

Time-resolved measurements of product formation in neopentane oxidation: a probe to investigate chain-branching mechanism

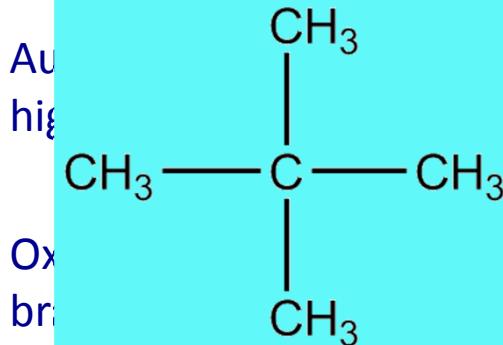
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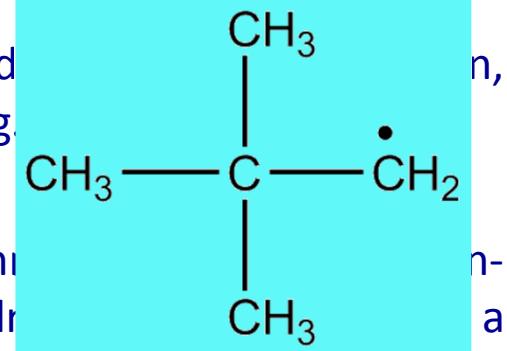
May 20th 2015, 9th U.S. National Combustion Meeting, Cincinnati, Ohio, USA

Introduction

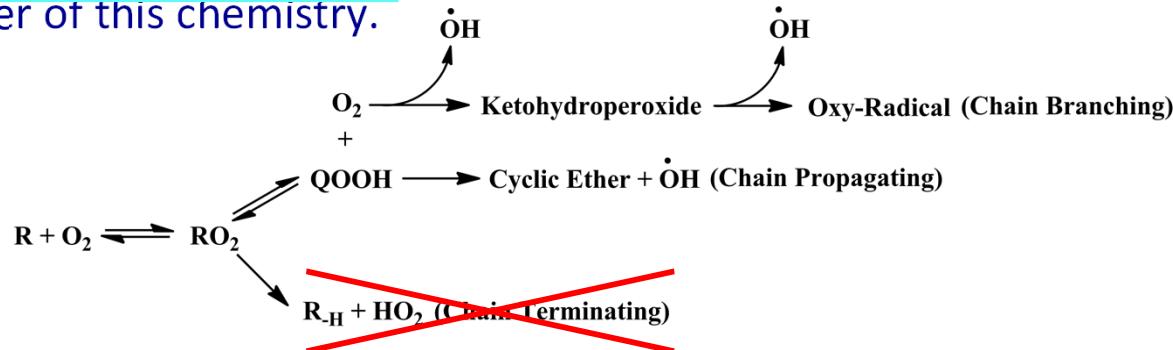
- Autoxidation
- Oxidative branching



lays a crucial role in the development of combustion engine technologies (e.g.,



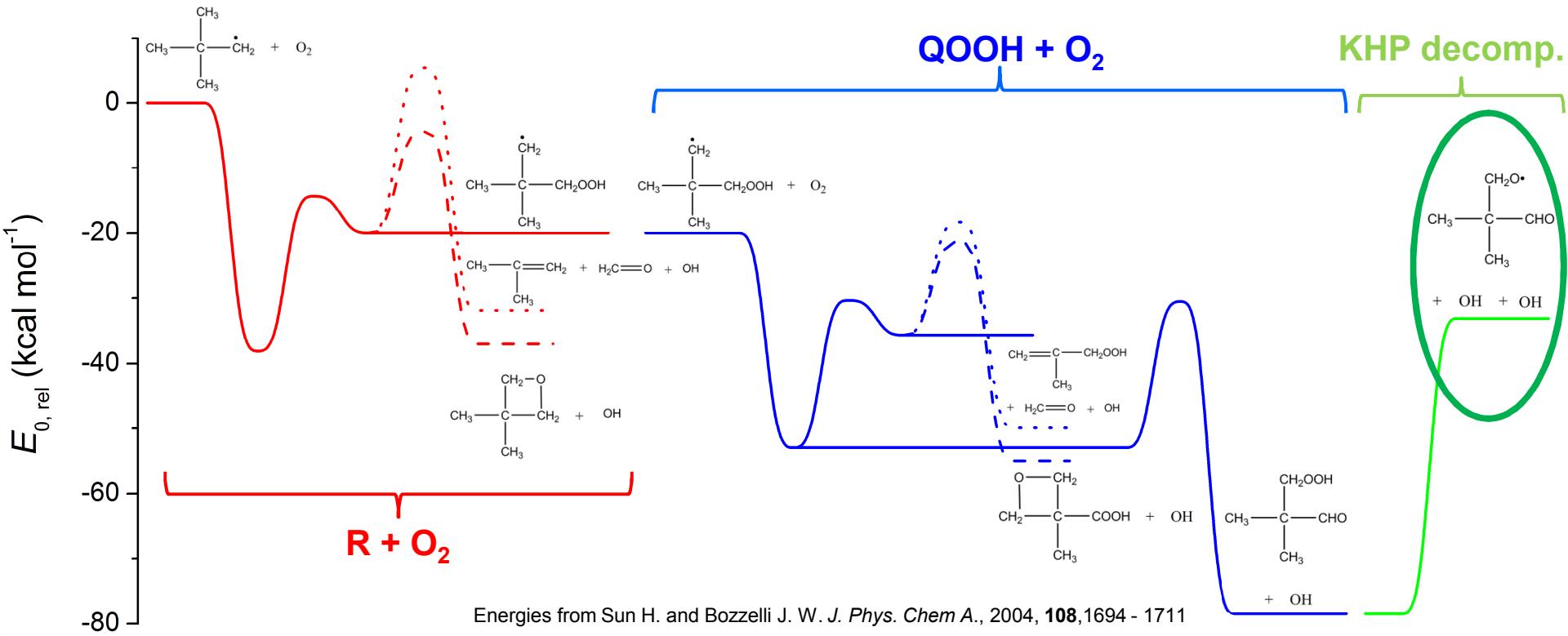
Oxidative branching, and especially their chain branching, for autoignition and ketohydroperoxide formation, a marker of this chemistry.



- Radical of interest in the current work, neopentyl radical, which is formed from neopentane by H-atom abstraction, is a good fuel radical to study chain-branching since no β -hydrogen is available and all hydrogen are primary.
- We study Cl-atom initiated oxidation chemistry of neopentane in the temperature range 550 – 700 K using both Low-Pressure (LP, $P \approx 8$ Torr) and High-Pressure (HP, $P \approx 1 - 2$ atm) reactors.

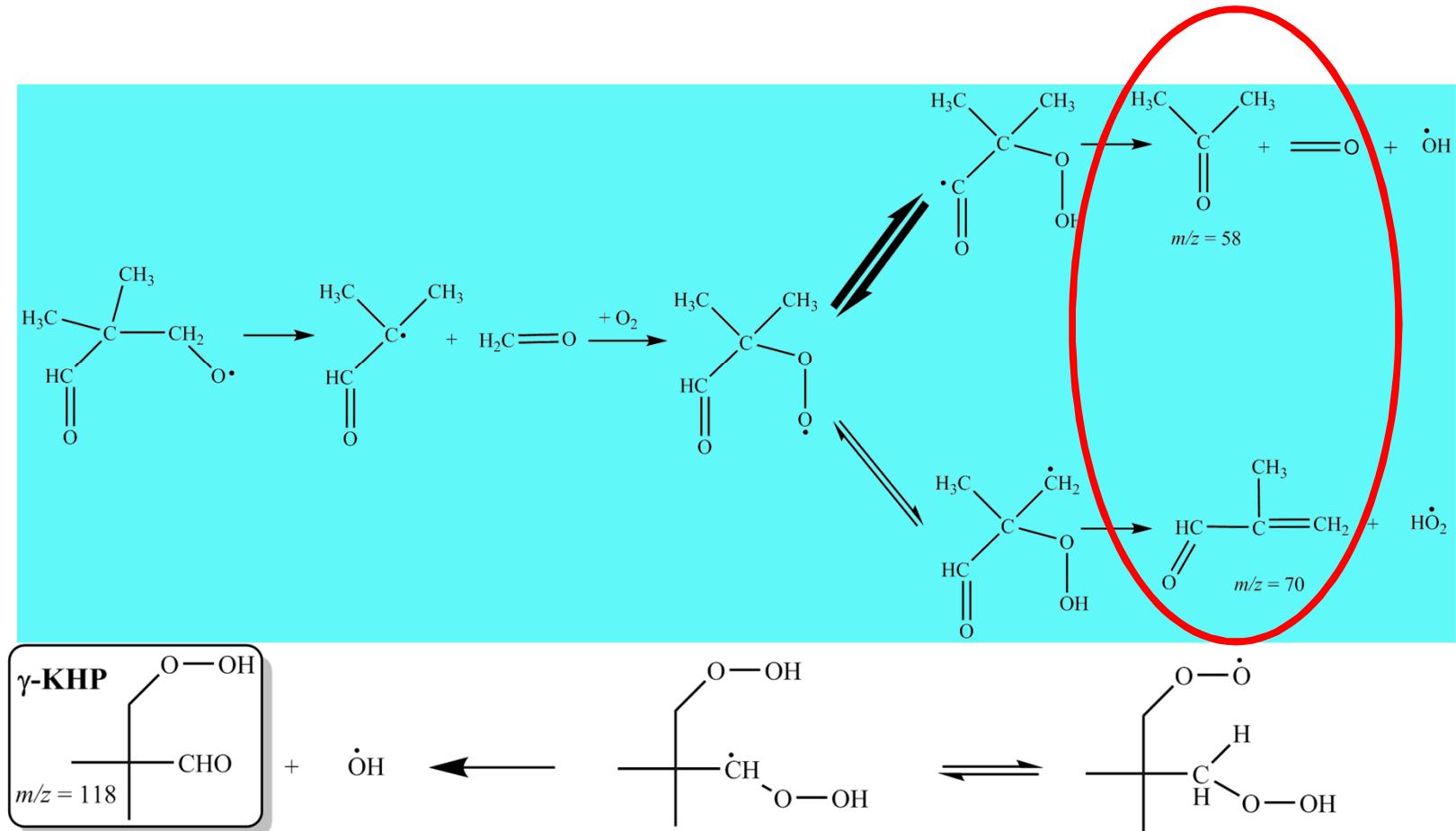
PESs of R + O₂, QOOH + O₂, and KHP decomposition

- Due to simple and symmetric molecular structures of neopentane and neopentyl radical, relatively compact representation is possible for the ketohydroperoxide formation under low-temperature combustion conditions.
- Ketohydroperoxide decomposition channel leading to oxo-radical + OH + OH results in chain-branched – particularly important for autoignition. But it might not be the sole KHP decomposition channel.



Reaction Mechanism

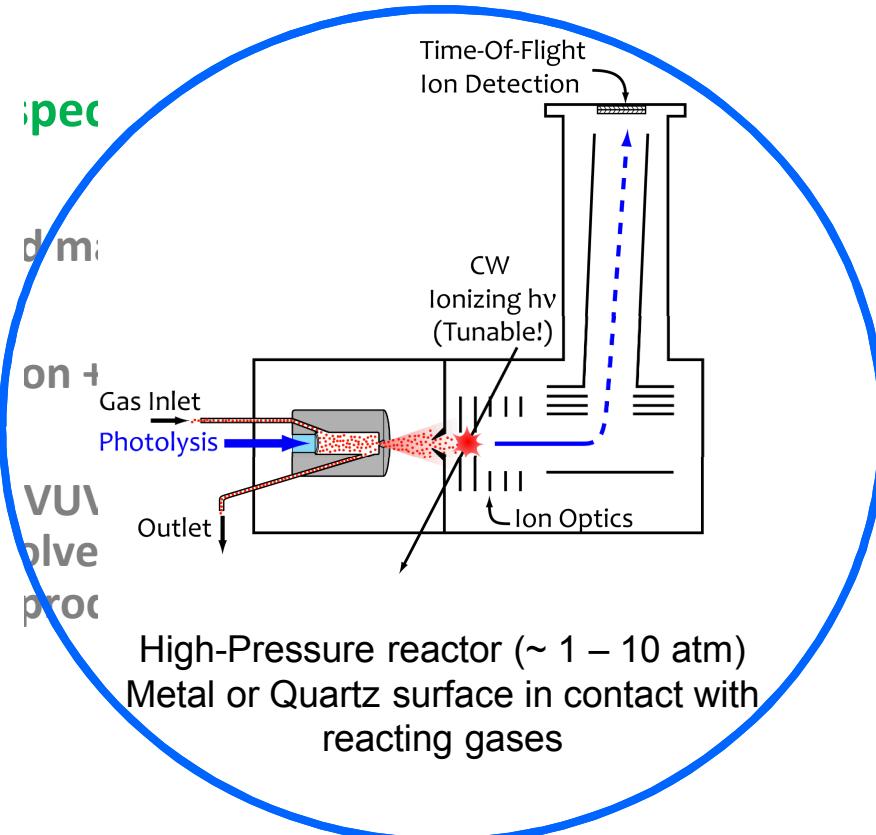
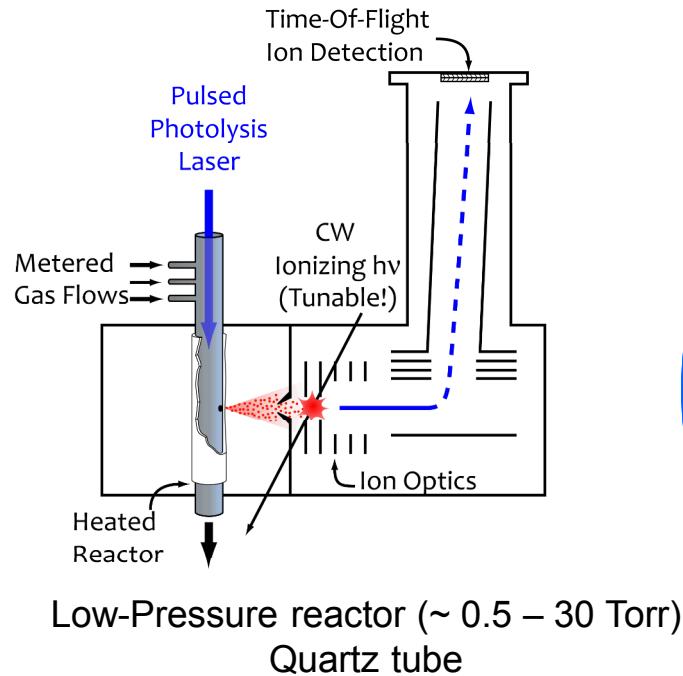
- Interestingly, Wang et al. also observed significant formic acid formation which they did not managed to explain.



Wang S. et al. Combust. Flame. 1999, 118, 415

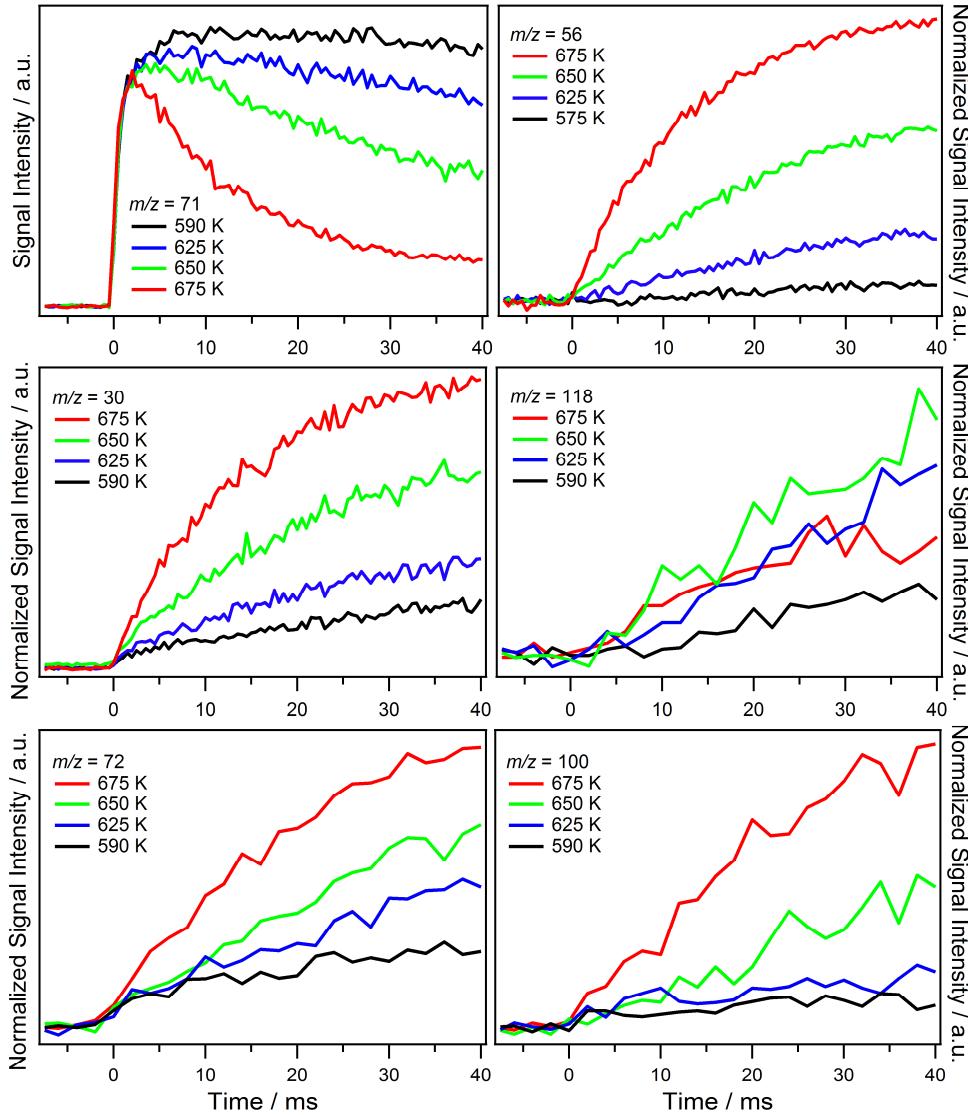
Experimental

Laser photolysis – flow reactors coupled to time-of-flight mass spectrometer with synchrotron photoionization

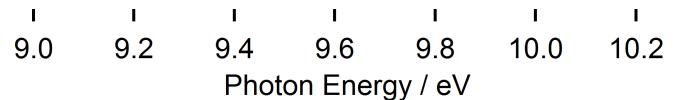


Results: Low-Pressure (8 Torr)

- Neopentane oxidation initiated by 248 nm photolysis of $(COCl)_2 \rightarrow 2 CO + 2 Cl$



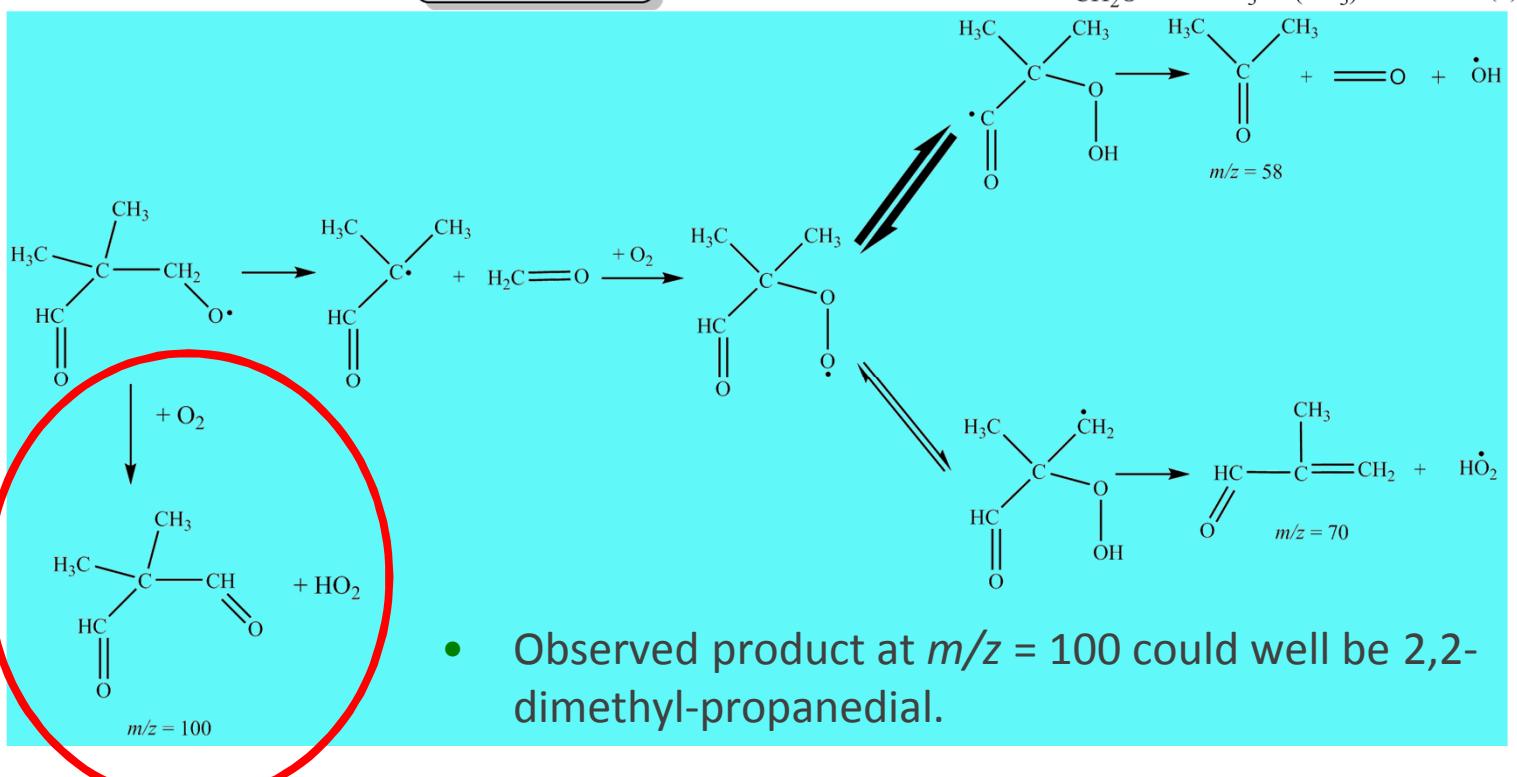
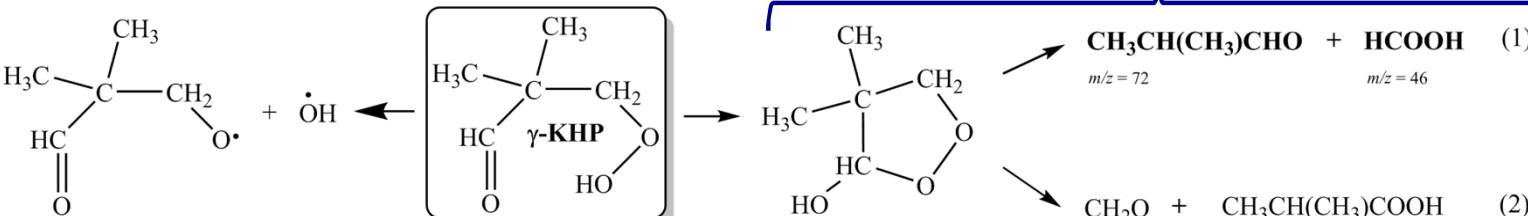
- Important products for autoignition observed at $m/z = 30$ (H_2CO), $m/z = 56$ (isobutene + 3,3-dimethyl-oxetane), $m/z = 71$ (RO_2), $m/z = 72$ (methyl propanal), $m/z = 100$, and $m/z = 118$ (KHP)
- Decay of RO_2 becomes faster with increasing temperature and $m/z = 30$ and $m/z = 56$ formation become faster as well. Intensity of KHP signal reaches maximum around 650 K
- Formation of both $m/z = 72$ and $m/z = 100$ products become faster with temperature. But what is (are) the mechanism(s) of their formation?



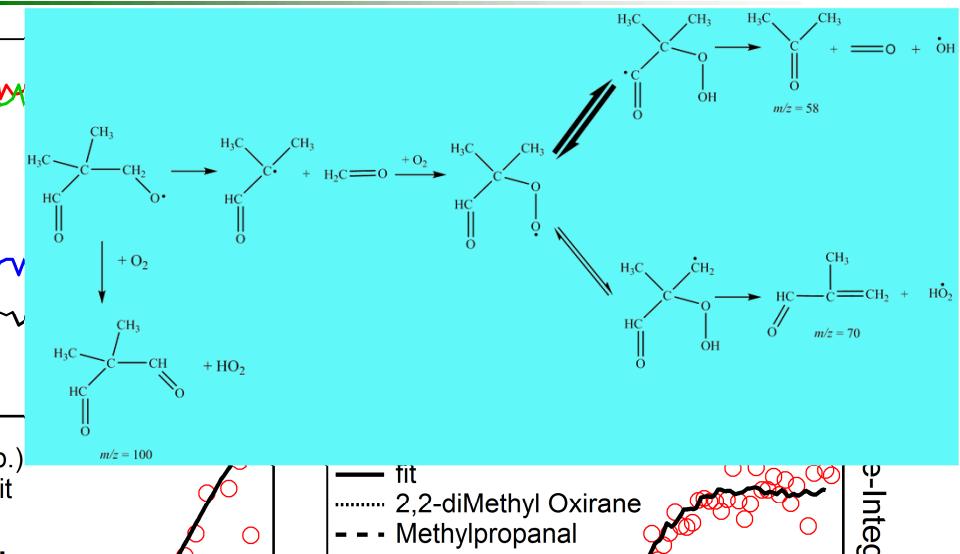
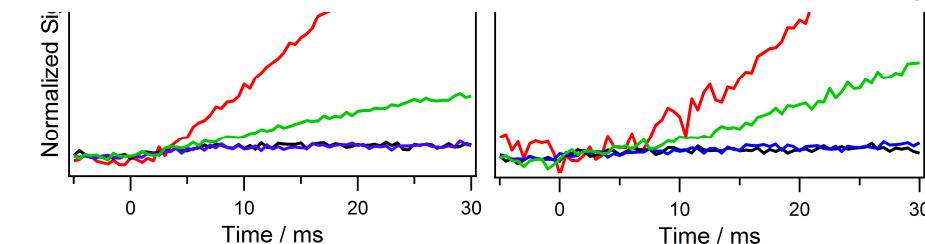
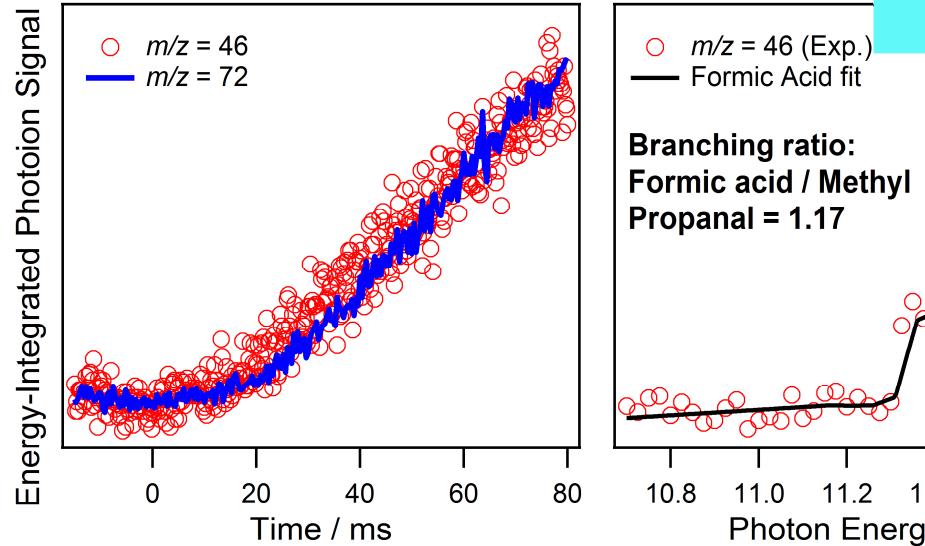
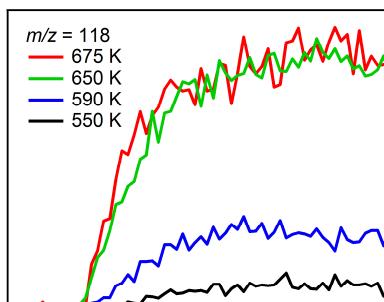
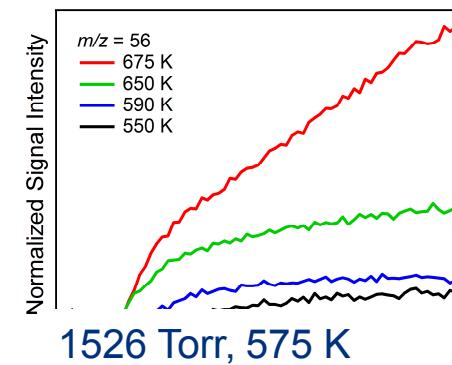
Results: Low-Pressure (8 Torr)

- Recently suggested Korcek decomposition of γ -ketohydroperoxide* might explain methylpropanal formation

* Jalan et al. et al. *J. Am. Chem. Soc.* 135 (2013), 11100

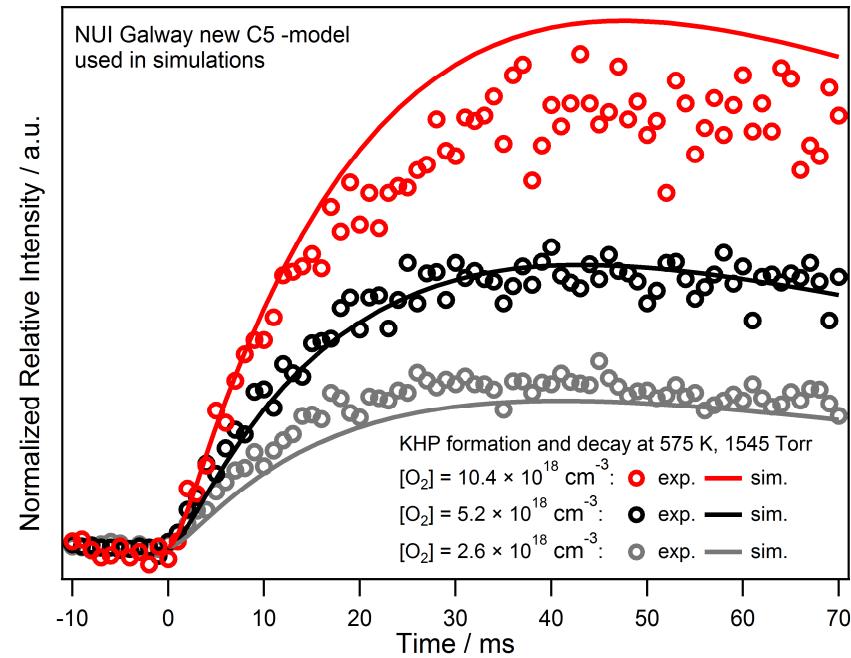
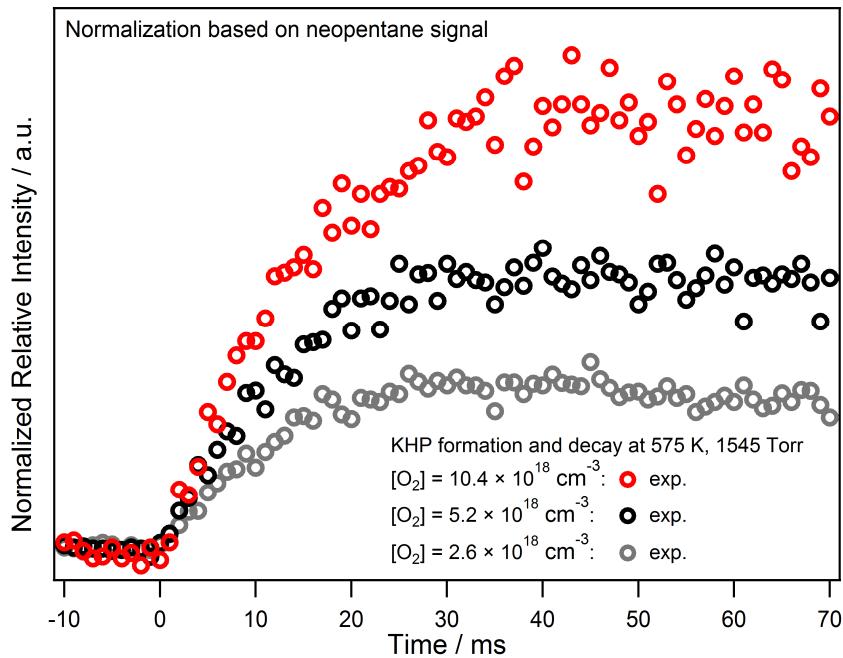


Results: High-Pressure (1 atm)



- Time dependency of signals at $m/z = 58$ and 70 lag behind $m/z = 100$ signal, in agreement with the suggested mechanism
- However, a stronger temperature dependency of $m/z = 100$ signal in comparison to $m/z = 58$ and 70 signals is not easily explained by the suggested mechanism

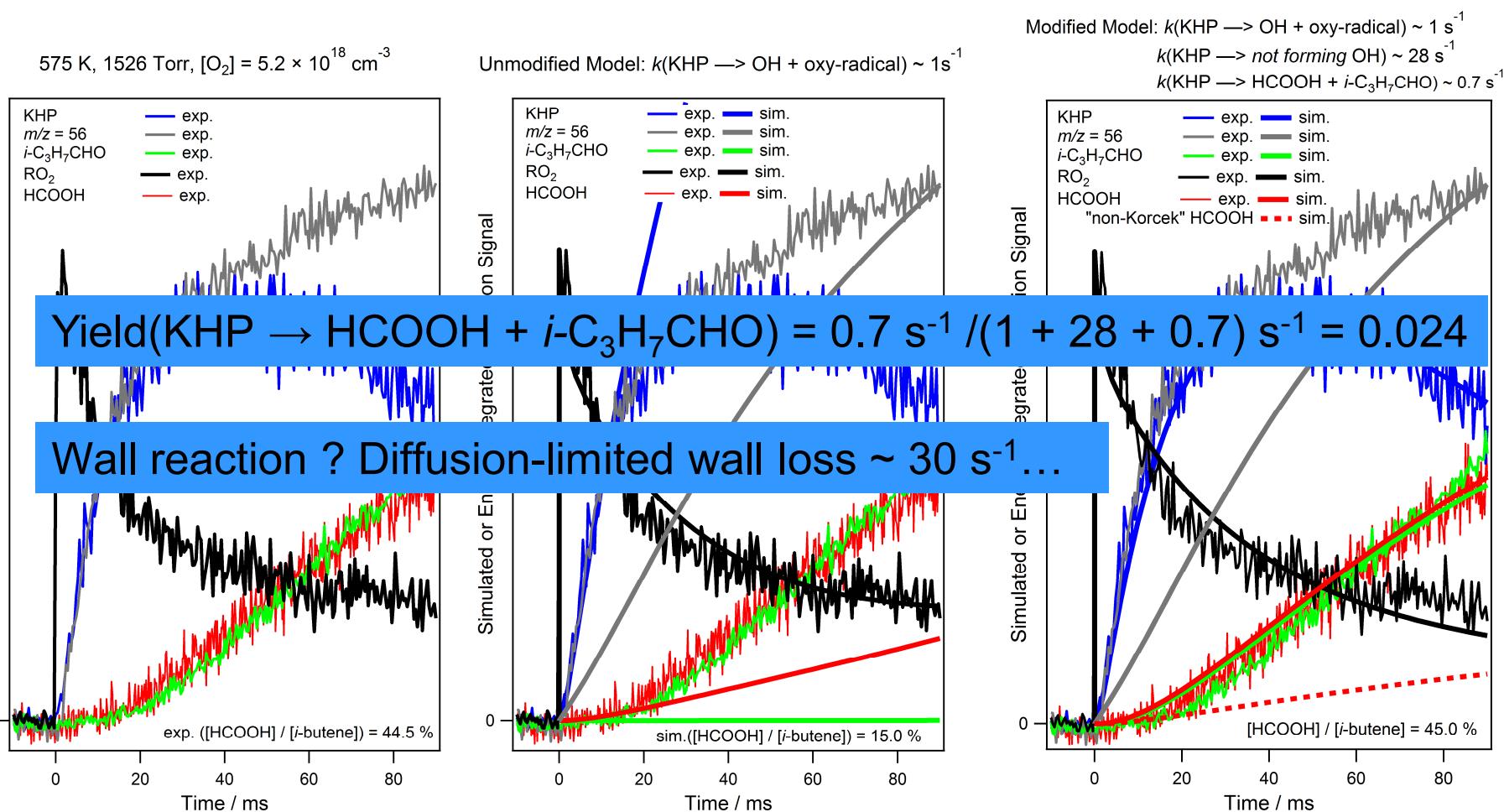
KHP formation kinetics and the effect of $[O_2]$



- Experimental time profiles are very similar at various $[O_2]$, only the signal intensities change due to increased interception of QOOH radicals by O_2 .
- Simulations reproduce experimental KHP time-behavior accurately once additional KHP decomposition rate 28 s^{-1} is added to the model
- In addition, simulations reproduce experimentally observed KHP signal intensity dependence on $[O_2]$ with good accuracy.

Exp. Kinetics vs. Model Simulations

- Cl + neopentane + O₂ –system was modelled using NUI Galway new C5-model. Without any adjustment, modelled [KHP] increases rapidly that is *not* observed in the experiments
- Upon including additional KHP decomposition mechanism in the model which does not produce OH, significantly better agreement observed between the model and the exp.



Conclusions and Acknowledgements

- Direct, time-resolved measurements of product formation in neopentane oxidation experiments were performed both at low (~ 8 Torr) and high (1 – 2 atm) pressures. Ketohydroperoxide (KHP) formation and decomposition clearly observed.
- Current observations of primary, secondary (e.g. KHP), and tertiary etc. product formation semi-quantitatively agree with a recent kinetic neopentane oxidation model.
- It is concluded that more direct studies of KHP decomposition, among other studies of KHP, would be greatly helpful to improve current autoignition models.

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