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Supplement of

Kinetic modeling of formation and evaporation of secondary organic aerosol from NO_3 oxidation of pure and mixed monoterpenes

Thomas Berkemeier et al.

Correspondence to: Thomas Berkemeier (t.berkemeier@mpic.de) and Nga L. Ng (ng@chbe.gatech.edu)

S.1 Particle-Phase Oligomerization Scheme

Gas-phase oxidation products may undergo reversible oligomerization in the particle phase, which is treated in the kinetic model. The volatility information of the monomeric building blocks is tracked in their oligomeric state and regained after decomposition into monomers. We assume both, formation and decomposition of oligomers, to be pseudo-first order processes that occur with a rate depending on the precursor material. Formation of hetero-oligomers is hence implicitly considered, but occurs with the speed of product from either precursor, not with a combined rate.

$$A_{\mathrm{monomer}} \xrightarrow{k_{\mathrm{form,A}}} A_{\mathrm{oligomer}} \quad (1)$$

$$A_{\mathrm{oligomer}} \xrightarrow{k_{\mathrm{decom,A}}} A_{\mathrm{monomer}} \quad (2)$$

Furthermore, gradual oligomerization will affect the availability of reaction sites for oligomerization reactions. This is accounted for with a conservatively chosen factor that can reduce the oligomer formation rate by up to a factor of 0.5, depending on the oligomer fraction, f_{oligomer}.

$$k^{*}_{\mathrm{form,A}} = k_{\mathrm{form,A}} \cdot \left(1 - 0.5 \cdot f_{\mathrm{oligomer}}\right) \quad (3)$$

This assumes that every monoterpene oxidation product has two possible reaction sites for oligomerization, but for simplicity, there is no further oligomerization beyond the dimer level. The real reduction in formation rate will depend on the exact number of reaction sites and average chain length of the oligomer in solution.

SI Figures

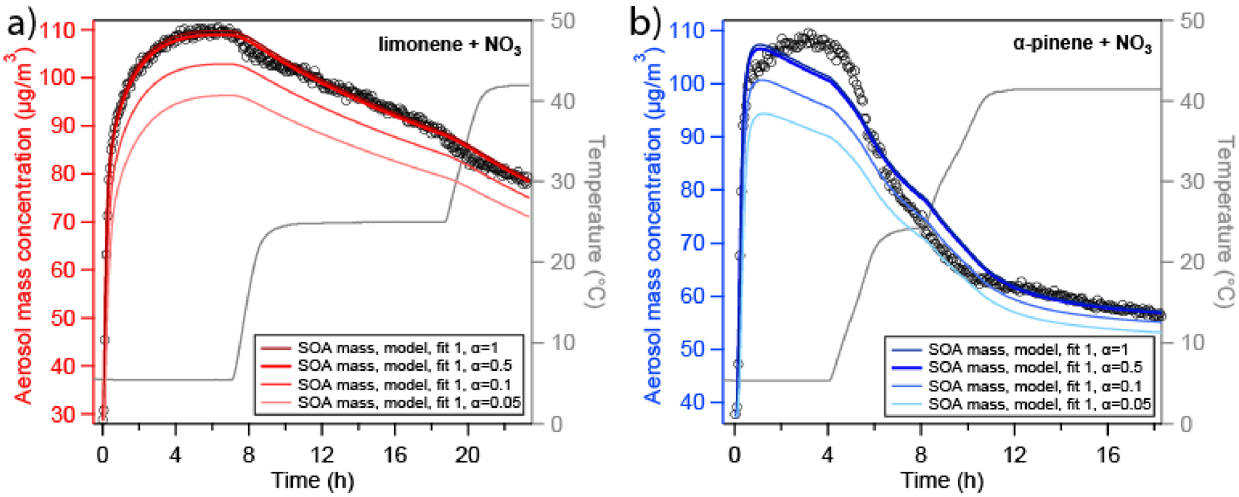

Fig. S1. Sensitivity runs of model fit 1 on the influence of the accommodation coefficient α_s on (a) the LIM experiment and (b) the APN experiment.

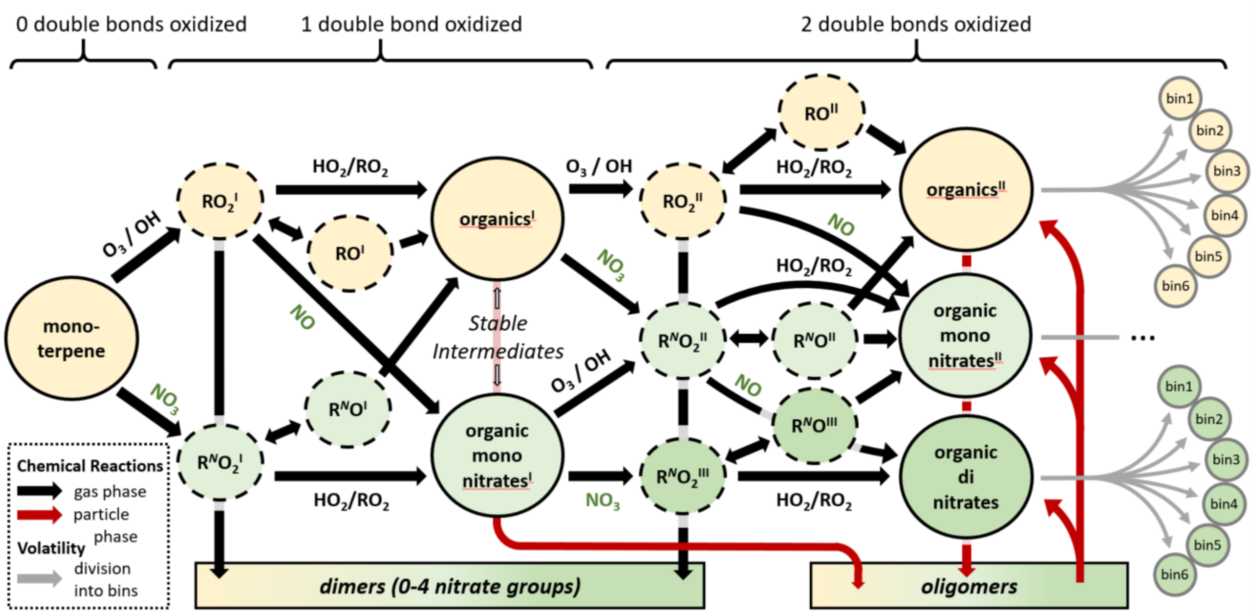

Fig. S2. Schematic representation of the extended lumped chemical mechanism for monoterpenes with two double bonds (e.g. limonene). Yellow colors denote non-nitrated products, while green colors denote mono-nitrated organics (light green), di-nitrated organics (green), and nitrogen oxides (dark green), respectively. Stable products are divided into product bins analogous to Fig. 1 (not depicted for clarity).

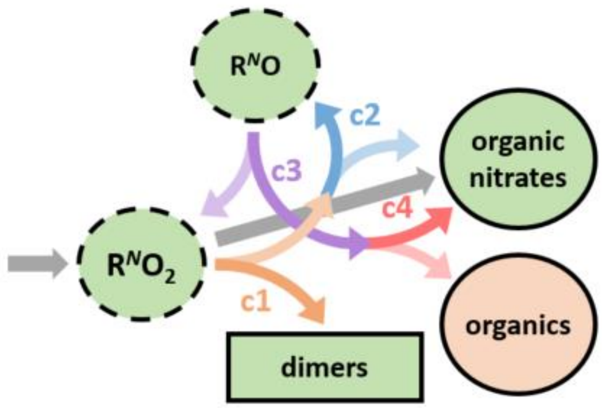

Fig. S3. Scheme detailing the branching ratios c1-c4 of RO_2 and RO radical chemistry used in the oxidation of α-pinene. The branching ratios detail the success of dimer formation (c1), RO yield from not-dimer-forming RO_2 self-reaction (c2), success of RO making product upon unimolecular decay (c3) and the branching between nitrated and non-nitrated products from stabilization of RO (c4). The darker color in the arrow pairs indicates which of the two branches is increased with increasing numerical value of the branching ratio. The formation of α-pinene oxidation products from RO_2^{II} and limonene oxidation products from RO_2^{IV} and RO_2^{V} was treated analogous.

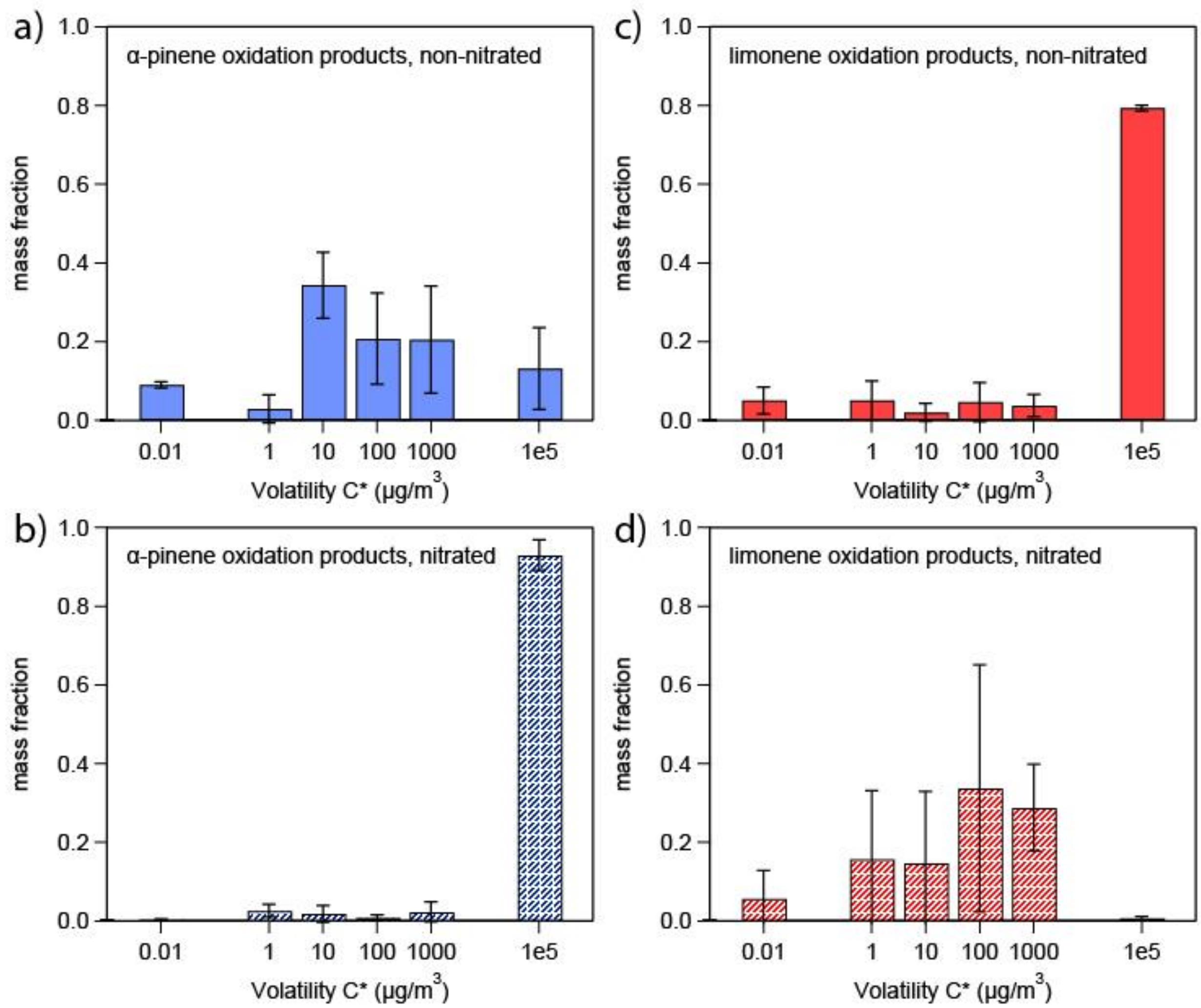

Fig. S4. Volatility distributions of monoterpene oxidation products as derived from kinetic model optimization to experimental data. These distribution keys are used to divide stable monomeric oxidation products into volatility bins. Volatility distributions were differentiated between nitrated and non-nitrated products as well as their precursor origin: (a) non-nitrated α-pinene oxidation products ($f_{apin,org,bi}$), (b) nitrated α-pinene oxidation products ($f_{apin,nitr,bi}$), (c) non-nitrated limonene products ($f_{lim,org,bi}$), and (d) nitrated limonene products ($f_{lim,nitr,bi}$). Dinitrated and mononitrated molecules were considered as following the same volatility distribution. The bars show arithmetic means obtained from multiple (N=11) model optimizations that each optimized six volatility bins while keeping all other model parameters constant. All fits possessed similar model-experiment correlation. Error bars represent standard deviations.

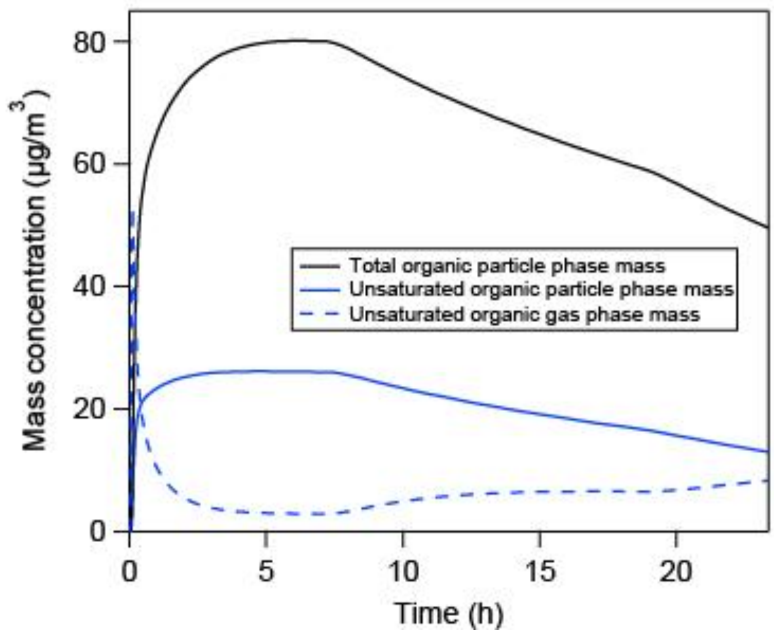

Fig. S5. Mass concentration of total (black solid line) and unsaturated (blue solid line) oxidation products in the particle phase during the LIM experiment according to the model in the best fit simulation. The mass concentration of gas phase unsaturated compounds is shown as blue dashed line.

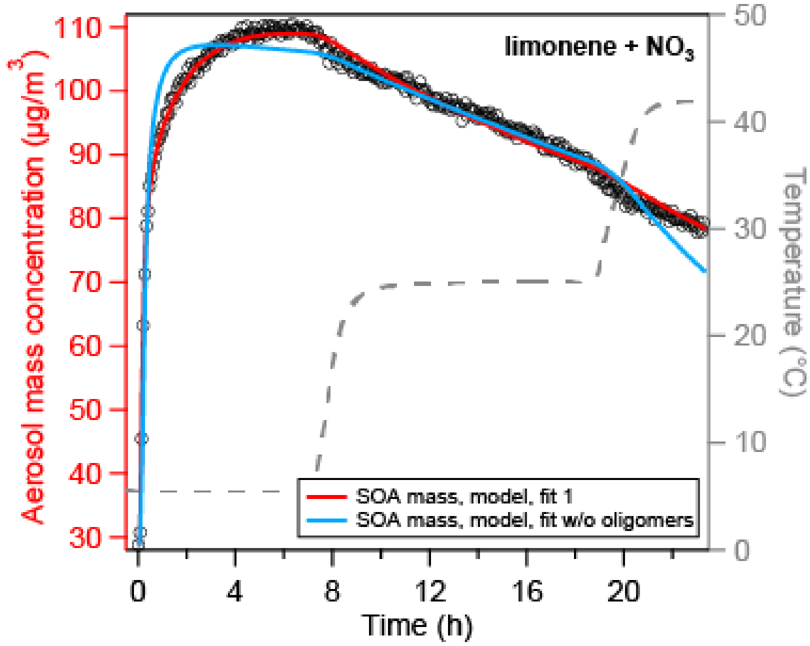

Fig. S6. Comparison of an alternative model optimization run without particle-phase oligomer formation to the best fitting scenario (fit 1) for the LIM experiment. The slow increase of SOA mass (0 – 5 hours) and the slow evaporation at 42 °C (19 – 21 hours) cannot be explained without oligomer formation.

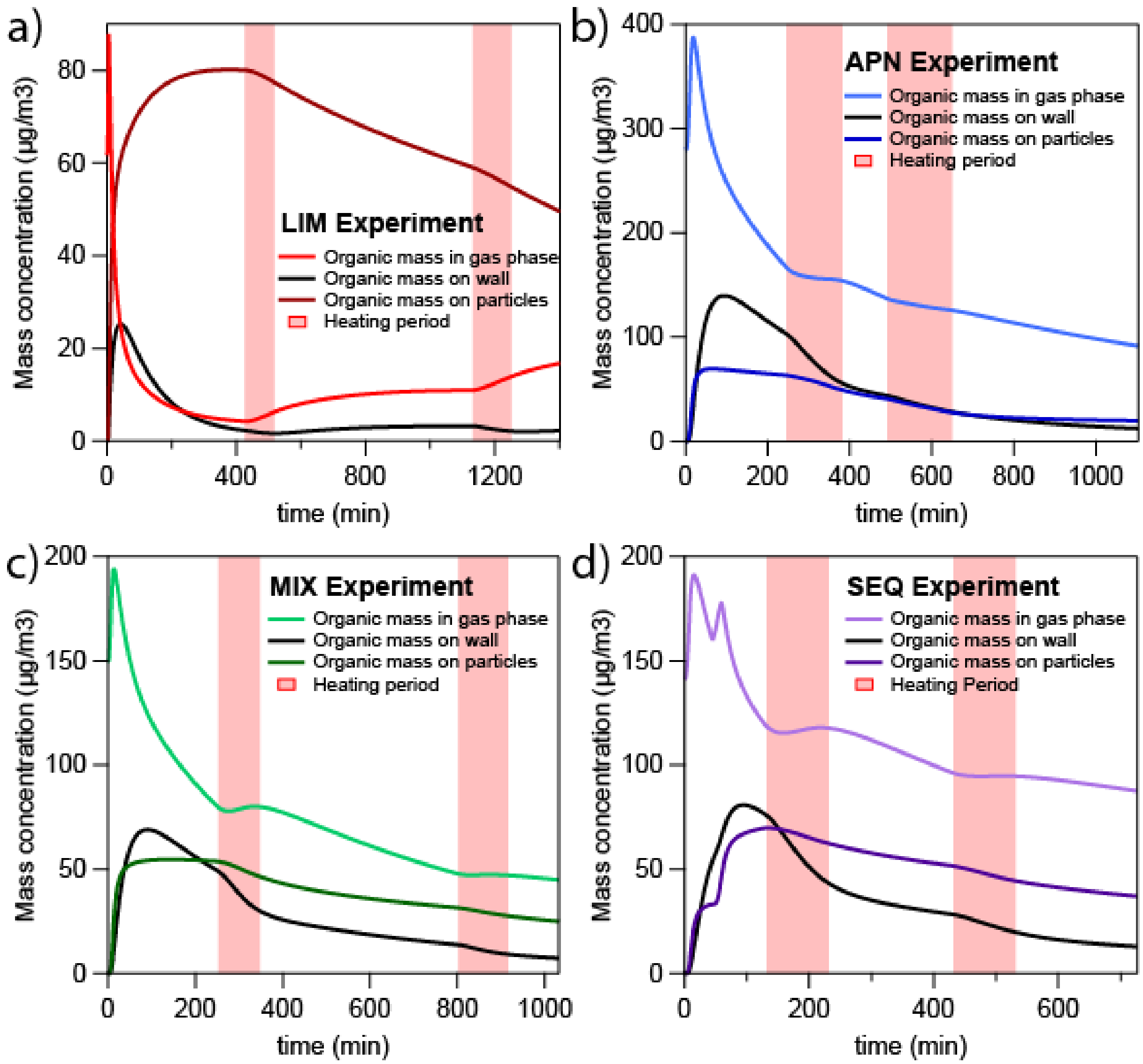

Fig. S7. Time evolution of organic mass concentrations in the chamber gas phase, the chamber wall and the particle phase for (a) the LIM experiment, (b) the APN experiment, (c) the MIX experiment and (d) the SEQ experiment. Heating periods are marked with red shadings to indicate areas where elevated evaporation of organic molecules from wall and particles to the gas phase is expected.

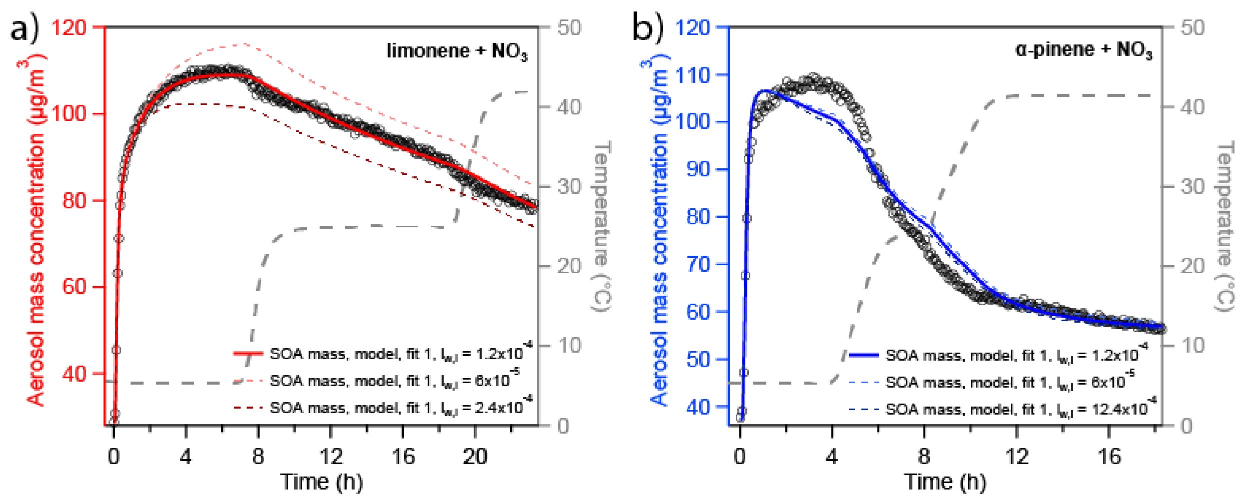

Fig. S8. Sensitivity runs of model fit 1 on the influence of the irreversible wall loss coefficient $l_{w,i}$ on (a) the LIM experiment and (b) the APN experiment.

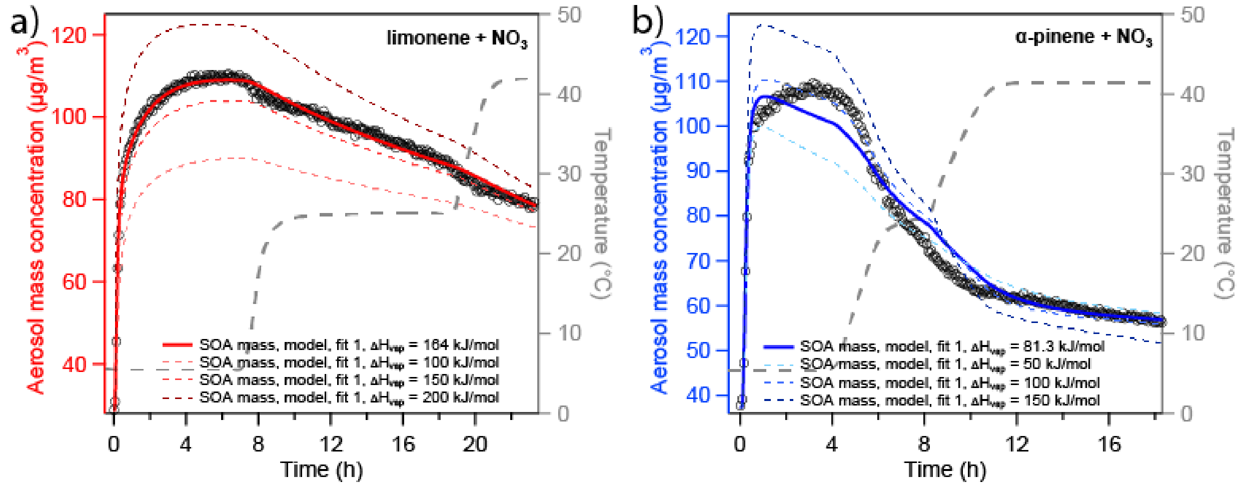

Fig. S9. Sensitivity runs of model fit 1 on the influence of the effective enthalpy of vaporization ΔH_{vap} on (a) the LIM experiment and (b) the APN experiment.

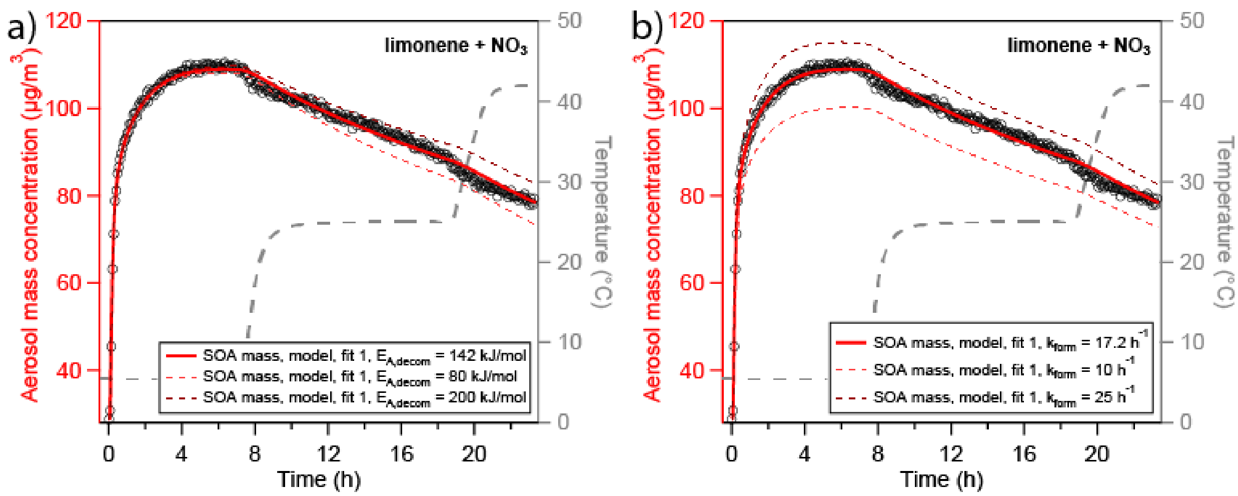

Fig. S10. Sensitivity runs of model fit 1 on the influence of (a) the activation energy of oligomer decomposition $E_{A,decom,lim}$ and (b) the oligomer formation rate $k_{form,lim}$ on the model simulation of the LIM experiment.

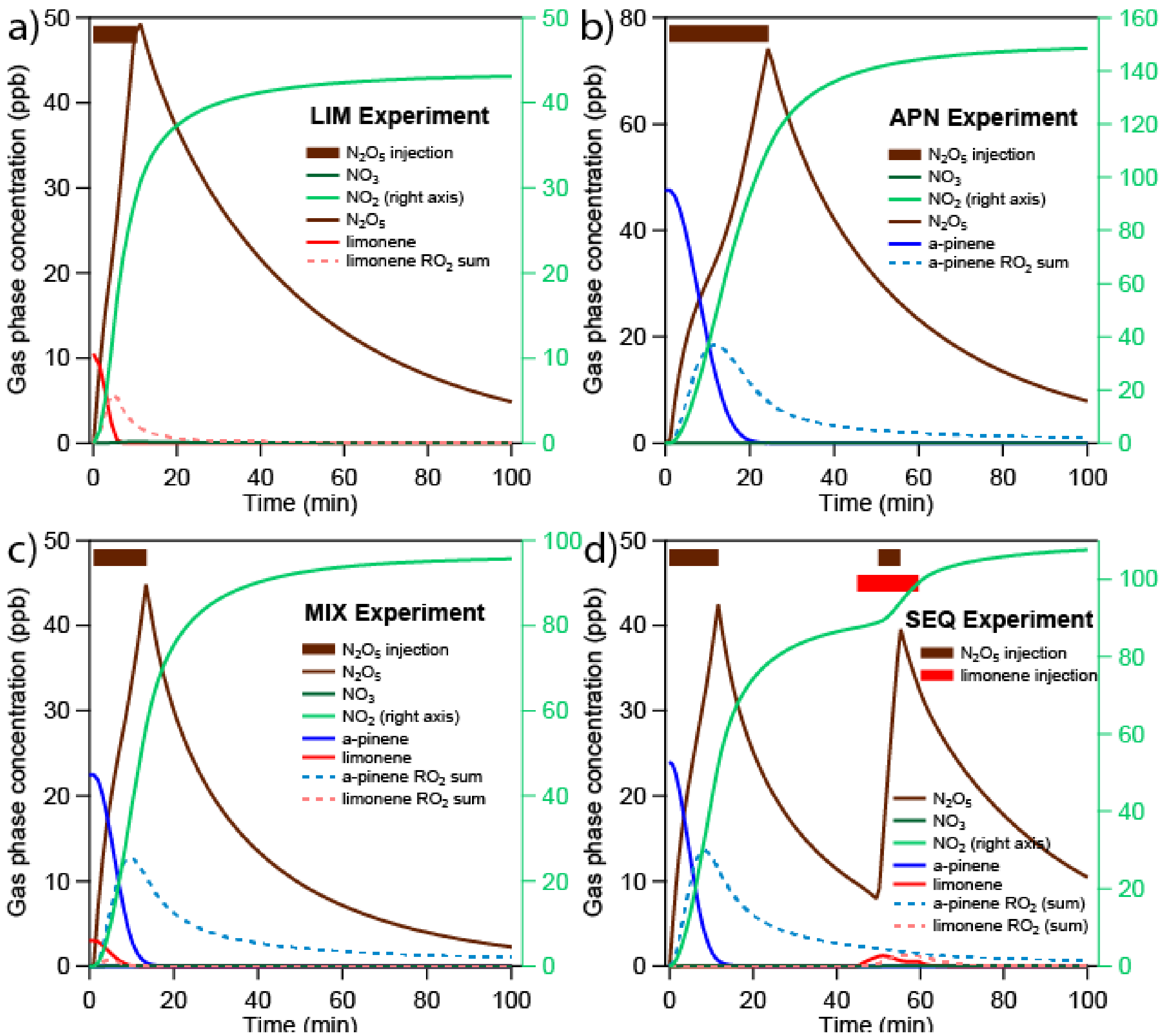

Fig. S11. Time evolution of the gas phase concentrations of selected chemical species according to the kinetic model (fit 1). Injection periods of N_2O_5 (brown rectangle) and limonene precursor (red rectangle) are marked at the top of the graph for the respective time frame.

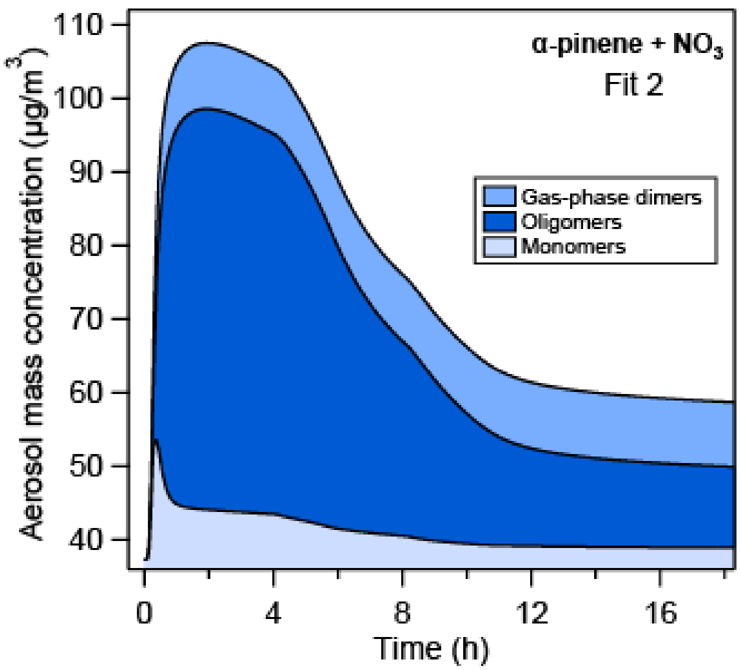

Fig. S12. Area plot of the time evolution of oligomerization state of particle-phase products in the model according to fit 2.

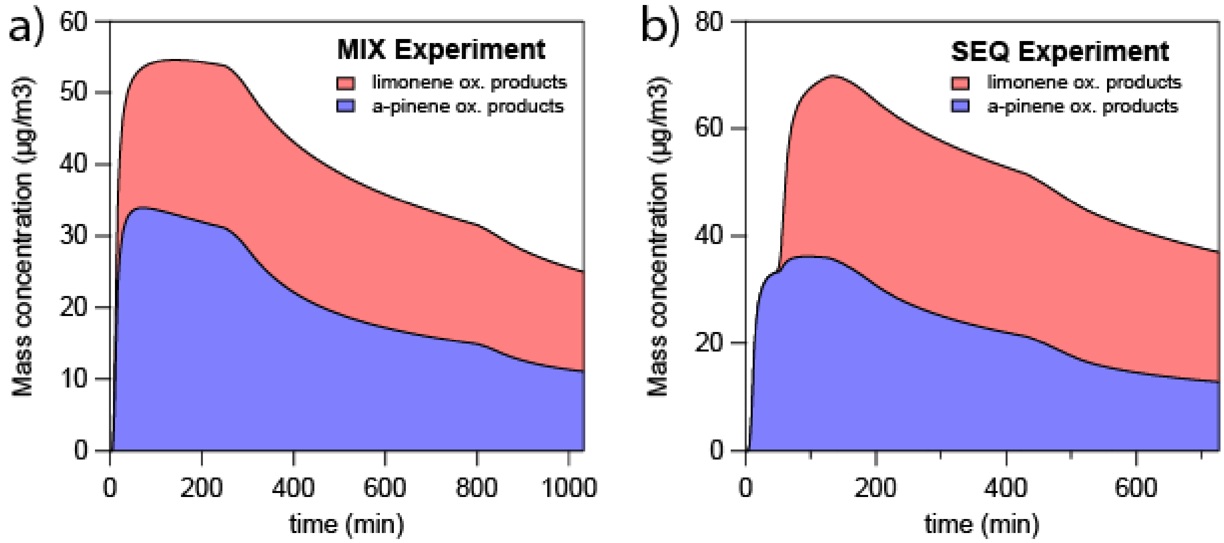

Fig. S13. Area plot of the time evolution of the quantity of α-pinene and limonene derived oxidation products in the particle phase according to model fit 1 for (a) the MIX experiment and (b) the SEQ experiment.

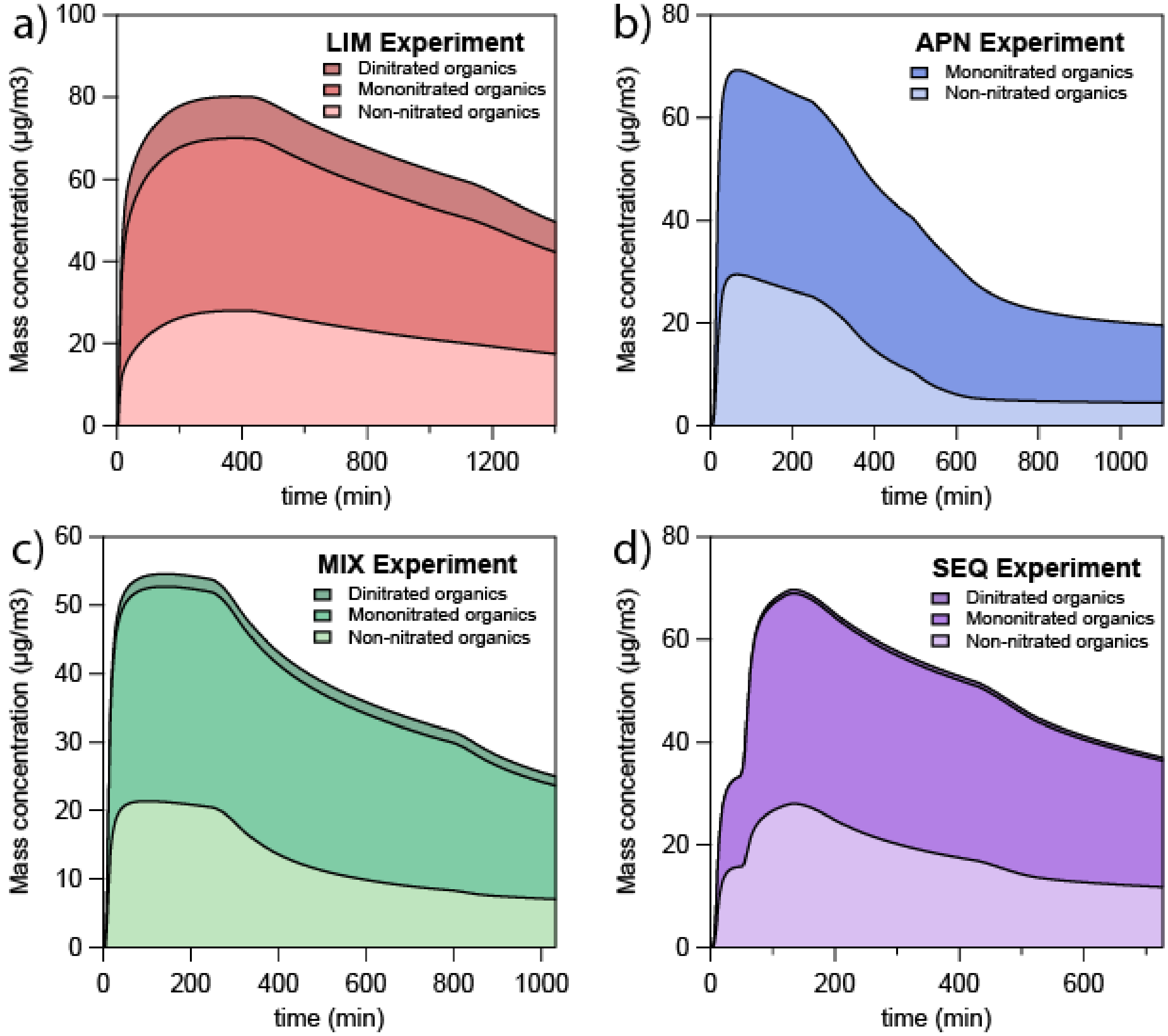

Fig. S14. Area plot of the time evolution of mass concentrations of dinitrated, mononitrated and non-nitrated organics in the particle phase for (a) the LIM experiment, (b) the APN experiment, (c) the MIX experiment and (d) the SEQ experiment. Mono- and dintrated dimers are counted as “mononitrated organics”, tri- and tetranitrated dimers are counted as “dinitrated organics” in this analysis.

SI Tables

Table S1. Lumped gas-phase chemical mechanism employed in this study. Rate coefficients of gas phase reactions involving inorganic reactants are ported from MCM and unless explicitly indicated displayed for a temperature of 5.5 °C and 1 bar pressure. Note that all stable organic products are further subdivided into 6 volatility bins according to a fitted volatility distribution. [RO_2] stands for the total concentration of RO_2 radicals, T is temperature, $f_{oligomer}$ the oligomer fraction, c_1-c_4 are fittest branching ratios, and TF_{apin} and TF_{lim} are temperature-dependence factors for α-pinene and limonene, respectively. In the names of chemical species, the suffix "org" denotes a non-nitrated product, the suffix "orgnitr" denotes an organic nitrate. Among these, a superscript "1N" denotes a mononitrated compound, a superscript "2N" denotes a dinitrated compound, etc.

Number	**Reaction Equation**	**Rate coefficients** (s-1 or cm3/s)
Gas Phase Reactions Involving Inorganics		
1	$O \rightarrow O_3$	$6.27 \cdot 10^{4} \cdot (T/300)^{-2.6}$
2	$O \rightarrow O_3$	$1.78 \cdot 10^{4} \cdot (T/300)^{-2.6}$
3	O + O3 →	$8.00 \cdot 10^{-12} \cdot \exp(-2060/T)$
4	$O + NO \rightarrow NO_2$	$2.63 \cdot 10^{-12}$
5	$O + NO_2 \rightarrow NO$	$5.50 \cdot 10^{-12} \cdot \exp(188/T)$
6	$O + NO_2 \rightarrow NO_3$	$2.33 \cdot 10^{-12}$
7	$O_3 + NO \rightarrow NO_2$	$1.40 \cdot 10^{-12} \cdot \exp(-1310/T)$
8	$O_3 + NO_2 \rightarrow NO_3$	$1.40 \cdot 10^{-13} \cdot \exp(-2470/T)$
9	$NO + NO \rightarrow NO_2 + NO_2$	$1.79 \cdot 10^{-20} \cdot \exp(530/T)$
10	$NO + NO_3 \rightarrow NO_2 + NO_2$	$1.80 \cdot 10^{-11} \cdot \exp(110/T)$
11	$NO_2 + NO_3 \rightarrow$ NO + NO2	$4.50 \cdot 10^{-14} \cdot \exp(-1260/T)$
12	$NO_2 + NO_3 \rightarrow N_2O_5$	$1.28 \cdot 10^{-12}$
13	$O_3 + OH \rightarrow HO_2$	1.70·10-12·exp(-940/T)
14	$OH + CO \rightarrow HO_2$	$2.33 \cdot 10^{-13}$

15	$OH + H_2O_2 \rightarrow HO_2$	$2.9 \cdot 10^{-12} \cdot \exp(-160/T)$
16	$O_3 + HO_2 \rightarrow OH$	$2.03 \cdot 10^{-16} \cdot (T/300)^{4.57} \cdot \exp(693/T)$
17	$OH + HO_2 \rightarrow$	$4.80 \cdot 10^{-11} \cdot \exp(250/T)$
18	$HO_2 + HO_2 \rightarrow H_2O_2$	$2.20 \cdot 10^{-13} \cdot \exp(600/T)$
19	$HO_2 + HO_2 \rightarrow H_2O_2$	$4.94 \cdot 10^{-14} \cdot \exp(980/T)$
20	$NO + OH \rightarrow HONO$	$1.12 \cdot 10^{-11}$
21	$NO_2 + OH \rightarrow HNO_3$	$1.15 \cdot 10^{-11}$
22	$NO_3 + OH \rightarrow NO_2 + HO_2$	$2.00 \cdot 10^{-11}$
23	$NO + HO_2 \rightarrow NO_2 + OH$	$3.45 \cdot 10^{-12} \cdot \exp(270/T)$
24	$NO_2 + HO_2 \rightarrow HO_2NO_2$	$8.55 \cdot 10^{-13}$
25	$OH + HO_2NO_2 \rightarrow NO_2$	$3.20 \cdot 10^{-13} \cdot \exp(690/T)$
26	$NO_3 + HO_2 \rightarrow NO_2 + OH$	$4.00 \cdot 10^{-12}$
27	$OH + HONO \rightarrow NO_2$	$2.50 \cdot 10^{-12} \cdot \exp(260/T)$
28	$OH + HNO_3 \rightarrow NO_3$	$5.00 \cdot 10^{-3}$
29	$HNO_3 \rightarrow NA$	$6.00 \cdot 10^{-6}$
30	$N_2O_5 \rightarrow NA + NA$	$4.00 \cdot 10^{-4}$
31	$N_2O_5 \rightarrow NO_2 + NO_3$	$3.50 \cdot 10^{-3}$
32	$HO_2NO_2 \rightarrow NO_2 + HO_2$	$5.00 \cdot 10^{-3}$
Gas Phase Reactions Involving Organics		
34	O_3 + APINENE → OH + APINENE_RO_2^{I}	$0.85 \cdot 8.05 \cdot 10^{-16} \cdot e^{-640/T}$
35	O_3 + APINENE → APINENE_RO_2^{II}	$0.15 \cdot 8.05 \cdot 10^{-16} \cdot e^{-640/T}$
36	OH + APINENE → APINENE_RO_2^{II}	$1.2e^{-11} \cdot e^{440/T}$
37	NO_3 + APINENE → APINENE_RO_2^{III}	$1.2e^{-12} \cdot e^{490/T}$

38	$NO + APINENE\_RO_2^{I} \rightarrow NO_2 + APINENE\_RO^{I}$	$9.10 \cdot 10^{-12}$
39	$NO_3 + APINENE\_RO_2^{I} \rightarrow NO_2 + APINENE\_RO^{I}$	$2.30 \cdot 10^{-12}$
40	$HO_2 + APINENE\_RO_2^{I} \rightarrow APINENE\_org$	$2.20 \cdot 10^{-11}$
41	$NO + APINENE\_RO_2^{II} \rightarrow APINENE\_orgnitr^{1N}$	$9.10 \cdot 10^{-12}$
42	$NO + APINENE\_RO_2^{II} \rightarrow NO_2 + APINENE\_RO^{I}$	$9.10 \cdot 10^{-12}$
43	$NO_3 + APINENE\_RO_2^{II} \rightarrow NO_2 + APINENE\_RO^{I}$	$2.30 \cdot 10^{-12}$
44	$HO_2 + APINENE\_RO_2^{II} \rightarrow APINENE\_org$	$2.20 \cdot 10^{-11}$
45	$NO + APINENE\_RO_2^{III} \rightarrow NO_2 + APINENE\_RO^{II}$	$9.10 \cdot 10^{-12}$
46	$NO_3 + APINENE\_RO_2^{III} \rightarrow NO_2 + APINENE\_RO^{II}$	$2.30 \cdot 10^{-12}$
47	$HO_2 + APINENE\_RO_2^{III} \rightarrow APINENE\_orgnitr^{1N}$	$2.20 \cdot 10^{-11}$
48	$APINENE\_RO_2^{I} \rightarrow APINENE\_RO^{I}$	$[RO_2] \cdot (1-c_1) \cdot c_2 \cdot 10^{-13}$
49	$APINENE\_RO_2^{I} \rightarrow APINENE\_org$	$[RO_2] \cdot (1-c_1) \cdot (1-c_2) \cdot 10^{-13}$
50	$APINENE\_RO_2^{II} \rightarrow APINENE\_RO^{I}$	$[RO_2] \cdot (1-c_1) \cdot c_2 \cdot 10^{-14}$
51	$APINENE\_RO_2^{II} \rightarrow APINENE\_org$	$[RO_2] \cdot (1-c_1) \cdot (1-c_2) \cdot 10^{-14}$
52	$APINENE\_RO_2^{III} \rightarrow APINENE\_RO^{II}$	$[RO_2] \cdot (1-c_1) \cdot c_2 \cdot 10^{-14}$
53	$APINENE\_RO_2^{III} \rightarrow APINENE\_orgnitr^{1N}$	$[RO_2] \cdot (1-c_1) \cdot (1-c_2) \cdot 10^{-14}$
54	$APINENE\_RO^{I} \rightarrow HO_2 + APINENE\_org$	$c_{3\_apin} \cdot 10^{6}$
55	$APINENE\_RO^{I} \rightarrow APINENE\_RO_2II$	$(1- c_{3\_apin}) \cdot 10^{6}$
56	$APINENE\_RO^{II} \rightarrow NO_2 + APINENE\_org$	$c_{3\_apin} \cdot (1-c_{4\_apin}) \cdot 10^{6}$
57	$APINENE\_RO^{II} \rightarrow APINENE\_orgnitr^{1N}$	$c_{3\_apin} \cdot c_{4\_apin} \cdot 10^{6}$
58	$APINENE\_RO^{II} \rightarrow APINENE\_RO_2^{III}$	$(1-c_{3\_apin}) \cdot 10^{6}$
59	$APINENE\_RO_2^{I} \rightarrow APINENE\_dimer\_org$	$c_1 \cdot [RO_2] \cdot 10^{-13}$
60	$APINENE\_RO_2^{II} \rightarrow APINENE\_dimer\_org$	$c_1 \cdot [RO_2] \cdot 10^{-14}$
61	$APINENE\_RO_2^{III} \rightarrow APINENE\_dimer\_orgnitr^{1N}$	$c_1 \cdot [RO_2] \cdot 10^{-14}$
62	$O_3 + LIMONENE \rightarrow OH + LIMONENE\_RO_2^{I}$	$0.865 \cdot 2.80 \cdot 10^{-15} \cdot \exp(-770/T)$

63	O_3 + LIMONENE → LIMONENE_RO_2^{I}	$0.135 \cdot 2.80 \cdot 10^{-15} \cdot \exp(-770/T)$
64	OH + LIMONENE → LIMONENE_RO_2^{I}	$4.28 \cdot 10^{-11} \cdot \exp(401/T)$
65	NO_3 + LIMONENE → LIMONENE_RO_2^{II}	$1.22 \cdot 10^{-11}$
66	NO + LIMONENE_RO_2^{I} → LIMONENE_intermed_orgnitr^{1N}	$0.228 \cdot 2.70 \cdot 10^{-12} \cdot \exp(360/T)$
67	NO + LIMONENE_RO_2^{I} → NO_2 + LIMONENE_RO^{I}	$0.772 \cdot 2.70 \cdot 10^{-12} \cdot \exp(360/T)$
68	NO_3 + LIMONENE_RO_2^{I} → NO_2 + LIMONENE_RO^{I}	$2.30 \cdot 10^{-12}$
69	HO_2 + LIMONENE_RO_2^{I} → LIMONENE_intermed_org	$0.914 \cdot 2.91 \cdot 10^{-13} \cdot \exp(1300/T)$
70	NO + LIMONENE_RO_2^{II} → LIMONENE_intermed_orgnitr^{1N}	$0.228 \cdot 2.70 \cdot 10^{-12} \cdot \exp(360/T)$
71	NO + LIMONENE_RO_2^{II} → NO_2 + LIMONENE_RO^{II}	$0.772 \cdot 2.70 \cdot 10^{-12} \cdot \exp(360/T)$
72	NO_3 + LIMONENE_RO_2^{II} → NO_2 + LIMONENE_RO^{II}	$2.30 \cdot 10^{-12}$
73	HO_2 + LIMONENE_RO_2^{II} → LIMONENE_intermed_orgnitr^{1N}	$0.914 \cdot 2.91 \cdot 10^{-13} \cdot \exp(1300/T)$
74	LIMONENE_RO_2^{I} → LIMONENE_RO^{I}	$[RO_2] \cdot (1-c_1) \cdot c_2 \cdot 8.80 \cdot 10^{-13}$
75	LIMONENE_RO_2^{I} → LIMONENE_intermed_org	$[RO_2] \cdot (1-c_1) \cdot (1-c_2) \cdot 8.80 \cdot 10^{-13}$
76	LIMONENE_RO_2^{II} → LIMONENE_RO_^{II}	$[RO_2] \cdot (1-c_1) \cdot c_2 \cdot 9.20 \cdot 10^{-14}$
77	LIMONENE_RO_2^{II} → LIMONENE_intermed_orgnitr_^{1N}	$[RO_2] \cdot (1-c_1) \cdot (1-c_2) \cdot 9.20 \cdot 10^{-14}$
78	LIMONENE_RO^{I} → HO_2 + LIMONENE_intermed_org	$c_{3,lim} \cdot 10^{6}$
79	LIMONENE_RO^{I} → LIMONENE_RO_2^{II}	$(1-c_{3,lim}) \cdot 10^{6}$
80	LIMONENE_RO^{II} → NO_2 + LIMONENE_intermed_org	$c_{3,lim} \cdot 10^{6}$
81	LIMONENE_RO^{II} → LIMONENE_RO_2^{III}	$(1-c_{3,lim}) \cdot 10^{6}$
82	O_3 + LIMONENE_intermed_org → OH + LIMONENE_RO_2^{III}	$0.67 \cdot 8.30 \cdot 10^{-18}$
83	O_3 + LIMONENE_intermed_org → LIMONENE_RO_2^{III}	$0.33 \cdot 8.30 \cdot 10^{-18}$
84	OH + LIMONENE_intermed_org → LIMONENE_RO_2^{III}	$1.10 \cdot 10^{-10}$

85	NO_3 + LIMONENE_intermed_org → LIMONENE_RO_2^{IV}	$2.60 \cdot 10^{-13}$
86	O_3 + LIMONENE_intermed_orgnitr^{1N} → OH + LIMONENE_RO_2^{IV}	$0.67 \cdot 8.30 \cdot 10^{-18}$
87	O_3 + LIMONENE_intermed_orgnitr^{1N} → LIMONENE_RO_2^{IV}	$0.33 \cdot 8.30 \cdot 10^{-18}$
88	OH + LIMONENE_intermed_orgnit_^{1N} → LIMONENE_RO_2^{IV}	$1.10 \cdot 10^{-10}$
89	NO_3 + LIMONENE_intermed_orgnitr^{1N} → LIMONENE_RO2^{V}	$2.60 \cdot 10^{-13}$
90	HO_2 + LIMONENE_RO2^{III} → LIMONENE_org	$0.914 \cdot 2.91 \cdot 10^{-13} \cdot \exp(1300/T)$
91	NO_3 + LIMONENE_RO2^{III} → NO_2 + LIMONENE_RO^{III}	$2.30 \cdot 10^{-12}$
92	NO + LIMONENE_RO_2^{III} → NO_2 + LIMONENE_RO^{III}	$0.772 \cdot 2.70 \cdot 10^{-12} \cdot \exp(360/T)$
93	NO + LIMONENE_RO_2^{III} → LIMONENE_orgnitr^{1N}	$0.228 \cdot 2.70 \cdot 10^{-12} \cdot \exp(360/T)$
94	LIMONENE_RO_2^{III} → LIMONENE_RO^{III}	$[RO_2] \cdot (1-c_1) \cdot c_2 \cdot 9.20 \cdot 10^{-14}$
95	LIMONENE_RO_2^{III} → LIMONENE_org	$[RO_2] \cdot (1-c_1) \cdot (1-c_2) \cdot 9.20 \cdot 10^{-14}$
96	HO_2 + LIMONENE_RO_2^{IV} → LIMONENE_orgnitr^{1N}	$0.914 \cdot 2.91 \cdot 10^{-13} \cdot \exp(1300/T)$
97	NO_3 + LIMONENE_RO_2^{IV} → NO_2 + LIMONENE_RO^{IV}	$2.30 \cdot 10^{-12}$
98	NO + LIMONENE_RO_2^{IV} → NO_2 + LIMONENE_RO^{IV}	$2.70 \cdot 10^{-12} \cdot \exp(360/T)$
99	NO + LIMONENE_RO_2^{IV} → LIMONENE_orgnitr^{2N}	$2.70 \cdot 10^{-12} \cdot \exp(360/T)$
100	LIMONENE_RO_2^{IV} → LIMONENE_RO^{IV}	$[RO_2] \cdot (1-c_1) \cdot c_2 \cdot 9.20 \cdot 10^{-14}$
101	LIMONENE_RO_2^{IV} → LIMONENE_orgnitr^{1N}	$[RO_2] \cdot (1-c_1) \cdot (1-c_2) \cdot 9.20 \cdot 10^{-14}$
102	HO_2 + LIMONENE_RO_2^{V} → LIMONENE_orgnitr^{2N}	$0.914 \cdot 2.91 \cdot 10^{-13} \cdot \exp(1300/T)$
103	NO_3 + LIMONENE_RO_2^{V} → NO_2 + LIMONENE_RO^{V}	$2.30 \cdot 10^{-12}$
104	NO + LIMONENE_RO_2V → NO_2 + LIMONENE_RO^{V}	$2.70 \cdot 10^{-12} \cdot \exp(360/T)$
105	LIMONENE_RO2^{V} → LIMONENE_RO^{V}	$[RO_2] \cdot (1-c_1) \cdot c_2 \cdot 9.20 \cdot 10^{-14}$

106	$LIMONENE\_RO_2^{V} \rightarrow LIMONENE\_orgnitr^{2N}$	$[RO_2]\cdot(1-c_1)\cdot(1-c_2)\cdot 9.20\cdot 10^{-14}$
107	$LIMONENE\_RO^{III} \rightarrow HO_2 + LIMONENE\_org$	$c_{3,lim}\cdot 10^6$
108	$LIMONENE\_RO^{III} \rightarrow LIMONENE\_RO2^{III}$	$(1 - c_{3,lim})\cdot 10^6$
109	$LIMONENE\_RO^{IV} \rightarrow NO2 + LIMONENE\_org$	$c_{3,lim}\cdot(1 - c_{4,lim})\cdot 10^6$
110	$LIMONENE\_RO^{IV} \rightarrow LIMONENE\_orgnitr^{1N}$	$c_{3,lim}\cdot c_{4,lim}\cdot 10^6$
111	$LIMONENE\_RO^{IV} \rightarrow LIMONENE\_RO2^{IV}$	$(1-c_{3,lim})\cdot 10^6$
112	$LIMONENE\_RO^{V} \rightarrow NO_2 + LIMONENE\_orgnitr^{1N}$	$c_{3,lim}\cdot(1 - c_{4,lim})\cdot 10^6$
113	$LIMONENE\_RO^{V} \rightarrow LIMONENE\_orgnitr^{2N}$	$c_{3,lim}\cdot c_{4,lim}\cdot 10^6$
114	$LIMONENE\_RO^{V} \rightarrow LIMONENE\_RO2^{V}$	$(1- c_{3,lim})\cdot 10^6$
115	$LIMONENE\_RO_2^{I} \rightarrow LIMONENE\_dimer\_org$	$c_1\cdot[RO_2]\cdot 9.20\cdot 10^{-14}$
116	$LIMONENE\_RO_2^{II} \rightarrow LIMONENE\_dimer\_orgnitr^{1N}$	$c_1\cdot[RO_2]\cdot 9.20\cdot 10^{-14}$
117	$LIMONENE\_RO_2^{III} \rightarrow LIMONENE\_dimer\_org$	$c_1\cdot[RO_2]\cdot 9.20\cdot 10^{-14}$
118	$LIMONENE\_RO_2^{IV} \rightarrow LIMONENE\_dimer\_orgnitr^{1N}$	$c_1\cdot[RO_2]\cdot 9.20\cdot 10^{-14}$
119	$LIMONENE\_RO_2^{V} \rightarrow LIMONENE\_dimer\_orgnitr^{2N}$	$c_1\cdot[RO_2]\cdot 9.20\cdot 10^{-14}$
Particle Phase Reactions		
120	$LIMONENE\_intermed\_org \rightarrow LIMONENE\_olig\_intermed\_org$	$k_{form,lim}\cdot(1-f_{oligomer}/2)$
121	$LIMONENE\_intermed\_orgnitr^{1N} \rightarrow LIMONENE\_olig\_intermed\_orgnitr^{1N}$	$k_{form,lim}\cdot(1-f_{oligomer}/2)$
122	$APINENE\_org \rightarrow APINENE\_olig\_org$	$k_{form,apin}\cdot(1-f_{oligomer}/2)$
123	$APINENE\_orgnitr\_^{1N} \rightarrow APINENE\_olig\_orgnitr^{1N}$	$k_{form,apin}\cdot(1-f_{oligomer}/2)$
124	$APINENE\_olig\_org \rightarrow APINENE\_org$	$k_{decom\_apin}\cdot \exp(TF_{apin}/T)$
125	$APINENE\_olig\_orgnitr^{1N} \rightarrow APINENE\_orgnitr^{1N}$	$k_{decom\_apin}\cdot \exp(TF_{apin}/T)$
126	$LIMONENE\_org \rightarrow LIMONENE\_olig\_org$	$k_{form,lim}\cdot(1-f_{oligomer}/2)$
127	$LIMONENE\_orgnitr^{1N} \rightarrow LIMONENE\_olig\_orgnitr^{1N}$	$k_{form,lim}\cdot(1-f_{oligomer}/2)$

128	LIMONENE_orgnitr^{2N} → LIMONENE_olig_orgnitr^{2N}	$k_{form,lim}\cdot(1-f_{oligomer}/2)$
129	LIMONENE_olig_org → LIMONENE_org	$k_{decom\_lim}\cdot exp(TF_{lim}/T)$
130	LIMONENE_olig_orgnitr^{1N} → LIMONENE_orgnitr^{1N}	$k_{decom\_lim}\cdot exp(TF_{lim}/T)$
131	LIMONENE_olig_orgnitr^{2N} → LIMONENE_orgnitr^{2N}	$k_{decom\_lim}\cdot exp(TF_{lim}/T)$
132	LIMONENE_olig_intermed_org → LIMONENE_intermed_org	$k_{decom\_lim}\cdot exp(TF_{lim}/T)$
133	LIMONENE_olig_intermed_orgnitr^{1N} → LIMONENE_intermed_orgnitr^{1N}	$k_{decom\_lim}\cdot exp(TF_{lim}/T)$

Table S2. Comparison of fit parameters of the kinetic model between default fit 1 and alternative fit 2. Error estimates are ranges in which a parameter can be varied until the model-experiment correlation decreases by 10 %.

Parameter	Value of fit 1	Value of fit 2	Description
$l_{\mathrm{w,i}}$	1.20 (0.97 – 1.51) × 10^{-4}	8.80 (7.18 – 11.5) × 10^{-5}	Transport rate in Teflon wall / irreversible loss rate (s^{-1})
$\Delta H_{\mathrm{vap,apin}}$	81.3 (66.2 – 96.5)	59.1 (49.5 – 67.8)	Effective enthalpy of vaporization of α-pinene SOA products (kJ/mol)
$\Delta H_{\mathrm{vap,lim}}$	164 (159 - 168)	133 (130 – 137)	Effective enthalpy of vaporization of limonene SOA products (kJ/mol)
C^*_{IM1}	5.5 (0.89 - ∞) × 10^5	3.5 (0.84 - ∞) × 10^5	Saturation mass concentration, non-nitrated limonene SOA intermediate at 298 K (μg/m^3)
C^*_{IM2}	7.43 (5.49 – 10.4) × 10^3	3.85 (3.33 – 4.57) × 10^3	Saturation mass concentration, nitrated limonene SOA intermediate at 298 K (μg/m^3)
c_1	1.96 (1.67 – 2.24) × 10^{-2}	1.80 (1.32 – 2.19) × 10^{-2}	Branching ratio, gas-phase dimer yield from RO_2 + RO_2
c_2	0.414 (0.381 – 0.451)	5.72 (1.52 – 10.9) × 10^{-2}	Branching ratio, RO yield from RO_2 + RO_2
$c_{3,\mathrm{apin}}$	5.93 (5.24 – 6.56) × 10^{-2}	7.98 (7.18 – 8.80) × 10^{-2}	Branching ratio, product yield from RO, α-pinene
$c_{3,\mathrm{lim}}$	0.337 (0.236 – 0.478)	0.690 (0.557 – 0.825)	Branching ratio, product yield from RO, limonene
$c_{4,\mathrm{apin}}$	0 (0 – 0.091)	0 (0 – 0.087)	Product ratio of non-nitrated to nitrate ratio species from RO, α-pinene
$c_{4,\mathrm{lim}}$	0.523 (0.303 – 0.730)	0.217 (0.126 – 0.307)	Product ratio of non-nitrated to nitrate ratio species from RO, limonene
$k_{\mathrm{form,apin}}$	0.124 (0 – 0.410)	9.0 (7.0 – 10.4)	Oligomerization rate coefficient, α-pinene (h^{-1})
$k_{\mathrm{form,lim}}$	17.2 (15.5 – 18.9)	7.2 (6.5 – 7.8)	Oligomerization rate coefficient, limonene (h^{-1})

$k_{\mathrm{decom,apin}}$	19.0 (7.45 – ∞)	5.8 (5.0 – 7.4)	Oligomer decomposition rate coefficient, α-pinene (h^{-1})
$k_{\mathrm{decom,lim}}$	9.0 (7.9 – 10) × 10^{-2}	8.0 (9.0 – 10.0) × 10^{-2}	Oligomer decomposition rate coefficient, limonene (h^{-1})
$E_{\mathrm{A,decom,apin}}$	795 (0 – 1077)	457 (376 - 501)	Activation energy of oligomer decomposition, α-pinene (kJ/mol)
$E_{\mathrm{A,decom,lim}}$	142 (112-180)	202 (170 – 237)	Activation energy of oligomer decomposition, limonene (kJ/mol)