

Supplement

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Table S1: SOA data compiled from published chamber studies for photooxidation and ozonolysis of α -pinene and limonene.

Condition	T (K)	[O ₃] _o (ppb)	NO _x (ppb)	[HC] _o (ppb)	Δ HC ($\mu\text{g m}^{-3}$)	SOA mass ($\mu\text{g m}^{-3}$)	SOA yield	Reference
α -Pinene photooxidation	312-306		230	150	804.6	44.0	0.06	Kim and Paulson (2013)
α -Pinene photooxidation	310-312-306		110	152	788.8	103.0	0.14	Kim and Paulson (2013)
α -Pinene photooxidation	306-309		50	142	743.9	107.0	0.16	Kim and Paulson (2013)
α -Pinene photooxidation	312-319-315		47	153	683.0	118.0	0.17	Kim and Paulson (2013)
α -Pinene photooxidation	300			51	260.0	46.0	0.18	Mcvay et al. (2016)
α -Pinene photooxidation	300			56	280.0	65.0	0.23	Mcvay et al. (2016)
α -Pinene photooxidation	300			53	240.0	52.0	0.22	Mcvay et al. (2016)
α -Pinene photooxidation	298			51	268.0	72.0	0.27	Mcvay et al. (2016)
α -Pinene photooxidation	297			53	205.0	35.0	0.17	Mcvay et al. (2016)
α -Pinene photooxidation	297			49	195.0	47.0	0.24	Mcvay et al. (2016)
α -Pinene photooxidation	293				616.6	199.0	0.32	Lee et al. (2006b)
α -Pinene photooxidation	298	0			76.8	29.3	0.38	Ng et al. (2007)
α -Pinene photooxidation	298	1			264.2	121.3	0.46	Ng et al. (2007)
α -Pinene photooxidation	296	198			73.4	15.6	0.21	Ng et al. (2007)
α -Pinene photooxidation	299	938			69.8	4.5	0.06	Ng et al. (2007)
α -Pinene photooxidation	298	968			259.2	40.8	0.16	Ng et al. (2007)
α -Pinene photooxidation		0			259.9	63.9	0.25	Chhabra et al. (2011)
α -Pinene photooxidation		400			265.6	53.7	0.20	Chhabra et al. (2011)
Limonene photooxidation	310-305	300	208		1110.4	96-287	0.35	Kim and Paulson (2013)
Limonene photooxidation	309-313	98	140		735.5	34-195	0.35	Kim and Paulson (2013)
Limonene photooxidation	297-299	120	157		801.0	32-214	0.37	Kim and Paulson (2013)
Limonene photooxidation	311-315	41	130		680.0	11-219	0.43	Kim and Paulson (2013)
Limonene photooxidation	308-312-307	39	130		690.6	14-275	0.47	Kim and Paulson (2013)
Limonene photooxidation	313.4	105			109.0	9.5	0.09	Griffin et al. (1999)
Limonene photooxidation	313.4	80.2			186.2	49.6	0.27	Griffin et al. (1999)
Limonene photooxidation	309.4	139			265.2	79.1	0.30	Griffin et al. (1999)
Limonene photooxidation	309.4	140			348.8	120.2	0.34	Griffin et al. (1999)
Limonene photooxidation	294				676.5	394.0	0.58	Lee et al. (2006b)
α -Pinene ozonolysis	299-300	500		143	592.2	28-230	0.46	Kim and Paulson (2013)
α -Pinene ozonolysis	296-299	500		150	724.3	39-271	0.44	Kim and Paulson (2013)
α -Pinene ozonolysis	296-301	500		170	866.2	37-271	0.40	Kim and Paulson (2013)
α -Pinene ozonolysis	296-295	500		160	897.5	71-349	0.45	Kim and Paulson (2013)
α -Pinene ozonolysis	291-293	500		126	669.8	34-215	0.39	Kim and Paulson (2013)
α -Pinene ozonolysis		200		49.5	282.0	42.3	0.15	Kourtchev et al. (2014)
α -Pinene ozonolysis		200		50.5	312.5	50.0	0.16	Kourtchev et al. (2014)
α -Pinene ozonolysis		200		55.2	349.4	55.9	0.16	Kourtchev et al. (2014)

α -Pinene ozonolysis	298	100	290.2 \pm 23.2	278.1	62.0 \pm 1.2	0.23	Nah et al. (2016)
α -Pinene ozonolysis	298	100	280.5 \pm 22.4	267.0	63.0 \pm 0.8	0.23	Nah et al. (2016)
α -Pinene ozonolysis	298	100	238.7 \pm 19.1	222.5	50.6 \pm 1.6	0.23	Nah et al. (2016)
α -Pinene ozonolysis	298	500	274 \pm 21.9	278.1	87.3 \pm 0.3	0.32	Nah et al. (2016)
α -Pinene ozonolysis	298	500	264 \pm 21.2	261.4	75.7 \pm 0.6	0.29	Nah et al. (2016)
α -Pinene ozonolysis	298	500	236.1 \pm 18.9	239.2	66.3 \pm 1.9	0.28	Nah et al. (2016)
α -Pinene ozonolysis	309.9			89.3	7.4	0.08	Griffin et al. (1999)
α -Pinene ozonolysis	309.9			97.3	8.5	0.09	Griffin et al. (1999)
α -Pinene ozonolysis	303.3			169.4	30.3	0.18	Griffin et al. (1999)
α -Pinene ozonolysis	303.3			248.7	46.0	0.18	Griffin et al. (1999)
α -Pinene ozonolysis	308			306.7	52.3	0.17	Griffin et al. (1999)
α -Pinene ozonolysis	308			349.8	65.1	0.19	Griffin et al. (1999)
α -Pinene ozonolysis	308	237	59.2	306.7	54.2	0.18	Yu et al. (1999)
α -Pinene ozonolysis	308	269	67.2	350.3	65.1	0.19	Yu et al. (1999)
α -Pinene ozonolysis	306	74	107.1	244.3	38.8	0.16	Yu et al. (1999)
α -Pinene ozonolysis	293			1052.2	417.0	0.41	Lee et al. (2006a)
α -Pinene ozonolysis	298.15 \pm 12	300		126.8	35.6	0.28	Chen et al. (2011)
α -Pinene ozonolysis	298.15 \pm 13	300		11.7	1.2	0.10	Chen et al. (2011)
α -Pinene ozonolysis	298.15 \pm 14	300		15.6	1.9	0.12	Chen et al. (2011)
α -Pinene ozonolysis	298.15 \pm 15	300		78.9	15.4	0.20	Chen et al. (2011)
α -Pinene ozonolysis	298.15 \pm 16	300		506.5	95.2	0.19	Chen et al. (2011)
α -Pinene ozonolysis	298.15 \pm 17	300		506.5	138.0	0.27	Chen et al. (2011)
α -Pinene ozonolysis	298.15 \pm 18	300		36.7	7.0	0.19	Chen et al. (2011)
α -Pinene ozonolysis	298.15 \pm 19	300		5.0	0.5	0.10	Chen et al. (2011)
α -Pinene ozonolysis		0		278.1	62.0	0.22	Chhabra et al. (2011)
Limonene ozonolysis	298-300	500	167	925.8	579.0	0.78	Kim and Paulson (2013)
Limonene ozonolysis	293-295	500	198	1116.3	614.0	0.72	Kim and Paulson (2013)
Limonene ozonolysis	294-296	500	150	842.8	454.0	0.72	Kim and Paulson (2013)
Limonene ozonolysis	295-296	69.7	33.7	154	257.0	0.49	Chen et al. (2017)
Limonene ozonolysis	295-296	71	35.2	150	269.0	0.51	Chen et al. (2017)
Limonene ozonolysis	295-297	72.1	58.9	158	220.0	0.73	Chen et al. (2017)
Limonene ozonolysis	296-297	70.3	62.4	153	228.0	0.72	Chen et al. (2017)
Limonene ozonolysis	296-297	1.1	67.1	155	144.0	0.27	Chen et al. (2017)
Limonene ozonolysis	295-296	0.9	68.2	159	138.0	0.30	Chen et al. (2017)

Table S2: Normalized emission factor (EF) for model surrogates representing top five monoterpenes (by EF) from black spruce, Douglas fir, and lodgepole pine (Hatch et al., 2015, 2017). In Assignment 1, α -pinene is used to represent all monoterpenes except limonene. In Assignment 2, camphene is represented as 50 % α -pinene and 50 % limonene. EFs of assignments 1 and 2 for lodgepole pine are the same, because camphene is not one of the top five monoterpenes by EF.

	Black Spruce		Douglas Fir		Lodgepole Pine	
	EF _{αpin}	EF _{lim}	EF _{αpin}	EF _{lim}	EF _{αpin}	EF _{lim}
Assignment 1	0.81	0.19	0.8	0.2	0.86	0.14
Assignment 2	0.62	0.38	0.6	0.4	0.86	0.14

Table S3: Two-product SOA yield parameters for α -pinene and limonene based on Griffin et al. (1999).

2-product				
	α_1	α_2	C* ₁	C* ₂
α -pinene	0.038	0.326	5.8	250.0
limonene	0.239	0.363	18.2	188.7

Table S4: Volatility basis set (VBS) parameters (low NO_x, dry) based on Pathak et al. (2007b) (for α -pinene) and Zhang et al. (2006) (for limonene).

VBS (low NO _x)					
C*	0	1	10	100	1000
α -pinene	-	0.07	0.038	0.179	0.3
limonene	0.03	0.29	0.31	0.3	0.6

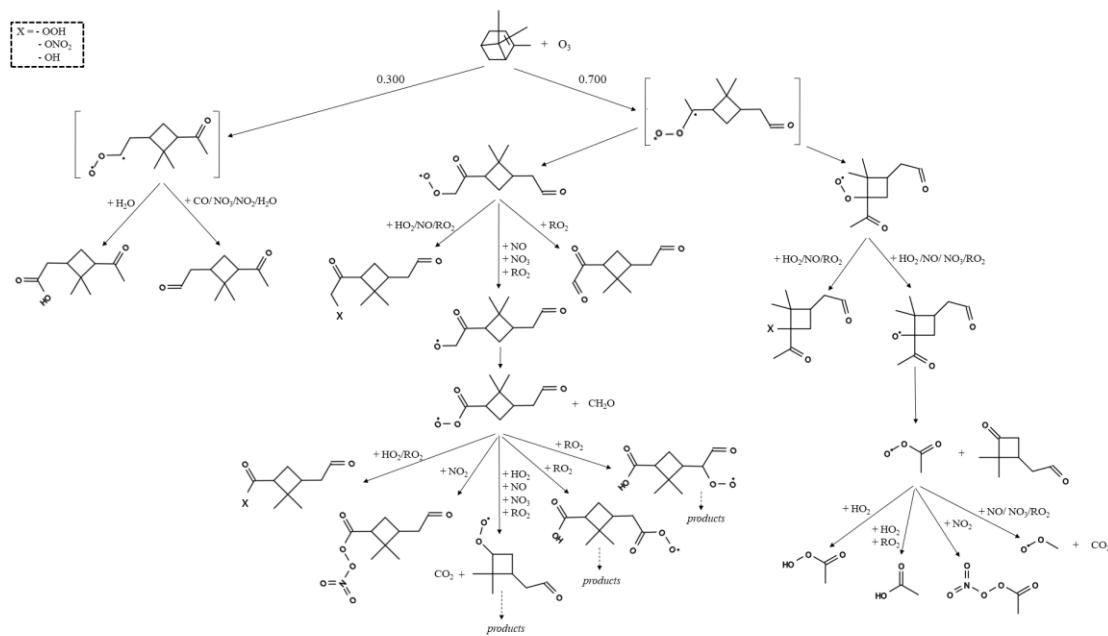


Figure S1: Initial oxidation pathways of α -pinene with O_3 as represented in GECKO-A.

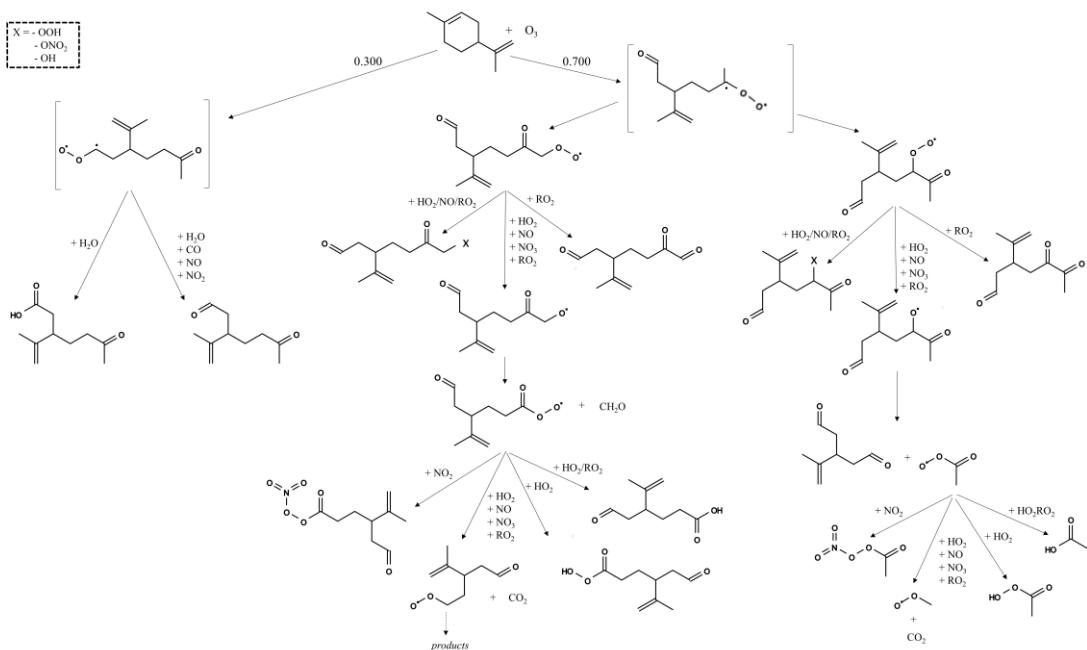


Figure S2: Initial oxidation pathways of limonene with O_3 as represented in GECKO-A.

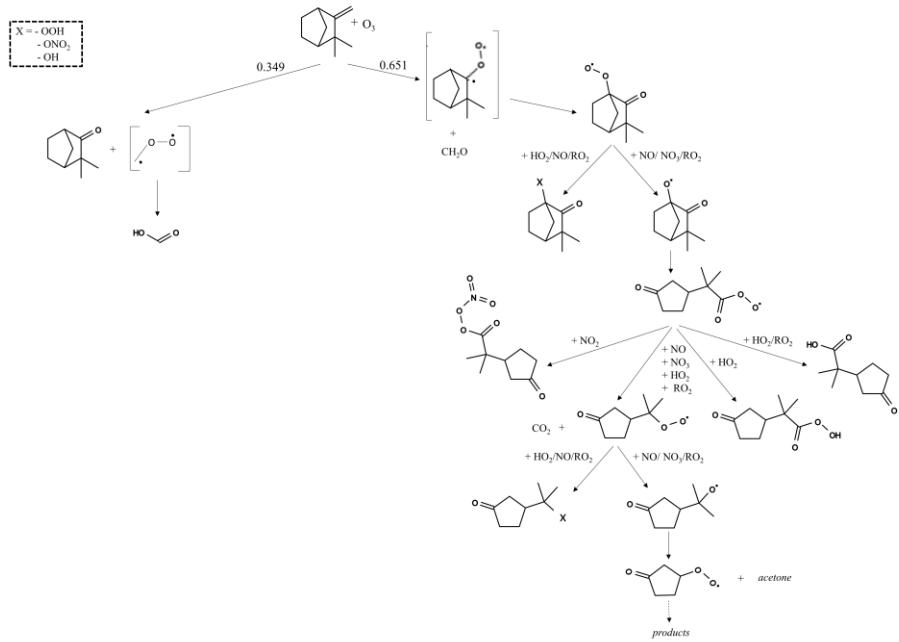


Figure S3: Initial oxidation pathways of camphene with O_3 as represented in GECKO-A.

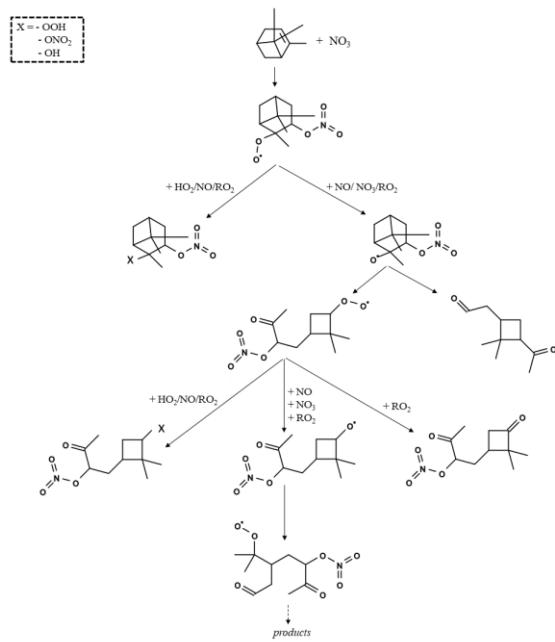


Figure S4: Initial oxidation pathways of α -pinene with NO_3 as represented in GECKO-A.

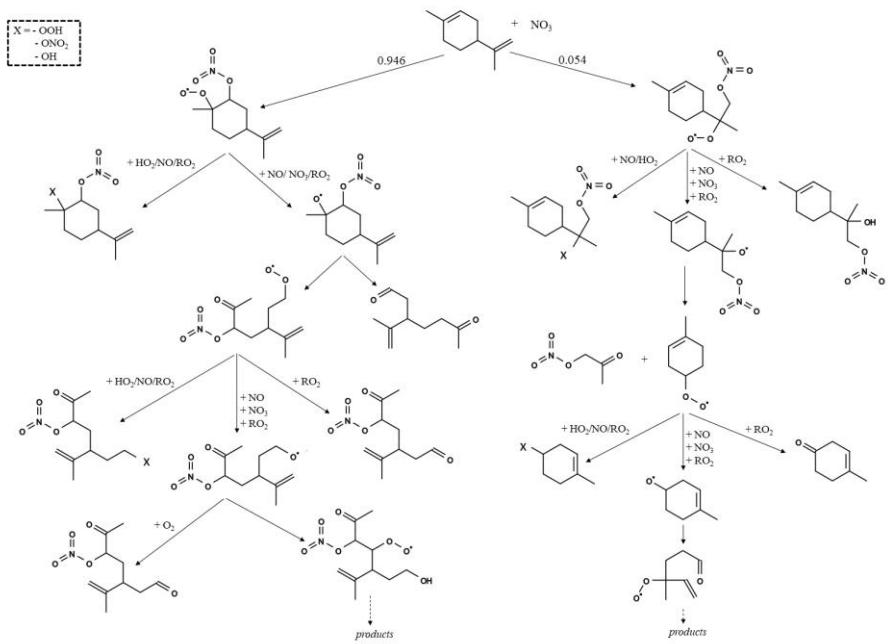


Figure S5: Initial oxidation pathways of limonene with NO_3 as represented in GECKO-A.

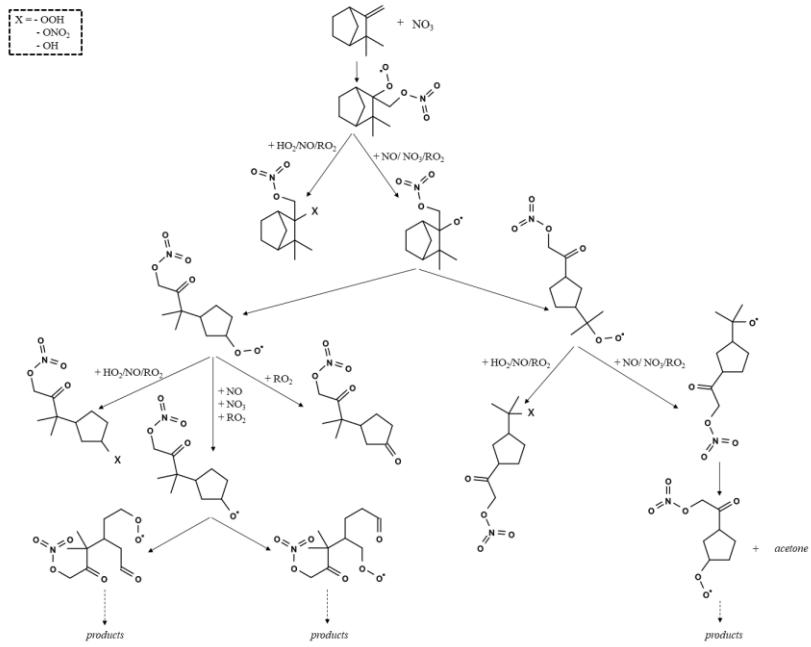


Figure S6: Initial oxidation pathways of camphene with NO_3 as represented in GECKO-A.

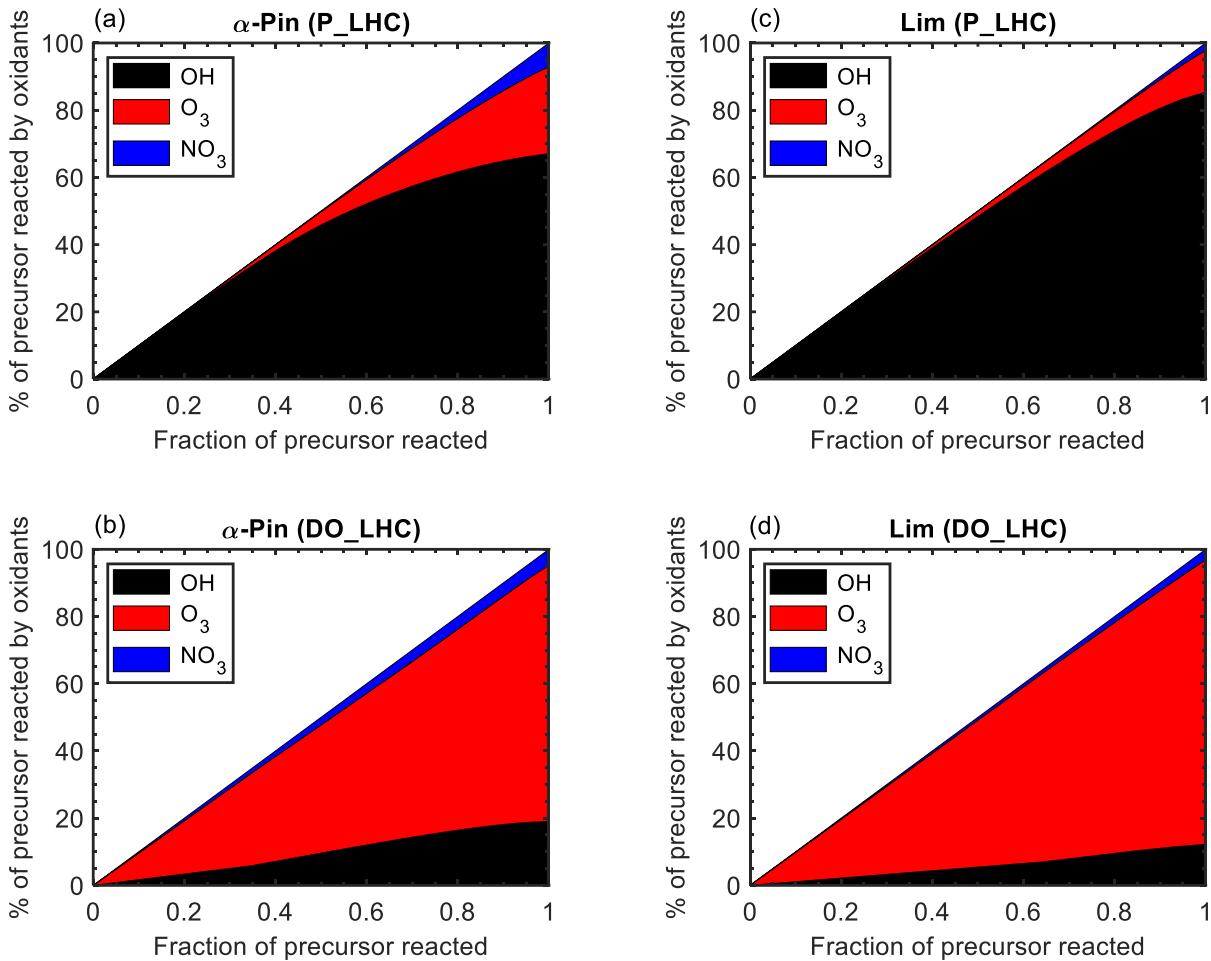


Figure S7: Percentage of precursor consumed by OH (black), O₃ (red), and NO₃ (blue) as a function of fraction of precursor reacted for α -pinene and limonene under photooxidation and ozonolysis (for lower initial precursor mixing ratio of 50 ppb).

Figure S7 shows the percentage of the simulated precursor consumption by the three main oxidants: hydroxyl radical (OH), ozone (O₃), and nitrate radical (NO₃). Under photooxidation, both α -pinene and limonene initially react predominantly with OH. As the reaction progresses (after $\sim 30\%$ of the precursor is reacted), removal of the precursor by O₃ and NO₃ begins to grow until the precursor is completely reacted. The results in Fig. S7a indicate that $\sim 67\%$ of α -pinene is removed by OH, 25 % by O₃, and $\sim 8\%$ by NO₃; similarly, as shown in Fig. S7c 85% of limonene is removed by OH, 12% by O₃ and 3 % by NO₃ during photooxidation. For α -pinene ozonolysis, the consumption is largely by O₃ ($\sim 75\%$) and OH($\sim 20\%$), to a lesser extent by NO₃; ($\sim 5\%$); for limonene, consumption is dominated by O₃ ($\sim 85\%$), followed by OH ($\sim 10\%$), and NO₃ ($\sim 5\%$). Unlike in many chamber experiments, there is no OH scrubber in the simulations. Also, as NO₃ is formed by reaction of O₃ with NO₂ during the dark ozonolysis simulation, a small percentage of the precursor reacts with NO₃ since no light is available to photolyze the NO₃.

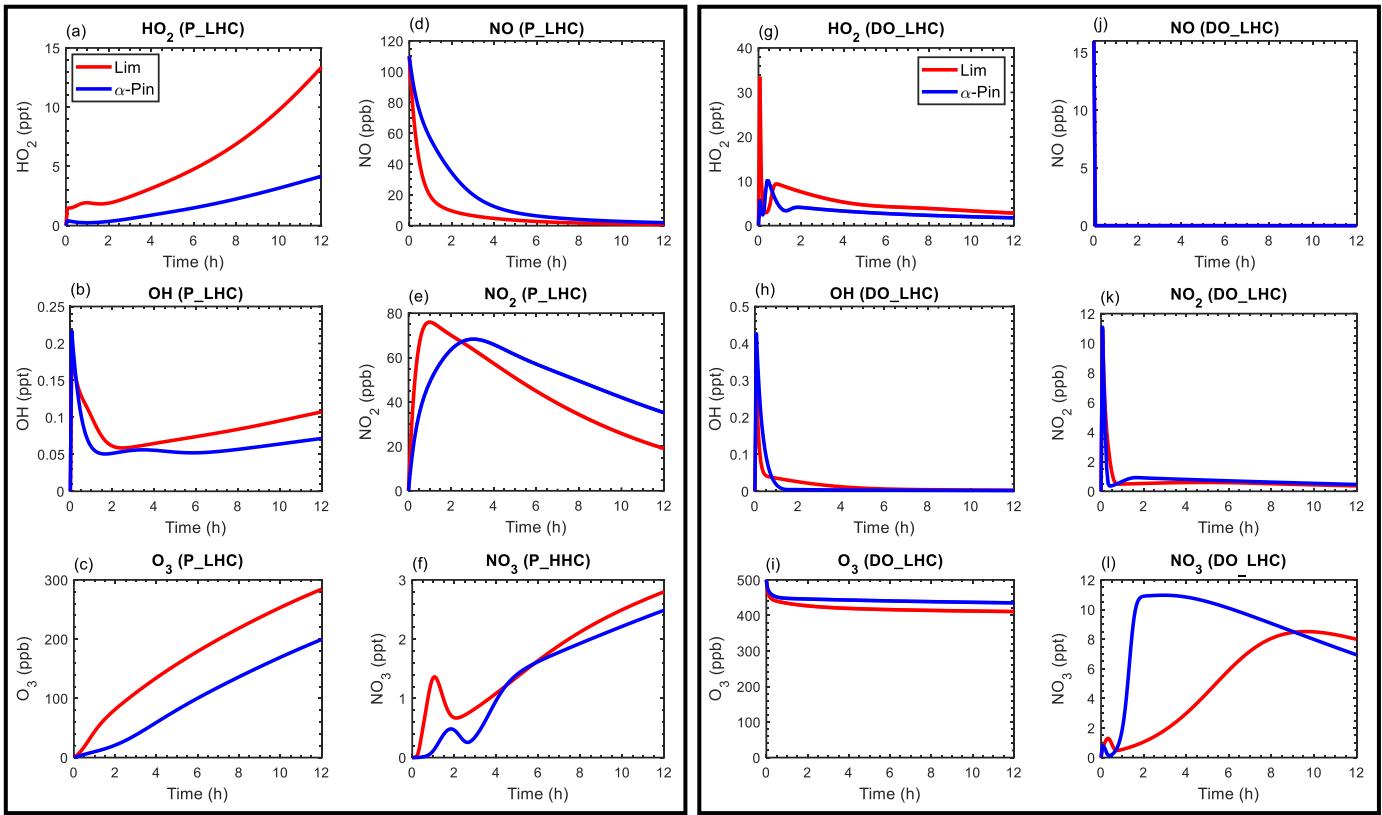


Figure S8: The mixing ratios of HO₂, OH, O₃, NO, NO₂, and NO₃ as a function of time for α -pinene (blue line) and limonene (red line) (with the low initial hydrocarbon (LHC) mixing ratio of 50 ppb) during photooxidation (P) and dark ozonolysis (DO) simulations.

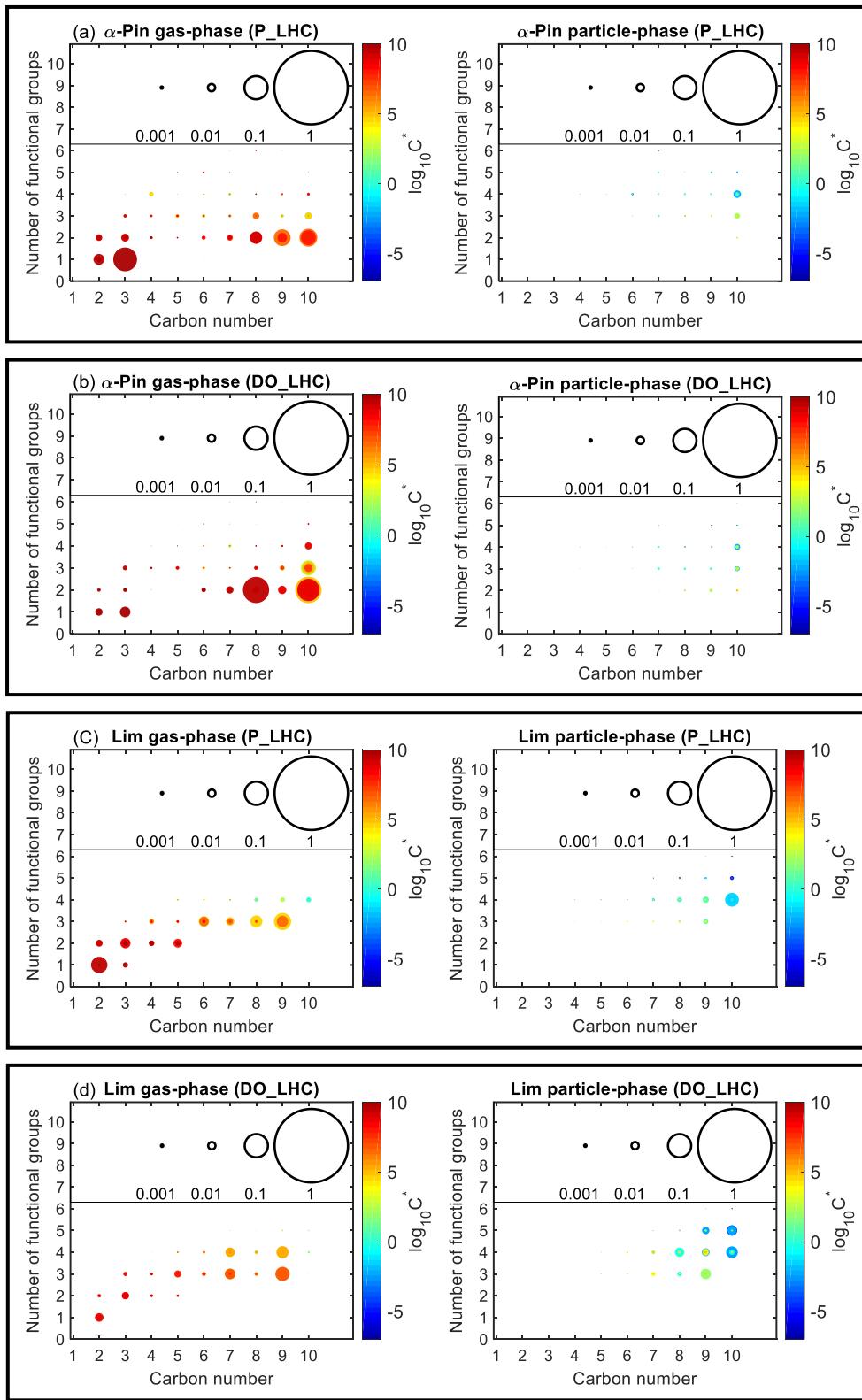


Figure S9: Number of functional groups associated with gas- and particle-phase species as a function of carbon number. Results are shown for camphene, α -pinene, and limonene after 12 hours of oxidation under photooxidation (P) and dark ozonolysis (DO) with lower hydrocarbon (LHC) mixing ratio of 50 ppb. The markers are sized by the ratio of their mixing ratio (in ppbC) to the initial mixing ratio of the precursor (in ppbC). The colors of the markers are scaled by volatility (represented by saturation concentration, C^*).

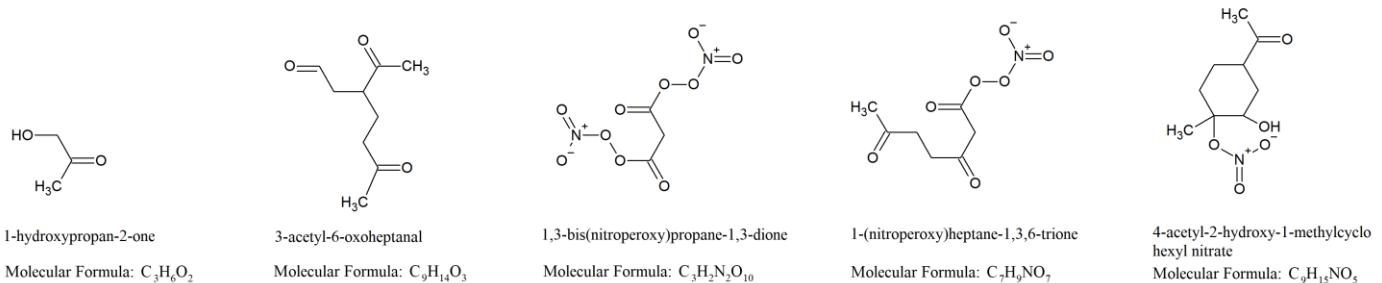
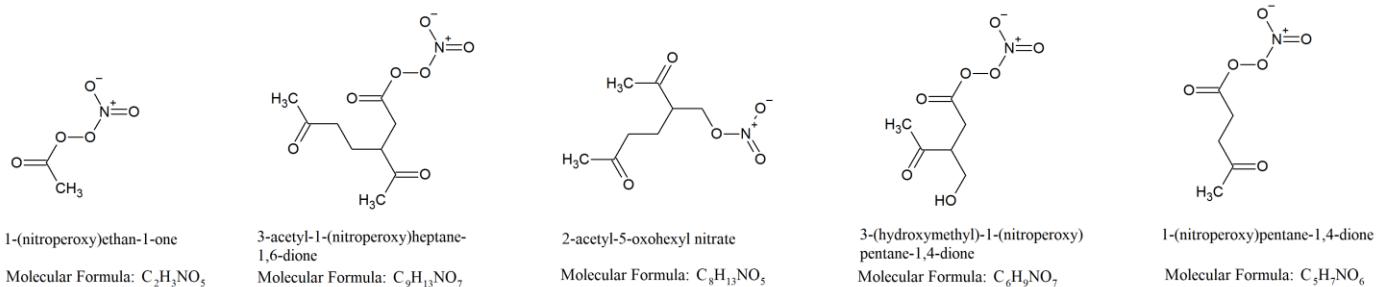


Figure S10: Top 10 gas-phase products from limonene photooxidation low hydrocarbon (P_LHC) simulation.

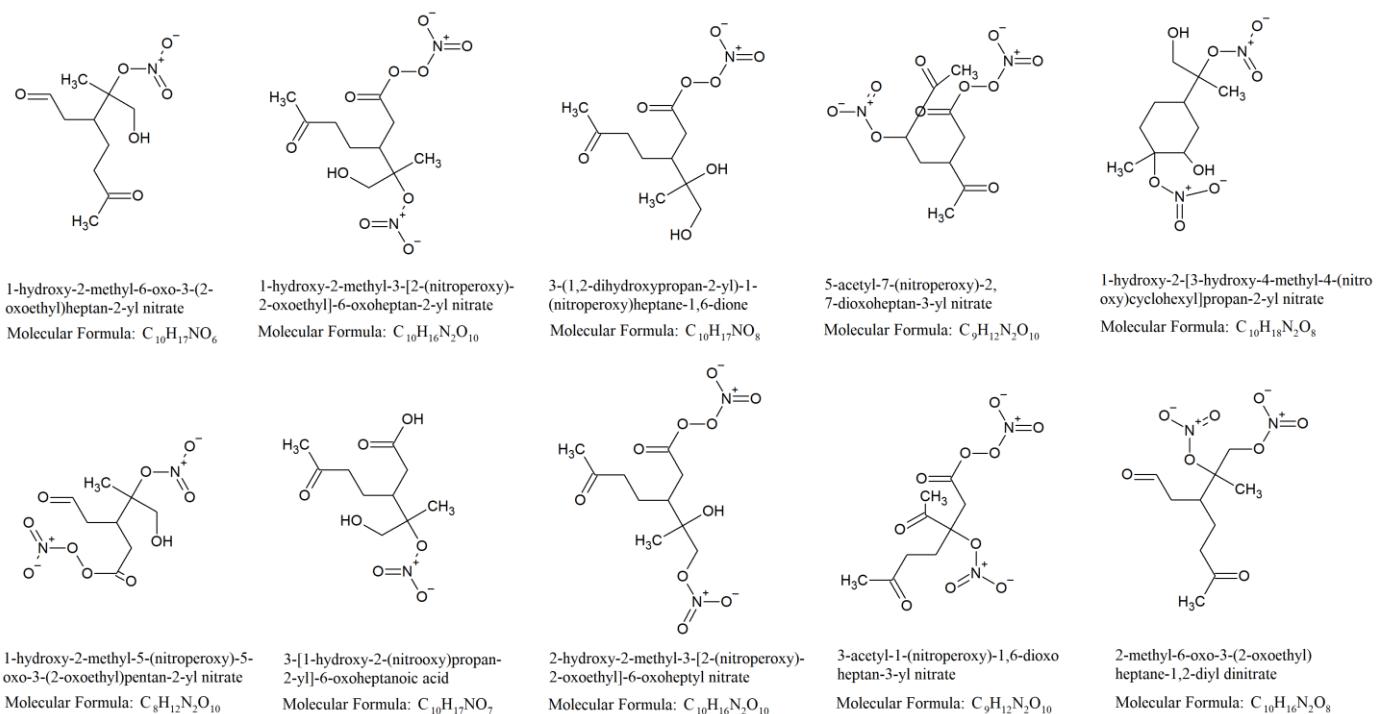


Figure S11: Top 10 particle-phase products from limonene photooxidation low hydrocarbon (P_LHC) simulation.

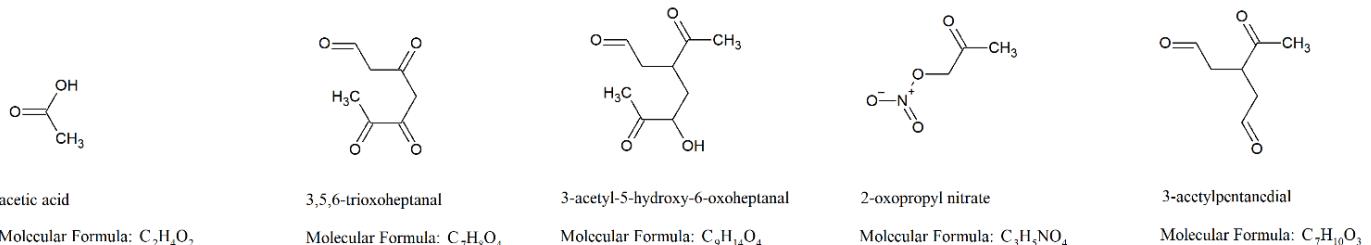
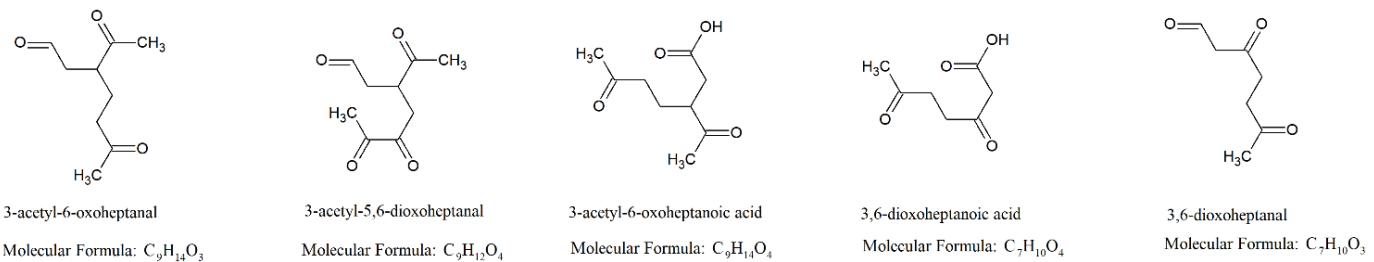


Figure S12: Top 10 gas-phase products from limonene dark ozonolysis low hydrocarbon (DO_LHC) simulation.

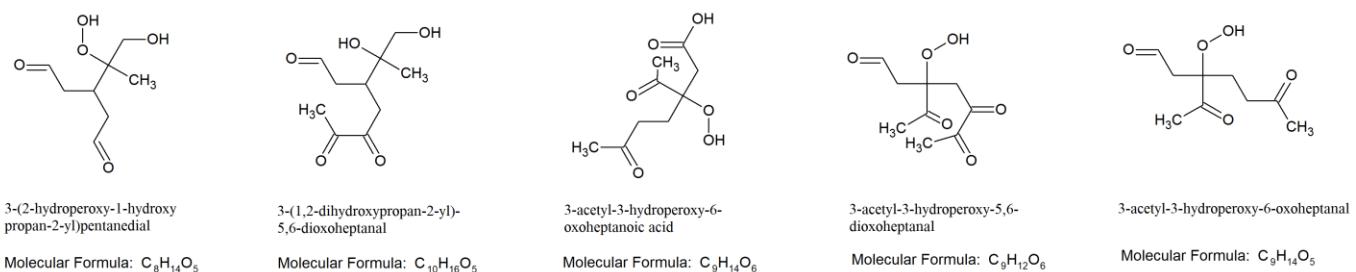
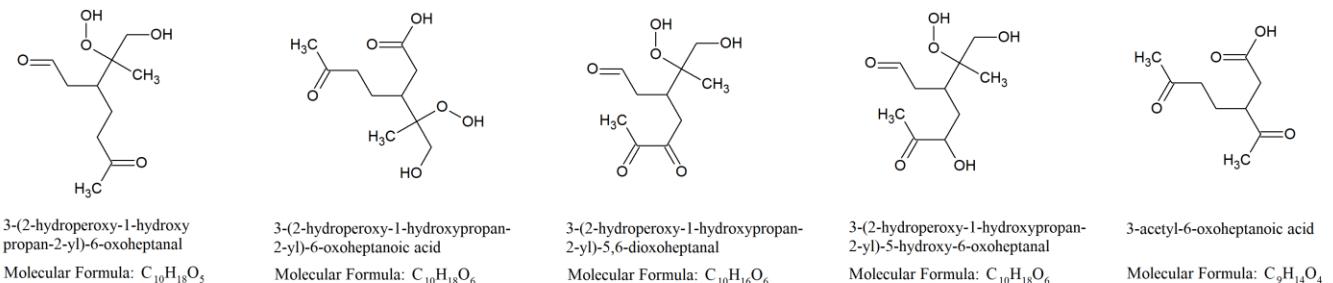


Figure S13: Top 10 particle-phase products from limonene dark ozonolysis low hydrocarbon (DO_LHC) simulation.

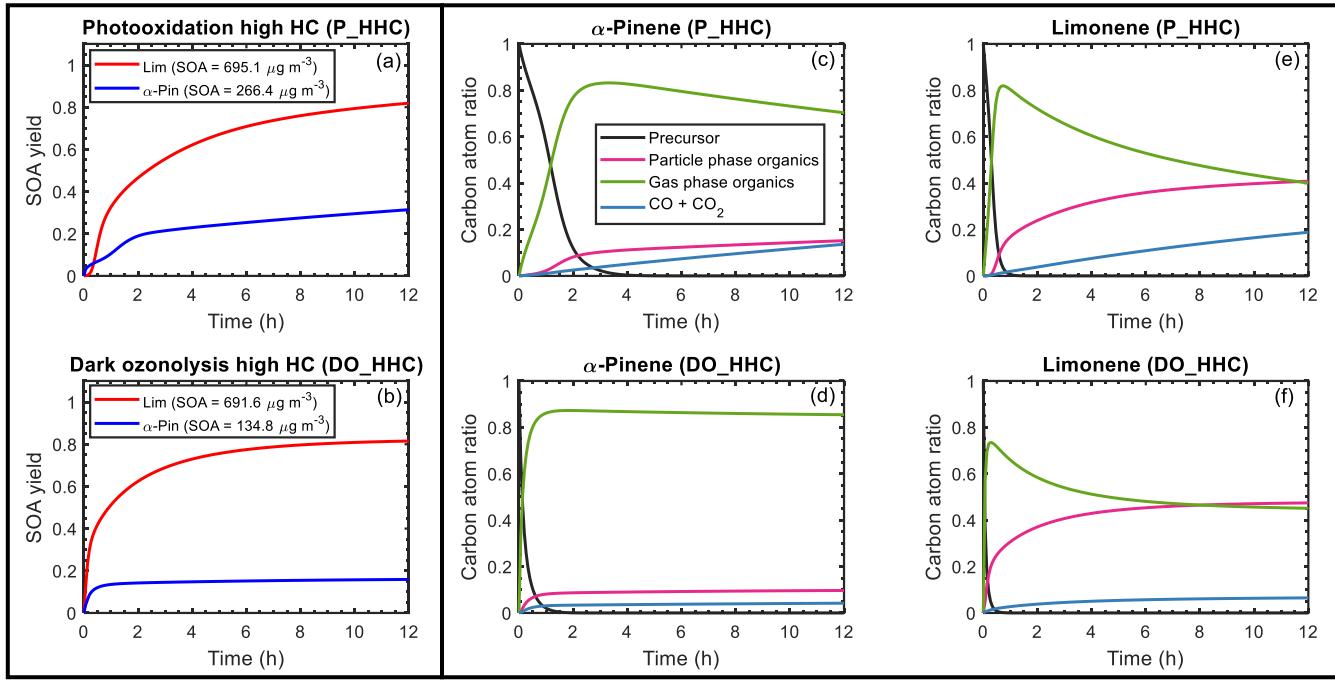


Figure S14: Simulated SOA yield as a function of time (a and b) and carbon budget (c to f) for α -pinene and limonene during photooxidation (a, c, e) and dark ozonolysis (b, d, f). The SOA yield curve for α -pinene is represented by a blue line; limonene is represented by a red line. For the carbon budget plots, the mixing ratios of the precursor (black line), particle-phase organics (magenta line), gas-phase organics (green line), and CO+CO₂ (blue line) are expressed as carbon atom ratios (in ppbC)/initial precursor (in ppbC). The results shown are for the high hydrocarbon mixing ratio (150 ppb) simulations.

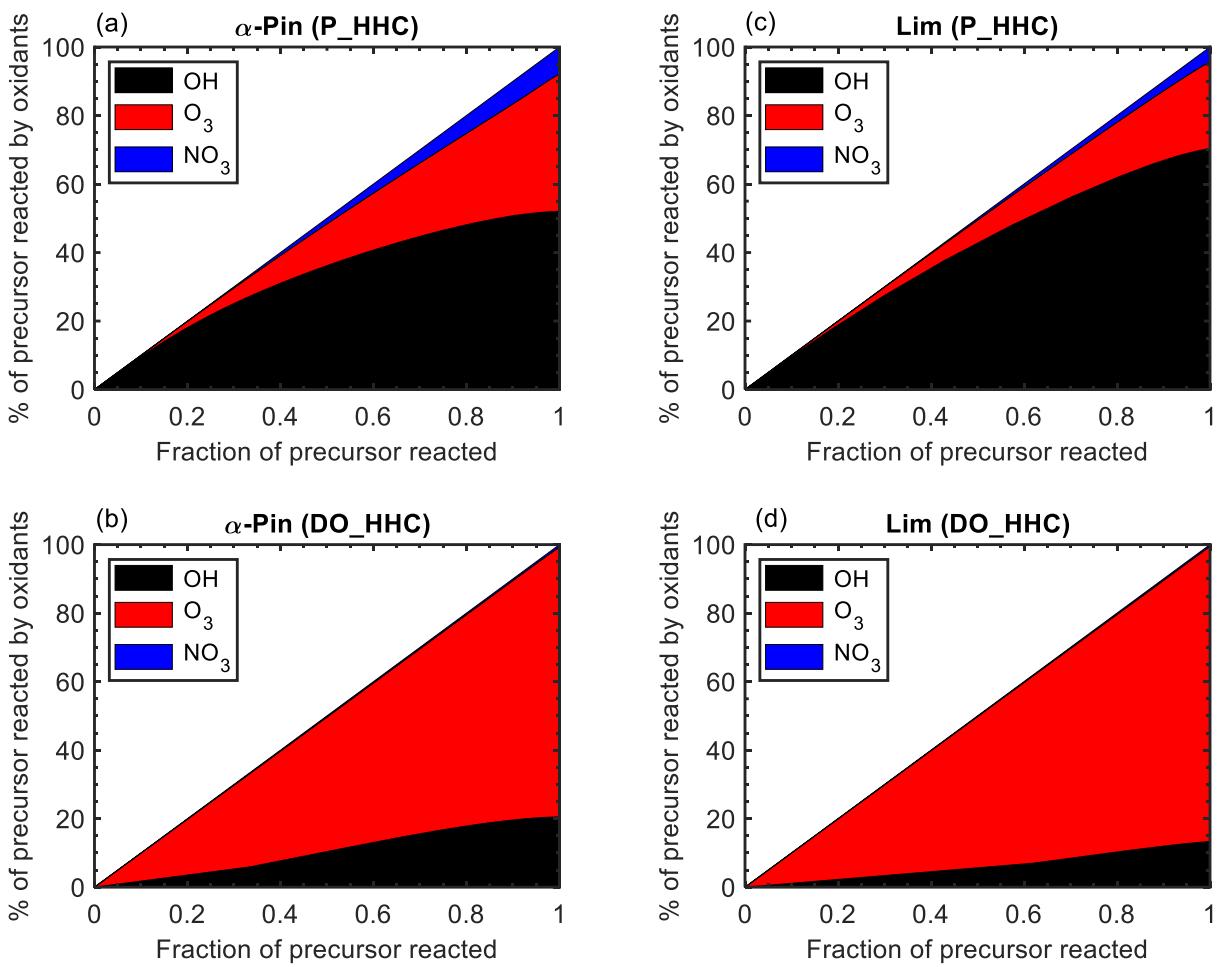


Figure S15: Percentage of precursor consumed by OH (black), O₃ (red), and NO₃ (blue) as a function of fraction of precursor reacted for α -pinene and limonene under photooxidation and ozonolysis (for higher initial precursor concentration of 150 ppb).

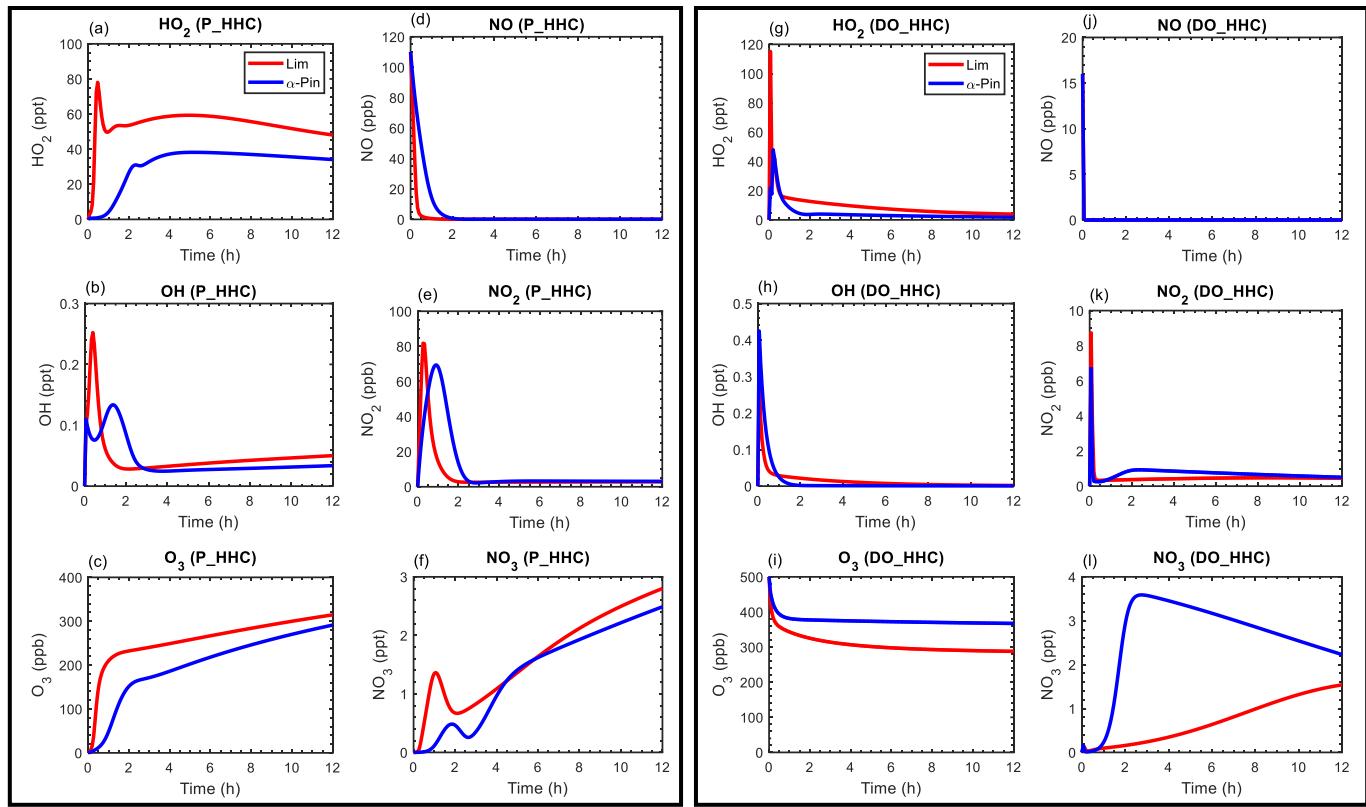


Figure S16: Mixing ratios of HO₂, OH, O₃, NO, NO₂, and NO₃ as function of time for limonene (red line), camphene (black line), and α -pinene (blue line) during the photooxidation and ozonolysis (with higher initial hydrocarbon mixing ratio of 150 ppb).

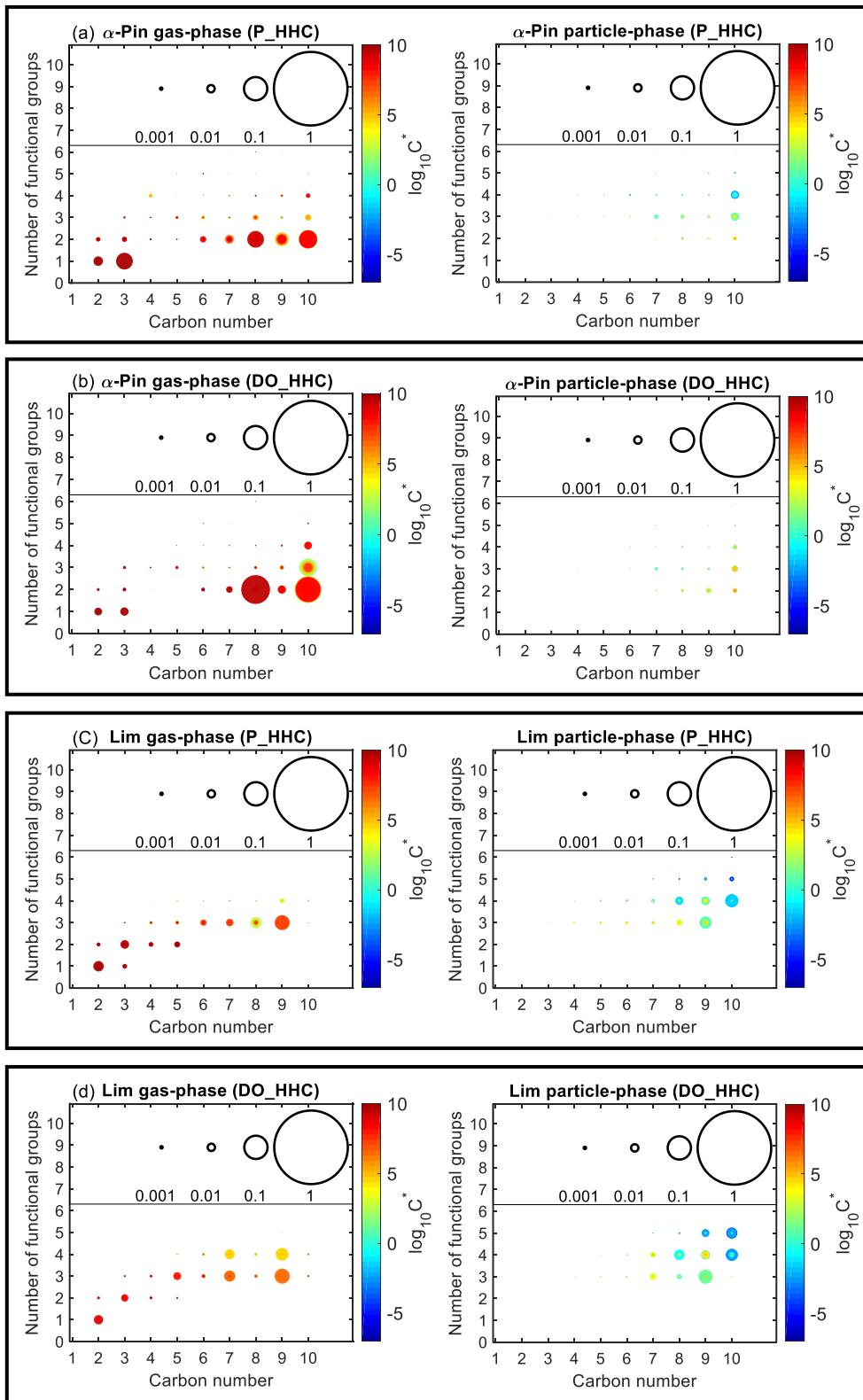


Figure S17: Number of functional groups associated with gas- and particle-phase species as a function of carbon number. Results are shown for camphene, α -pinene, and limonene after 12 hours of oxidation under photooxidation (P) and dark ozonolysis (DO) with higher hydrocarbon (LHC) mixing ratio of 150 ppb. The markers are sized by the ratio of their mixing ratio (in ppbC) to the initial mixing ratio of the precursor (in ppbC). The colors of the markers are scaled by volatility (represented by saturation concentration, C^*).

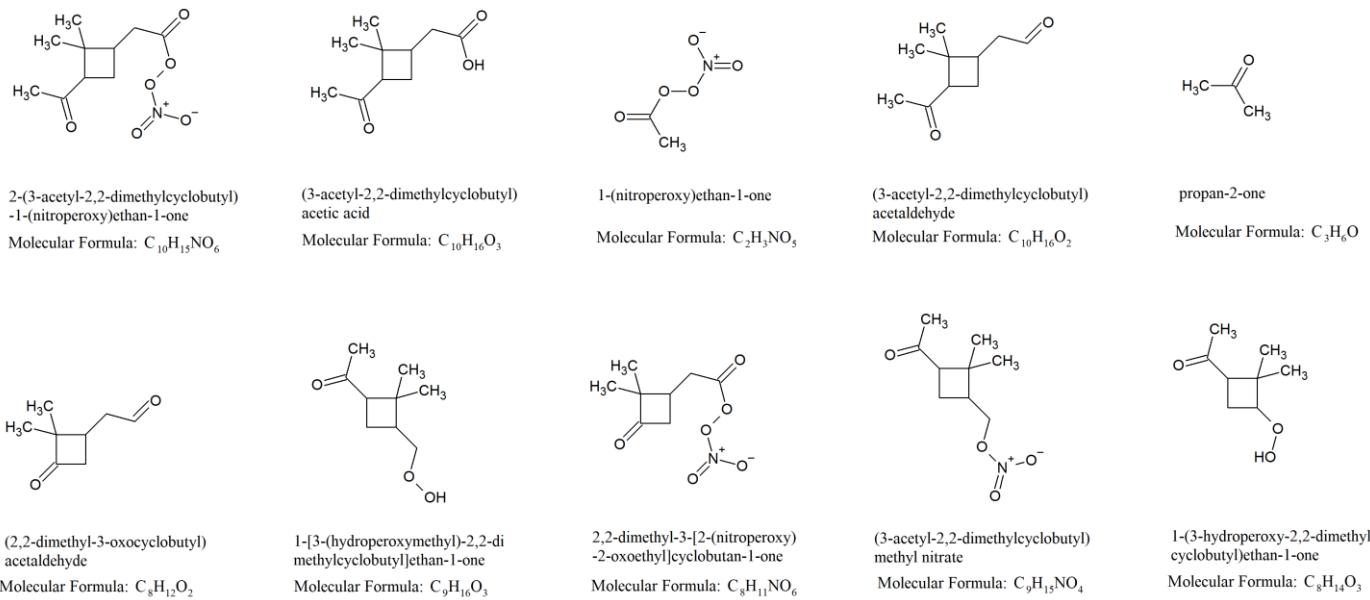


Figure S18: Top 10 gas-phase products from α -pinene photooxidation high hydrocarbon (P_HHC) simulations.

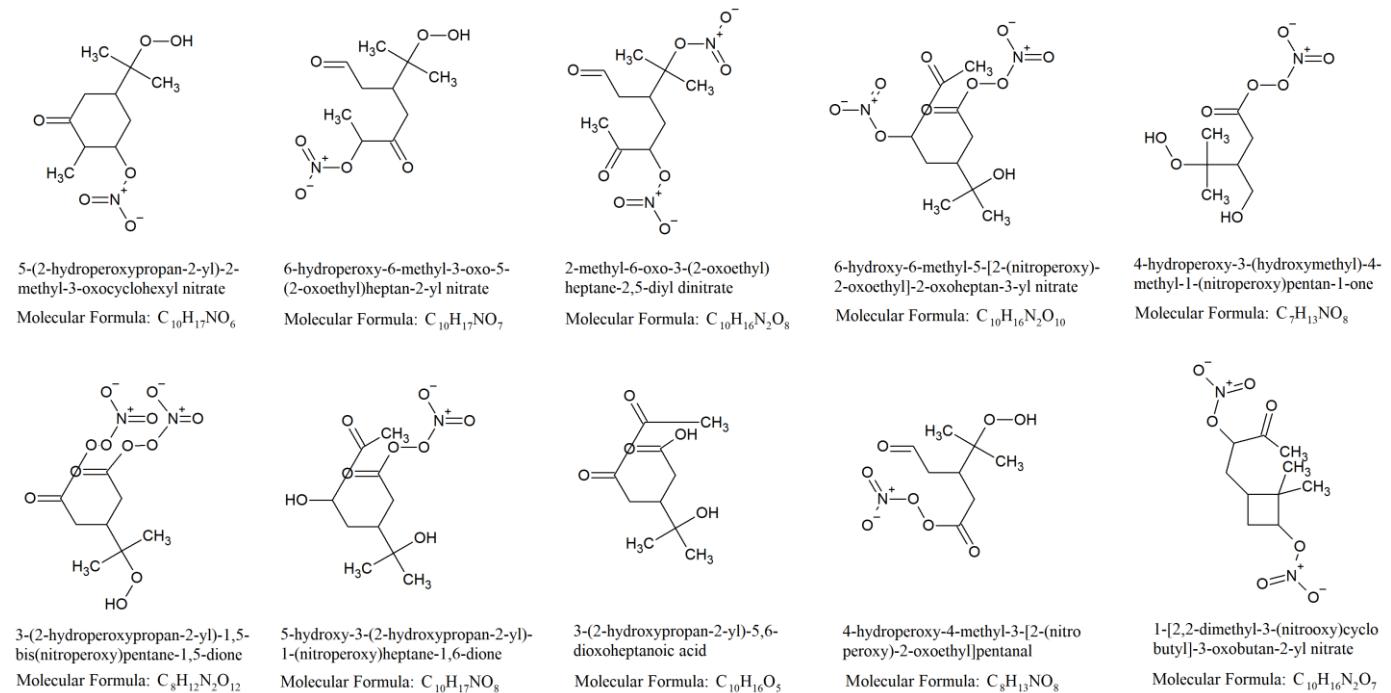


Figure S19: Top 10 particle-phase products from α -pinene photooxidation high hydrocarbon (P_HHC) simulations.

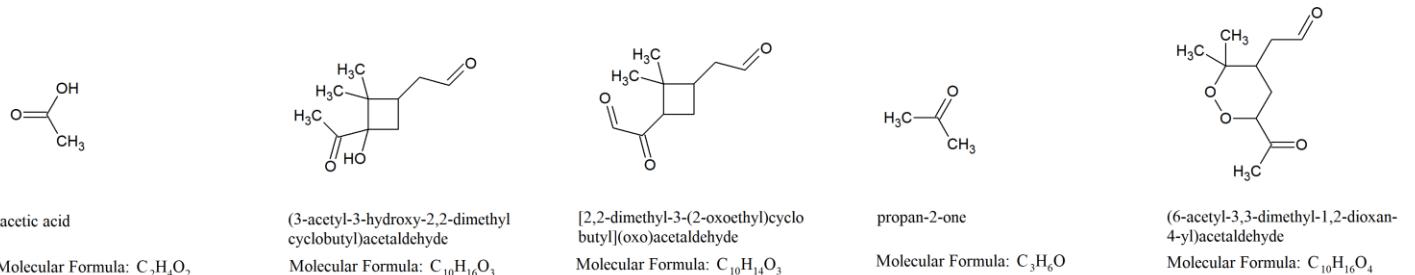
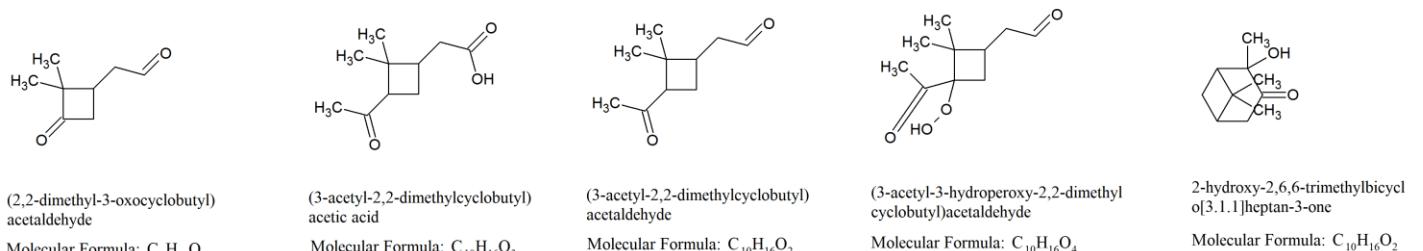


Figure S20: Top 10 gas-phase products from α -pinene dark ozonolysis high hydrocarbon (DO_HHC) simulations.

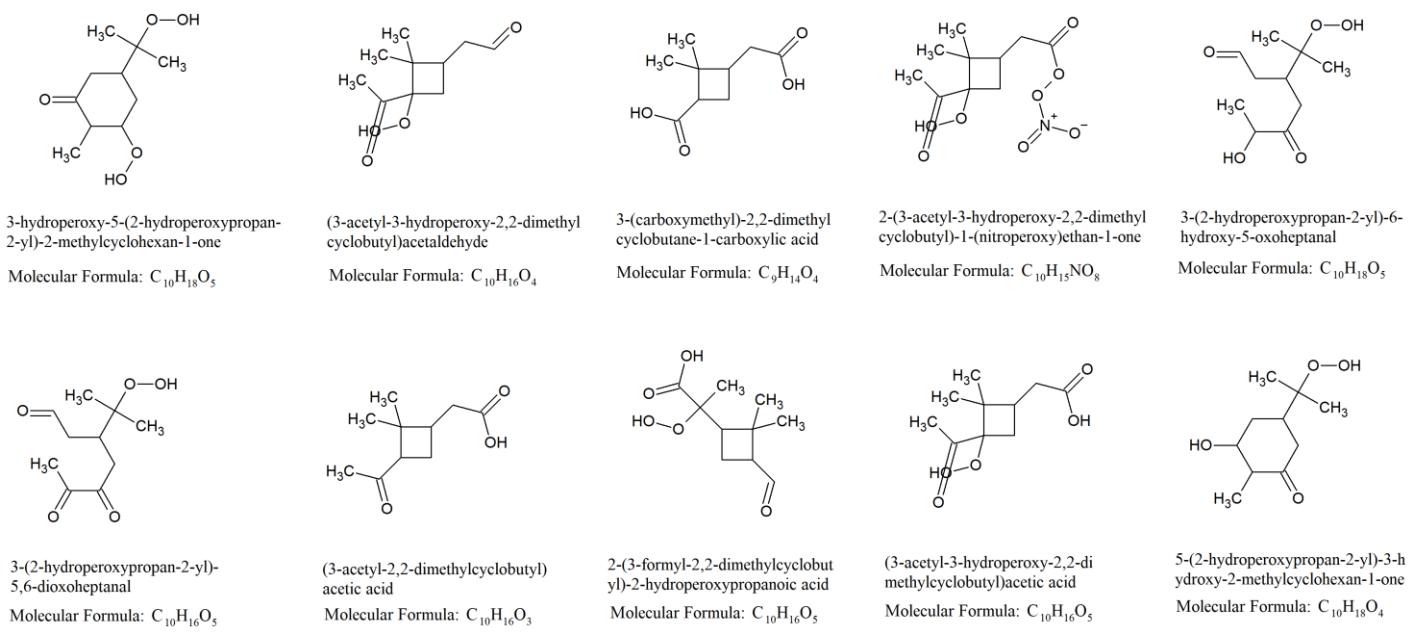


Figure S21: Top 10 particle-phase products from α -pinene dark ozonolysis high hydrocarbon (DO_HHC) simulations.

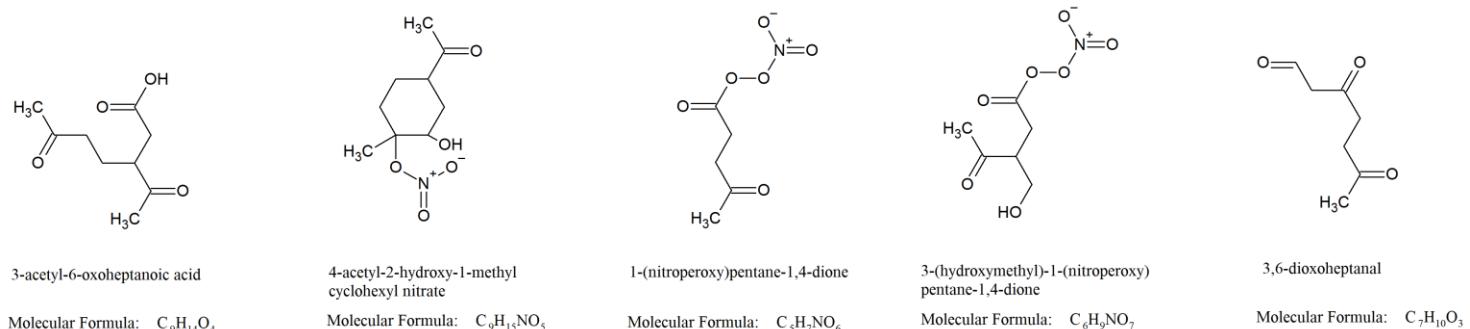
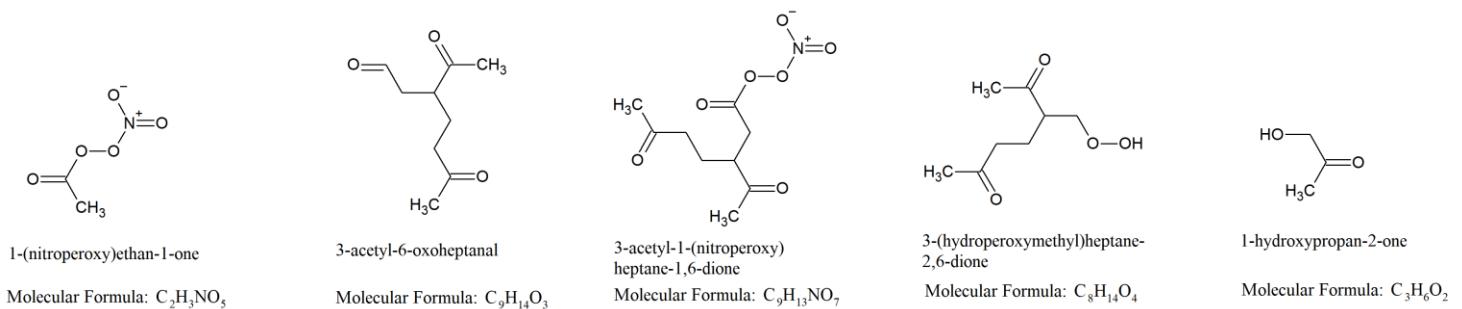


Figure S22: Top 10 gas-phase products from limonene photooxidation high hydrocarbon (P_HHC).

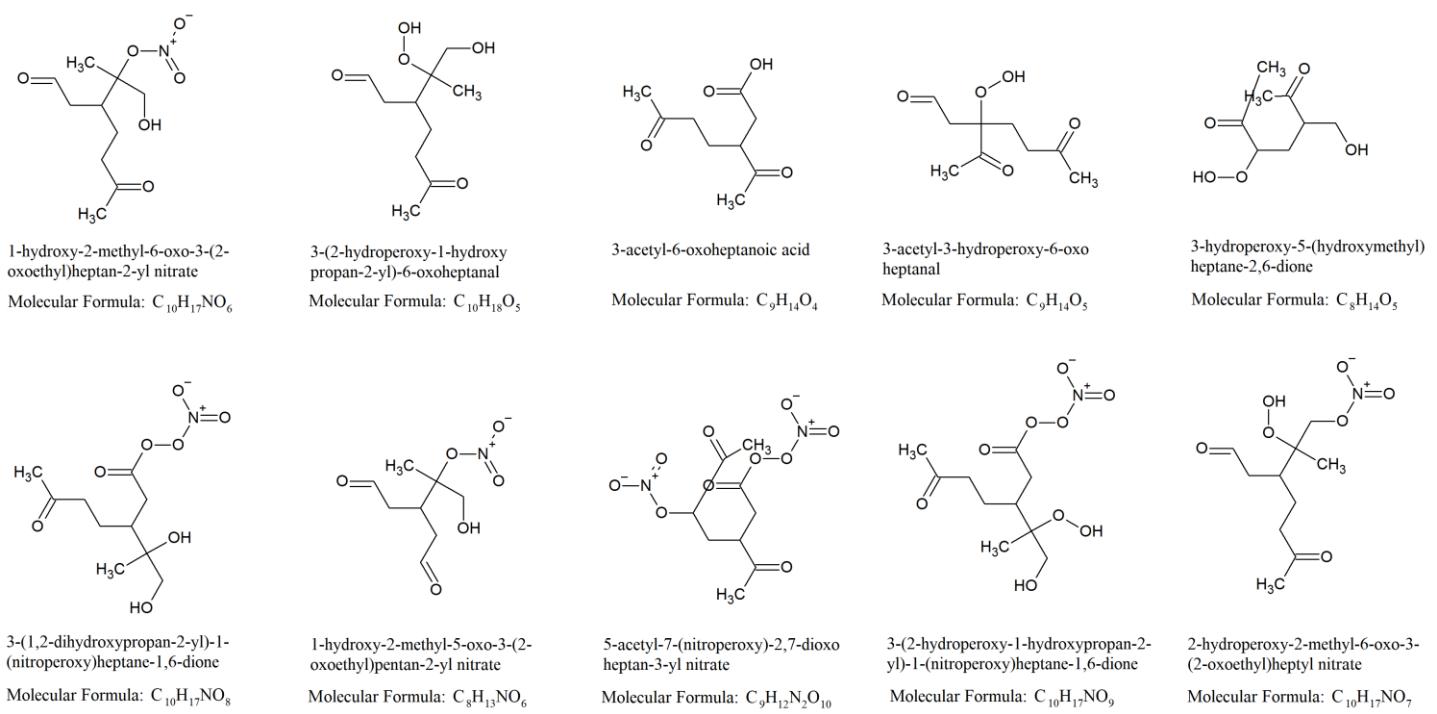


Figure S23: Top 10 particle-phase products from limonene photooxidation high hydrocarbon (P_HHC).

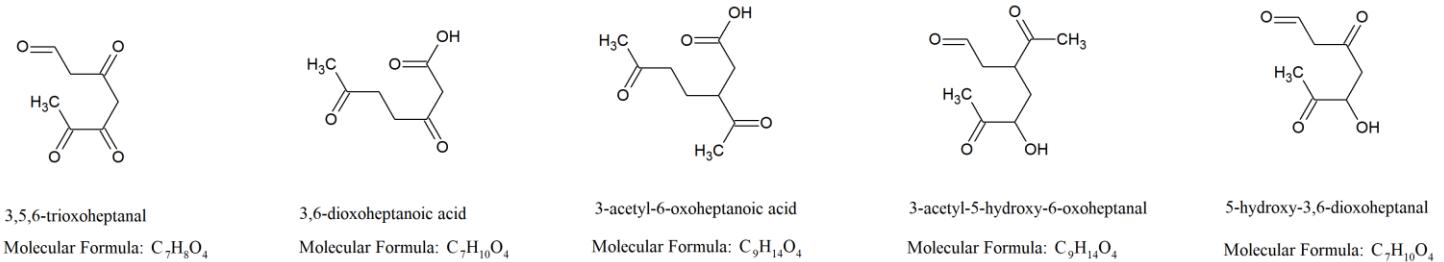
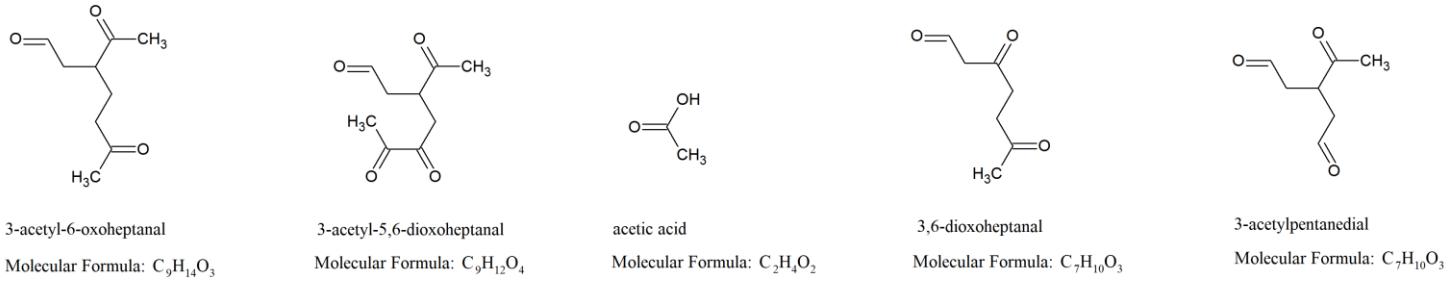


Figure S24: Top 10 gas-phase products from limonene dark ozonolysis high hydrocarbon (DO_HHC).

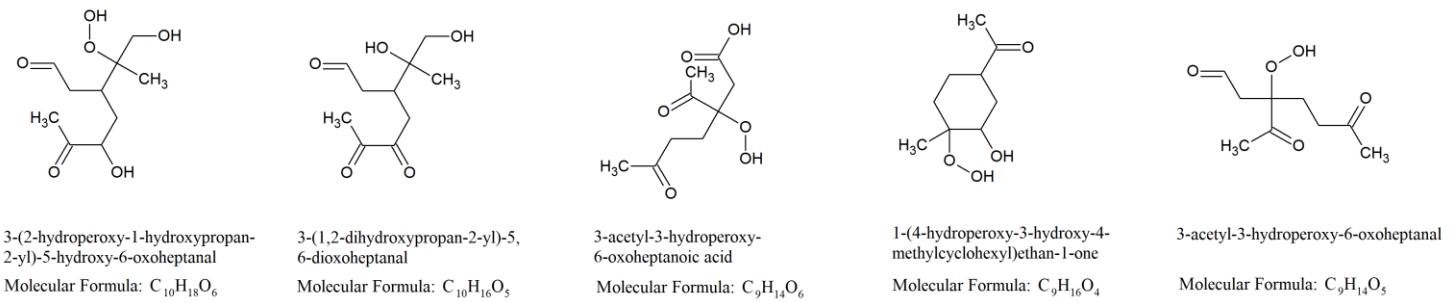
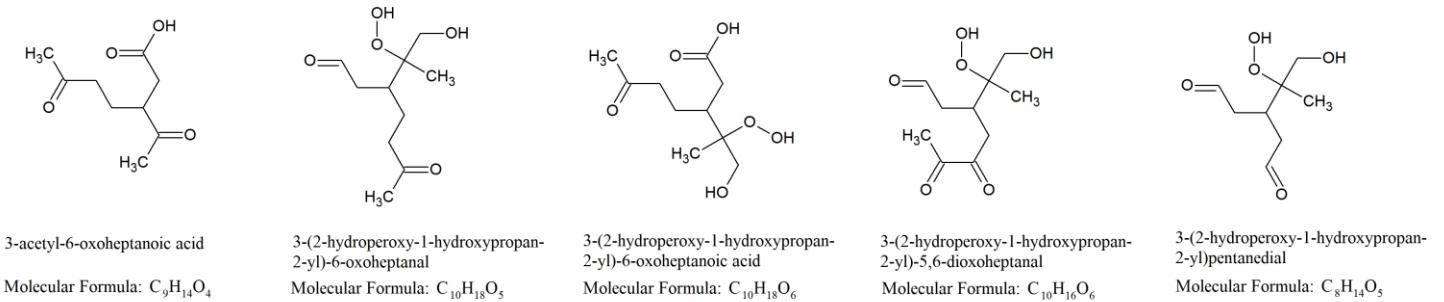


Figure S25: Top 10 particle-phase products from limonene dark ozonolysis high hydrocarbon (DO_HHC).

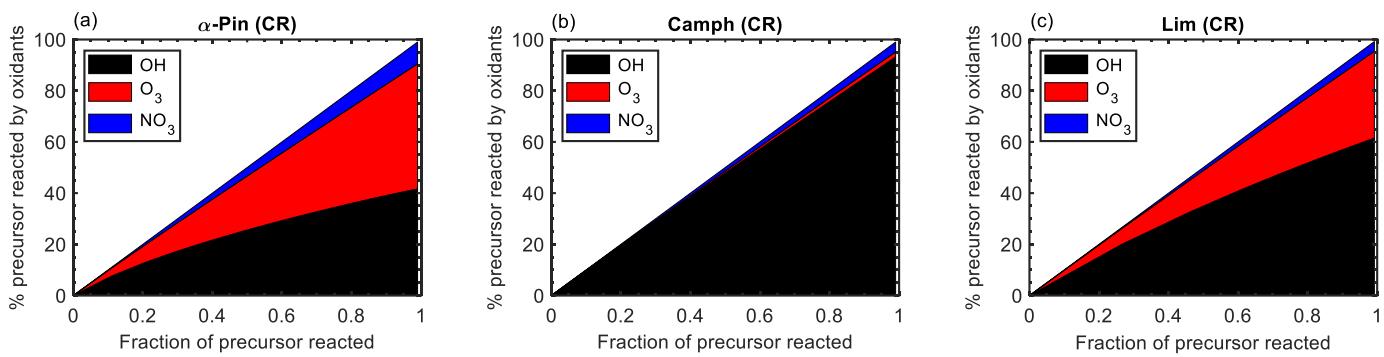


Figure S26: Percentage of precursor reacted by OH (black), O_3 (red), and NO_3 (blue) as a function of fraction of precursor reacted for α -pinene, camphene, and limonene during controlled reactivity (CR) simulations.

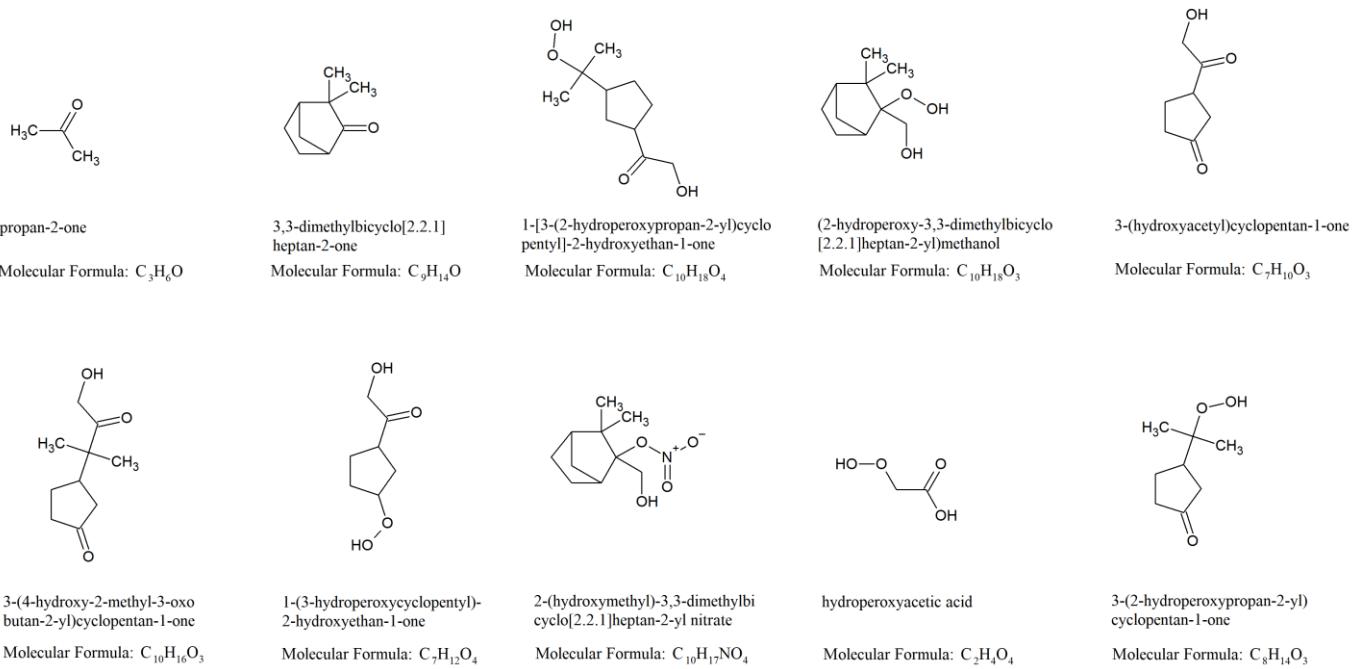


Figure S27: Top 10 gas-phase products from camphene controlled reactivity simulation.

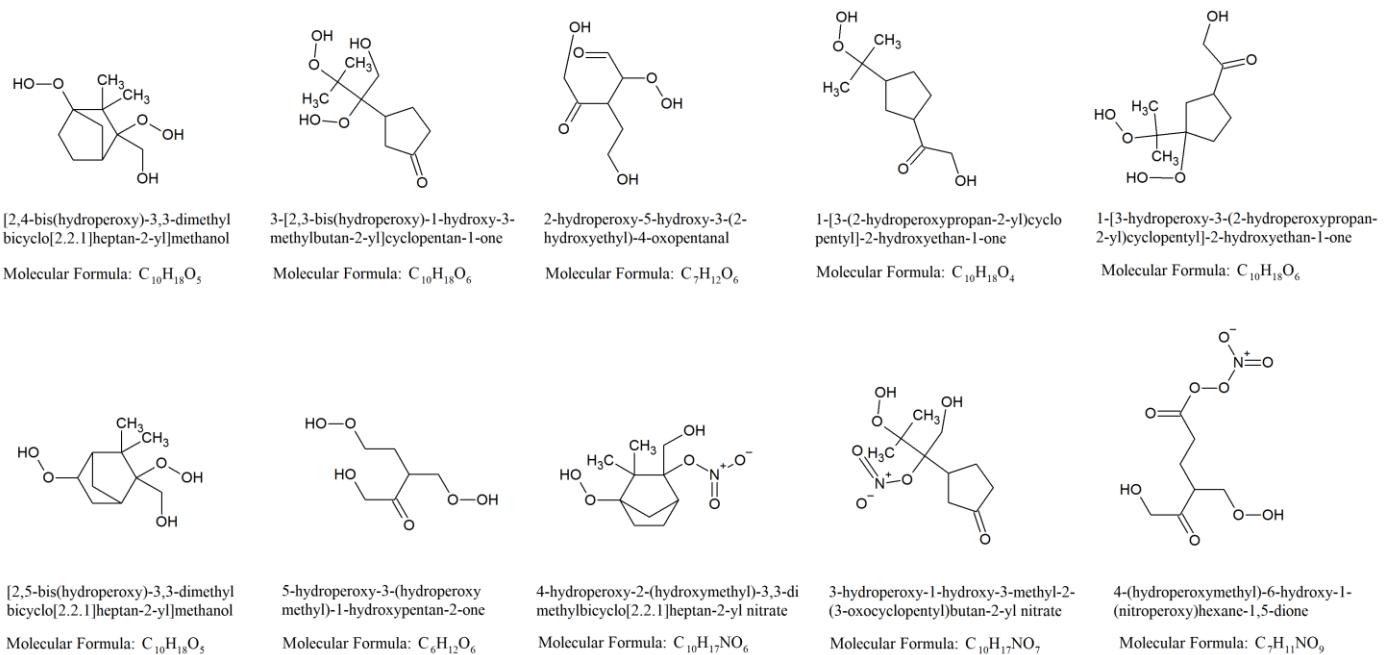


Figure S28: Top 10 particle-phase products from camphene controlled reactivity simulation.

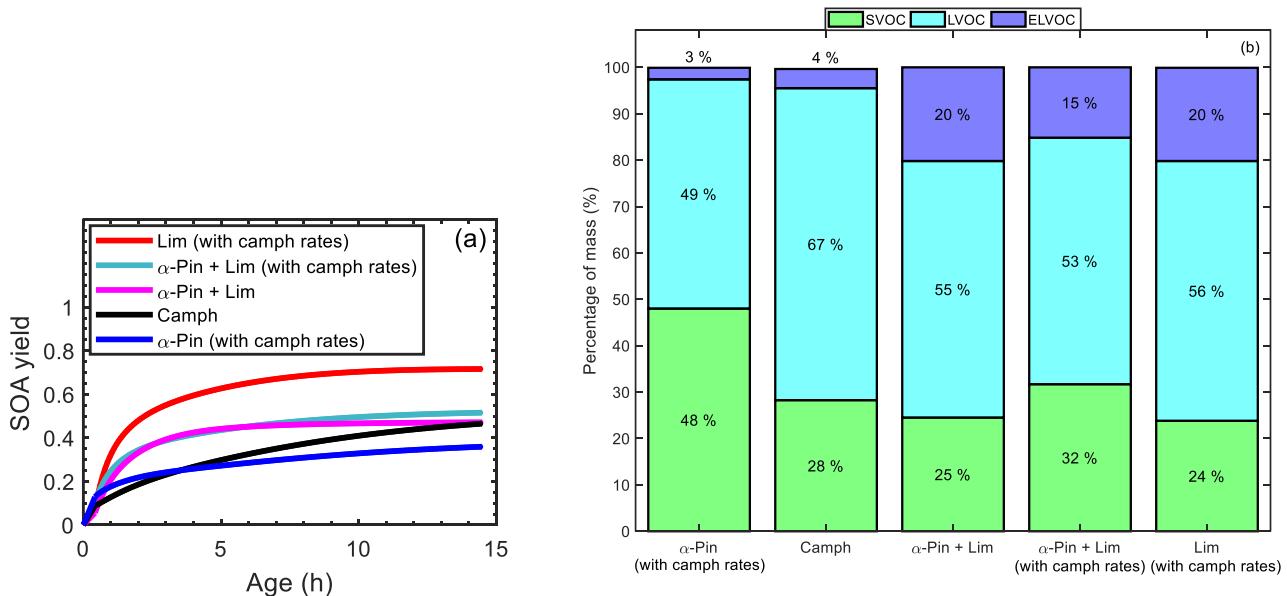


Figure S29: (a) Simulated SOA yield as a function of atmospheric aging time for camphene (black line), 50 % α -pinene + 50 % limonene (magenta line), α -pinene with camphene rate constants (blue line), limonene with camphene rate constants (red line), and 50 % α -pinene + 50 % limonene where the rate constants of α -pinene and limonene were replaced with the rate constants of camphene (green line); and (b) mass percentage of four volatility categories in the particle phase at the end of the controlled reactivity simulations for camphene, 50 % α -pinene + 50 % limonene, α -pinene with camphene rate constants, limonene with camphene rate constants, and 50 % α -pinene + 50 % limonene where the rate constants of α -pinene and limonene were replaced with the rate constants of camphene.