Supplementary Information

for

The Effect of Sub-Zero Temperature on the Formation and Composition of Secondary Organic Aerosol from Ozonolysis of Alpha-Pinene

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Calculating chamber volume

The following procedure was developed to accurately determine the volume of the smog chamber once inflated with dry purified air.

At 293 K, the smog chamber is flushed and filed to an initial volume ($V_{Chamber}$) with dry purified air. Ozone is then added to the chamber at 10 L min^{-1} for 18 min resulting in an initial ozone concentration ($[O_3]_i$) of 103.1 ppb ozone. During ozone addition, chamber volume is increased by 180 L (10 Lmin^{-1} x 18 min, V_{O3}^{add}). A known volume (2029 L, $V_{removed}$) is then removed from the chamber by pump and flow meter, during which the ozone concentration inside the chamber remains the same. A known volume of ozone-free purified air is added to the chamber (V_{clean}^{add}), thus diluting the ozone concentration. The new ozone concentration ($[O_3]_{new}$) is measured and used for calculation of the initial chamber volume, $V_{Chamber}$, using the following equation:

$$V_{Chamber} = \frac{\left(\frac{[O_3]_{new}}{[O_3]_i}\right) * V_{clean}^{add}}{1 - \left(\frac{[O_3]_{new}}{[O_3]_i}\right)} + V_{removed} - V_{O3}^{add}$$

$$V_{Chamber} = \frac{\left(\frac{87.5ppb}{103.1ppb}\right) * 557L}{1 - \left(\frac{87.5ppb}{103.1ppb}\right)} + 2029L - 180L = \underline{4971L}$$

Subsequent additions of ozone-free air are performed and the above calculations repeated with new V_{clean}^{add} and $[O_3]_{new}$values. The above mentioned chamber volume experiment was conducted twice to evaluate on the repeatability of filling the smog chamber. Table 1S shows the calculated $V_{Chamber}$ values for different $\frac{[O_3]_{new}}{[O_3]_i}$ ratios obtained during the two experiments.

Tabel 1S. Calculated chamber volumes for fully inflated camber

Exp. #	$\frac{[O_3]_{new}}{[O_3]_i}$	$V_{Chamber}$ (L)
1	0.85	4971.0
	0.75	4989.7
	0.67	4995.1
	0.60	4888.3
2	0.95	4995.8
	0.89	5001.2
	0.84	5108.2
	0.79	4921.6
Average		**4983.9**
Std.dev.		64.6

Table 2S. Smog chamber specification overview comparing the AURA chamber with other similar chamber facilities. [a] Particle type (AS = Ammonium sulfate, BC =Black carbon, SOA = Secondary Organic Aerosol) associated with listed wall loss rates is shown in parenthesis.

Chamber	Volume (m^3)	S/V (m^{-1})	Material	Active mixing	Particle Wall Loss Rate (h^{-1})[a]	Ozone Wall Loss Rate (h^{-1})	NO_2 photolysis rate (min^{-1})	Reference
AURA	5	3.5	FEP	No	0.06 (AS), 0.08 (SOA)	0.01	0.19	This study
Ilmari	29	2	FEP	No	0.09 (AS)	n/a	0.62	[1]
TSC	3	5	FEP	No	0.07	0.04	0.23	[2]
GIG-CAS	30	2.1	FEP	Yes	0.17 (AS)	0.02	0.49	[3]
PSI	27	2	FEP	No	0.21 (SOA)	0.04	0.12 (Xenon arc lamp)	[4], [5]
PSI-mobile	9	2.9	FEP	No	0.25 (BC)	n/a	0.48	[6]
EUPHORE	200	1	FEP	Yes	0.18 (SOA)	0.03	n/a	[7], [8]
Caltech	28	2.1	FEP	No	0.09-0.18 (SOA)	n/a	1.5	[9]
UCR	90	1.4	FEP	No	0.29 (SOA)	n/a	0.19	[10]
SAPHIR	270	1	FEP	Yes	0.27 (SOA)	n/a	n/a	[11]
CMU	12	n/a	FEP	No	0.40 (SOA)	n/a	n/a	[12]

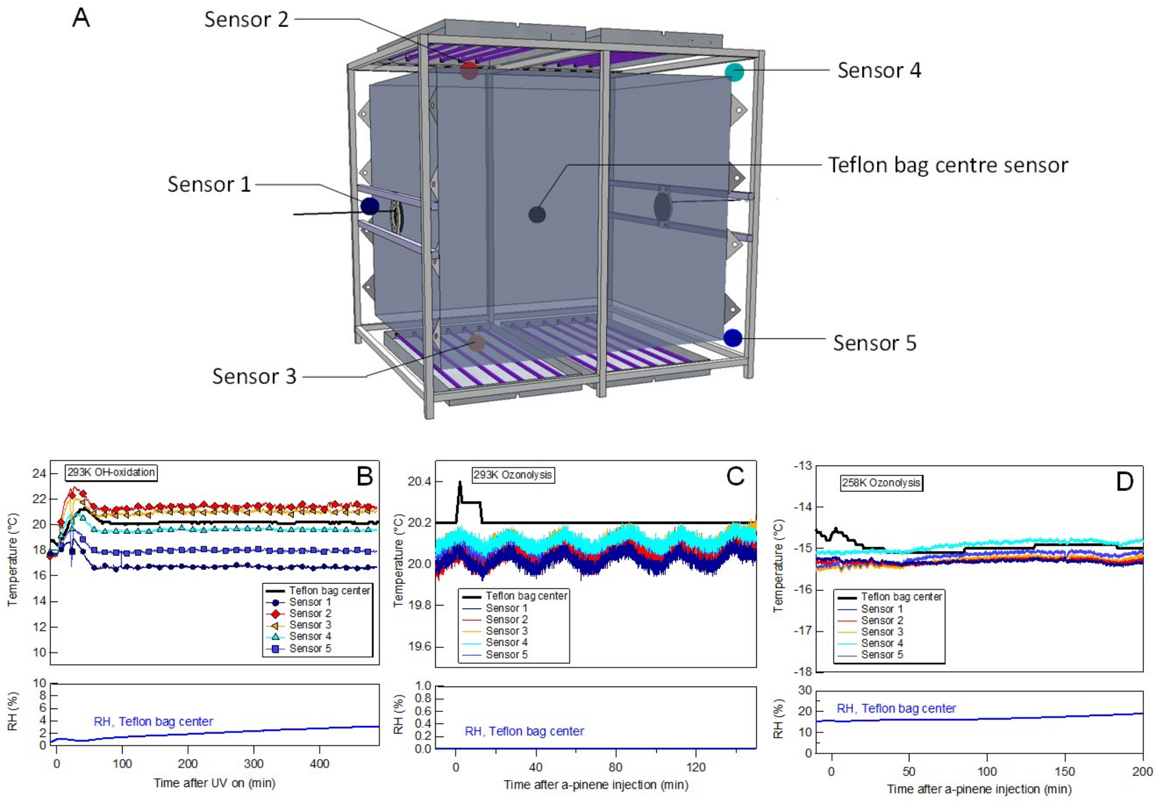


Figure 1S. A) Chamber illustration with placement of the six temperature sensors (five outside Teflon bag and one at Teflon bag centre). **B)** Temperature and RH measurements during OH-oxidation experiment with all 24 UV lights on. **C)** Temperature and RH measurements during dark ozonolysis experiment at 293 K. **D)** Temperature and RH measurements during dark ozonolysis experiment at 258 K.

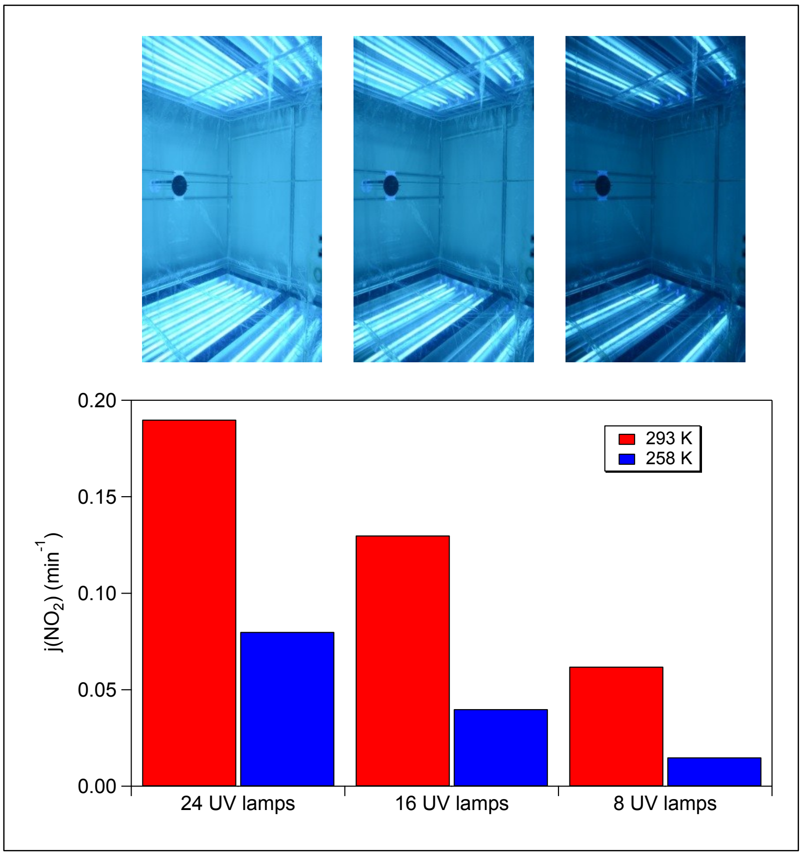


Figure 2S. The NO_2 photolysis rates (min^{-1}, bottom) at 293 K and 258 K with 24, 16, and 8 UV lamps on (top).

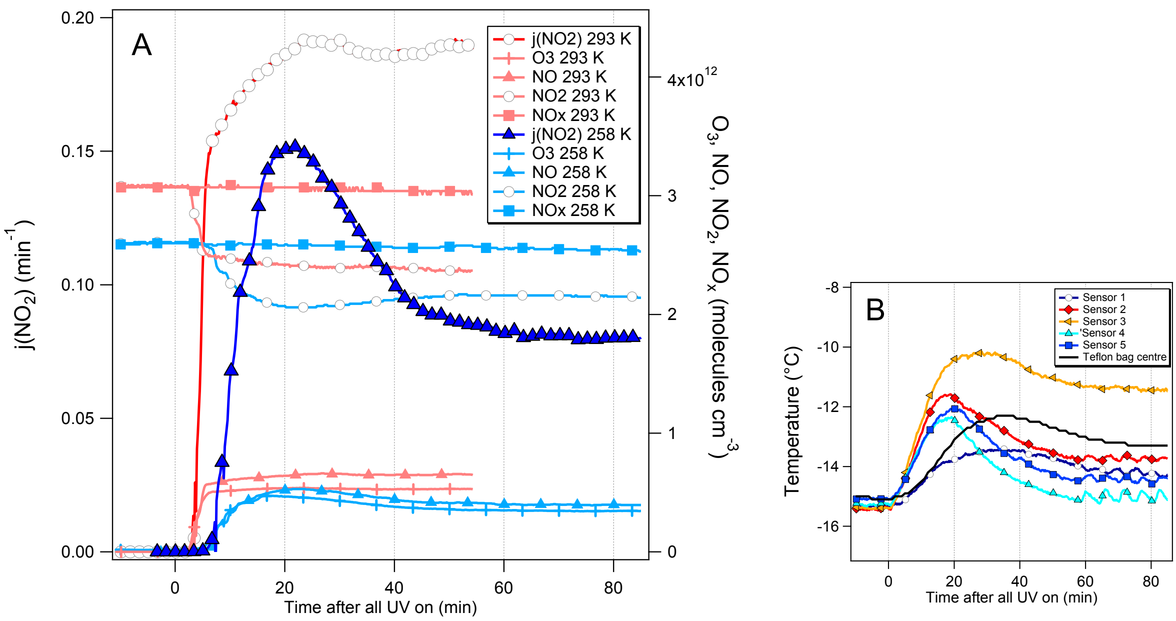


Figure 3S. A) The NO_2 photolysis rates (min^{-1}, bottom) after correction for dark chemistry at 293 K (red) and 258 K (blue) and mixing ratios (not corrected) of O_3, NO, NO_2, and NO_x (molecules cm^{-3}) after all 24 UV lamps are turned on (t=0 min). **B)** Temperatures during the NO_2 photolysis experiment at 258 K as measured by the temperature sensors shown in Figure 1S. Changes in photolysis rate at 258 K is attributed to changes in UV output as a consequence of changing temperatures initiated by heating from the UV lamps and subsequent cooling by the cold-room cooling system.

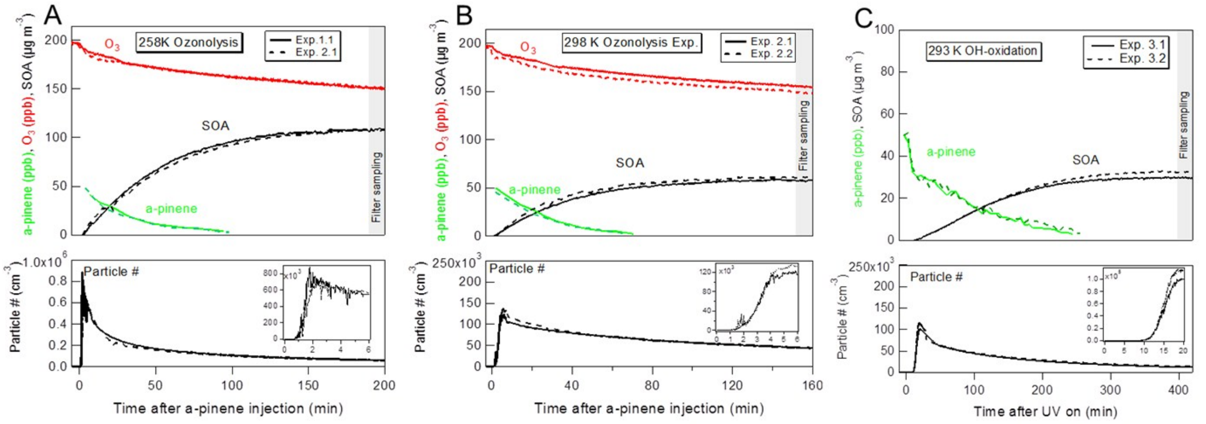


Figure 4S. Concentration of O_3 (ppb), α-pinene (ppb), wall loss corrected SOA mass (μg m^{-3}), particle number (cm^{-3}, not wall loss corrected) during the two dark ozonolysis of α-pinene experiment performed at 258 K (**A**, Exp. 1.1 & 1.2) and 293 K (**B**, Exp. 2.1 & 2.2) **C)** Concentration of α-pinene (ppb), wall loss corrected SOA mass (μg m^{-3}), particle number (cm^{-3}, not wall loss corrected) during the two OH-initiated oxidation experiment performed at 293 K (Exp. 3.1 & 3.2).

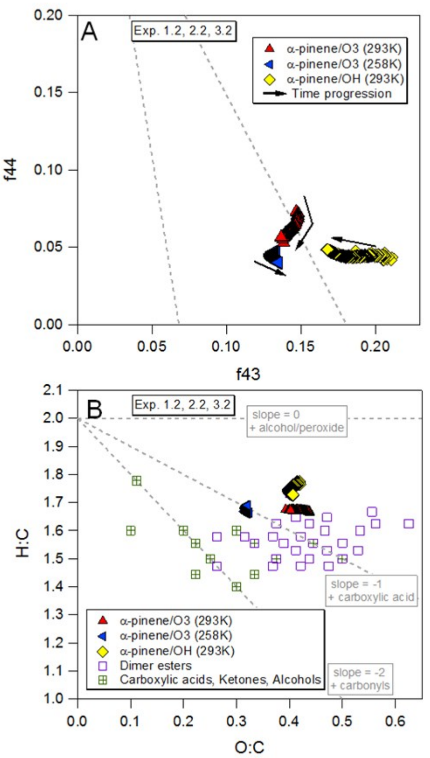
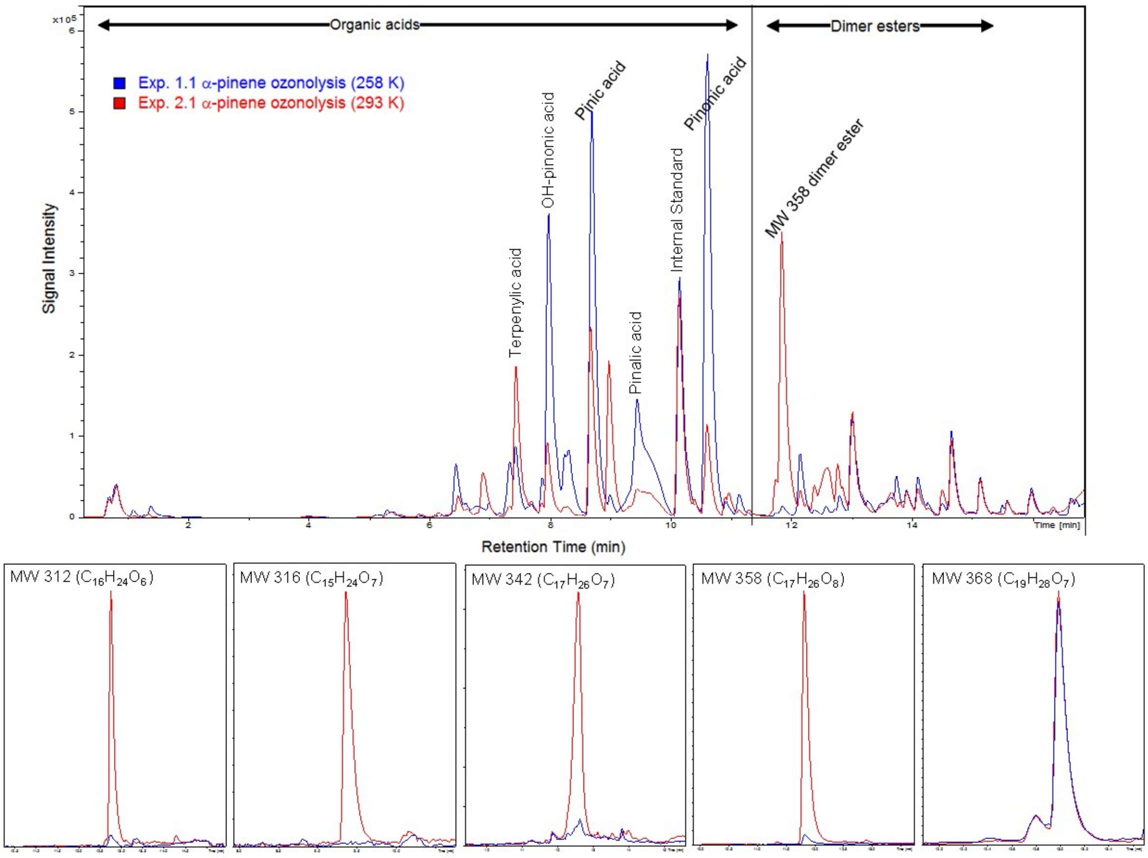


Figure 5S. **A)** "Triangle plot" for α-pinene SOA formed from ozonolysis at 293 K (Exp. 2.2, red) and 258 K (Exp. 1.2, blue) and photooxidation at 293 K (Exp. 3.2, yellow). The outline of the triangle (Ng et al., 2010) is shown in grey dashed line. **B)** Van Krevelen diagram for SOA formed from α-pinene ozonolysis and photooxidation experiments. The green crosshair squares denotes known alcohol, aldehyde carboxylic acid oxidation products from α-pinene oxidation. The purple squares denote dimer esters identified in α-pinene SOA from ozonolysis experiments. Lines with slopes of 0, −1 and −2 are represented by grey dashed lines.



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gure 6S. Top: Example of UHPLC/ESI-qTOF-MS chromatogram of particle filter sample collected from 258 K (Blue) and 293 K (red) ozonolysis of α-pinene experiments. Bottom: Extracted Ion Chromatograms of five of the total 31 identified dimer esters.

Table 3S. Carboxylic acids identified by UHPLC/ESI-qToF-MS analysis of collected particle samples along with observed m/z, molecular formula, O:C, H:C, suggested molecular structure and contribution to SOA mass formed at 293 K and 258 K ozonolysis of α-pinene and 293 K photooxidation of α-pinene.

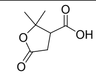
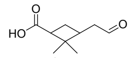
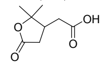
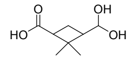
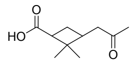
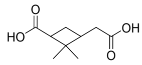
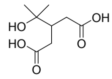
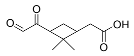
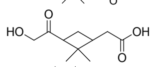
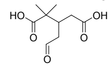
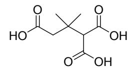
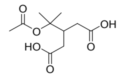
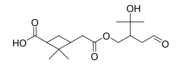
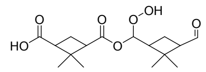
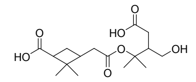
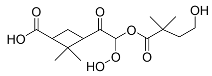
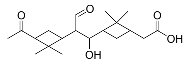
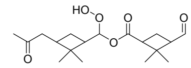
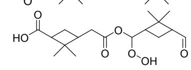
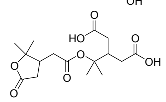
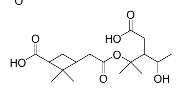
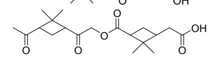
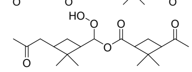
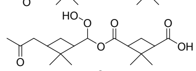
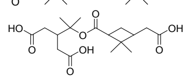
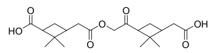
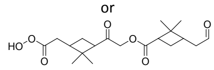
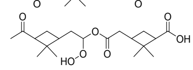
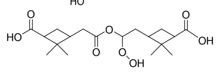
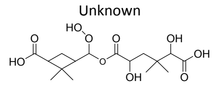
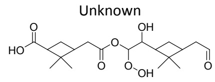
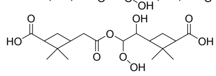
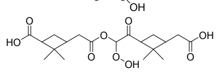
Carboxylic acid ID	Observed m/z (-)	Molecular formula	Error (ppm)	O:C	H:C	Suggested Molecular Structure	% of SOA mass		
							293 K	258 K	293 K OH
Terebic acid	157.052	$C_7H_{10}O_4$	1.9	0.58	1.42		0.45	0.14	0.80
Pinalic acid	169.087	$C_9H_{14}O_3$	0.5	0.33	1.55		4.00	5.41	5.75
Terpenylic acid	171.067	$C_8H_{12}O_4$	1.3	0.50	1.50		2.20	1.07	1.87
MW 174	173.083	$C_8H_{14}O_4$	1.6	0.50	1.75		0.28	0.08	0.23
MW 176	175.061	$C_7H_{12}O_5$	0.4	0.71	1.71	Unknown	0.12	0.02	0.13
Pinonic acid	183.103	$C_{10}H_{16}O_3$	0.9	0.30	1.60		1.17	6.40	1.29
Pinic acid	185.083	$C_9H_{14}O_4$	1.6	0.44	1.55		4.50	7.25	4.51
Diaterpernylic acid (DTA)	189.076	$C_8H_{14}O_5$	0.3	0.63	1.75		0.23	0.10	0.23
MW 190	189.076	$C_8H_{14}O_5$	0.3	0.63	1.75	Unknown	0.24	0.20	0.21
Oxopinonic acid	197.098	$C_{10}H_{14}O_4$	0.3	0.40	1.40		1.28	1.61	0.42
Hydrooxy-pinonic acid (OH-pinonic acid)	199.098	$C_{10}H_{16}O_4$	1.0	0.40	1.60		2.28	5.51	1.23
MW 202	201.077	$C_9H_{14}O_5$	0.7	0.44	1.55		0.29	0.77	0.56
3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)	203.056	$C_8H_{12}O_6$	0.4	0.75	1.50		0.38	0.01	0.77
MW 206	205.072	$C_8H_{14}O_6$	0.8	0.75	1.75	Unknown	1.10	0.48	1.19
MW 214	213.077	$C_{10}H_{14}O_5$	0.7	0.50	1.40	Unknown	1..73	2.61	0.61
Diaterpenylic acid acetate (DTAA)	231.087	$C_{10}H_{16}O_6$	0.1	0.60	1.60		0.22	0.09	0.25
Total							**20.47**	**31.73**	**20.06**

Table 4S. Dimer esters identified by UHPLC/ESI-qToF-MS analysis of collected particle samples along with observed m/z, molecular formula, O:C, H:C, suggested molecular structure and contribution to SOA mass formed at 293 K and 258 K ozonolysis of α-pinene and 293 K OH-initiated oxidation of α-pinene. b.d. = below detection limit

Dimer ester ID	Observed m/z (-)	Molecular formula	Error (ppm)	O:C	H:C	Suggested Molecular Structure	% of SOA mass		
							293 K	258 K	293 K OH
MW302	301.164	$C_{15}H_{26}O_6$	2.4	0.40	1.73	Unknown	0.03	0.02	0.03
MW310	309.168	$C_{17}H_{26}O_5$	2.2	0.29	1.53	Unknown	0.15	0.03	b.d.
MW312	311.149	$C_{16}H_{24}O_6$	1.2	0.38	1.50	Unknown	0.36	0.01	b.d.
MW314	313.164	$C_{16}H_{26}O_6$	4.2	0.38	1.63	Unknown	0.29	0.06	b.d.
MW316†	315.144	$C_{15}H_{24}O_7$	2.2	0.47	1.60		0.06	0.01	b.d.
MW328+	327.145	$C_{16}H_{24}O_7$	-1.6	0.44	1.50		0.10	b.d.	b.d.
MW330+	329.160	$C_{16}H_{26}O_7$	2.5	0.44	1.63		0.12	0.05	b.d.
MW332+	331.139	$C_{15}H_{24}O_8$	0.0	0.53	1.60		0.05	b.d.	b.d.
MW336	335.185	$C_{19}H_{28}O_5$	4.0	0.26	1.48	Unknown	0.15	0.10	b.d.
MW338ǂ	337.200	$C_{19}H_{30}O_5$	5.9	0.26	1.56		0.53	0.19	b.d.
MW340+	339.180	$C_{18}H_{28}O_6$	2.3	0.30	1.56		0.32	0.17	b.d.
MW342*	341.159	$C_{17}H_{26}O_7$	4.2	0.41	1.53		0.72	0.10	b.d.
MW344a*	343.138	$C_{16}H_{24}O_8$	2.9	0.50	1.50		0.12	b.d.	b.d.
MW344b+	343.174	$C_{17}H_{28}O_7$	4.0	0.41	1.65		0.08	0.05	b.d.
MW352	351.183	$C_{19}H_{28}O_6$	2.4	0.32	1.48		0.58	0.49	b.d.
MW354ǂ	353.194	$C_{19}H_{30}O_6$	6.0	0.32	1.58		0.21	0.25	b.d.
MW356+	355.173	$C_{18}H_{28}O_7$	7.0	0.39	1.56		0.23	0.11	b.d.
MW358*	357.155	$C_{17}H_{26}O_8$	0.1	0.47	1.53		1.26	0.08	b.d.
MW360	359.170	$C_{17}H_{28}O_8$	2.8	0.47	1.64	Unknown	0.21	0.02	b.d.
MW362	361.147	$C_{16}H_{26}O_9$	8.5	0.56	1.63	Unknown	0.02	b.d.	b.d.
MW368*	367.174	$C_{19}H_{28}O_7$	3.8	0.37	1.47	 or 	0.94	0.74	b.d.
MW370+	369.190	$C_{19}H_{30}O_7$	4.1	0.37	1.58		0.23	0.11	b.d.
MW372+	371.170	$C_{18}H_{28}O_8$	2.1	0.44	1.56		0.45	0.07	b.d.
MW374	373.149	$C_{17}H_{26}O_9$	2.6	0.53	1.53	Unknown	0.04	0.02	b.d.
MW378+	377.144	$C_{16}H_{26}O_{10}$	1.5	0.63	1.63		b.d.	b.d.	b.d.
MW384	383.172	$C_{19}H_{28}O_8$	-2.6	0.42	1.47	Unknown	0.23	0.06	b.d.
MW386+	385.183	$C_{19}H_{30}O_8$	7.9	0.42	1.58		0.07	0.03	b.d.
MW388+	387.164	$C_{18}H_{28}O_9$	3.9	0.50	1.56		0.24	0.05	b.d.
MW400+	399.164	$C_{19}H_{28}O_9$	4.5	0.47	1.47		0.77	0.18	b.d.
MW405	405.174	$C_{18}H_{30}O_{10}$	4.6	0.55	1.67	Unknown	0.02	0.01	b.d.
Total							**8.58**	**2.99**	**0.03**

Molecular structures suggested by *Yasmeen et al., (2010)[13], ǂ Witkowski et al. (2014)[14], †Zhang et al., (2015)[15], +Kristensen et al., (2016)[16]

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