

1 **Contrasting impacts of humidity on the ozonolysis of** 2 **monoterpenes: insights into the multi-generation** 3 **chemical mechanism**

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5 Shan Zhang, Lin Du*, Zhaomin Yang, Narcisse Tsona Tchinda, Jianlong Li, Kun Li*
6 Environment Research Institute, Shandong University, Qingdao 266237, China.

7 *Correspondence to:* Lin Du (lindu@sdu.edu.cn) and Kun Li (kun.li@sdu.edu.cn)
8

9 **Abstract.** Secondary organic aerosol (SOA) formed from the ozonolysis of biogenic monoterpenes is a
10 major source of atmospheric organic aerosol. It has been previously found that relative humidity (RH)
11 can influence the SOA formation from some monoterpenes, yet most studies only observed the increase
12 or decrease in SOA yield without further explanations of molecular-level mechanisms. In this study, we
13 chose two structurally different monoterpenes (limonene with an endocyclic double bond and an
14 exocyclic double bond, Δ^3 -carene with only an endocyclic double bond) to investigate the effect of RH
15 in a set of oxidation flow reactor experiments. We find contrasting impacts of RH on the SOA formation:
16 limonene SOA yield increases by ~100% as RH increases, while there is a slight decrease in Δ^3 -carene
17 SOA yield. By analyzing SOA chemical composition and reaction mechanisms, the enhancement in
18 limonene SOA yield can be attributed to the water-influenced reactions after ozone attack on the
19 exocyclic double bond of limonene, which leads to the increment of lower volatile organic compounds
20 under high RH condition. However, as Δ^3 -carene only has an endocyclic double bond, it cannot undergo
21 such reactions. This hypothesis is further proved by the SOA yield enhancement of β -caryophyllene, a
22 sesquiterpene that also has an exocyclic double bond. These results greatly improve our understanding
23 of how water vapor influences the ozonolysis of biogenic organic compounds and subsequent SOA
24 formation processes.

25 **1 Introduction**

26 Secondary organic aerosol (SOA), as an important type of ambient fine particulate matter (PM_{2.5}:
27 aerosols with aerodynamic diameter $\leq 2.5 \mu\text{m}$) (Guo et al., 2014; Huang et al., 2014), has caused a series
28 of negative impacts on human health (Pye et al., 2021), air quality (Zhang et al., 2016) and global climate
29 (Levy et al., 2013). SOA produced from the oxidation of biogenic volatile organic compounds (BVOCs)
30 is a major component of SOA in heavy forest regions during summer (Sindelarova et al., 2014; Ahmadov

31 et al., 2012), and contributes by a large fraction (~40%-80%) to global OA budget (Cholakian et al.,
32 2019).

33 Monoterpenes, mostly emitted from coniferous trees, account for ~11% in total BVOCs
34 (Sindelarova et al., 2014; Kanakidou et al., 2005). Limonene is one of the most abundant monoterpenes,
35 with the annual emission budget of 11.4 Tg yr⁻¹ (Guenther et al., 2012). Apart from the biogenic source,
36 limonene can also be released from the indoor emission, mainly from essential oils (Ravichandran et al.,
37 2018; De Matos et al., 2019; Mot et al., 2022). Limonene has an endocyclic double bond and an exocyclic
38 double bond, and is thus more reactive than other monoterpenes towards oxidants such as ozone (O₃),
39 hydroxyl radical (OH), and nitrate radical (NO₃) (Chen and Hopke, 2010; Atkinson and Arey, 2003). Δ³-
40 carene is another kind of monoterpene that dominates the monoterpene emission from Scots pine (Bäck
41 et al., 2012). Different from limonene, Δ³-carene contains only one endocyclic double bond, which is
42 similar to most other monoterpenes.

43 Ozonolysis is an important reaction pathway for limonene and Δ³-carene. Although reactions with
44 OH and NO₃ are faster than that with O₃ for both two monoterpenes (Atkinson, 1991; Khamaganov and
45 Hites, 2001; Chen et al., 2015; Shaw et al., 2018), the atmospheric concentration of the latter
46 monoterpene is much higher than that of the former (Sbai and Farida, 2019). The contributions of O₃-
47 reactions with limonene and Δ³-carene to tropospheric degradation are 47% and 24%, respectively, in
48 the daytime (Ziemann and Atkinson, 2012). In pristine areas where NO₃ concentration is very low,
49 ozonolysis is also the dominant fate for limonene and Δ³-carene in the nighttime. In addition, it has been
50 previously found that the ozonolysis of monoterpenes can produce more extremely low volatility
51 products than OH-initiated oxidation, which contributes by a large fraction to the SOA production
52 (Jokinen et al., 2015). For either limonene or Δ³-carene, the first step for ozonolysis is attacking on the
53 endocyclic double bond to form two types of stabilized Criegee intermediates (sCI) with low energy (Fig.
54 S1) (Drozd and Donahue, 2011; Chen et al., 2019). The sCI will then trigger a series of chemical reactions,
55 like isomerization, decomposition and addition reactions. Correspondingly, the major components in Δ³-
56 carene SOA are caric acid, OH-caronic acid, and caronic acid (Ma et al., 2009; Thomsen et al., 2021),
57 while the major components from limonene SOA are limonaldehyde, keto-limonon aldehyde, limononic
58 acid and keto-limononic acid (Pathak et al., 2012; Wang and Wang, 2021).

59 Water is ubiquitous in the atmosphere and can affect the formation mechanism of SOA and its

60 relevant physical and chemical properties (Sun et al., 2013). A number of field measurements have shown
61 that the average molecular weight of the water/organic phase and activity coefficient of condensed
62 organics would be changed due to the change of relative humidity (RH) (Seinfeld et al., 2001; Li et al.,
63 2020). In addition, several laboratory studies have demonstrated that RH can influence the ozonolysis of
64 monoterpenes in different ways. Most of those studies have reported either an inhibitory effect or a
65 negligible effect of high RH on the particle formation (Bonn and Moortgat, 2002; Fick et al., 2002; Zhao
66 et al., 2021; Ye et al., 2018). Nevertheless, few other studies found that high RH can promote SOA
67 formation from the ozonolysis of limonene (Yu et al., 2011; Gong et al., 2018; Xu et al., 2021), but the
68 reason of this promotion effect remains unclear.

69 To fully examine the effects of water on SOA formation from the ozonolysis of monoterpenes,
70 especially the related chemical processes, we used an oxidation flow reactor (OFR) to investigate the
71 ozonolysis of limonene and Δ^3 -carene under different RH conditions in this study. An ultra-high
72 performance liquid chromatography with a quadrupole time-of-flight mass spectrometer (UPLC-Q-TOF-
73 MS) was deployed to analyze the molecular chemical composition of the SOA, which provided insights
74 into the physical and chemical processes influenced by the water content. With these state-of-the-art
75 techniques, we proposed mechanisms that may explain the inhibitory or enhancing RH effects on SOA
76 formation for different monoterpenes.

77 **2 Experimental methods**

78 **2.1 Oxidation flow reactor experiments**

79 A series of dark ozonolysis experiments of limonene and Δ^3 -carene were conducted in a custom-
80 made oxidation flow reactor (OFR). The OFR is a 602 mm long stainless cylinder with a volume of 2.5
81 L (Fig. S2) (Liu et al., 2019; Liu et al., 2014). A zero-air generator (XHZ2000B, Xianhe, China) was
82 used to generate dry clean air as the carrier gas for the OFR. As shown in Fig. S2, there are four gas paths
83 upstream of the OFR: the first path is the precursor gas channel through which monoterpenes are injected
84 via a syringe pump (ISPLab 01, Shenchen, China); the second path is for the flow of 300 sccm dry zero
85 air passing through a mercury lamp ($\lambda = 185$ nm) to generate O_3 ; the third path is connected to a water
86 bubbler to generate wet air; the fourth path is the extra dry zero air entering the OFR. The RH in the OFR
87 was controlled by adjusting the ratio of the wet and dry zero air flows. A water recycle system was

88 equipped to keep the temperature (T) around at 298 K. The total flow was 0.9 L min⁻¹, resulting in an
 89 average residence time of 167 s. The RH and T in the OFR were monitored by a T/RH Sensor (HM40,
 90 VAISALA, Finland). The concentration of ozone and the consumption of the precursor gas were
 91 measured with an ozone monitor (Model 106L, 2B Technologies, USA) and a gas chromatography with
 92 flame ionization detector (GC-FID 7890B, Agilent Technologies, USA), respectively. The GC was
 93 equipped with a DB-624 column (30 m × 0.32 mm, 1.8 μm film thickness) whose temperature was set
 94 to ramp from 100 °C to 180 °C at a rate of 20 °C min⁻¹, and then held at 180 °C for 2 min. Before each
 95 experiment, O₃ was introduced into the OFR to clean it until the background aerosol mass concentration
 96 reached < 1 μg m⁻³.

97 The experimental conditions are shown in Table 1. In these OFR experiments, the precursor
 98 (limonene or Δ³-carene) concentration was set to ~320-340 ppb. A high O₃ concentration of ~6 ppm was
 99 used to realize an equivalent aging time of 0.41 day in the real atmosphere, assuming an average ambient
 100 O₃ concentration of 28 ppb (Sbai and Farida, 2019) (see Section S1 for the calculation). Under such
 101 conditions, most of the precursors were consumed, since the residence time was almost five and three
 102 times of the half-life for limonene and Δ³-carene, respectively. Correspondingly, the O₃ consumption for
 103 limonene and Δ³-carene were ~250 ppb and ~100 ppb, respectively. A series of RH conditions ranging
 104 from dry (1-2%) to 60% with a step of ~10% were used to investigate the effects of water content on
 105 SOA production and composition (see Table 1). All materials used in the experiments have been
 106 described in Section S2.

107 **Table 1.** Experimental conditions and results.

Exp.	[Precursor] (ppb)	[O] ₃ (ppm)	T (K)	RH (%)	N _{(13.8-723.4 nm)^a} (cm ⁻³)	M _{(13.8-723.4 nm)^b} (μg m ⁻³)	D _{(mean)^c} (nm)	SOA yield (%)
limonene								
1	321±39	5.7	298	1–2	6.9×10 ⁵	980.9	138.2	62.9
2	321±39	6.0	298	10±2	1.3×10 ⁶	1377.5	126.8	88.4
3	321±39	5.9	298	20±2	9.0×10 ⁵	1573.3	150.9	90.2
4	321±39	5.9	298	30±2	1.4×10 ⁶	1573.3	128.9	100.9
5	321±39	6.0	298	40±2	1.7×10 ⁶	2051.4	130.7	131.6

6	321±39	5.5	298	50±2	1.5×10 ⁶	1962.7	137.8	125.9
7	321±39	5.5	298	60±2	1.5×10 ⁶	2211.1	139.0	141.8
Δ³-carene								
8	341±28	6.1	298	1–2	9.5×10 ⁴	346.0	195.8	19.4
9	341±28	6.4	298	10±2	1.4×10 ⁵	300.3	163.4	16.8
10	341±28	6.4	298	20±2	9.4×10 ⁴	244.9	176.9	13.7
11	341±28	6.0	298	30±2	5.9×10 ⁴	241.2	205.1	13.5
12	341±28	6.3	298	40±2	4.6×10 ⁴	205.8	203.2	11.5
13	341±28	6.3	298	50±2	6.8×10 ⁴	196.7	180.7	11.0
14	341±28	6.3	298	60±2	5.6×10 ⁴	198.5	190.2	11.1

108 ^a N_(14.1-735 nm) means the total particle number concentration from size 13.8 nm to 723.4 nm. ^b M_{(13.8-723.4}
109 nm) means the total particle mass concentration from size 13.8 nm to 723.4 nm. ^c D_(mean) means the particle
110 mean diameter.

111 2.2 SOA particle analysis

112 2.2.1 SOA yield

113 The SOA particle size distribution was measured with a scanning mobility particle sizer (SMPS),
114 which consists of a differential mobility analyzer (DMA) (model 3082, TSI Inc., USA) and a
115 condensation particle counter (CPC) (model 3776, TSI Inc., USA). The samples were measured by SMPS
116 every 5 minutes with a sampling flow and a sheath flow of 0.3 L min⁻¹ and 3 L min⁻¹, respectively. The
117 SOA mass concentration was calculated from the volume concentration measured with SMPS and the
118 aerosol density, which was estimated to be 1.25 cm⁻³ for limonene- and 1.09 g cm⁻³ for Δ³-carene-SOA
119 (Thomsen et al., 2021; Watne et al., 2017).

120 The SOA yield (Y) for individual organic gas can be calculated as:

$$121 Y = \frac{\Delta M}{\Delta HC}$$

122 Where ΔM is the total mass concentration of SOA, ΔHC is the mass concentration of reacted precursor
123 (Ng et al., 2007; Odum et al., 1996).

124 2.2.2 Ultra-high performance liquid chromatography quadrupole time-of-flight mass spectrometry 125 analysis

126 An ultra-high performance liquid chromatography (UPLC, UltiMate 3000, Thermo Scientific)

127 coupled with a quadrupole time-of-flight mass spectrometry (Q-TOFMS, Bruker Impact HD) was used
128 to analyze the molecular-level chemical composition of SOA. First, the SOA particles were collected on
129 the PTFE filters (47 mm diameter, 0.22 μm pore size, Jinteng, China). Next, these filters were dissolved
130 and extracted by 5 mL methanol for two times. Extracts were then filtered through PTFE syringe filters
131 (0.22 μm pore size), and were concentrated to near dryness by nitrogen-blowing. At last, the samples
132 were redissolved in a 200 μL solution with 0.1% (v/v) formic acid in 50:50 methanol/ultrapure water
133 mixture.

134 The parameters of LC-MS were set as follows: capillary voltage 4000 V, nebulizer pressure 0.4 bar,
135 dry heater temperature 200°C, end plate voltage -500 V, and flow of dry gas 4 L min^{-1} . A C_{18} column
136 (100 \AA , 3 mm particle size, 2.1 mm \times 50 mm, Waters, USA) was used with a column temperature of 35°C.
137 The mobile phase was 0.1 % formic acid in methanol (A) and 0.1 % formic acid in ultra-high purity
138 water (B) with a flow of 200 $\mu\text{L min}^{-1}$. The injection volume was 5 μL . The MS was operated in negative
139 ion mode, and the detection molecular weight range was from m/z 50 to 1500. The temperature ramp
140 program was: 0–3min with 0%–3% phase B, 3–25min with 3%–50% phase B, 25–43min with 50%–90%
141 phase B, 43–48 min with 90%–3% phase B, 48–60min with 3% phase B.

142 **3 Results and discussion**

143 **3.1 SOA production under different RH conditions**

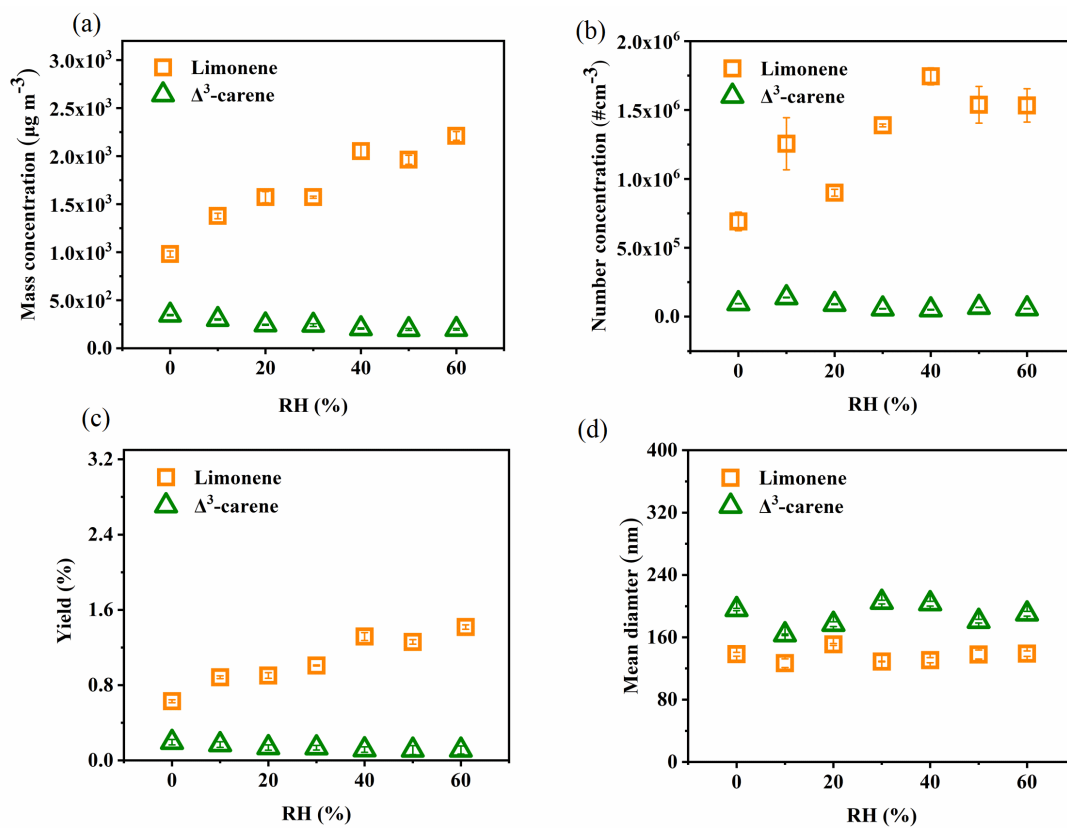
144 SOA formation of a representative experiment is shown in Fig. S3. It is found that the formed SOA
145 are mainly in the size range of 60-200 nm, and the number concentration and mass concentration are
146 relatively stable during the course of the OFR experiment. SOA formation from limonene and Δ^3 -carene
147 in terms of particle number concentration, particle mass concentration, and SOA yield as a function of
148 RH are illustrated in Fig. 1a-c. We find that all the above-mentioned 3 parameters of limonene-SOA
149 increase with the increasing RH. The increment of particle mass concentration and SOA yield from the
150 ozonolysis of limonene is \sim 100% higher at wet (60% RH) than at dry conditions. In contrast, SOA
151 formation from Δ^3 -carene is suppressed by \sim 40% under high RH. The distinct effects of RH on SOA
152 formation from the ozonolysis of limonene and Δ^3 -carene found in this study agree with most previous
153 studies (Yu et al., 2011; Jonsson et al., 2006b; Bonn et al., 2002; Gong and Chen, 2021; Li et al., 2019b).
154 As shown in Table 2, Yu et al. (2011) reported a positive correlation between SOA production and RH

155 for the ozonolysis of limonene in the chamber experiments without OH scavenger. Their experimental
156 condition is similar to that in our study regarding the absence of OH scavenger and, thus, similar results
157 were observed. However, in the presence of OH scavenger, results are quite different. Jonsson et al. (2006)
158 observed a similar enhancement effect of high RH on SOA production with 2-butanol as the OH
159 scavenger, while Bonn et al. (2002) found a negligible or suppressive effect with cyclohexane as the OH
160 scavenger. It should be noted that the OH scavenger not only has the ability to scavenge OH but also
161 produces additional products which may influence the reactions of target precursors. For example, there
162 is no difference between 2-butanol and cyclohexane in the scavenging ability of OH radical, though 2-
163 butanol will produce more HO₂· than cyclohexane and, consequently, R· will react with HO₂· to produce
164 more hydroxyl acids and hydroxyl per-acid products, most of which have low volatility and, thus high
165 partitioning into the particle phase. According to previous studies, the influence of different OH
166 scavengers can vary (Jonsson et al., 2008). This may explain the different findings with and without OH
167 scavenger for limonene-SOA. With regard to Δ³-carene, similar results are found in the absence of OH
168 scavenger, namely, high RH has negligible or slightly suppressive effect on SOA production (Bonn et al.,
169 2002; Fick et al., 2002). Same as limonene, the presence of OH scavenger and its different chemical
170 nature can explain the different results found previously (Jonsson et al., 2006a; Bonn et al., 2002).

171 The enhancement in limonene-SOA production under high RH can be due to several reasons from
172 either physical or chemical processes. First, the hygroscopic growth of the particles (i.e., absorption of
173 water content) can lead to higher mass concentration under higher RH, but the enhancement should be
174 at most ~30% as the growth factor (GF, the ratio of wet and dry diameter: $D_{\text{wet}}/D_{\text{dry}}$) of limonene-SOA is
175 ≤ 1.1 (Varutbangkul et al., 2006). However, we do not observe an obvious change in the mean diameter
176 when comparing dry and wet conditions (Fig. 1d). In addition, hygroscopic growth should also occur for
177 Δ³-carene SOA, but no obvious enhancement in particle mass is observed (Fig. 1a). Therefore, it is
178 suggested that physical processes regarding hygroscopic growth play a minor role in the enhancement in
179 limonene-SOA under high RH. As a consequence, we believe that chemical processes are likely the
180 reason of the enhancement in limonene-SOA under high RH. Water can influence chemical processes in
181 the gas phase or in the particle phase. Particle-phase reactions can promote the growth of small particles
182 and, thus, mainly lead to larger particle sizes. As the observed SOA enhancement is mainly from high
183 number concentration particles rather than the large size particles (Fig. 1b and 1d), it is likely that the

184 water-participated gas-phase reactions are the most possible reasons for the limonene-SOA enhancement.

185 The reaction mechanism is analyzed below based on the mass spectra information on the SOA.



186

187 **Figure 1.** The effect of RH on the SOA formation: (a) number concentration, (b) mass concentration, (c)

188 SOA yield, (d) mean diameter.

189

Table 2. Comparison with previous studies on the effect of RH.

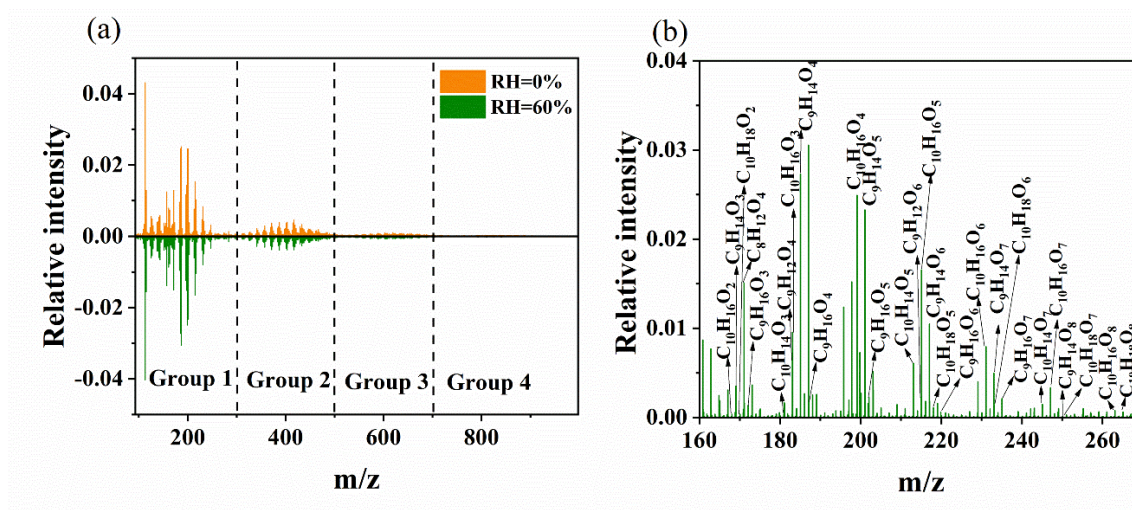
Precursor concentration (ppb)	Precursor concentration (ppb)	O ₃ concentration (ppb)	Reactor	OH scavenger	T (K)	RH (%)	SOA Mass		M ^a	N ^b	Reference
							Concentration (µg/m ³)	SOA Yield (%)			
1000	1000		flow reactor	cyclohexane	295±2	0.02 and 32.5	N.M. ^c	N.M. ^c	no effect	- ^e	Bonn et al. (2002)
320	100±5		chamber	N.M. ^c	296±2	18±2, 50±3 and 82±2	24; 58; 120	7.0 ± 0.7; 17.4±1.3; 53.4±1.9	+ ^d (7 times)	+ ^d (8 times)	Yu et al. (2011)
15 and 30	430.9		flow reactor	2-butanol	298±0.4	< 2-85	2.7-10.5 and 62-229	6.8-26.4 and 77.4-285.7	+ ^d	+ ^d	Jonsson et al. (2006)
endocyclic (24.6) and exocyclic (15.2)	endocyclic (270) and exocyclic (12200)		flow reactor	2-butanol	298	10-50	endocyclic (~11) and exocyclic (22-51)	endocyclic (~7.4) and exocyclic (23.8-55.3)	exocyclic (+ ^d) and endocyclic (- ^e)	N.M. ^c	Gong and Chen (2021)
1085	900±10		flow reactor	none	298	3-62	150; 200; 210	N.M	+ ^d	- ^e	Li et al. (2019)

321±39	5786±203	flow reactor	none	298	0-60	980.9-2211.1	62.9-141.8	+ ^d (2 times)	+ ^d (3 times)	this study
1000	1000	flow reactor	cyclohexane	295±2	0.02 and 32.5	N.M. ^c	N.M. ^c	no effect	- ^e	Bonn et al. (2002)
14.2 and 29.4	2300	flow reactor	2-butanol	298±0.4	< 2-85	0.78-3.8 and 15.3-94;	2.1-10.1 and 19.8- 116.7	+ ^d	+ ^d	Jonsson et al. (2006)
1111	900±10	flow reactor	none	298	3-62	75; 80; 90	N.M	- ^e	- ^e	Li et al. (2019)
341±28	6257±140	flow reactor	none	298	0-60	346.0-198.5	19.4-11.1	- ^e	no effect	this study

191 ^a M means the change trend total particle mass concentration. ^b N means total particle number concentration. ^c N.M. means not mentioned. ^d Positive sign (+) means the
192 mass or number concentration increases with RH. ^e Negative sign (-) means the mass or number concentration decreases with RH.

193 **3.2 Molecular analysis of SOA particles**

194 The UPLC/ESI-Q-TOF-MS was used to examine the SOA molecular composition under high and
 195 low RH conditions. As shown in Fig. 2a, the mass spectra of limonene-SOA are divided into four groups:
 196 monomeric group (<m/z 300), dimeric group (m/z 300-500), trimeric group (m/z 500-700), and
 197 tetrameric group (m/z 700-1000), corresponding to products containing one, two, three, and four
 198 oxygenated limonene units, respectively (Bateman et al., 2009). Most of the SOA molecules are
 199 monomers (>60%) (Fig. 2b) and dimers (~25%), while trimers and tetramers contribute to very small
 200 fractions (<10% and ~3%) (Table S1). Correspondingly, the distribution of Δ^3 -carene-SOA can be
 201 divided into four groups (Fig. S4), comparable to that of limonene-SOA. Most of the SOA molecules are
 202 monomers (~70%) and dimers (~25%), while trimers and tetramers contribute to smaller proportions (~2%
 203 and <1%, respectively) (Table S2). Although the SOA mass concentration increases by ~100% under
 204 high RH condition, the relative intensities of MS peaks do not significantly change with varying RH
 205 conditions. In other words, we did not observe an obvious change in the overall MS patterns, and the
 206 fractions of the four groups only slightly differed under different RH conditions, e.g., the fraction of
 207 monomers was 62% under dry condition and 66% under wet conditions. However, if we take a closer
 208 look, the intensities and contributions of specific peaks are quite different with varying RH. For example,
 209 the relative intensity of $C_{10}H_{16}O_2$, a possible first-generation product (Gong et al., 2018), decreases by
 210 ~20% with increasing RH from dry to 60% (Table S3). This is likely due to the multi-generation reactions
 211 influenced by water vapor concentration, as discussed below with the proposed reaction mechanism of
 212 limonene ozonolysis.



213

214 **Figure 2.** UPLC/ (-) ESI-Q-TOF-MS mass spectra of SOA from limonene ozonolysis. (a) MS under
215 high and low RH conditions; (b) the identification of monomers under high RH condition.

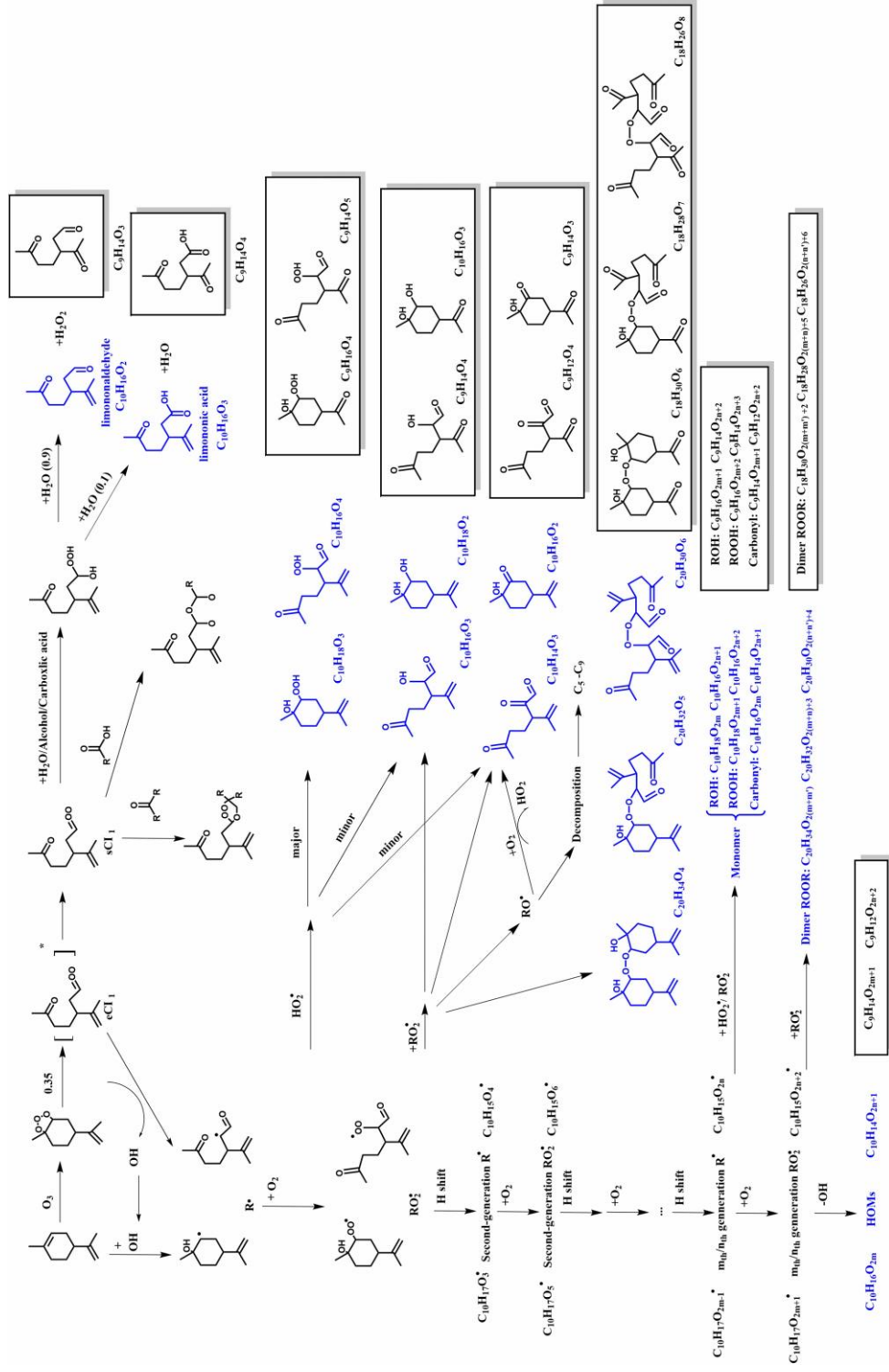
216 The proposed reaction mechanism of limonene ozonolysis is shown in Fig. 3 and Fig. 4. The initial
217 step in the reaction of O₃ with limonene is the attack of the endocyclic double bond to form eCI₁ and
218 eCI₂ (with branching ratios of 0.35 and 0.65, respectively). In the context of eCI₁, several complex
219 reactions occur, with the most dominant reaction being the generation of hydroxyl radicals (OH) and a
220 reaction pathway known as sCI₁. The sCI₁ pathway can proceed through three distinct reactions, as
221 depicted in Fig. 3. The first pathway is the reaction with H₂O, alcohol or carboxylic acid to form a
222 carboxylic acid species with hydroxyl, which would subsequently lose a molecule of water to form
223 limononaldehyde or lose a molecule of hydrogen peroxide to form limononic acid (Grosjean et al., 1992;
224 Li et al., 2019b). The second and third pathways involve reactions of sCI₁ with carboxylic acids and
225 carbonyls, respectively, leading to the formation of anhydrides and secondary ozonides. Additionally, the
226 generated OH radicals can react with limonene, giving rise to another alkyl radical, C₁₀H₁₇O·. These
227 alkyl radicals react with O₂ and form peroxy radicals (RO₂·). The atmospheric fate of produced RO₂· in
228 the absence of NO_x includes the reaction with RO₂· or HO₂· (Atkinson and Arey, 2003) and the
229 unimolecular H shift. The RO₂·+HO₂· route mainly form hydroperoxide (ROOH), and the minor fraction
230 is to form alcohols and carbonyls (Atkinson and Arey, 2003). The products of bimolecular reactions
231 between RO₂· and RO₂· are alcohols, carbonyls, alkoxy radicals, peroxides and ROOR dimers (Hammes
232 et al., 2019; Peng et al., 2019). The H shift of RO₂· can form second-generation R· and trigger a main
233 generation channel of highly oxidized molecules (HOMs), i.e., R· would go through a process of repeated
234 oxygen addition and hydrogen-atom shift to form HOMs with high O/C ratios of > 0.7–0.8 (Molteni et
235 al., 2018; Bianchi et al., 2019).

236 In addition to the eCI₁ route, the eCI₂ pathway is also responsible for the generation of various
237 products (Fig. 4). Since the reaction of the hydroxyl radical (OH) attacking limonene is already depicted
238 in Fig. 3, our main emphasis in Fig. 4 is on the pathways involved in the generation of sCI. First, sCI₂
239 reacts with H₂O and decomposes to limononaldehyde and H₂O₂. Additionally, sCI₂ could experience an
240 O₂ addition, ·OH loss and isomerization to produce two types of RO₂·, which can undergo the similar
241 reactions as the RO₂· formed from the sCI₁ route, and the major products are also shown in Fig. 4.

242 Since limonene and Δ³-carene both have an endocyclic double bond, the similar reactions as

243 mentioned above can occur for the ozonolysis of Δ^3 -carene (Fig. S5), and most corresponding formula
244 in Fig. S5 could be identified in Table S4. However, the reactivity of limonene towards O_3 is expected to
245 be higher owing to its exocyclic double bond. As shown in Fig. 4, the attack of O_3 to the exocyclic double
246 bond mainly leads to sCl_3 (highlighted in red) with the unpaired electrons outside the ring (Leungsakul
247 et al., 2005). sCl_3 can react with H_2O to form a carbonyl called keto-limonene. It should be noted that
248 this reaction can occur not only for limonene, but also for all the products that retain the exocyclic double
249 bond. As a result, the compounds that are colored in blue in Fig. 3 and Fig. 4 can undergo further reactions
250 to generate products with an additional carbonyl (see the boxes in Fig. 3 and Fig. 4). Furthermore, their
251 molecular formula shown in Table S5 have been identified using the Q-TOF-MS. This mechanism can
252 well explain the decrease in the relative intensity of $C_{10}H_{16}O_2$ from high RH to low RH and the increase
253 in the relative intensity of $C_9H_{14}O_3$ from low RH to high RH (Table S3).

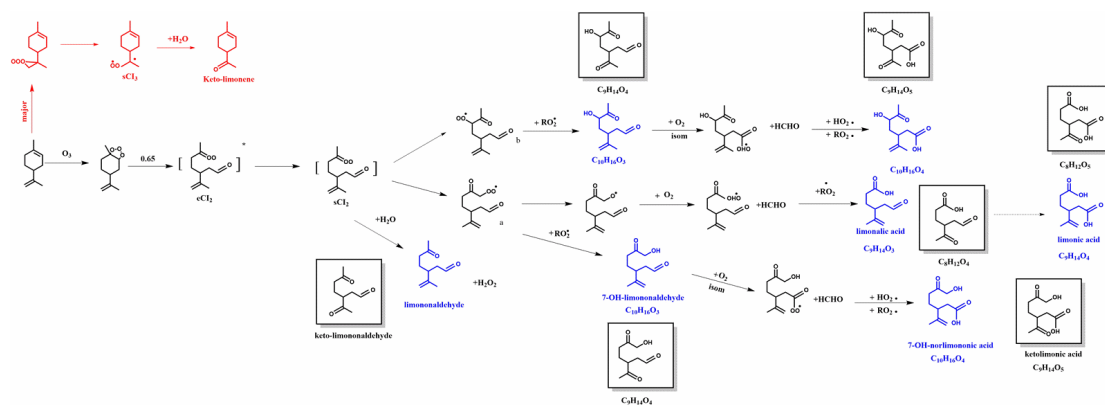
254 In such progress, we cannot rule out the possibility that relative humidity (RH) may influence the
255 generation of other free radicals (Ma et al., 2009), thereby impacting the formation of secondary organic
256 aerosols (SOA), such as, OH-radical reactions (Bonn et al., 2002; Fick et al., 2002). However, Molar OH
257 radical yields were reported as 0.65 ± 0.10 (Hantschke et al., 2021), 0.86 ± 0.11 (Aschmann et al., 2002)
258 and 0.56 to 0.59 (Wang et al., 2019) for Δ^3 -carene, while for limonene, the reported yields were 0.67 ± 0.10
259 (Aschmann et al., 2002) and 0.76 ± 0.06 (Herrmann et al., 2010). It seems that the OH radicals produced
260 from limonene and Δ^3 -carene are quite similar within the range of uncertainties. Therefore, the increased
261 ozone consumption by limonene is primarily attributed to the presence of its exocyclic double bond.



262

263 **Figure 3.** Proposed formation mechanism for SOA formation from eCI₁ oxidation under high RH. The compounds in blue and in boxes are identified using UPLC/ (-) ESI-Q-

264 TOF-MS.



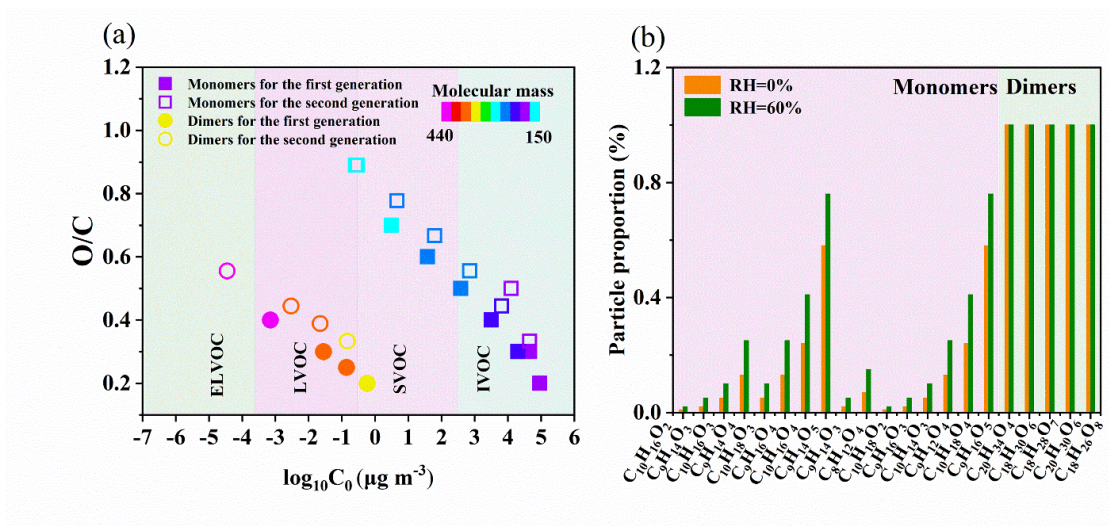
265

266 **Figure 4.** Proposed formation mechanisms for SOA formation from eCl₂ and exocyclic double bond
 267 oxidation under high RH. The compounds in blue and in boxes are identified using UPLC/ (-) ESI-Q-
 268 TOF-MS.

269

270 **3.3 Processes leading to the increase or decrease in SOA formation**

271 Based on the results and mechanisms shown above, we present evidence that high humidity
 272 enhances limonene-SOA formation. First, the presence of water vapor enhances the formation of
 273 carbonyls from the reaction of exocyclic double bond, and the oligomerization of these carbonyls
 274 generates more dimers including hemiacetal (or acetal) formation and aldol condensation (Zhang et al.,
 275 2022; Kroll et al., 2005; Jang et al., 2003). As shown in Table S6, 54 out of the total 187 dimers were
 276 exclusively observed for limonene under high humidity conditions, contributing to a corresponding
 277 intensity of ~19%. These dimers can be classified as low-volatile organic compounds (LVOC; $3 \times 10^{-4} <$
 278 $C_0 < 0.3 \mu\text{g m}^{-3}$) and extremely low-volatile organic compounds (ELVOCs; $C_0 < 3 \times 10^{-4} \mu\text{g m}^{-3}$) (Fig.
 279 5a), and thus promote the nucleation and new particle formation in different ways. This finding is similar
 280 to that from a previous study showing that high RH can promote dimer formation from the ozonolysis of
 281 α -pinene (Kristensen et al., 2014). Second, we find that high RH can also promote the formation of
 282 HOMs, although the mechanism remains unclear. As shown in Table S3, many HOMs proposed from the
 283 mechanism are detected under high RH condition but not detected under low RH condition, including
 284 both monomers and dimers. Many HOMs have low volatilities and, thus, can also promote new particle
 285 formation. Overall, the promoted dimer and HOM formation greatly enhance the new particle number
 286 concentration under high RH condition (Fig. 6).

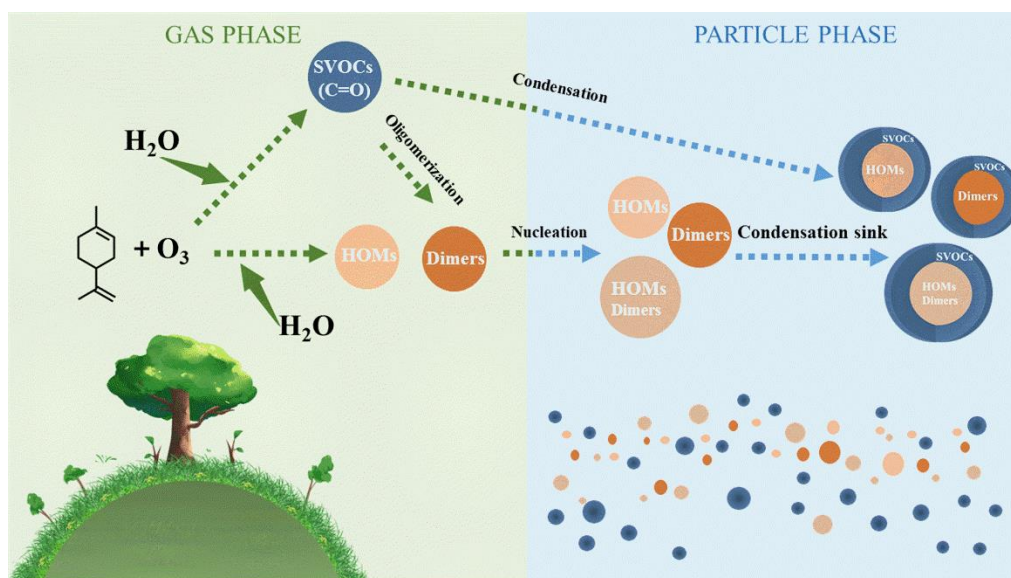


287

288 **Figure 5.** (a) Distribution of the limonene-SOA in the two-dimensional volatility basis set (2D-VBS)

289 space. (b) Partitioning coefficients of limonene monomers and dimers under low and high RH conditions.

290



291

292 **Figure 6.** Schematic diagram of the possible mechanisms for the enhancement of limonene-SOA.

293

294 High particle number concentration generally provides more surface areas for semi-volatile organic
 295 compounds (SVOCs; $0.3 < C_0 < 300 \mu\text{g m}^{-3}$) to condense on, which results in higher condensation sink
 296 (CS). In the OFR, the fates of SVOCs include condensing on aerosol, getting lost on the wall, and reacting
 297 with OH radicals to form functionalization and/or fragmentation products (Palm et al., 2016; Li et al.,
 298 2019a). The promoted condensation by higher CS leads to a higher fraction of SVOCs getting into the
 299 particle phase rather than getting lost on the wall or becoming smaller fragments staying in the gas phase,

300 and thus promoting SOA formation (Li et al., 2019a). Furthermore, the transformation from C-C double
301 bond to carbonyl shown in Fig. 3 and Fig. 4 decreases the volatility of molecules, which can largely
302 influence the gas-particle partitioning of the monomeric compounds (Fig. 5b). For example, the C_0 values
303 of $C_{10}H_{16}O_2$ and $C_{10}H_{16}O_3$ are 90701 and 19968 $\mu\text{g m}^{-3}$, corresponding to partitioning coefficients of
304 0.01 and 0.05, respectively (Fig. 5b and Table S3), with an SOA mass concentration of $\sim 1000 \mu\text{g m}^{-3}$
305 under dry condition. When they are converted to carbonyls $C_9H_{14}O_3$ and $C_9H_{14}O_4$, the values of C_0
306 become 45556 and 6479 $\mu\text{g m}^{-3}$, corresponding to partitioning coefficients of 0.02 and 0.13, respectively
307 (Fig. 5b and Table S3), with the same SOA loading. This enhancement in partitioning coefficient can
308 largely promote the condensation of SVOCs and, thus, enhance the SOA mass concentration. In addition,
309 the enhanced SOA formation can further influence the equilibrium, e.g., the partitioning coefficient of
310 $C_{10}H_{16}O_3$ increases from 0.05 to 0.10 when SOA mass concentration increases from $\sim 1000 \mu\text{g m}^{-3}$ under
311 dry condition to $\sim 2000 \mu\text{g m}^{-3}$ under wet condition (Fig. 5b and Table S3). The distribution of saturation
312 vapor pressure for monomers and dimers identified by MS has also been shown in Fig. 5a. As can be
313 seen from this figure, around 50% monomers are categorized as SVOCs, thus having the large fraction
314 in the particle phase when converting from dry to wet conditions. Overall, the different fate and
315 partitioning of SVOCs largely enhance the amount of SVOCs in the particle phase (Fig. 6).

316 Concluding the analysis above, high humidity promotes the SOA formation from the ozonolysis of
317 limonene in two steps: nucleation of new particles and condensation of SVOCs on them (Fig. 6). These
318 two steps are closely related to the multi-generation reactions of the exocyclic C=C bond, which are
319 unlikely to happen for the ozonolysis of Δ^3 -carene. Interestingly, Gong and Chen (2021) have found that
320 high RH can inhibit the SOA formation from the first-generation oxidation of limonene ozonolysis, but
321 enhance the SOA formation from the second-generation oxidation (Gong and Chen, 2021), their results
322 agree well with the results and analysis shown here. In contrast, Li et al. (2019b) found negligible change
323 in dimers and HOMs in limonene- O_3 system when changing RH from 0 to 60%. The discrepancy is
324 mainly attributed to the different experimental conditions. The ozone exposure in this study is ~ 18 times
325 higher than in Li et al. (2019b), while the limonene concentration in this study is only $\sim 30\%$ of that in
326 their study. These two conditions both favor the multi-generation reactions occurred at the exocyclic
327 double bond of limonene and its products. Thus, we believe this leads to the different results regarding
328 the formation of HOMs and dimers.

329 Regarding Δ^3 -carene, the mechanisms and processes are almost opposite to those of limonene. First,
330 water vapor reacts with sCl₁ or sCl₂ to promote the formation of α -hydroxyalkyl-hydroperoxides (Fig.
331 S5). Their subsequent products without second ozonolysis of exocyclic double bond have higher
332 volatility, and may most likely prevail in the gas phase. In addition, it has been found that α -hydroxyalkyl
333 hydroperoxides preferentially decompose into aldehydes and H₂O₂ (Kumar et al., 2014; Chen et al., 2016),
334 i.e., 3-caronaldehyde for Δ^3 -carene, which has higher volatility than the products from other reaction
335 pathways. Correspondingly, the number and relative intensity of HOMs and dimers detected under high
336 RH conditions are both lower than those under low RH conditions (Table S7). Furthermore, out of a total
337 of 178 dimers, 63 dimers were exclusively identified under low RH conditions (Table S6). As a result,
338 high RH shows an inhibitory effect on the SOA formation from Δ^3 -carene ozonolysis.

339 To investigate the multi-generation reactions of limonene under low-concentration conditions, we
340 conducted low-concentration limonene ozonolysis experiments, and the results are shown in Fig. S6. In
341 these experiments, the limonene and O₃ concentrations were 20.5 ppb and 5.7 ppm, respectively.
342 According to the experimental results, the number concentration of SOA formed from limonene
343 ozonolysis increased by approximately 1.4 times under high RH, which is similar to the increase observed
344 under high-loading conditions. The mass concentration increased by approximately 1.3 times at a
345 precursor concentration of 20.5 ppb. The relatively small increase in mass concentration compared to the
346 high-concentration conditions may be attributed to the less pronounced distribution of SVOCs at low
347 mass concentrations. This result indicates that the enhancement effect on limonene SOA by high RH is
348 still valid for low precursor concentrations.

349 To further confirm the assumption that water-influenced multi-generation reactions of the exocyclic
350 double bond enhance the SOA formation, we conducted two comparative analyses: firstly, we examined
351 the ozonolysis of the endocyclic double bond in limonene, leaving the exocyclic double bond unreacted.
352 This was done by applying a low O₃ concentration (~67 ppb), since the reaction of O₃ with endocyclic
353 double bond is ~30 times faster than the reaction of O₃ with exocyclic double bond (Shu and Atkinson,
354 1994). Interestingly, when limonene was oxidized at only the endocyclic double bond, we observed a
355 slight decrease in both the number and mass concentrations as the RH increased (Fig. S7). This is similar
356 to the results obtained for Δ^3 -carene, which contains only one endocyclic double bond. Secondly, we
357 compared the ozonolysis of structurally similar β -caryophyllene, which has an exocyclic C-C double

358 bond that can undergo further reactions (Fig. S8). As expected, we observe a large enhancement in SOA
359 formation under high RH condition (Table S8 and Fig. S9). This implies that monoterpenes,
360 sesquiterpenes, and other BVOCs with two unsaturation double bonds may follow similar reaction
361 mechanisms during ozonolysis, and thus have a RH dependency in SOA production.

362 **4 Conclusions**

363 In this study, the effect of humidity on SOA production from the ozonolysis of two monoterpenes
364 (limonene and Δ^3 -carene) was investigated with an OFR. Contrasting impacts of RH on the SOA
365 formation were observed: limonene-SOA yield increases by $\sim 100\%$ when RH changes from $\sim 1\%$ to
366 $\sim 60\%$, while Δ^3 -carene-SOA yield slightly decreases. By analyzing the chemical composition of SOA
367 with ESI-Q-TOF-MS, we find that the multi-generation reactions of the exocyclic C-C double bond are
368 likely the driving force of the enhancement in limonene-SOA. The presence of water promotes the
369 formation of carbonyls from the reaction of exocyclic double bond, and further favors the formation of
370 dimers and HOMs. This leads to promoted new particle formation and subsequent condensation of
371 SVOCs. These reactions also lower the volatilities of the SVOCs, and further promote the gas-particle
372 partitioning. Moreover, this hypothesis is proved by a similar behavior of the ozonolysis of β -
373 caryophyllene (sesquiterpene with an exocyclic double bond) in SOA enhancement under high RH
374 condition. The results in this study suggest that multi-generation reactions play an important role in SOA
375 formation from the ozonolysis of BVOCs, which are significantly influenced by humidity. This impact
376 is largely dependent on the molecular structure of the SOA precursors (e.g., with or without the exocyclic
377 double bond), thus highlighting the importance to consider the molecular structure of monoterpenes in
378 modeling and field studies of biogenic SOA.

379

380 **Data availability.** Experimental data are available upon request to the corresponding authors.

381 **Supplement.** The supplement related to this article is available online.

382 **Author contributions.** LD and SZ designed the experiments and SZ carried them out. SZ performed
383 data analysis with assistance from KL, LD, ZY, and JL. SZ and KL wrote the paper with contributions
384 from all co-authors.

385 **Declaration.** The authors declare that they have no conflict of interest.

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