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Direct observation of low temperature QOOH chemistry using *tert*-butyl hydroperoxide as precursor

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Introduction

The hydroperoxyalkyl (QOOH) radical is one of the most important classes of intermediate radicals in alkane oxidation reactions, responsible for low-temperature chain branching. However, no QOOH has ever been directly observed because of its high reactivity and hence short lifetime. The information about their reactions in current combustion mechanisms is only inferred. Thus, direct observation or measurement is needed to establish a full model of hydrocarbon oxidation.
We have used reactions of Cl atom with alkylhydroperoxides (ROOH), e.g., *tert*-Butyl hydroperoxide (TBHP), as a precursor to generate QOOH directly through a Cl atom initiated reaction system in the temperature range of 296K – 500K. The Cl atoms are produced through photolysis of Cl_2 at 355nm.

$(CH_3)_3COOH + Cl \rightarrow (CH_3)_2C(CH_2)OOH + HCl$

The products are analyzed in detail by our multiplexed chemical kinetic photoionization mass spectrometer using the synchrotron light at Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. For TBHP we have directly observed the dissociation of the generated QOOH to OH radical and 2,2-dimethyloxirane:

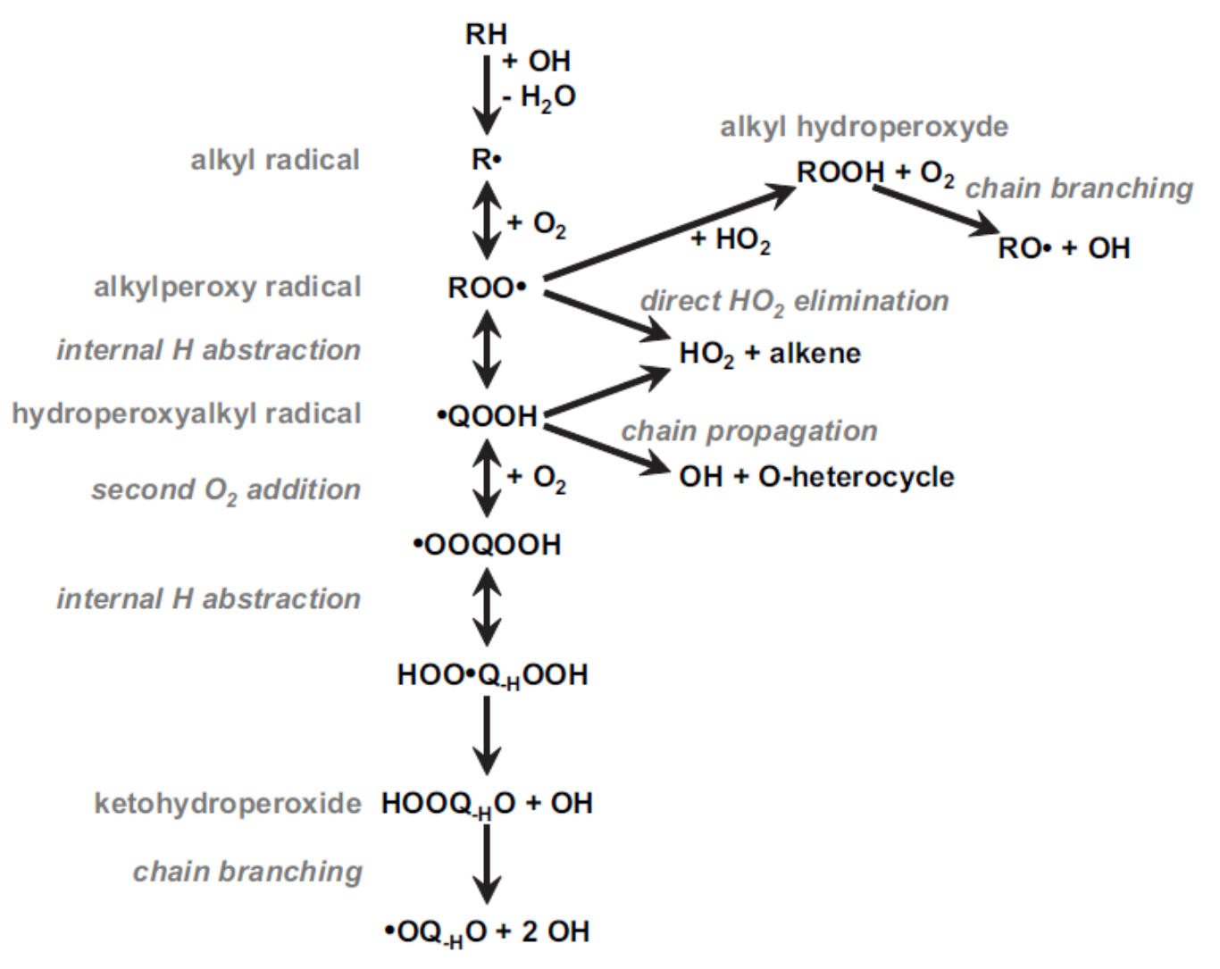
$(CH_3)_2C(CH_2)OOH \rightarrow OH$ + 2,2-dimethyloxirane with rate constant k_D

Under our experimental conditions we did not observe HO_2 + isobutene production, in accordance with the calculated PES. But with oxygen in the reaction system, the reaction between QOOH and oxygen can compete with its dissociation:

$(CH_3)_2C(CH_2)OOH + O_2 \rightarrow$ products with rate constant k_{Bi}

The yield of 2,2-dimethyloxirane decreases versus the concentration of oxygen in the system, while the yield of formaldehyde increases with oxygen concentration. Measurement of the change in product composition enables a direct, although relative, measurement of QOOH + O_2 reaction kinetics. In a separate set of experiments, the OH radical generated in the reactions was monitored by IR absorption spectroscopy at 3484.599 cm^{-1} in a pulsed laser photolysis flow reactor.

Mechanism of low temperature hydrocarbon oxidation and auto-ignition chemistry:

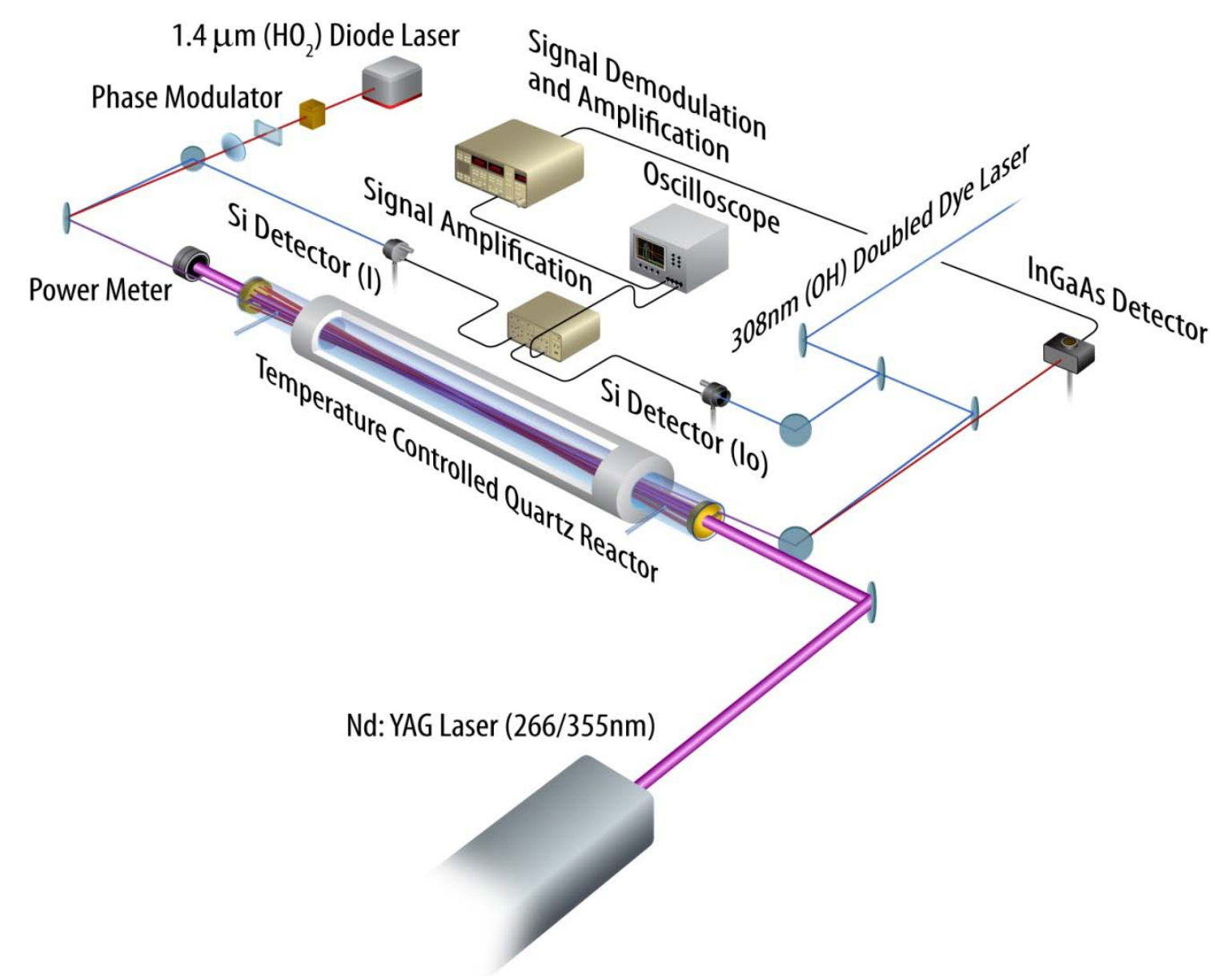


[1] Progress in Energy and Combustion Science **2011**, 37, 371-421

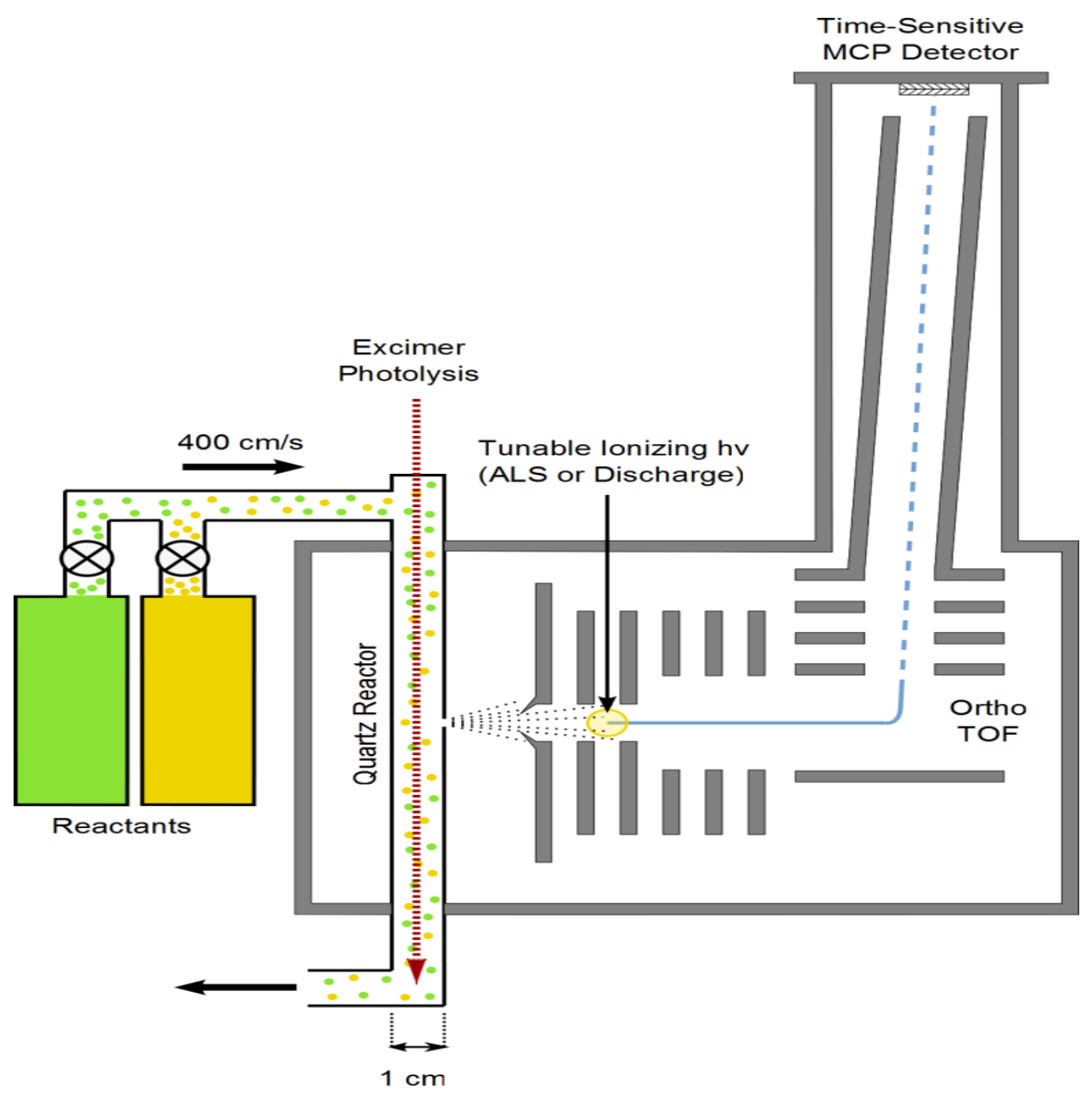
[2] Angew. Chem. Int. Ed. **2010**, 49, 3169-3172

Experiment

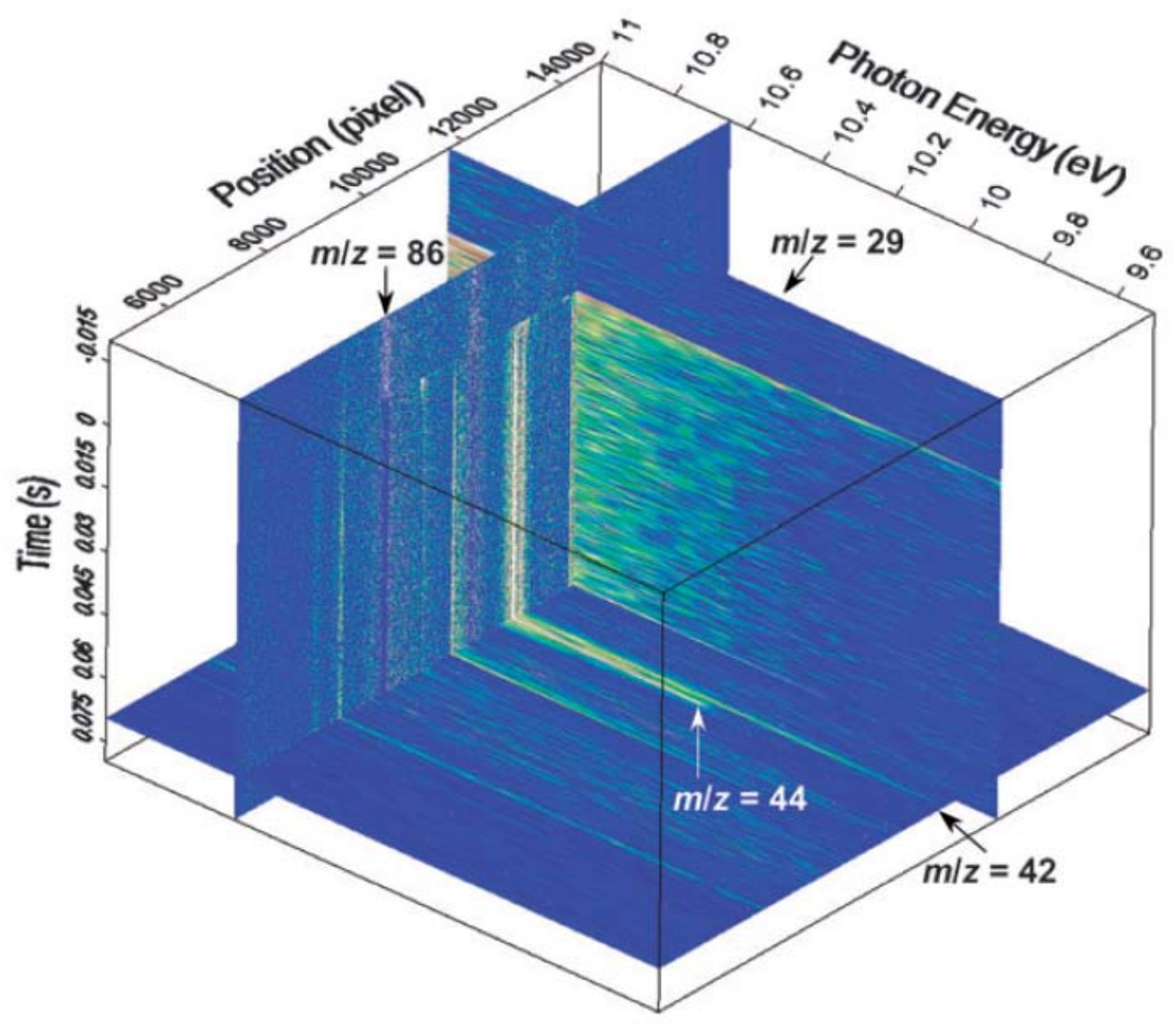
1. Pulsed laser photolysis flow reactor with multi-pass absorption probe:



2. Multiplexed chemical kinetic photoionization mass spectrometer:



- •3-D data cube, ion signal is a function of m/z, synchrotron photon energy and time delay after photolysis
- •Integrating over a small range of photon energy gives a time-resolved mass spectrum.
- •Integrating over the kinetic time generates a photoionization efficiency (PIE) spectrum for each mass, which is utilized to identify isomeric species by their ionization energy and their photoionization spectra.
- •Integrating over a single mass gives the time dependence of the PIE spectrum of the mass, which can reveal the dynamics of isomerization process.



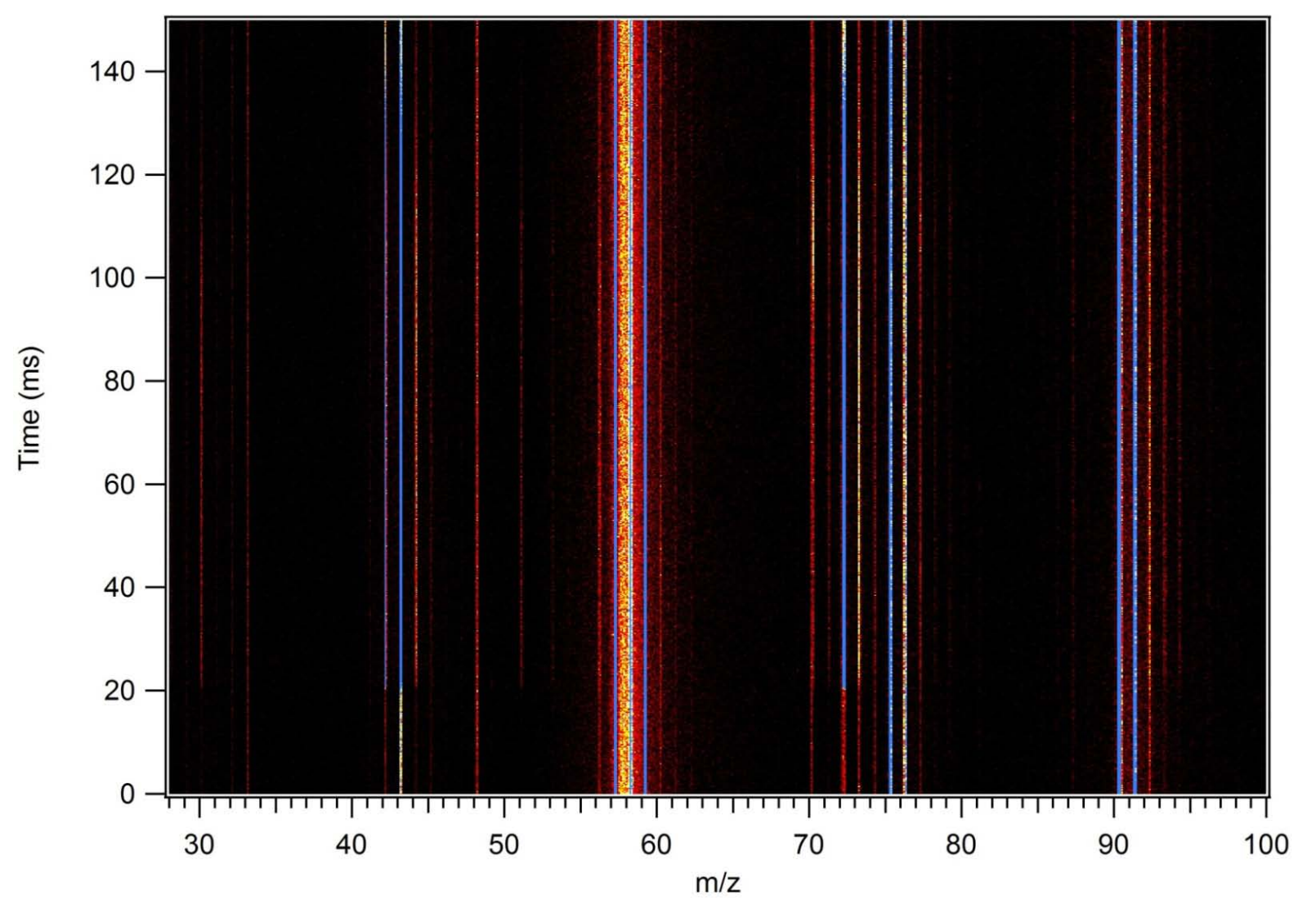
[3] RSI, **1997**, 68, 1875-1878

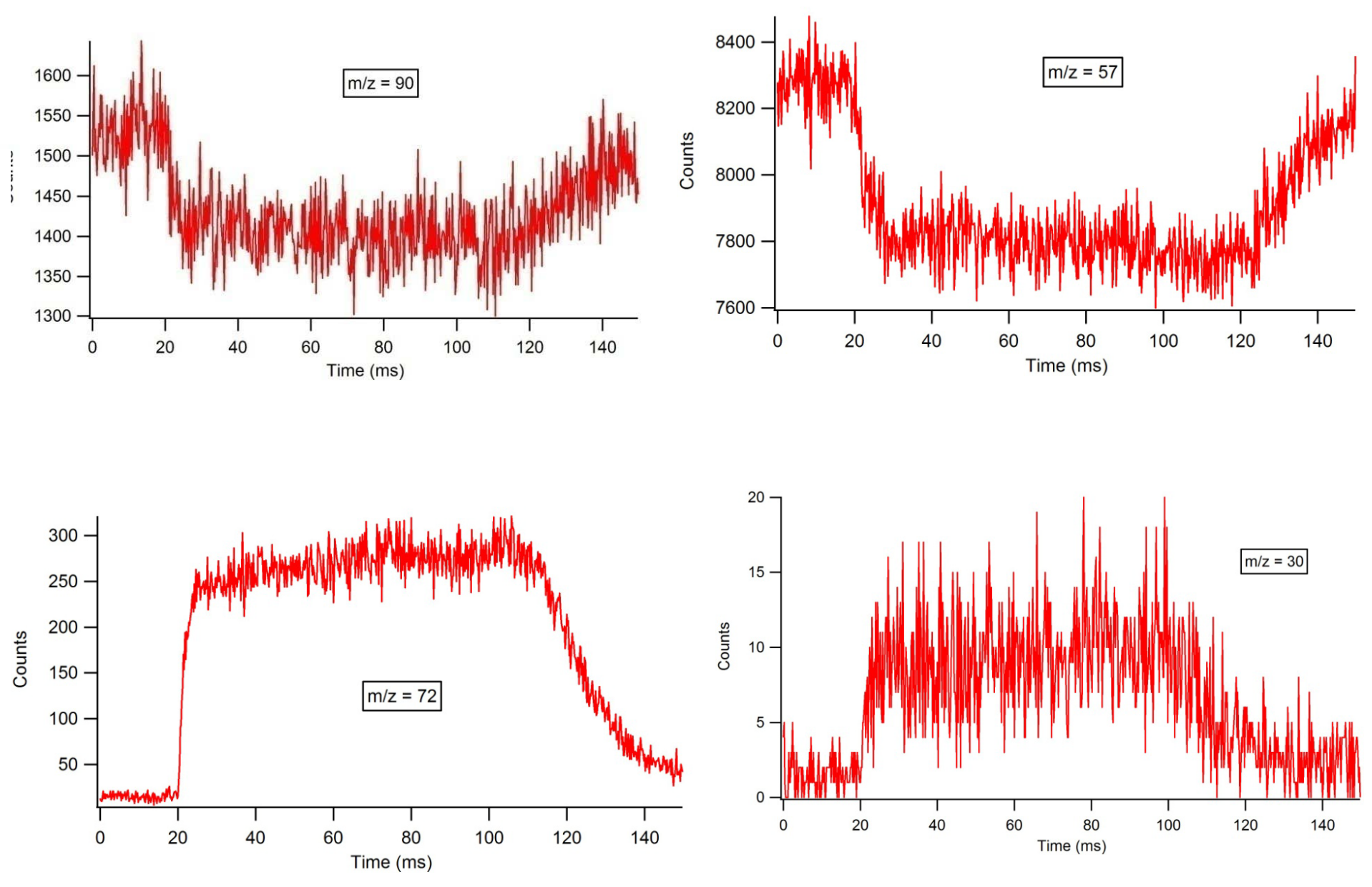
[4] PCCP, 2008, 10, 20-34

Results and discussion

1. Main products

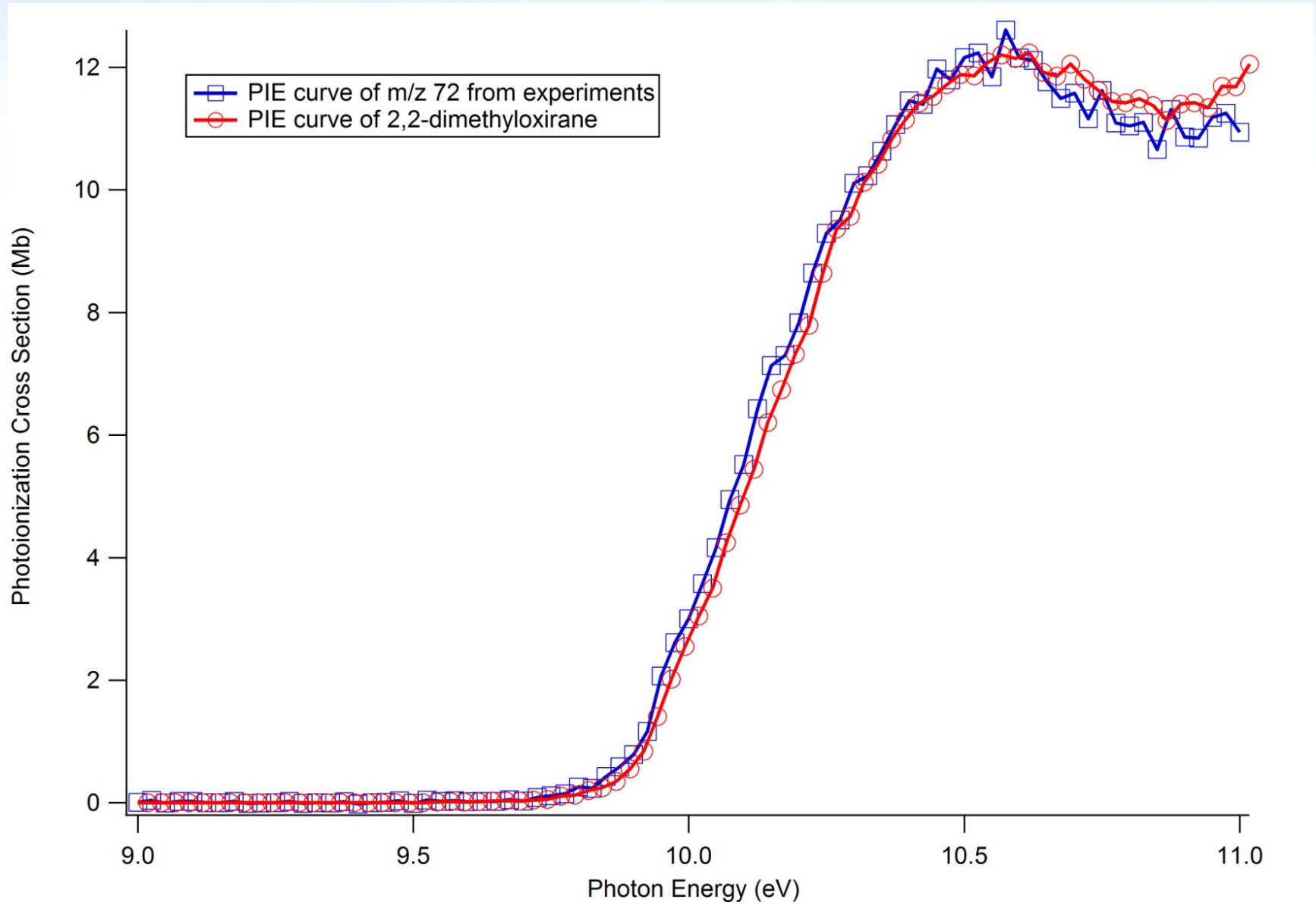
Time-resolved mass spectrum of products

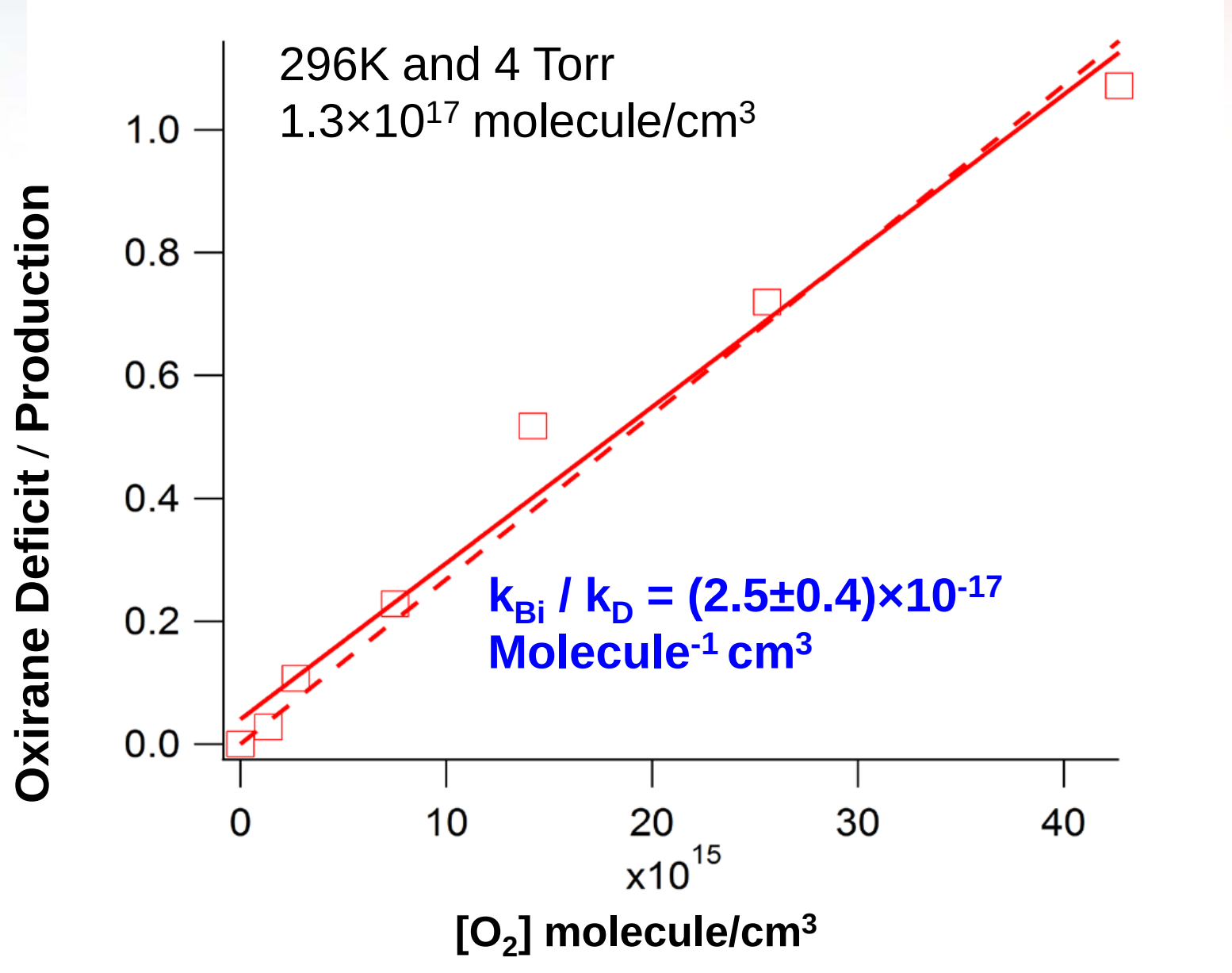




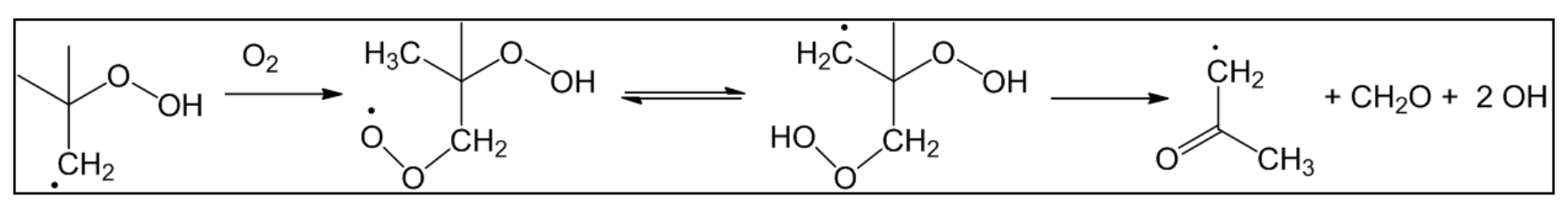
Dissociative ionization products: m/z = 42, 43, 44 from m/z = 72 and m/z = 57 from m/z = 90
Main products: m/z = 72, 2,2-dimethyloxirane and m/z = 30, formaldehyde
No QOOH observed at m/z = 89.
Although there exist some stable $QOOH^+$, the $QOOH^+$ from TBHP is not bounded.

Results and discussion





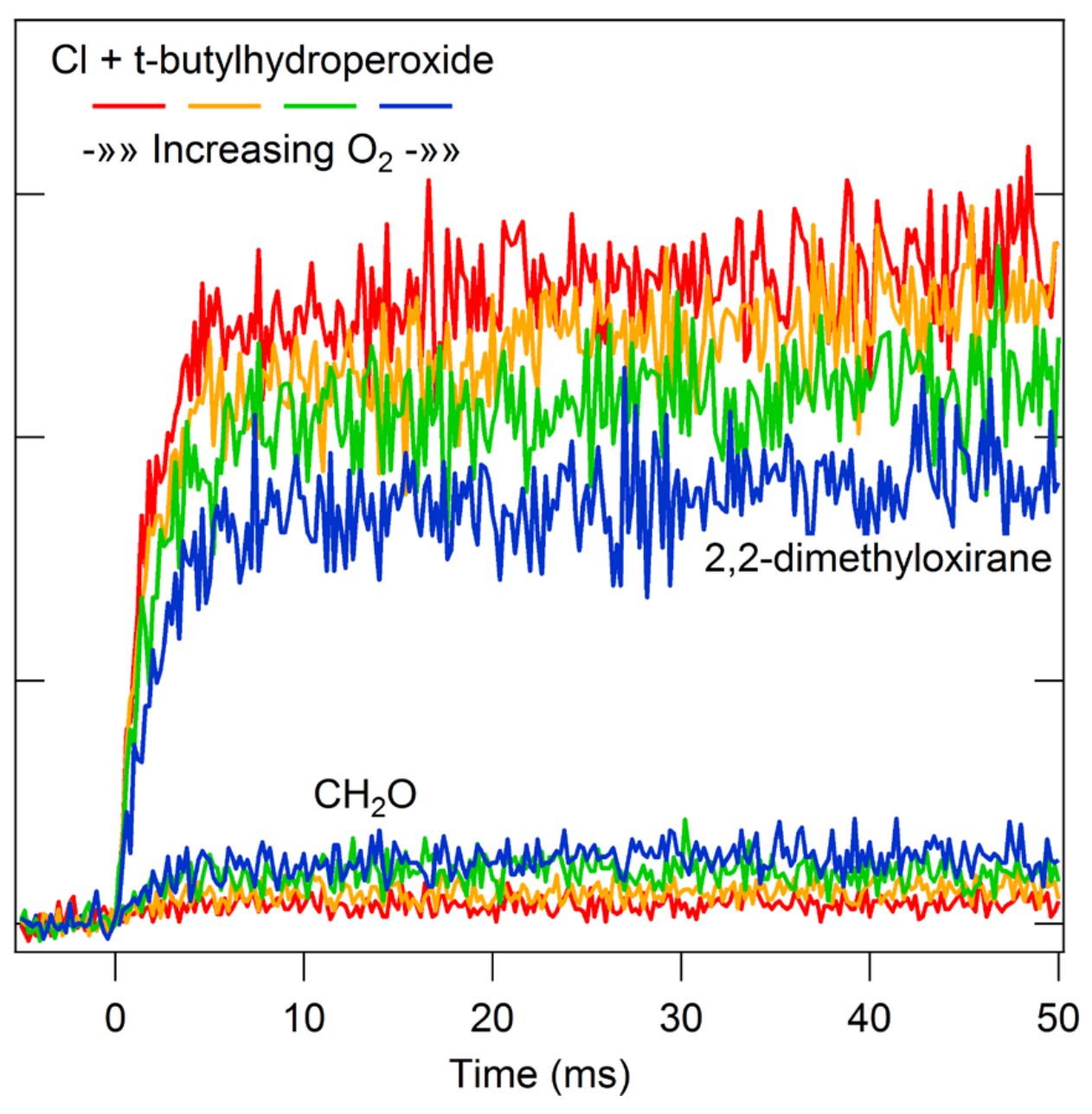
2. Competition between dissociation and O_2 addition



- •The production of 2,2-dimethyloxirane decreases but that of CH_2O increases with O_2 concentration.
- •By neglecting the effect of OH from the reaction O_2 + QOOH, the ratio between oxirane deficit and its production is proportional to the ratio between two rate coefficients:

{oxirane (no O_2) – oxirane (O_2)} / oxirane (O_2)
= k_{Bi} [O_2] / k_D

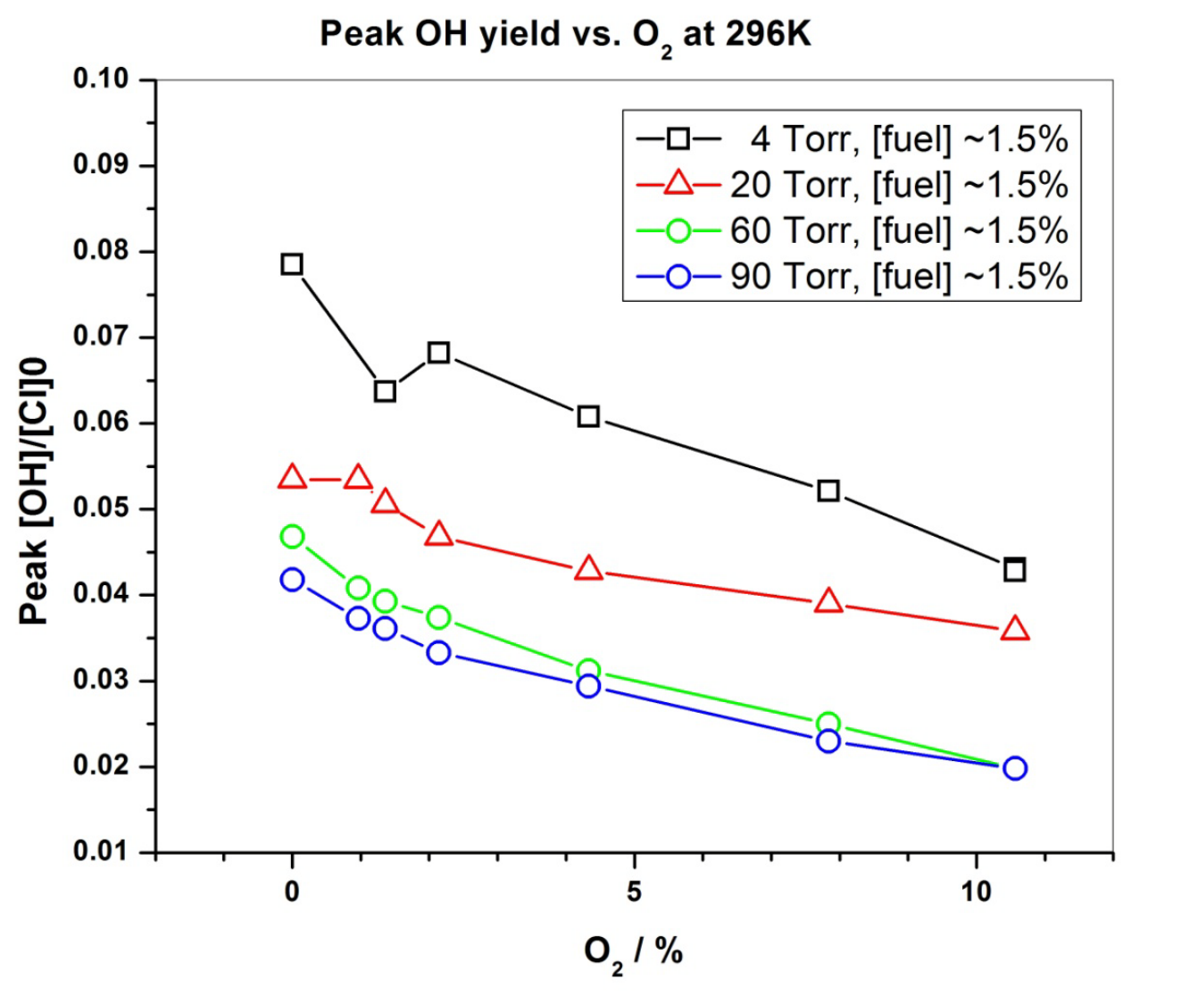
The ratio kBi/kD is estimated to be $(2.5\pm0.4)\times10^{-17}$ molecule^{-1} cm^3 (95% confidence) at 296K and 4 Torr.

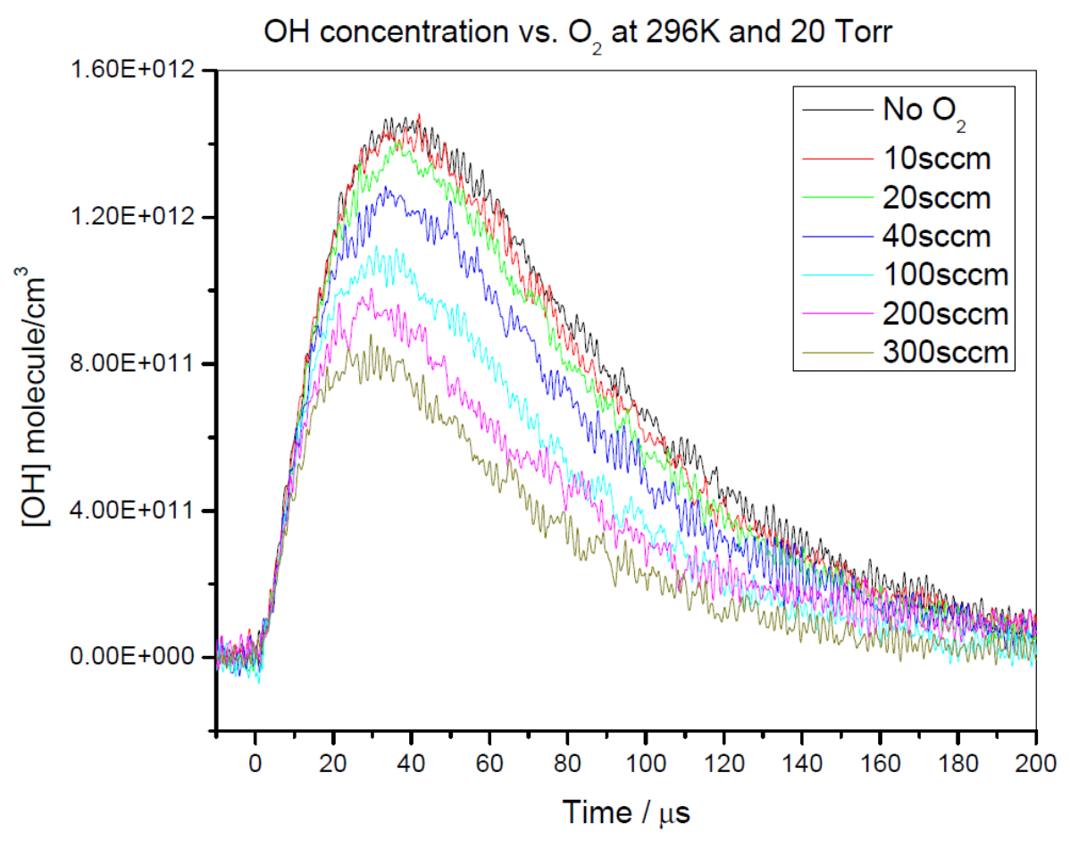


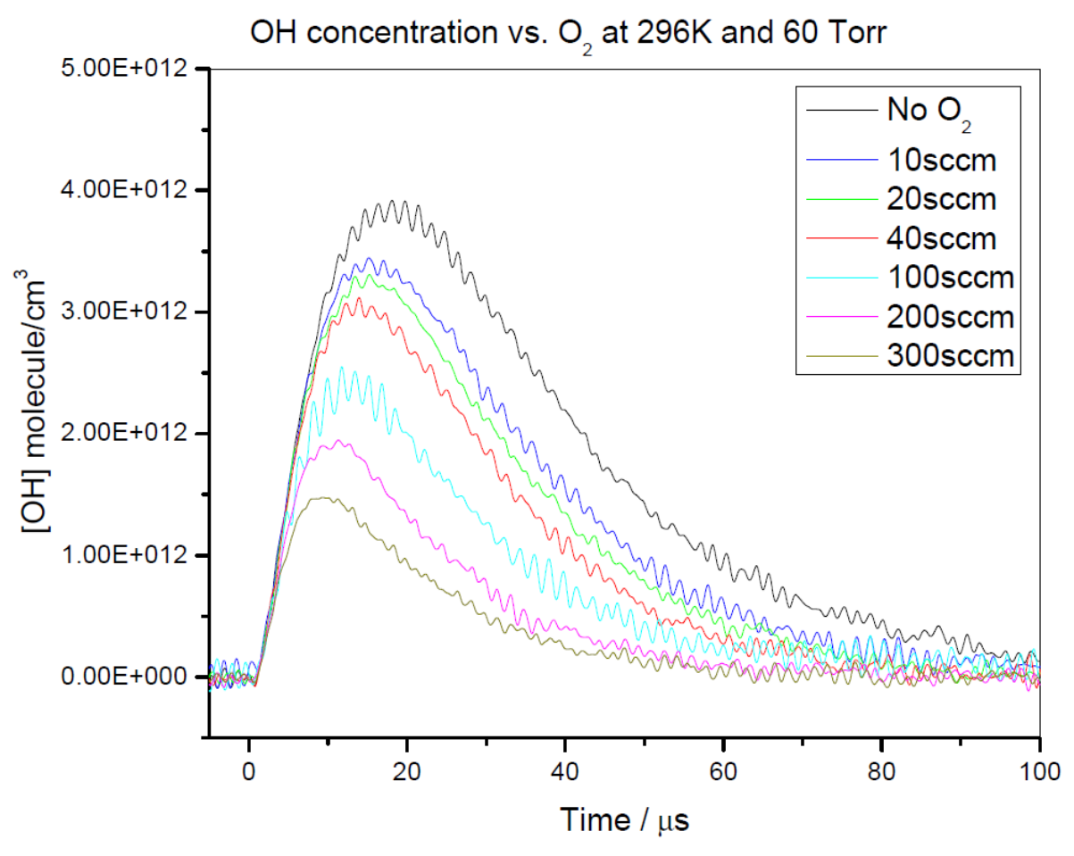
- •O_2 addition to QOOH is the chain branching step.
- •At higher temperature, O_2 addition competes less with QOOH dissociation, because its dissociation is faster than at room temperature.

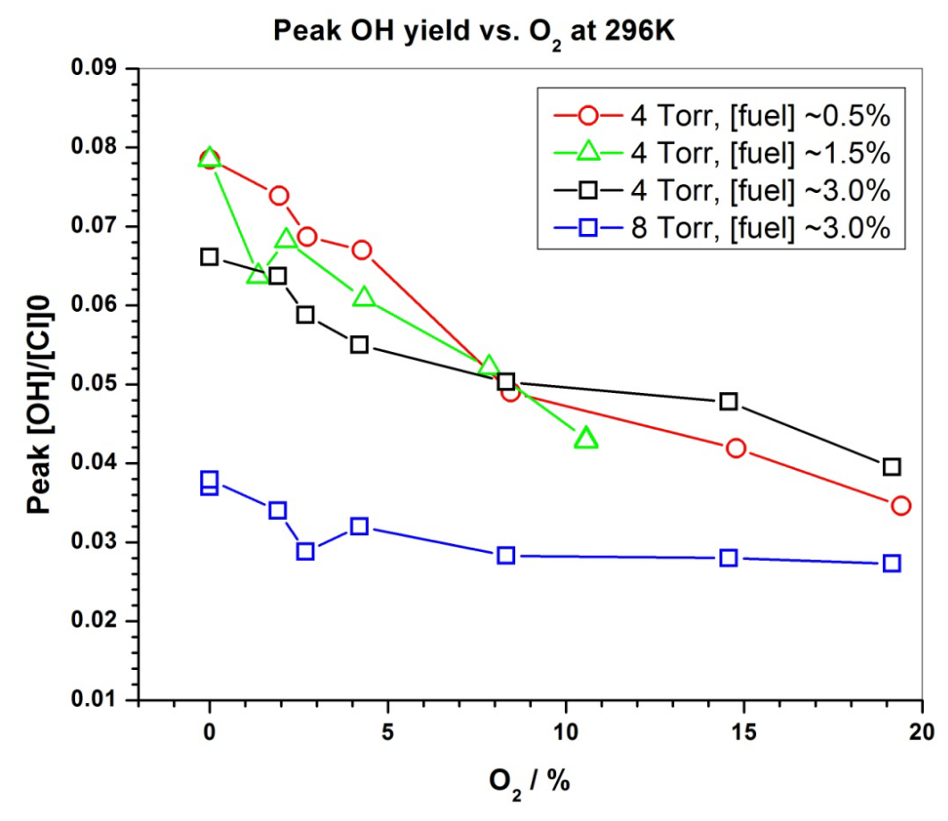
2. OH measurement at 3484.599 cm^{-1}

- •In the pressure range from 4 Torr to 90 Torr, peak OH yield decreases with O_2 concentration.
- •For highest fuel percentage (~3%), peak OH yield data show stabilization when O_2 is larger than 8%.
- •Measured time profiles of OH radical concentration in the reactions can constrain both **k_D** and **k_{Bi}** if the data is fitted to a detailed kinetic model.









Conclusions

TBHP has been used as a precursor to generate hydroperoxyalkyl radical (QOOH) directly in pulsed laser photolysis flow reactors, employing Cl-initiation after photolysis. The products are analyzed by our time-resolved multiplexed photoionization mass spectrometer using the synchrotron light source at ALS. We have observed 2,2-dimethyloxirane as the direct product of the dissociation of generated QOOH, and CH_2O as another key product when O_2 is added to the reaction mixture.

When the O_2 concentration increases, the production of oxirane decreases while that of CH_2O increases, showing the competition between QOOH dissociation and O_2 + QOOH reaction. By monitoring this competition, we have measured the ratio between **k_{Bi}** and **k_D** to be $(2.5\pm0.4)\times10^{-17}$ molecule^{-1} cm^3 at 296K and 4 Torr.

With our multi-pass IR absorption spectrometer, we have recorded the time profiles of the concentration of OH radical in the reactions. Our preliminary results suggest that the QOOH-O_2 complex can be stabilized at pressures from 4 Torr to 90 Torr. At highest relative fuel concentration (~3.0%), the OH yield displays stabilization for large O_2 pencentage, suggesting the effect of feedback loop OH + TBHP → QOOH → OH + 2,2-dimethyloxirane.

Ongoing efforts include:

- •Master equation calculations on QOOH and O_2 + QOOH which give the base for the simulation of the measured OH time signal to constrain **k_{Bi}** and **k_D**
- •Measuring time-resolved CH_2O concentration profiles with spectroscopic method, supplying more kinetic information on this QOOH reaction system
- •Derive **k_{Bi}** and **k_D** of this QOOH at other temperatures

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