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Contrasting impacts of humidity on the ozonolysis of monoterpenes: insights into the multi-generation chemical mechanism

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Section S1. Calculation of equivalent aging days

The equivalent aging days can be calculated by $\text{Age (days)}=k\frac{O_{3\text{exp}}}{[O_3]}=k\frac{[O_3]_0\times RT}{[O_3]}$, where $[O_3]_0$ is the initial ozone concentration in OFR, RT is the residence time, k is a constant coefficient which is equals to 1.03 and $[O_3]$ is the mean ozone concentration in the atmosphere for 1 day, estimated to be 6.05×10^{16} molec cm^{-3} s (Sbai and Farida, 2019).

Section S2. Materials

Limonene (>99%, TCI), Δ^3-carene (>97%, Sigma Aldrich), methanol (Optima® LC-MS grade, Fisher Scientific), formic acid (Optima® LC-MS grade, Fisher Scientific), pressured nitrogen gas (99.999%, DEYI) were directly used for nitrogen-blowing without further purification. Ultrapure water with a resistivity of 18.2 MΩ cm was generated with a water purification system (Millipore, France).

Section S3. Calculation of the pure-compound saturation concentrations

The pure-compound saturation concentrations (C_0) of SOA from limonene and Δ^3-carene have been predicted using the following nonlinear expression (Li et al., 2016):

$$\text{Log}_{10}C_0 = \left(n_C^0\text{-}n_C\right)b_C\text{-}n_O b_O\text{-}2\frac{n_C n_O}{n_C+n_O}b_{CO}$$

The four free parameters n_C^0, b_C, b_O and b_{CO} represent the carbon number of 1 μg m^{-3} alkane, the carbon-carbon interaction term, the oxygen-oxygen interaction term and the carbon-oxygen nonideality respectively. The two independent variates n_C and n_O are the numbers of carbon and oxygen, respectively. Based on the calculated saturation mass concentration of organic aerosols, they can be classified into five groups (Donahue et al., 2012): extremely low-volatile organic compound (ELVOC; $C_0 < 3\times10^{-4}$ μg m^{-3}); low-volatile organic compound (LVOC; $3\times10^{-4} < C_0 < 0.3$ μg m^{-3}); semi-volatile organic compound (SVOC; $0.3 < C_0 < 300$ μg m^{-3}); intermediate volatility organic compound (IVOC; $300 < C_0 < 3\times10^6$ μg m^{-3}) and volatile organic compounds (VOC; $C_0 > 3\times10^6$ μg m^{-3}).

Table S1. The number and intensity proportion of four groups for limonene

Groups	Monomers	Dimers	Trimers	Tetramers
Number (L)[a]	242	162	122	116
Number (H)[b]	272	187	134	105
Intensity proportion (L)[a]	61.8%	25.7%	9.4%	3.1%
Intensity proportion (H)[b]	65.6%	24.4%	7.9%	2.0%

[a] L means under low RH. [b] H means under high RH.

Table S2. The number and intensity proportion of four groups for Δ^3-carene

Groups	Monomers	Dimers	Trimers	Tetramers
Number (L)[a]	239	178	76	4
Number (H)[b]	216	151	26	1
Intensity proportion (L)[a]	69.8%	28.6%	1.6%	0.5%
Intensity proportion (H)[b]	72.5%	26.9%	2.0%	0.2%

[a] L means under low RH. [b] H means under high RH.

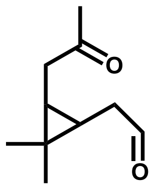
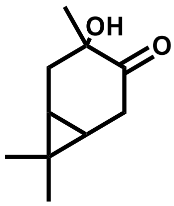
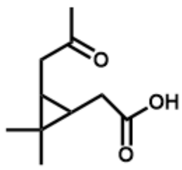
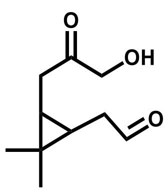
Table S3. Intensity and partitioning coefficient for limonene products identified by MS (can be found in the proposed mechanism).

	Molecular formula	**Low RH**		**High RH**		**Partitioning coefficient**	
		Absolute intensity	**Relative intensity**	**Absolute intensity**	**Relative intensity**	**Low RH**	**High RH**
Monomers	$C_{10}H_{16}O_2$	9.01×10^2	1.72×10^{-4}	1.27×10^3	1.42×10^{-4}	0.01	0.02
	$C_9H_{14}O_3$	1.49×10^4	2.85×10^{-3}	3.00×10^4	3.33×10^{-3}	0.02	0.05
	$C_{10}H_{16}O_3$	4.99×10^4	9.54×10^{-3}	8.58×10^4	9.55×10^{-3}	0.05	0.10

	$C_9H_{14}O_4$	1.29×10^{5}	2.46×10^{-2}	2.46×10^{5}	2.73×10^{-2}	0.13	0.25
	$C_{10}H_{18}O_3$	1.21×10^{3}	2.31×10^{-4}	1.64×10^{3}	1.82×10^{-4}	0.05	0.10
	$C_9H_{16}O_4$	7.60×10^{3}	1.45×10^{-3}	1.51×10^{4}	1.68×10^{-3}	0.13	0.25
	$C_{10}H_{16}O_4$	1.28×10^{5}	2.45×10^{-2}	2.24×10^{5}	2.49×10^{-2}	0.24	0.41
	$C_9H_{14}O_5$	1.28×10^{5}	2.45×10^{-2}	2.08×10^{5}	2.33×10^{-2}	0.58	0.76
	$C_9H_{14}O_3$	1.49×10^{4}	2.85×10^{-3}	3.00×10^{4}	-	0.02	0.05
	$C_8H_{12}O_4$	6.71×10^{4}	1.28×10^{-2}	1.35×10^{5}	-	0.07	0.15
	$C_{10}H_{18}O_2$	2.62×10^{2}	5.01×10^{-5}	4.60×10^{2}	5.12×10^{-5}	0.01	0.02
	$C_9H_{16}O_3$	7.20×10^{3}	1.38×10^{-3}	1.48×10^{4}	1.64×10^{-3}	0.02	0.05
	$C_{10}H_{14}O_3$	7.34×10^{3}	1.40×10^{-3}	1.34×10^{4}	1.50×10^{-3}	0.05	0.10
	$C_9H_{12}O_4$	3.49×10^{4}	6.66×10^{-3}	5.94×10^{4}	6.61×10^{-3}	0.13	0.25
	$C_{10}H_{14}O_5$	4.00×10^{4}	7.64×10^{-3}	5.44×10^{4}	6.06×10^{-3}	0.71	0.85
	$C_9H_{12}O_6$	1.25×10^{4}	2.38×10^{-3}	2.08×10^{4}	2.31×10^{-3}	0.94	0.97
	$C_{10}H_{16}O_6$	-	8.32×10^{-3}	7.12×10^{4}	7.93×10^{-3}	0.96	0.98
	$C_{10}H_{18}O_4$	-	1.49×10^{-3}	1.29×10^{5}	1.44×10^{-3}	0.24	0.41
	$C_9H_{16}O_5$	1.40×10^{4}	2.67×10^{-3}	2.76×10^{4}	3.08×10^{-3}	0.58	0.76
	$C_{10}H_{18}O_6$	-	1.39×10^{-3}	1.31×10^{5}	1.46×10^{-3}	0.96	0.98
	$C_{10}H_{16}O_5$	8.02×10^{3}	1.53×10^{-2}	1.49×10^{4}	1.65×10^{-2}	0.72	0.85
	$C_9H_{14}O_6$	-	-	9.40×10^{4}	1.05×10^{-2}	0.94	0.97
	$C_{10}H_{18}O_5$	9.05×10^{3}	1.73×10^{-3}	1.65×10^{4}	1.84×10^{-3}	0.72	0.85
	$C_9H_{16}O_6$	-	-	1.41×10^{4}	1.57×10^{-3}	0.94	0.97
HOMs	$C_9H_{14}O_7$	-	4.19×10^{-3}	4.44×10^{4}	4.95×10^{-3}	1.00	1.00
	$C_{10}H_{14}O_7$	8.75×10^{3}	1.67×10^{-3}	1.32×10^{4}	1.47×10^{-3}	1.00	1.00
	$C_{10}H_{14}O_{11}$	-	-	3.68×10^{2}	4.10×10^{-5}	1.00	1.00
	$C_{10}H_{14}O_{13}$	-	-	3.88×10^{2}	4.32×10^{-5}	1.00	1.00
	$C_9H_{16}O_7$	7.71×10^{3}	1.47×10^{-3}	1.91×10^{4}	2.13×10^{-3}	1.00	1.00
	$C_{10}H_{16}O_7$	1.63×10^{4}	3.12×10^{-3}	3.00×10^{4}	3.35×10^{-3}	1.00	1.00
	$C_9H_{14}O_8$	-	-	4.12×10^{3}	4.60×10^{-4}	1.00	1.00
	$C_{10}H_{18}O_7$	4.70×10^{3}	8.99×10^{-4}	8.90×10^{3}	9.91×10^{-4}	1.00	1.00

	$C_9H_{16}O_8$	-	-	2.54×10^3	2.82×10^{-4}	1.00	1.00
	$C_{10}H_{16}O_8$	3.63×10^3	6.94×10^{-4}	7.08×10^3	7.67×10^{-4}	1.00	1.00
Dimers	$C_{20}H_{34}O_4$	-		4.98×10^2	5.55×10^{-5}	1.00	1.00
	$C_{18}H_{30}O_6$	-	-	2.74×10^3	3.04×10^{-4}	1.00	1.00
	$C_{18}H_{28}O_7$	-	-	1.53×10^4	1.70×10^{-3}	1.00	1.00
	$C_{20}H_{30}O_8$	3.61×10^2	1.97×10^{-4}	1.25×10^4	1.40×10^{-3}	1.00	1.00
	$C_{18}H_{26}O_8$	1.29×10^4	2.47×10^{-3}	2.34×10^4	2.62×10^{-3}	1.00	1.00

Table S4. Δ^3-carene-SOA identified under high RH in Fig. S3.

[M–H]-	Theo. Mass	Error (ppm)	DBE	Suggested Formula	Molecular Structure
167.10657	167.107753	7.081	3	$C_{10}H_{16}O_2$	 
183.101733	183.102668	5.105	3	$C_{10}H_{16}O_3$	 

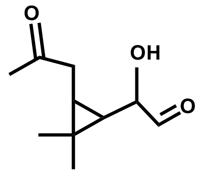
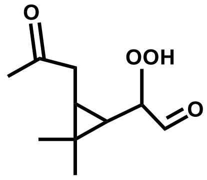
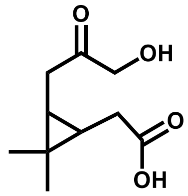
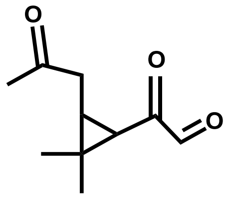
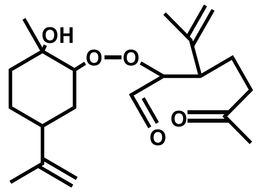
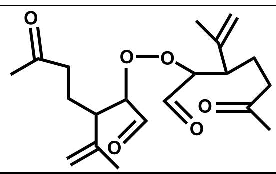
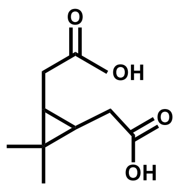
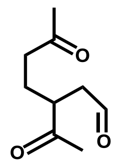
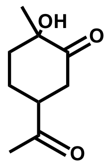
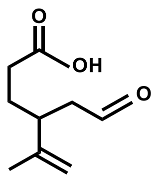
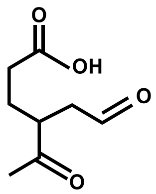
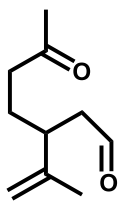
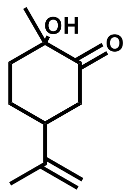
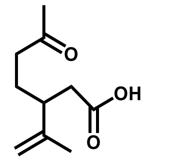
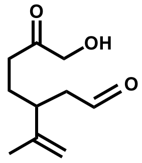
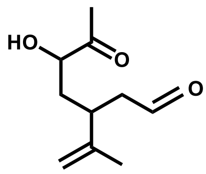
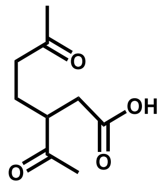
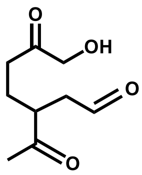
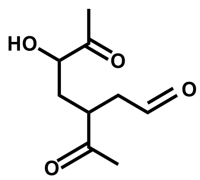
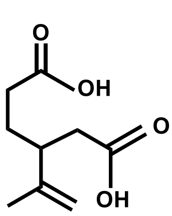
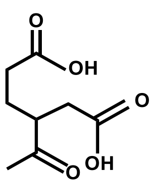
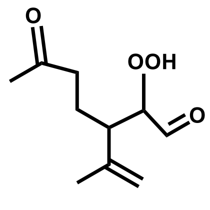
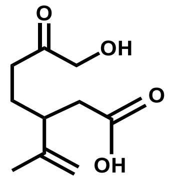
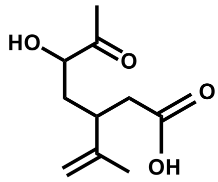
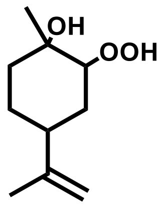
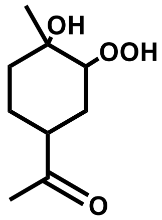
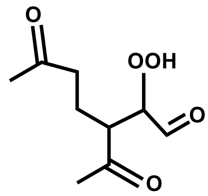
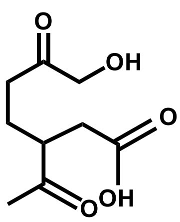
169.122233	169.123403	6.921	2	$C_{10}H_{18}O_2$	
199.096239	199.097583	6.747	3	$C_{10}H_{16}O_4$	 
181.085655	181.087018	7.526	3	$C_{10}H_{14}O_3$	
351.214938	351.217698	7.858	5	$C_{20}H_{32}O_5$	
365.194982	365.196962	5.421	6	$C_{20}H_{30}O_6$	
185.080938	185.081932	5.374	3	$C_9H_{14}O_4$	

Table S5. Limonene-SOA under high RH identified in Fig. 3 and Fig. 4.

[M–H]⁻	**Theo. Mass**	**Error (ppm)**	**DBE**	**Suggested Formula**	**Molecular Structure**
169.086288	169.087018	4.319	3	$C_9H_{14}O_3$	
					
					
183.065329	183.066282	5.208	4	$C_9H_{12}O_4$	
167.107219	167.107753	3.198	2	$C_{10}H_{16}O_2$	
					

183.102508	183.102668	0.874	3	$C_{10}H_{16}O_3$	
					
					
185.081203	185.081932	3.943	3	$C_9H_{14}O_4$	
					
					
					
187.060122	187.061197	5.749	3	$C_8H_{12}O_5$	

199.096857	199.097583	3.644	3	$C_{10}H_{16}O_4$	
					
					
185.117126	185.118318	6.441	2	$C_{10}H_{18}O_3$	
187.096428	187.097583	6.172	2	$C_9H_{16}O_4$	
201.075661	201.076847	5.896	3	$C_9H_{14}O_5$	
					

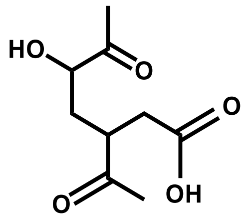
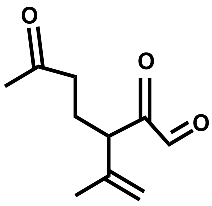
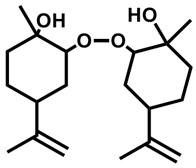
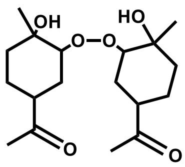
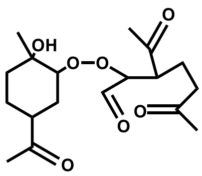
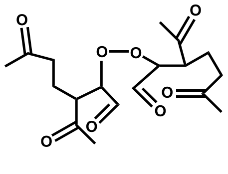
					
181.086015	181.087018	5.536	4	$C_{10}H_{14}O_3$	
337.237472	337.238433	2.851	4	$C_{20}H_{34}O_4$	
341.196189	341.196962	2.266	4	$C_{18}H_{30}O_6$	
355.17525	355.176227	2.749	5	$C_{18}H_{28}O_7$	
369.154689	369.155491	2.174	6	$C_{18}H_{26}O_8$	

Table S6. The intensity of dimers from multi-carbonyls under high RH and low RH

Molecular formula	Absolute intensity (Low RH)	Relative intensity (Low RH)	Absolute intensity (High RH)	Relative intensity (High RH)
$C_{19}H_{28}O_5$	3.60×10^{2}	6.87×10^{-5}	9.28×10^{3}	2.06×10^{-3}
$C_{19}H_{28}O_7$	5.00×10^{3}	9.50×10^{-4}	2.73×10^{4}	6.08×10^{-3}

$C_{19}H_{28}O_6$	1.78×10^3	3.40×10^{-4}	1.39×10^4	3.10×10^{-3}
$C_{18}H_{28}O_6$	3.19×10^3	6.08×10^{-4}	4.30×10^3	9.56×10^{-4}
$C_{18}H_{24}O_6$			6.06×10^2	1.35×10^{-4}
$C_{18}H_{26}O_5$			6.28×10^2	1.40×10^{-4}

Table S7. Dimers: RH-dependent discoveries for limonene and Δ[3]-carene.

54 dimers exclusively detected under high RH (limonene)		**63 dimers exclusively detected under low RH (Δ^3-carene)**	
Molecular formula	**Absolute intensity (High RH)**	**Molecular formula**	**Absolute intensity (Low RH)**
$C_{18}H_{26}O_4$	4.66×10^2	$C_{17}H_{24}O_5$	1.59×10^3
$C_{16}H_{20}O_6$	7.24×10^2	$C_{10}H_{14}O_{11}$	3.90×10^3
$C_{13}H_{18}O_9$	3.36×10^2	$C_{14}H_{14}O_8$	4.02×10^3
$C_{17}H_{22}O_6$	6.63×10^3	$C_{20}H_{40}O_2$	4.60×10^3
$C_{18}H_{26}O_5$	6.28×10^2	$C_{12}H_{10}O_{10}$	4.00×10^3
$C_{19}H_{32}O_4$	1.58×10^3	$C_{13}H_{16}O_9$	8.34×10^3
$C_{15}H_{18}O_8$	1.65×10^3	$C_{19}H_{26}O_4$	4.96×10^3
$C_{13}H_{12}O_{10}$	8.85×10^3	$C_{17}H_{22}O_6$	1.05×10^3
$C_{14}H_{20}O_9$	8.44×10^2	$C_{13}H_{12}O_{10}$	5.46×10^3
$C_{16}H_{28}O_7$	9.89×10^3	$C_{13}H_{18}O_{10}$	4.68×10^3
$C_{15}H_{26}O_8$	2.18×10^3	$C_{15}H_{12}O_9$	4.22×10^3
$C_{10}H_8O_{13}$	6.33×10^3	$C_{10}H_{12}O_{13}$	5.00×10^3
$C_{18}H_{24}O_6$	6.06×10^2	$C_{22}H_{28}O_3$	8.88×10^3
$C_{11}H_{14}O_{12}$	7.70×10^2	$C_{19}H_{26}O_6$	1.54×10^3
$C_{21}H_{22}O_4$	4.80×10^3	$C_{16}H_{20}O_9$	1.64×10^3
C20H34O4	2.53×10^3	$C_{15}H_{18}O_{10}$	5.00×10^3
$C_{23}H_{32}O_2$	2.12×10^3	$C_{16}H_{22}O_9$	1.69×10^3
$C_{18}H_{32}O_6$	3.68×10^2	$C_{18}H_{22}O_8$	3.32×10^3
$C_{17}H_{30}O_7$	7.46×10^3	$C_{12}H_{16}O_{13}$	4.00×10^3
$C_{14}H_{22}O_{10}$	4.04×10^3	$C_{20}H_{32}O_6$	8.21×10^3
$C_{21}H_{36}O_4$	1.36×10^4	$C_{16}H_{18}O_{10}$	4.50×10^3
$C_{17}H_{30}O_8$	4.68×10^2	$C_{16}H_{20}O_{10}$	5.20×10^3
$C_{12}H_{16}O_{13}$	2.43×10^3	$C_{19}H_{24}O_8$	8.21×10^3
$C_{11}H_{14}O_{14}$	4.46×10^2	$C_{20}H_{28}O_7$	2.38×10^3
$C_{18}H_{30}O_8$	4.46×10^2	$C_{17}H_{20}O_{10}$	4.16×10^3
$C_{16}H_{26}O_{10}$	7.44×10^2	$C_{21}H_{36}O_6$	8.03×10^3
$C_{17}H_{20}O_{10}$	2.12×10^3	$C_{16}H_{26}O_{11}$	1.16×10^3
$C_{16}H_{24}O_{11}$	1.48×10^3	$C_{17}H_{26}O_{11}$	1.32×10^3
$C_{20}H_{24}O_8$	3.96×10^3	$C_{18}H_{18}O_{11}$	4.02×10^3
$C_{17}H_{22}O_{11}$	2.48×10^3	$C_{18}H_{22}O_{11}$	4.54×10^3
$C_{21}H_{34}O_8$	1.28×10^4	$C_{18}H_{26}O_{11}$	1.49×10^3
$C_{13}H_{22}O_{15}$	4.06×10^2	$C_{22}H_{28}O_8$	4.62×10^3

$C_{19}H_{32}O_{10}$	5.30×10^{2}	$C_{15}H_{18}O_{14}$	4.08×10^{3}
$C_{22}H_{32}O_{8}$	5.90×10^{3}	$C_{20}H_{32}O_{10}$	5.97×10^{3}
$C_{20}H_{28}O_{10}$	1.53×10^{3}	$C_{17}H_{22}O_{13}$	5.10×10^{3}
$C_{18}H_{18}O_{13}$	4.49×10^{3}	$C_{21}H_{28}O_{10}$	4.25×10^{3}
$C_{19}H_{24}O_{12}$	1.49×10^{4}	$C_{19}H_{22}O_{12}$	5.44×10^{3}
$C_{19}H_{30}O_{12}$	6.10×10^{2}	$C_{22}H_{34}O_{9}$	7.52×10^{3}
$C_{15}H_{18}O_{16}$	1.14×10^{3}	$C_{21}H_{34}O_{10}$	2.12×10^{3}
$C_{23}H_{38}O_{9}$	4.34×10^{2}	$C_{14}H_{24}O_{16}$	4.80×10^{3}
$C_{32}H_{44}O_{2}$	8.96×10^{2}	$C_{15}H_{22}O_{16}$	4.04×10^{3}
$C_{21}H_{36}O_{11}$	3.74×10^{2}	$C_{17}H_{30}O_{14}$	3.51×10^{3}
$C_{14}H_{26}O_{17}$	1.00×10^{3}	$C_{22}H_{36}O_{10}$	4.02×10^{3}
$C_{20}H_{26}O_{13}$	1.26×10^{4}	$C_{18}H_{24}O_{14}$	4.44×10^{3}
$C_{22}H_{34}O_{11}$	1.92×10^{3}	$C_{19}H_{28}O_{13}$	6.68×10^{3}
$C_{20}H_{30}O_{13}$	9.36×10^{2}	$C_{20}H_{22}O_{13}$	3.90×10^{3}
$C_{18}H_{24}O_{15}$	2.05×10^{3}	$C_{21}H_{26}O_{12}$	4.48×10^{3}
$C_{21}H_{38}O_{12}$	9.16×10^{2}	$C_{22}H_{30}O_{11}$	2.29×10^{3}
$C_{24}H_{38}O_{10}$	3.78×10^{3}	$C_{15}H_{24}O_{17}$	4.70×10^{3}
$C_{16}H_{24}O_{17}$	1.26×10^{3}	$C_{25}H_{38}O_{9}$	5.24×10^{3}
$C_{21}H_{24}O_{14}$	4.80×10^{3}	$C_{17}H_{26}O_{16}$	5.18×10^{3}
$C_{20}H_{34}O_{4}$	4.98×10^{2}	$C_{21}H_{26}O_{13}$	4.82×10^{3}
$C_{18}H_{30}O_{6}$	2.74×10^{3}	$C_{22}H_{30}O_{12}$	2.47×10^{3}
$C_{18}H_{28}O_{7}$	1.53×10^{4}	$C_{16}H_{24}O_{17}$	5.16×10^{3}
		$C_{17}H_{28}O_{16}$	6.58×10^{3}
		$C_{29}H_{44}O_{6}$	5.82×10^{3}
		$C_{17}H_{30}O_{16}$	2.06×10^{3}
		$C_{22}H_{38}O_{12}$	3.86×10^{3}
		$C_{16}H_{32}O_{17}$	7.04×10^{3}
		$C_{23}H_{30}O_{12}$	1.26×10^{3}
		$C_{24}H_{34}O_{11}$	6.82×10^{3}
		$C_{20}H_{30}O_{10}$	4.14×10^{3}
		$C_{20}H_{32}O_{11}$	3.41×10^{3}

Table S8. Intensity and partitioning coefficient for Δ^3-carene products identified by MS (can be found in the proposed mechanism).

	Molecular formula	**Low RH**		**High RH**		**Partitioning coefficient**	
		Absolute intensity	**Relative intensity**	**Absolute intensity**	**Relative intensity**	**Low RH**	**High RH**
HOMs	$C_{10}H_{14}O_{11}$	3.41×10^{2}	5.44×10^{-5}	-	-	1.00	1.00

	$C_{10}H_{16}O_8$	1.42×10^3	2.26×10^{-4}	8.31×10^2	1.89×10^{-4}	1.00	1.00
	$C_{10}H_{18}O_{11}$	2.32×10^3	3.70×10^{-4}	1.61×10^3	3.65×10^{-4}	1.00	1.00
	$C_{10}H_{18}O_8$	4.60×10^2	7.34×10^{-5}	-	-	1.00	1.00
Dimers	$C_{20}H_{30}O_6$	1.25×10^4	1.97×10^{-3}	7.55×10^3	1.71×10^{-3}	1.00	1.00
	$C_{20}H_{30}O_8$	6.99×10^3	1.11×10^{-3}	4.16×10^3	9.44×10^{-4}	1.00	1.00
	$C_{20}H_{30}O_{10}$	3.62×10^3	5.77×10^{-4}	-	-	1.00	1.00
	$C_{20}H_{32}O_7$	1.58×10^4	2.51×10^{-3}	7.45×10^3	1.69×10^{-3}	1.00	1.00
	$C_{20}H_{32}O_9$	1.31×10^4	2.09×10^{-3}	8.76×10^3	1.99×10^{-3}	1.00	1.00
	$C_{20}H_{32}O_{11}$	2.98×10^3	4.76×10^{-4}	-	-	1.00	1.00
	$C_{20}H_{32}O_{13}$	5.11×10^2	8.15×10^{-5}	3.12×10^2	7.09×10^{-5}	1.00	1.00

Table S9. The experimental data and results of β-caryophyllene oxidation.

Exp.	**[Precursor] (ppb)**	**$[O]_3$ (ppm)**	**T (K)**	**RH (%)**	**$N_{(14.1\text{-}735nm)}$[a] (no.cm^{-3})**	**$M_{(14.1\text{-}735nm)}$[b] (μg m^{-3})**	**$D_{(mean)}$[c] (nm)**	**SOA yield (%)**
1	234.9	6.3	298	3.2	(2.3±0.1)×10^6	168.2±13.8	49.9±2.5	9.4±0.8
2	255.3	6.4	298	58	(3.6±0.5)×10^6	584.1±10.9	64.3±0.7	25.1±0.5

[a] $N_{(14.1\text{-}735\ nm)}$ means the total particle number concentration from size 13.8 nm to 723.4 nm. [b] $M_{(13.8\text{-}723.4\ nm)}$ means the total particle mass concentration from size13.8 nm to 723.4 nm. [c] $D_{(mean)}$ means the particle mean diameter.

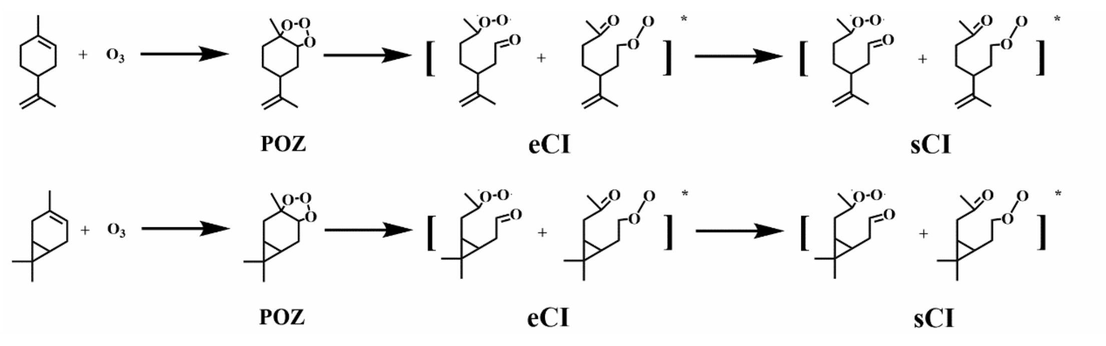


Fig S1. The formation of sCIs from the ozonolysis of limonene and Δ^3-carene.

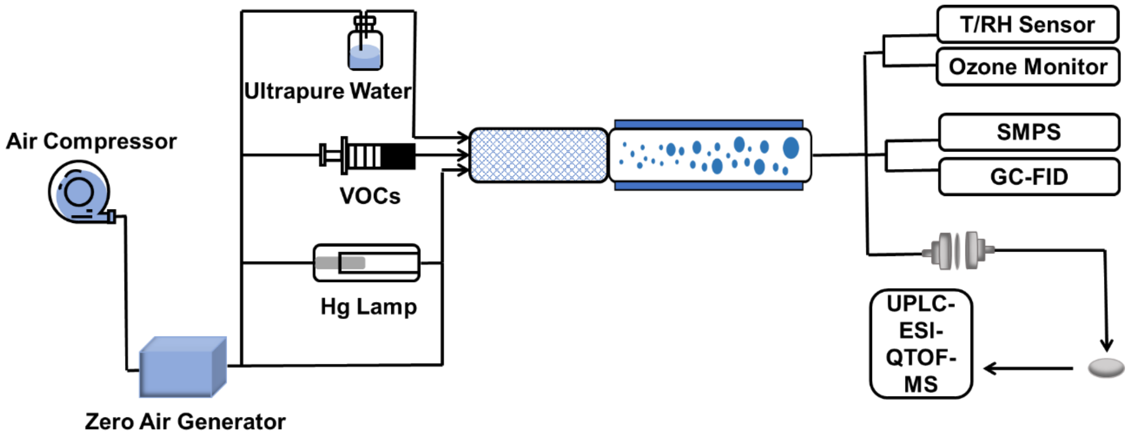


Figure S2. Schematic description of the experiment.

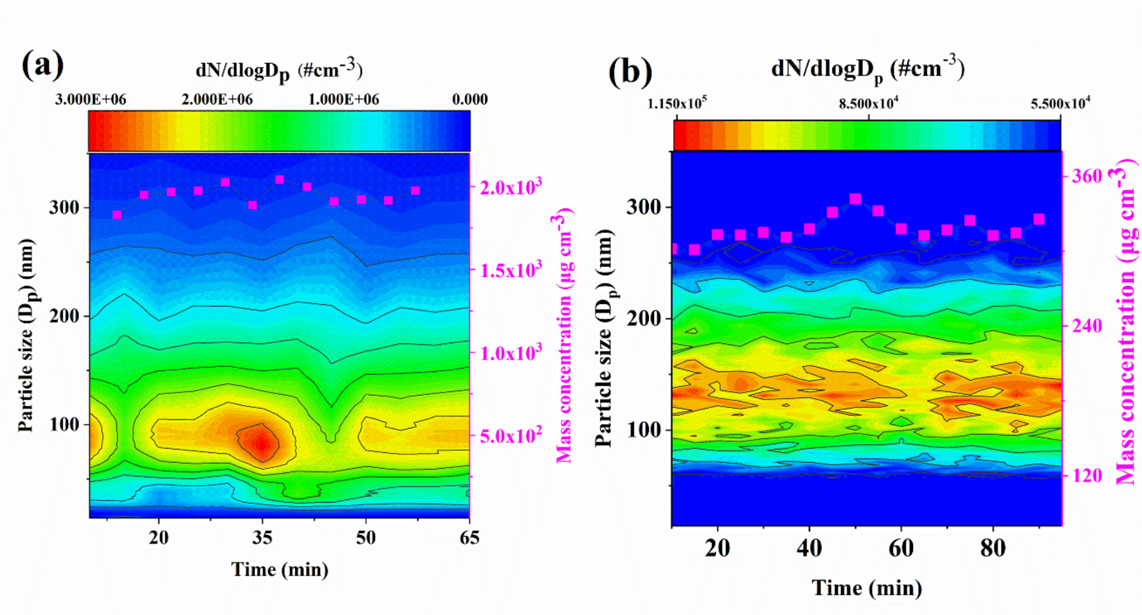


Figure S3. Time evolution of SOA size (electromobility diameter) and mass concentration obtained from limonene/O_3 and Δ^3-carene/O_3 experiments (Exp. 6 and Exp. 11).

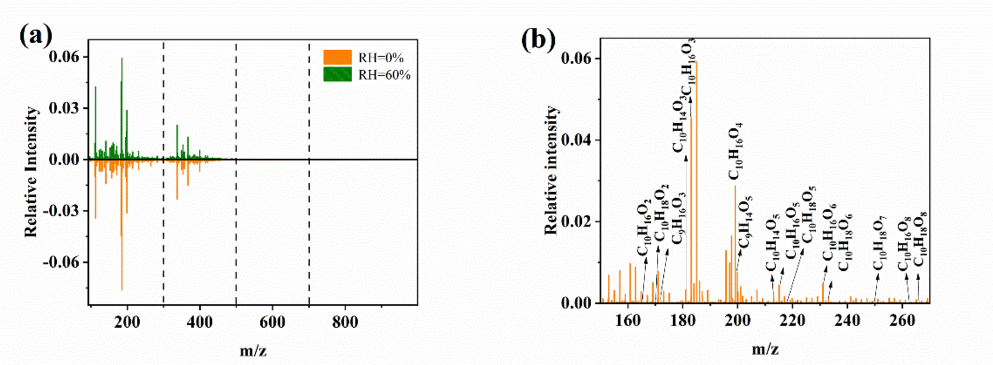


Fig. S4. UPLC/ (−) ESI-Q-TOF-MS mass spectra of SOA from Δ^3-carene ozonolysis. (a) MS under high and low RH conditions; (b) the identification of monomers under low RH condition.

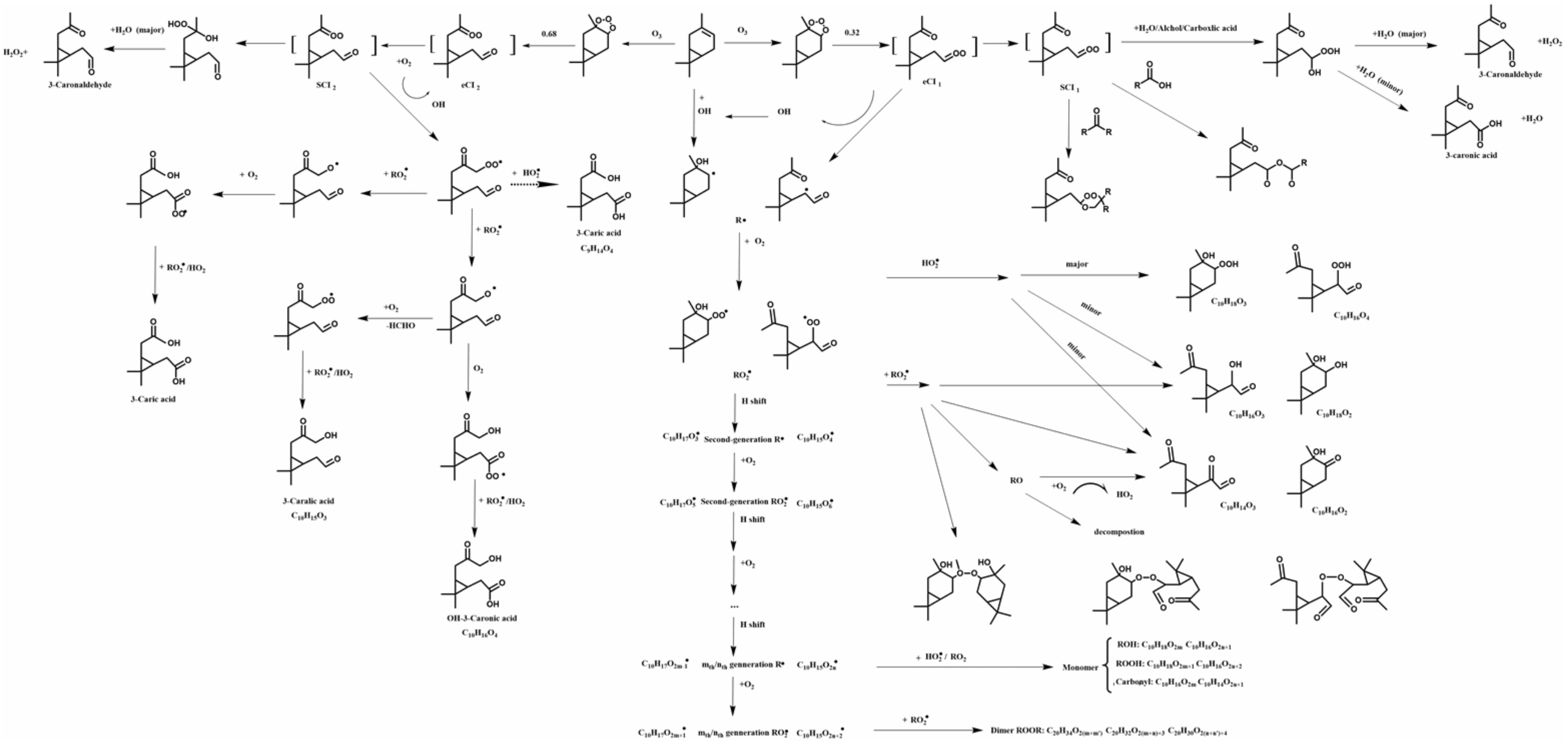


Figure S5. Proposed formation mechanisms for SOA formation from Δ^3-carene ozonolysis under high RH.

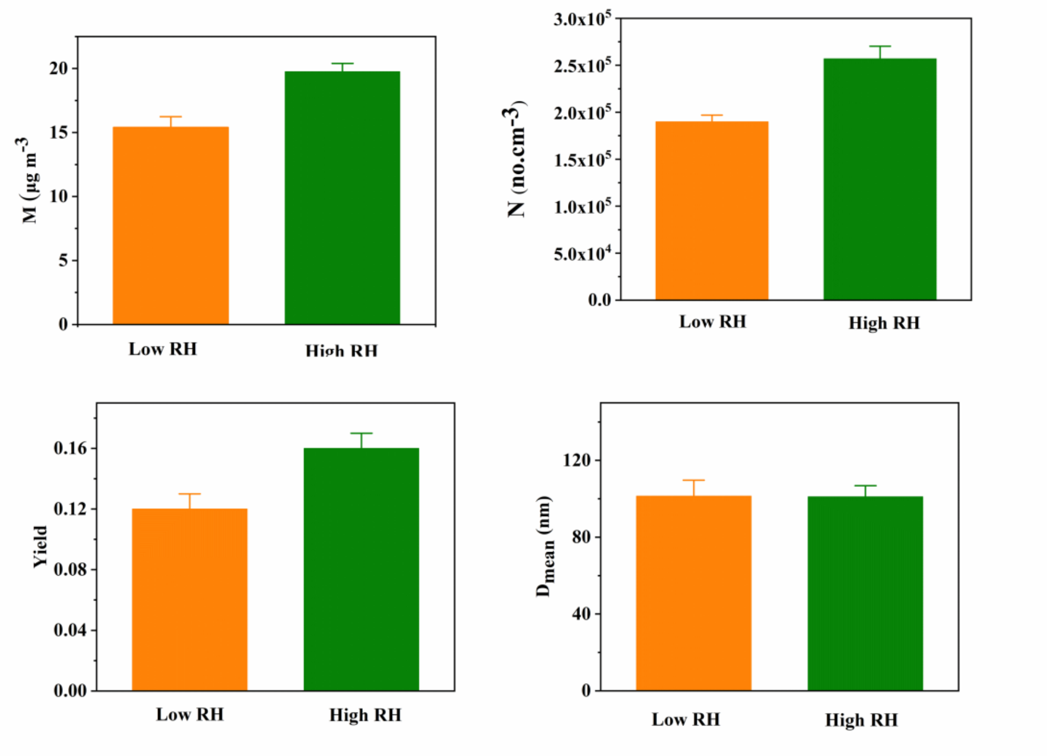


Figure S6. The SOA formation of low-concentration limonene under low and high RH (a) mass concentration (b) number concentration (c) SOA yield (d) mean diameter.

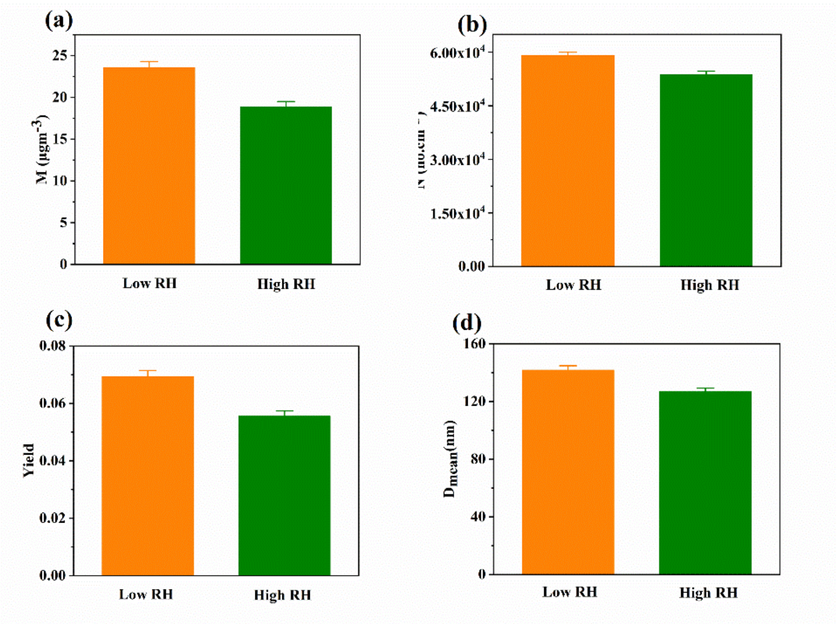


Figure S7. The SOA formation from endocyclic ozonolysis of limonene under low and high RH (a) mass concentration (b) number concentration (c) SOA yield (d) mean diameter. The initial concentration of limonene is 450 ppb and the concentration of O_3 is 67 ppb. Limonene ozonolysis primarily took place on endo-double bonds, with a rate constant of 2.01×10^{-16} cm^3 $molec.^{-1}$ s^{-1} (Shu and Atkinson, 1994).

Based on this rate constant, it can be estimated that approximately 10% of the limonene was consumed by O_3 upon exiting the reactor.

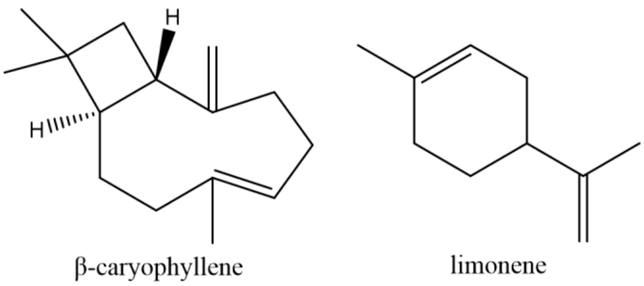


Figure S8. The molecular structure of β-caryophyllene and limonene.

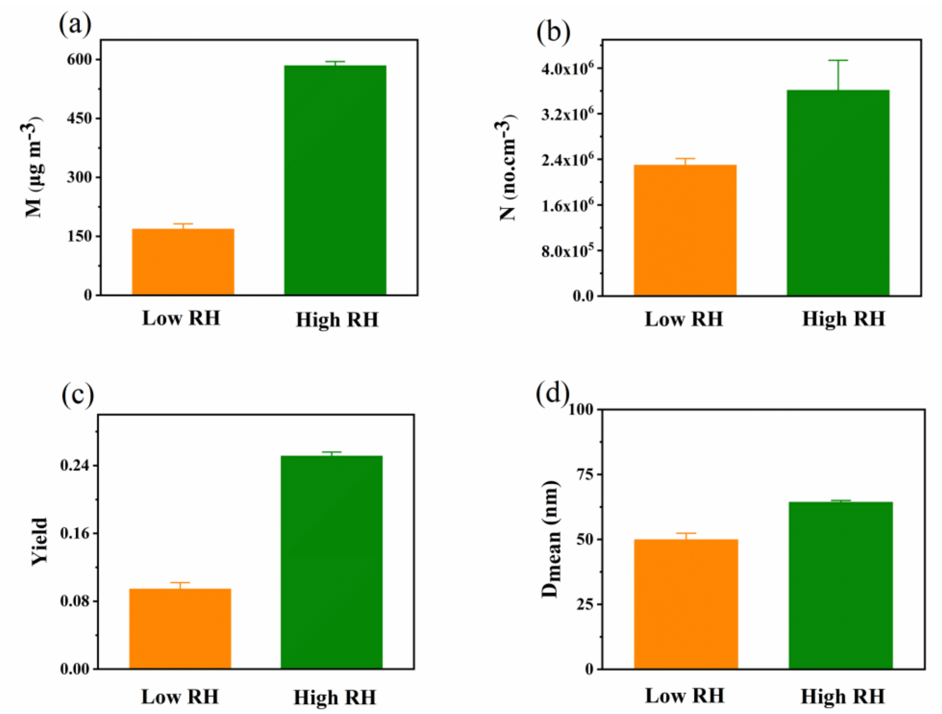


Figure S9. The SOA formation of β-caryophyllene under low and high RH (a) mass concentration (b) number concentration (c) SOA yield (d) mean diameter.

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