Photochemical Experiment Product Yield Study: α-Pinene + OH

It is recommended that the following procedure be carried out by each participating chamber as part of the ICARUS inter-comparison study. The purpose of this study is to compare SOA and individual product yields using vapor/particle wall loss corrections and the photon flux protocol to determine modeled vs. experimental OH (via decay of VOC).

I. Suggested Procedures

- α-Pinene photooxidation experiments will be carried out at ambient temperature (~295 K), atmospheric pressure (~1 atm), and low relative humidity (15% RH). At Caltech, temperature and RH will be monitored with a Vaisala HMM211 probe.
- Experiments will be performed in the presence of $(NH_4)_2SO_4$ seed aerosol, and at an initial NO_x mixing ratio of 15 ppb (injected as pure NO). At Caltech, O_3 and NO_x mixing ratios are quantified by a Horiba APOA-360 O_3 absorption monitor and a Teledyne T200 NO_x monitor, respectively. The detection limits for O_3, NO, and NO_2 are 0.5, 0.4, and 0.4 ppb, respectively.
- Prior to each experiment, the chamber should be flushed with dry, purified air for 24 h such that the particle number and volume concentrations are < 10 cm^{-3} and 0.01 μm^3 cm^{-3}, respectively.
- α-Pinene (≥99%, Sigma-Aldrich) should be injected into the chamber such that the initial mixing ratio is ~100 ppb.
- Polydisperse seed aerosol should be generated via atomization of a dilute (0.06 M) aqueous solution of $(NH_4)_2SO_4$, followed by diffusive drying and neutralization. The target volume concentration and mean particle diameter are ~70 μm^3 cm^{-3} and ~100 nm, respectively.
- H_2O_2 should serve as the source of OH on photolysis under broadband UV irradiation. At the slow H2O2 photolysis rate in the Caltech chamber (350 nm backlights) and the relatively high initial mixing ratios of H2O2, steady-state OH and HO2 concentrations are achieved (Eddingsaas 2012). The initial H_2O_2 mixing ratio should produce steady-state OH and HO_2 concentrations of ~2 x 10^6 and ~1 x 10^{10} molecules cm^{-3}, respectively. At Caltech, this requires an initial H_2O_2 mixing ratio of ~2 ppm
- Experiments should be run for 4-h.

II. Instrumentation

1. Required Instruments

- An instrument to monitor α-pinene mixing ratio, such as PTR-MS, SIFT-MS, GC-FID, GC-ECD, IMS, or similar.
- An instrument to monitor gaseous oxidation products, such as negative ion CIMS (any reagent ion), PTR-MS, SIFT-MS, or similar.

- An instrument to monitor particle size and concentration, such as SMPS, AMS, or similar.

2. Optional Instruments

- An instrument to monitor particle composition, PILS coupled with HPLC, FIGAERO, or similar.

III. Example Calibration and Data Analysis Protocols for Caltech Chamber

1. Gas Phase α-pinene Mixing Ratio using GC-FID

α-Pinene mixing ratios are quantified with an Agilent 6890N gas chromatograph equipped with a flame ionization detector (GC-FID) and operated with an Agilent HP-5 column (30 m × 0.32 mm, 0.25 μm). The GC-FID is calibrated with a commercial α-pinene standard (>99%, Sigma- Aldrich) over a mixing ratio range from 100 to 200 ppb using a gas-tight volumetric syringe and a mass-controlled dilution flow of N_2 into a 100 L Teflon bag.

At Caltech, the GC-FID is also calibrated with ppm-level bags (10-20 ppm) prepared via an analogous method and cross-calibrated using Fourier transform infrared spectroscopy (FT-IR) with tabulated absorption cross sections for α-pinene (Sharpe 2002).

2. SMPS Data Analysis

At Caltech, SMPS data analysis is carried out through data inversion based on finite element analysis of particle trajectories along the TSI 3081A long column DMA, Monte Carlo simulation of particle Brownian motion, and residence time distribution modeling of the TSI 3010 CPC (Mai 2018). Based on instrumental limitations and inversion accuracies, the SMPS used in the Caltech chamber can measure particle size distributions from 20 nm up to 800 nm, which is sufficient to cover the SOA size range in this experiment. Noted that using different DMA transfer functions (Stolzenburg 1988, Russell 1995, Collins 2004, Mamakos 2008, Dubey 2011) and instrumentation setup may result in differences in SOA yield calculations.

As a result of particle growth driven by gas/particle-phase chemistry and gas-particle partitioning, mean geometric diameters typically shift from ~100 nm to ~230 nm after a 4-hr experiment. Aerosol volume concentrations are calculated from particle size distributions assuming homogenous spherical particles. Aerosol mass concentrations are derived assuming an effective density for α-pinene SOA of 1.25 g mL^{-1}.

3. AMS Data Analysis

AMS ionization efficiency is calibrated using dry, 350 nm NH_4NO_3 particles, generated from a dilute (0.01 M) aqueous solution of NH_4NO_3 and size-selected with a DMA. Detection limits for each class of chemical constituents are calculated as three times the

standard deviation of blank signals measured from HEPA filter samples (~30 min) taken before each experiment.

AMS data are analyzed using the SQUIRREL and PIKA modules for Igor Pro, and are corrected for gas-phase interferences (Allan 2005, Aiken 2008) and composition-dependent collection efficiencies (Middlebrook 2012). Elemental O:C and H:C ratios are calculated using the "Improved-Ambient" elemental analysis method for AMS spectra (Canagaratna 2015).

IV. References:

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