Quantification of intermediates in dimethyl ether oxidation

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Summary

Dimethyl ether (DME) is a proven biodiesel fuel and aids ignition of other fuels. The chemical pathways responsible for its autoignition are generally known, yet several key intermediates have never been observed or quantified experimentally. **We have quantified three important intermediates in the chain-branching reactions of DME – RO_2, OOQOOH, and KHP – enabling quantitative comparison with detailed chemical models**. In addition, our experimentally determined cross sections enable quantification of these species in other experiments.

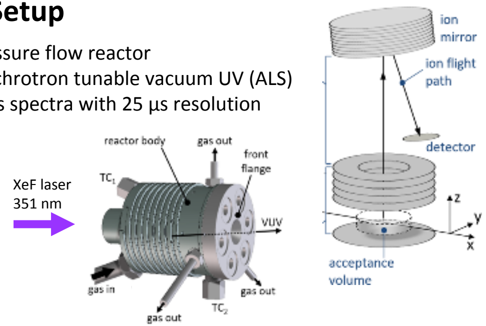
Setup

- Photolysis of Cl_2 initiates reactions in a high pressure flow reactor
- Gas is continuously sampled and ionized by synchrotron tunable vacuum UV (ALS)
- Mass spectrometer provides time-resolved mass spectra with 25 µs resolution

Reactor conditions

- P = 10 bar
- T = 450-575 K
- 50 ms residence time

- [DME] = 8×10^{14} /cm^3
- [Cl_2] = 1×10^{15} /cm^3
- [O_2] = 3×10^{18} /cm^3
- [He] ≈ 10^{20} /cm^3 (varies with T)
- $[Cl]_{t=0}$ = 7×10^{12} /cm^3 after photolysis



Sheps et al., JPCA 123, 10804 (2019)

Analysis

$$\text{Concentration} \propto \frac{\text{Ion signal}}{\text{Sensitivity} \cdot \text{Cross section}}$$

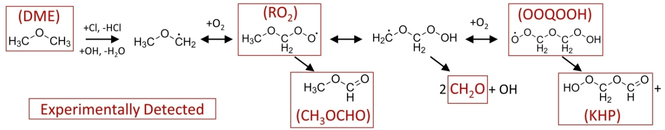
Chemical species with known photoionization cross sections:

- Concentration is quantified relative to DME, which has a known (supplied) pre-photolysis concentration

Species without known cross-sections:

- We can find experimental conditions where C atom balance reveals concentration
- Using experimentally determined concentrations, we derive cross-sections

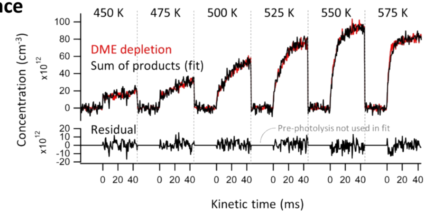
Quantification



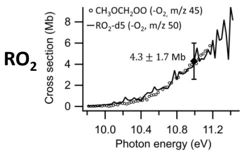
Carbon balance

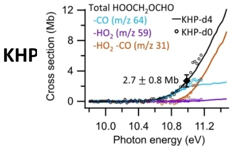
$$\text{DME Depletion}(t) = [\text{DME}](t=0) - [\text{DME}](t)$$
$$= \sum [\text{species}](t)\left(\frac{\#\text{ C atoms in species}}{\#\text{ C atoms in DME}}\right)$$
$$= [RO_2](t) + [\text{OOQOOH}](t) + [\text{KHP}](t) + [CH_3OCHO](t) + \tfrac{1}{2}[CH_2O](t)$$

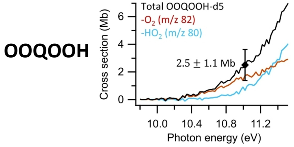
- 2 free parameters: cross sections for and KHP
- OOQOOH cross section was determined in a separate measurement comparing RO_2 and OOQOOH as they come into equilibrium immediately after photolysis



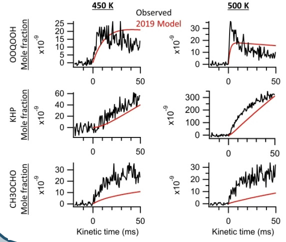
Absolute photoionization cross sections







Comparison to models



- These time-resolved quantified measurements provide a new, critical benchmark for theory-based master equation models
- Three recent models predict time-average concentrations of major chemical intermediates within a factor of 5 of our measurements
- However, these models do not reproduce the time evolution of OOQOOH and methyl formate, suggesting areas for improvement.

Model shown: *Hashemi et al. Comb. & Flame 205, 80 (2019)*
Also compared to: *Dames et al. Comb. & Flame 168, 310 (2016), Burke et al. Comb. & Flame 162, 315 (2015)*

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