Supplement of Atmos. Chem. Phys., 22, 1467–1482, 2022
https://doi.org/10.5194/acp-22-1467-2022-supplement

Supplement of

Secondary organic aerosol and organic nitrogen yields from the nitrate radical (NO_3) oxidation of alpha-pinene from various RO_2 fates

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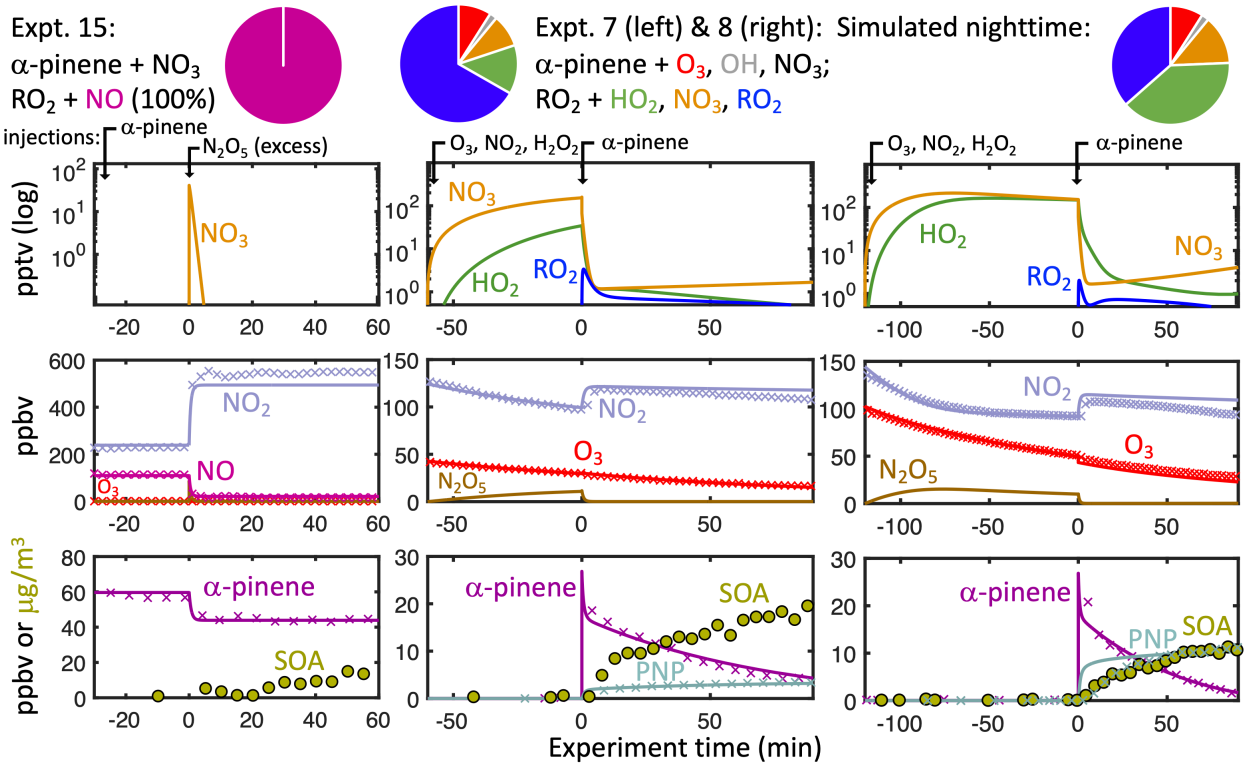

Figure S1. Modelled (solid lines) and measured (points) concentrations of key reactive species and products in three example chamber experiments. Timings of chamber injections are demarcated at top. Experiment time of 0 corresponds to the beginning of α-pinene oxidation. Pie charts show the percent contribution of each α-pinene oxidative pathway (α-pinene + O_3 in red, α-pinene + OH in grey and α-pinene + NO_3 speciated by subsequent RO_2 reaction partner: pink for NO, orange for NO_3, blue for RO_2, green for HO_2).

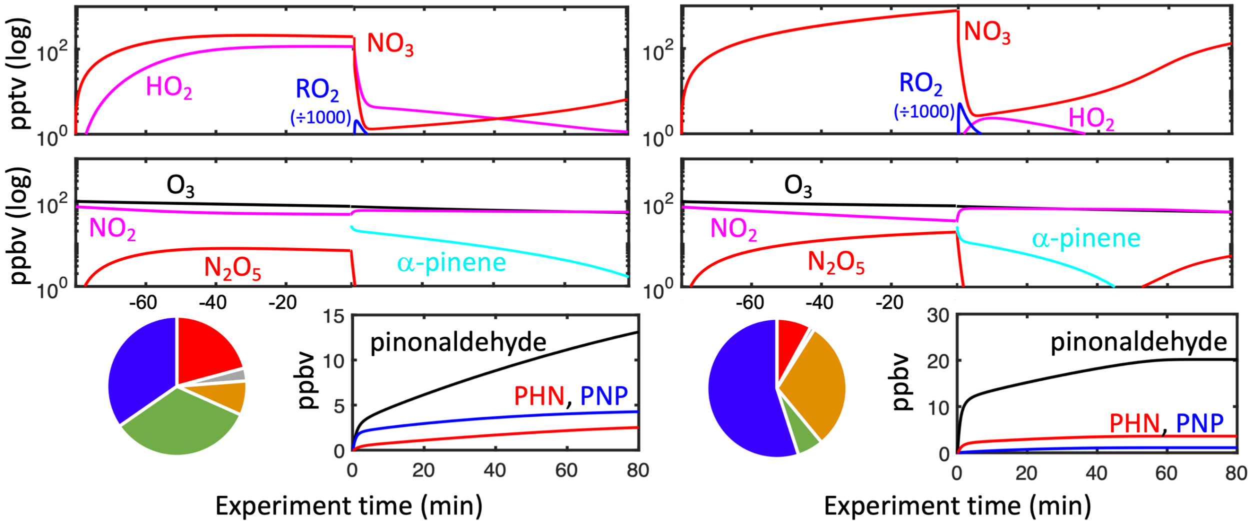

Figure S2. Modeled concentrations of key reactive species (top) and contributions of reactive pathways (bottom) in an example 'simulated nighttime' experiment with (left) and without (right) inclusion of the $NO_3 + H_2O_2$ reaction to produce HO_2. Experiment time of 0 corresponds to the a-pinene injection and beginning of its oxidation. Pie charts show the percent contribution of each α-pinene oxidative pathway (α -pinene+O_3 in red, α -pinene+OH in grey and α -pinene+NO_3 speciated by subsequent RO_2 reaction partner: orange for NO_3, blue for RO_2, green for HO_2).Without the $NO_3 + H_2O_2$ reaction, the *n*RO_2 + HO_2 pathway only contributes 6% of the total α-pinene fate, which is incompatible with our high (~22%) measured yields of PNP. In our kinetic model, we use a rate constant of $k_{NO3+H2O2} = 1.1\times10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}, estimated from ($k_{NO3+CH2O}$ / $k_{OH+CH2O}$) × $k_{OH+H2O2}$. This is well below the upper limit of 2×10^{-15} cm^3 $molecule^{-1}$ s^{-1} estimated by Burrows, Tyndall, & Moortgat.[1]

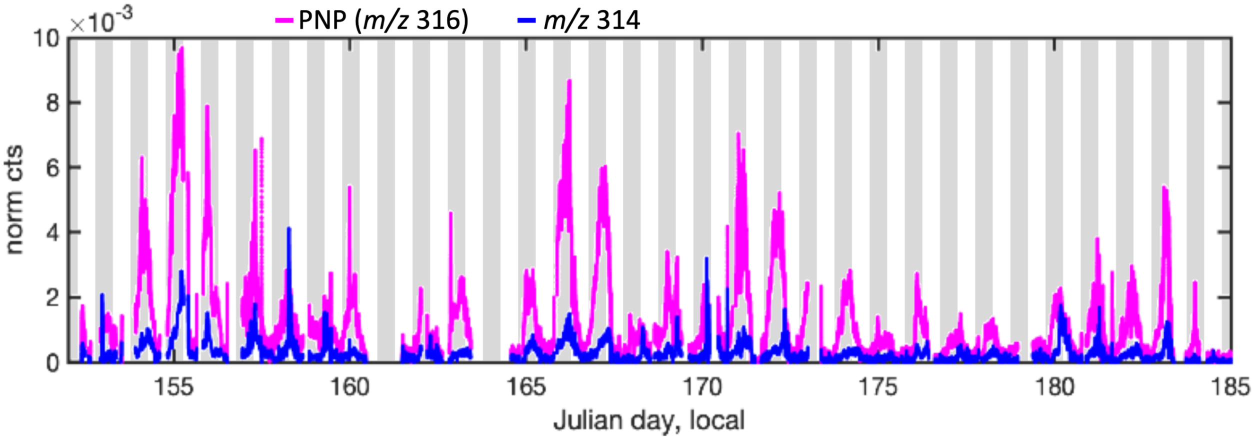

Figure S3. Select gas-phase organonitrates observed by CF_3O^- CIMS during the Southern Oxidant and Aerosol Study (SOAS), including PNP (*m/z* 316) and an unknown compound at *m/z* 314. Both compounds were had similar diurnal cycles at SOAS (peaking at night), and were also observed during 'simulated nighttime' experiments in this work (**Fig. 4**)

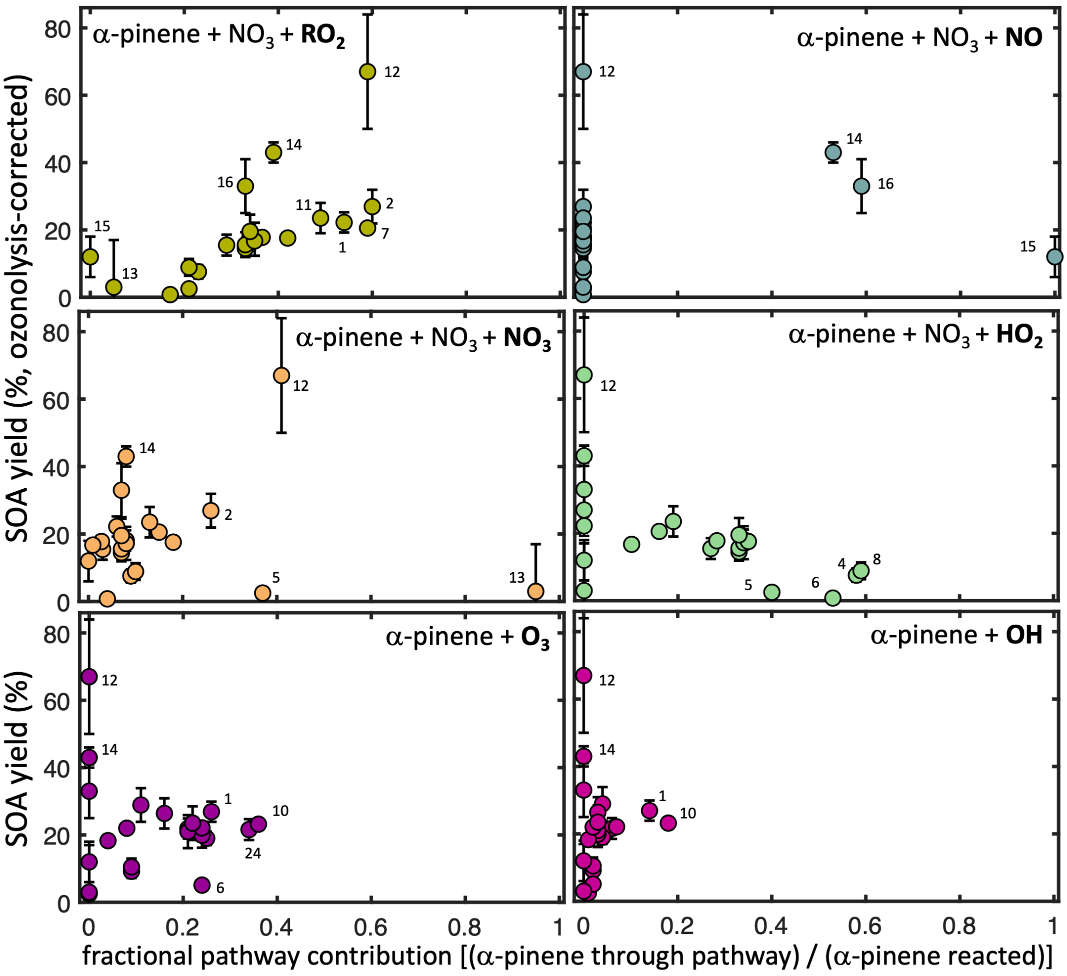

Figure S4. Measured SOA yields from chamber experiments plotted against modeled contributions of each reactive pathway. Select points are labeled with their experiment numbers from **Tables 1 & 2**. Error bars denote uncertainty from SMPS measurements.

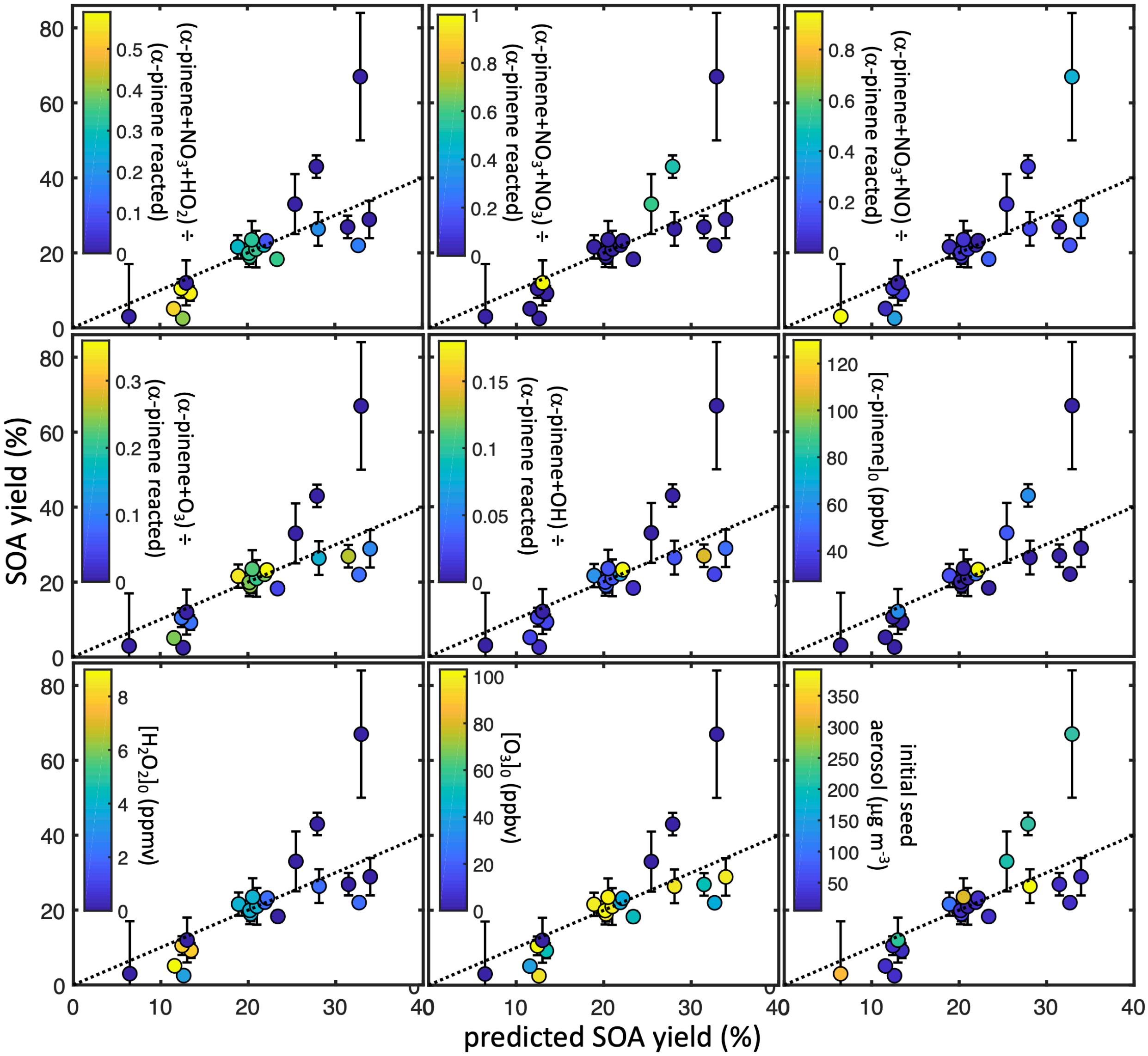

Figure S5. Measured (non-ozonolysis-corrected) SOA mass yields from each experiment as a function of the predicted SOA yield from the sum of each pathway contribution, with points colored by various experimental or modelled parameters. Error bars denote uncertainty from SMPS measurements.

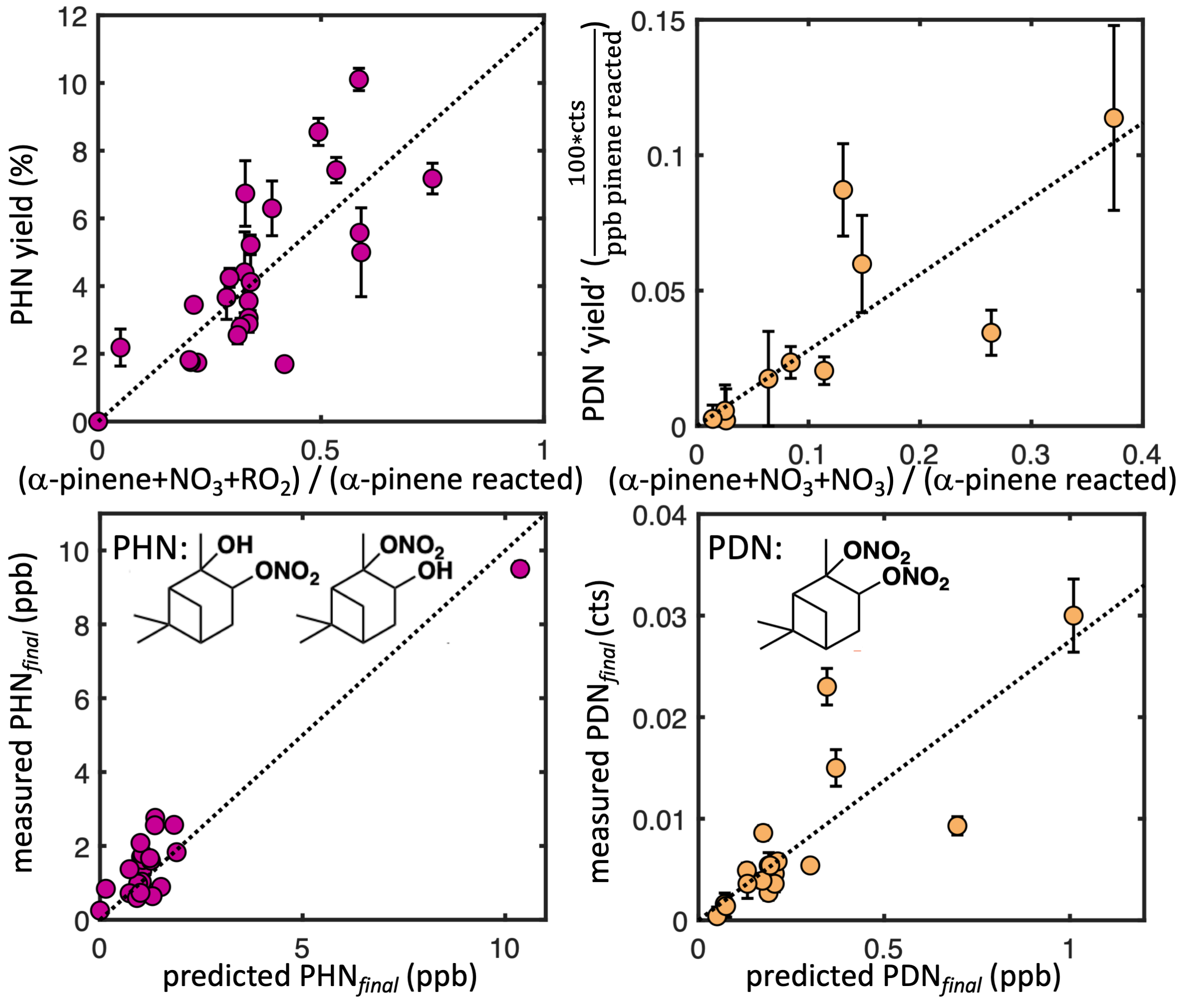

Figure S6. Measured yields of α-pinene hydroxynitrate (PHN, left, a product of RO_2 + RO_2 chemistry) and α-pinene dinitrate (PDN, right, a product of RO_2 + NO and/or RO_2 + NO_3 chemistry) as a function of the modeled contribution of their formation pathway (top) and plotted against the yields predicted by the simple kinetic model. For PDN, the CIMS cannot be properly calibrated due to a lack of standards or calibrant analogs, so the measurement values are reported as normalized CIMS counts. Dotted lines denote ordinary least squares regressions, constrained to pass through the origin, with R^2 of (clockwise from top left) 0.58, 0.66, 0.67, and 0.91.

Table S1 provides additional details on the ozonolysis control experiments performed individually for each simulated nighttime experiment described in the main text. Control experiments were initialized with the same $[H_2O_2]_0$ and seed aerosol loadings as in the main experiments (as listed in **Tables 1 & 2**), but with lower $[O_3]_0$ designed to approximately match the $[O_3]_0$ value at the time when pinene was injected in the main experiment (at which point it had diminished from the value listed in **Table 1** due to reactions with the other inorganic reactants present). Reported SOA mass yields in **Table S1** are averages over the course of the experiment. In preparing the "ozonolysis-adjusted" SOA mass yields in **Table 2**, we subtracted instantaneous SOA yields from each time point in the ozonolysis control experiment from the corresponding time point in the main experiment (weighted by the modeled ozonolysis contribution to the overall α-pinene reactivity).

Table S1. Initial conditions and SOA yields for ozonolysis control experiments

Expt # (**Tab. 1 & 2**)	α-pinene (ppb)	H_2O_2 (ppm)	O_3 (ppb)	seed mass (μg/m^3)	SOA mass yield (%)	Ozonolysis contribution to main expt (%, modelled)	SOA mass yield to subtract from main expt (%)
1	27	0	50	23.4	20.4	27	5.5
2	27	0	88	23.2	18.3	11	2.0
3	27	4	35	23.8	20.8	5	1.0
4	27	8	35	23.7	19.3	9	1.7
5	27	3.5	41	23.5	4.8	1	0.05
6	27	9	27	25.3	24.7	24	5.9
7	27	2	30	24.2	21.3	8	1.7
8	27	8	55	27.7	17.7	9	1.6
9	54	2	34	24.8	11.9	24	2.9
10	130	2	32	27.3	12.4	36	4.5
11	27	2	116	253	18.3	13	2.4
17	27	4	87	0	18.0	21	3.8
18	27	4	78	2.5	20.4	22	4.5
19	27	4	79	2.5	19.1	21	4.0
20	27	4	82	5.3	21.1	20	4.2
21	27	4	82	10.8	21.4	20	4.3
22	27	4	86	24.3	22.9	23	5.3
23	27	4	80	57.2	21.4	23	4.9
24	42	4	79	101	16.7	34	5.7
25	27	4	105	245	17.1	21	3.6

Table S2. Masses of proposed α-pinene RO$_2$ dimers as observed in HRMS analysis of SOA from filters collected during experiments 26 (*n*RO$_2$ + *n*RO$_2$) and 27 (simulated nighttime).[a]

Positive[b]		*n*RO$_2$ α $C_{10}H_{16}NO_5$	*n*RO$_2$ β $C_{10}H_{16}NO_6$	*n*RO$_2$ χ $C_{10}H_{16}NO_7$	*n*RO$_2$ δ $C_7H_{10}NO_7$	*n*RO$_2$ ε $C_{10}H_{15}N_2O_{10}$	$_{OH}$RO$_2$ 1 $C_{10}H_{17}O_5$	$_{OH}$RO$_2$ 2 $C_{10}H_{17}O_7$	$_{O3}$RO$_2$ i $C_{10}H_{15}O_4$	$_{O3}$RO$_2$ ii $C_{10}H_{15}O_6$	$_{O3}$RO$_2$ iii $C_{10}H_{15}O_8$
*n*RO$_2$ α	$C_{10}H_{16}NO_5$	*357.204[c]	*467.200	*483.195	*441.148	*544.175	438.210	*470.200	420.199	452.189	484.179
*n*RO$_2$ β	$C_{10}H_{16}NO_6$	*467.200	*483.195	*499.190	*457.143	*560.170	*454.205	*486.195	436.194	*468.184	*500.174
*n*RO$_2$ χ	$C_{10}H_{16}NO_7$	*483.195	*499.190	*515.185	473.138	576.165	*470.200	502.190	452.189	484.179	516.169
*n*RO$_2$ δ	$C_7H_{10}NO_7$	*441.148	*457.143	473.138	431.091	534.118	428.153	460.143	410.142	442.132	474.122
*n*RO$_2$ ε [d]	$C_{10}H_{15}N_2O_{10}$	*544.175	*560.170	576.165	534.118	637.145	531.180	563.170	513.169	545.159	577.149

Negative[e]		*n*RO$_2$ α $C_{10}H_{16}NO_5$	*n*RO$_2$ β $C_{10}H_{16}NO_6$	*n*RO$_2$ χ $C_{10}H_{16}NO_7$	*n*RO$_2$ δ $C_7H_{10}NO_7$	*n*RO$_2$ ε $C_{10}H_{15}N_2O_{10}$	$_{OH}$RO$_2$ 1x [f] $C_{10}H_{18}NO_9$
*n*RO$_2$ α	$C_{10}H_{16}NO_5$	*490.204	*506.199	*522.194	*480.147	*583.174	*556.200
*n*RO$_2$ β	$C_{10}H_{16}NO_6$	*506.199	*522.194	*538.189	496.142	*599.169	572.195
*n*RO$_2$ χ	$C_{10}H_{16}NO_7$	*522.194	*538.189	554.184	512.137	615.164	588.190
*n*RO$_2$ δ	$C_7H_{10}NO_7$	*480.147	496.142	512.137	470.090	573.117	546.143
*n*RO$_2$ ε [d]	$C_{10}H_{15}N_2O_{10}$	*583.174	*599.169	615.164	573.117	676.144	649.170

[a] As in Figure 10, dimers in pink are observed only in the 'simulated nighttime' experiment, and those marked with a * have moderate-to-high signal (40>S/N). Dimers in blue are observed in both the 'simulated nighttime' and *n*RO$_2$ + *n*RO$_2$ experiments, while dimers in black are not observed. *n*RO$_2$ ϕ is omitted as no dimers unique to its chemical formula were observed with moderate-to-high S/N (though some dimers attributed to *n*RO$_2$ δ may instead derive from *n*RO$_2$ ϕ). [b] Positive mode ions are generally sodium clusters ($M+Na^+$). [c] This mass corresponds to the parent compound $-2HNO_2$, presumably lost during ionization; the sodiated parent mass (451.205) was also observed but with low signal due to a lack of carbonyl groups on this dimer. [d] Dimers of *n*RO$_2$ ε are observed as the oxidation product (as in Figure 10 in the main text). [e] Negative mode ions are generally nitrate clusters ($M+NO_3^-$). [f] $_{OH}$RO$_2$ (1x) is an oxidation product of $_{OH}$RO$_2$ (1) in Figure 10.

Mechanism S1.

Here we provide the list of new species (with SMILES strings for stable products) and reactions added to the kinetic model in this work. The mechanism accurately simulates measured decay of α-pinene (Figure 2), production of α-pinene nitrooxy-hydroperoxide (PNP, Figure 6), production of α-pinene hydroxy-nitrate (PHN, Figure S2), and concentrations of inorganic species (Figure 2) under the range of experimental conditions, but is not meant to simulate SOA formation or later-generation chemistry. While dimer formation from RO_2 + RO_2 reactions is included to approximate the levels observed in SOA, a complete representation of dimer formation would require more detailed treatment of peroxy radical isomerization as shown in Figure 9. Additional reactions of inorganic species relevant to radical dynamics in the chamber are taken from the JPL Chemical Kinetics and Photochemical Data Evaluation,[2] and the reaction of NO_3 with H_2O_2 (producing HO_2 and HNO_3) was added (see Fig. S1). In reaction rates, T denotes temperature (K).

{Species}
APIN = a-pinene;
{SMILES: C/C1=C/CC2CC1C2(C)C}
APINNO2a = tertiary (major) peroxy radical from APIN + NO_3 + O_2;
APINNO2b = secondary (minor) peroxy radical from APIN + NO_3 + O_2;
PNP = pinene nitrooxy-hydroperoxide;
{SMILES: CC1(C)C2CC(O[N+](=O)O)C(C)(OO)C1C2 (major)}
{SMILES: CC1(C)C2CC(OO)C(C)(O[N+](=O)O)C1C2 (minor)}
PHN = pinene hydroxy-nitrate;
{SMILES: CC1(C)C2CC(O[N+](=O)O)C(C)(O)C1C2 (major)}
{SMILES: CC1(C)C2CC(O)C(C)(O[N+](=O)O)C1C2 (minor)}
PDN = pinene dinitrate;
{SMILES: CC1(C)C2CC(O[N+](=O)O)C(C)(O[N+](=O)O)C1C2}
PINAL = pinonaldehyde;
{SMILES: CC(=O)C1CC(CC=O)C1(C)C}
DIMER = dimers from RO_2 + RO_2 reactions;
{SMILES: CC3(C)C4CC(O[N+](=O)O)C(OOC1(C)C(O[N+](=O)O)CC2CC1C2(C)C)C3C4 (Fig. 6D.a)}
{SMILES: CC(=O)CC(CC(CC=O)OOC1(C)C(O[N+](=O)O)CC2CC1C2(C)C)O[N+](=O)O (Fig. 6D.b)}
{SMILES: CC(=O)C(CC2CC(OOC1CC(CC(O[N+](=O)O)C(C)=O)C1(C)C)C2(C)C)O[N+](=O)O (Fig. 6D.c)}
{SMILES: CC(=O)C(CC(C(=O)CO[N+](=O)O)C(C)(C)OOC1(C)C(O[N+](=O)O)CC2CC1C2(C)C)O[N+](=O)O (Fig. 6D.d)}
APINO2a = tertiary (major) peroxy radical from APIN + OH + O_2;
APINO2b = secondary (minor) peroxy radical from APIN + OH + O_2;
APINO2c = peroxy radical from APIN + O_3;
APINP = generic product of APINO2 reactions;

{Reactions}
APIN + NO3 = 0.65 APINNO2a + 0.35APINNO2b : $1.2\times10^{-12}\times e^{(490/T)}$;
APIN + O3 = 0.16 PINAL + 0.16 H2O2 + 0.8 OH + 0.8 APINO2c : $0.48\times10^{-15}\times e^{(-550/T)}$;
APIN + OH = 0.65 APINO2a + 0.35APINO2b : $1.34\times10^{-11}\times e^{(410/T)}$;
APINNO2a + HO2 = 0.37 PNP + 0.63 PINAL + 0.63 HO2 + 0.63 OH : $2.66\times10^{-13}\times e^{(1300/T)}$;
APINNO2a + NO = 0.3 PDN + 0.7 PINAL + 1.4 NO2 : $2.55\times10^{-12}\times e^{(380/T)}$;
APINNO2a + NO3 = 0.1 PDN + 0.9 PINAL + 1.8 NO2 : 2.3×10^{-12} ;
APINNO2b + HO2 = PNP : $2.66\times10^{-13}\times e^{(1300/T)}$;
APINNO2b + NO = 0.3 PDN + 0.7 PINAL + 1.4 NO2 : $2.55\times10^{-12}\times e^{(380/T)}$;

APINNO2b + NO3 = 0.1 PDN + 0.9 PINAL + 1.8 NO2 : 2.3×10^{-12} ;
APINNO2a + APINNO2a = 0.16 DIMER + 1.68 PINAL + 1.68 NO2 : 1×10^{-14} ;
APINNO2a + APINNO2b = 0.34 PHN + 0.16 DIMER + 1.34 PINAL + 1.34 NO2 : 1×10^{-14} ;
APINNO2b + APINNO2b = 0.68 PHN + 0.16 DIMER + 1.00 PINAL + 1.00 NO2 : 1×10^{-14} ;
APINO2a + HO2 = 0.5 PINAL + 0.5APINP + 0.5 HO2 + 0.5 OH : $2.66\times10^{-13}\times e^{(1300/T)}$;
APINO2a + NO = 0.3 PHN + 0.7 PINAL + 0.7 HO2 + 0.7 NO2 : $2.55\times10^{-12}\times e^{(380/T)}$;
APINO2a + NO3 = 0.1 PHN + 0.9 PINAL + 0.9 HO2 + 0.9 NO2 : 2.3×10^{-12} ;
APINO2b + HO2 = 0.5 PINAL + 0.5APINP + 0.5 HO2 + 0.5 OH : $2.66\times10^{-13}\times e^{(1300/T)}$;
APINO2b + NO = 0.3 PHN + 0.7 PINAL + 0.7 HO2 + 0.7 NO2 : $2.55\times10^{-12}\times e^{(380/T)}$;
APINO2b + NO3 = 0.1 PHN + 0.9 PINAL + 0.9 HO2 + 0.9 NO2 : 2.3×10^{-12} ;
APINO2c + HO2 = APINP : $2.66\times10^{-13}\times e^{(1300/T)}$;
APINO2c + NO = APINP + 0.7 NO2 : $2.55\times10^{-12}\times e^{(380/T)}$;
APINO2c + NO3 = APINP : 2.3×10^{-12} ;
APINNO2a + APINO2a = 0.16 DIMER + 1.68 PINAL + 0.84 NO2 + 0.84 HO2 : 1×10^{-14} ;
APINNO2a + APINO2b = 0.16 DIMER + 1.68 PINAL + 0.84 NO2 + 0.84 HO2 : 1×10^{-14} ;
APINNO2a + APINO2c = 0.16 DIMER + 0.84 PINAL + 0.84 APINP + 0.84 NO2 + 0.84 HO2 : 1×10^{-14} ;
APINNO2b + APINO2a = 0.16 DIMER + 1.68 PINAL + 0.84 NO2 + 0.84 HO2 : 1×10^{-14} ;
APINNO2b + APINO2b = 0.16 DIMER + 1.68 PINAL + 0.84 NO2 + 0.84 HO2 : 1×10^{-14} ;
APINNO2b + APINO2c = 0.16 DIMER + 0.84 PINAL + 0.84 APINP + 0.84 NO2 + 0.84 HO2 : 1×10^{-14} ;
APINO2a + APINO2a = 2 PINAL + 2 HO2 : 1×10^{-14} ;
APINO2a + APINO2b = 2 PINAL + 2 HO2 : 1×10^{-14} ;
APINO2a + APINO2c = PINAL + HO2 + APINP : 1×10^{-14} ;
APINO2b + APINO2b = 2 PINAL + 2 HO2 : 1×10^{-14} ;
APINO2b + APINO2c = PINAL + HO2 + APINP : 1×10^{-14} ;
APINO2c + APINO2c = 2 APINP : 1×10^{-14} ;

References:

1. J. P. Burrows, G. S. Tyndall, and G. K. Moortgat: Absorption spectrum of NO_3 and kinetics of the reactions of NO_3 with NO_2, Cl, and several stable atmospheric species at 298 K. *J. Phys. Chem.*, 89 (22), 4848-4856, DOI: 10.1021/j100268a038, 1985.

2. J. B. Burkholder, S. P. Sander, J. Abbatt, J. R. Barker, C. Cappa, J. D. Crounse, T. S. Dibble, R. E. Huie, C. E. Kolb, M. J. Kurylo, V. L. Orkin, C. J. Percival, D. M. Wilmouth, and P. H. Wine "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 19," JPL Publication 19-5, Jet Propulsion Laboratory, Pasadena, 2019 http://jpldataeval.jpl.nasa.gov