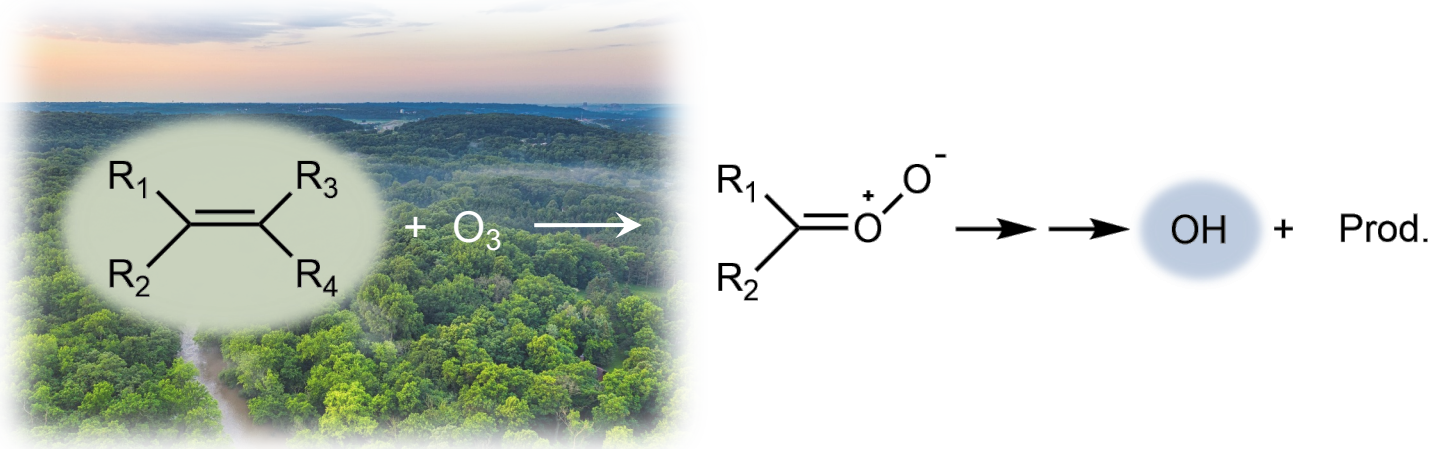
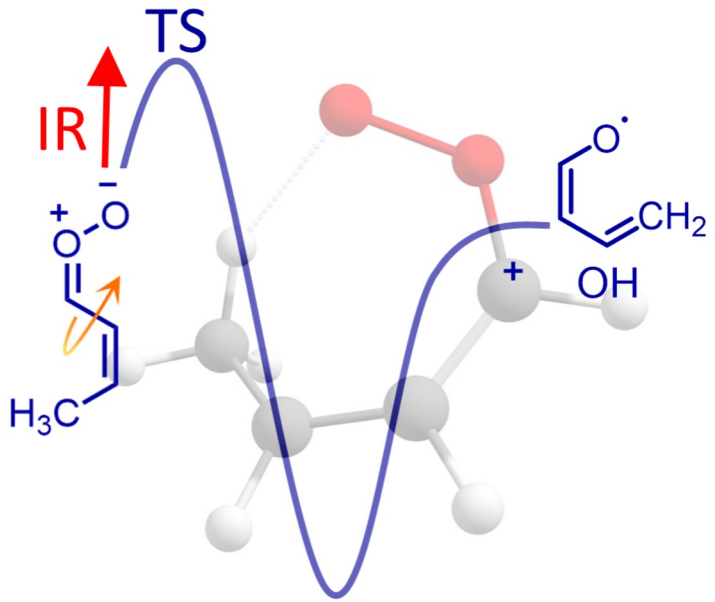
Rapid Allylic 1,6 H-Atom Transfer in a Criegee Intermediate with Unsaturated Substituents

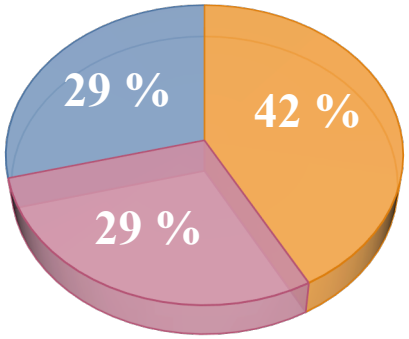
Anne S. Hansen[1], Yujie Qian[1], Stephen J. Klippenstein[2] and Marsha I. Lester[1]
[1]*Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA*
[2]*Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA*



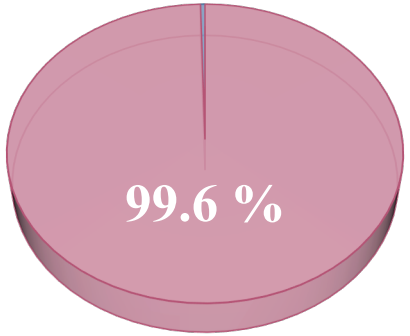


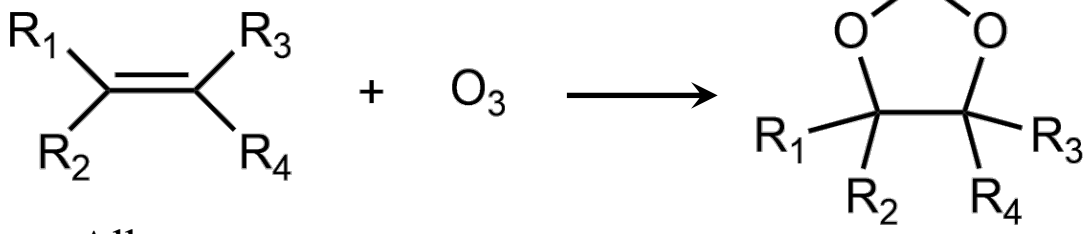
Alkene Ozonolysis: Significant Source of OH Radicals

DAYTIME



NIGHTTIME





Alkene

Primary Ozonide (POZ)

$O_3 \xrightarrow{+h\nu} O(^1D) + O_2$

$O(^1D) + H_2O \rightarrow OH$

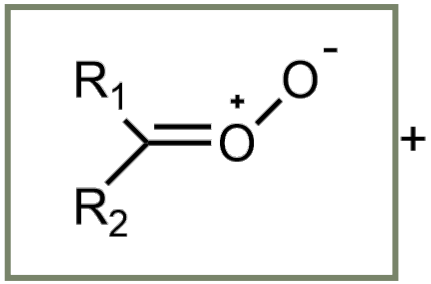
$HONO \xrightarrow{+h\nu} OH + NO$

Alkene + O_3 → OH

Alkene + O_3 → OH

OH + coproduct

Unimolecular decay



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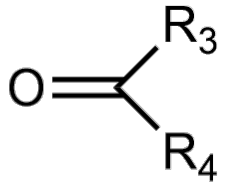


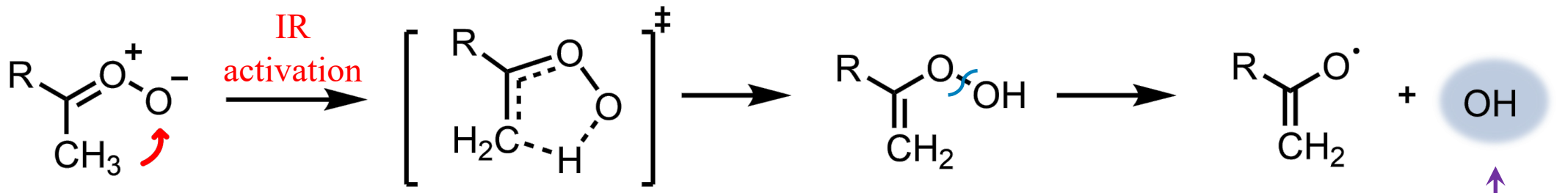
Criegee Intermediate (CI)

carbonyl product

Initiates oxidation of many trace atmospheric species

Unimolecular Decay of Criegee Intermediates

Typical 1,4 Alkyl H-Atom Shift



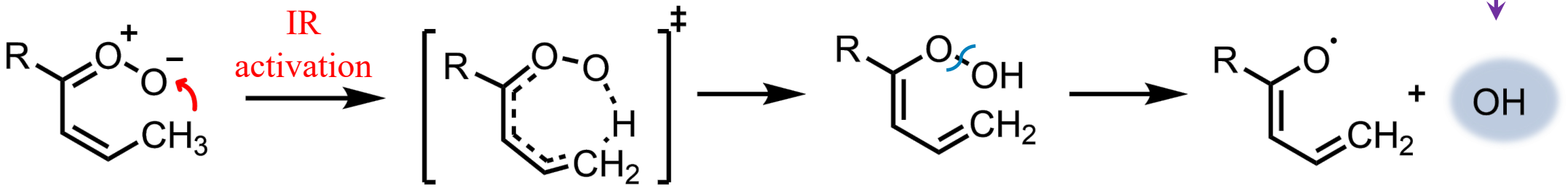
Criegee Intermediate

Transition State (TS)
~ 16-18 kcal mol^{-1}
or overtone CH stretch ($2\nu_{CH}$)

Vinyl hydroperoxide (VHP)

Vinoxy

Novel 1,6 Allylic H-Atom Shift



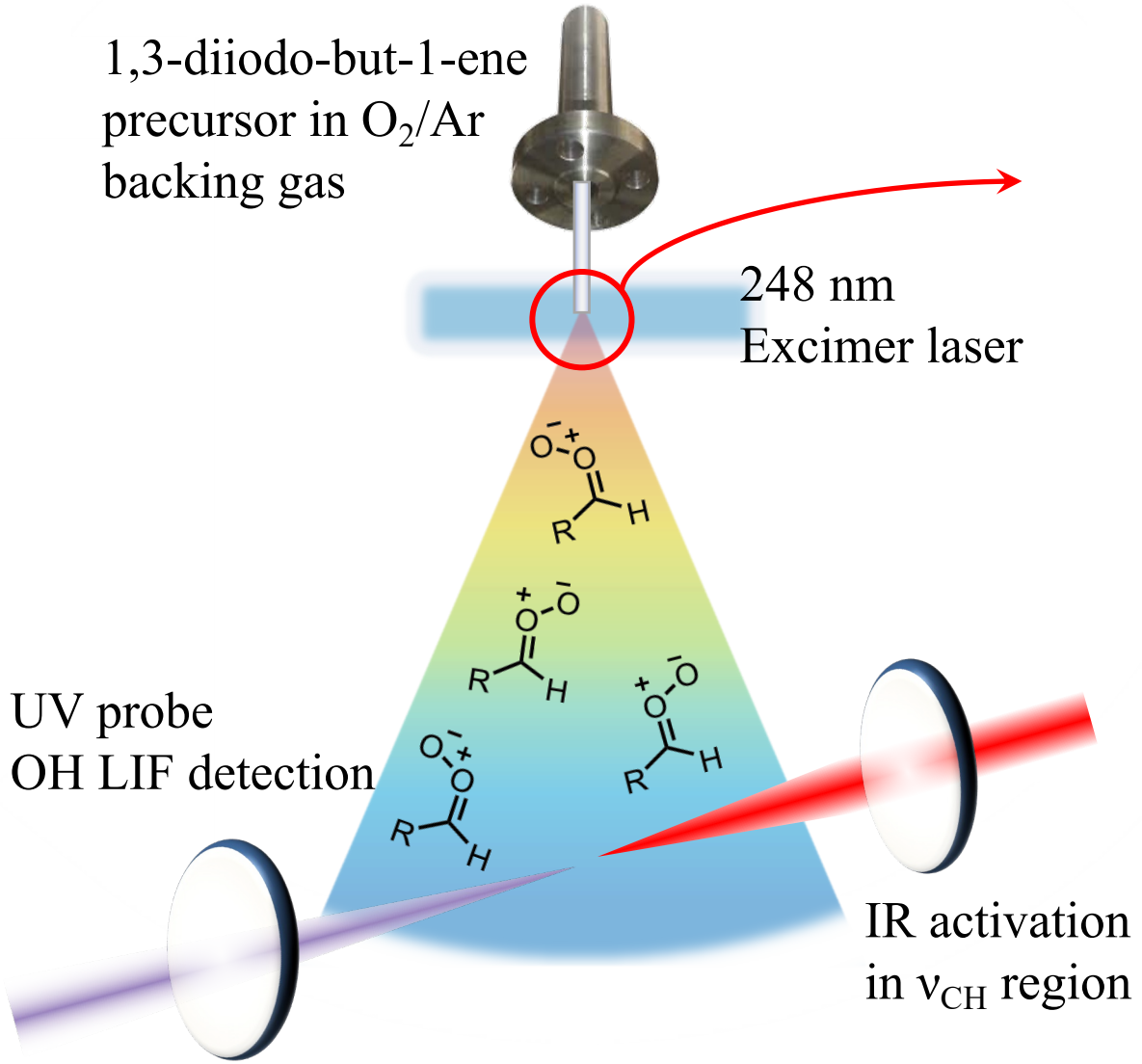
Criegee Intermediate

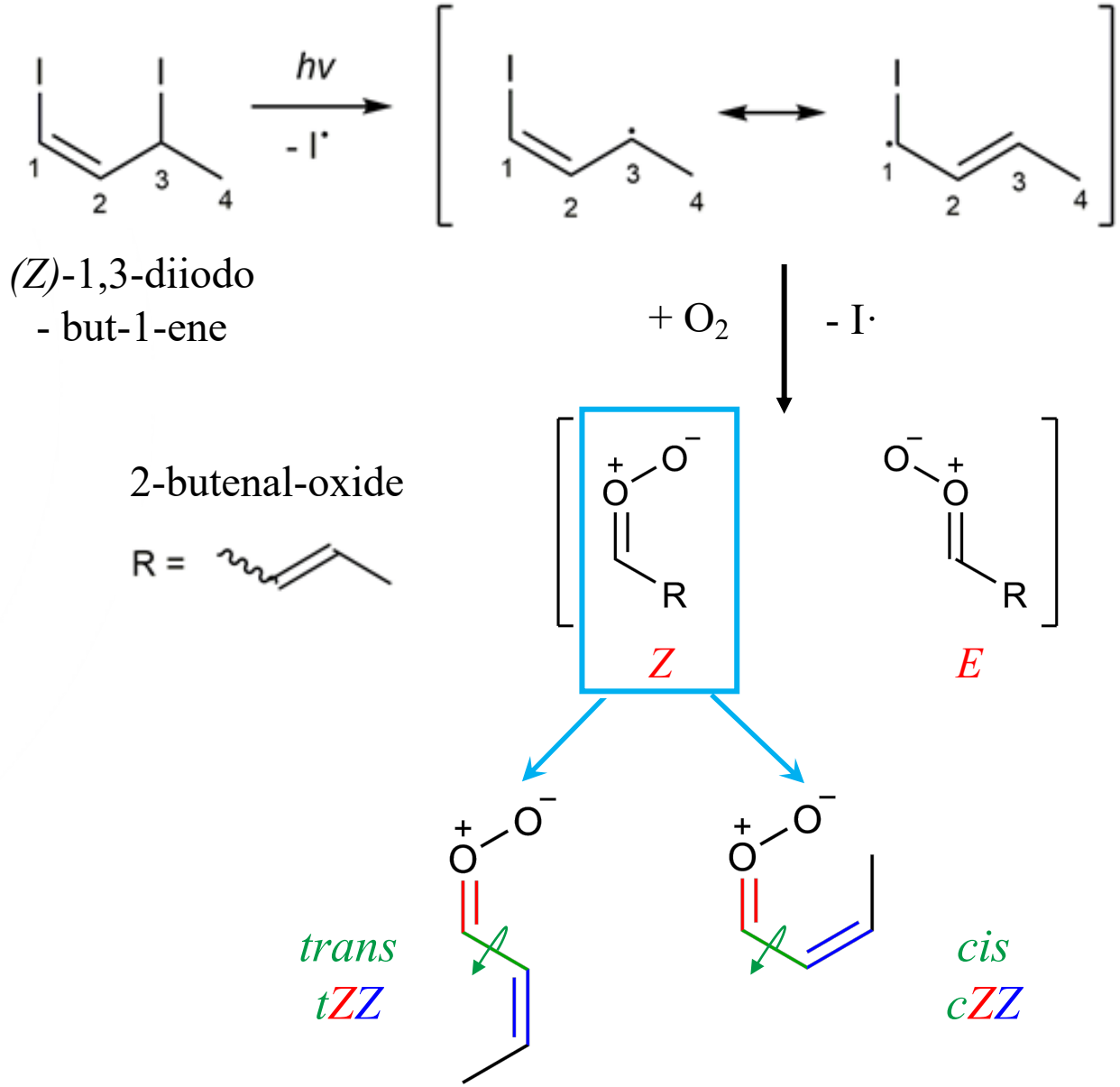
Transition State (TS)
~ 5 kcal mol^{-1}
or fundamental CH stretch (ν_{CH})

(E)-1-hydroperoxy buta-1,3-diene (HPBD)

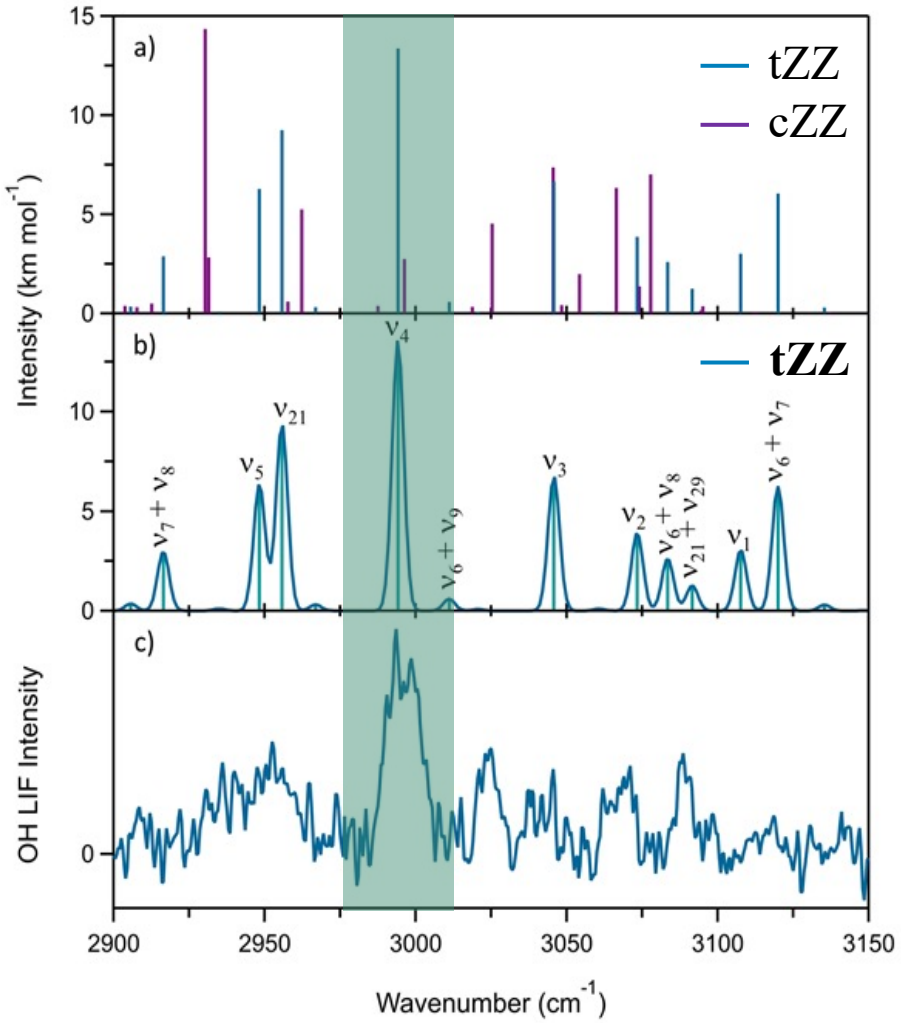
1-oxobut-3-enyl (OBD)

IR Action Spectroscopy





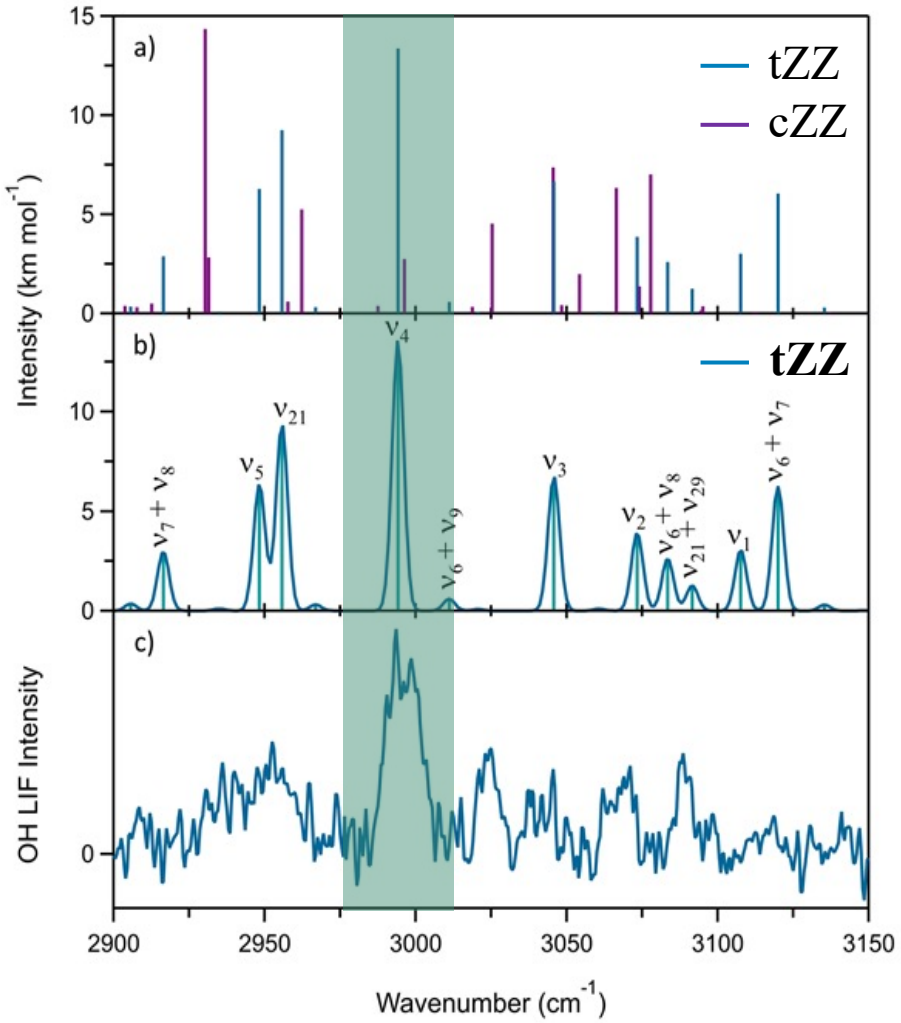
Experimental Spectroscopy Results



VPT2 anharmonic vibrational frequencies.
Level of theory: B2PLYP-D3/cc-pVTZ

tZZ stick spectrum broadened to reflect rotational band contour at T_{rot} ~ 10 K, laser bandwidth (0.9 cm^{-1}), and Lorentzian broadening (1.7 cm^{-1}) due to rapid IVR of 3 ps

Experimental Spectroscopy and Appearance of OH Products



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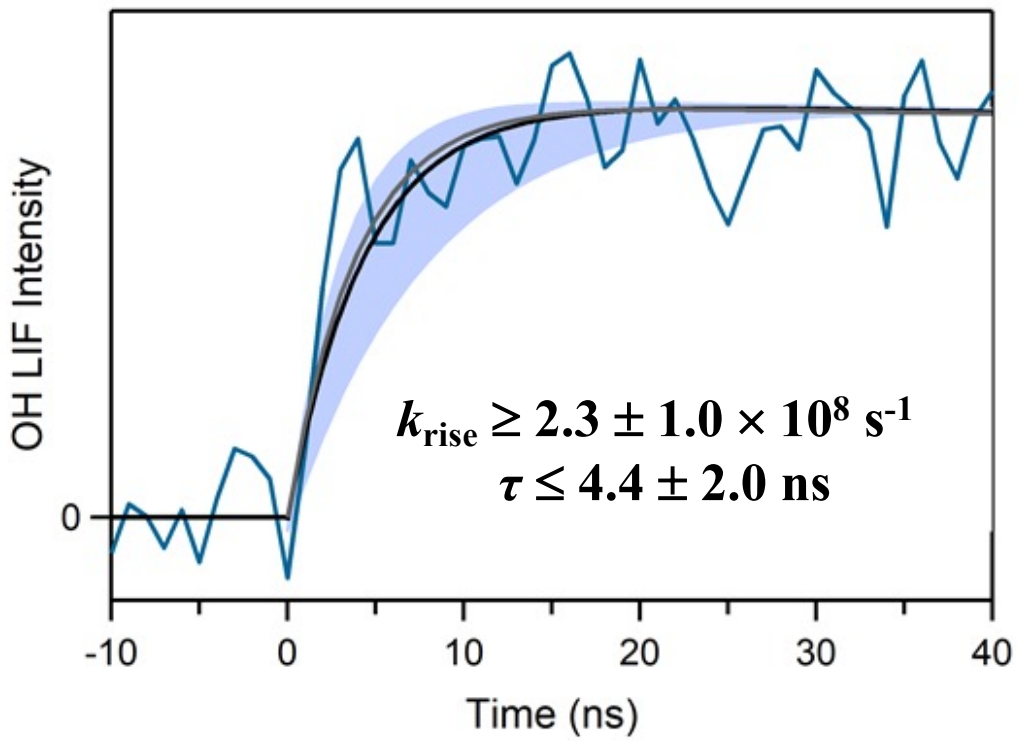
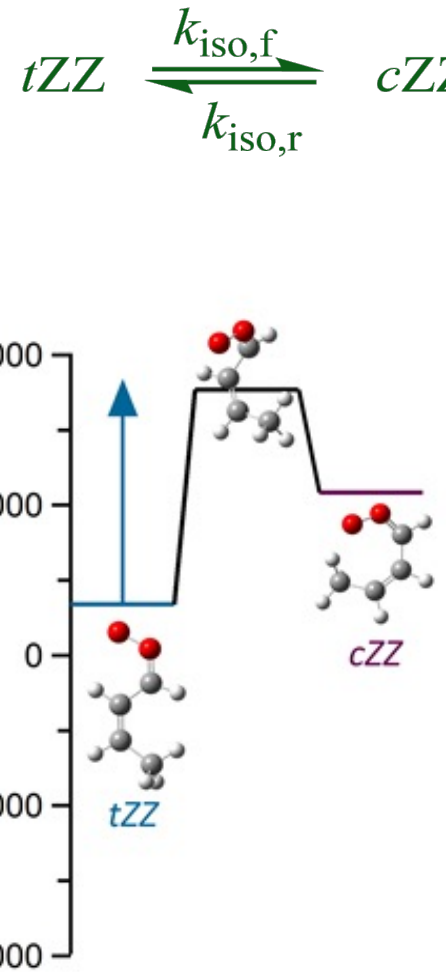


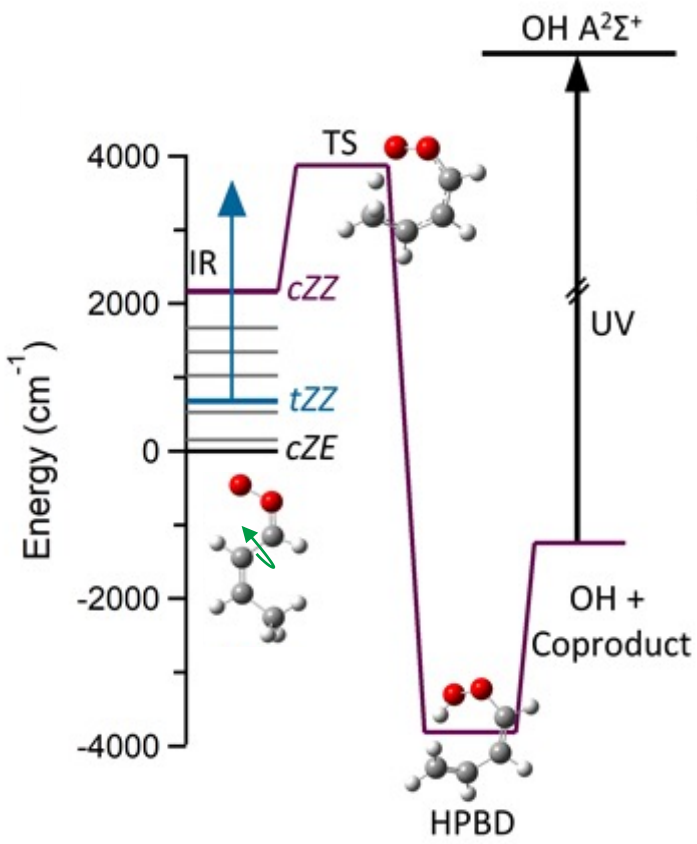
IR pump at 3000 cm^{-1}, UV probe OH LIF detection
Rapid time-resolved appearance of OH products

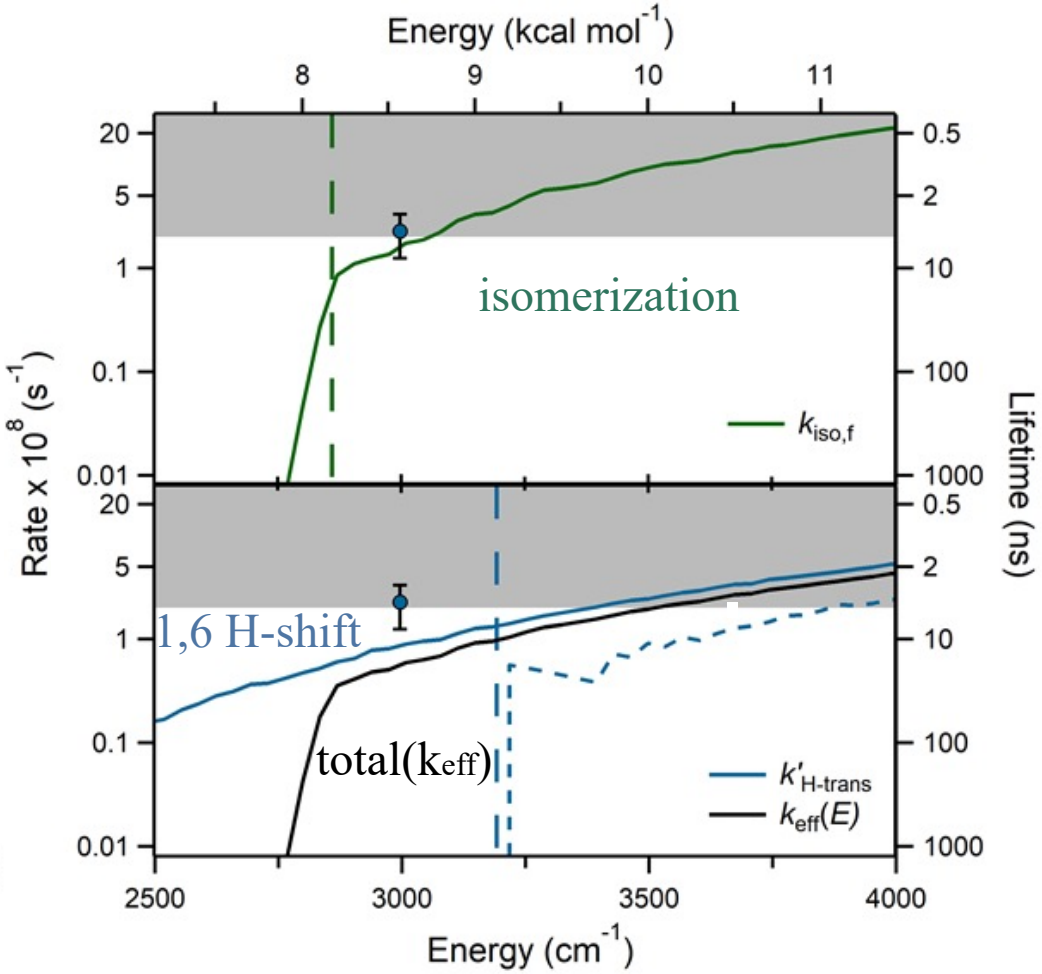
tZZ stick spectrum broadened to reflect rotational band contour at T_{rot} ~ 10 K, laser bandwidth (0.9 cm^{-1}), and Lorentzian broadening (1.7 cm^{-1}) due to rapid IVR of 3 ps

Isomerization and Unimolecular Reaction Kinetics



$$tZZ \underset{k_{iso,r}}{\overset{k_{iso,f}}{\rightleftharpoons}} cZZ \qquad cZZ \xrightarrow{k_{H\text{-}trans}} product$$

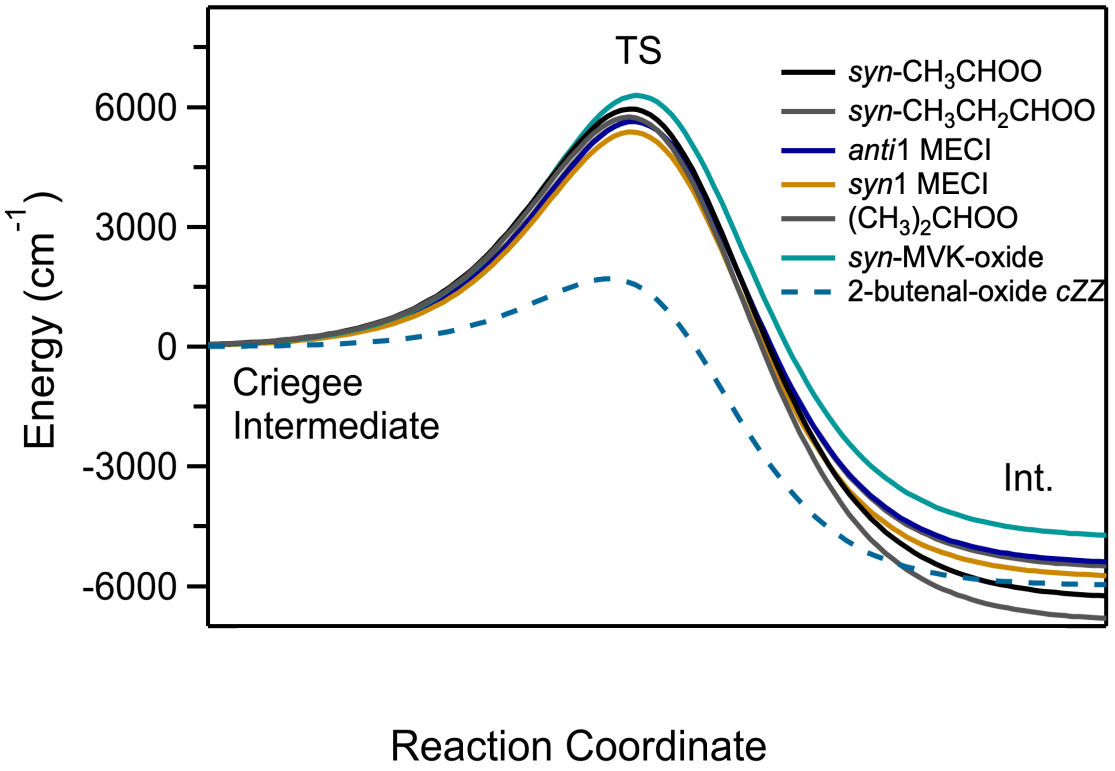




RRKM calculation: at 3000 cm^{-1}

$k_{eff}(E) = 5.6 \times 10^7\ s^{-1}$ or $\tau_{eff}(E) \leq 5$ ns

Comparison of 1,4 and 1,6 H-Atom Transfer



Alkyl 1,4 H-atom transfer

TS: ~ 16-18 kcal mol^{-1} or $2\nu_{CH}$

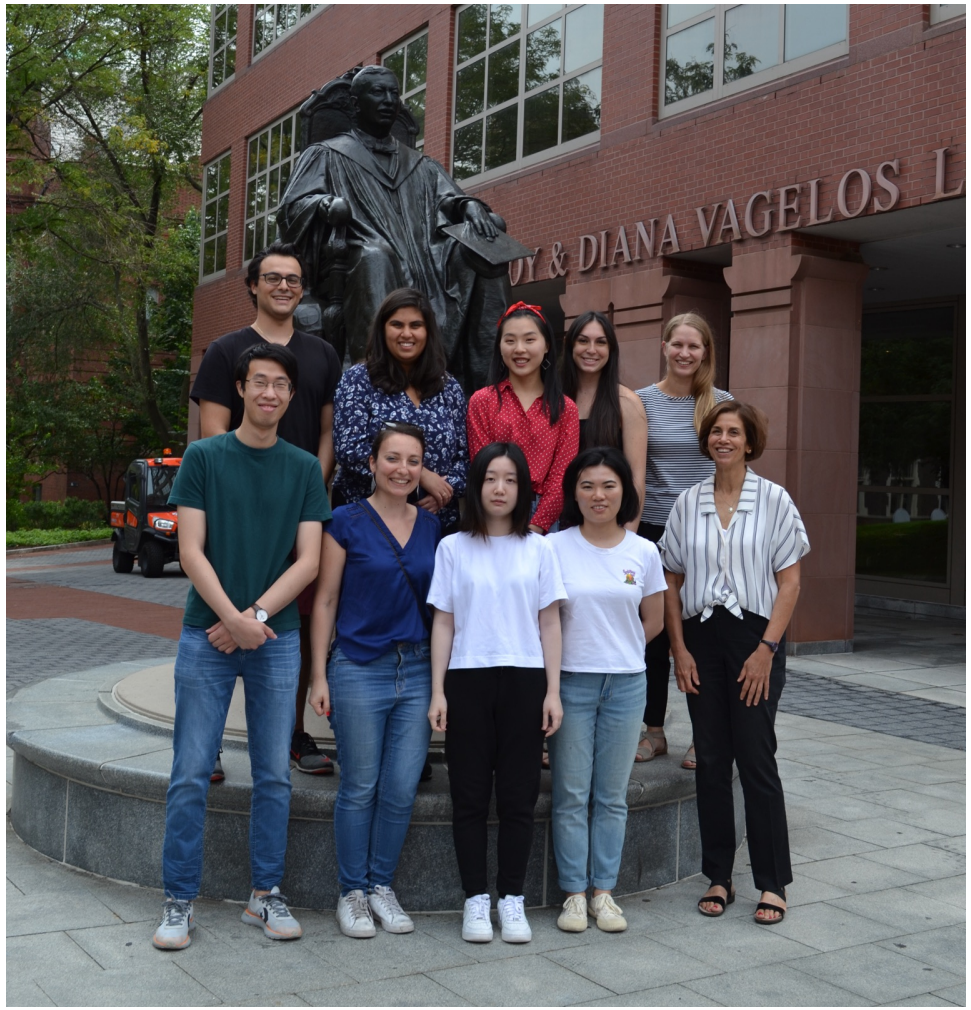
Allylic 1,6 H-atom transfer

TS: ~ 4.9 kcal mol^{-1} or ν_{CH}

Lower TS barrier results in much faster 1,6 H-atom transfer than 1,4 H-atom transfer !

Rapid allylic 1,6 H-atom transfer in an unsaturated Criegee intermediate. *J. Am. Chem. Soc.* 2022, 144, 13, 5945–5955

Acknowledgement



Thank you for listening!

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