Low pressure yields of stabilized Criegee Intermediates produced from ozonolysis of a series of alkenes

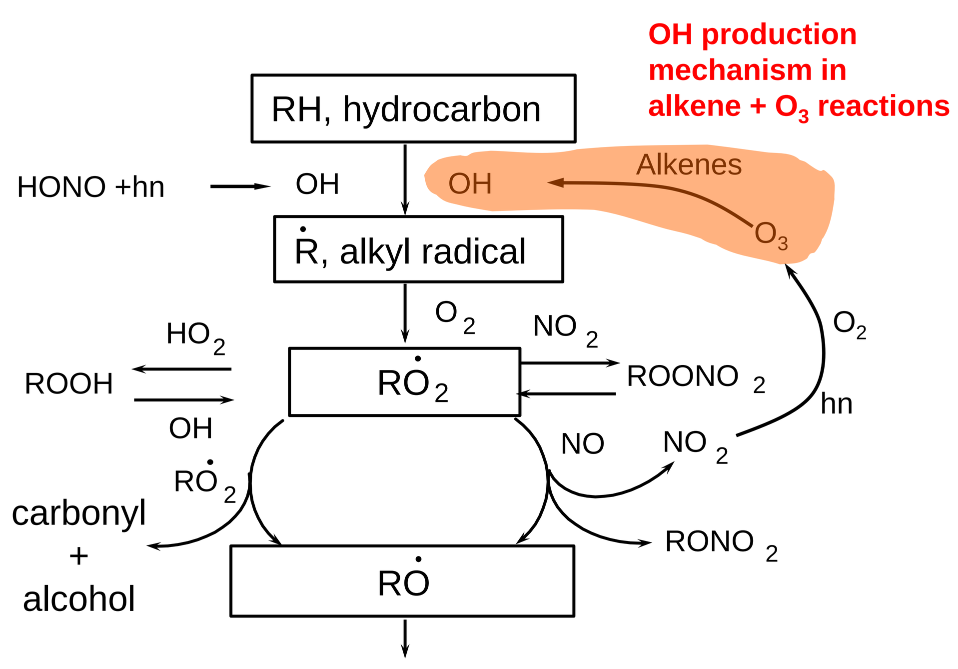
Lei Yang, Mixtli Campos-Pineda, and Jingsong Zhang

Department of Chemistry, University of California, Riverside, CA 92521

Introduction

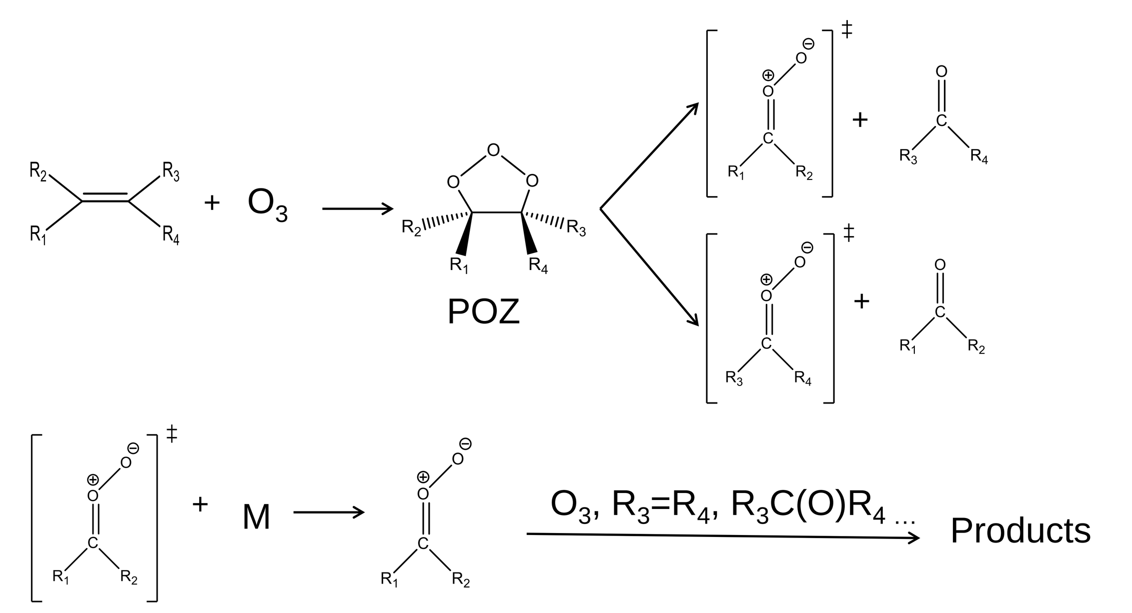
Ozonolysis of alkenes

- Important oxidation pathway of alkenes in the troposphere.
- Involved in the production of organic aerosol.
- Involved in OH radical production.



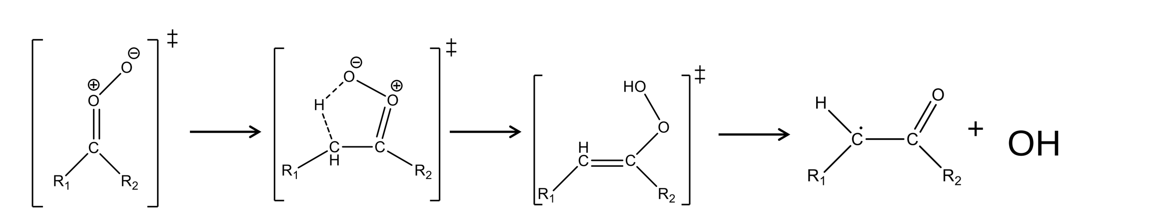
Mechanism of ozonolysis of alkenes

- Formation of a primary ozonide (POZ).
- Production of a carbonyl and a high-energy carbonyl oxide (Criegee Intermediate).
- Stabilization of the Criegee Intermediate leads to further reactions.



Criegee intermediates

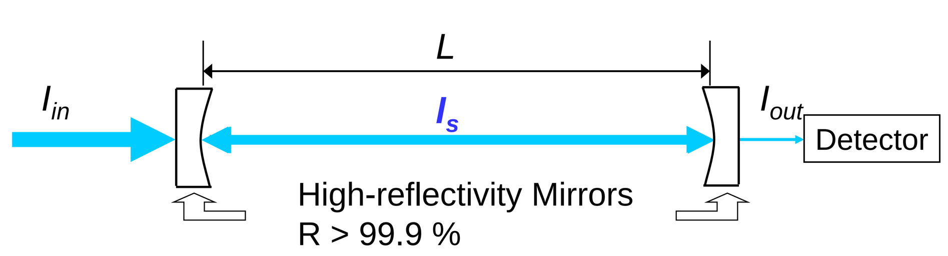
- Criegee intermediates are produced with a broad internal energy distribution.
- High energy Criegee intermediates (tCI) decompose into atmospherically important compounds (e.g. vinoxy, OH radical).



- Stabilized Criegee intermediates (sCI) undergo reactions to produce secondary ozonides and organic aerosols.

Method and Apparatus

Cavity Ring-Down Spectroscopy



τ_0: ringdown time without sample
τ: ringdown time with sample
c: speed of light

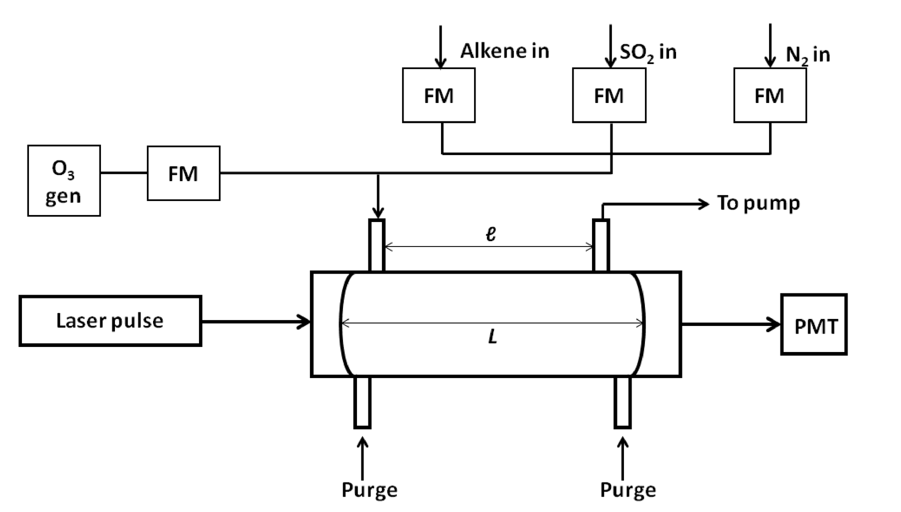
R: cavity mirror reflectivity
L: length of the cell
l_s: single path absorption length

Absorption coefficient

$$\alpha = \frac{L}{cl_s}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) = \sigma n$$

Alkene ozonolysis gas flow reactor

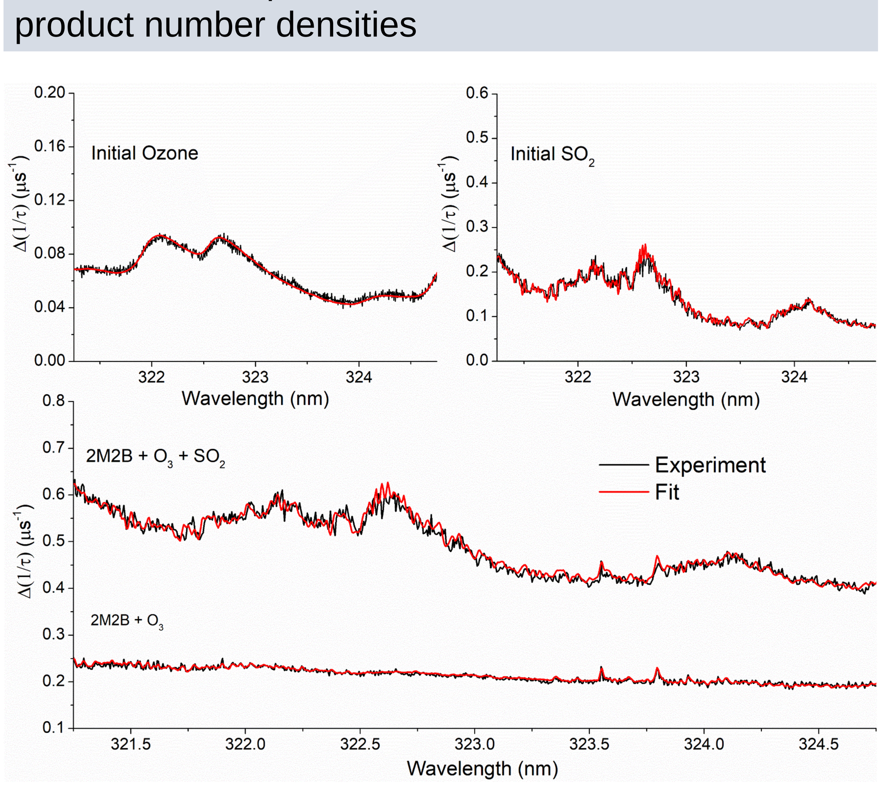
- Spectroscopy of the reaction products is performed in real time.
- Spectra are scanned from 320-325 nm.
- Reaction is carried out under various flow and pressure conditions.
- Scavenging of the stabilized Criegee Intermediate (sCI) is done using SO_2



Spectra analysis

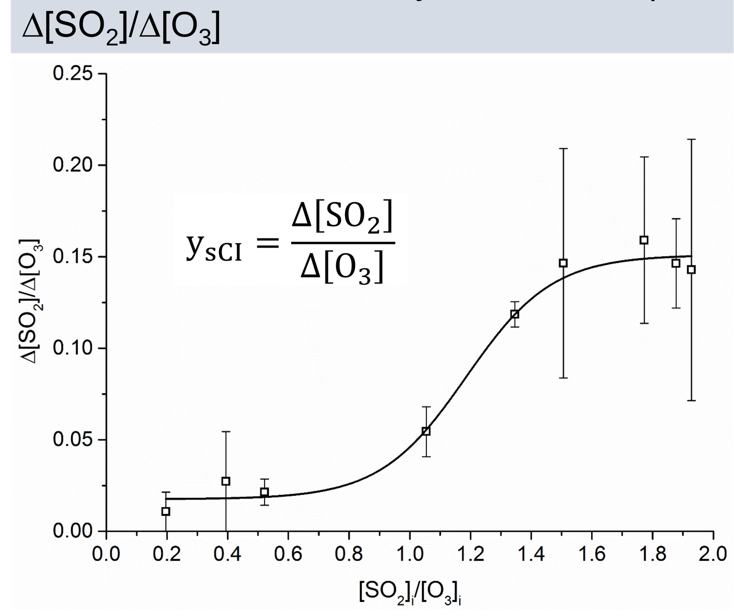
$$\left(\frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)}\right) = \frac{dc}{L}\alpha(\lambda) = \frac{dc}{L}\sum_i^n \sigma_i(\lambda) N_i$$

Reference cross-section of products and reactants are fitted to spectral features in order to obtain product number densities



The ratios of initial SO_2 and O_3 ($[SO_2]/[O_3]_i$) were measured and compared to the ratio of consumed SO_2 and O_3 ($\Delta[SO_2]/\Delta[O_3]$).

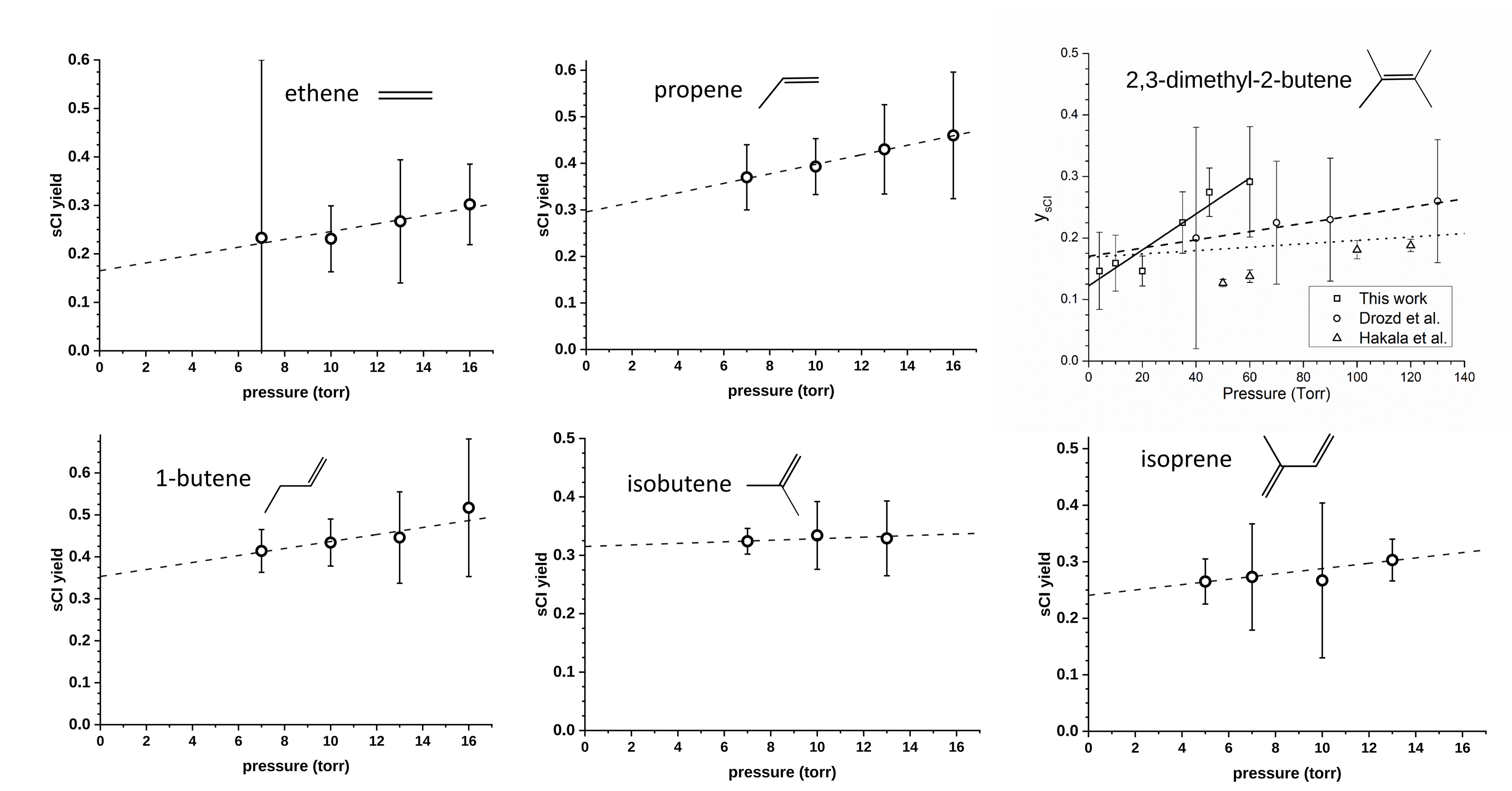
At $[SO_2]/[O_3]_i$ ratios of ~2, SO_2 effectively titrates the sCI and the yield of sCI equals $\Delta[SO_2]/\Delta[O_3]$



Results

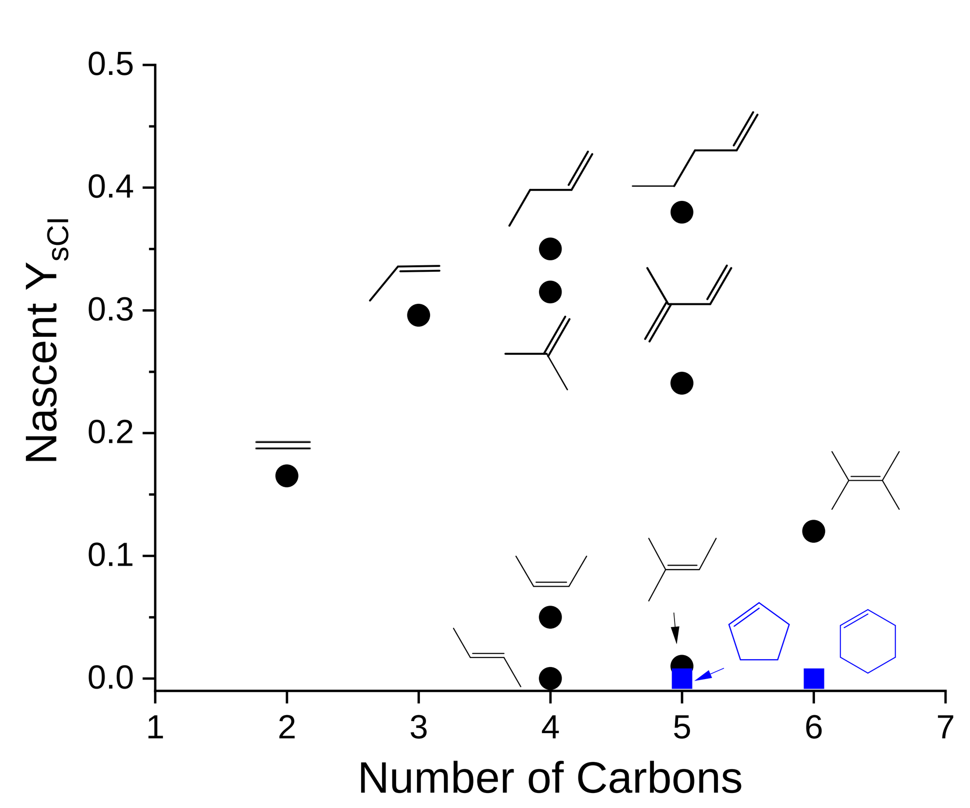
Low pressure yields of sCI produced by ozonolysis of a series of alkenes

The yields of stabilized Criegee intermediates were measured at different low pressures and the nascent /zero pressure yields were determined by extrapolation. Endocyclic alkenes show no sCI production at the pressures studied. However, acyclic alkenes show pressure-dependent sCI yields. The sCI yields of 2,3-dimethyl-2-butene were compared to existing data to assess this new technique.



Drozd, G. T. & Donahue, N. M. *The Journal of Physical Chemistry A* **115,** 4381–4387 (2011).
Hakala, J. P. & Donahue, N. M. *The Journal of Physical Chemistry A* **120,** 2173–2178 (2016).

Nascent sCI yields from ozonolysis of a series of alkenes



- Stabilized formaldehyde oxide (CH_2OO) has a high nascent yield due to its relatively high energy barrier for dissociation with respect to the alkenes studied.
- The nascent yield of stabilized CH_2OO increases with increasing carbon number of the carbonyl co-product. As the size of the carbonyl co-product increases, the energy that is taken by the CI decreases. Thus, CI ends up with a lower mean energy distribution.
- *cis*-2-butene produces higher nascent sCI than *trans*-2-butene, perhaps due to different syn- and anti-CI branching ratios, or different POZ conformations.
- Endocyclic alkene ozonolysis produced effectively no nascent sCI.

Summary

- Measurement of consumed SO_2 during scavenging can be used to indirectly measure the yield of sCI.
- The yields of sCIs produced by ozonolysis of a series of alkenes were measured at low pressures.
- Nascent yields were determined by extrapolation at zero pressure and compared with existing data.
- New information of nascent yields can be used as benchmark for theoretical calculations.

Acknowledgements

W. M. Keck Foundation

UC-MEXUS Fellowship