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

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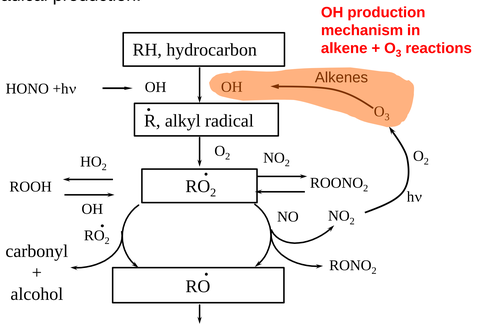
Introduction

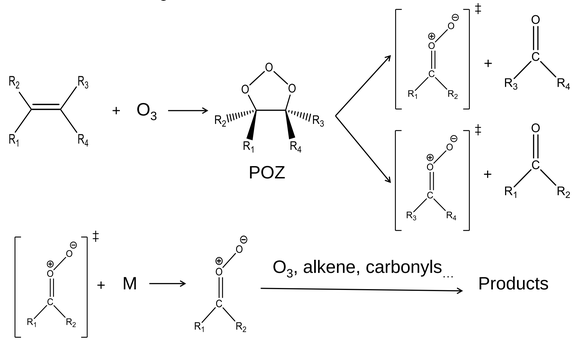
Ozonolysis of alkenes

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



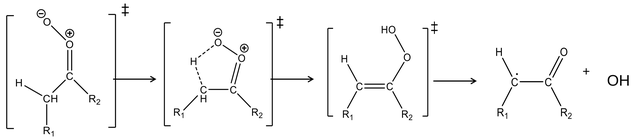
Mechanism of ozonolysis of alkenes

- 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

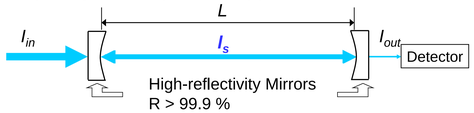
- Criegee intermediates are produced with a broad internal energy distribution.
- High energy Criegee intermediates (tCI) decompose into atmospherically important compounds (e.g. vinoxy, OH radical).



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

Method and Apparatus

Cavity Ring-Down Spectroscopy

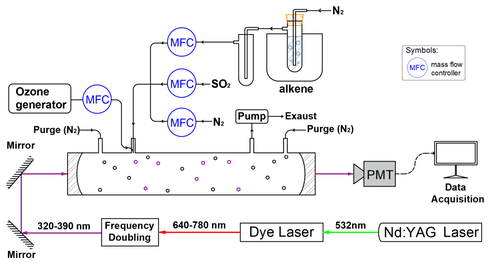


Absorption coefficient $\alpha = \frac{L}{cl_s}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) = \sigma N$

τ_0: ringdown time without sample
τ : ringdown time with sample
c: speed of light
R: cavity mirror reflectivity
σ: absorption cross-section
N: number density
L: length of the cell
l_s: single path absorption length

Alkene ozonolysis gas flow reactor

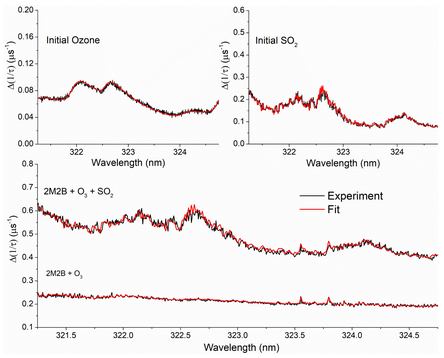
- Spectroscopy of the reaction products is performed in real time.
- Spectra are scanned from 320-325 nm.
- Reaction is carried out under various flow and pressure conditions.
- Scavenging of the stabilized Criegee Intermediate (sCI) is done using SO_2



Spectra analysis

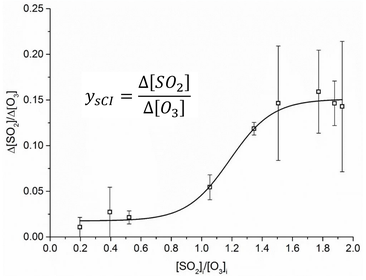
$$\Delta\left(\frac{1}{\tau}\right) = \frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)} = \frac{cl_s}{L}\alpha(\lambda) = \frac{cl_s}{L}\sum_i^n \sigma_i(\lambda)N_i$$

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

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



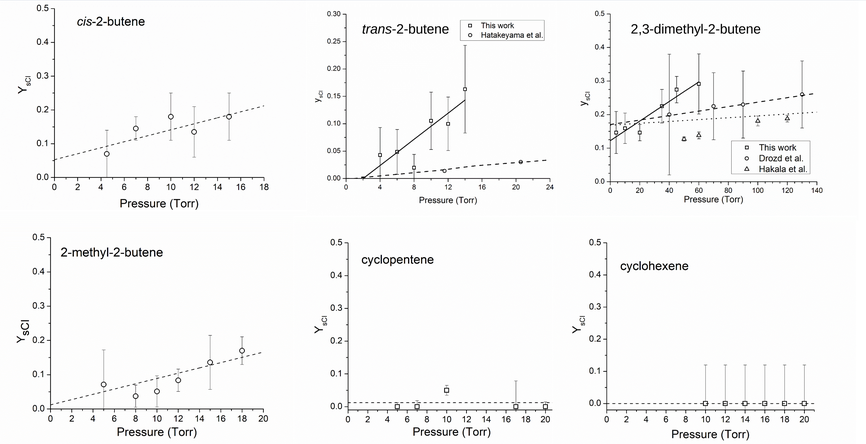
Summary

- 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.

Results

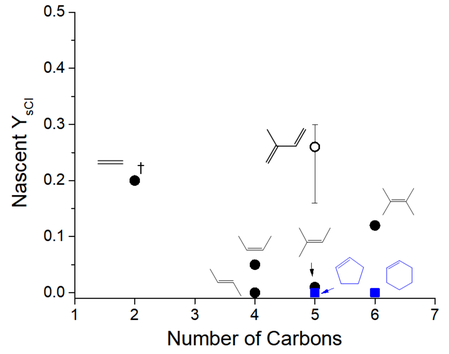
Low pressure yields of sCI produced by ozonolysis of a series of alkenes

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 *trans*-2-butene and 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).
Hatakeyama, S., Kobayashi, H. and Akimoto, H. *The Journal of Physical Chemistry* **88,** 4736 (1984).

Nascent sCI yields from ozonolysis of a series of alkenes



- Formaldehyde oxide has a high nascent yield (data from Hatakeyama et al.) due to its relatively high energy barrier for dissociation with respect to the alkenes studied.
- Endocyclic alkene ozonolysis produced effectively no nascent sCI.
- *cis*-2-butene has a higher nascent total sCI yield than *trans*-2-butene, perhaps due to different syn- and anti-CI branching ratios, or different POZ conformations.
- There is indication that alkenes larger than 2,3-dimethyl-2-butene will have higher nascent sCI yields.

†Hatakeyama, S., Kobayashi, H., Lin, Z. Y., Takagi, H. & Akimoto, H. *The Journal of Physical Chemistry* **90,** 4131–4135 (1986).

Acknowledgements

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