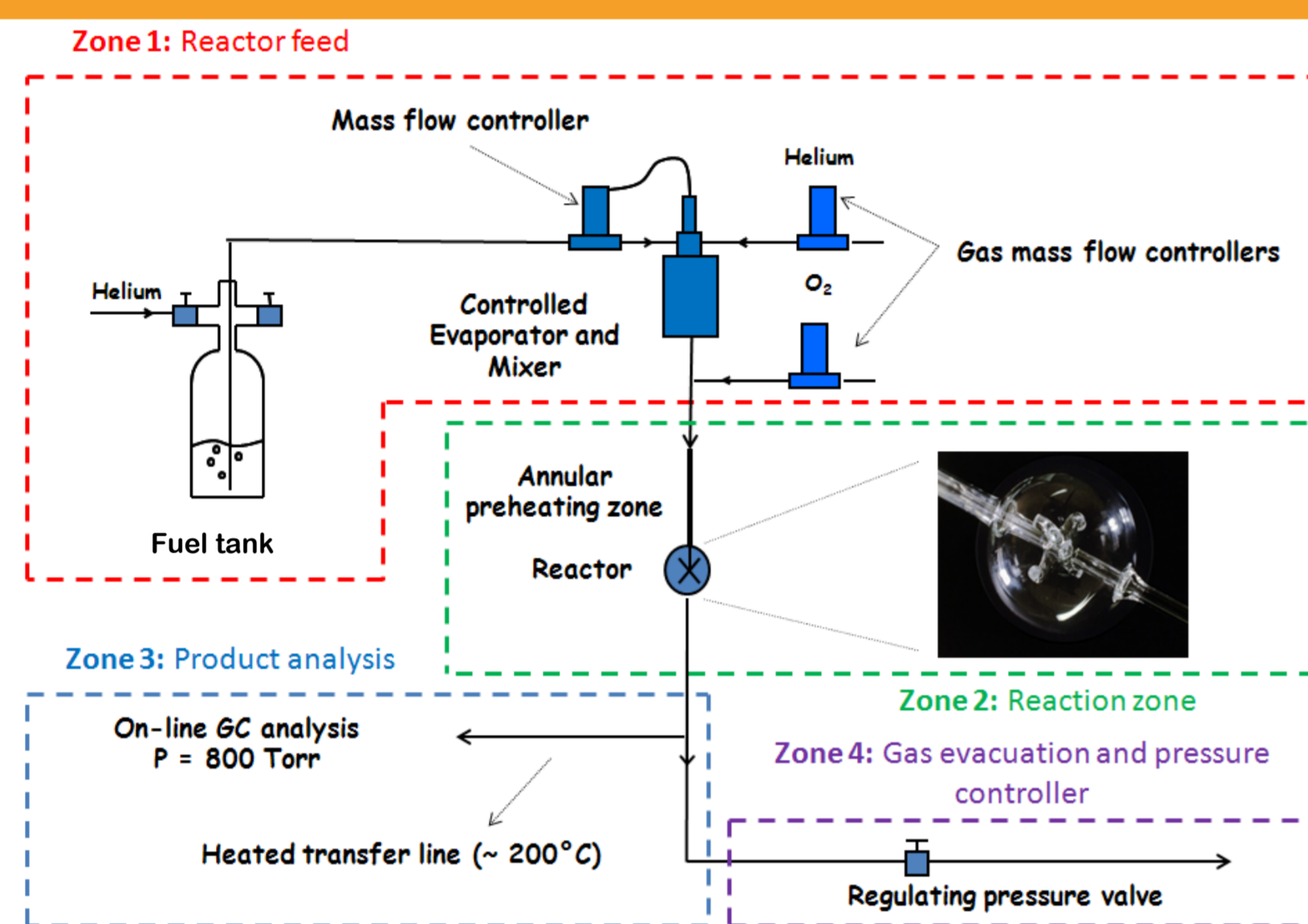


Fig. 1a JSR-GC system at LRGP-CNRS Nancy

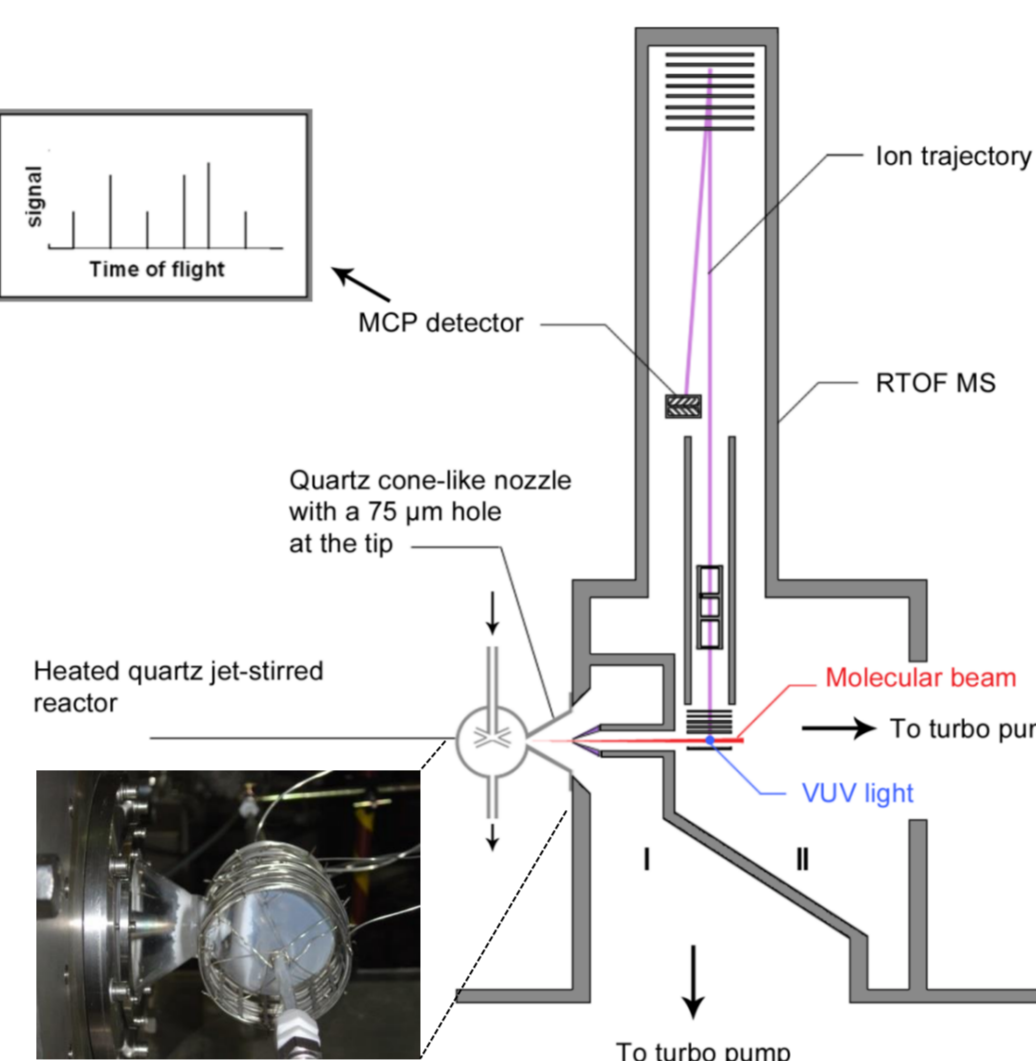


Fig. 1b JSR-PI-MBMS system at NSRL Hefei

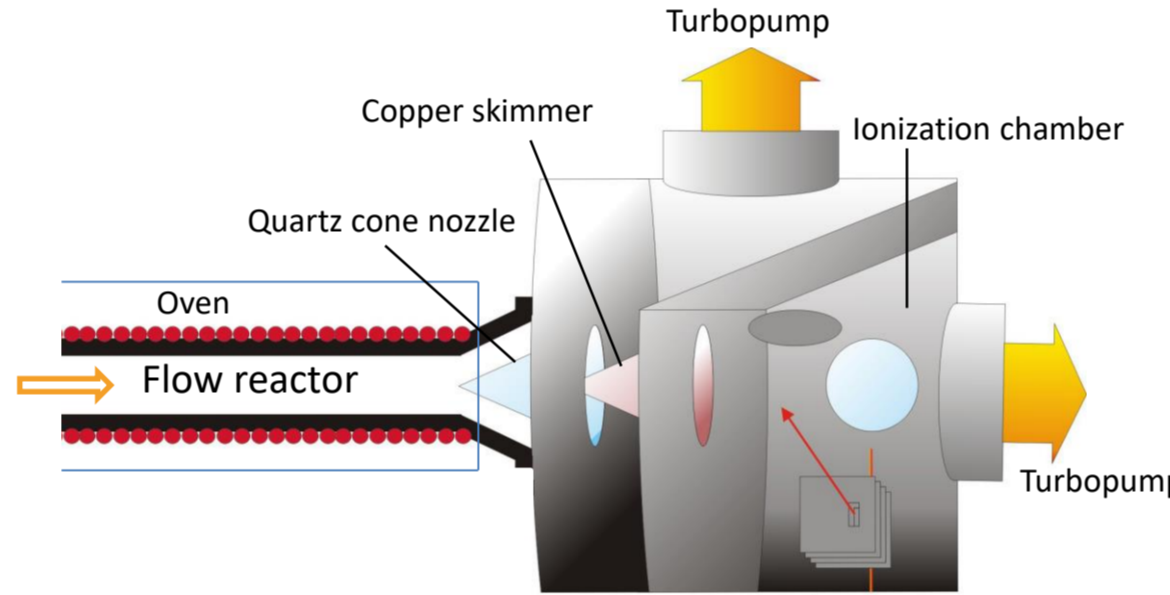


Fig. 1c PFR-EI-MBMS system at Bielefeld University

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	ϕ	t (s)	T (K)	Initial gas mole fraction			
				He or Ar ^a	O ₂	DBE	
JSR	1	2	435-1100	0.870	0.12	0.01	GC
							PI-MBMS
PFR	1	2 ^b	448-1015	0.935	0.06	0.005	EI-MBMS
							EI-MBMS
	1	1 ^b	448-900	0.935	0.06	0.005	EI-MBMS
							EI-MBMS
0.7	2 ^b	448-900	0.909	0.086	0.005	EI-MBMS	

^a He: GC experiments, Ar: MBMS experiments. ^b at ~1000 K

Results

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

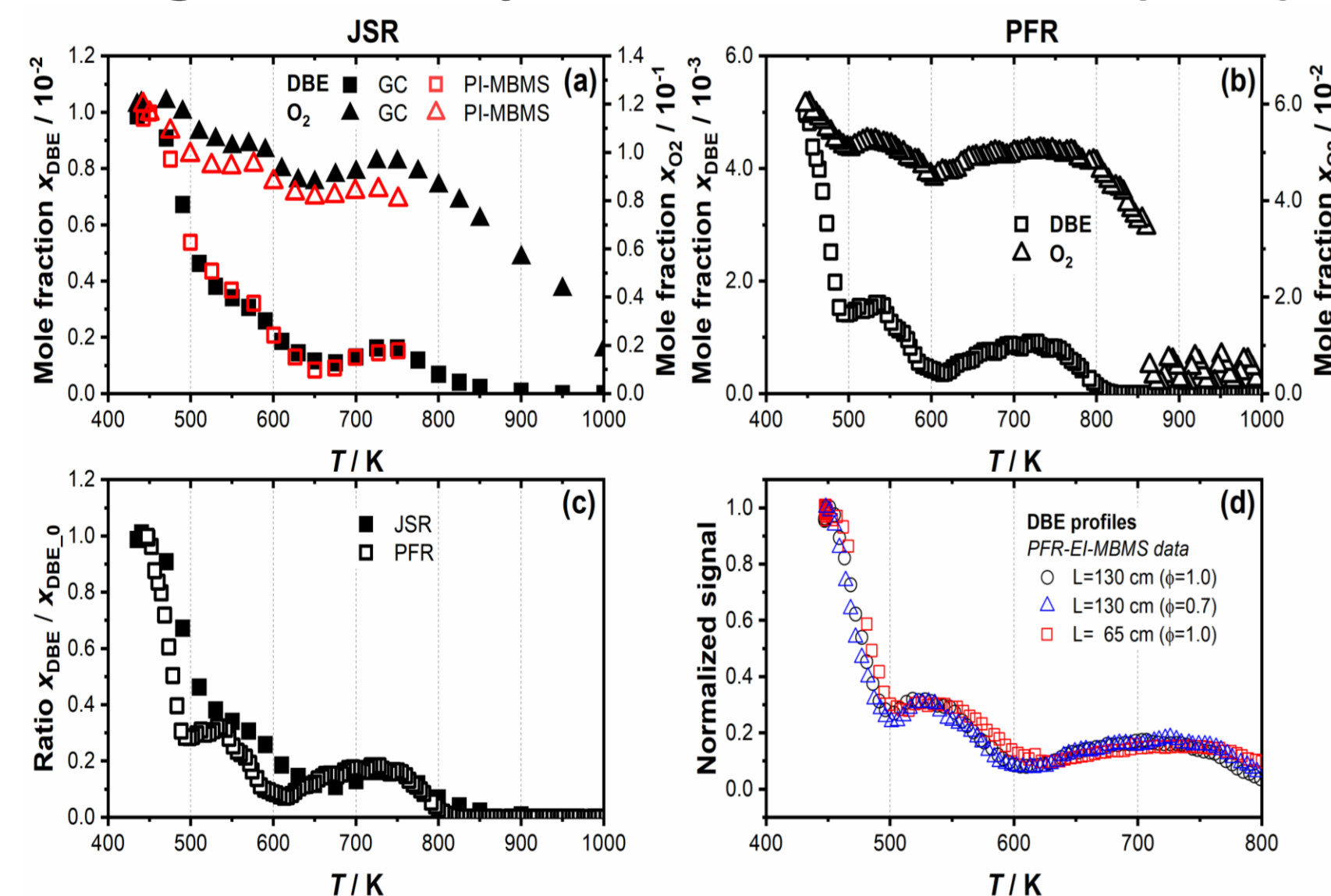


Fig. 2. Experimental mole fraction profiles of DBE and O₂. (a) JSR ($\phi=1.0$, 1% DBE), (b) PFR ($\phi=1.0$, 0.5% DBE), (c) DBE profile in JSR-GC and PFR-EI-MBMS experiments, (d) DBE profiles for different ϕ and PFR lengths L . Profiles in (c) and (d) are normalized by the respective inlet DBE mole fractions.

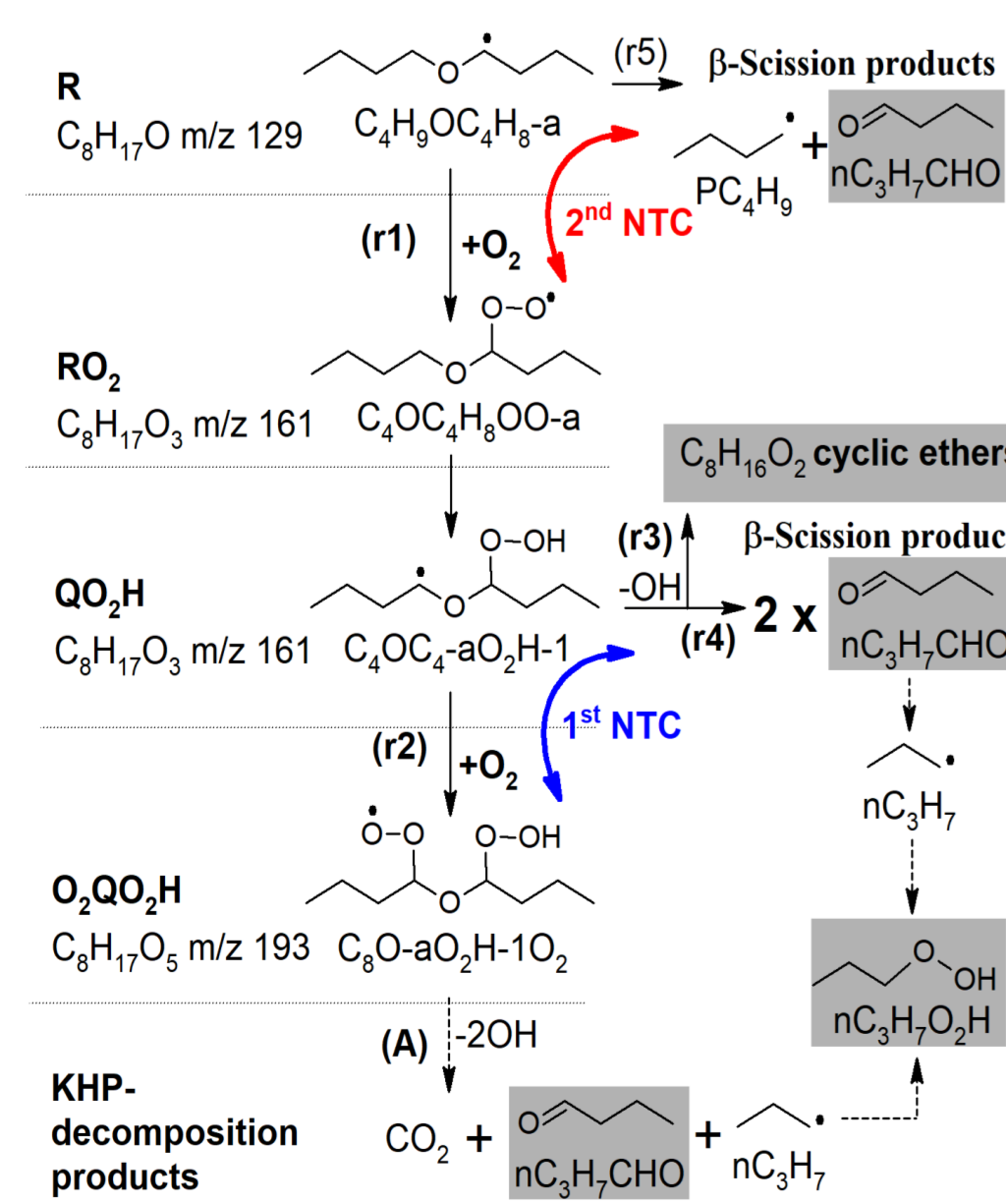


Fig. 3. Proposed mechanism of DBE oxidation resulting in two NTC zones. Dashed arrows represent series of reactions.

Detection of previously unobserved oxygenated components

Acids

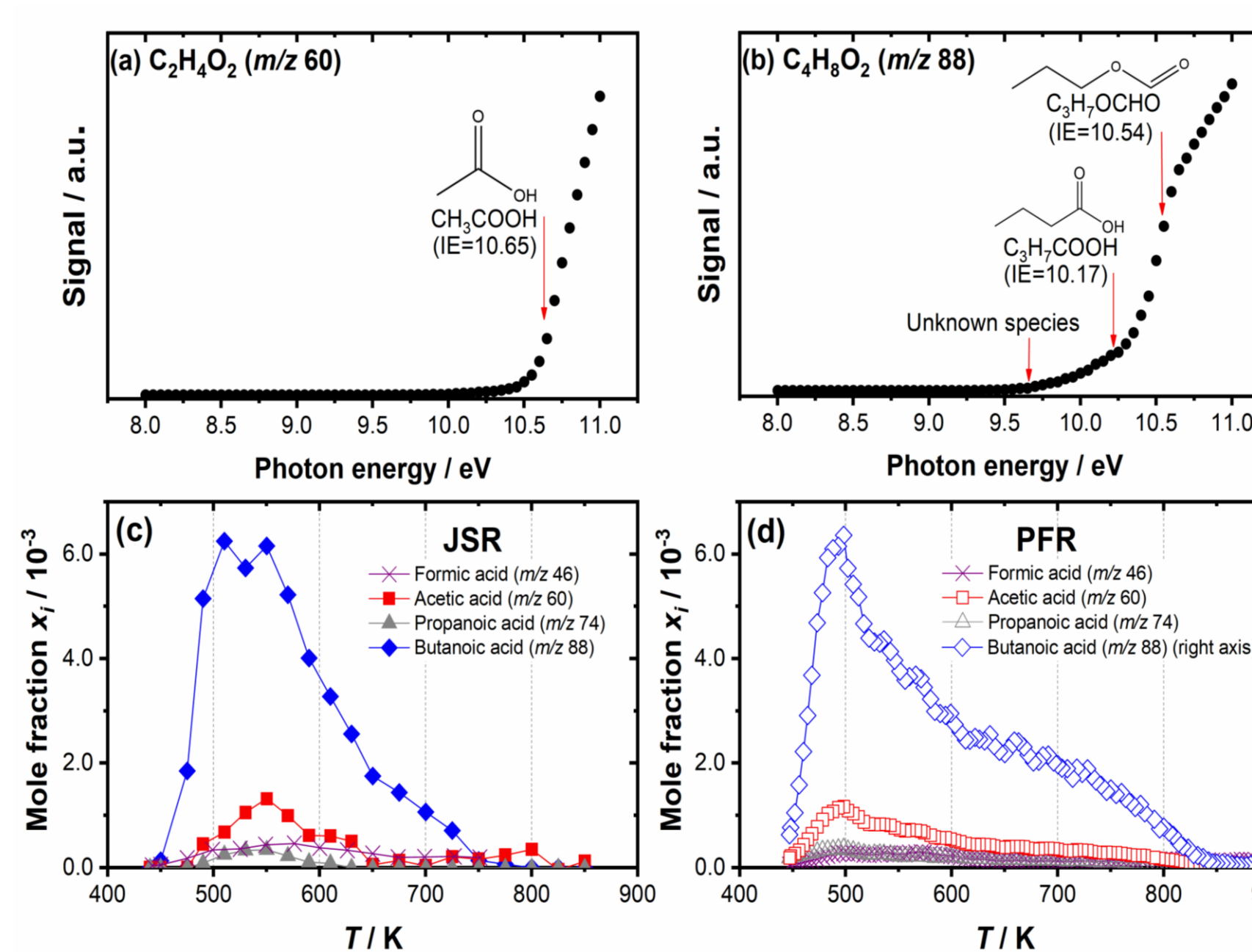


Fig. 4. Photoionization efficiency curves at 500 K from the JSR-PI-MBMS experiment for m/z 60 (a) and 88 (b), corresponding to acetic acid (CH₃COOH) and butanoic acid (C₃H₇COOH), respectively. Profiles of the detected acids: (c) JSR, (d) PFR.

C₈H₁₆O₂ cyclic ethers

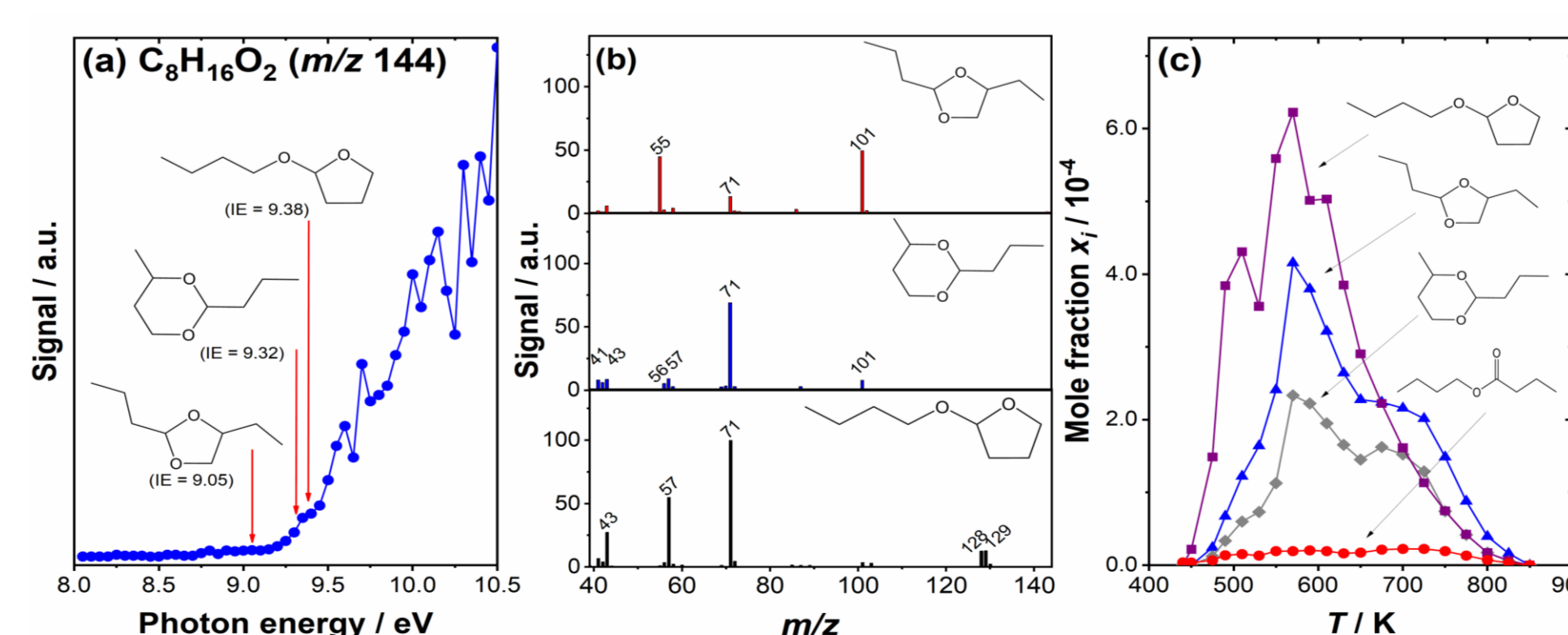


Fig. 5. (a) PIE curves for the C₈H₁₆O₂ cyclic ethers, (b) fragmentation mass spectra from GC-MS, (c) mole fraction profiles of the C₈H₁₆O₂ isomers identified by the JSR-GC experiments.

Diones (C₈H₁₄O₃)

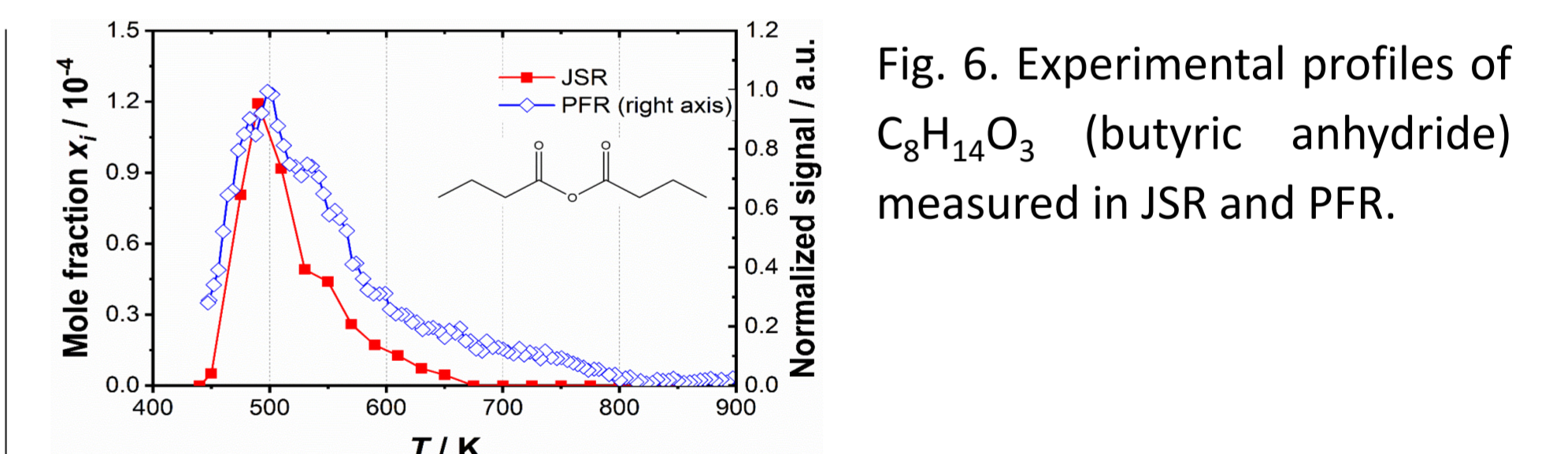


Fig. 6. Experimental profiles of C₈H₁₄O₃ (butyric anhydride) measured in JSR and PFR.

Highly-oxygenated reactive species

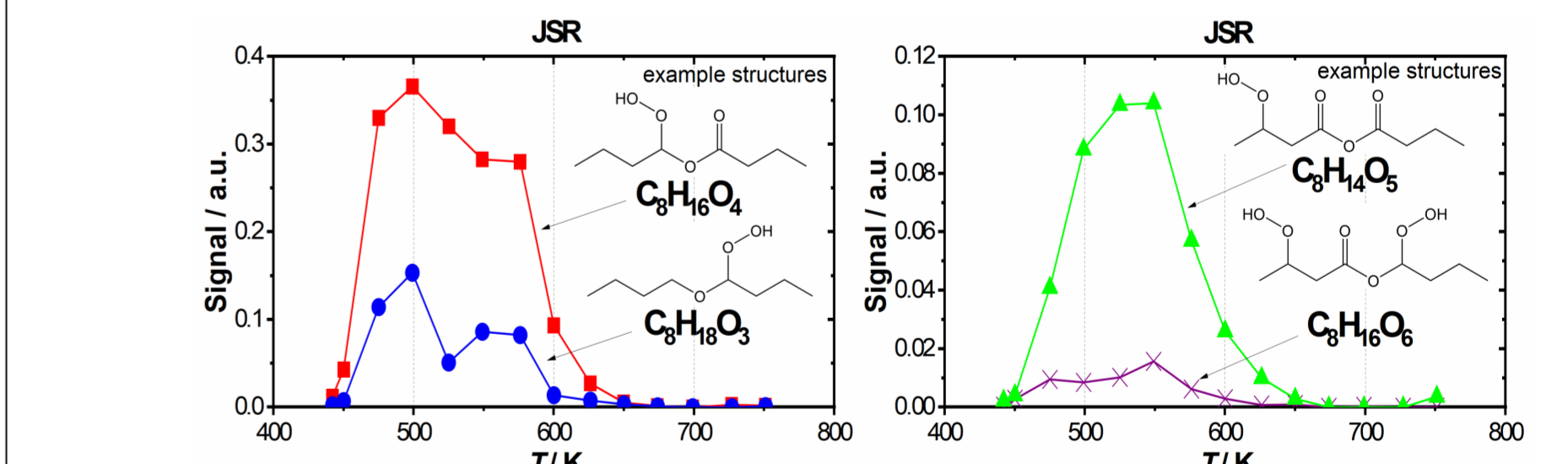


Fig. 7. Profiles of fuel-specific peroxides: hydroperoxides C₈H₁₈O₃ (products of the first O₂ addition), keto-hydroperoxides C₈H₁₆O₄ (products of the second O₂ addition), di-keto-hydroperoxides C₈H₁₄O₅ and keto-di-hydroperoxides C₈H₁₆O₆ (products of the third O₂ addition).

Examples of newly-proposed reaction pathways

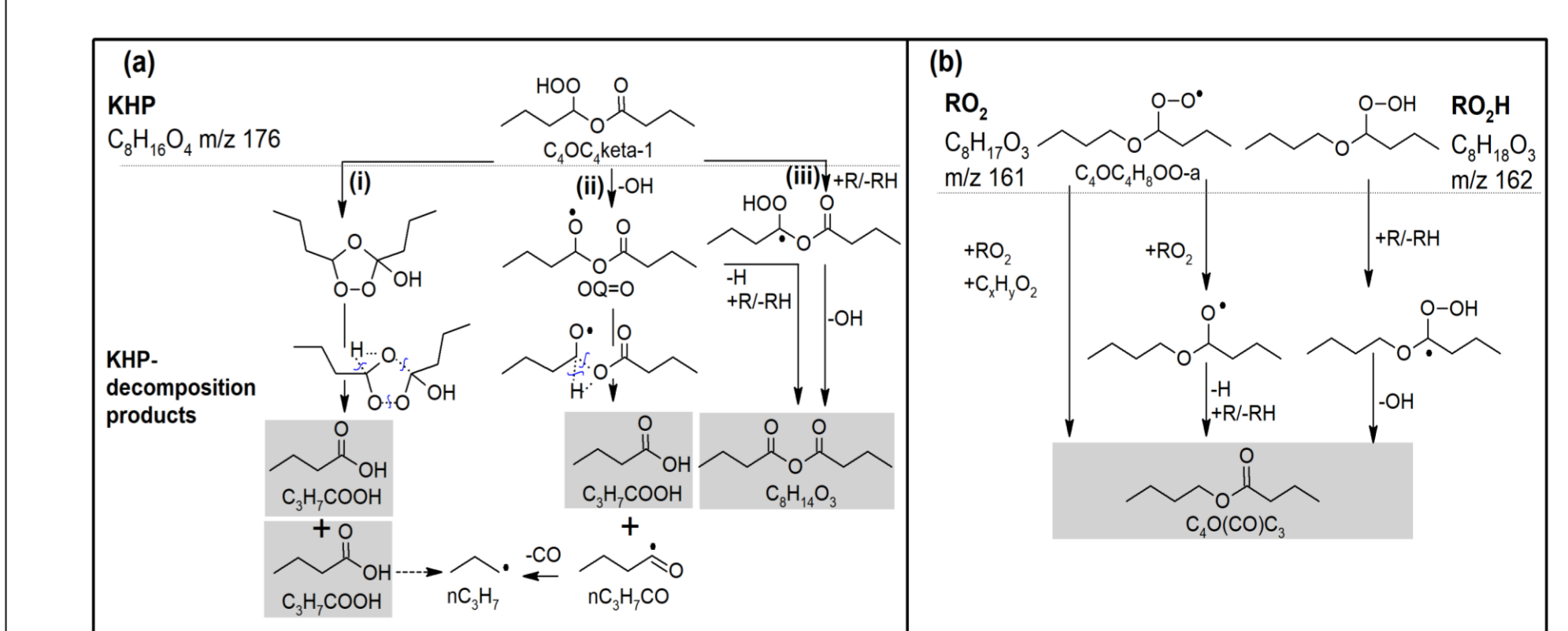


Fig. 8. Newly-proposed paths for DBE LT mechanism. (a) Formation of butanoic acid (C₃H₇COOH) and butyric anhydride (C₈H₁₄O₃). (b) Formation of *n*-butyl butanoate (C₄O(CO)C₃).

Acknowledgements

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