



Chamber Study Exploring Aerosol Formation from NO₃ Oxidation of α -pinene and Δ -carene under Different HO₂/RO₂/NO₃ Regimes



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Major Results

Aerosol Yields

- α -pinene products from nitrate radical oxidation tend not to partition into the aerosol (typically < 5 % yields)
- Δ -carene nitrate radical oxidation products have much higher aerosol mass yields (~ 60 %) for all RO₂ regimes.
- The nitrate/organic aerosol mass ratio measured in all the regimes for both α -pinene and Δ -carene is ~ 0.1.
- Organic peroxides (ROOR) were observed with I⁻ CIMS in all three regimes, likely a product of RO₂ + RO₂ reactions.

Background

Why Aerosol?

Aerosols are liquid or solid phase particles suspended in air. As they grow in size, they scatter and absorb light and act as seeds for cloud formation. As a result, they impact climate by reflecting solar radiation back into space, which causes a net cooling effect, although soot causes warming. Thus, it is necessary to understand the mechanisms by which they form to develop accurate climate models. Furthermore, aerosols are known to reduce visibility and have negative effects on health.

How does RO₂ fate affect mass yields in NO₃-initiated SOA chamber experiments at low NO conditions?

The nitrate radical (NO₃) will oxidize monoterpenes to form R^{*}, which subsequently reacts with oxygen gas to form RO₂. In the atmosphere, RO₂ radical will react with either another RO₂, HO₂, NO, NO₂ or NO₃ (Figure 2, Atkinson [1]).

During the summer of 2014, experiments were conducted to explore the effect of RO₂ reaction fate on secondary organic aerosol (SOA) mass yields from α -pinene and Δ -carene in a series of chamber experiments under different HO₂/RO₂/NO₃ regimes.

Methods

The products of 23 experiments (mostly conducted in batch mode, that is no dilution) at the CU Boulder chamber (8000 L Teflon bag), were analyzed with

- NO₃/N₂O₅ Cavity Ringdown Spectrometer (CRDS)
- Aerodyne High-Resolution Aerosol Mass Spectrometer (AMS)
- Scanning Mobility Particle Sizer (SMPS)
- Ultrafine Condensation Particle Counter (UCPC)
- Aerodyne High-Resolution Chemical Ionization Mass Spectrometer using iodide ion chemistry (I⁻ CIMS)
- Chemiluminescence NO_x detector and an ozone monitor.
- GC-FID (Tenax samples)

Several seeded experiments began with aerosolizing a 7.5 mM solution of (NH₄)₂SO₄ and passing it through a drying tube and into the chamber. A known volume of VOC was injected by gently heating a round bottom flask and pushing with nitrogen gas for 10 min. The collection line was then passivated for 20 min. Finally, a Tenax sample was collected for 10 min. at 250 sccm.

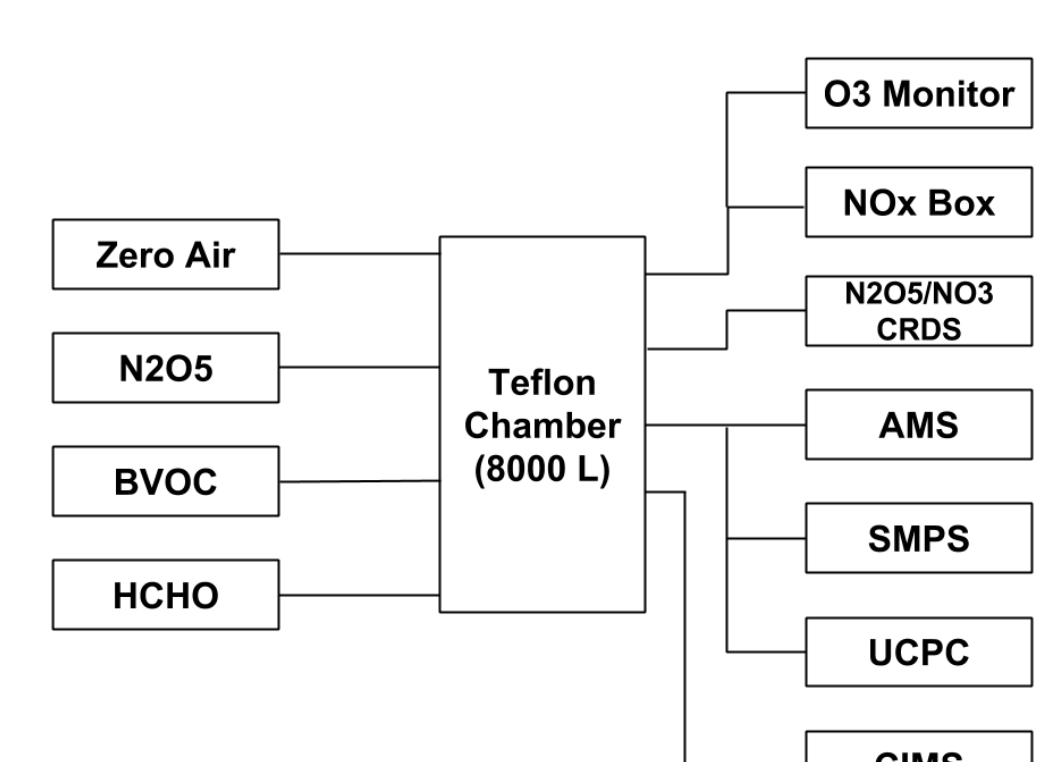


Figure 3. Diagram of chamber with instruments.

Oxidation Methods

NO₃ + RO₂: These experiments would begin with 100 ppb of N₂O₅ injected into the chamber, followed by a 10 ppb VOC injection. Although NO₃ + RO₂ is likely not very important in the atmosphere, it may be important in NO₃-radical initiated chambers studies where high NO₃ concentrations are employed.

RO₂ + RO₂: 10 ppb of N₂O₅ was injected into the chamber, followed by a 100 ppb VOC injection.

HO₂ + RO₂: A constant flow of N₂O₅ was provided to the chamber to keep its concentration at 10 ppb. Then, formaldehyde (50 ppm) was injected into the chamber by heating paraformaldehyde to form HO₂ via reaction with NO₃, which was followed by a 10 ppb injection of VOC. Multiple (4 or 5) Tenax samples were collected for these experiments, but the last measurement was used to calculate yields as the aerosol growth was slow and the last collection was closest to the aerosol peak.

Model

| # | Reaction | Rate Constant (cm ³ molecule ⁻¹ s ⁻¹) |
|----|---|---|
| 1 | NO ₂ + O ₃ -> NO ₃ + O ₂ | 2.97×10 ⁻¹⁷ |
| 2 | NO ₃ + NO ₂ -> N ₂ O ₅ | 1.17×10 ⁻¹² |
| 3 | N ₂ O ₅ -> NO ₃ + NO ₂ (reverse of 2) | 0.0324 |
| 4 | NO + O ₃ -> NO ₂ + O ₃ | 1.86×10 ⁻¹⁴ |
| 5 | NO + NO ₃ -> 2NO ₂ | 2.67×10 ⁻¹¹ |
| 6 | NO ₃ + HCHO -> CO + HO ₂ + HNO ₃ | 5.80×10 ⁻¹⁶ |
| 7 | HO ₂ + HO ₂ -> H ₂ O ₂ + O ₂ | 1.43×10 ⁻¹² |
| 8 | HO ₂ + NO ₃ -> HO + NO ₂ + O ₂ | 3.50×10 ⁻¹² |
| 9 | VOC + NO ₃ -> RO ₂ | 9.10×10 ⁻¹¹ |
| 10 | RO ₂ + NO ₃ -> NO ₃ RO ₂ | 2.0×10 ⁻¹² [6] |
| 11 | RO ₂ + HO ₂ -> HO ₂ RO ₂ | 2.39×10 ⁻¹¹ [7] |
| 12 | RO ₂ + RO ₂ -> RO ₂ RO ₂ | 2.0×10 ⁻¹⁵ [8] |

Table 1. Rate constants from the 17th JPL Data Evaluation (jpldataeval.jpl.nasa.gov) at 0.83 atm and 295 K. Ozone oxidation reactions were not included as the rate constants for those reactions are much slower.

A simple box model was developed to design the experiments and to better understand the kinetics. There is not a consensus on the rate constants for each of the three RO₂ fates (reactions 10, 11, 12) for the nitrate-substituted C₁₀ R groups present in these reactions. The estimated rate constants used for this model are based on the references indicated and are shown in Table 1.

Improving this modeling analysis by conducting sensitivity studies on rate constants is a major area for future work. Currently, the N₂O₅ and NO₃ wall loss constants are 1.5 × 10⁻⁴ and 1.4 × 10⁻³ respectively for exp. 13 and 16. For exp. 11, the fan is on, and so the wall constants are higher; 2.0 × 10⁻² and 2.0 × 10⁻¹ respectively.

Modeling of Oxidant Regimes: Δ -carene oxidation

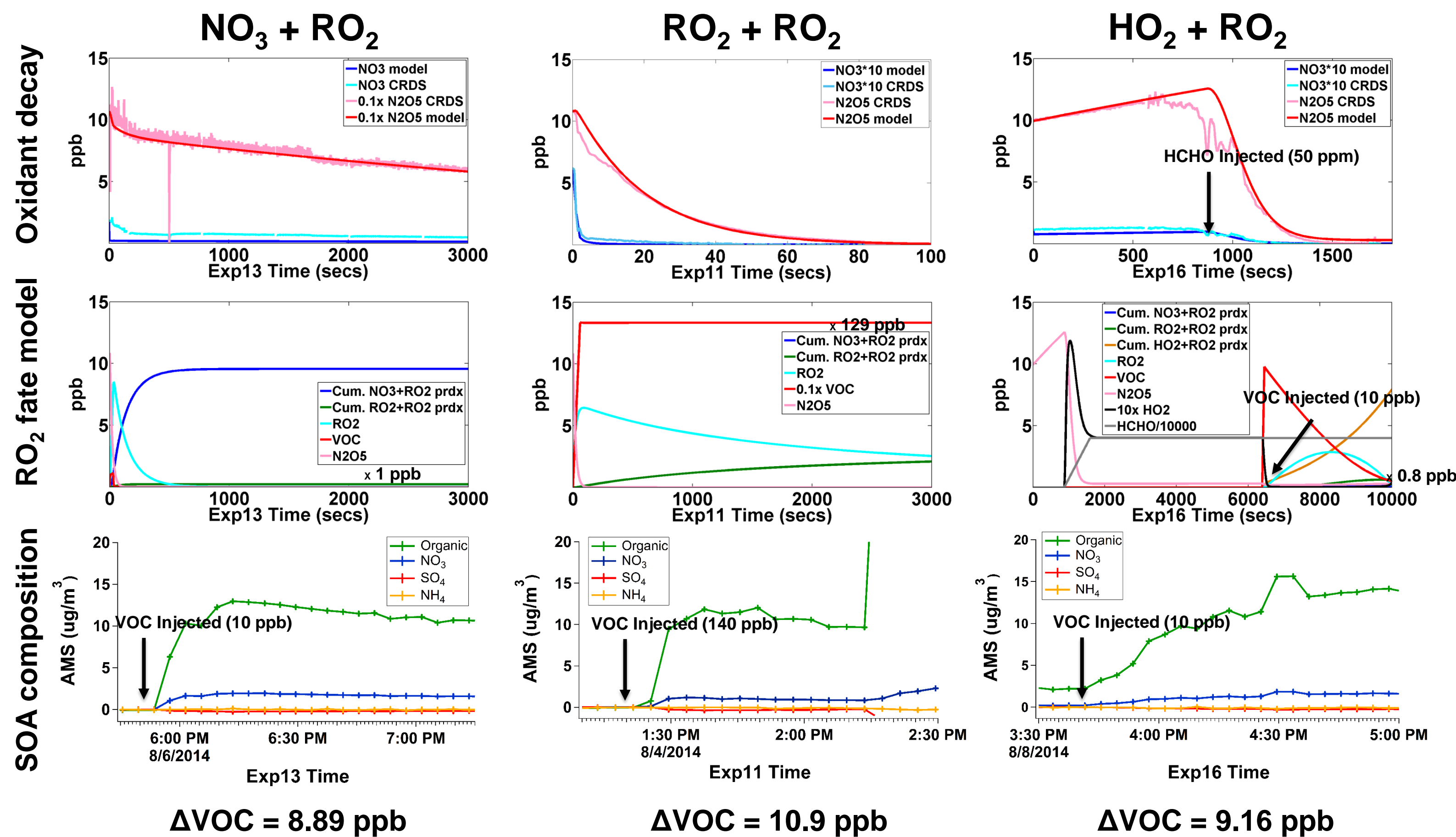


Figure 4. The top row shows comparisons of NO₃/N₂O₅ traces from representative experiments with the model as VOC is injected. The second row are the model predictions of growth for respective reaction pathways, and the Tenax measurements of VOC left in the chamber are indicated. The final row shows the AMS data for the 90 minutes following VOC injection, and the reaction regimes are represented by each of the columns.

The RO₂ fate model of HO₂ + RO₂ (second row) was generated to reflect the entirety of the experiment, not just following VOC injection. It was difficult to achieve constant NO₃/N₂O₅ in the chamber, and as a result the experiment began when it was not quite at equilibrium, to which the model was fit.

As shown in the top row of Figure 4, one of the current issues with the model is that it under-predicts the concentration of nitrate radical. In the AMS data of the RO₂ + RO₂ regime, an additional 900 ppb is injected at the 2:14 mark, resulting in the sudden jump in aerosol. The aerosol mass yields in all three regimes are interestingly all similar, although the HO₂ + RO₂ seems to grow slower than the other two.

CIMS/AMS Observations of Gas/Aerosol Composition

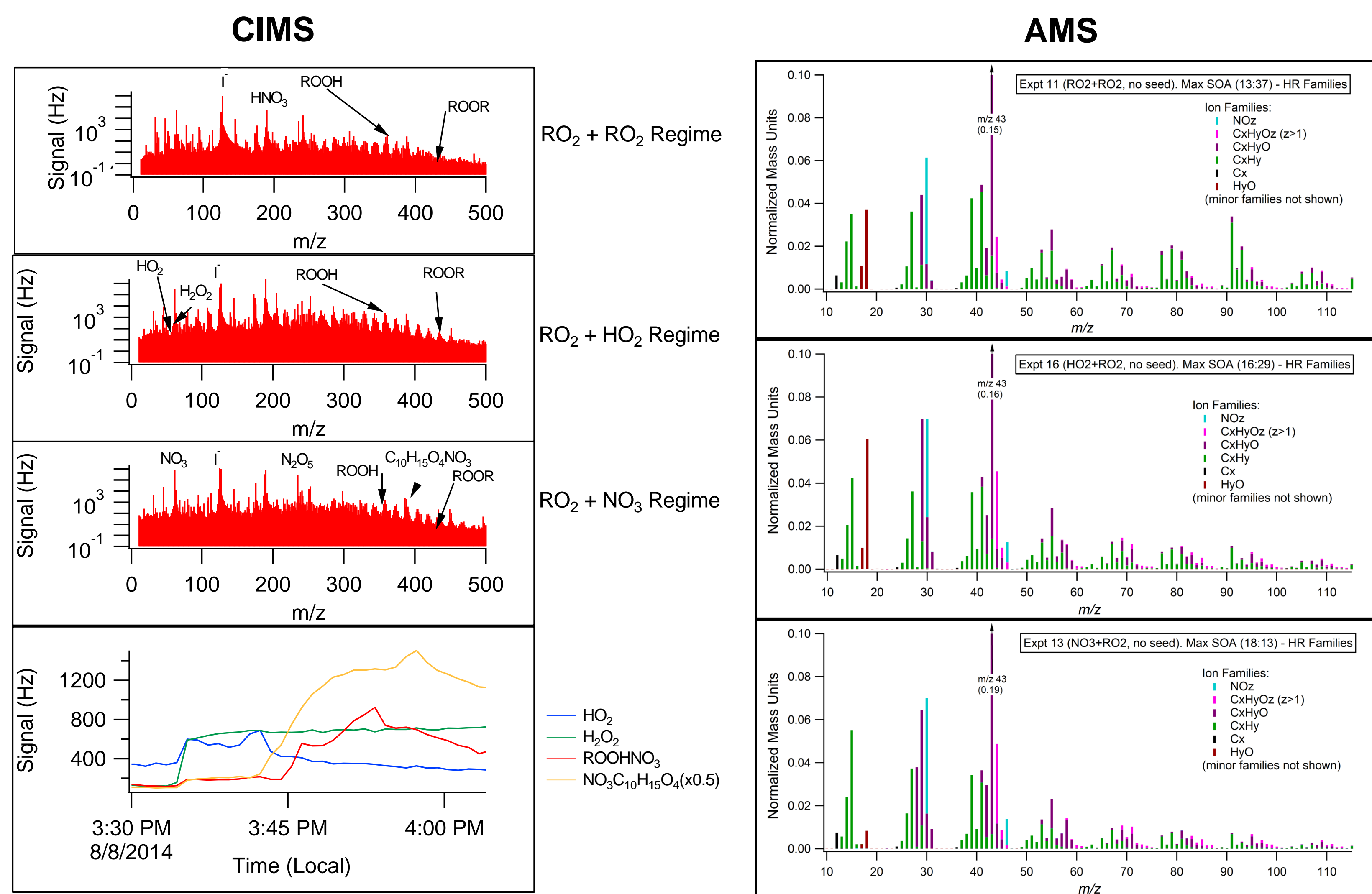


Figure 5. The top 3 figures on the left are I⁻ CIMS spectra from the 3 oxidation regimes. The bottom figure is a timeseries plot for the HO₂ + RO₂ experiment (Δ -carene was injected at 3:40). The figures on the right are the AMS spectra corresponding to each oxidant regime.

As shown in Figure 5, ROOR was detected in all three of the regimes studied. A previous study of RO₂ fate (Kwan et al. 2012, [5]) in the NO₃ + isoprene system found a 3-4% branching ratio for organic peroxide formation; here we might expect even higher branching ratio due to larger the size of the RO₂.

We note a generally greater degree of hydrocarbon oxidation in the AMS spectrum of the NO₃ + RO₂ experiment than the other two regimes. Furthermore, the fragment masses in the RO₂ + RO₂ mass spectrum appear heavier. This is possibly due to some contamination in the Δ -carene, as non-oxidant organic aerosol was observed forming at high concentrations of Δ -carene.

Aerosol Mass Yields and NO₃/Organic Ratios

| Exp. # | Regime | % Yield | Nitrate/Organic Ratio |
|--------|--|---------|-----------------------|
| 4 | RO ₂ + RO ₂ | 0.06 | 0.08 |
| 14 | RO ₂ + RO ₂ + seed | 1.5 | 0.09 |
| 6 | NO ₃ + RO ₂ | 8.1 | 0.09 |
| 8 | HO ₂ + RO ₂ | 0.05 | 0.53 |
| 17 | HO ₂ + RO ₂ | 2.9 | 0.15 |

Table 2. Aerosol yield results from NO₃-initiated α -pinene SOA experiments. These experiments are consistent with the low yields reported by Fry et al [1], Hallquist et al [4], and Spittler et al [3]. The nitrate/organic ratio is the ratio of the mass of the nitrate aerosol and the organic aerosol in μ g/m³ as detected by the AMS. Only one Tenax sample was collected for experiment 8. The high ratio from exp. 8 is likely caused by noise as very little aerosol is formed. Furthermore, experiment 8 data should be erroneous due to the fact that a constant flow of N₂O₅ was not maintained during the experiment. However, yields are comparable to experiment 17 which was carried out under a constant N₂O₅ flow.

| Exp. # | Regime | % Yield | Nitrate/Organic Ratio |
|--------|--|---------|-----------------------|
| 11 | RO ₂ + RO ₂ | 38.4 | 0.10 |
| 12 | RO ₂ + RO ₂ | 75.8 | 0.03 |
| 22 | RO ₂ + RO ₂ | 95.3 | 0.07 |
| 18 | RO ₂ + RO ₂ + seed | 68.5 | 0.05 |
| 13 | NO ₃ + RO ₂ | 69.4 | 0.15 |
| 16 | HO ₂ + RO ₂ | 62.2 | 0.12 |
| 23 | HO ₂ + RO ₂ | 25.6 | 0.15 |
| 19 | HO ₂ + RO ₂ + seed | 47.8 | 0.11 |
| 21 | HO ₂ + RO ₂ + O ₃ + NO ₂ | 15.6 | 0.16 |

Table 3. Aerosol yield results from NO₃-initiated Δ -carene SOA experiments. Experiment 21 attempted to more closely simulate nitrate formation in atmosphere by reacting ozone (30 ppb) with NO₂ (500 ppb) instead of directly injecting N₂O₅.

Analysis

The nitrate/organic ratio for all of the experiments were around 0.1, which suggests that dimerization could be occurring (NO₃: 62 m/z, VOC: 136 m/z, NO₃/(R(NO₃)-OO-(NO₃)R) = 0.098), or more likely that substantial amounts of non-nitrate oxidation products are condensing alongside nitrates. The I⁻ CIMS (Figure 5) suggests both. The formula for aerosol yield is:

$$\% \text{ yield} = \frac{\Delta \text{aerosol mass}}{\Delta \text{VOC mass}} \times 100 \%$$

and so the addition of functional groups to the VOCs allow high yields without having significant portions of the carbon partition to the aerosol.

Preliminary analysis of the seeded vs. unseeded aerosol mass yields does not appear to support a large effect. This suggests that vapor-phase losses of ELVOCs do not compete substantially on the fast timescale of aerosol formation in these experiments.

Future Work

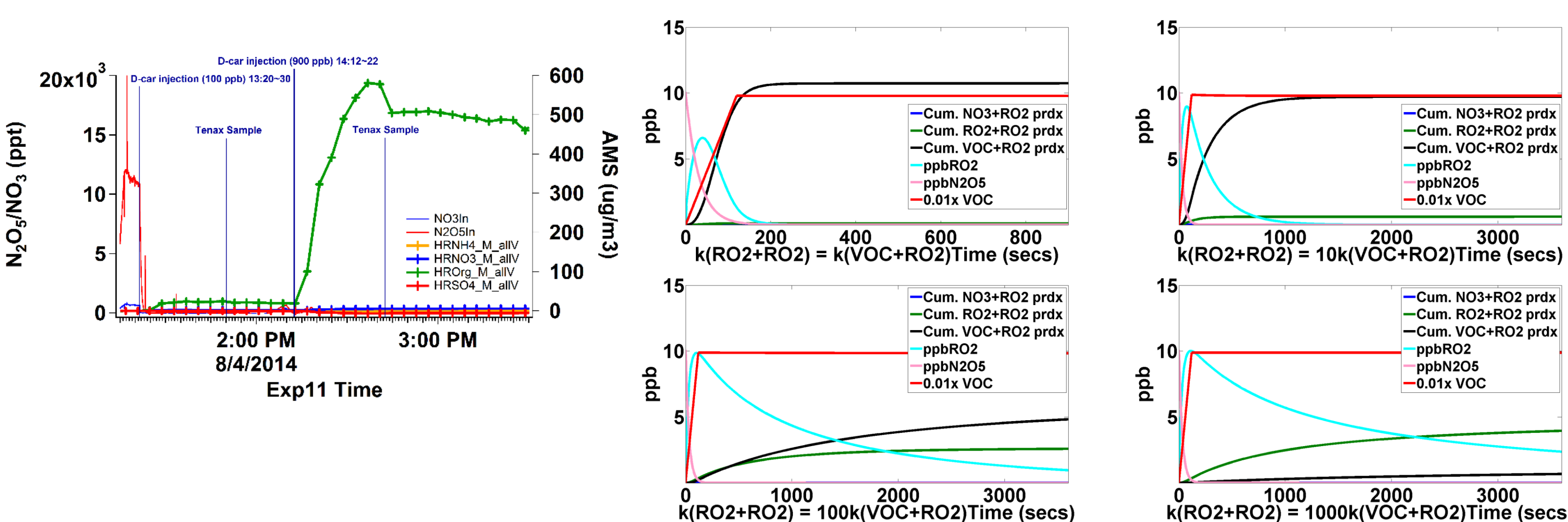


Figure 6. Expansion of experiment 11 with models of VOC + RO₂ reactions at various hypothetical rates. The plot on the left is the AMS data including the 900 ppb injection, and the plots on the right are model simulations for each reaction pathway when the VOC + RO₂ rate constant is at various multiples of the RO₂ + RO₂ (1, 1/10, 1/100, 1/1000 times).

In experiment 11, an additional 900 ppb of Δ -carene was injected at 14:12. In the lack of oxidant, it should have yielded no more aerosol, but it grew, which suggests that Δ -carene was reacting with some oxidant. The model (Figure 4) suggests that there should be no more nitrate, and perhaps it is possible that the RO₂ was reacting with the VOC to partition into the aerosol. We hope to explore this possibility. As the rate constant for this reaction is unknown, we will have to consider hypothetical rate constants (Figure 6) to compare with the results from experiments.

Another consideration to make is the production of OH from reaction 8 (Table 1), which was discussed by Kwan et al [5]. Future improvements will be made on the model to account for this.

References and Acknowledgements

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