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Large differences of highly oxygenated organic molecules (HOMs) and low-volatile species in secondary organic aerosols (SOAs) formed from ozonolysis of β-pinene and limonene

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SOA formation

Figure S1 indicates that at 565 ppb O_3 condition, the peak concentration of limonene SOA (1484 μg m^{-3} for 626 nm particles) is much higher than β-pinene SOA (1152 μg m^{-3} for 684 nm particles), partially reflecting the higher SOA yield of limonene ozonolysis. The SOA concentration difference is not as high as ten times, which may be due to the exact concentration of limonene in the flow tube is lower than β-pinene. The evidence is that we observed substantial large particles (diameter > 600 nm) during the β-pinene SOA formation process (Figure S1a). The mass-size distribution of these particles does not change significantly and rapidly when the UV lights are turned off. We infer these large particles (Figure S1a) are β-pinene microdroplets produced during the precursor evaporation or due to condensation. In contrast, negligible number of big particles were observed during the limonene SOA formation process (Figure S1b).

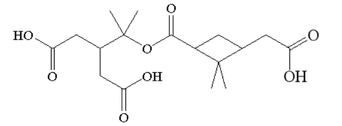
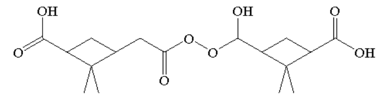
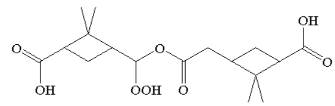
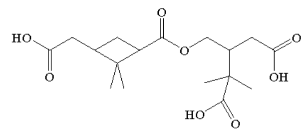
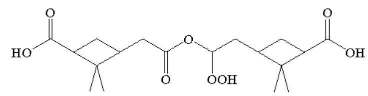
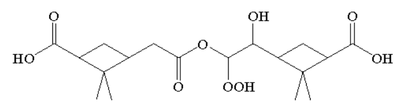
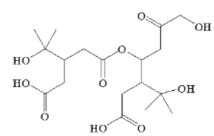
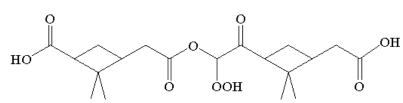
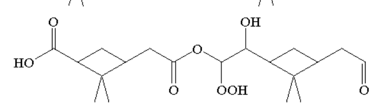
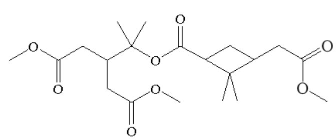
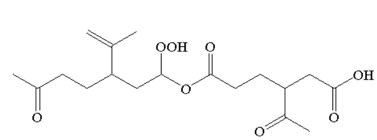
Table S1. The experimental conditions, the collected SOA particles quality of β-pinene and limonene SOA. The concentration of gas phase β-pinene and limonene are estimated to be 2-4 ppm and 1-3 ppm, respectively. The number concentration ($[SOA]_{number}$) and mass concentrations of SOA ($[SOA]_{mass}$) are for particles with sizes ranging from 10 to 1093 nm.

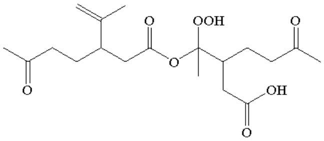
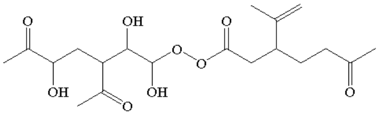
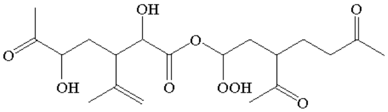
VOC	Date	$[O_3]$	$[SOA]_{number}$	$[SOA]_{mass}$	Sampling time		Collected SOA
		ppb	cm^{-3}	$\mu g\ m^{-3}$	Beginning	Ending	µg
β-pinene	13/08/2019	315	1.61E+06	2085.16	15:24	15:57	130
β-pinene	13/08/2019	315	1.81E+06	1767.30	16:00	16:31	110
β-pinene	13/08/2019	565	2.08E+06	693.11	19:01	19:37	190
β-pinene	13/08/2019	565	1.80E+06	646.12	19:39	20:25	220
β-pinene	13/08/2019	50	8.05E+05	3966.64	22:50	23:15	70
β-pinene	13/08/2019	50	8.04E+05	4696.83	23:17	23:40	60
β-pinene	14/08/2019	50	8.15E+05	5557.75	7:38	8:42	90
Limonene	09/09/2019	50	3.06E+05	24.99	12:52	13:56	30
Limonene	09/09/2019	50	3.32E+05	28.57	13:56	15:52	30
Limonene	09/09/2019	50	3.54E+05	43.20	15:53	17:52	30
Limonene	10/09/2019	565	1.90E+06	599.65	17:12	17:46	130
Limonene	10/09/2019	565	1.89E+06	603.14	17:48	18:45	230
Limonene	10/09/2019	565	1.84E+06	603.34	18:46	19:46	260
Limonene	11/09/2019	315	1.22E+06	293.89	12:27	13:37	220
Limonene	11/09/2019	315	1.20E+06	298.18	13:38	14:44	150
Limonene	11/09/2019	315	1.16E+06	300.47	14:46	15:48	210

Table S2. Summary of the top fifteen molecules in relative abundance in β-pinene and limonene SOA that formed at 50, 315, and 565 ppb ozone, respectively.

Classified	Molecular formula	Molecular weight	Relative abundance (%)					
			β-pinene SOA			limonene SOA		
			50 ppb O_3	315 ppb O_3	565 ppb O_3	50 ppb O_3	315 ppb O_3	565 ppb O_3
Monomer	$C_8H_{12}O_4$	172	3	18	17	5	2	2
	$C_9H_{18}O_2$	158	11	7	1	15	< 0.5	< 0.5
	$C_9H_{16}O_3$	172	7	48	21	11	1	1
	$C_9H_{14}O_3$	170	19	39	17	53	41	55
	$C_9H_{14}O_4$	186	10	78	57	37	29	22
	$C_{10}H_{16}O_2$	168	9	3	< 0.5	14	< 0.5	< 0.5
	$C_{10}H_{16}O_3$	184	86	95	35	88	52	66
	$C_{10}H_{16}O_4$	200	9	32	19	100	100	100
Dimer	$C_{17}H_{26}O_3$	278	2	1	< 0.5	42	2	2
	$C_{17}H_{26}O_4$	294	100	44	8	13	1	2
	$C_{17}H_{26}O_7$	342	4	28	17	20	22	15
	$C_{17}H_{26}O_8$	358	2	21	43	10	15	12
	$C_{18}H_{22}O_4$	302	4	2	1	1	< 0.5	< 0.5
	$C_{18}H_{26}O_5$	322	2	25	10	5	2	2
	$C_{18}H_{28}O_6$	340	2	34	31	19	16	15
	$C_{18}H_{28}O_7$	356	1	10	15	27	26	22
	$C_{18}H_{30}O_7$	358	1	31	25	7	6	6
	$C_{18}H_{26}O_8$	370	< 0.5	1	0	13	19	13
	$C_{18}H_{28}O_8$	372	1	3	5	25	25	19
	$C_{18}H_{30}O_9$	390	2	18	14	3	4	3
	$C_{19}H_{28}O_4$	320	9	12	2	17	7	6
	$C_{19}H_{32}O_4$	324	5	3	1	5	1	< 0.5
	$C_{19}H_{30}O_5$	338	3	100	100	74	73	69
	$C_{19}H_{28}O_6$	352	1	15	14	51	36	32
	$C_{19}H_{30}O_6$	354	2	39	32	48	36	28
	$C_{19}H_{28}O_7$	368	< 0.5	5	7	48	62	47
	$C_{19}H_{30}O_7$	370	4	78	52	85	35	27
	$C_{19}H_{28}O_8$	384	1	2	2	30	23	18
	$C_{19}H_{30}O_8$	386	1	4	7	21	18	15
	$C_{19}H_{28}O_9$	400	< 0.5	< 0.5	< 0.5	17	24	16
Unclassified	$C_{16}H_{24}O_6$	312	2	26	8	5	5	4
	$C_{23}H_{30}O_3$	354	4	2	1	2	0	< 0.5
	$C_{32}H_{42}O_3$	474	12	0	0	0	0	0

Table S3. Dimer HOMs identified by FT-ICR MS analysis of collected particle samples along with observed m/z, proposed molecular formula and molecular structure in SOA produced from ozonolysis of β-pinene and limonene.

Dimer ID	Observed m/z (-)	Molecular formula	Proposed molecular structure	Reference
		β-Pinene SOA		
MW 358	357.155	$C_{17}H_{26}O_8$		Kahnt et al. (2018) Kristensen et al. (2017)
				Müller et al. (2009) Mohr et al. (2017)
				Mohr et al. (2017)
				Mohr et al. (2017)
MW 372	371.171	$C_{18}H_{28}O_8$		Kristensen et al. (2017)
MW 388	387.166	$C_{18}H_{28}O_9$		Kristensen et al. (2017) Kristensen et al. (2016)
MW 406	405.177	$C_{18}H_{30}O_{10}$		Kenseth et al. (2018)
MW 400	399.166	$C_{19}H_{28}O_9$		Kristensen et al. (2017)
MW 386	385.187	$C_{19}H_{30}O_8$		Kristensen et al. (2017)
MW 400	399.202	$C_{20}H_{32}O_8$		Kahnt et al. (2018)
		Limonene SOA		
MW 372	371.171	$C_{18}H_{28}O_8$		Hammes et al. (2019)

MW 386	385.187	$C_{19}H_{30}O_8$		Hammes et al. (2019)
MW 402	401.182	$C_{19}H_{30}O_9$		Kundu et al. (2012)
				Kundu et al. (2012)

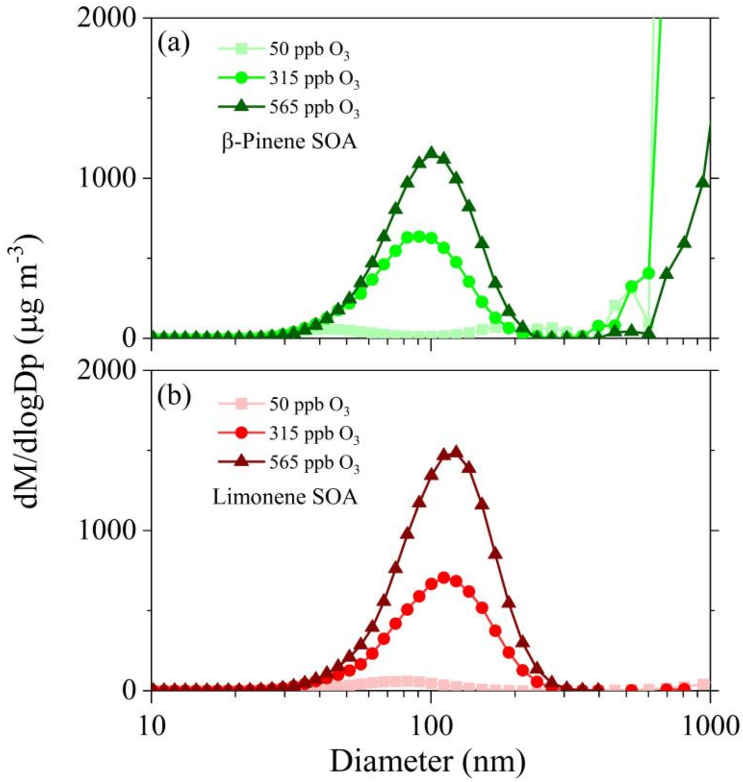


Figure S1. Particle size and mass concentration distributions of β-pinene SOA (a) and limonene SOA (b) from SMPS measurement.

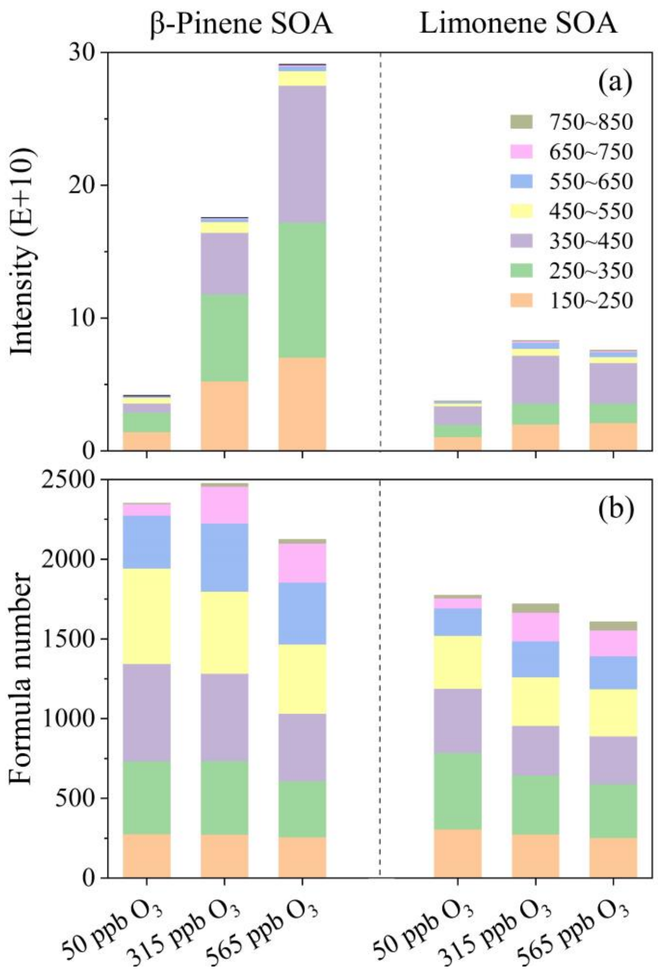


Figure S2. The intensity (a) and formula number (b) of molecular weight distributions for β-pinene and limonene SOA at 50 ppb, 315 ppb and 565 ppb ozone concentrations.

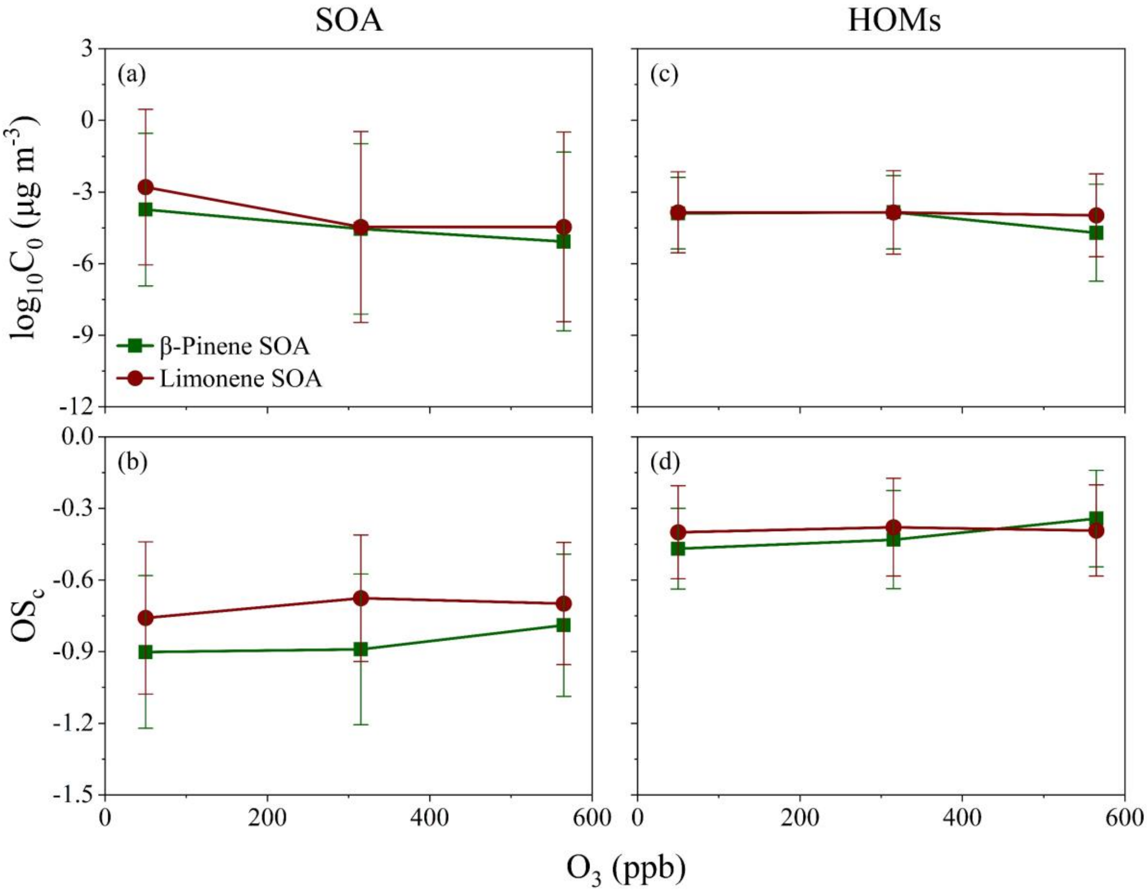


Figure S3. Average saturation mass concentration (C_0) (a, c) and carbon oxidation state (OS_C) (b, d) for organic compounds from β-pinene SOA (green square) and limonene SOA (red circle) and the corresponding HOMs at different ozone concentrations.

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