A Steady State Continuous Flow Chamber for the Study of Daytime and Nighttime Chemistry at Atmospherically Relevant NO levels

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Overview

- We present here the development and characterization of the NCAR Atmospheric Simulation Chamber, along with initial results on isoprene oxidation.
- Focus is on use of the chamber in a continuous flow mode, allowing experiments to be conducted under realistic atmospheric daytime and nighttime conditions.
- Box modeling exercises demonstrate the ranges of conditions that can be achieved.
- Yields of MVK + MACR from the OH-initiated oxidation of isoprene over ranges of NOx are presented, and compared to box model results.

Application to Isoprene + OH System

- Experiments conducted over a range of [NOx]. High NOx expts. done in 'batch mode', low NOx expts. in continuous flow mode (as shown below).
- MVK and MACR yields determined as a function of NOx, and compared with recent isoprene mechanism developments. Provides test of recent discoveries regarding RO2 reversible formation, isomerizations, etc.
- Below: Results from a typical OH / isoprene experiment, showing the approach to and achievement of steady-state conditions.

NCAR Atmospheric Simulation Chamber

- 10 m3 FEP Teflon bag housed in an Al enclosure.
- 128 wall-mounted blacklights emitting from 180 to 600 nm.
- Chamber constantly flushed w/ purified dry air at ≈ 40 L min⁻¹ ⇒ chamber residence time of 4.2 hrs.
- Incoming and outgoing flows balanced ⇒ constant chamber P, slightly above ambient.

Standard Operating Conditions

- ‘DAYTIME’ EXPERIMENTS: Lights on, H2O2 and NO inflow, balanced by outgoing flow of chamber air. Run to steady-state.
- ‘Daytime’ box model-derived HOx/NOx/O3 levels for various H2O2 and NO input flow rates are shown below.
- Data not shown, can create 10⁸ – 10⁹ NO3 radicals in SS.

Conclusions and References

- Development and characterization of the NCAR Atmospheric Simulation Chamber, operated in steady-state continuous flow mode, is described.
- Proof-of-principal experiments: MVK and MACR production from OH/isoprene chemistry. Yield determinations are consistent (maybe) with latest isoprene mechanism developments.
- Current and future work ⇒ mechanisms for the following systems: 1) NO3 + isoprene; 2) NO3 + monoterpenes; 3) OH+ pyrogenic VOCs (substituted furans and phenols).

References

2. Leeds MCM, v.3.3.1, http://mcm.leeds.ac.uk/MCM/
3. P. Wennberg et al., Chemical Reviews, DOI: 10.1021/acs.chemrev.7b00439.