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Direct observation of ketohydroperoxide formation and decomposition in photolytically initiated oxidation of *n*-butane, neopentane, and diethylketone (DEK)

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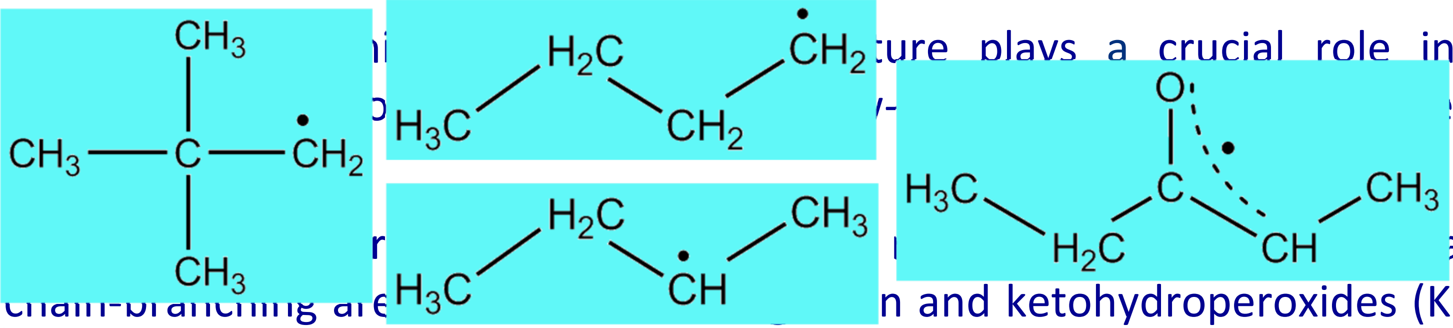
Introduction



- i ture plays a crucial role in the
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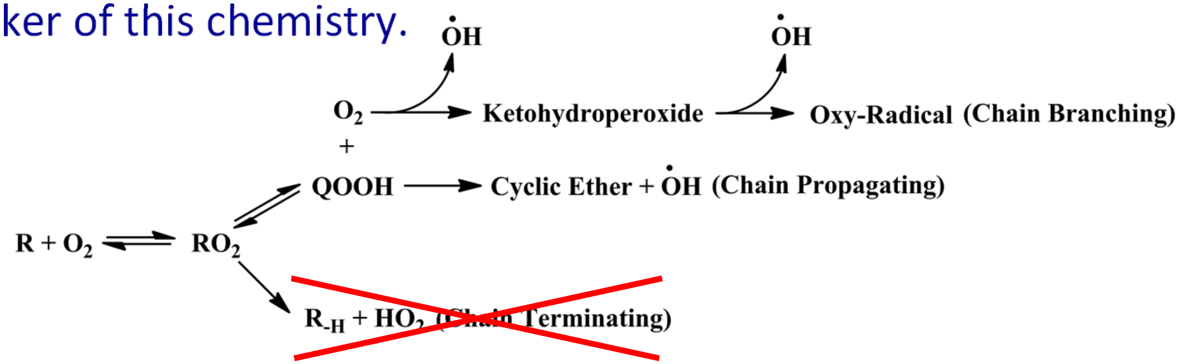
- r r ad to chain-branching are n and ketohydroperoxides (KHP's) are a marker of this chemistry.



$R + O_2 \rightleftharpoons RO_2$

$RO_2 \rightleftharpoons QOOH$

$QOOH \longrightarrow$ Cyclic Ether + $\dot{O}H$ (Chain Propagating)

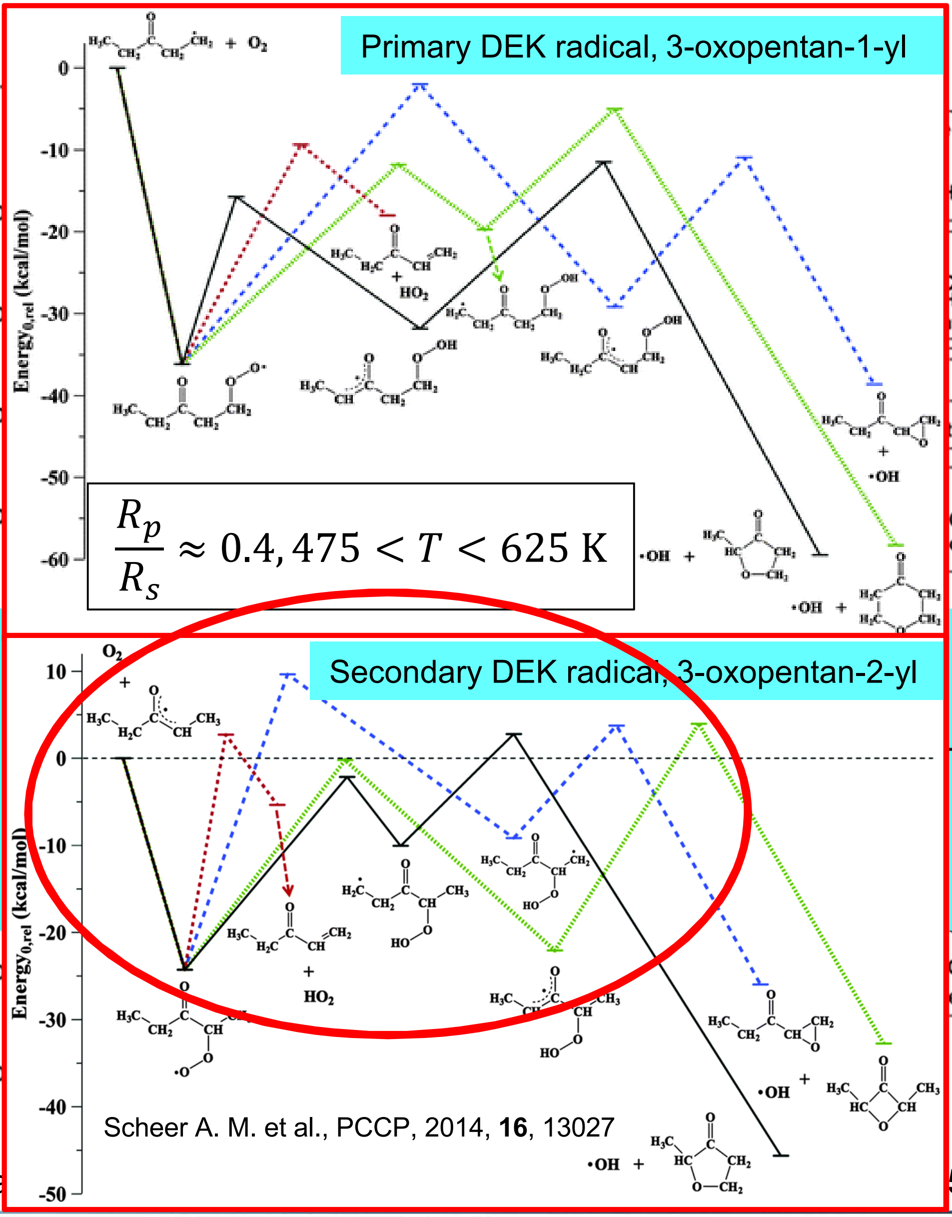
O_2 + QOOH $\longrightarrow$ Ketohydroperoxide + $\dot{O}H$ $\longrightarrow$ Oxy-Radical + $\dot{O}H$ (Chain Branching)

$RO_2 \longrightarrow$ ~~$R_{-H} + HO_2$ (Chain Terminating)~~

- Fuel radicals of the current work are different: neopentyl radical has no β-hydrogens, 1-butyl + O_2 and 2-butyl + O_2 radicals constitute a smallest system with low-temperature behavior of larger hydrocarbons, and secondary DEK radical (3-oxopental-2-yl, main radical of the system) is resonantly stabilized.

- We study Cl-atom initiated oxidation chemistry of neopentane, *n*-butane, and 3-pentanone using a High-Pressure (HP) reactor under 475 – 700 K and 1 – 7 atm conditions.

PESs of R + O_2, QOOH + O_2, and KHP decomposition



Primary DEK radical, 3-oxopentan-1-yl

$$\frac{R_p}{R_s} \approx 0.4, 475 < T < 625\text{ K}$$

Secondary DEK radical, 3-oxopentan-2-yl

Scheer A. M. et al., PCCP, 2014, **16**, 13027

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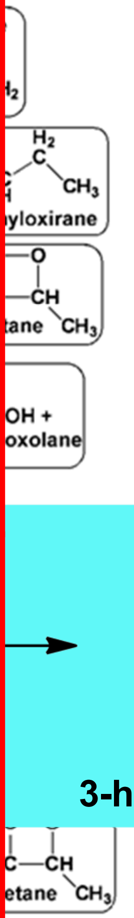
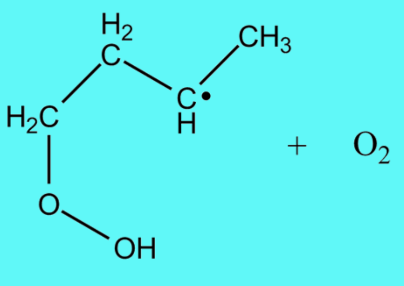
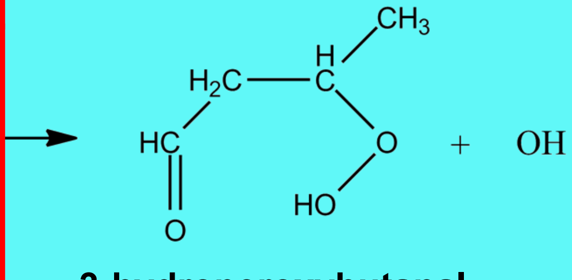


P decomp.





3-hydroperoxybutanal

$E_{0,}$

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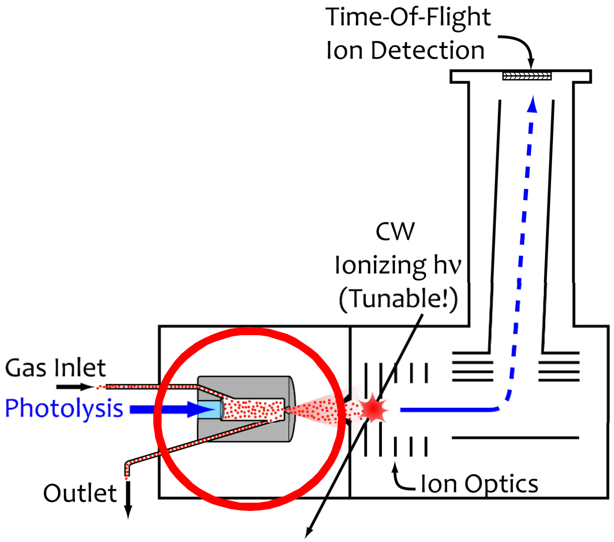
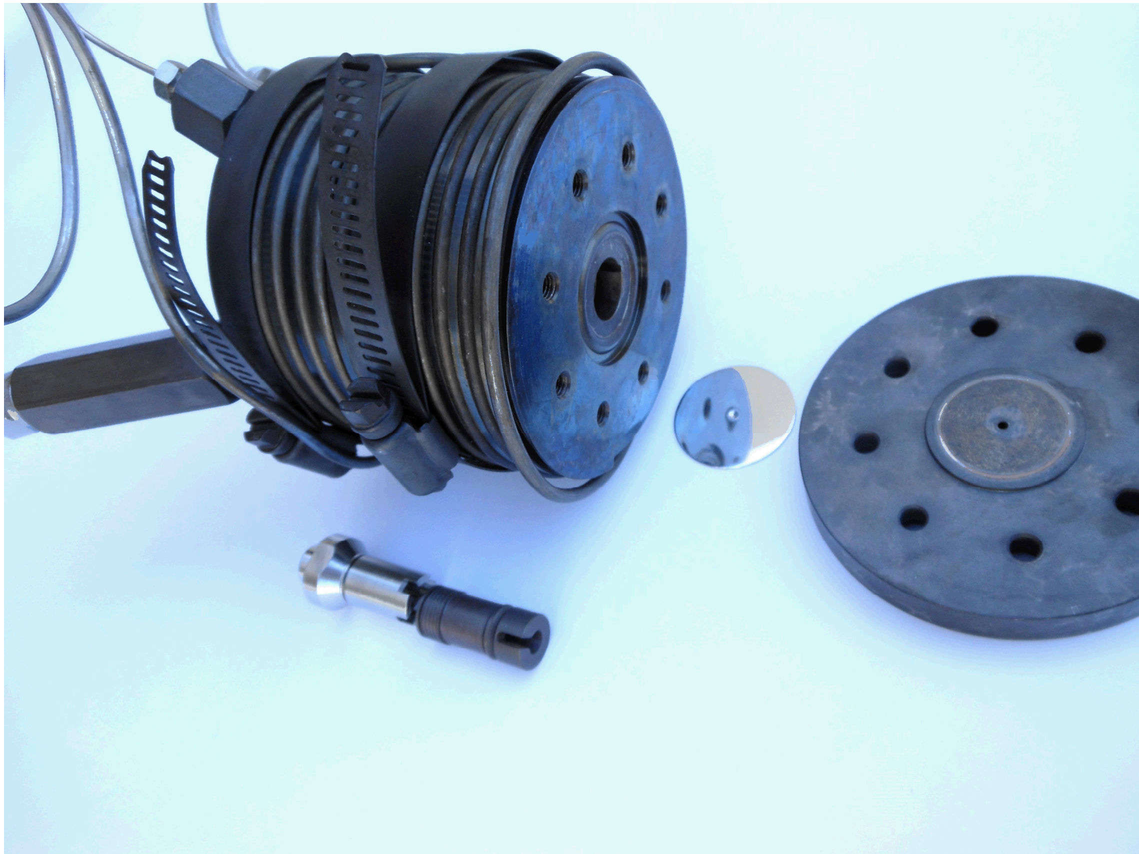
5, **35(1)**, 291 – 298.

Experimental

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



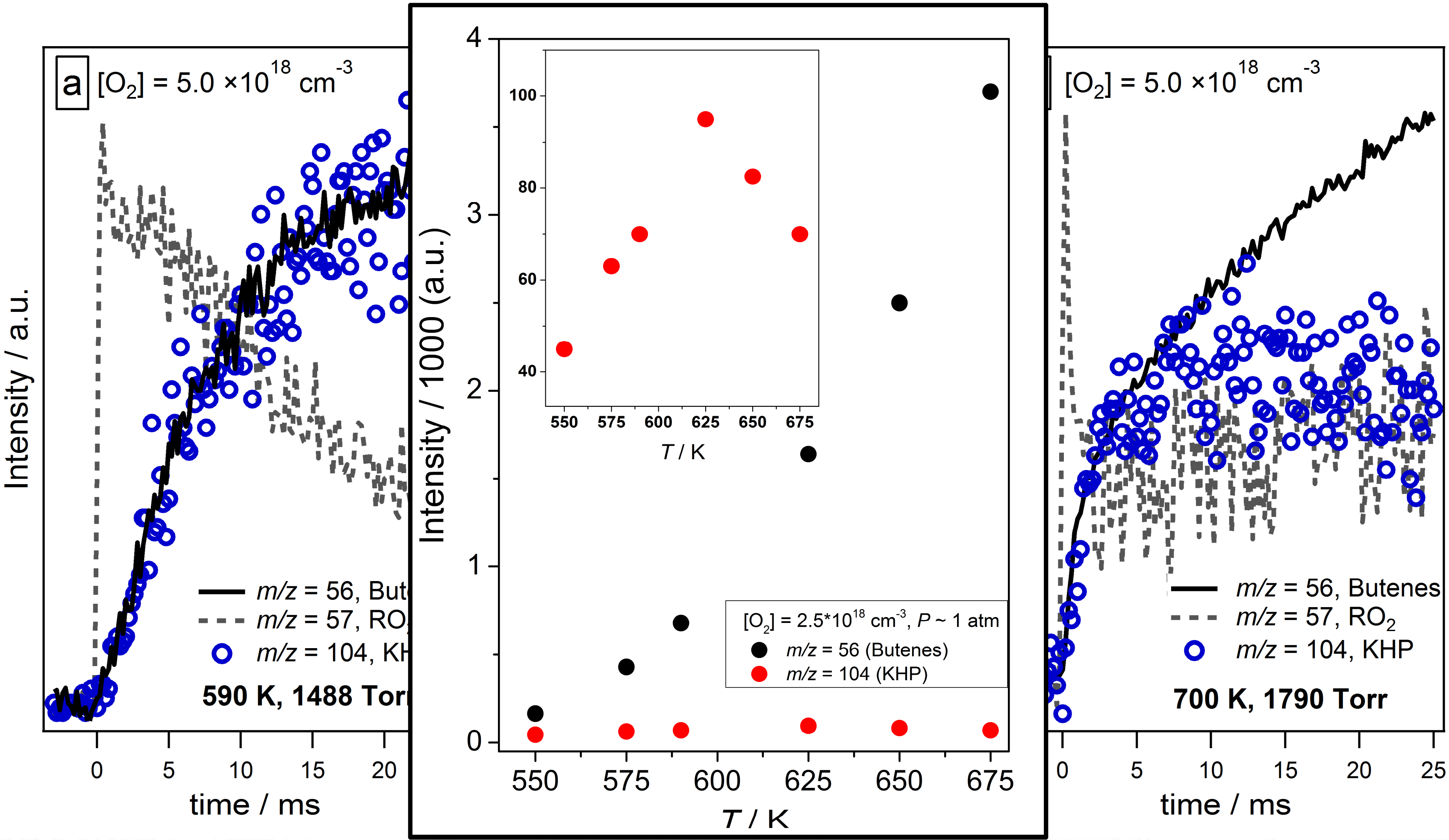
High-Pressure reactor (~ 1 – 10 atm)
Metal or Quartz surface in contact with reacting gases



- Oxidation initiated by 193 nm photolysis of $CFCl_3 \rightarrow CFCl_2 + Cl$ or 248 nm photolysis of $(ClCO)_2 \rightarrow 2{*}Cl + 2{*}CO$

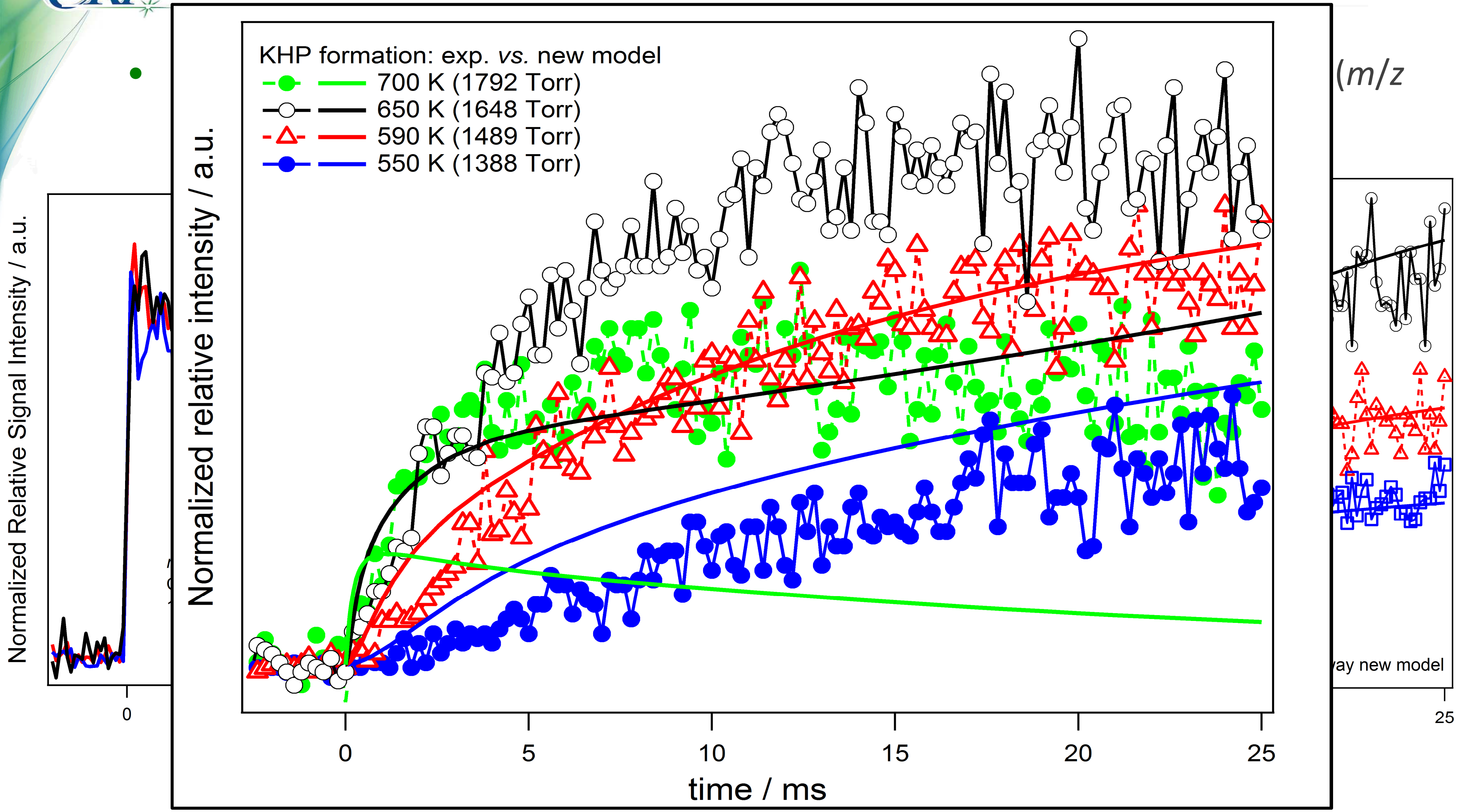
KHP formation and decomposition: *n*-butane

- Important products for autoignition observed at *m/z* = 56 (butenes), *m/z* = 57 (RO_2), *m/z* = 72 (oxygenates), and *m/z* = 104 (KHP, ketohydroperoxide)



KHP and *n*-butane: The effect of $[O_2]$ and *T*

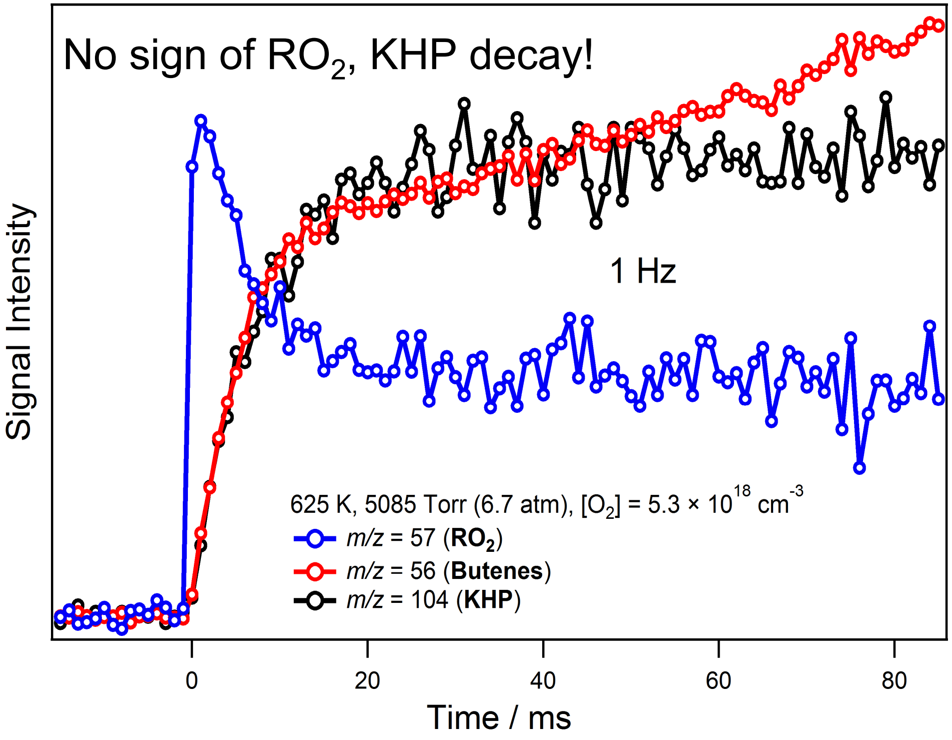
- (*m*/*z*

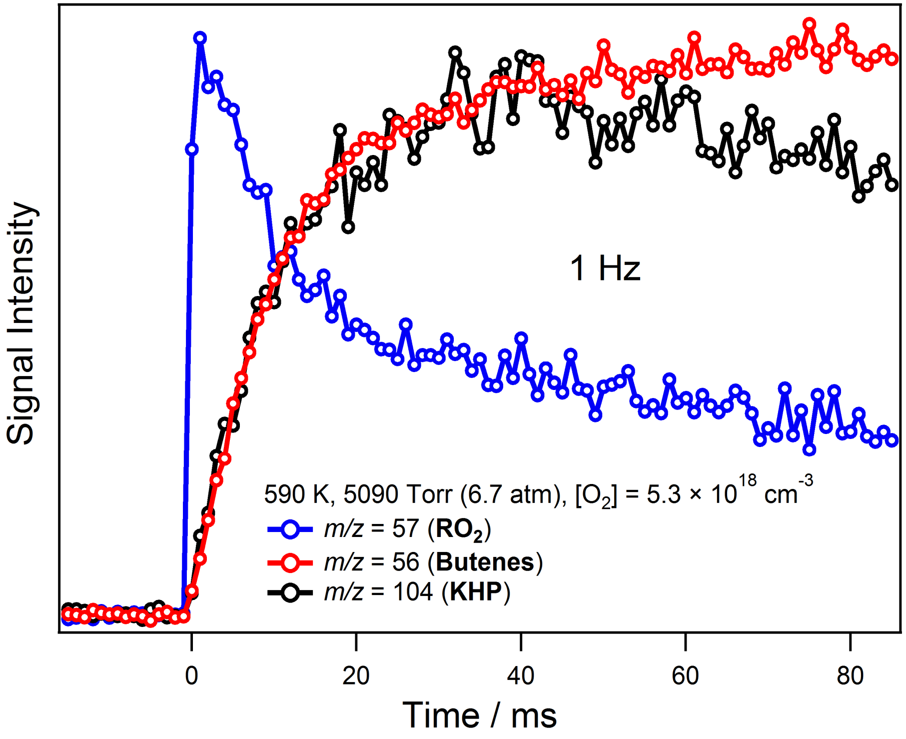


- Under constant conditions (total density, $[O_2]$) KHP signal intensity and formation rate increases with temperature up to about 650 K. At higher *T* KHP signal intensity decreases, probably due to unimolecular decomposition of KHP.

KHP and *n*-butane: The effect of pressure

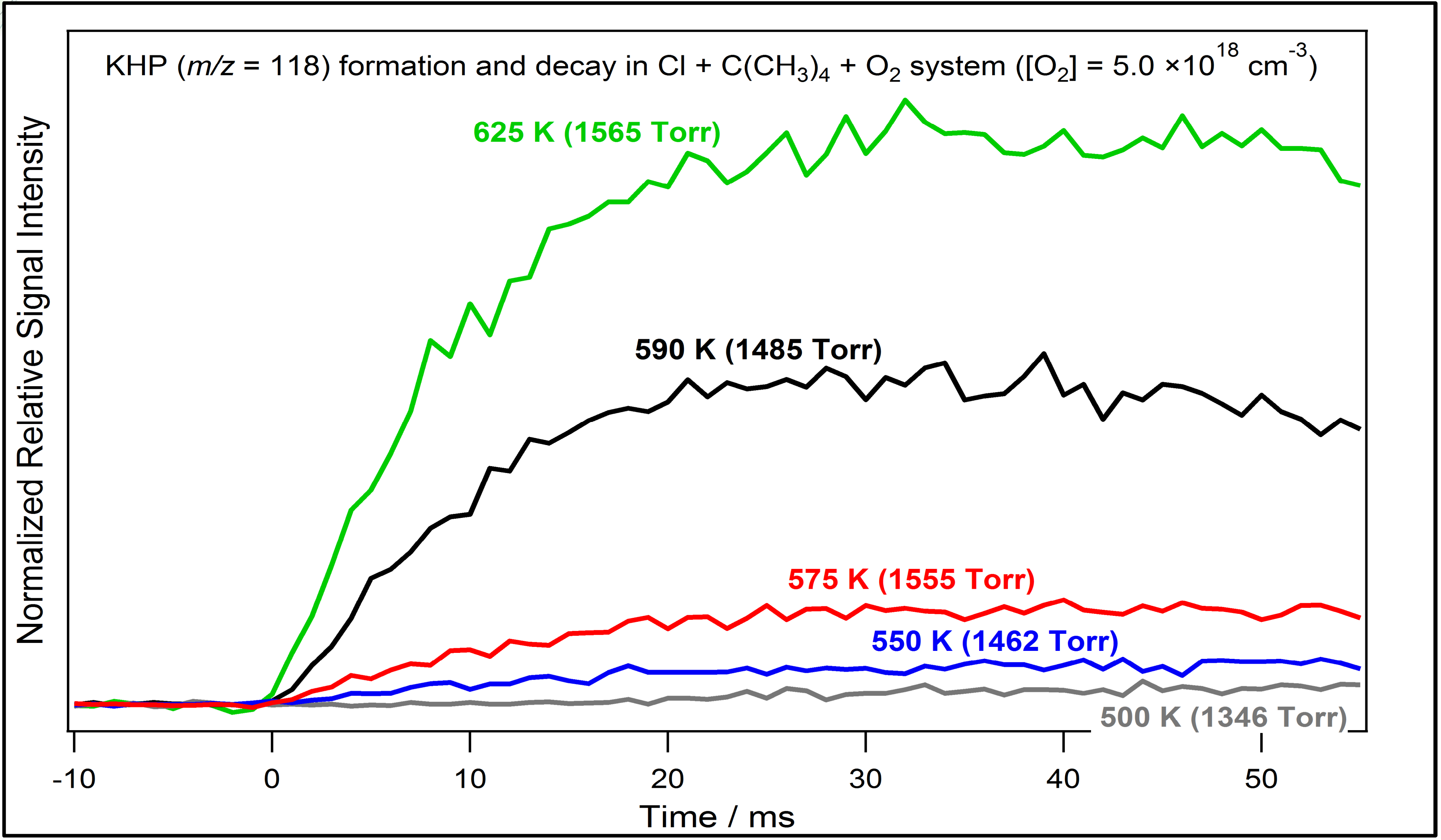
- We estimate that diffusion-limited wall-loss rate of KHP at 2 atm, 590 K is ~ 35 s^{-1} and at 6.7 atm, 590 K ~ 10 s^{-1}.


No sign of RO_2, KHP decay!



- Once temperature was increased from 625 to 640 K (or higher) at 6.7 atm and $[O_2]$ = 5.3 × 10^{18} cm^{-3}, spontaneous oxidation was observed, i.e. oxidation products appeared at several masses without laser initiation.

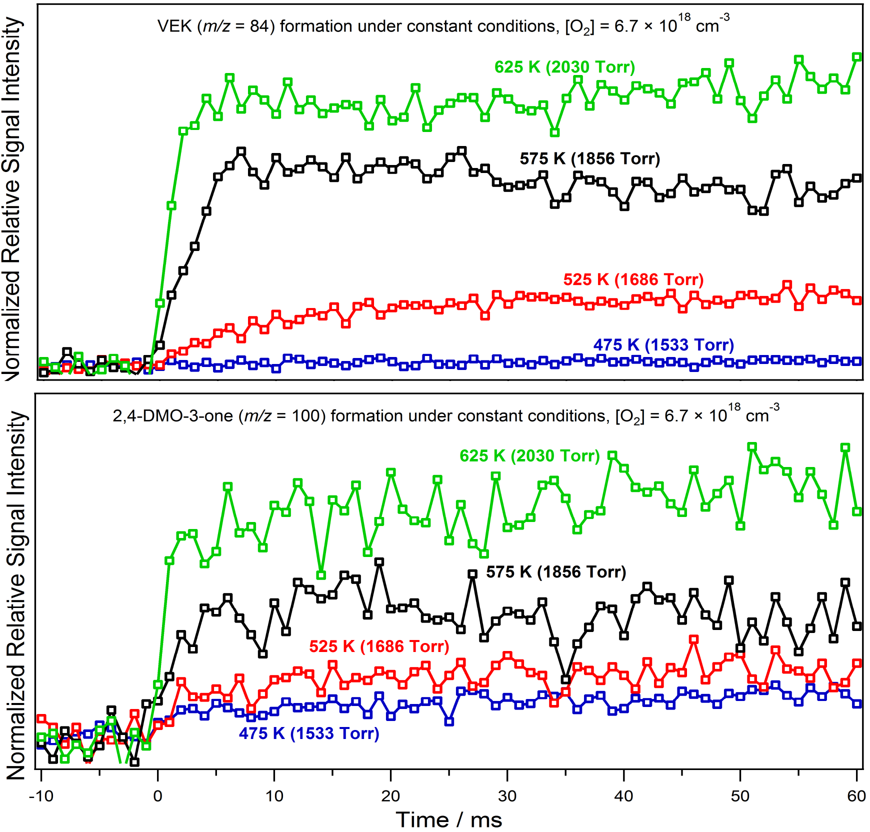
KHP formation and decomposition: neopentane

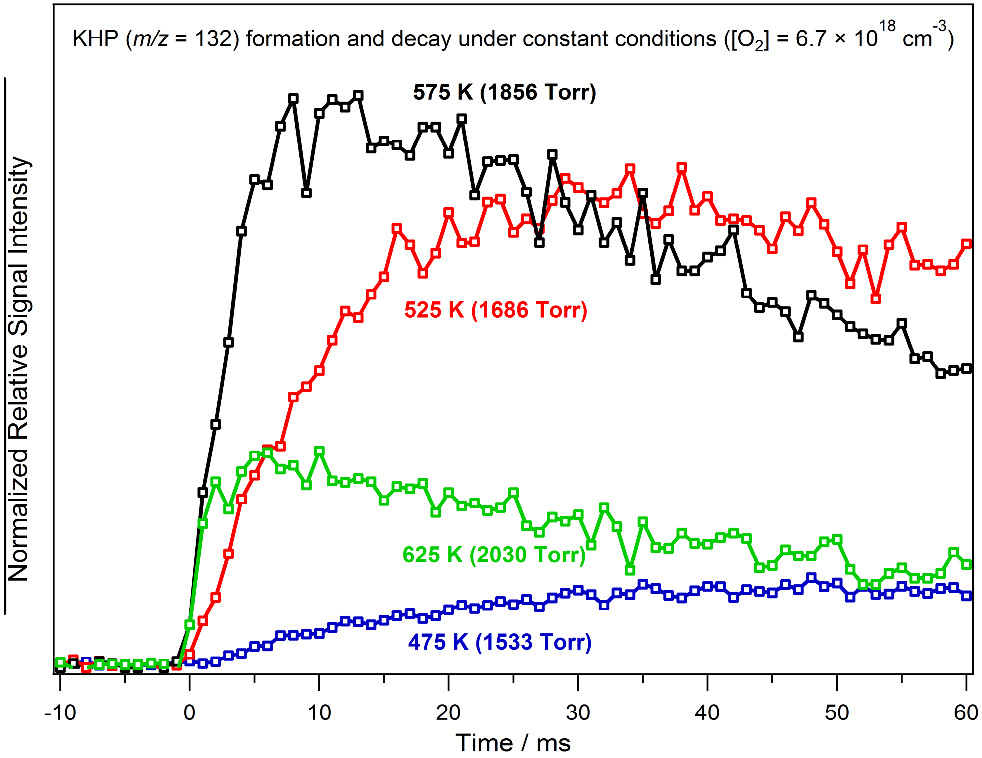


- In neopentane oxidation experiments at 2 atm, KHP signal formation rate and intensity increased with temperature until above ~ 625 K spontaneous oxidation was observed.

KHP formation and decomposition: DEK

- In DEK oxidation experiments, KHP signal (m/z = 132) intensity increases with a factor of ~ 2 as [O_2] is doubled, *i.e.* faster than in case of *n*-butane and neopentane.





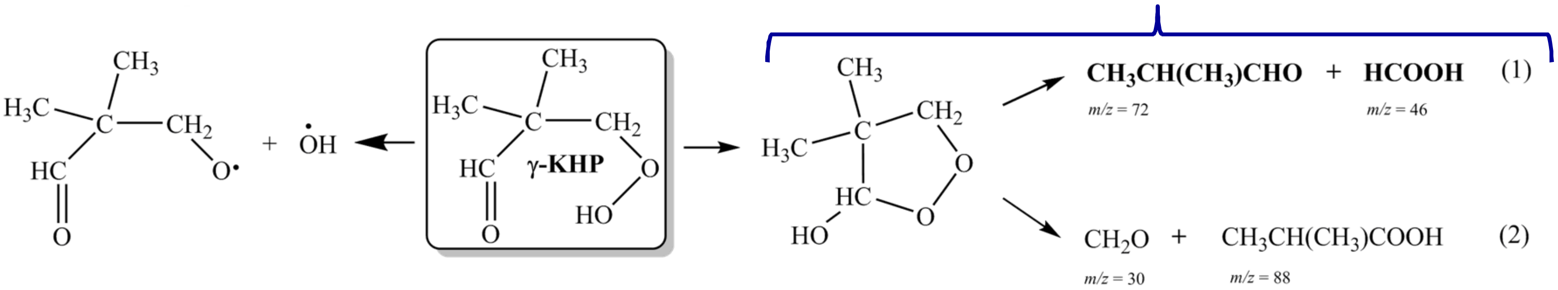
- Probably due to resonance stabilization of both secondary DEK radical (3-oxopental-2-yl) *and* corresponding QOOH radical, intense KHP signal starts to appear at lower *T* than in case of *n*-butane and neopentane, it reaches maximum around 575 K, after which KHP signal intensity starts to decrease with *T*.

KHP decomposition: neopentane

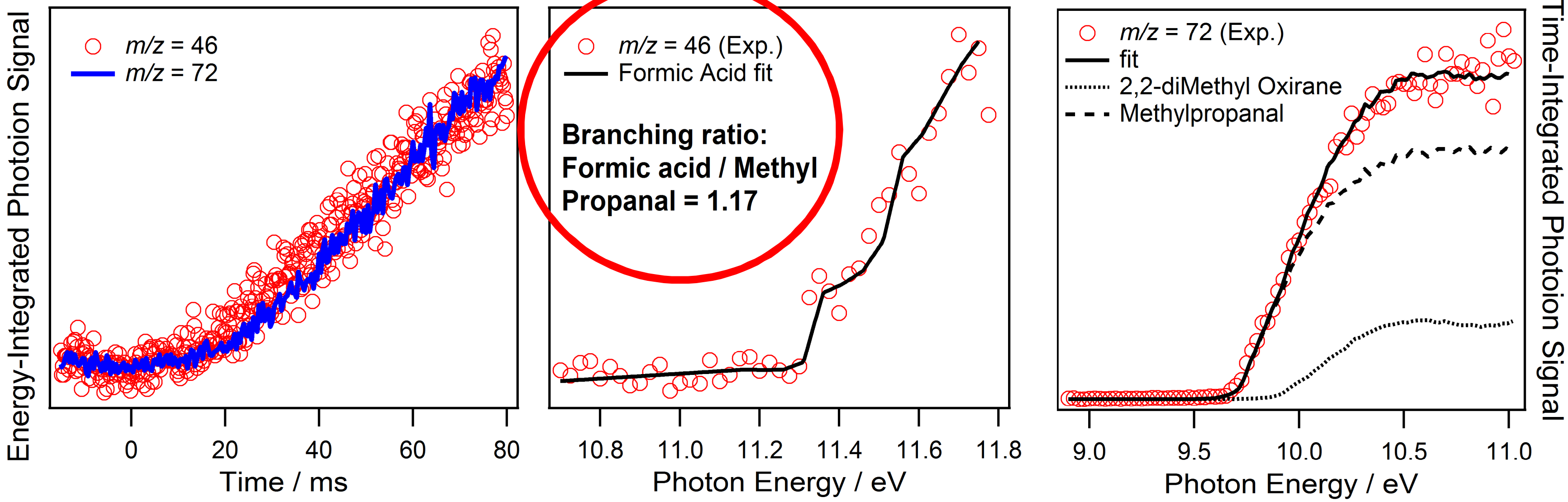
- KHP decomposition *via* suggested Korcek decomposition of γ-ketohydroperoxide * mechanism leads to aldehyde + acid products, *not* to reactive OH + oxy-radicals that are needed for chain-branching, thus this new mechanism reduces system reactivity.

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

Korcek decomposition of γ-ketohydroperoxide

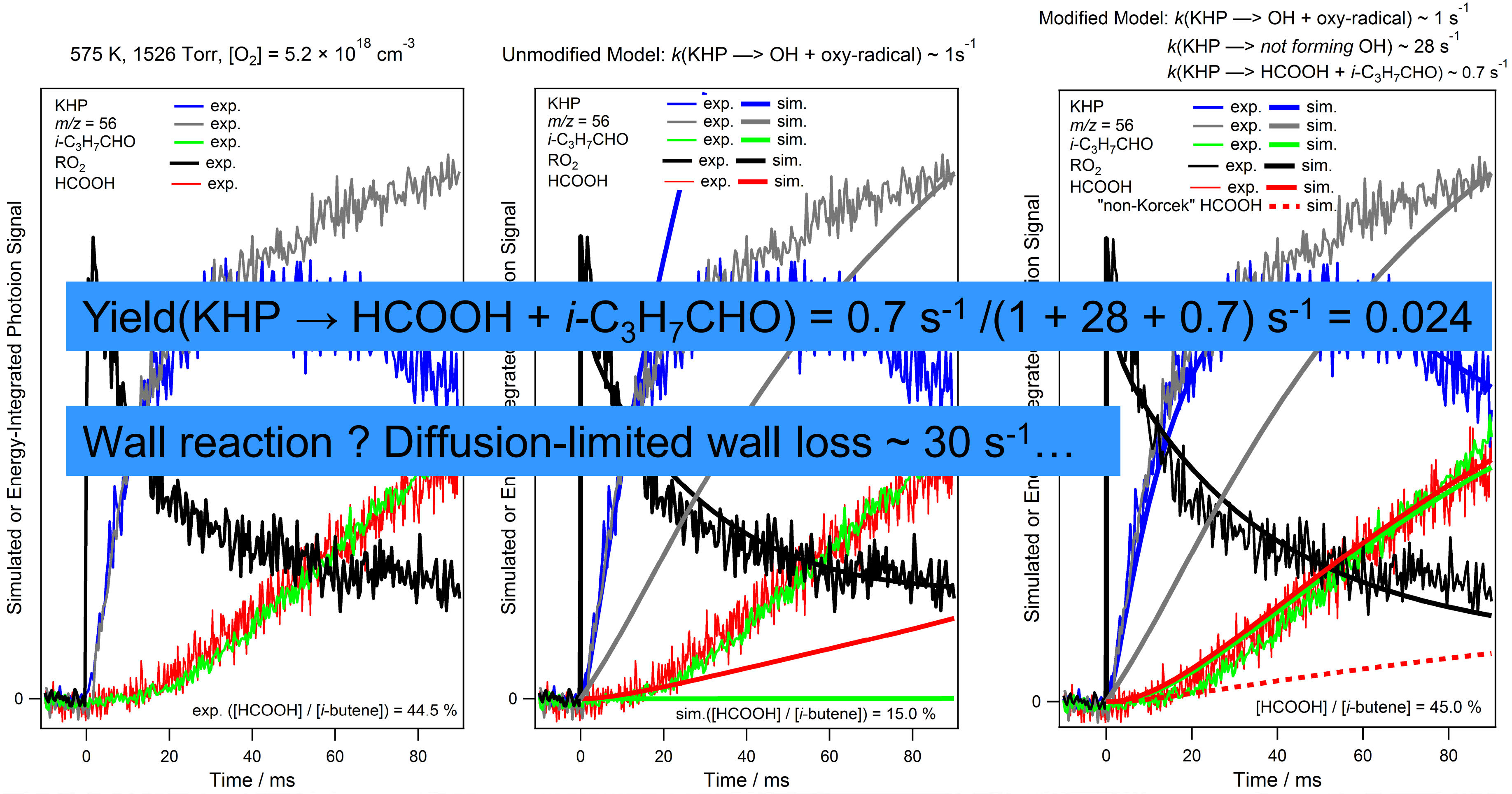


1526 Torr, 575 K



neopentane γ-KHP decomposition: Exp. vs. Model

- Cl + neopentane + O_2 –system was modelled using NUI Galway new C5-model. Without any adjustment, modelled [KHP] increases rapidly that is *not* observed in the 2 atm experiments
- Upon including additional KHP decomposition mechanism in the model which does not produce OH, significantly better agreement is observed between the model and the exp.


575 K, 1526 Torr, $[O_2] = 5.2 \times 10^{18}$ cm^{-3}

Unmodified Model: k(KHP —> OH + oxy-radical) ~ 1s^{-1}

Modified Model: k(KHP —> OH + oxy-radical) ~ 1 s^{-1}
k(KHP —> *not forming* OH) ~ 28 s^{-1}
k(KHP —> HCOOH + i-C_3H_7CHO) ~ 0.7 s^{-1}

Yield(KHP → HCOOH + i-C_3H_7CHO) = 0.7 s^{-1} /(1 + 28 + 0.7) s^{-1} = 0.024

Wall reaction ? Diffusion-limited wall loss ~ 30 s^{-1}…

Conclusions and Acknowledgements

- Direct, time-resolved measurements of ketohydroperoxide formation in Cl-atom initiated *n*-butane, neopentane, and DEK oxidation experiments were performed at high, 2 – 7 atm, pressures.

- Current KHP formation measurements clearly show differences among systems studied: intensity and rate of KHP formation in neopentane oxidation experiments increase with temperature up to a point of spontaneous oxidation, while both in *n*-butane and DEK experiments KHP formation was observed to first increase and then decrease with temperature. Also, KHP formation was observed in DEK experiments at ~ 75 K lower temperatures than in *n*-butane measurements.

- It is concluded that more direct study of KHP decomposition and other studies of KHP, e.g. absolute photoionization cross section and reaction kinetics with OH radical, would be greatly helpful to better understand chain-branching mechanism.

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