Contents:

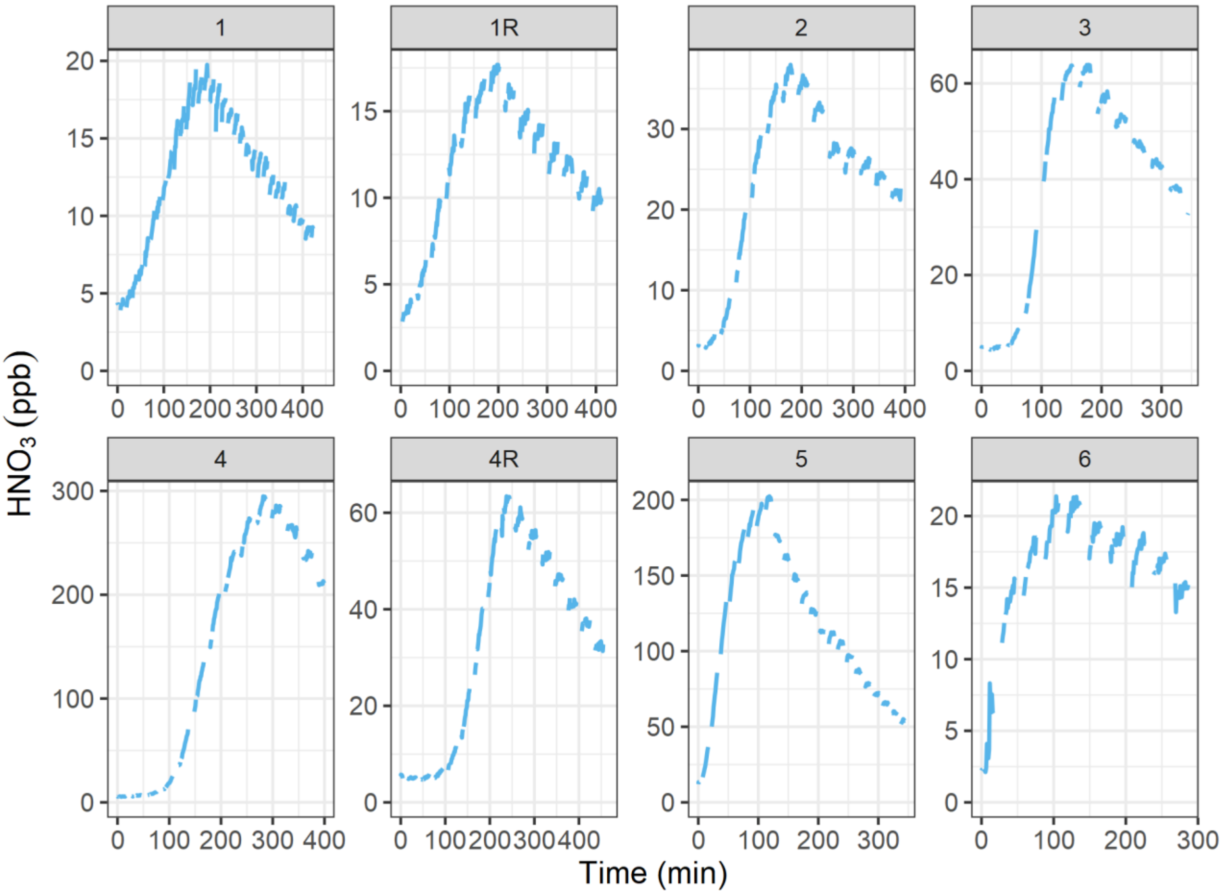

Fig. S1. The measured HNO_3 concentrations for the various conducted experiments. The measurements were made using CIMS. A substantial "chamber blank" was observed before the start (time = 0) of the experiments.

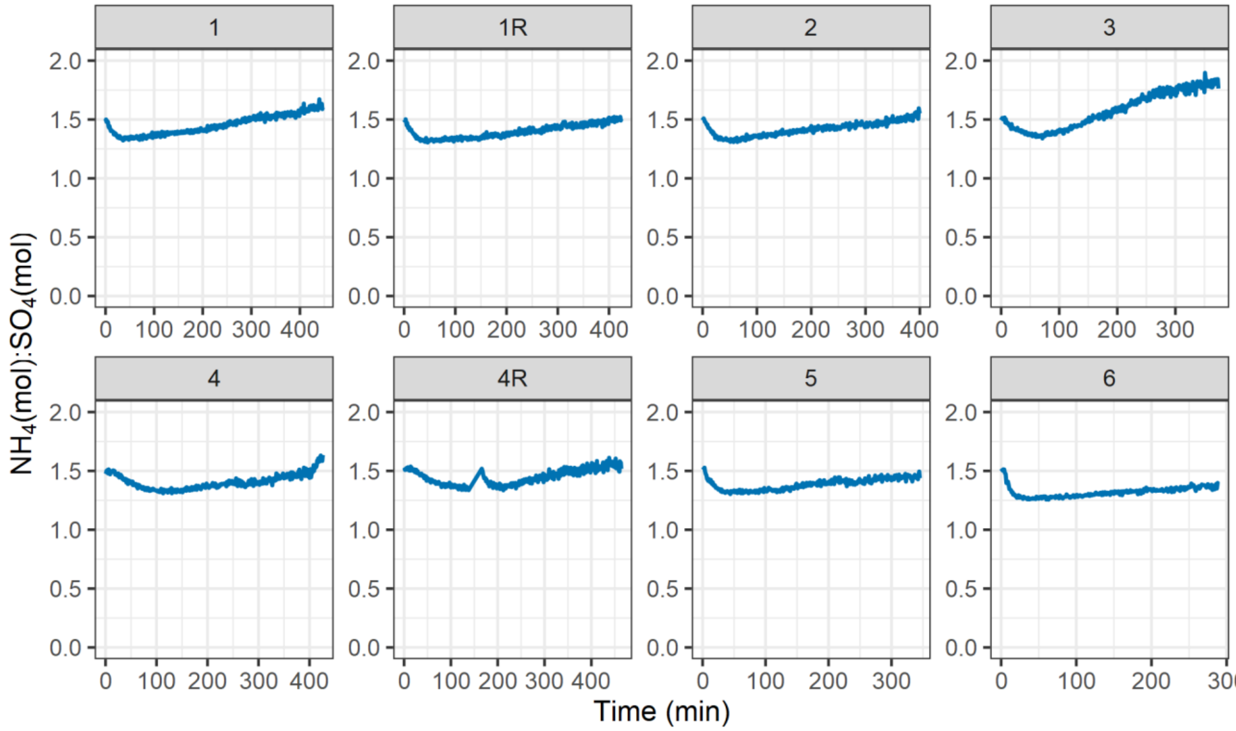

Fig. S2. The measured NH_4(mol):SO_4(mol) ratio for each conducted experiment from the HR-ToF-AMS. The ratios remained consistent and below 2 during the experiment indicative of minor contributions of pNO_3 derived from HNO_3.

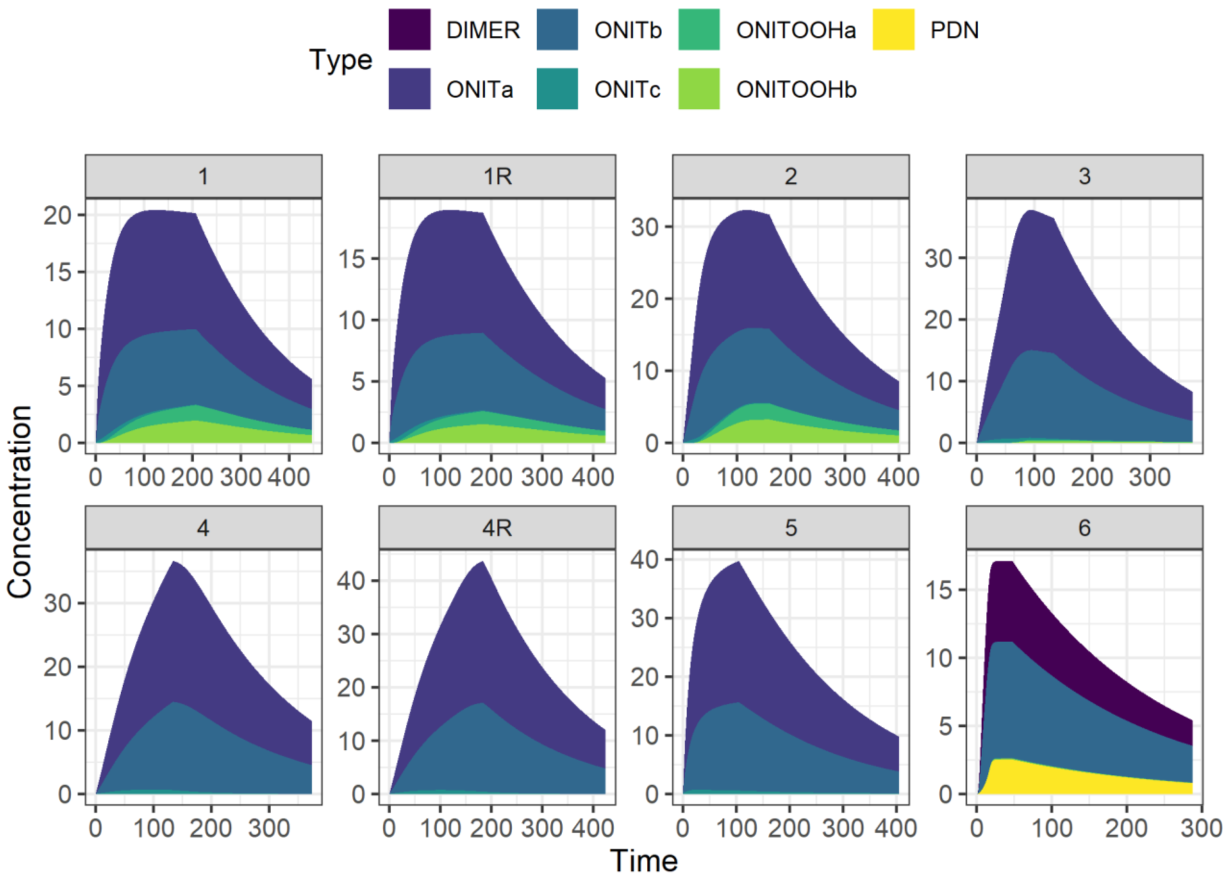

Fig. S3. The simulated types of organic nitrate and isomers formed during the various *α*-pinene/NO_x oxidation experiments using the USC-API mechanism. The mechanism includes 2 pinene hydroxyl-nitrate (ONITa (tertiary) and ONITb (secondary)), pinene carbonyl nitrate (ONITc), pinene nitrooxy-hydroperoxide (ONITOOHa (tertiary) and ONITOOHb (secondary)), dimer (DIMER), and pinene dinitrate (PDN).

Table S1. Summary of the USC-API Species List.

Species	Description	SMILES
	Inorganic	
CO	Carbon monoxide	C=O
CO2	Carbon dioxide	O=C=O
H2	Hydrogen	[H][H]
H2O2	Hydrogen peroxide	OO
HNO3	Nitric acid	O=N(=O)O
HO2	Hydroperoxy radical	[O]O
HO2NO2	Pernitric acid	OO[N+](=O)[O-]
HONO	Nitrous acid	O=N[O]
N2O5	Dinitrogen pentoxide	O=[N+](=O)O[N+](=O)[O-]
NO	Nitric oxide	[N]=O
NO2	Nitrogen dioxide	[O-][N+](=O)
NO3	Nitrate radical	[O-][N+](=O)O
O1D	Excited state oxygen atom $O(^1D)$	[O]
O3	Ozone	O=O=O
O3P	Ground state oxygen atom $O(_3P)$	[O]
OH	Hydroxl radical	[OH]
	Organic	
ACT	Acetone	CC(=O)C
API	A-pinene	C/C1=C/CC2CC1C2(C)C
APINAO	alpha-pinene alkoxy radical	OC1CC2CC(C1(C)[O])C2(C)C
APINAO2	tertiary (major) peroxy radical from APIN + OH + O2	[O]OC1(C)C(O)CC2CC1C2(C)C
APINAOOH	pinene-derived hydroxy hydroperoxide	OOC1(C)C(O)CC2CC1C2(C)C
APINBO	alpha-pinene alkoxy radical	[O]C1CC2CC(C1(C)O)C2(C)C
APINBO2	secondary (minor) peroxy radical from APIN + OH + O2	[O]OC1CC2CC(C1(C)O)C2(C)C
APINBOOH	pinene-derived hydroxy hydroperoxide	OOC1CC2CC(C1(C)O)C2(C)C
APINCO	alpha-pinene alkoxy radical	CC1=CCC(CC1O)C(C)(C)[O]
APINCO2	tertiary (minor) peroxy radical from APIN + OH + O2	[O]OC(C)(C)C1CC=C(C)C(O)C1
APINCOOH	pinene-derived hydroxy hydroperoxide	OOC(C)(C)C1CC=C(C)C(O)C1

DIMER	Dimers from nRO_2 + RO_2 reactions	CC3(C)C4CC(O[N+](=O)O)C(OOC1(C)C(O[N+](=O)O)CC2CC1C2(C)C)C3C4
MO2	Generic RO_2	N/A
NAPINAO2	tertiary (major) peroxy radical from APIN + NO3 + O2;	[O]OC1CC2CC(C1(C)ON(=O)=O)C2(C)C
NAPINBO2	secondary (minor) peroxy radical from APIN + NO3 + O2;	[O]OC1(C)C(ON(=O)=O)CC2CC1C2(C)C
ONITa	Tertiary (major) alpha-pinene hydroxynitrate	O=N(=O)OC1(C)C(O)CC2CC1C2(C)C
ONITb	Secondary (minor) alpha-pinene hydroxynitrate	O=N(=O)OC1CC2CC(C1(C)O)C2(C)C
ONITc	Tertiary alpha-pinene carbonyl nitrate	O=N(=O)OC(C)(C)C1CC=C(C)C(O)C1
ONITOOHa	Tertiary alpha-pinene nitrate hydroperoxide	OOC1CC2CC(C1(C)ON(=O)=O)C2(C)C
ONITOOHb	Secondary alpha-pinene nitrate hydroperoxide	OOC1(C)C(ON(=O)=O)CC2CC1C2(C)C
P	Generic Product	N/A
PAN	Peroxyacetyl nitrate	CC(=O)OON(=O)=O
PDN	Pinene dinitrate	CC1(C)C2CC(O[N+](=O)O)C(C)(O[N+](=O)O)C1C2
PINAL	pinonaldehyde	CC(=O)C1CC(CC=O)C1(C)C
PINO3	pinonaldehyde-derived acyl peroxy radical	[O]OC(=O)CC1CC(C(=O)C)C1(C)C
PINPAN	C10 peroxyacyl nitrate	O=N(=O)OOC(=O)CC1CC(C(=O)C)C1(C)C
RO	Generic Aloxy Radical	N/A
RO3	Generic acyl peroxy radical	N/A

Table S2. Summary of the USC-API Mechanism.

Label	Reaction	Reaction Rate (*k*)
Inorganic Photolysis		
R001	O3 → O3P + O2	JO3P*
R002	O3 → O1D + O2	JO1D*
R003	H2O2 → OH + OH	JH2O2*
R004	NO2 → O3P + NO	JNO2*
R005	NO3 → O2 + NO	JNO3_NO*
R006	NO3 → O3P + NO2	JNO3_NO2*
R007	HONO → OH + NO	JHONO*
R008	HNO3 → OH + NO2	JHNO3*
R009	HO2NO2 → 0.2 OH + 0.2 NO3 + 0.8 HO2 + 0.8 NO2	JHO2NO2*
Inorganic Reactions		
R010	O3 + OH → HO2 + O2	1.70E-12 * exp(-940 / T)
R011	O3 + HO2 → OH + O2 + O2	1.00E-14 * exp(-490 / T)
R012	O3 + NO → NO2 + O2	1.40E-12 * exp(-1310 / T)
R013	NO2 + O3 → NO3 + O2	1.40E-13 * exp(-2470 / T)
R014	O3P + O2 → O3	M * 5.60E-34 * (T / 300)^-2.6 * 0.21 * M
R015	O3P + O3 → O2 + O2	8.00E-12 * exp(-2060 / T)
R016	O1D + O2 → O3P + O2	3.20E-11 * 0.21 * M
R017	O1D + N2 → O3P + N2	1.80E-11 * exp(107 / T) * 0.78 * M
R018	O1D + H2O → OH + OH	2.20E-10 * H2O
R019	OH + H2 → HO2 + H2O	7.70E-12 * exp(-2100 / T)
R020	OH + HO2 → H2O + O2	4.80E-11 * exp(250 / T)
R021	HO2 + HO2 → H2O2 + O2	2.20E-13 * exp(600 / T) + 1.90E-33 * M * exp(980 / T)
R022	HO2 + HO2 + H2O → H2O2 + H2O + O2	(3.08E-34 * exp(2800 / T) + 2.59E-54 * M * exp(3180 / T)) * H2O
R023	H2O2 + OH → HO2 + H2O	2.90E-12 * exp(-160 / T)
R024	NO + O3P → NO2	K_O3P_NO**
R025	NO + OH → HONO	K_OH_NO**
R026	HO2 + NO → OH + NO2	3.45E-12 * exp(270 / T)
R027	HO2 + NO → HNO3	K_HO2_NO_HNO3**

R028	NO + NO → NO2 + NO2	3.30E-39 * exp(530 / T) * 0.21 * M
R029	HONO + OH → NO2 + H2O	2.50E-12 * exp(260 / T)
R030	O3P + NO2 → NO + O2	5.50E-12 * exp(188 / T)
R031	O3P + NO2 → NO3	K_O3P_NO2**
R032	OH + NO2 → HNO3	K_OH_NO2_HONO2**
R033	OH + HNO3 → NO3 + H2O	K_OH_HNO3**
R034	OH + NO3 → HO2 + NO2	2.00E-11
R035	HO2 + NO3 → 0.7 OH + 0.7 NO2 + 0.3 HNO3	4.00E-12
R036	NO + NO3 → NO2 + NO2	1.80E-11 * exp(110 / T)
R037	NO2 + NO3 → NO + NO2 + O2	4.50E-14 * exp(-1260 / T)
R038	NO3 + NO3 → NO2 + NO2 + O2	8.50E-13 * exp(-2450 / T)
R039	NO2 + NO3 → N2O5	K_NO2_NO3**
R040	N2O5 → NO2 + NO3	K_N2O5**
R041	N2O5 + H2O → HNO3 + HNO3	2.50E-22 * H2O
R042	HO2 + NO2 → HO2NO2	K_HO2_NO2**
R043	HO2NO2 → HO2 + NO2	K_HO2NO2**
R044	OH + HO2NO2 → NO2 + H2O + O2	1.30E-12 * exp(380 / T)
R045	OH + CO → HO2 + CO2	K_OH_CO**
	API Oxidation	
R046	API + OH → 0.572 APINAO2 + 0.353 APINBO2 + 0.075 APINCO2	1.2e-11 * exp(440 / T)
R047	API + O3 → RO2 + OH	8.05e-16 * exp(-640 / T)
R048	API + NO3 → 0.65 NAPINAO2 + 0.35 NAPINBO2	1.2e-12 * exp(490 / T)
	APIO2 Rxns	
R049	APINAO2 + NO → 0.23 ONITa + 0.77 PINAL + 0.77 HO2 + 0.77 NO2	2.70e-12 * exp(360 / T)
R050	APINBO2 + NO → 0.23 ONITb + 0.77 PINAL + 0.77 HO2 + 0.77 NO2	2.70e-12 * exp(360 / T)
R051	APINCO2 + NO → 0.125 ONITc + 0.875 ACT + 0.875 P + 0.875 NO2	2.70e-12 * exp(360 / T)
R052	APINAO2 + HO2 → APINAOOH	2.91e-13 * exp(1300 / T) * 0.914
R053	APINBO2 + HO2 → APINBOOH	2.91e-13 * exp(1300 / T) * 0.914
R054	APINCO2 + HO2 → APINCOOH	2.91e-13 * exp(1300 / T) * 0.914
R055	APINAO2 + NO3 → APINAO + NO2	KRO2NO3**
R056	APINBO2 + NO3 → APINBO + NO2	KRO2NO3**
R057	APINCO2 + NO3 → APINCO + NO2	KRO2NO3**

PINAL Chemistry		
R058	PINAL + hv → RO2 + CO + HO2	J.JPINAL[*]
R059	PINAL + OH → PINO3 + RO2	5.2e-12 * exp(600 / T)
R060	PINAL + NO3 → PINO3 + HNO3	2.00E-14
R061	PINO3 + NO → RO2 + NO2	7.5E-12 * exp(290 / T)
R062	PINO3 + NO3 → RO2 + NO2	4.00E-12
R063	PINO3 + NO2 → PINPAN	K_ACO3_NO2[**]
R064	PINO3 + HO2 → 0.44 RO2 + 0.44 OH + 0.15 O3 + 0.55 P	5.20E-13 * exp(980 / T)
R065	PINPAN → PINO3 + NO2	K_PAN[**]
General RO2 Rxns		
R066	MO2 + NO → NO2 + RO	2.7e-12 * exp(360 / T)
R067	MO2 + HO2 → P	2.91e-13 * exp(1300 / T)
R068	MO2 + NO3 → RO + NO2	2.30E-12
R069	MO2 + MO2 → P	1.30E-12
R070	MO2 + PINO3 → P	5.00E-12
ACT Chemistry		
R071	ACT + OH → RO2	1.39E-13 + 3.72E-11 exp(-2044 / T)
R072	ACT + hv → RO3 + RO2	JACT[*]
PAN Chemistry		
R073	RO3 + NO2 → PAN	K_ACO3_NO2[**]
R074	PAN → RO3 + NO2	K_PAN[**]
R075	PAN + hv → RO3 + NO2	JPAN1[*]
R076	PAN + hv → MO2 + NO3 + CO2	JPAN2[*]
RO3 Chemistry		
R077	RO3 + NO → RO2 + NO2	8.10E-12 * exp(270 / T)
R078	RO3 + HO2 → P	4.30E-13 * exp(1040 / T)
R079	RO3 + RO2 → HO2 + P	2.00E-12 * exp(500 / T)
R080	RO3 + RO3 → P	2.50E-12 * exp(500 / T)
APIOOH Chemistry		
R081	APINAOOH + hv → P + OH	J.JAPINAOOH[*]
R082	APINAOOH + OH → RO2	1.83E-11
R083	APINBOOH + hv → P + OH	J.JAPINAOOH[*]
R084	APINBOOH + OH → P + OH	3.28E-11
R085	APINCOOH + hv → P + OH	J.JAPINAOOH[*]
R086	APINCOOH + OH → RO2	1.03E-10
NAPINO2 Chemistry		
R087	NAPINAO2 + HO2 → 0.37 ONITa + 0.63 PINAL + 0.63 HO2 + 0.63 OH	2.66e-13 * exp(1300 / T)

R088	NAPINAO2 + NO → 0.9 PINAL + 1.9 NO2 + 0.1 ONITa	2.55e-12 * exp(380 / T)
R089	NAPINAO2 + NO3 → 0.1 PDN + 0.9 PINAL + 1.8 NO2	2.30E-12
R090	NAPINAO2 + NAPINAO2 → 0.16 DIMER + 1.68 PINAL + 1.68 NO2	1.00E-14
R091	NAPINAO2 + NAPINBO2 → 0.34 ONITb + 0.08 DIMER + 1.34 PINAL + 0.08 DIMER + 1.34 NO2	1.00E-14
R092	NAPINBO2 + HO2 → ONITOOHb	2.66e-13 * exp(1300 / T)
R093	NAPINBO2 + NO → 0.9 PINAL + 1.9 NO2 + 0.1 ONITb	2.55e-12 * exp(380 / T)
R094	NAPINBO2 + NO3 → 0.1 PDN + 0.9 PINAL + 1.8 NO2	2.30E-12
R095	NAPINBO2 + NAPINBO2 → 0.68 ONITb + 0.16 DIMER + PINAL + NO2	1.00E-14
RO2 Cross Reactions		
R096	APINAO2 + APINAO2 → 2 PINAL + 2 HO2	1.00E-14
R097	APINAO2 + APINBO2 → 2 PINAL + 2 HO2	1.00E-14
R098	APINAO2 + APINCO2 → 2 PINAL + 2 HO2	1.00E-14
R099	APINBO2 + APINBO2 → 2 PINAL + 2 HO2	1.00E-14
R0100	APINBO2 + APINCO2 → 2 PINAL + 2 HO2	1.00E-14
R101	APINCO2 + APINCO2 → 2 PINAL + 2 HO2	1.00E-14
R102	RO + O2 → MO2	1E-11 * M * 0.21
ONIT Reactions		
R103	ONITa + OH → PINAL + NO2	5.50E-12
R104	ONITb + OH → P + NO2	3.64E-12
R105	ONITc + OH → ACT + P + NO2	9.87E-11
R106	ONITc + hv → ACT + RO2 + NO2	JONIT*

*The photolysis frequencies (J) were calculated inline using the F0AM Box model based on the MCMv3.2 cross-sections

**The complex reaction rate constants (K) were from the MCMv3.2

Table S3. Summary of the organic nitrate hydrolysis reactions incorporated into the USC-API ("USC-API-Hydro") mechanism that was utilized for a sensitivity simulation. Note: the DIMER and pinene dinitrate were not included in the hydrolysis scheme since the nighttime oxidation experiment exhibited low organic nitrate filter hydrolysis efficiency.

Label	**Reaction**	**Rate (*k*)**
Hydro-01	ONITa=HNO3+P	2.78E-04
Hydro-02	ONITb=HNO3+P	2.78E-04
Hydro-03	ONITc=HNO3+P	2.78E-04
Hydro-04	ONITOOHa=HNO3+P	2.78E-04
Hydro-05	ONITOOHb=HNO3+P	2.78E-04

Table S4. Summary of the measured NO_y isotope data ($\Delta^{17}O$, $\delta^{18}O$, and $\delta^{15}N$) and uncertainties (±σ) for the various conducted experiments.

	NO_2 (‰)			HNO_3 (‰)			pNO_3 (‰)		
Exp	$\delta^{15}N$	$\Delta^{17}O$	$\delta^{18}O$	$\delta^{15}N$	$\Delta^{17}O$	$\delta^{18}O$	$\delta^{15}N$	$\Delta^{17}O$	$\delta^{18}O$
1	-67.8±1.7	13.4±0.7	43.6±1.8	-37.0±1.7	15.6±0.7	49.0±1.8	-79.6±2.4	5.2±0.8	21.7±0.7
1R	-63.3±1.7	10.8±0.7	45.3±1.8	-37.7±1.7	16.6±0.7	49.0±1.8	-76.3±2.6	5.6±0.8	22.3±0.8
2	-68.3±1.7	18.9±0.7	65.8±1.8	-34.3±1.7	13.4±0.7	43.7±1.8	-78.5±1.1	9.2±0.7	29.2±0.6
3	-70.2±1.7 -71.8±1.7 -68.7±1.7	32.4±0.7 32.6±0.7 31.2±0.7	92.6±1.8 86.6±1.8 80.6±1.8	-32.0±1.7 -20.1±1.7 -19.1±1.7	16.5±0.7 16.3±0.7 16.7±0.7	49.5±1.8 48.5±1.8 49.3±1.8	-73.1±1.8	11.1±0.8	37.7±0.8
4	-67.8±1.7 -71.0±1.7 -71.4±1.7	40.8±0.7 39.3±0.7 38.6±0.7	108.7±1.8 107.8±1.8 112.1±1.8	-32.8±1.7 -47.0±1.7 -49.7±1.7	18.1±0.7 21.1±0.7 21.7±0.7	48.1±1.8 60.2±1.8 61.3±1.8	-90.3±1.9	12.0±0.7	42.4±0.8
4R	-67.6±1.7 -62.9±1.7 -68.2±1.7 -68.7±1.7	39.6±0.7 39.4±0.7 40.7±0.7 41.2±0.7	107.8±1.8 115.3±1.8 108.5±1.8 108.7±1.8	-29.6±1.7 -30.6±1.7 -26.8±1.7 -26.8±1.7	17.8±0.7 18.1±0.7 17.9±0.7 18.4±0.7	53.9±1.8 55.0±1.8 52.2±1.8 54.7±1.8	-87.5±4.1	11.8±0.9	40.4±1.4
5	-5.5±1.7 -6.0±1.7 -6.0±1.7 -7.1±1.7	39.1±0.7 36.9±0.7 37.0±0.7 38.1±0.7	103.0±1.8 100.8±1.8 98.0±1.8 101.0±1.8	-8.0±1.7 -6.3±1.7 -4.0±1.7 -4.7±1.7	14.7±0.7 15.7±0.7 15.3±0.7 15.2±0.7	48.5±1.8 48.3±1.8 48.7±1.8 46.8±1.8	-22.5±1.0	15.6±0.9	51.0±1.4
6	-46.0±1.7 -45.8±1.7 -45.5±1.7	7.0±0.7 7.3±0.7 7.4±0.7	31.2±1.8 31.7±1.8 32.7±1.8	-24.8±1.7 -21.6±1.7 -24.4±1.7	14.5±0.7 15.3±0.7 15.3±0.7	45.4±1.8 47.0±1.8 45.8±1.8	NA	NA	NA