Supplemental Material for Fry, Draper, Barsanti, Smith, Ortega, Winkler, Lawler, Brown, Edwards, Cohen, and Lee, “Secondary organic aerosol formation and organic nitrate yield from NO_3 oxidation of biogenic hydrocarbons.”

Contains 8 figures and 2 tables, on 10 pages.

Supplemental Material

NCAR Chamber Facility description

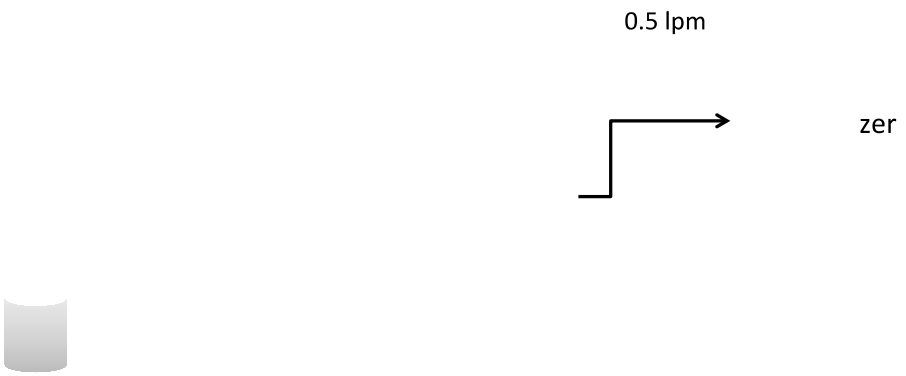


Figure S1. Schematic of the NCAR environmental chamber facility. Alternating inlet and outlet NO_3 and N_2O_5 measurements are made using two 3-way valves (grey circles). Full instrument names corresponding to acronyms used here are in Table S1.

The NCAR chamber consists of a 10 m^3 bag made of 0.005 inch thick fluorinated ethylene propylene (FEP) Teflon film suspended in a cubic enclosure. All gaps were sealed to eliminate any light penetration, thus avoiding possible photochemical reactions. Prior to each experiment, the chamber was cleaned using a pulse of ppm-level ozone (20 ppm for ~ 5 minutes) from an electrical discharge ozone generator (Welsbach, Inc.), using pure oxygen to avoid the generation of NO_x, followed by 20-30 hours of purified air at a flow of 40 lpm from a zero air generator (Model 737, Aadco Instruments) through HEPA filters (Pall Life Sciences model 12144). The chamber was considered clean after ozone levels had dropped to below 1 ppb, and total particle concentrations were below 10 cm^{-3}. Relative humidity was consistently below 5%. Ammonium sulfate seed aerosol was added during one experiment, generated from a 0.1 g/L aqueous solution of ammonium sulfate using an atomizer followed by a diffusion drier, resulting in polydisperse dry ammonium sulfate seed with mode diameter of 40 nm. All flows into and out of the chamber were through 22.2 mm inner diameter stainless steel tubes, which penetrated the chamber through compression fittings. For these experiments, the chamber was run in flow-through mode with a total input flow rate of 40 lpm zero air with slight positive pressure (1-2 mm H_2O). Gas-phase and aerosol-phase measurements were extracted from the chamber on the wall opposite to the zero air and reactant inputs.

Each experiment was initiated by filling the chamber with the NO_3 + N_2O_5 oxidant at the desired concentration (nominally either 10 ppb or 50 ppb). An N_2O_5 trap source was used in these experiments in order to provide a source of pure NO_3 oxidant with no O_3. A calibrated concentration was provided by flowing approximately 20-200 mL min^{-1} of

zero air through a trap containing N_2O_5 crystals, submerged in an isopropyl alcohol and dry ice bath held at a temperature of -65 to -60°C. The temperature settings depended upon daily trap condition, so before each experiment, flows and temperatures were tuned to achieve the desired N_2O_5 concentration as measured by cavity ringdown spectroscopy (CRDS) and then kept constant for the remainder of that experiment. After N_2O_5 concentrations had reached steady state in the chamber, BVOC was introduced to the inlet flow. In all cases except *β*-caryophyllene, the BVOC was introduced using a constant flow of a quantified ppm-level gas standard (balance N_2) that was subsequently diluted by the 40 liters per minute zero air flow to obtain the desired final chamber concentrations of ~20-60 ppb. Cylinder concentrations were verified using a cryo-focused GC-FID system calibrated against a NIST-certified butane/benzene gas standard. In the case of *β*-caryophyllene, a small flow (4-18 mL/min) of zero air was fed through a heated trap held at 30-77°C containing the liquid hydrocarbon into the chamber input zero air flow. In this case, the *β*-caryophyllene concentration was verified by sampling 200 mL of the BVOC + air mixture onto a two stage adsorbent cartridge (filled with Tenax T and Carbograph B) and analyzed by thermo-desorption GC-MS-FID.

Table S1. Instruments used in chamber experiments.

Instrument	**Measurement**	**Flow rate (sampling on INlet or OUTlet flow)**	**Time resolution**
Thermo Scientific chemiluminescence NO_x Analyzer (Model 17i)	NO and NO_2	0.6 lpm (OUT)	1 s
2-channel cavity ringdown spectroscopy (CRDS)	NO_3 and N_2O_5	20-200 mL/min, 0.5 lpm (IN, OUT)	1 s
Ozone monitor (Thermo scientific model 49)	O_3	1 lpm (OUT)	1 s
Scanning Mobility Particle Sizer (SMPS)	Particle size distribution (10-350 nm)	0.5 lpm (OUT)	4 min
Thermal Dissociation / Laser Induced Fluorescence	$\Sigma ANs+PNs_{(gas)}$ and $\Sigma ANs+PNs_{(aero)}$	0.5 lpm (OUT)	1 s

Wall loss analysis

The total chamber flow (Q) was 40 liters per minute (or 0.667 L s^{-1}), and the total volume (V) was 10,000 L. The resulting β is plotted against particle diameter (d_p).

These wall loss rates were used to correct all SMPS data collected during chamber experiments. Size-dependent rates were applied to each raw size distribution to determine the number of particles lost to the walls at each time step. It was assumed that particles were lost to the walls irreversibly and no longer able to act as a gas-condensation reservoir. Thus, to get accurate gross mass yields, these losses were cumulatively added back to the size distributions.

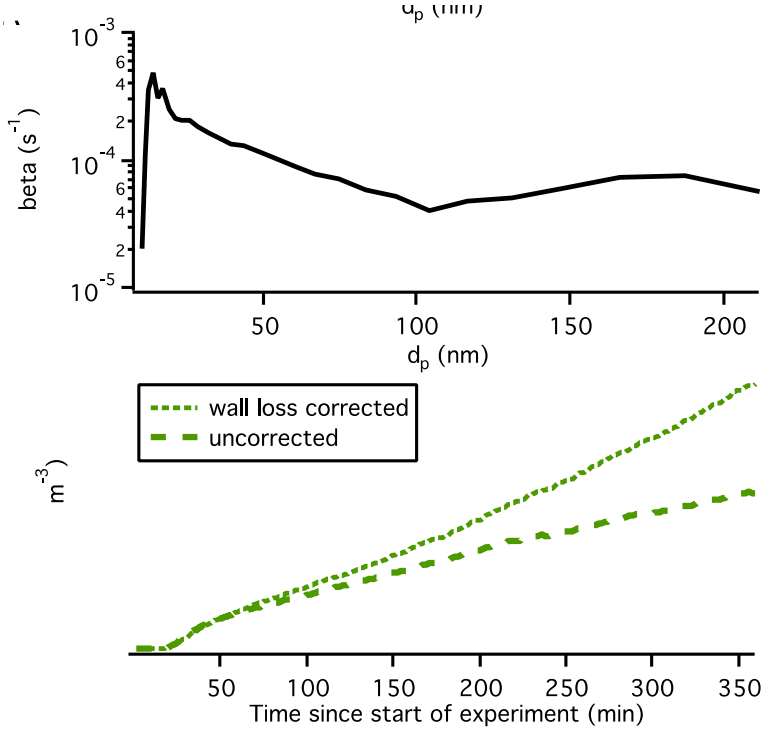


Figure S2. Wall loss characterization for the NCAR chamber. (a) Aerosol number size distribution entering (red) and exiting (blue) the chamber at steady state with total flow of 40 lpm, as used in SOA experiments. (b) Calculated values of $\beta(d_p)$ based on the size distributions shown in 3a and using Eqn. 1. (c) Uncorrected (long dash) and corrected (dotted) mass concentration for the low-concentration β-pinene experiment (Experiment 2), to show magnitude of wall-loss correction.

Determination of Δ*VOC*: method 1: NO_3 observation constrained

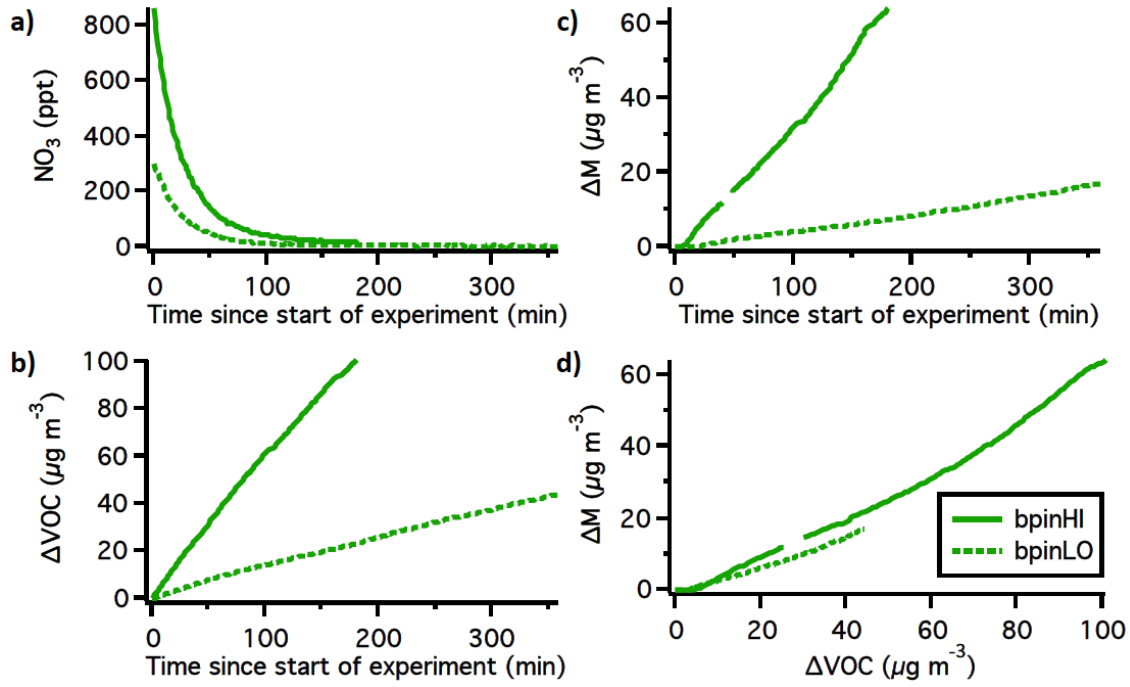


Figure S3. Derivation of cumulative *β*-pinene Δ*VOC* time series for Experiments 2 & 3 (panel b) from NO_3 decay (panel a) and known BVOC addition rate, for the high (solid) and low (dotted) concentration experiments. This is then compared with aerosol mass loading timeseries (Δ*M*) (panel c), to determine how aerosol mass formed responds to reacted VOC (panel d), from which yields are calculated. Panel d shows the different Δ*VOC* ranges over which the "high" and "low" concentration experiments are run.

Determination of Δ*VOC*: method 2: Model constrained

For this determination of ΔVOC, the model (see equation 3 in the main text for general structure) is initiated with an empty chamber. N_2O_5 is added for 24 hours to achieve steady-state concentrations matching the initial [N_2O_5] and [NO_3] observed for each experiment, using wall loss rate constants that were optimized for the set of all experiments. At hour 24, we begin adding BVOC to the chamber at the rate known from experiment conditions, with continuing addition of N_2O_5 at the same rate as previously. The reactions included are shown below, with a table of rate constants. The model is run at 295 K and 0.8 atm (Boulder, CO).

The greatest uncertainty is in the RO_2 rate constants, for which we followed Ziemann and Atkinson [1] in combination with this useful structure-function relationship page on the MCM: http://mcm.leeds.ac.uk/MCM/categories/saunders-2003-4_6_5-gen-master.htt?rxnId=12891 We assume our RO_2 radical to all be tertiary, with an enhancement of 2 orders of magnitude due to the beta-NO_3 functional group, which we assume to have the same effect as a beta-hydroxy substitution. We further assume that no HO_2 will be generated in this system (via NO_3+RO_2 reactions), because the RO2 are all tertiary.

Based on our reading of these sources, there appear to be at least 2 orders of magnitude uncertainty in RO_2+RO_2 rate constants, and at least one in NO_3+RO_2.

1.	VOC + NO_3 → RO_2	k_1
2.	RO_2 + NO_3 → products	k_2
3.	RO_2 + RO_2 → products	k_3
4.	RO_2 + NO_2 → RO_2NO_2	k_4
5.	RO_2NO_2 → RO_2 + NO_2	k_5
6.	NO_3 + NO_2 → N_2O_5	k_6
7.	N_2O_5 → NO_3 + NO_2	k_7
8.	N_2O_5 → walls	k_8
9.	NO_3 → walls	k_9

Figure S4: Kinetics box model mechanism.

Table S2: Rate constants used in the above model.

Parameter	Value	Source
k_1	*α*-pinene : 6.4×10^{-12} cm^3 $molec^{-1}$ s^{-1} *β*-pinene : 2.5×10^{-12} cm^3 $molec^{-1}$ s^{-1} Δ-carene: 9.1×10^{-12} cm^3 $molec^{-1}$ s^{-1} limonene : 1.2×10^{-11} cm^3 $molec^{-1}$ s^{-1} *β*-caryophyllene : 1.9×10^{-11} cm^3 $molec^{-1}$ s^{-1} sabinene : 1.0×10^{-11} cm^3 $molec^{-1}$ s^{-1}	Calvert, 2000 [2]
k_2	2×10^{-12} cm^3 $molec^{-1}$ s^{-1}	Vaughan, 2006 [3]
k_3	2×10^{-15} cm^3 $molec^{-1}$ s^{-1}	Ziemann & Atkinson [1] assuming 100-fold enhancement from beta-NO_3

k_4	7.4×10^{-12} cm^3 molec^{-1} s^{-1}	JPL kinetics eval. 2011
k_5	3.3 s^{-1}	JPL kinetics eval. 2011
k_6	1.2×10^{-12} cm^3 molec^{-1} s^{-1}	JPL kinetics eval. 2011
k_7	3.2×10^{-2} s^{-1}	JPL kinetics eval. 2011
k_8	0 s^{-1}	fit to all model spin-ups
k_9	1.5×10^{-3} s^{-1}	fit to all model spin-ups

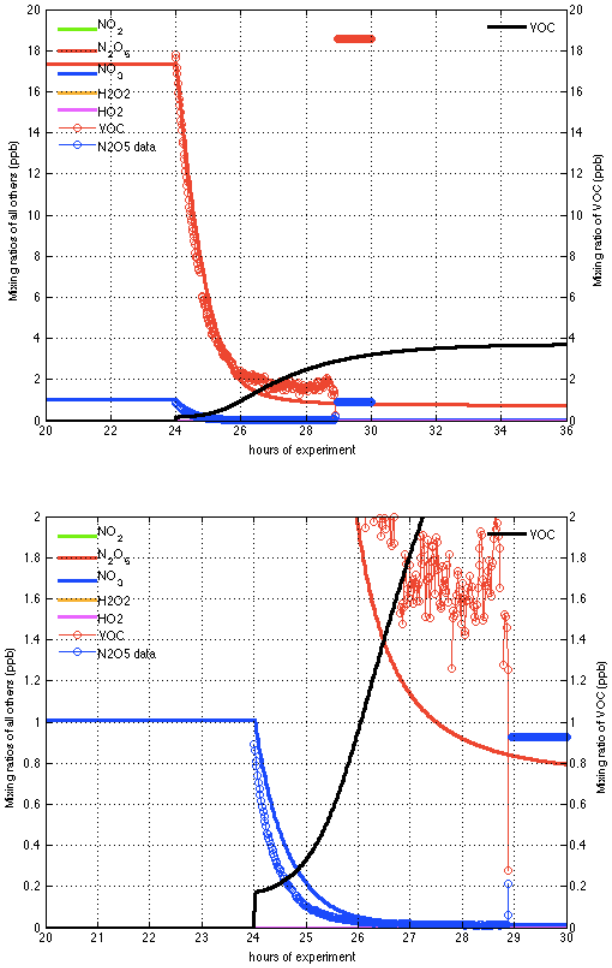


Figure S5: Exemplary model run for β-pinene high concentration experiment N2O5 data in red markers, model in red line; NO_3 data in blue markers, model in blue line, and VOC model in black line. There is no HO_2 or H_2O_2 in these experiments. Lower panel is a zoom-in on upper panel, showing discrepancies in decay timescale of NO_3/N_2O_5. As NO_3 decays, VOC is predicted to build up in the chamber. The cumulative VOC lost to reaction with NO3 in this model is used as the ΔVOC timeseries.

Molecular structural effects on alkoxy radical fate

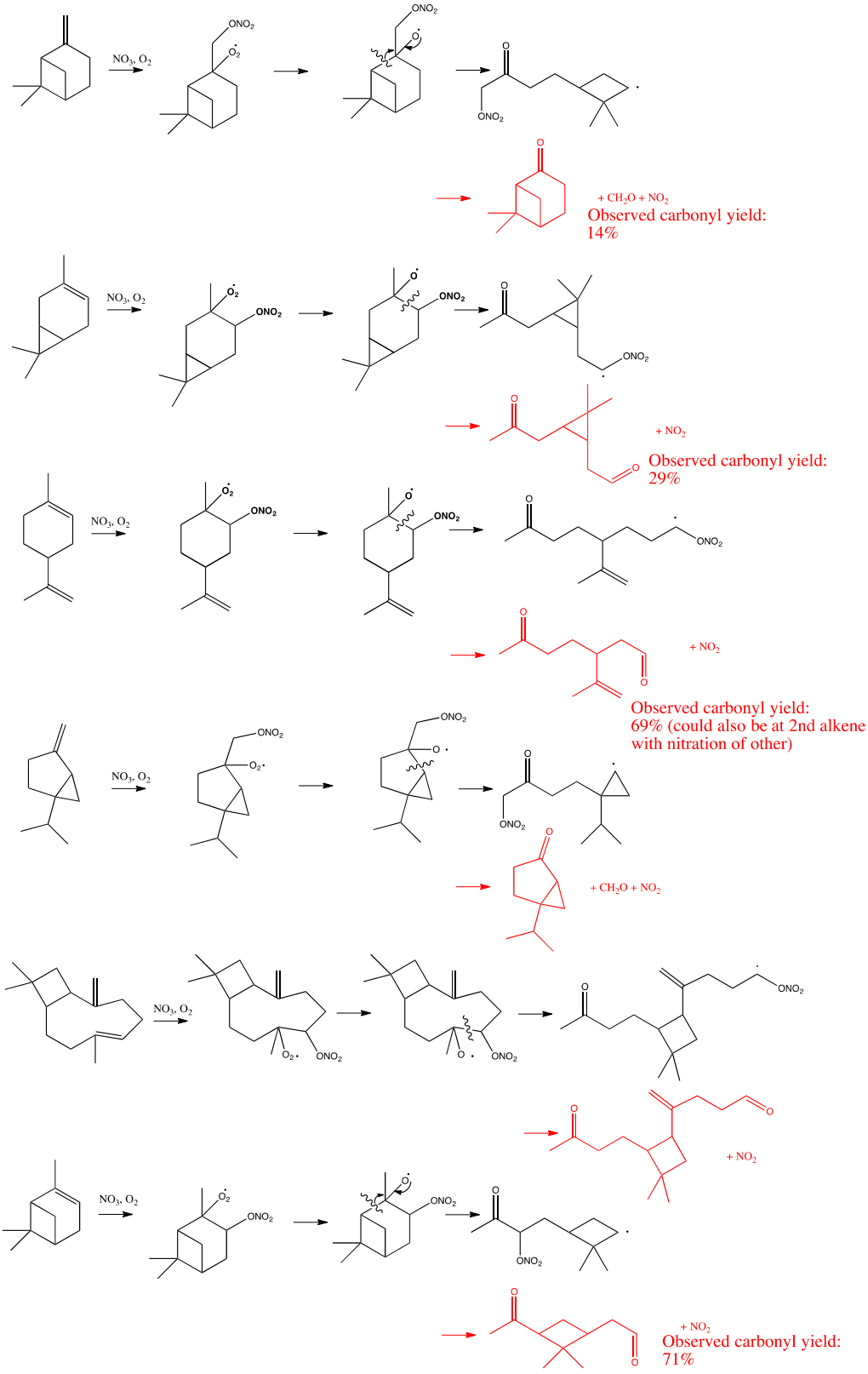


Figure S6. Proposed initial steps of nitrate oxidation of (from top to bottom) β-pinene, Δ-carene, limonene, sabinene, β-caryophyllene and α-pinene. Shown in black are the predicted nitrato-carbonyl products based on Vereecken and Peeters [4]; in red are the alternate NO_2-shedding dicarbonyl products, with yields reported by Hallquist et al. [5] Note that the carbonyl is not necessarily mutually exclusive with organonitrate formation, especially in the limonene case with two double bonds.

Organonitrate production

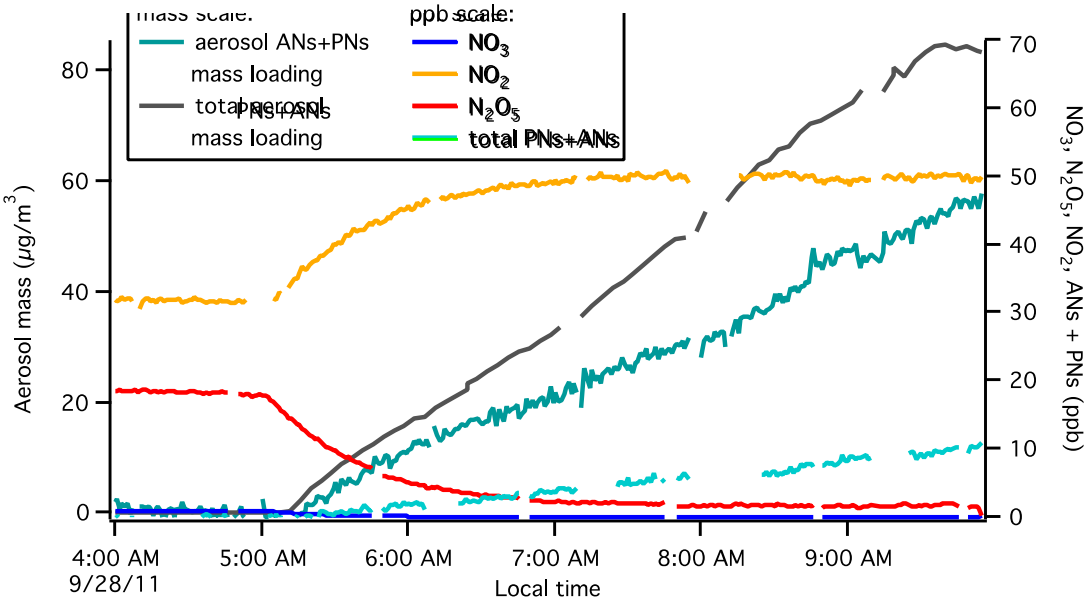
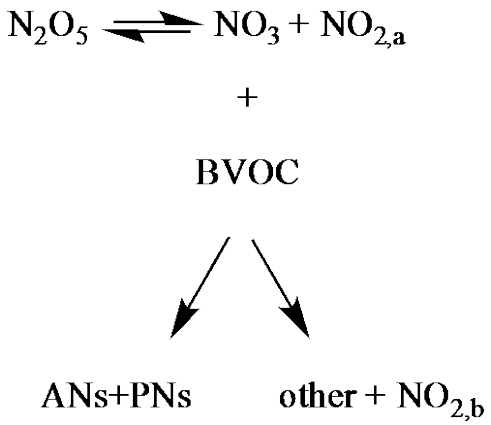


Figure S7. Top: Full time series of organonitrate measurements for β-pinene high concentration experiment (#2), in which BVOC was added at 5:20. Bottom: fraction of total aerosol mass that is organonitrate, assuming a mono-nitrate with MW ~ 230 g/mol.

Figure S8. Schematic of nitrogen balance, to aid interpretation of Table 3 in the manuscript text.



As reactions proceed, N flows from N_2O_5 to products:

$$-\Delta[N_2O_5] = \Delta[NO_2]_a + \Delta[ANs+PNs] + \Delta[NO_2]_b$$

And the sum of molar NO_2 and ANs+PNs production should equal 2, since each N_2O_5 precursor contains 2 equivalents N:

$$\frac{\Delta[ANs + PNs]}{-\Delta[N_2O_5]} + \frac{\Delta[NO_2]}{-\Delta[N_2O_5]} = 2$$

References:

1. Ziemann, P. J.; Atkinson, R., Kinetics, products, and mechanisms of secondary organic aerosol formation. *Chemical Society Reviews* **2012,** *41* (19), 6582-6605.
2. Calvert, J. G.; Atkinson, J. A.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G., *Mechanisms of the atmospheric oxidation of the alkenes*. Oxford University Press: New York, NY, 2000.
3. Vaughan, S.; Canosa-Mas, C. E.; Pfrang, C.; Shallcross, D. E.; Watson, L.; Wayne, R. P., Kinetic studies of reactions of the nitrate radical (NO3) with peroxy radicals (RO2): an indirect source of OH at night? *Physical Chemistry Chemical Physics* **2006,** *8* (32), 3749-3760.
4. Vereecken, L.; Peeters, J., Decomposition of substituted alkoxy radicals-part I: a generalized structure-activity relationship for reaction barrier heights. *Physical Chemistry Chemical Physics* **2009,** *11* (40), 9062-9074.
5. Hallquist, M.; Wangberg, I.; Ljungstrom, E.; Barnes, I.; Becker, K. H., Aerosol and product yields from NO3 radical-initiated oxidation of selected monoterpenes. *Environ. Sci. Technol.* **1999,** *33* (4), 553-559.