

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

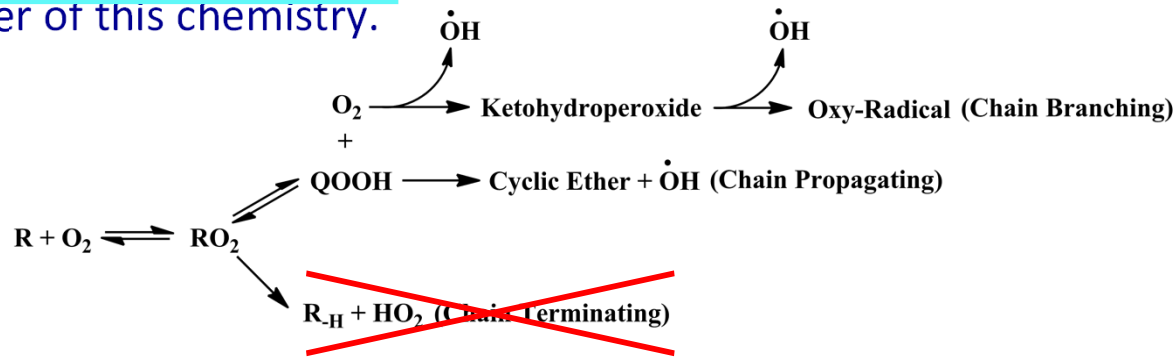
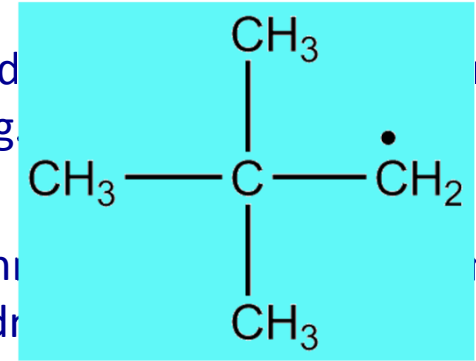
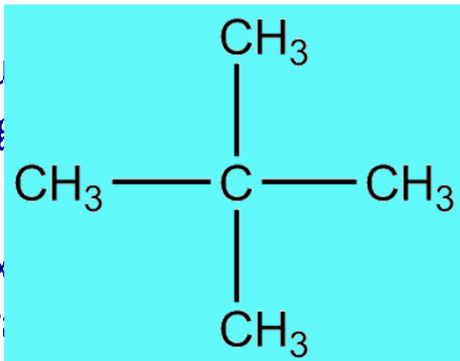
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# Introduction

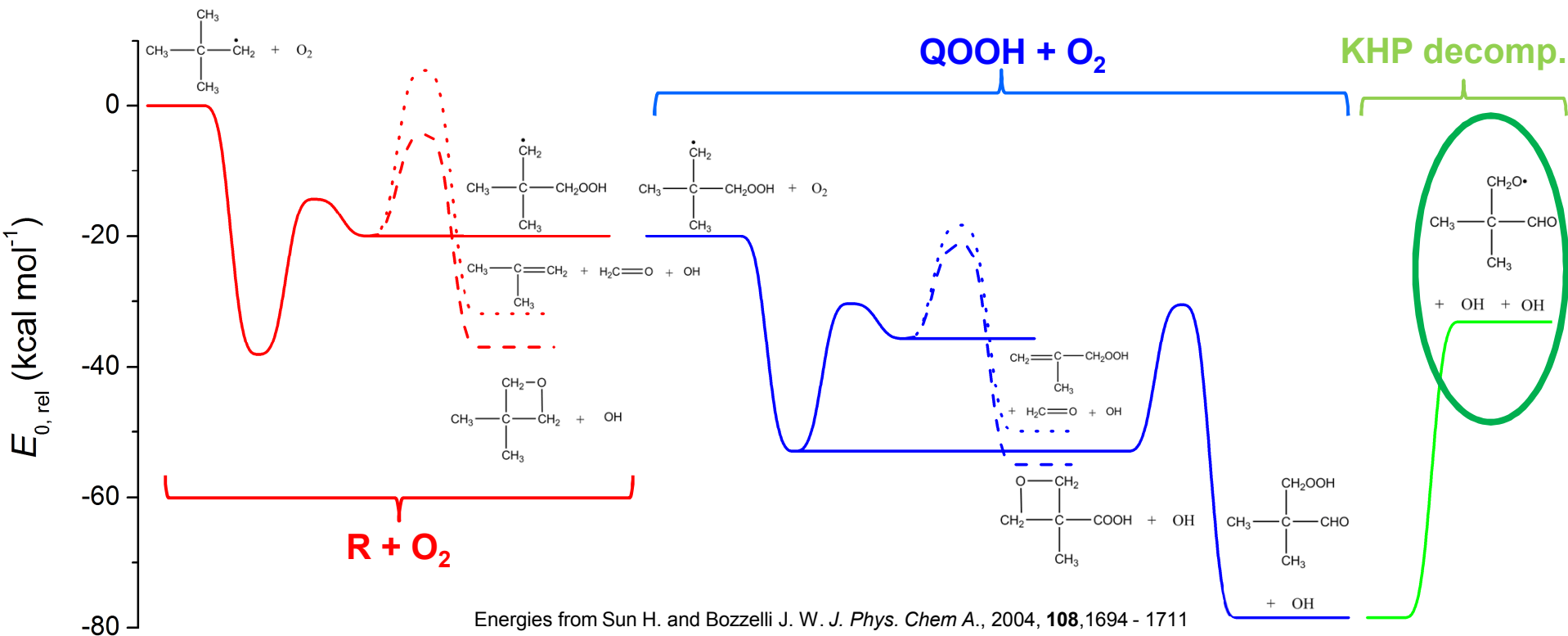
- Autoignition plays a crucial role in the development of new combustion engine technologies (e.g. HCCI, PCCI, etc.).
- Oxidation chemistry of hydrocarbons, and especially their chain branching, is a key factor for autoignition and ketohydroperoxide formation, a marker of this chemistry.



- 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  $\beta$ -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 $R + O_2$ , QOOH + $O_2$ , and KHP decomposition

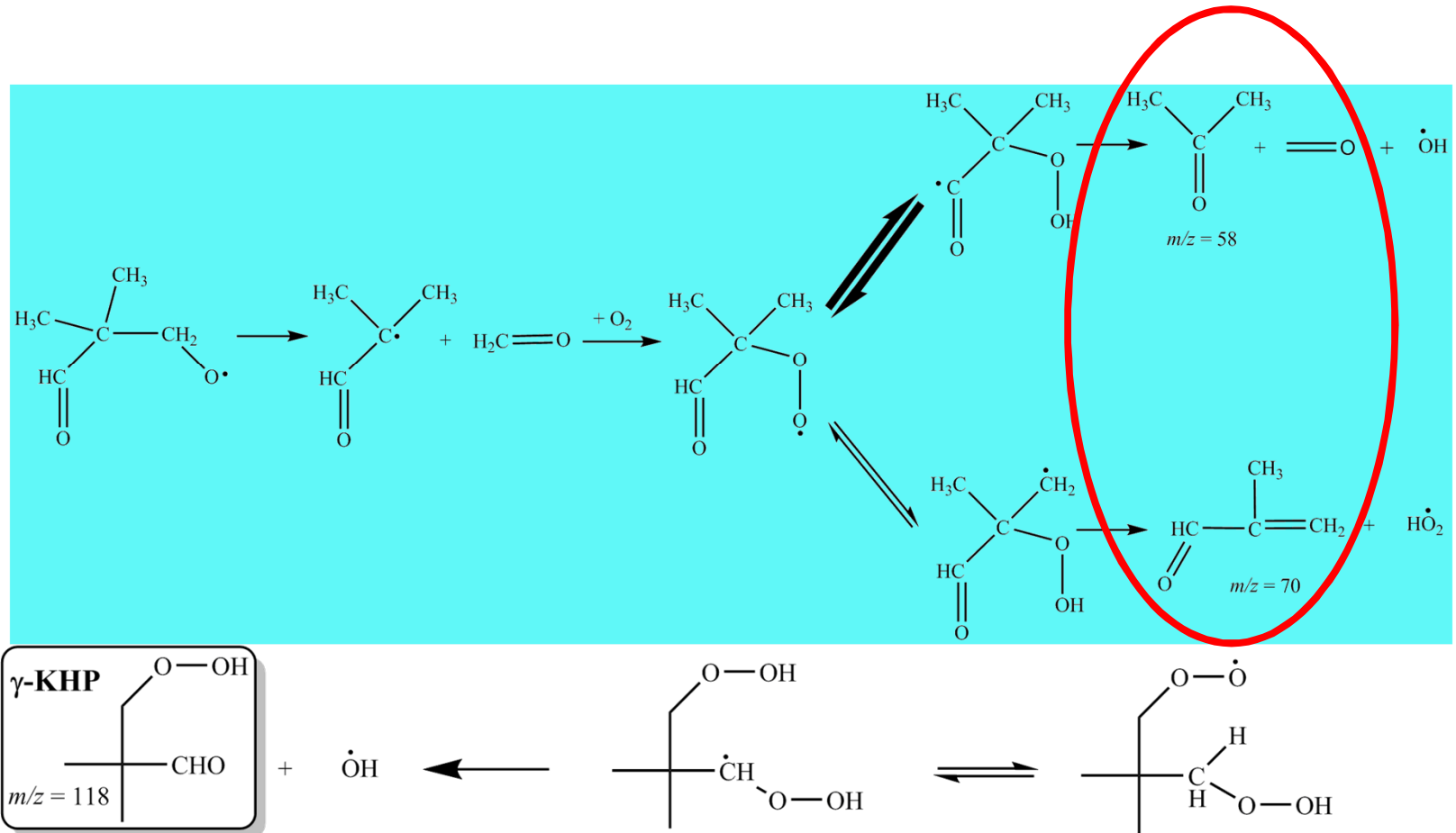
- Due to simple and symmetric molecular structures of neopentane and neopentyl radical, relatively compact representation is possible for the ketohydroperoxide formation under low-temperature combustion conditions.
- Ketohydroperoxide decomposition channel leading to oxo-radical + OH + OH results in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



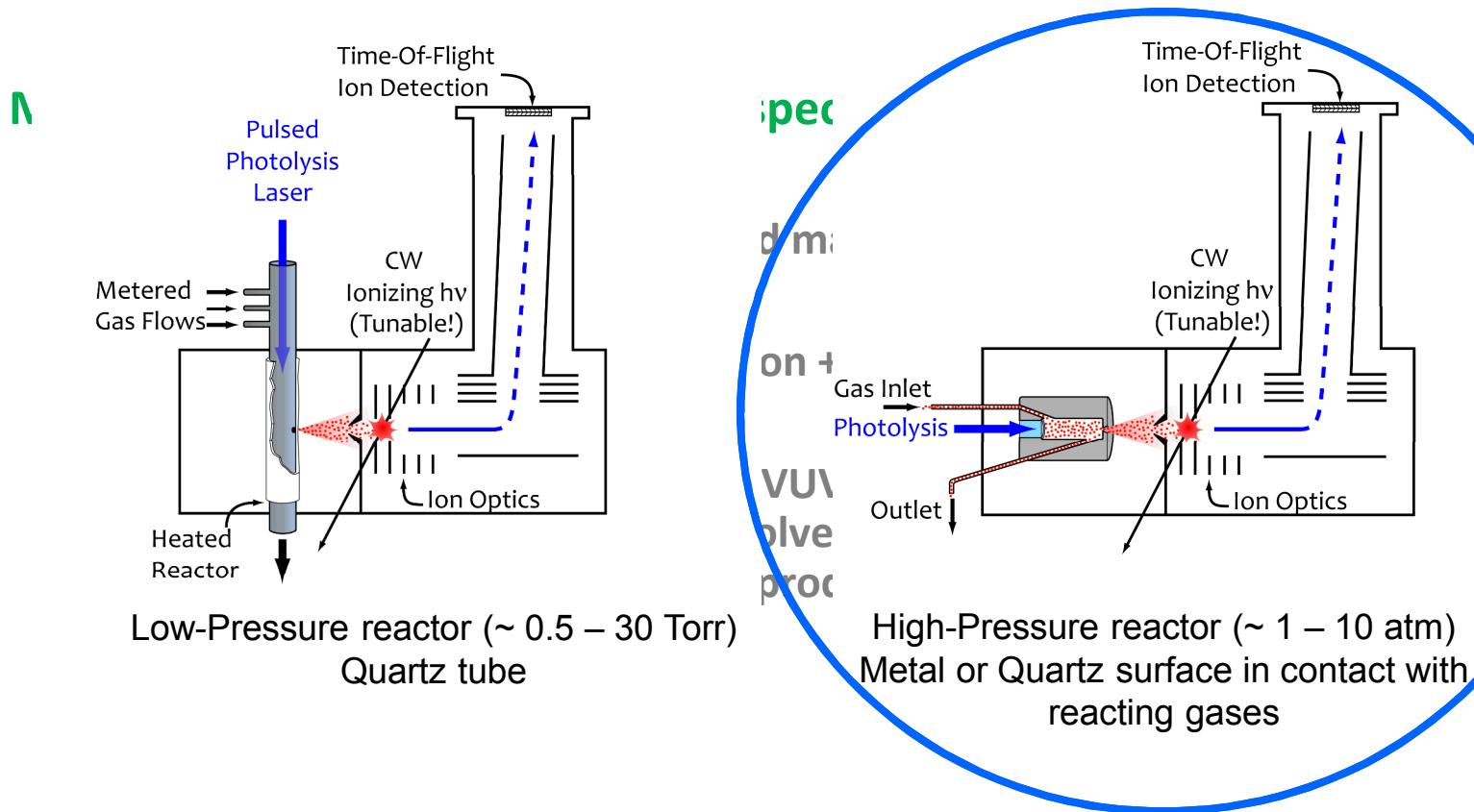
Energies from Sun H. and Bozzelli J. W. *J. Phys. Chem. A.*, 2004, **108**, 1694 - 1711

# Reaction Mechanism

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

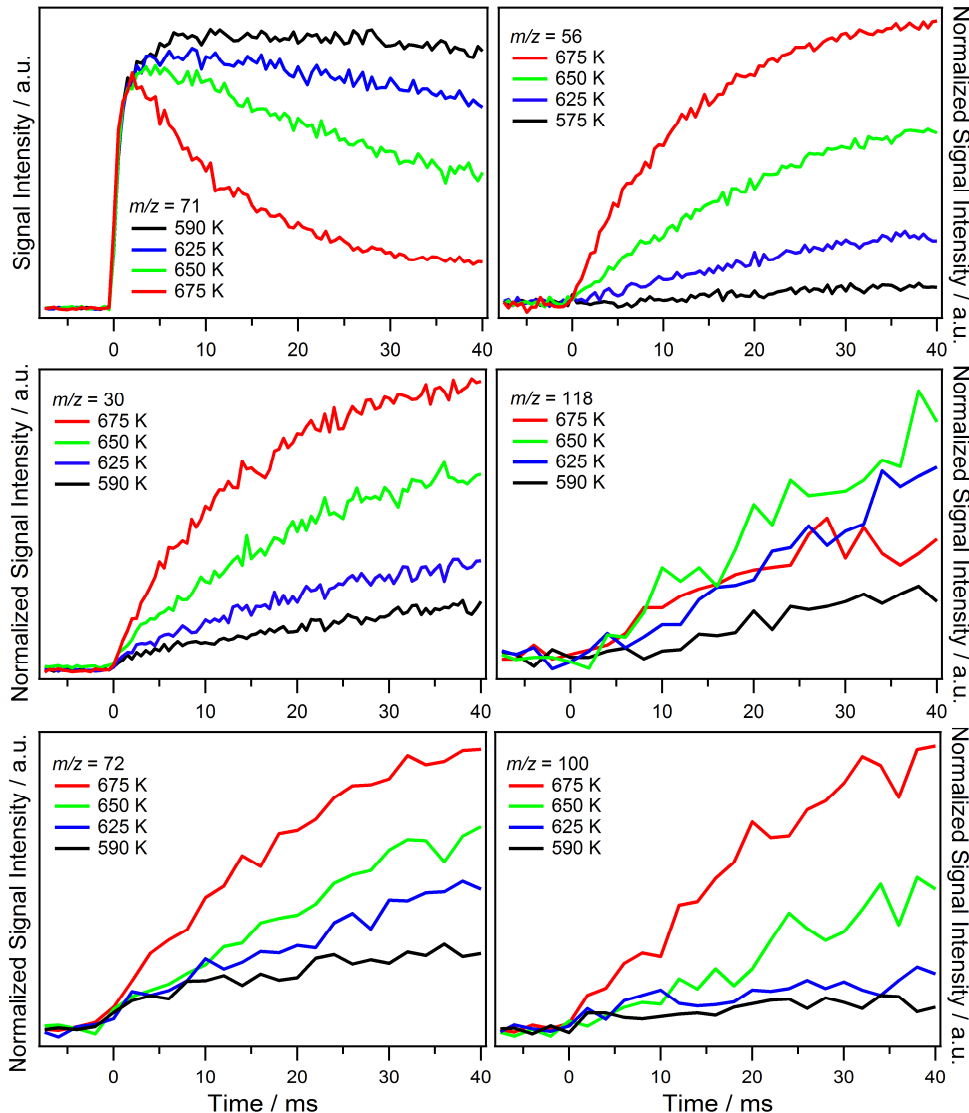


## Laser photolysis – flow reactors coupled to time-of-flight mass spectrometer with synchrotron photoionization

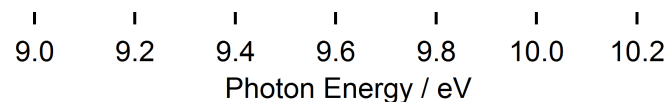


# Results: Low-Pressure (8 Torr)

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



- Important products for autoignition observed at  $m/z = 30$  ( $\text{H}_2\text{CO}$ ),  $m/z = 56$  (isobutene + 3,3-dimethyloxetane),  $m/z = 71$  ( $\text{RO}_2$ ),  $m/z = 72$  (methyl propanal),  $m/z = 100$ , and  $m/z = 118$  (KHP)
- Decay of  $\text{RO}_2$  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?

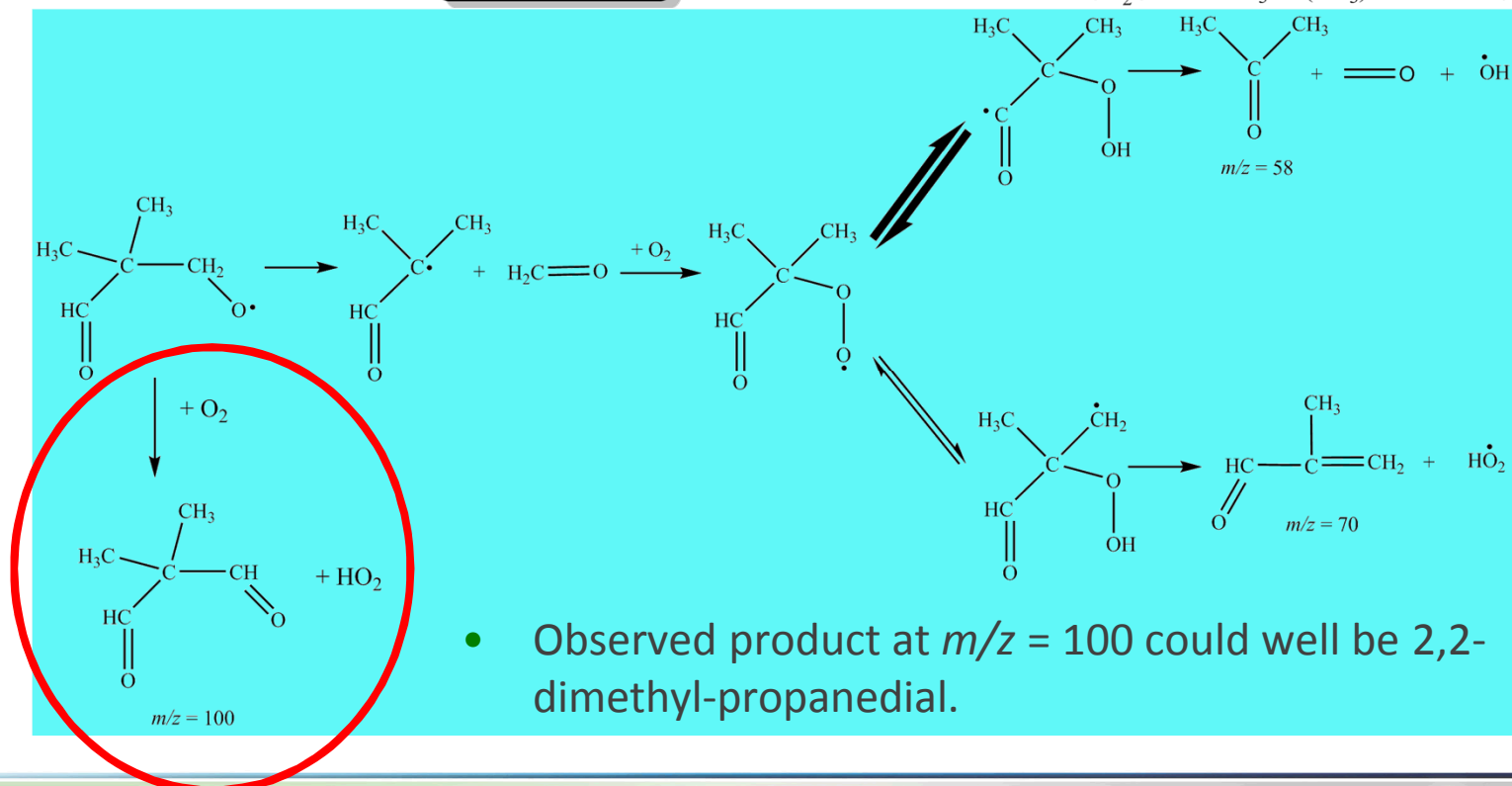
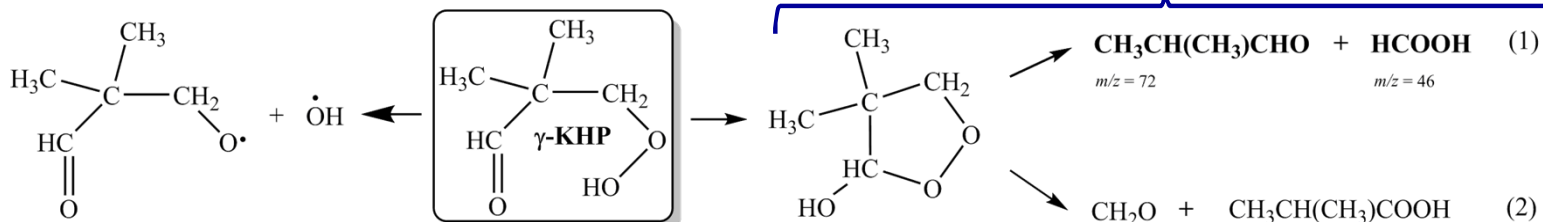


# Results: Low-Pressure (8 Torr)

- Recently suggested Korcek decomposition of  $\gamma$ -ketohydroperoxide\* might explain methylpropanal formation

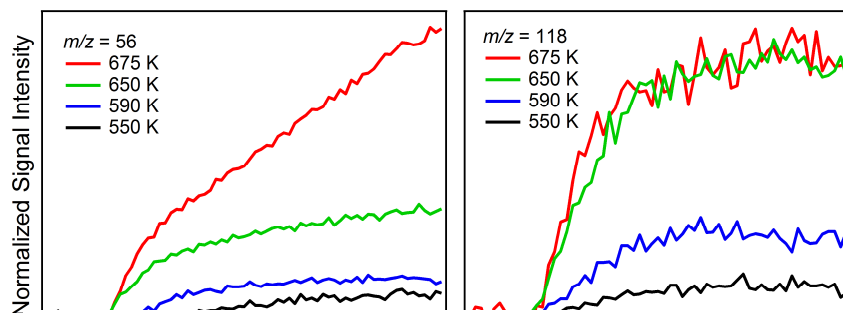
\* Jalan et al. et al. *J. Am. Chem. Soc.* 135 (2013), 11100

## Korcek decomposition of $\gamma$ -ketohydroperoxide

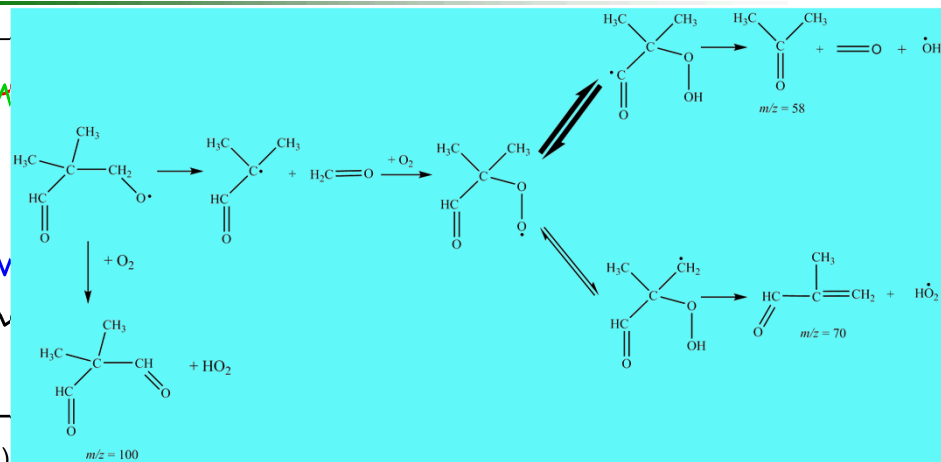
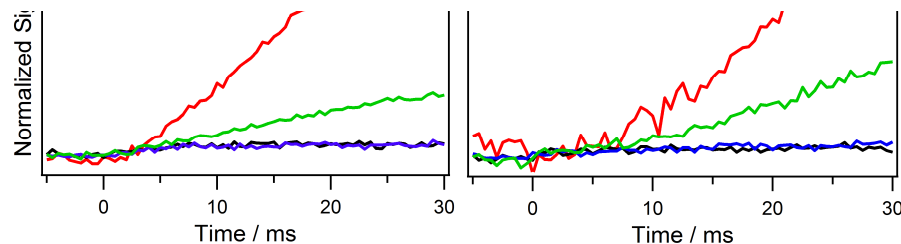
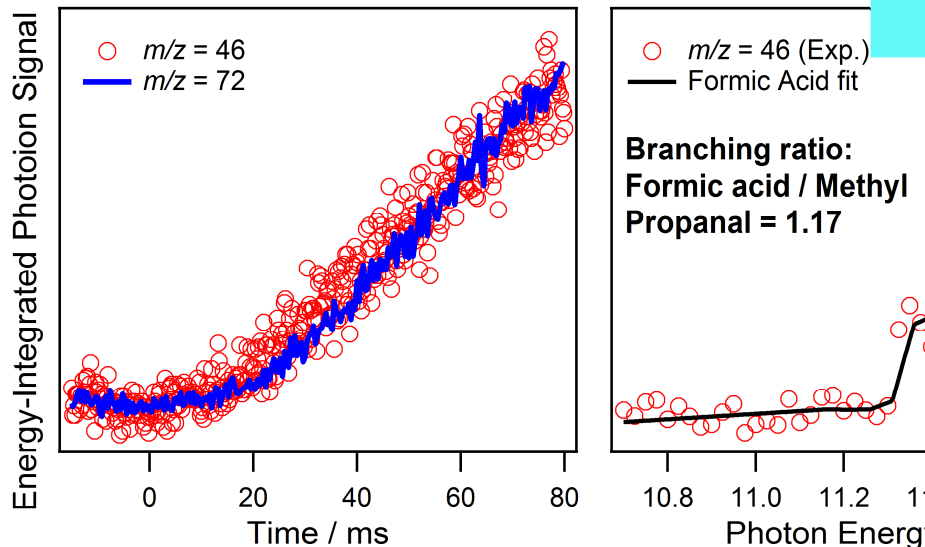


- Observed product at  $m/z = 100$  could well be 2,2-dimethyl-propanedial.

# Results: High-Pressure (1 atm)



1526 Torr, 575 K

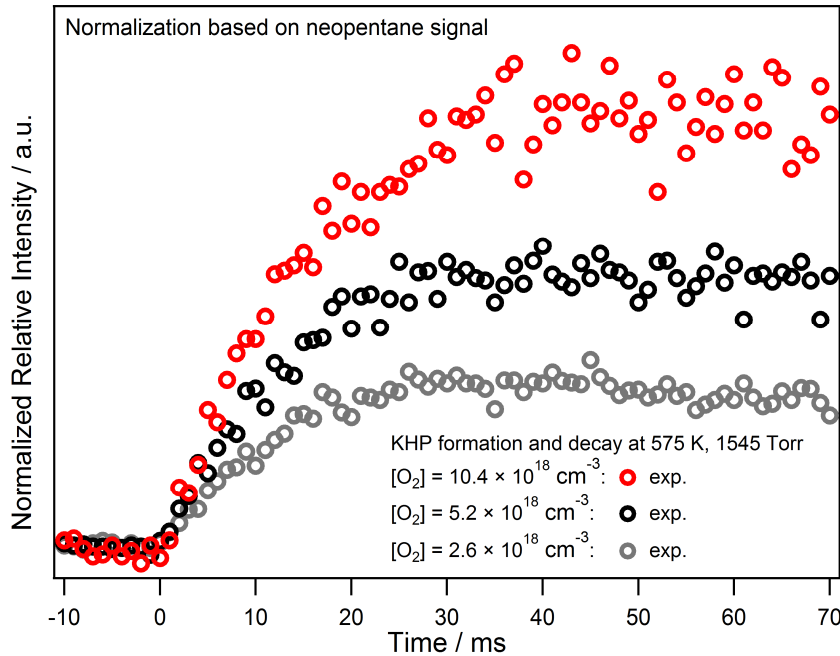


- Time dependency of signals at  $m/z = 58$  and  $70$  lag behind  $m/z = 100$  signal, in agreement with the suggested mechanism
- However, a stronger temperature dependency of  $m/z = 100$  signal in comparison to  $m/z = 58$  and  $70$  signals is not easily explained by the suggested mechanism

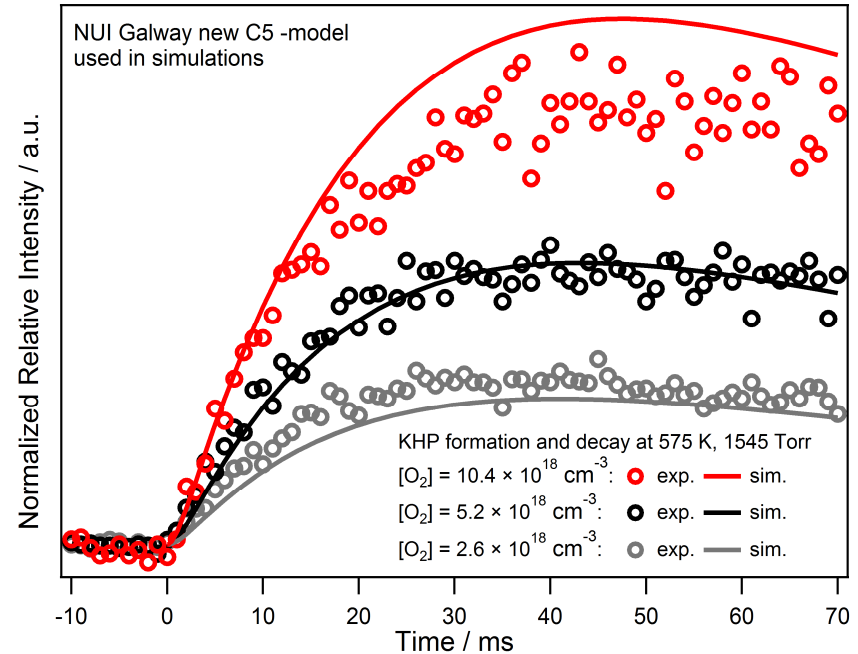
Photon Energy / eV



# 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  $28 \text{ s}^{-1}$  is added to the model
- In addition, simulations reproduce experimentally observed KHP signal intensity dependence on  $[O_2]$  with good accuracy.

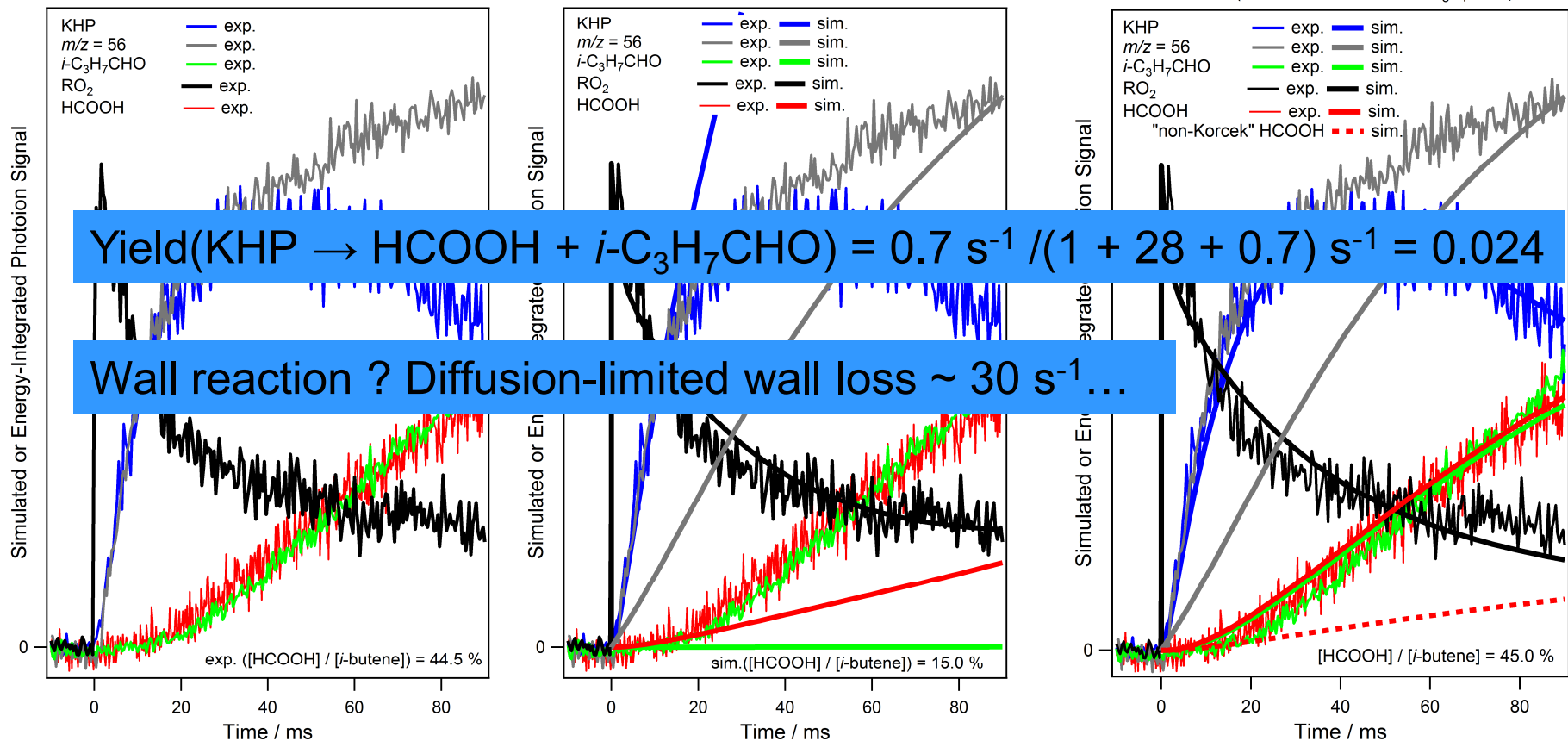
# Exp. Kinetics vs. Model Simulations

- Cl + neopentane + O<sub>2</sub> –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.

575 K, 1526 Torr, [O<sub>2</sub>] =  $5.2 \times 10^{18} \text{ cm}^{-3}$

Unmodified Model:  $k(\text{KHP} \rightarrow \text{OH} + \text{oxy-radical}) \sim 1 \text{ s}^{-1}$

Modified Model:  $k(\text{KHP} \rightarrow \text{OH} + \text{oxy-radical}) \sim 1 \text{ s}^{-1}$   
 $k(\text{KHP} \rightarrow \text{not forming OH}) \sim 28 \text{ s}^{-1}$   
 $k(\text{KHP} \rightarrow \text{HCOOH} + i\text{-C}_3\text{H}_7\text{CHO}) \sim 0.7 \text{ s}^{-1}$





# Conclusions and Acknowledgements

- Direct, time-resolved measurements of product formation in neopentane oxidation experiments were performed both at low ( $\sim 8$  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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