Direct detection of Criegee Intermediates and reaction products using time-resolved spectroscopy

Daniel Stone

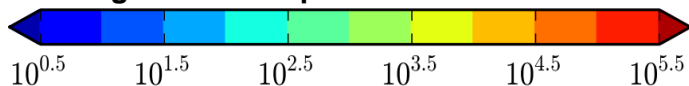School of Chemistry, University of Leeds

Criegee intermediates long predicted to be key reaction intermediates

Criegee & Wenner, *J. Liebigs. Ann. Chem.,* 1949

Produced in the atmosphere following the ozonolysis of unsaturated volatile organic compounds (VOCs)

O_3

Primary ozonide

Excited Criegee intermediate

OH, HO₂, CO

M

Stabilised Criegee intermediate
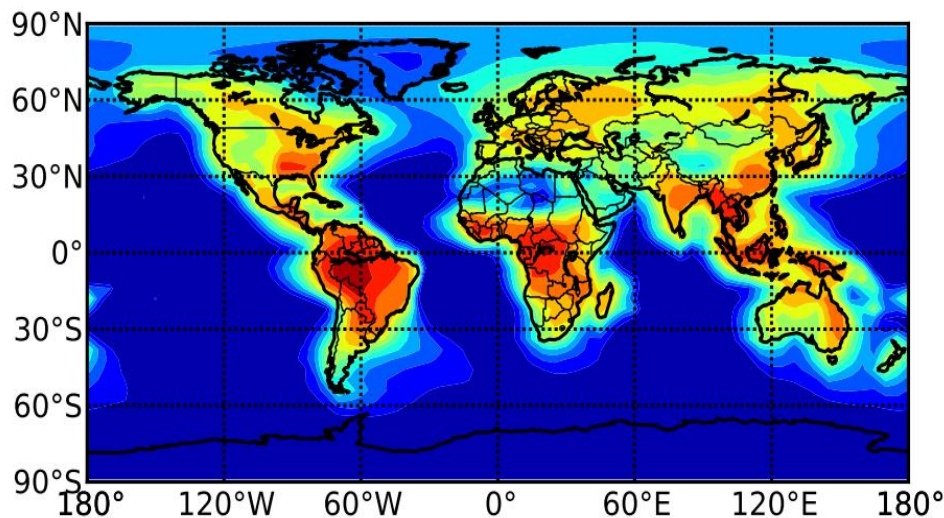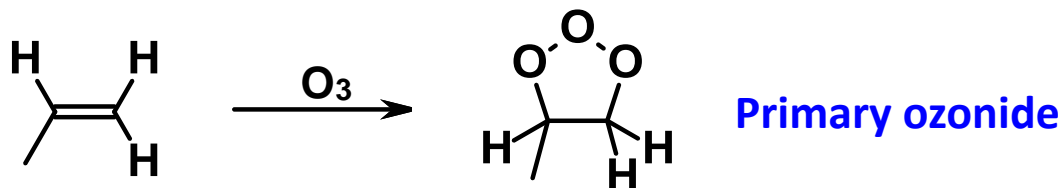
Criegee biradical production rate / cm³ s⁻¹

$10^{0.5}$ $10^{1.5}$ $10^{2.5}$ $10^{3.5}$ $10^{4.5}$ $10^{5.5}$

Pierce *et al.*, Atmos. Chem. Phys., 2013

Kinetics of Criegee intermediates

Kinetics of Criegee intermediate reactions are highly uncertain

Johnson & Marston, *Chem. Soc. Rev.,* **2008**

Data often derived from chamber experiments of ozonolysis reactions

- Complex reaction mechanisms

- Information regarding Criegee intermediates derived from observations of stable species

- Often multiple routes to production of stable species

- Extraction of Criegee kinetics requires modelling of production, stabilisation and removal processes

Large uncertainties in Criegee intermediate chemistry and impacts on atmospheric composition
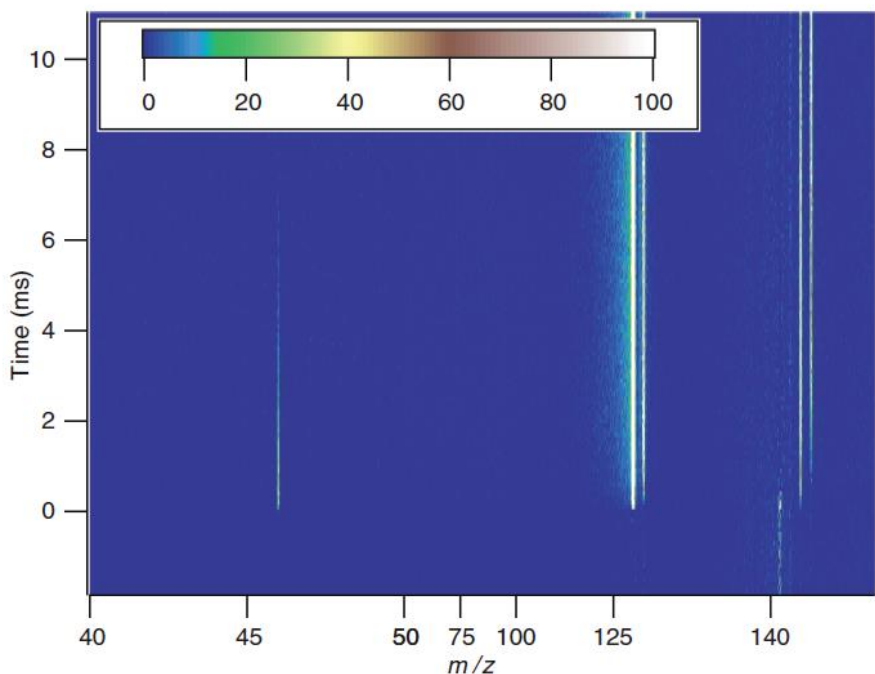
First direct measurements of Criegee intermediate kinetics by Welz *et al.* in 2012

Welz et al., Science, **2012**

Production of CH$_2$OO following photolysis of CH$_2$I$_2$ in excess O$_2$

$$CH_2I_2 + h\nu \text{ } (\lambda=248 \text{ nm}) \rightarrow CH_2I + I$$

$$CH_2I + O_2 \rightarrow CH_2OO + I$$

Tunable synchrotron photoionisation mass spectrometry used to detect CH$_2$OO

- And to distinguish from possible isomers

- Criegee ionisation threshold at 10.5 eV

  Isomers ionise at higher energies

     Dioxirane 10.82 eV

     Formic acid 11.33 eV

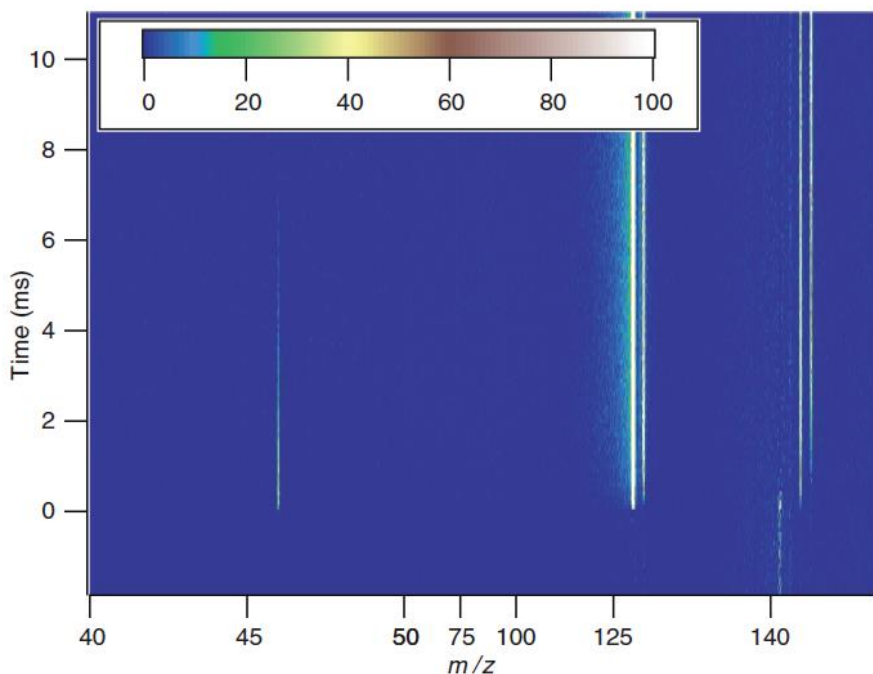First direct measurements of Criegee intermediate kinetics by Welz *et al*. in 2012

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Production of CH$_2$OO following photolysis of CH$_2$I$_2$ in excess O$_2$

$$CH_2I_2 + h\nu \text{ (}\lambda=248 \text{ nm)} \rightarrow CH_2I + I$$

$$CH_2I + O_2 \rightarrow \textcolor{red}{CH_2OO + I}$$

Availability of photolytic Criegee sources has generated a lot of interest in Criegee kinetics

  - More reactive than previously expected

  - Greater role in atmospheric chemistry

Numerous studies of bimolecular reactions

Fewer studies of unimolecular decomposition

This work aims to look at Criegee decomposition as *f(T,p)*

CH$_2$OO Decomposition

CH$_2$OO generated by laser flash photolysis of CH$_2$I$_2$/O$_2$/He at λ = 266 nm

- Experiments at Combustion Research Facility, Sandia National Labs

Monitoring of CH$_2$OO by broadband multipass UV absorption spectroscopy

Absorbance spectra contain contributions from CH$_2$OO, the CH$_2$I$_2$ precursor and IO (2° chem)

Normalised lit. spectra

CH$_2$OO
CH$_2$I$_2$
IO

Normalised absorption spectrum / arb. units vs *Wavelength / nm*
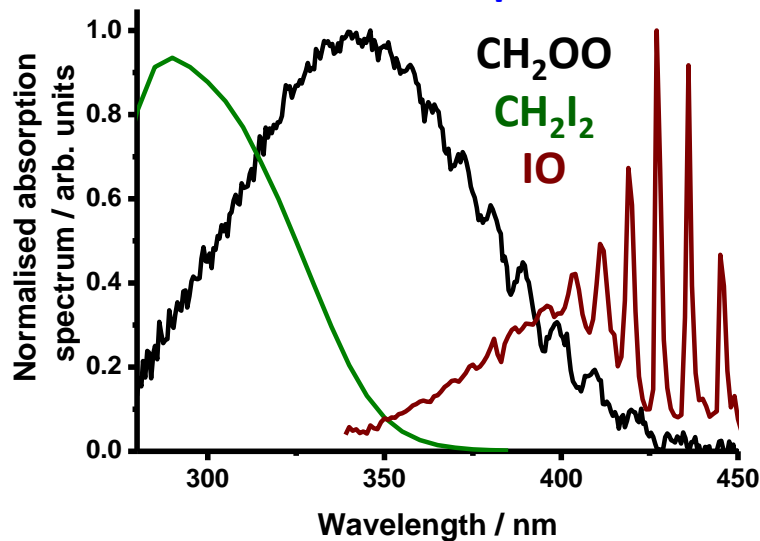
Fit absorption cross-sections to observed absorbance to monitor CH$_2$OO throughout the reaction
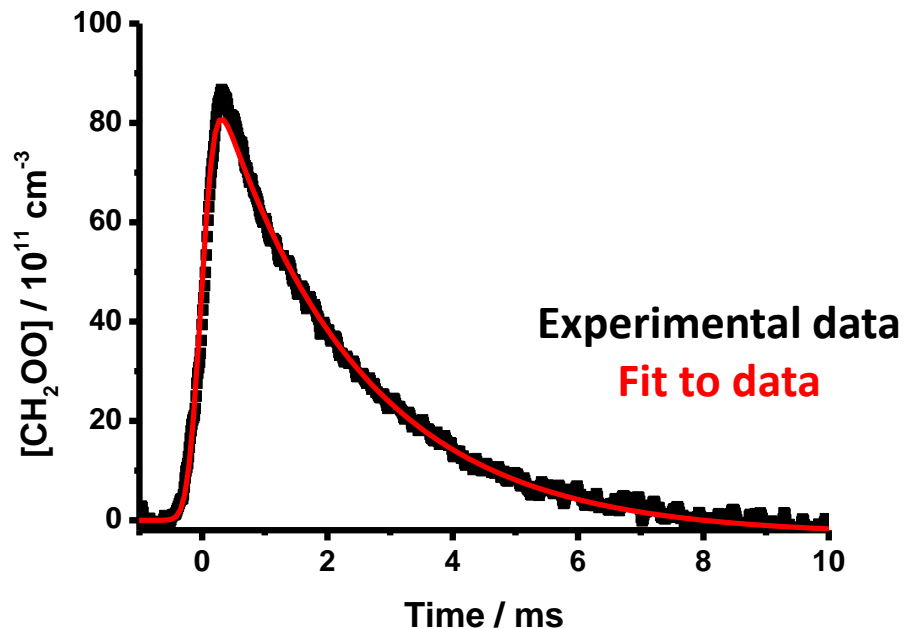
Experiments at temperatures between 450 K and 650 K and pressures ranging from 2 to 300 Torr

k_{obs} = (440 ± 5) s^{-1}

T = 525 K, p = 5 Torr

Decay of CH$_2$OO well-described by first-order kinetics

Fit first-order loss to find k_{obs}

$$[CH_2OO]_t = [CH_2OO]_0 \exp(-k_{obs}t)$$
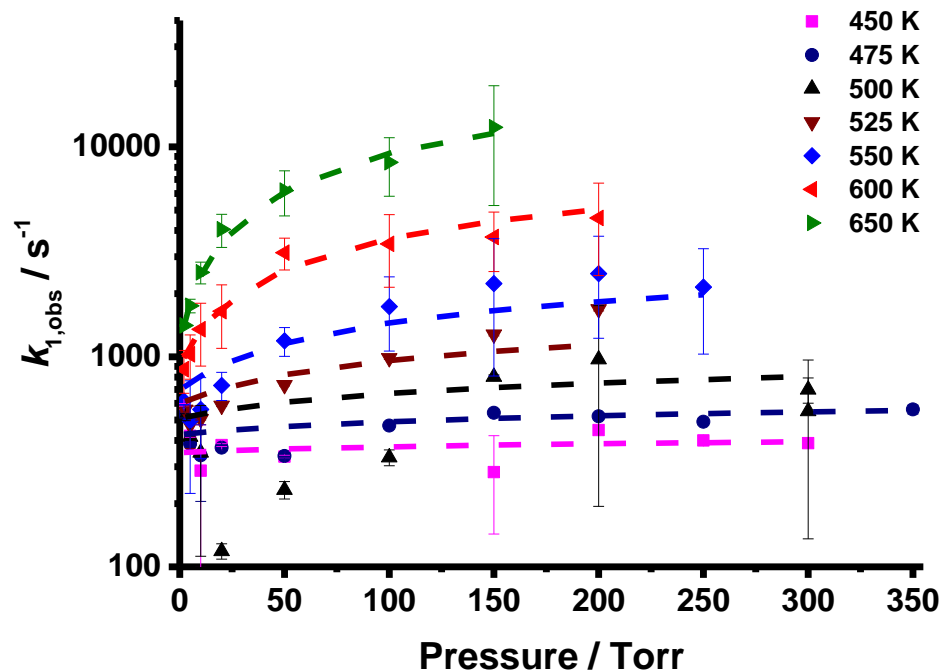
Rate coefficients describing CH_2OO loss increase with increasing temperature

Rate coefficients at $T < 500$ K independent of pressure

Rate coefficients at $T \geq 500$ K show pressure dependence

$$k_{obs} = k(p,T) + k(T)$$

Decomposition reaction gives pressure dependent term

Background losses ($CH_2OO + CH_2I_2$) give pressure independent term

Legend:
- 450 K
- 475 K
- 500 K
- 525 K
- 550 K
- 600 K
- 650 K

Fit $k(p,T) + k(T)$ to determine contributions from background losses
Likely contribution from $CH_2OO + CH_2I_2$ at high temperatures used

Master equation calculations in progress using MESMER

- **M**aster **E**quation **S**olver for **M**ulti-**E**nergy well **R**eactions

Glowacki *et al.*, *J. Phys. Chem. A,* 2012

Glowacki *et al.*, *J. Phys. Chem. A,* 2012

Master equation calculations in progress using MESMER

- **M**aster **E**quation **S**olver for **M**ulti-**E**nergy well **R**eactions

Glowacki *et al.*, *J. Phys. Chem. A,* 2012

0.0
CH₂OO

TS2
78.2

-107.5
cyc-H₂COO

TS6
-3.3

TS6a
-19.2

-78.2
open-H₂COO

TS6b
-68.2

TS4
-204.2

-41.4
HCO + OH

-500.4
H₂ + CO₂

-482.4
***t*-HC(O)OH**

-465.7
H₂O + CO

Energies in kJ mol⁻¹

Nyugen *et al.*, *J. Chem. Phys.,* 2015

Master equation calculations in progress using MESMER

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Nyugen *et al., J. Chem. Phys.,* **2015**

Master Equation Modelling

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Glowacki *et al., J. Phys. Chem. A,* **2012**

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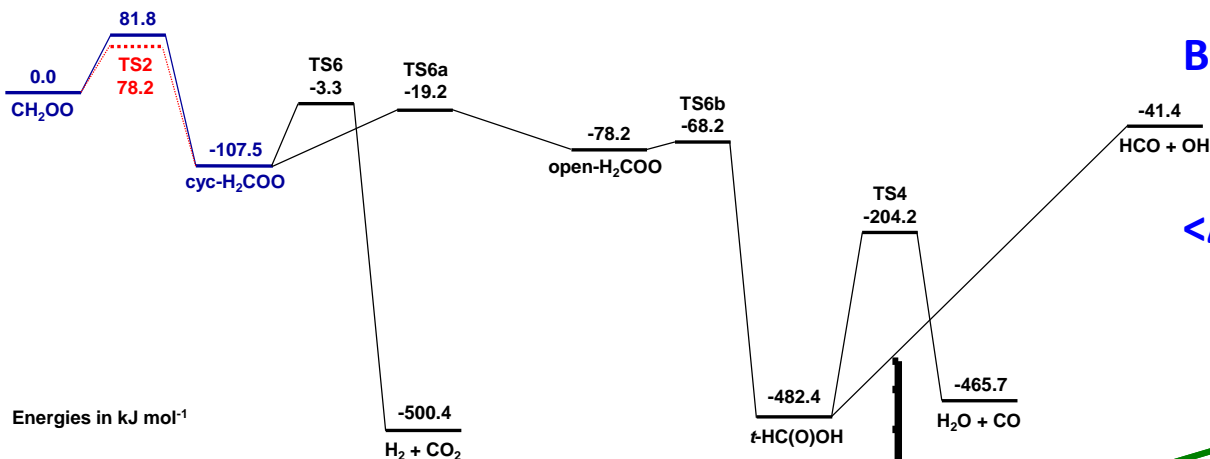
Barrier to decomposition increased by 2.6 kJ mol^{-1} to fit data

$<\Delta E_{down}> = 32.56 \ (T/298 \ K)^{1.68} \ cm^{-1}$

k_{dec} (298 K, 760 Torr) = 1 × 10^{-3} s^{-1}

MESMER simulations give product yields
63. 7 % H$_2$ + CO$_2$
36.0 % H$_2$O + CO
0.3 % HCO + OH
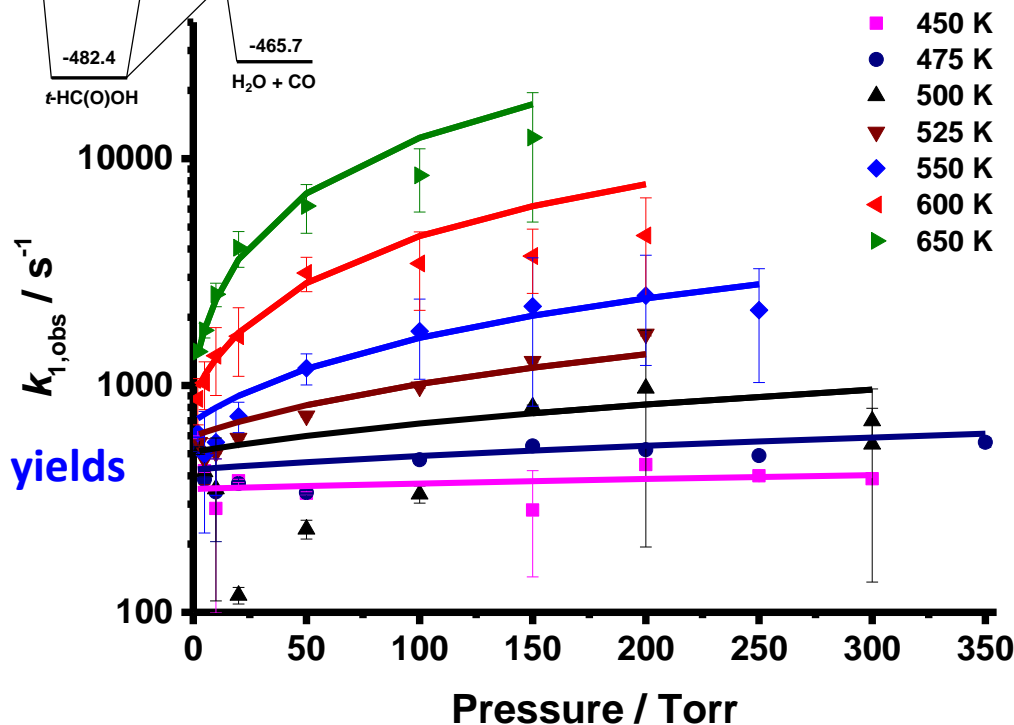
Legend:
- 450 K
- 475 K
- 500 K
- 525 K
- 550 K
- 600 K
- 650 K

y-axis: $k_{1,obs}$ / s^{-1}

x-axis: Pressure / Torr

CH$_2$OO generated by laser flash photolysis of CH$_2$I$_2$/O$_2$/N$_2$ at λ = 248 nm

OH(v=0) fluorescence excited at λ = 282 nm, detection at λ = 308 nm

OH(v=1) fluorescence excited at λ ~ 288 nm, detection at λ = 308 nm
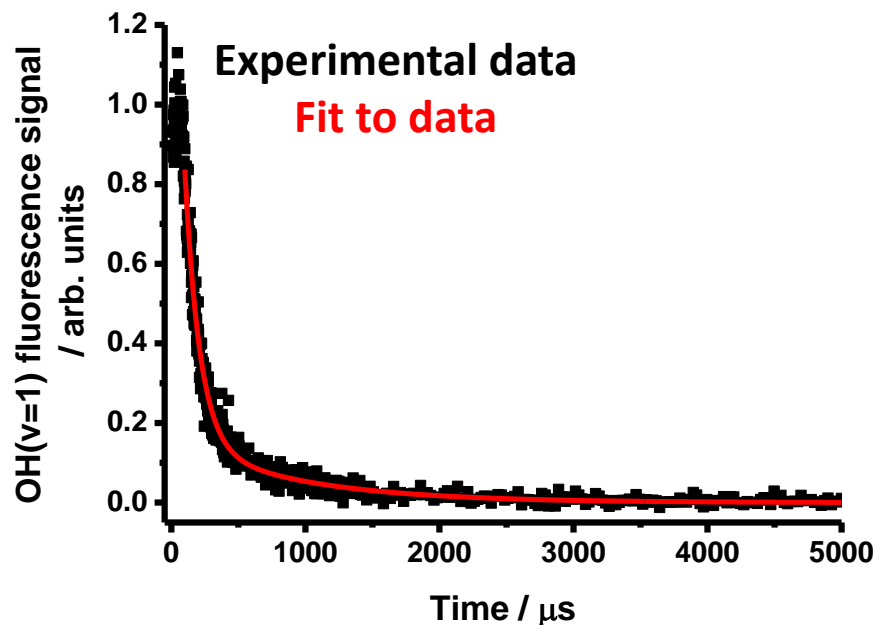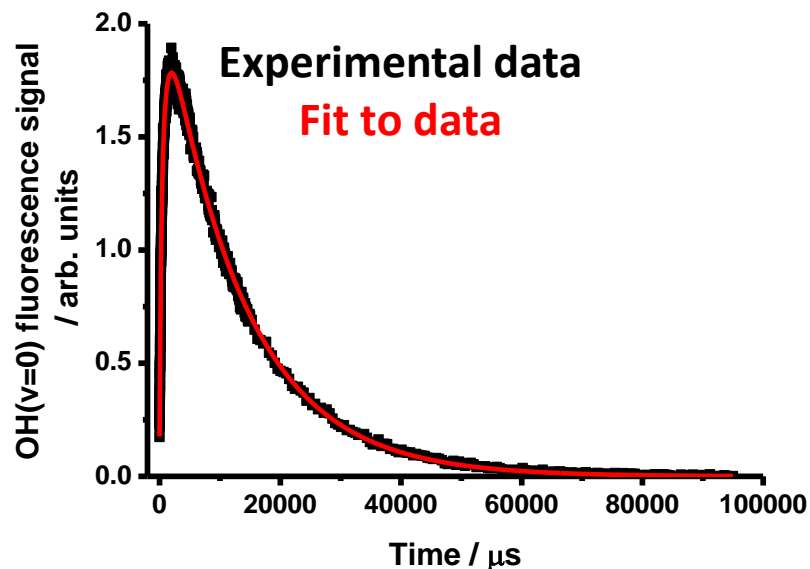
**General agreement between direct experiments monitoring CH$_2$OO
and indirect experiments monitoring OH**
OH(v=0,1) radicals produced in low yields

CH_3CHOO generated by laser flash photolysis of $CH_3CHI_2/O_2/He$ at $\lambda = 266$ nm

 - Experiments at Combustion Research Facility, Sandia National Labs

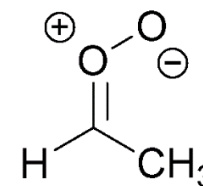Monitoring of CH_3CHOO by broadband multipass UV absorption spectroscopy

Absorbance spectra contain contributions from CH_3CHOO, CH_3CHI_2 precursor and IO (2° chem)

CH_3CHOO conformers display distinct absorption spectra and conformer dependent kinetics

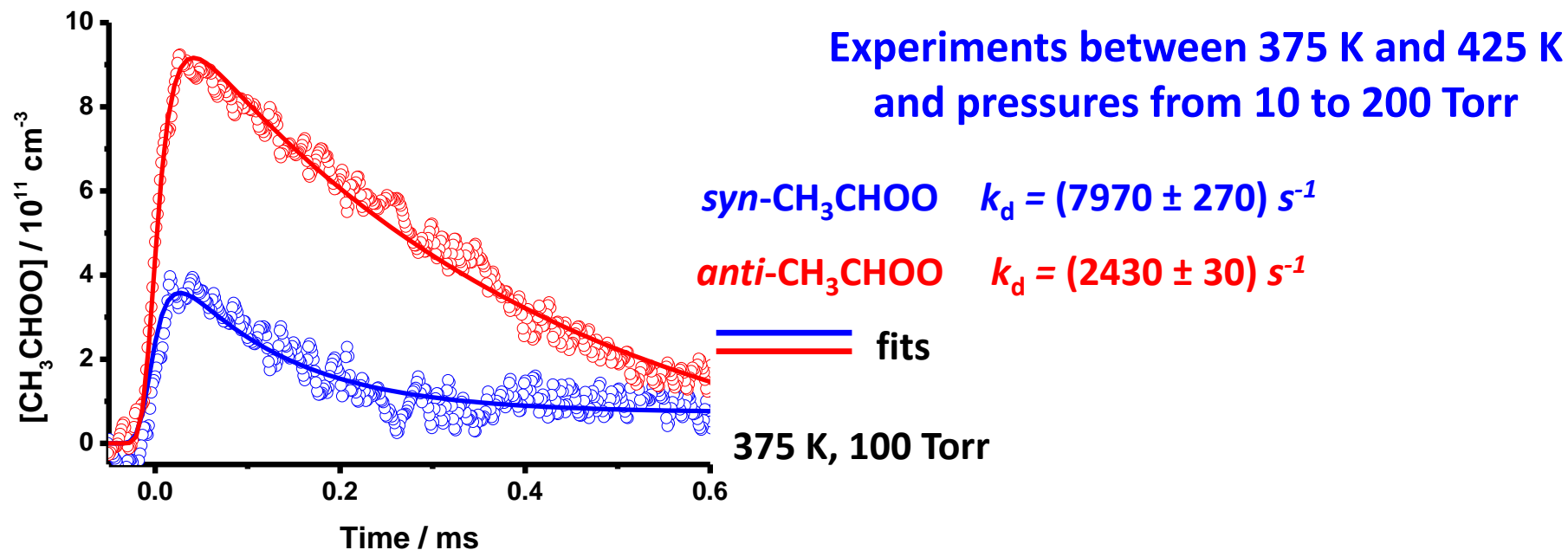**Sheps *et al.*, *Phys. Chem. Chem. Phys.*, 2014**
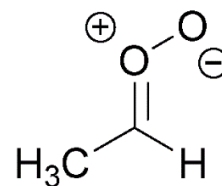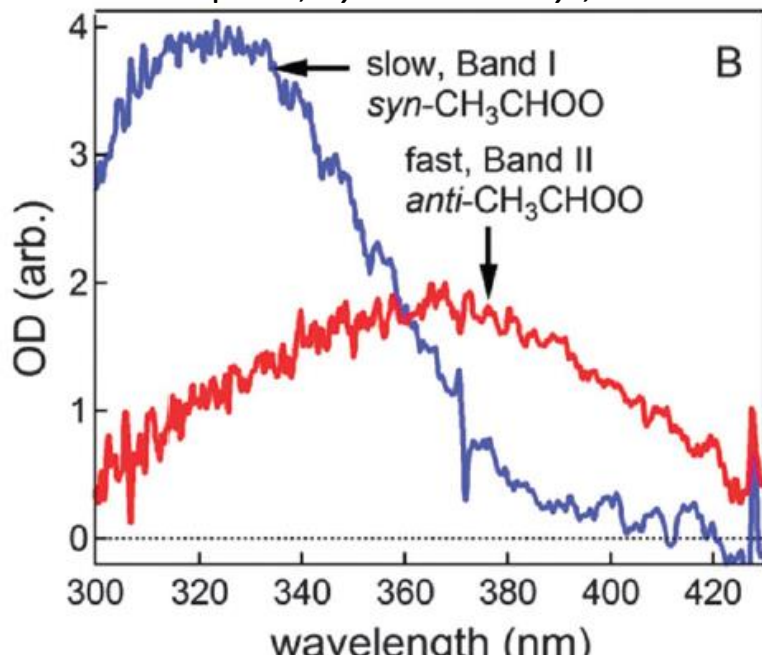
anti-CH₃CHOO   *syn*-CH₃CHOO

Fit reference spectra for *syn*- and *anti*-CH₃CHOO, CH₃CHI₂ and IO to observed absorbance (300-450 nm) to determine contributions from each species

CH₃CHOO Decomposition

Experiments between 375 K and 425 K and pressures from 10 to 200 Torr

syn-CH₃CHOO k_d = (7970 ± 270) s^{-1}

anti-CH₃CHOO k_d = (2430 ± 30) s^{-1}

fits

375 K, 100 Torr

CH₃CHOO conformers exhibit clear differences in decomposition kinetics

syn-**conformer decomposes more rapidly than** *anti*-**conformer**

- Note previous work shows *syn*-conformer to have slower bimolecular kinetics
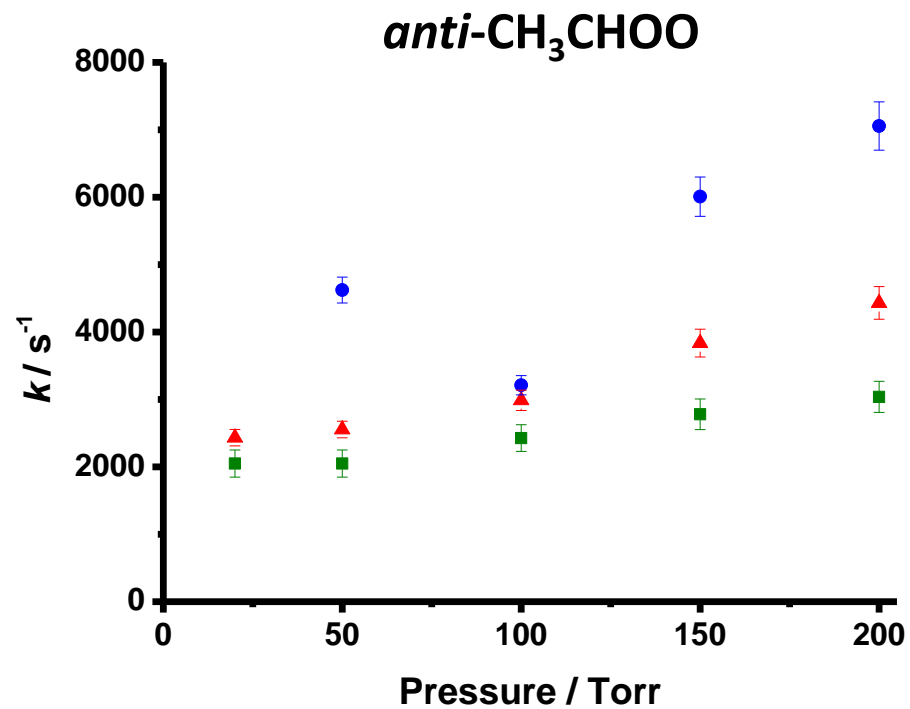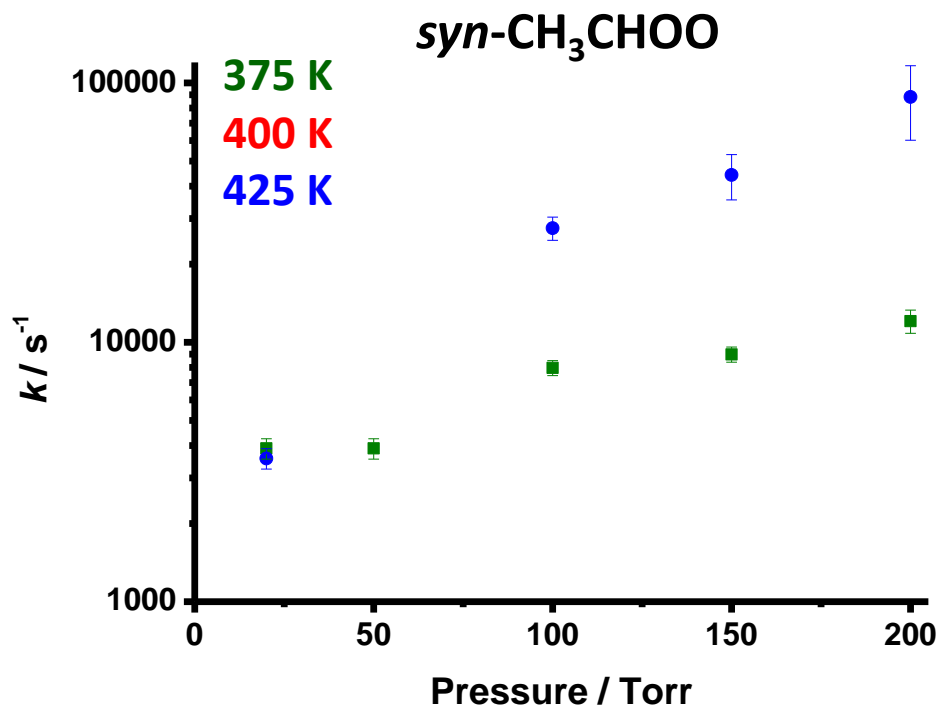
Decays are well-described by first-order kinetics

Fit first-order loss to decays find k_{dec} for each conformer

$$[CH_3CHOO]_t = [CH_3CHOO]_0 \exp(-k_{dec}\, t)$$

syn-CH₃CHOO

anti-CH₃CHOO

Effects of Temperature & Pressure

UNIVERSITY OF LEEDS

syn-CH₃CHOO

375 K
400 K
425 K

k / s⁻¹

Pressure / Torr

Kidwell *et al.*, *Nature Chem.*, 2016

syn-CH₃CHOO

Transition state
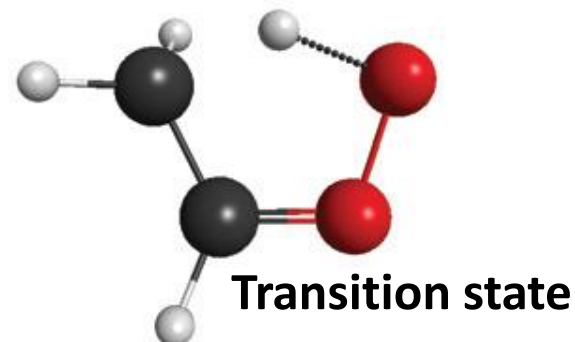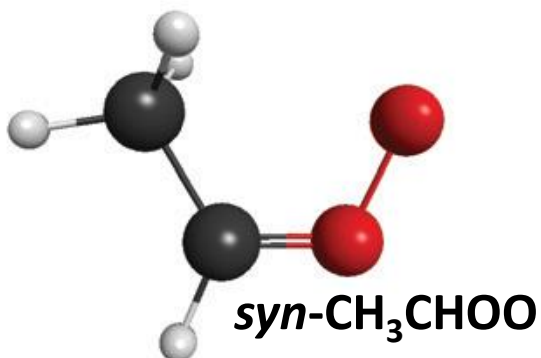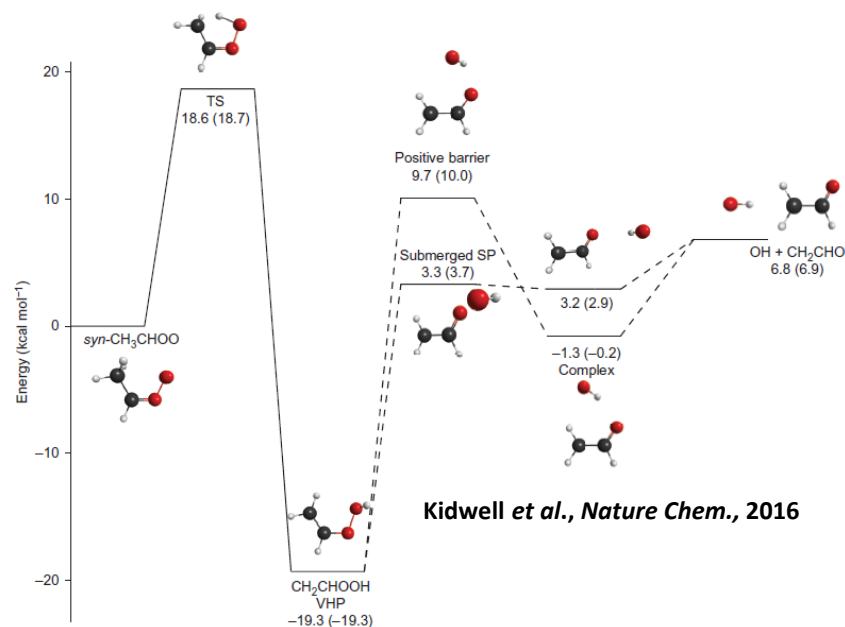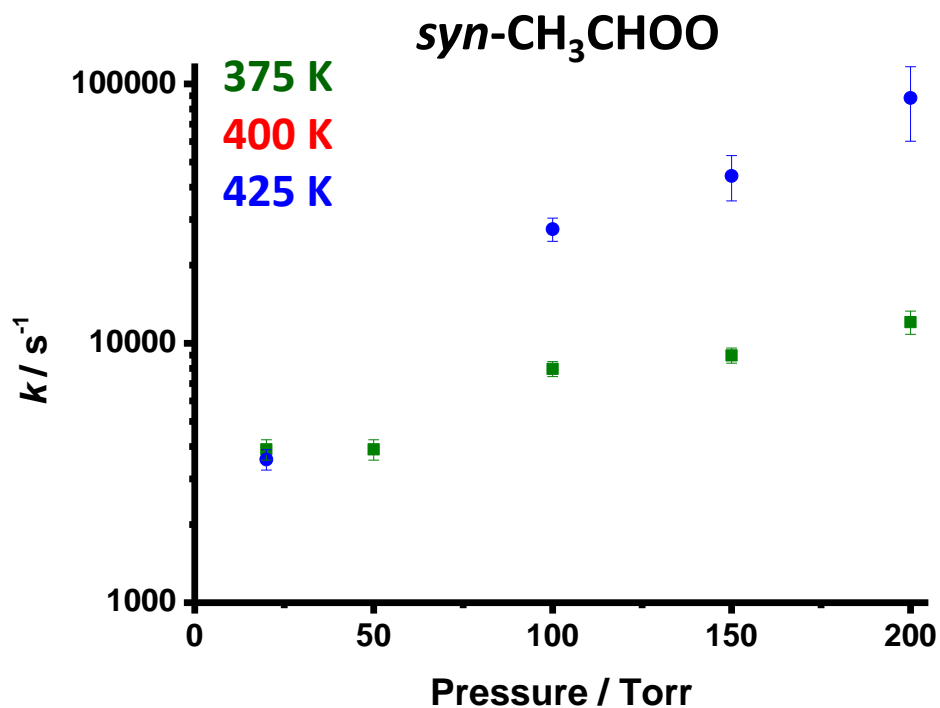
Experiments in progress to extend temperature range

Conclusions & Future Work

CH_2OO Criegee intermediate decomposition studied as a function of temperature and pressure

 - Slow decomposition under ambient conditions, $k_{dec} = 1 \times 10^{-3}$ s^{-1} at 298 K, 760 Torr

 - MESMER simulations give product yields 63.7 % H_2 + CO_2, 36.0 % H_2O + CO, 0.3 % OH + HCO

 - Low yields of OH(v=0) and OH(v=1) observed by laser-induced fluorescence

CD_2OO shows similar kinetics

- Experiment and theory indicate no kinetic isotope effect

CH_3CHOO decomposition experiments in progress

 - Conformer dependent kinetics, *syn*-CH_3CHOO decomposes more rapidly than *anti*-CH_3CHOO

Slow CH_2OO decomposition under ambient conditions

CH_3CHOO decomposition more rapid

Experiments and data analysis still in progress

Acknowledgements

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Kendrew Au

Thank you for your attention