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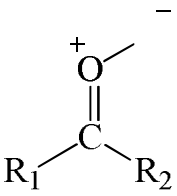

Isomers and Isomerizations in Tropospheric Chemistry: Opening the Black Box of Criegee Intermediate Reactions

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24th Conference on the Dynamics of Molecular Collisions

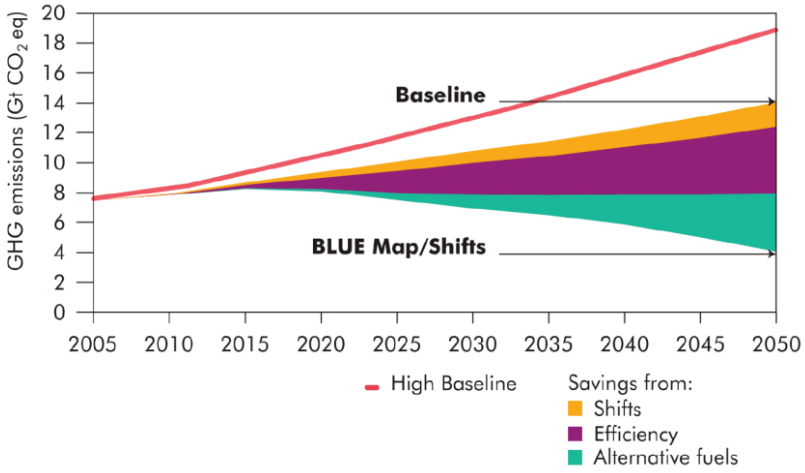
July 12, 2013

Granlibakken

Hydrocarbon Oxidation Powers Our Society and Is a Key Process in Earth's Atmosphere

Combustion produces ~ 85% of the United States' energy

- Hydrocarbon combustion provides nearly all of the energy for transportation
- Clean, efficient combustion is part of global energy strategies

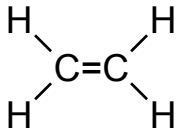


Karol M Wikimedia commons

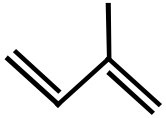
Tropospheric Chemistry:

- **Oxidation "cleanses" the troposphere**
- **Oxidation also produces aerosols, smog, other unwanted byproducts**

Alkenes are emitted into the troposphere in substantial amounts



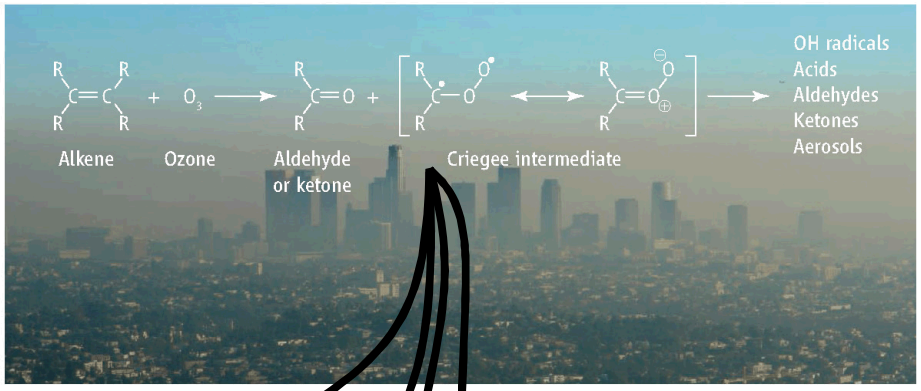
- Plants emit ~ 5 x 10^{11} kg / year of isoprene and also produce monoterpenes and sesquiterpenes in large amounts



- Anthropogenic sources contribute to alkene emission

- Alkenes account for 15% of non-methane hydrocarbons
- Tropospheric reactions consume alkenes
  - OH
  - NO_3
  - O_3

Ozonolysis of Alkenes Contributes to Important Atmospheric Processes



G. Marston, *Science* **335**, 178 (2012)

Sources / sinks of carbonyls

OH formation (in the dark)

$SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$

Source of organic acids

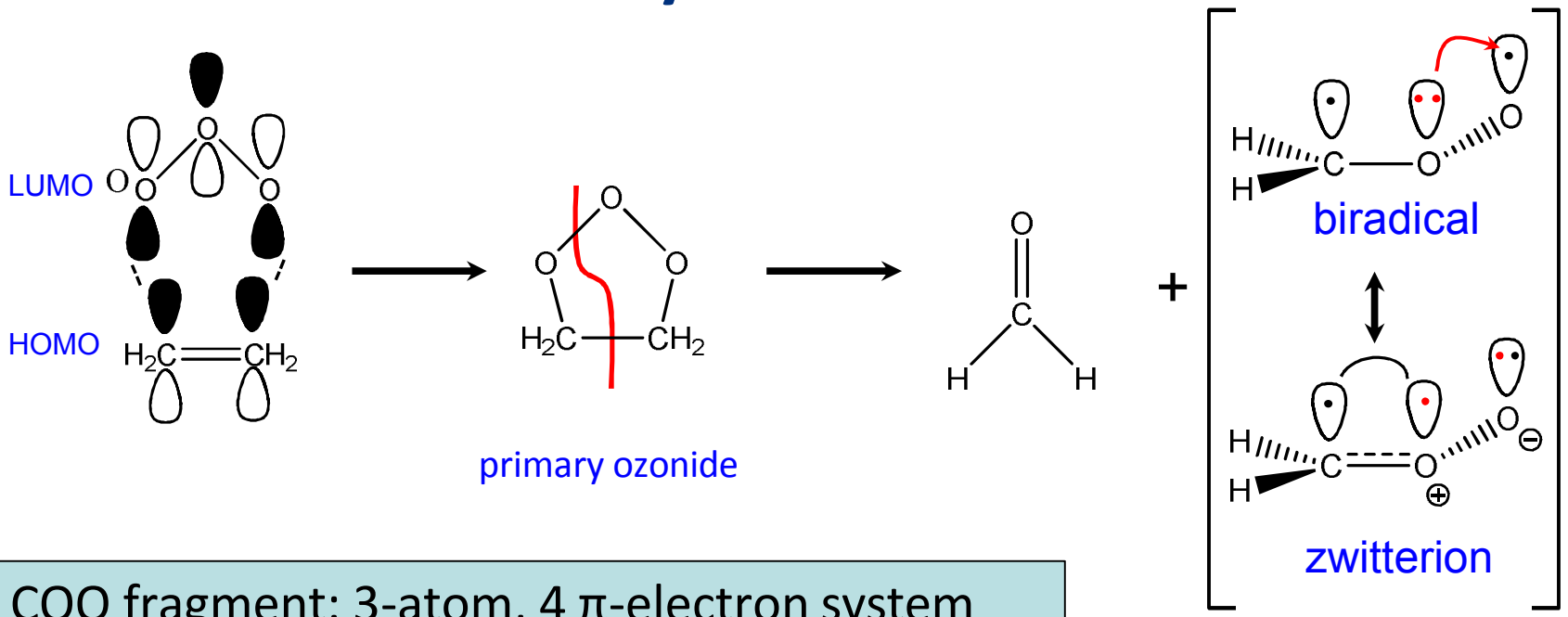
Secondary Organic Aerosols

Health

Visibility

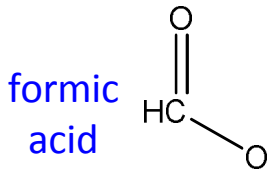
Climate

The Criegee Intermediate (Carbonyl Oxide) formed in ozonolysis



- COO fragment: 3-atom, 4 π-electron system
- Zwitterion is the dominant electronic configuration
- High barrier (38 kcal/mol) for rotation around C-O bond → slow at tropospheric conditions

Criegee Intermediate (Carbonyl Oxide)

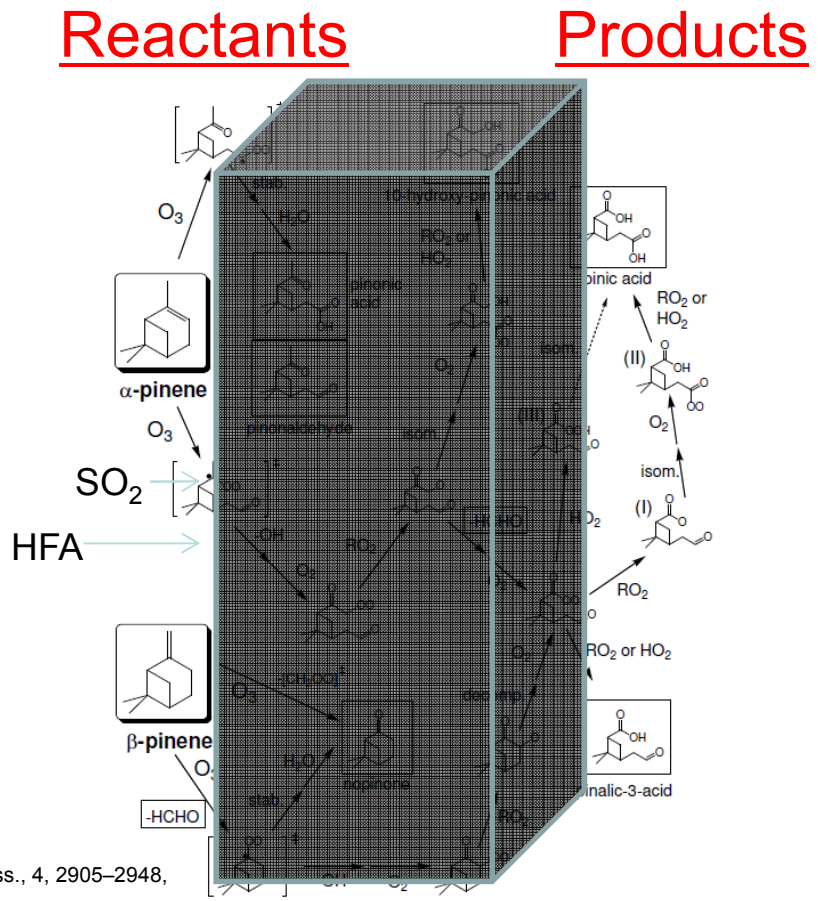


Traditional approach to study Criegee chemistry: Measurements of ozonolysis products

- Compare measured products to theory and models
- Add scavengers that are thought to remove Criegee intermediates, see what happens to stable product yields

Rate coefficients for Criegee reactions are uncertain by orders of magnitude!

Need direct measurements!

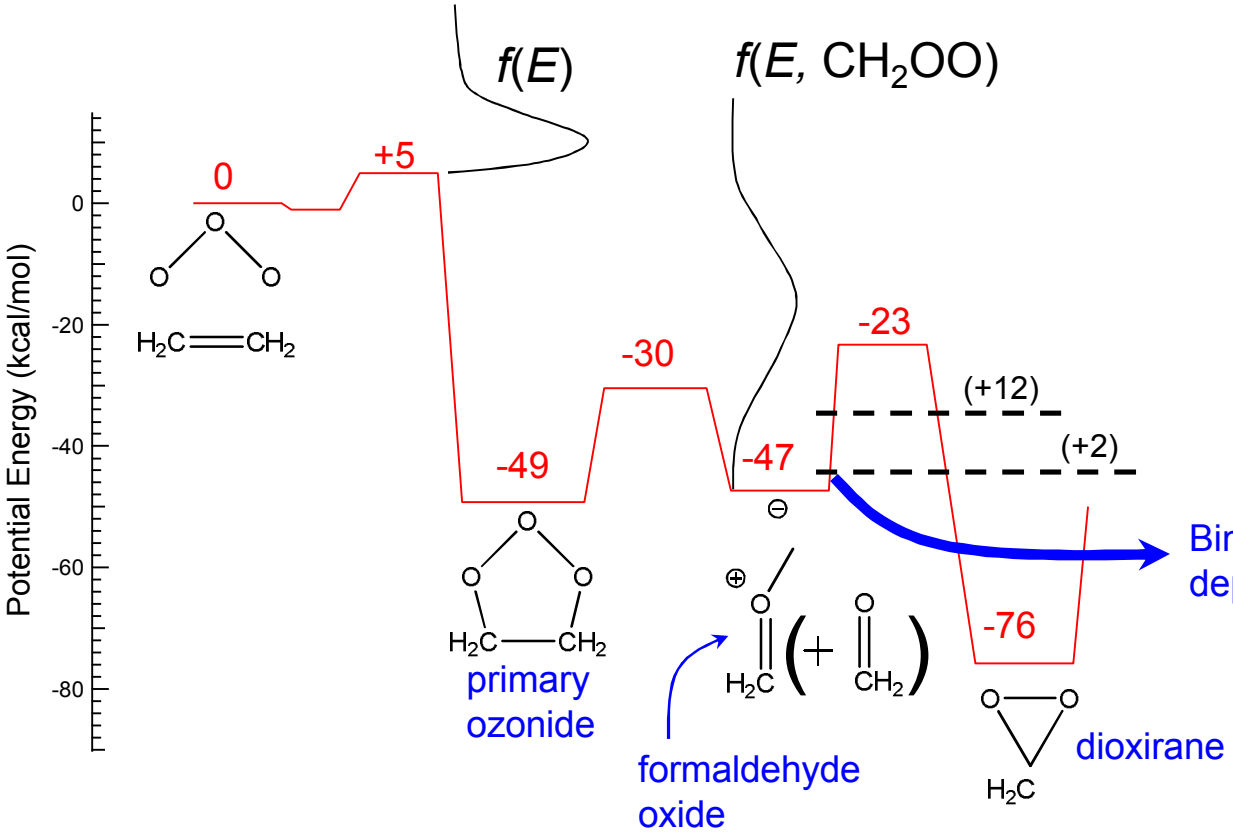


Atmos. Chem. Phys. Discuss., 4, 2905–2948, 2004

Why are Criegee Intermediates so hard to detect?

Ozonolysis forms Criegee intermediates slowly, but they react away rapidly

The hole in the bottom of the bucket is big, and the rate of water going in is small



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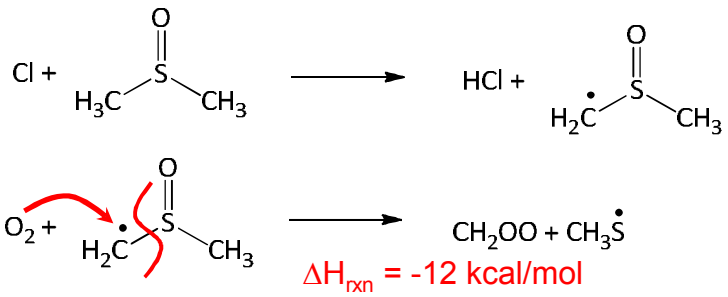
“Recipe” for directly measuring Criegee reactions

1. Make a lot of *cold* Criegee Intermediate quickly

2. Have a sensitive and selective detection technique for Criegee Intermediates

1. Make a lot of *internally cold* Criegee Intermediate

Asatryan and Bozzelli *Phys. Chem. Chem. Phys.* 10, 1769 (2008) predicted CH_2OO formation in dimethyl sulfoxide oxidation



First detection of a gas phase Criegee intermediate

Taatjes et al., JACS **130**, 11883 (2008)

Make it internally cold

Make a lot of it cold

Arkke Eskola et al. *Phys. Chem. Chem. Phys.* 8, 1416 (2006) studied $CH_2I + O_2 \rightarrow I + ??$

$$CH_2I_2 \xrightarrow{248 \text{ or } 351 \text{ nm}} I + CH_2I$$

$$CH_2I + O_2 \longrightarrow I + CH_2OO$$

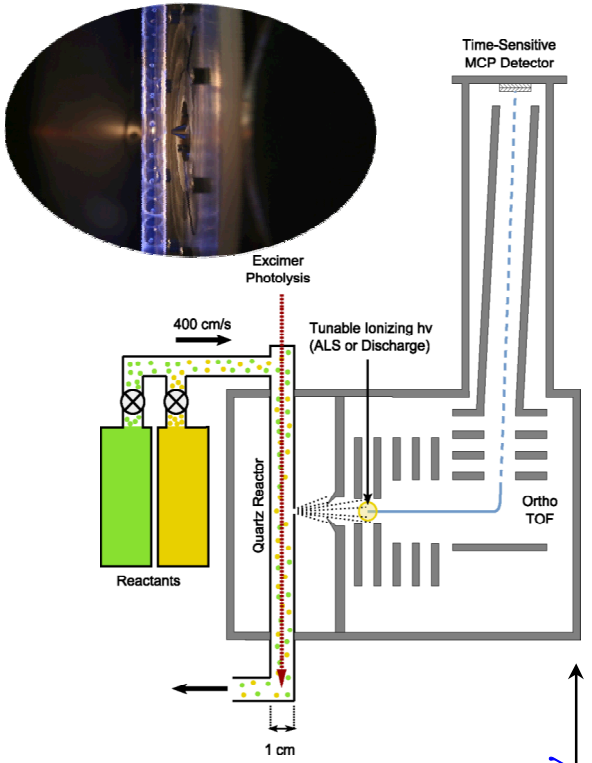
ΔH_{rxn} ~ -2 kcal/mol

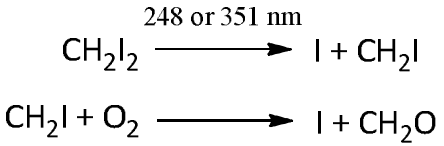
T = 300 K, P = 4 Torr

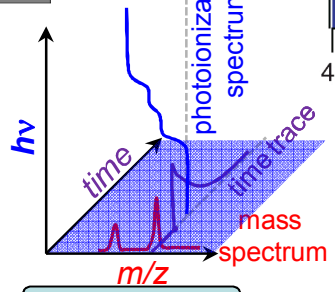
O. Welz, J.D. Savee, D. L. Osborn, S. V. Vasu, C. P. Percival, D. E. Shallcross, C. A. Taatjes, *Science* **335**, 204 (2012)

2. Have a sensitive and selective detection technique

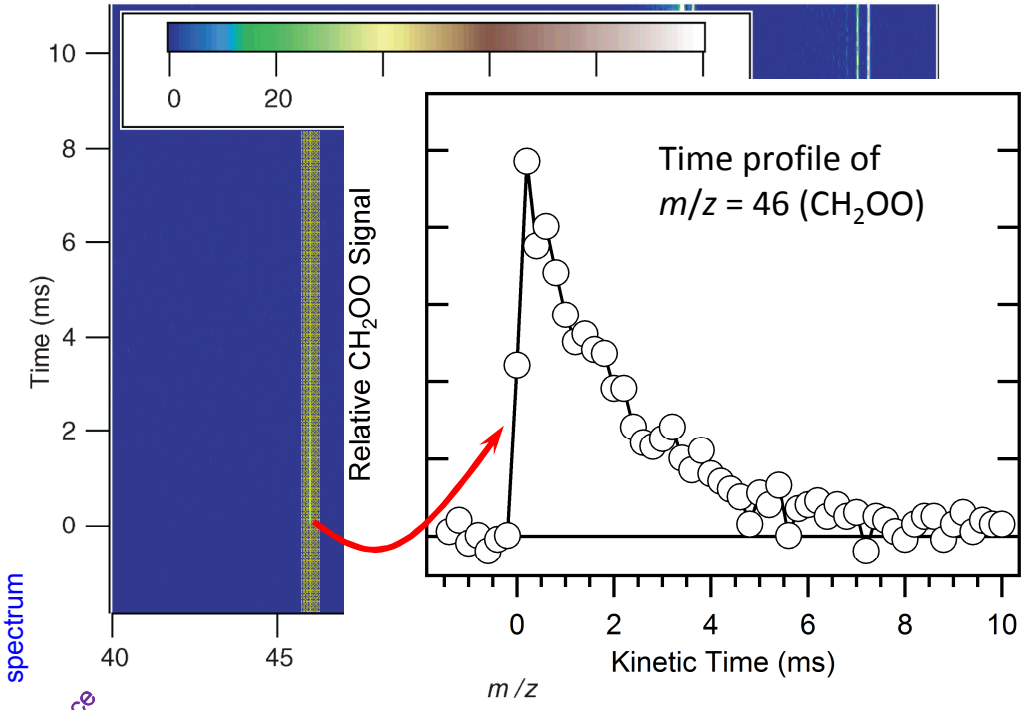
→ Multiplexed Photoionization Mass Spectrometry (MPIMS)







3-D Data



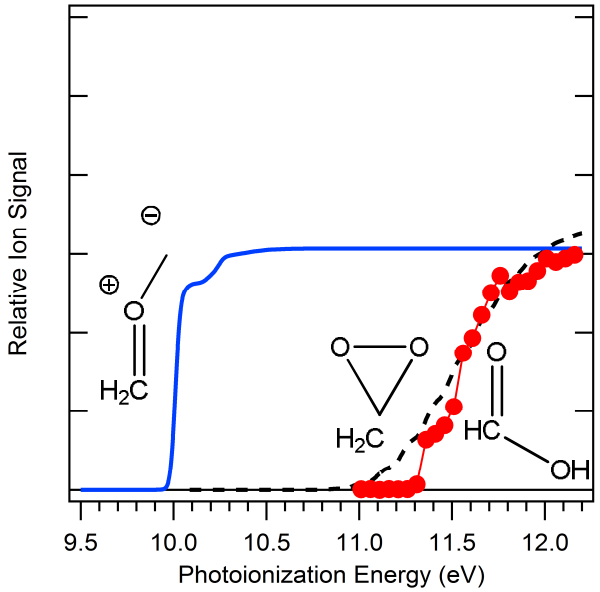
The Criegee intermediate is an isomer of more stable products
→ Need isomer-resolved detection!

T = 300 K, P = 4 Torr (25 ns between collisions)

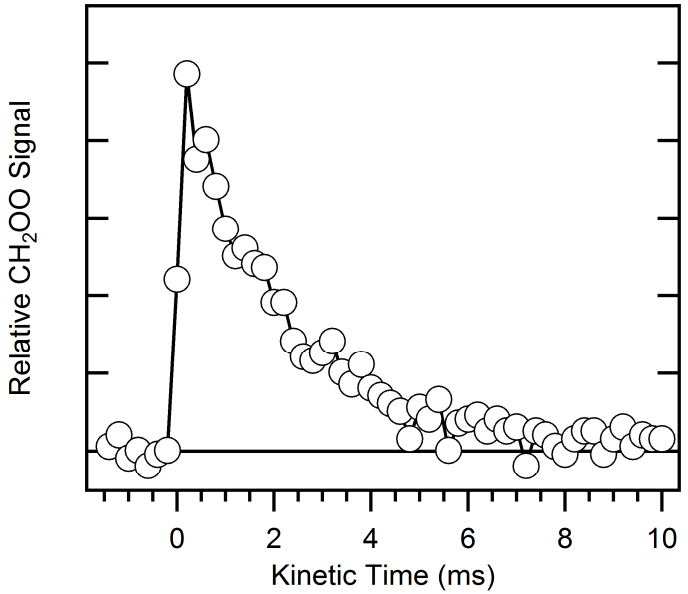
2. Have a sensitive and selective detection technique

→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

Photoionization spectra of CH_2OO isomers



Time profile of m/z = 46 (CH_2OO)



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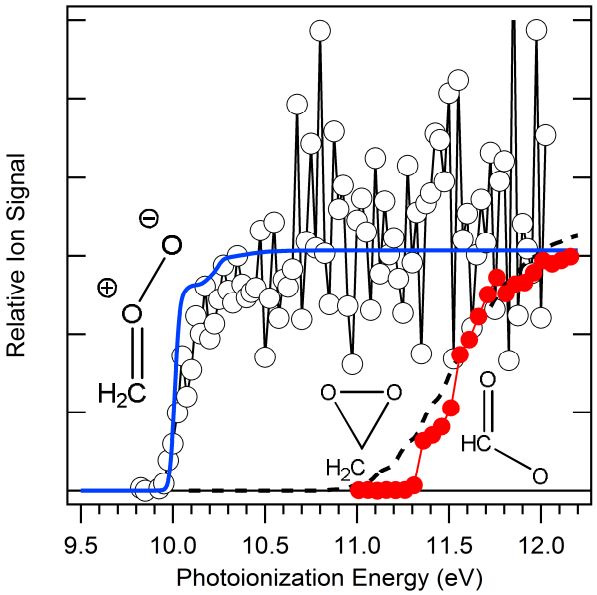
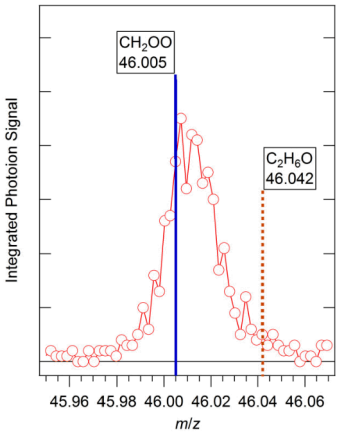
2. Have a sensitive and selective detection technique

→ Multiplexed Photoionization Mass Spectrometry (MPIMS)

m/z = 46 photoionization product spectrum



Definitive Evidence:
1) IE matches theory
2) Franck-Condon factors match theory
3) Exact mass is correct



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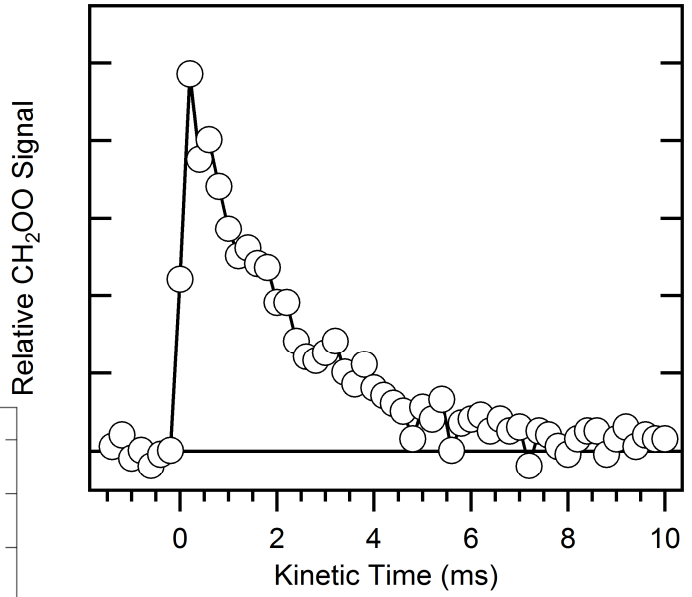

Measuring CH_2OO reactions with important tropospheric species

$CH_2OO + SO_2$: $k = (3.9 \pm 0.7) \times 10^{-11}$ cm^3 s^{-1}

→ up to **10 000 times** faster than what is used in models

If other Criegee intermediates react similarly, they could be major SO_2 oxidants

$CH_2OO + NO_2$: $k = (7\ ^{+3}/_{-2}) \times 10^{-12}$ cm^3 s^{-1}

→ **50 times** faster than what is used models

If other Criegee intermediates react similarly, Criegee reactions might play an important role in NO_x chemistry

Reactions of CH_2OO with NO and H_2O are too slow to be measured

→ only upper limits could be obtained

$CH_2OO + NO$: $k \leq 6 \times 10^{-14}$ cm^3 s^{-1}

→ At least two orders of magnitude slower than literature estimates

$CH_2OO + H_2O$: $k \leq 4 \times 10^{-15}$ cm^3 s^{-1}

→ Tends to confirm values used in models

$[SO_2]$ ($10^{\quad}$ cm^{-3})

Media Interest in Chemical Kinetics!

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Pollution-gobbling molecules in global warming SMACKDOWN

Boffins: Newly observed particles scrub our filthy air

By **Chris Williams** • **Get more from this author**

Posted in Science, 16th January 2012 10:17 GMT

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Elusive pollution-busting molecules are scrubbing our planet's atmosphere at a much faster rate than first imagined, according to gas-bothering boffins.

Reactions by the cleaning agents, known as Criegee intermediates, are also emitting a by-product that forms solar radiation-reflecting clouds that could help cool Earth and reduce the effects of global warming.

The Criegee biradicals were first hypothesised in the 1950s by German chemist Rudolf Criegee, but only now have they been recreated in a lab and directly measured for the first time. Specifically, the scientists took formaldehyde oxide – a species of Creigee intermediate – and observed it reacting with sulphur dioxide and nitrogen dioxide.

These dioxides are said to initiate climate change in our atmosphere, yet it's now understood they are removed from the troposphere by helpful Criegee biradicals – described as pivotal atmospheric reactants. The reaction also spews sulphate and nitrate into the atmosphere, creating aerosol droplets

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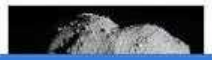
SPOTLIGHT

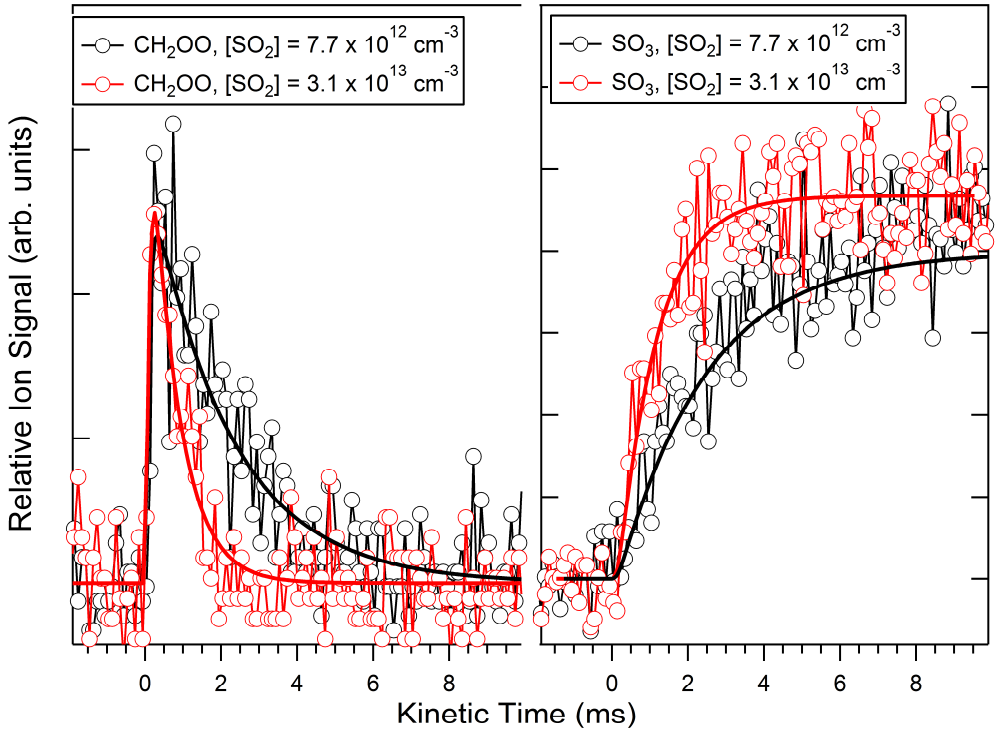
Look out! PEAK WIND is COMING, warns top Harvard physicist Last out of the windpower future turn out the lights ... Oh

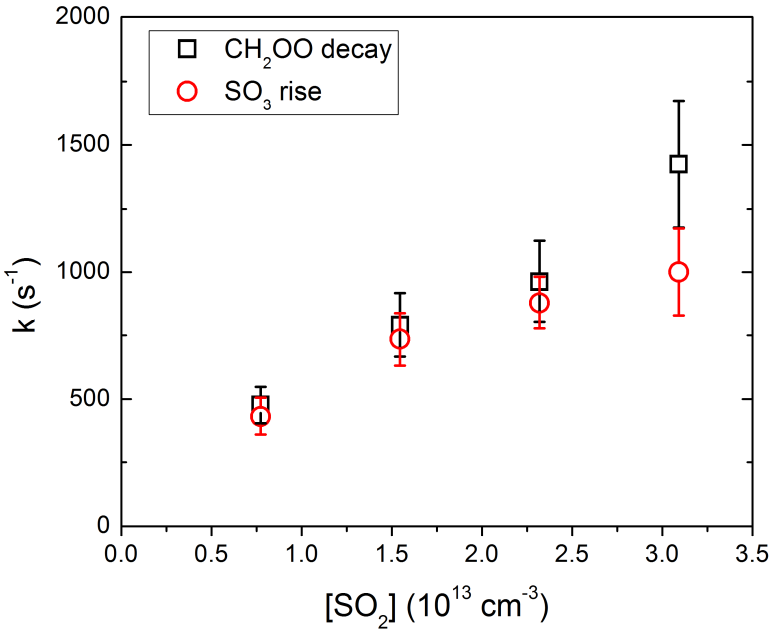
Chip daddy Mead: 'A bunch of big egos' are strangling science **ISSCC** The scientific revolution has stalled, here's how to kickstart it



The universe speaks: 'It's time to get off your

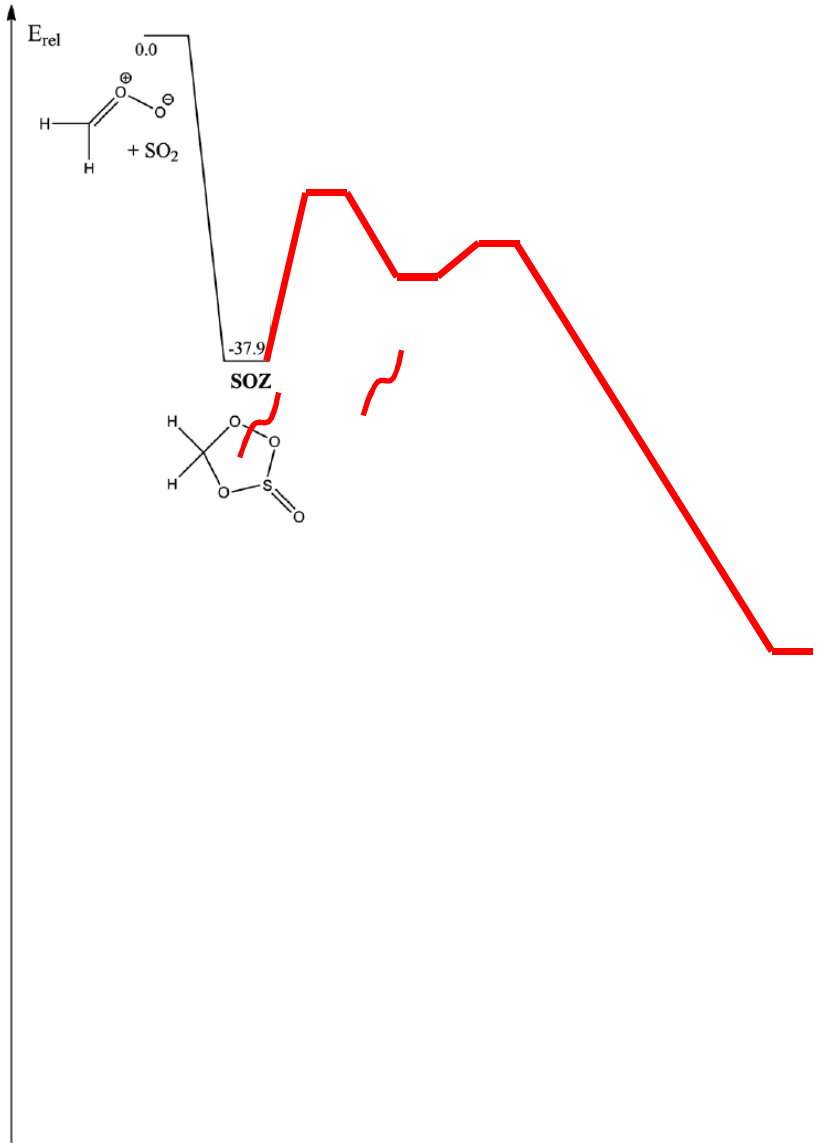
SO_3 is a direct product of $CH_2OO + SO_2$ at 4 Torr





Theoretical work of Vereecken et al. Phys. Chem. Chem. Phys. 14, 14682 (2012) predicts that $CH_2O + SO_3$ is the major product channel at atmospheric conditions.

Why is CH_2OO ($^1A'$) + SO_2 ($^1A_1$) so fast?



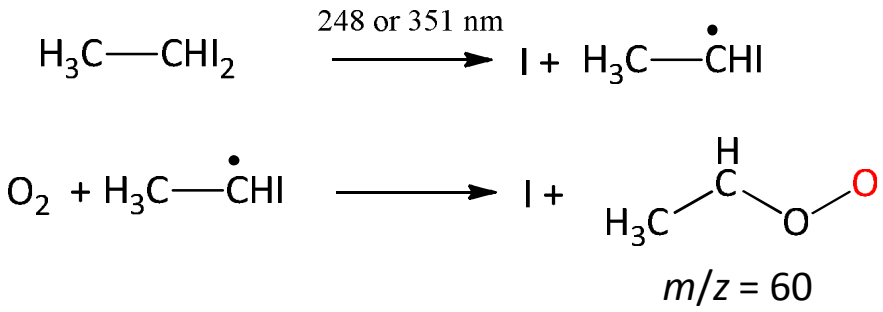
Our experiments are at 4 torr pressure.

How will stabilization of SOZ affect SO_3 production?

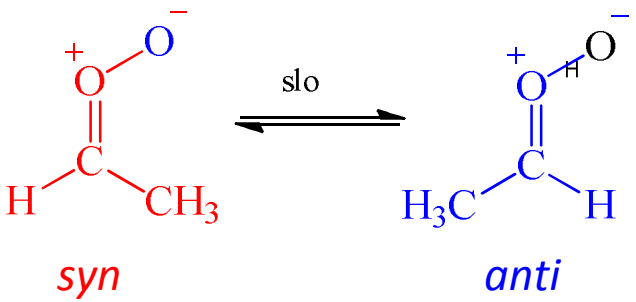
L. Vereecken, H. Harder, and A. Novelli, Phys. Chem. Chem. Phys. **14**, 14682 (2012).

The next larger Criegee Intermediate: acetaldehyde oxide (CH_3CHOO) shows richer chemistry

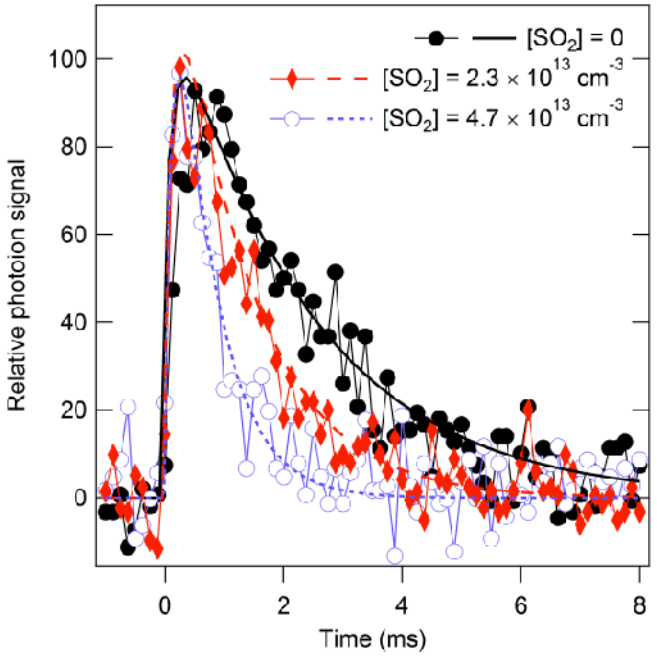
Similar strategy:



CH_3CHOO exists in two distinct conformeric forms



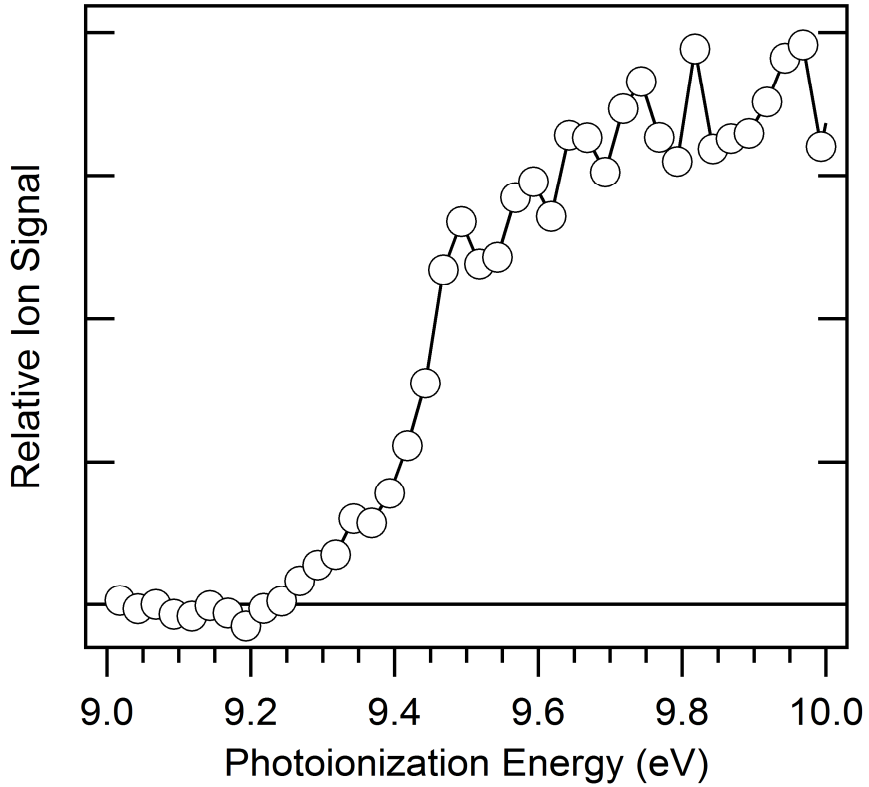
m/z = 60 time profile



Calculations predict that *anti*-CH_3CHOO reacts with H_2O five orders of magnitude faster than *syn*-CH_3CHOO

(Phys. Chem. Chem. Phys. 13, 13034 (2011)

The *m/z* = 60 photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of CH_3CHOO



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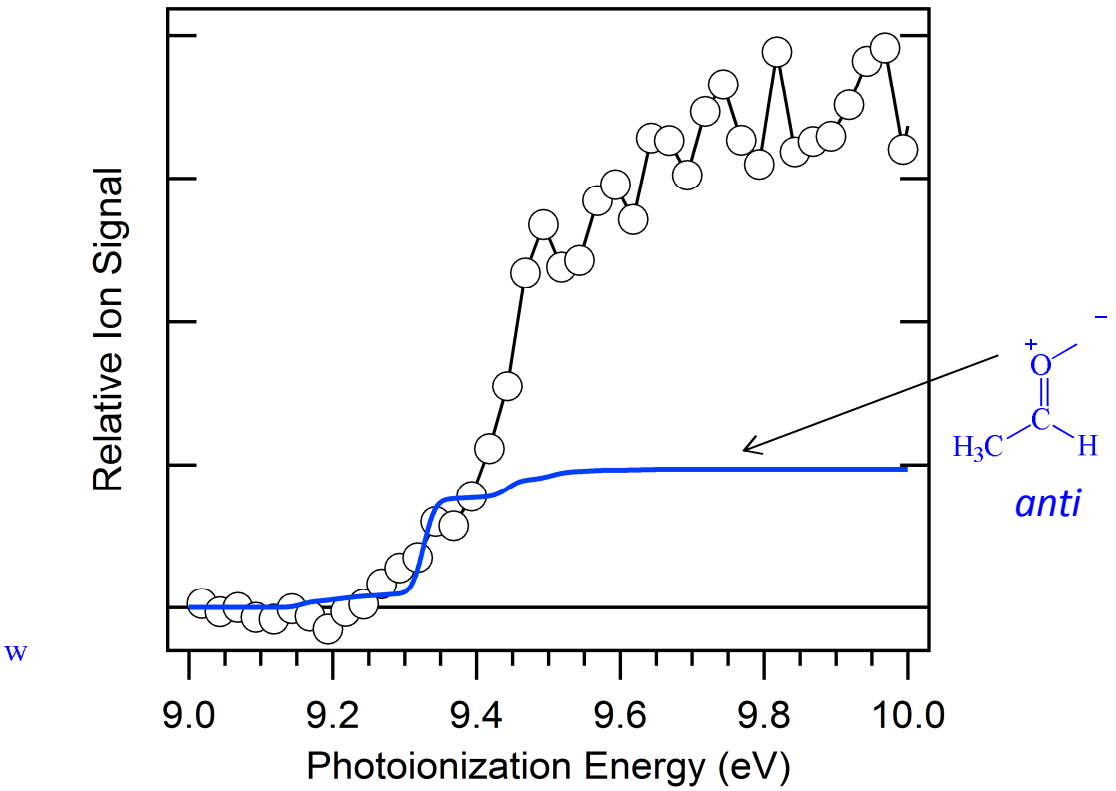

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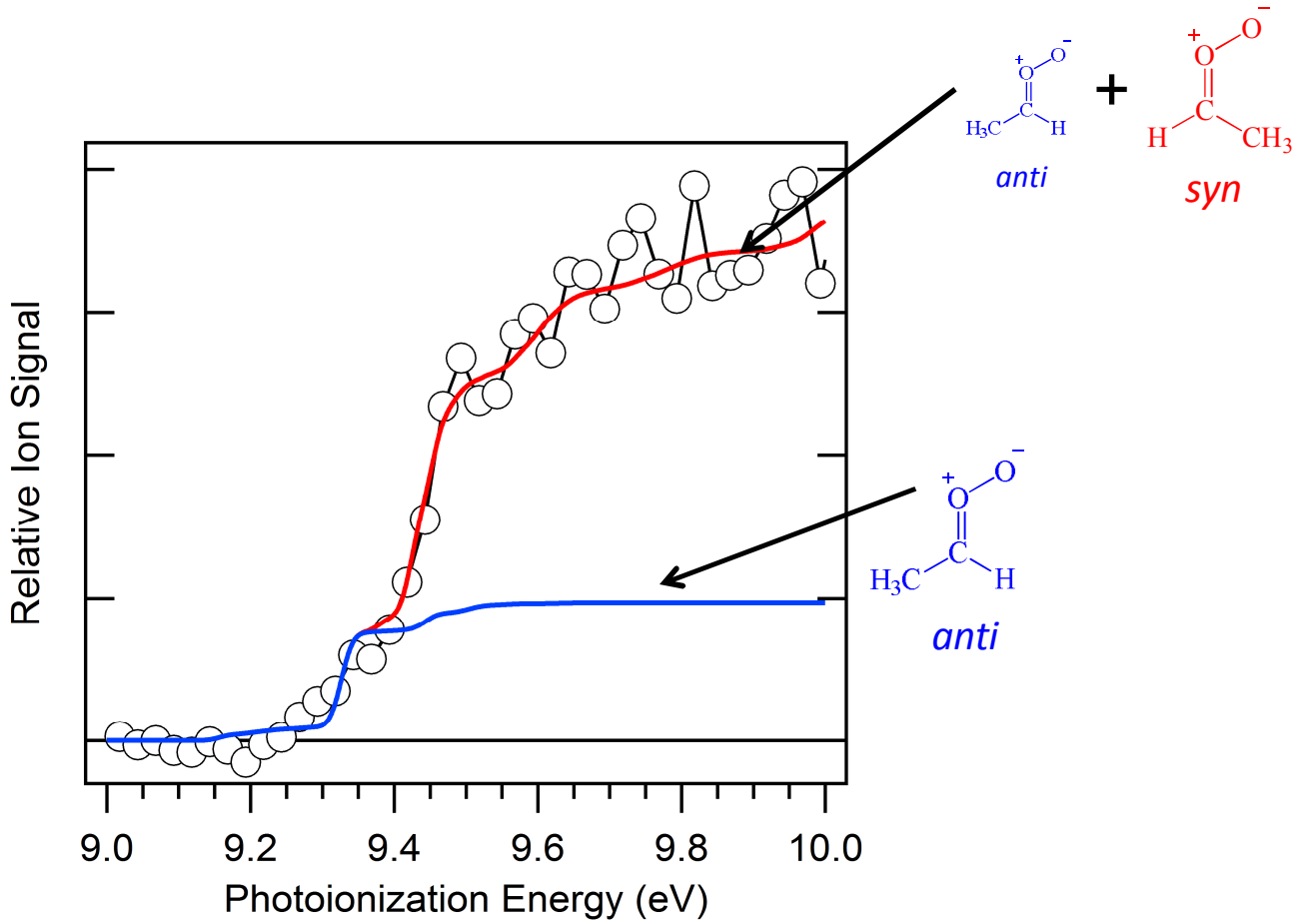
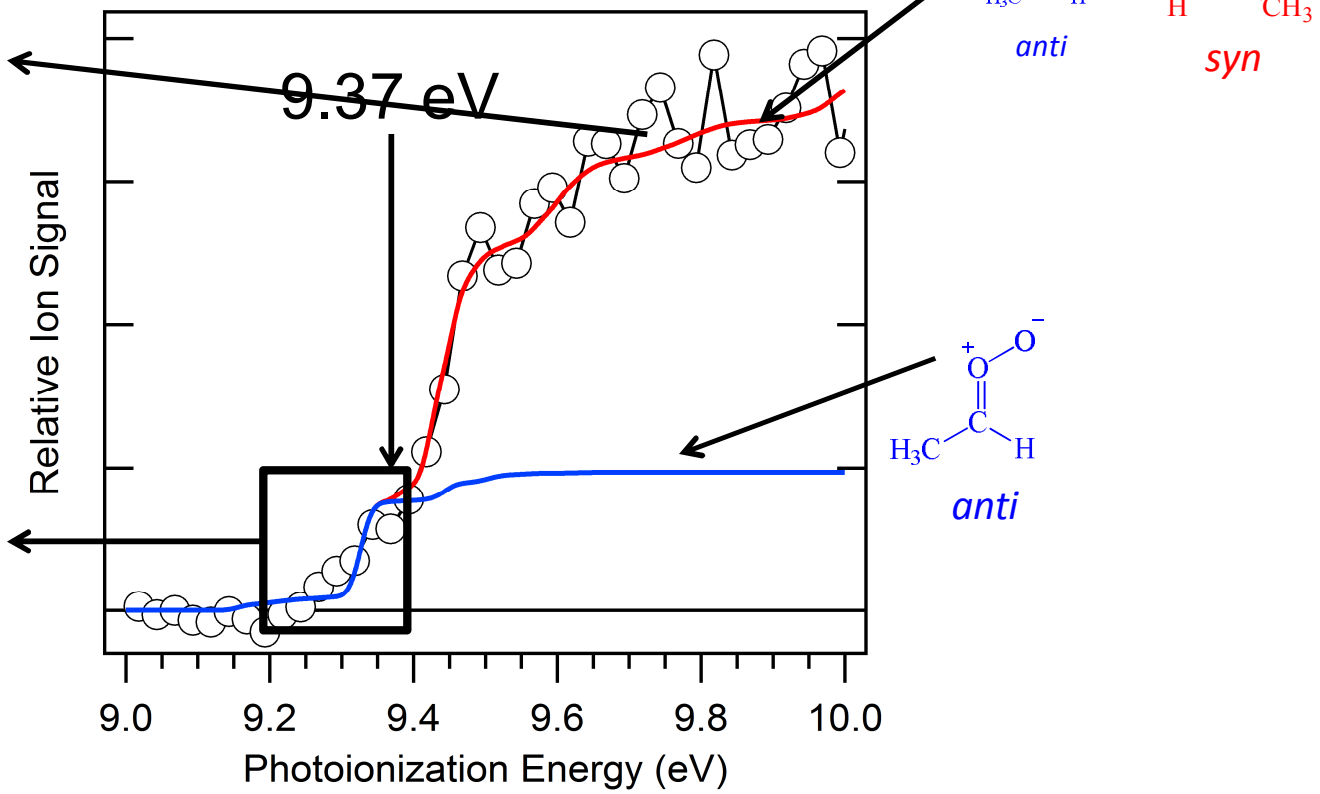


The low-energy part *m/z* = 60 photoionization spectrum is dominated by *anti*-CH_3CHOO

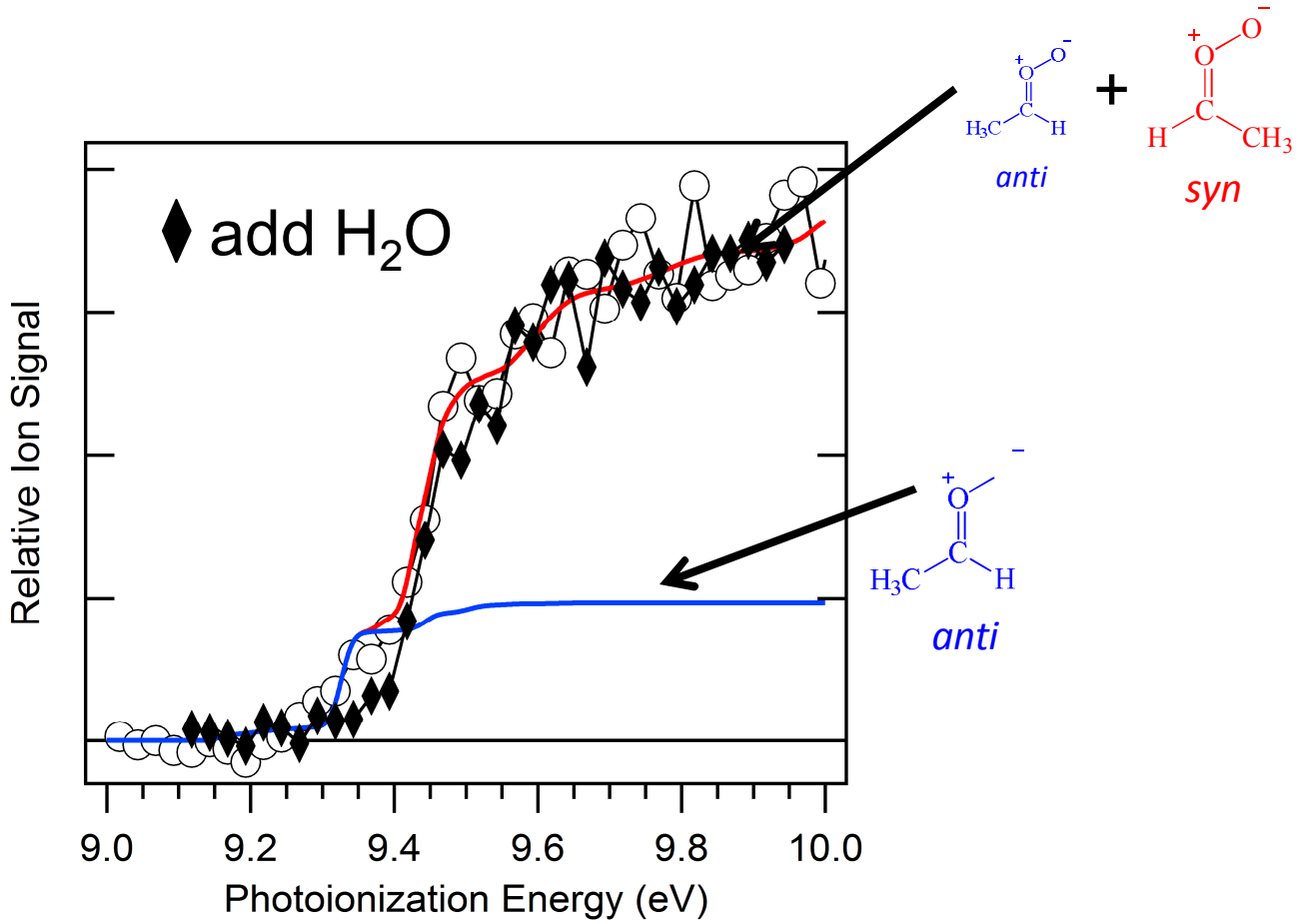
both conformers contribute, but *syn*- dominates

10.5 eV: ~ 85% of the signal is *syn*-

anti- conformer can be probed separately from *syn*-



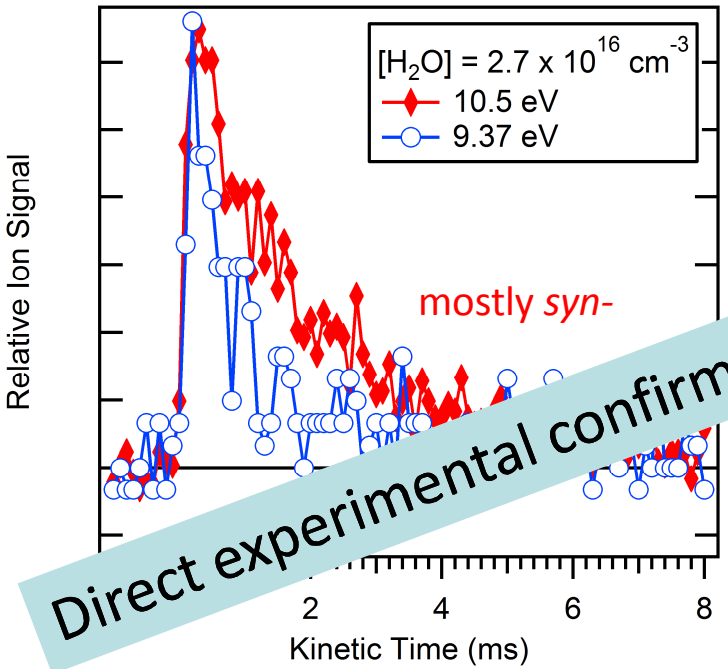
Addition of water preferentially removes the *anti-* conformer of CH_3CHOO

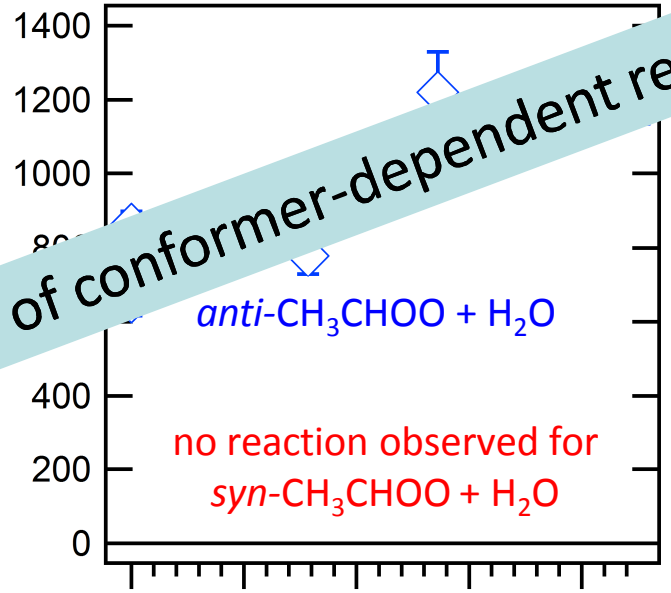


Conformer-dependent reactivity!

Taatjes *et al.*, *Science* **340**, 177 (2013)

A direct measurement of the rate coefficient of *anti*-CH_3CHOO with H_2O





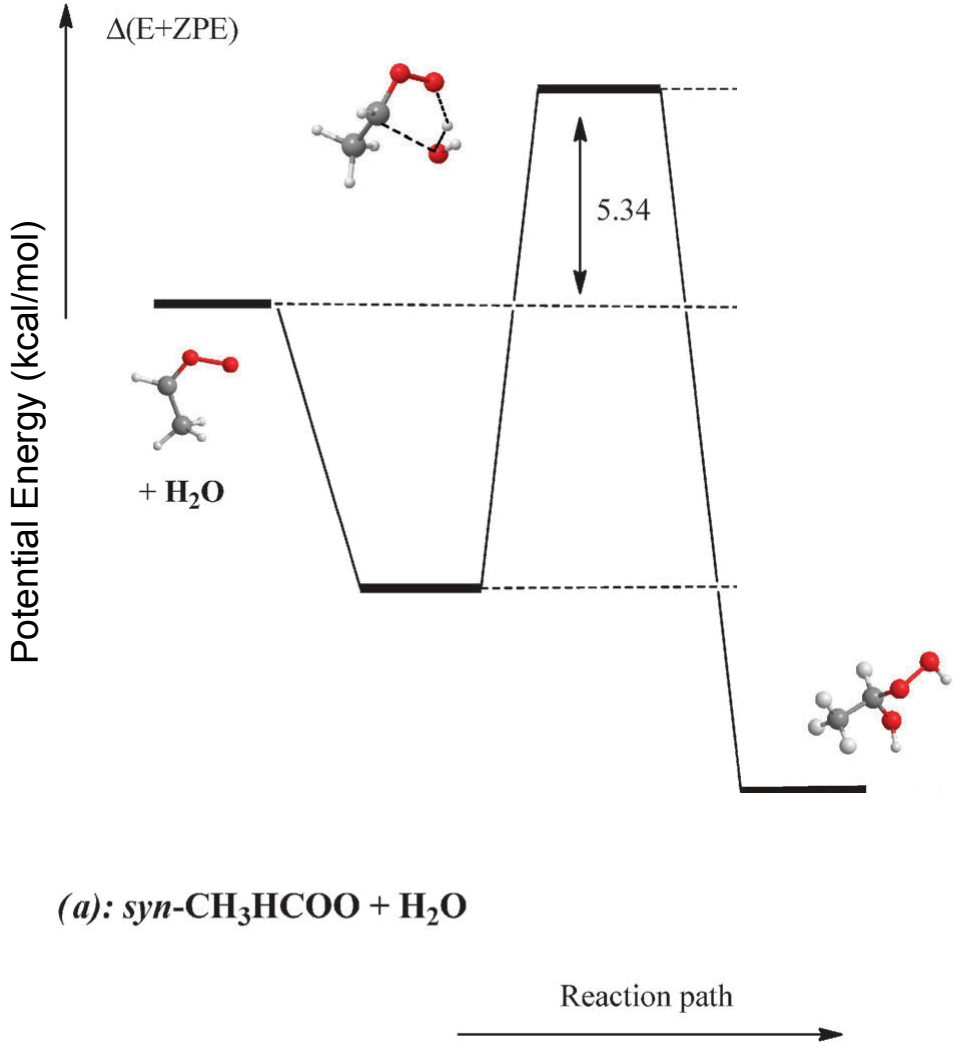
Direct experimental confirmation of conformer-dependent reactivity

$k(\textit{anti}\text{-}CH_3CHOO + H_2O) = (1.0 \pm 0.4) \times 10^{-14}$ cm^3 s^{-1}

$k(\textit{syn}\text{-}CH_3CHOO + H_2O) \leq 4 \times 10^{-15}$ cm^3 s^{-1}

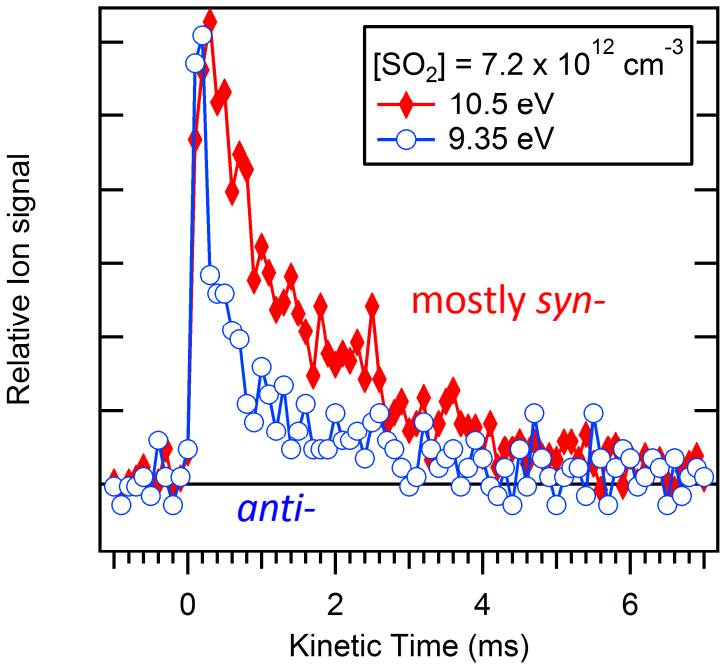
- A factor of 10 lower than predictions for the high-pressure limit from Anglada et al. (Phys. Chem. Chem. Phys. 13, 13034 (2011)), but larger than other calculations
- Substantially larger than prediction for other Criegee Intermediates

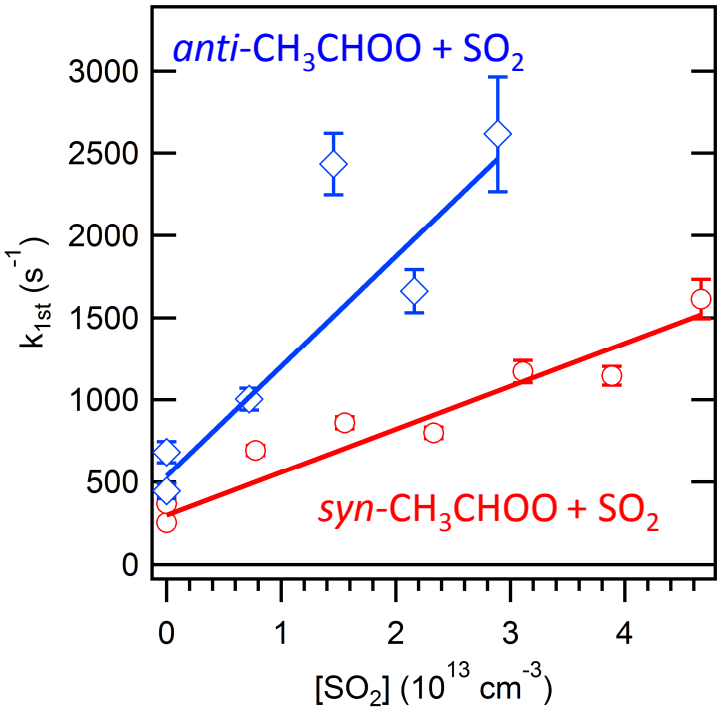
Explanation of Conformer Dependent Reactivitv



Anglada et al., Phys. Chem. Chem. Phys. 13, 13034 (2011)

$CH_3CHOO + SO_2$ also shows conformer-dependent reactivity



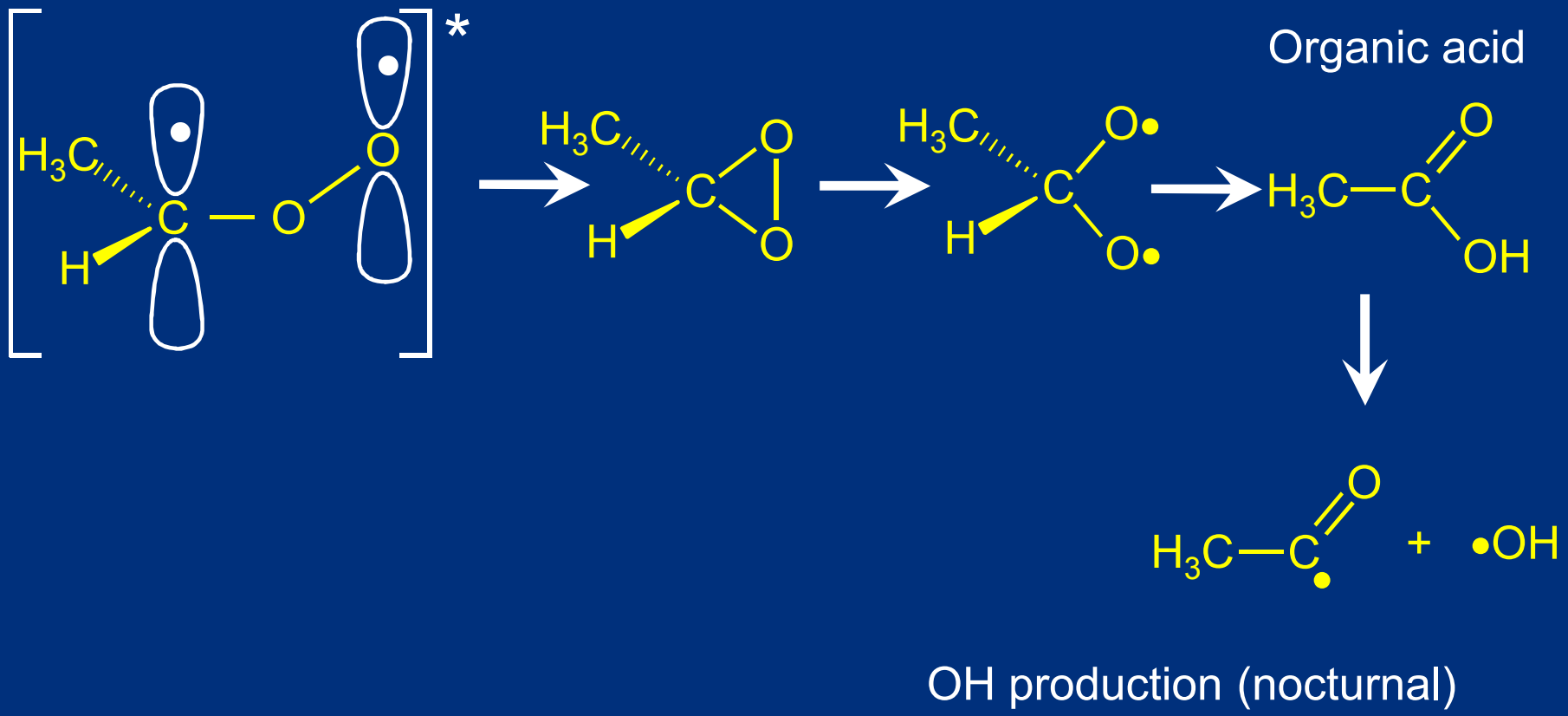


$k(anti\text{-}CH_3CHOO + SO_2) = (6.7 \pm 1.0) \times 10^{-11}$ cm^3 s^{-1}

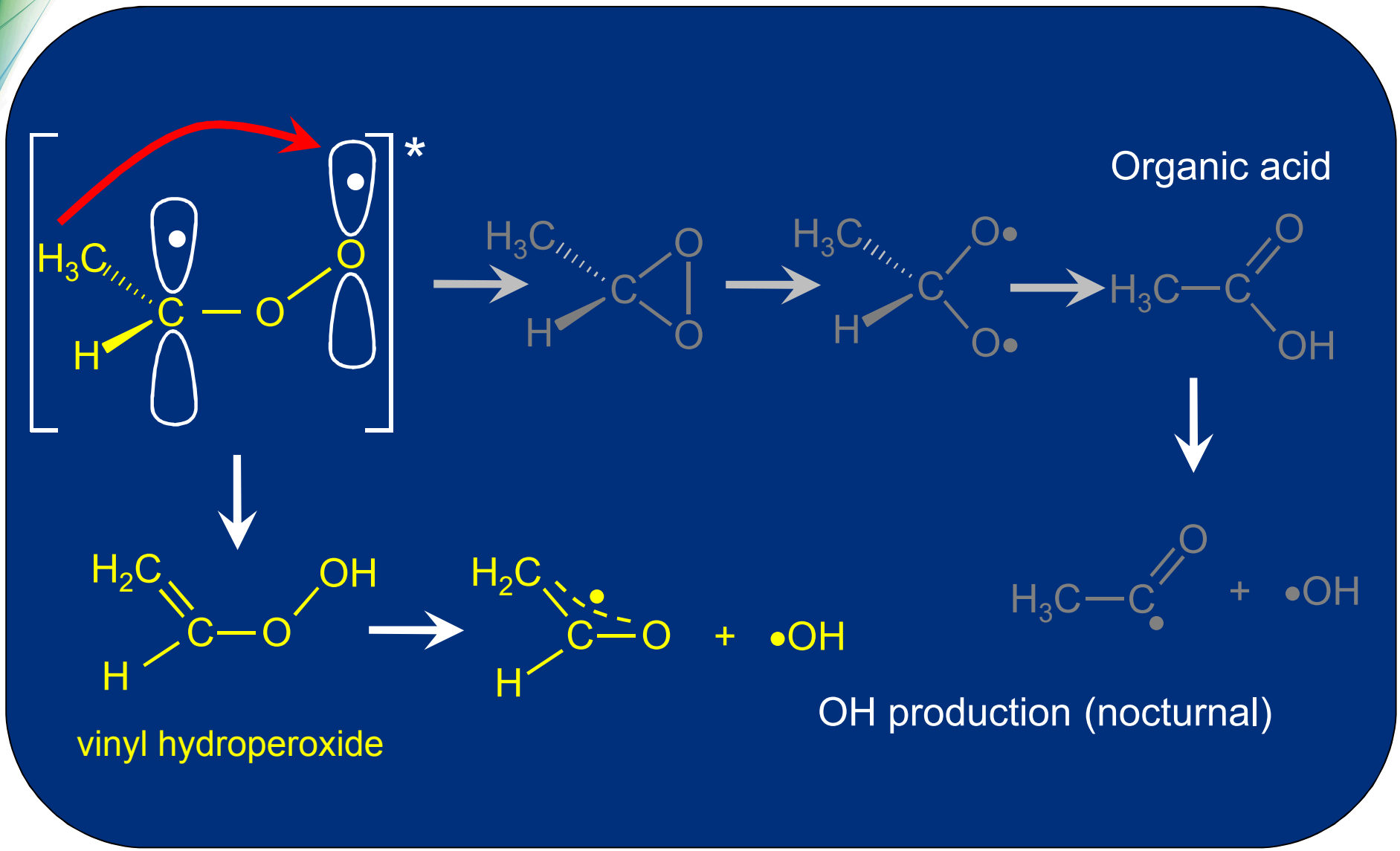
$k(syn\text{-}CH_3CHOO + SO_2) = (2.4 \pm 0.3) \times 10^{-11}$ cm^3 s^{-1}

Similarly fast as CH_2OO reaction

Unimolecular reactions of Criegee intermediates?

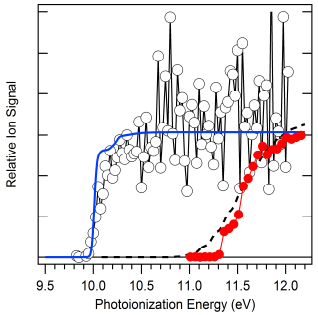


Unimolecular reactions of Criegee intermediates?



Summary

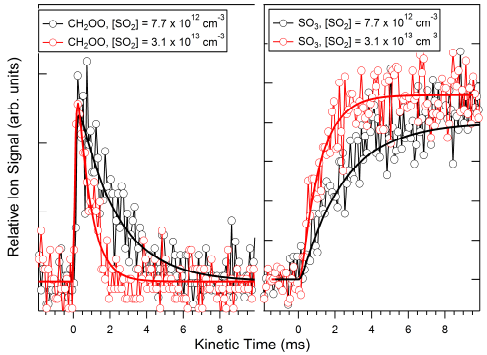
1,1-Diiodoalkane oxidation combined with MPIMS is a suitable strategy to directly probe reactions of Criegee Intermediates



$$CH_2I_2 \xrightarrow{248 \text{ or } 351 \text{ nm}} I + CH_2I$$

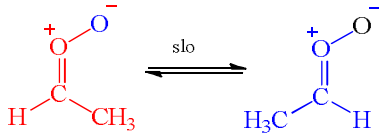
$$CH_2I + O_2 \longrightarrow I + CH_2OO$$

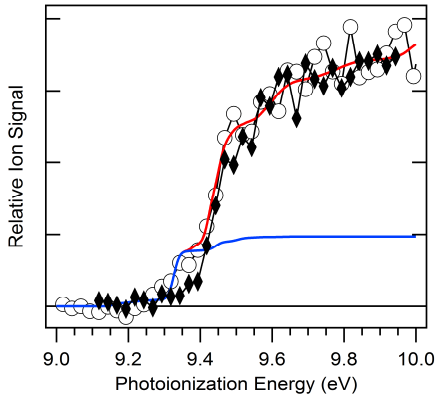
Tunability of the photo-ionization energy is key to distinguish isomers



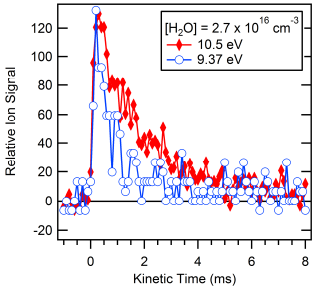
We determined rate coefficients for CH_2OO reactions with atmospherically relevant species; substantial differences to values used in tropospheric models exist in some cases

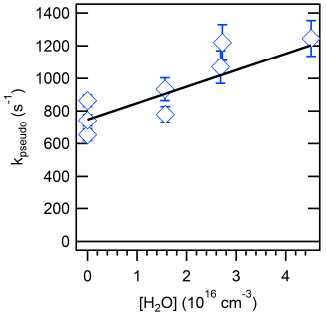
The two conformers of CH_3CHOO can be distinguished by their photoionization spectra





anti-CH_3CHOO reacts faster with H_2O and SO_2 than *syn-;* direct determination of the *anti*-$CH_3CHOO + H_2O$ rate coefficient





Tropospheric Implications

- $CH_2OO + SO_2 \rightarrow$ carbonyl + SO_3 similar importance to $OH + SO_2 \rightarrow H + SO_3$ oxidation of SO_2.
  - Pot… quires sun…
- Criege… els:
  - NO…
- *anti*-CH… r.
- *syn*-CH… nay compe…

We are just beginning to understand how Criegee Intermediates react

- Need to understand larger Criegee molecules
- Need to understand more reactions
- Need to understand reactions at different conditions

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The *m/z* = 60 photoionization spectrum shows evidence of both *syn*- and *anti*- conformers of CH_3CHOO