

# 1 **Heterogeneous Ozonolysis of Squalene: Gas-Phase Products Depend** 2 **on Water Vapor Concentration**

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16

## 17 **Abstract**

18 Previous work examining the condensed-phase products of squalene particle ozonolysis found  
19 that an increase in water vapor concentration led to lower concentrations of secondary ozonides,

20 increased concentrations of carbonyls, and smaller particle diameter, suggesting that water  
21 changes the fate of the Criegee intermediate. To determine if this volume loss corresponds to an  
22 increase in gas-phase products, we measured gas-phase volatile organic compound (VOC)  
23 concentrations via proton-transfer-reaction time-of-flight mass spectrometry. Studies were  
24 conducted in a flow-tube reactor at atmospherically relevant ozone ( $O_3$ ) exposure levels (5-30  
25 ppb h) with pure squalene particles. An increase in water vapor concentration led to strong  
26 enhancement of gas-phase oxidation products at all tested  $O_3$  exposures. An increase in water  
27 vapor from near zero to 70% relative humidity (RH) at high  $O_3$  exposure increased the total mass  
28 concentration of gas-phase VOCs by a factor of three. The observed fraction of carbon in the  
29 gas-phase correlates with the fraction of particle volume lost. Experiments involving  $O_3$   
30 oxidation of shirts soiled with skin oil confirms that the RH dependence of gas-phase reaction  
31 product generation occurs similarly on surfaces containing skin oil under realistic conditions.  
32 Similar behavior is expected for  $O_3$  reactions with other surface-bound organics containing  
33 unsaturated carbon bonds.

## 34 **Introduction**

35       People spend 90% of their lives indoors<sup>1</sup>. Each day, adult humans inhale 12-15 kg of air,  
36 making indoor air an important route of exposure to many chemicals, including volatile organic

37 compounds (VOCs). People can be the dominant indoor VOC emission source in densely  
38 occupied spaces, and, in the presence of ozone (O<sub>3</sub>), the oxidation of skin lipids adds ketones and  
39 aldehydes to the composition of indoor air<sup>2-8</sup>.

40 Indoor O<sub>3</sub> concentrations are commonly 20-70% of outdoor levels, with the ratio  
41 depending on building air-change rate (ACR), type of ventilation system, and the nature of  
42 indoor surfaces<sup>9</sup>. Indoor air is estimated to contribute 25-60% of an individual's daily O<sub>3</sub>  
43 exposure.<sup>10</sup> In densely occupied spaces, occupants may be the dominant indoor sinks for O<sub>3</sub>,  
44 mainly due to reactions with lipids on their skin, hair, and clothing.<sup>11</sup>

45 Squalene (C<sub>30</sub>H<sub>50</sub>) constitutes 10% of the mass of human skin lipids, and contributes 50%  
46 of the unsaturated carbon bonds.<sup>12</sup> When exposed to O<sub>3</sub>, squalene is quickly oxidized to products  
47 that span a wide range of volatility; some products remain in the condensed phase while others  
48 become gaseous.<sup>5</sup>

49 Researchers have investigated effects of human occupancy on aircraft cabin air,  
50 considering that interior O<sub>3</sub> levels are sometimes elevated in airplanes.<sup>13</sup> Weschler et al.  
51 conducted experiments in a simulated aircraft cabin section and found that more than half of the  
52 observed oxidation products in the gas phase came from O<sub>3</sub> reacting with human skin lipids.<sup>4</sup>  
53 Further work studied O<sub>3</sub> deposition on materials common to aircraft cabin interiors, finding that  
54 soiled clothing exposed to O<sub>3</sub> emits 6-methyl-5-hepten-2-one (6-MHO).<sup>14,15</sup> Surface bound

55 squalene was found to have a high reaction probability with O<sub>3</sub>, in the range of 0.5-1 × 10<sup>-3</sup>, and  
56 reaction of ozone with squalene on soiled clothing has been shown to be mass-transport  
57 limited.<sup>16-18</sup> Both 4-oxopentanal (4-OPA) and 6-MHO are known respiratory irritants.<sup>19,20</sup>  
58 Acetone and 6-MHO are among the most prominent VOCs emitted from human skin.<sup>21</sup> While  
59 acetone is known to originate from a wide variety of sources, including breath, 6-MHO is  
60 thought to be specific to squalene oxidation. The high emission rate suggests that squalene  
61 oxidation contributes significantly to VOC emissions from human skin.

62 Heine et al. investigated the influence of RH on squalene ozonolysis using pure squalene  
63 particles in a flow-tube reactor.<sup>22</sup> They showed that water vapor concentration does not affect the  
64 rate of squalene ozonolysis, but does substantially change the product composition. Under dry  
65 conditions, as O<sub>3</sub> consumes squalene, secondary ozonide concentrations increase in the  
66 condensed phase and initial particle volume is reduced by 15%. At 60% RH, condensed-phase  
67 ozonolysis products shift from secondary ozonides to carbonyls, and particle volume is reduced  
68 by as much as 50%. Such losses of particle volume should correspond to an increase in gas-  
69 phase oxidation products.

70 For this study, we designed experiments specifically to observe the mass lost to the gas  
71 phase and the products formed by O<sub>3</sub>-squalene reactions as a function of RH, and to understand  
72 the implications for the fate of the Criegee intermediate on squalene particle surfaces and skin-oil

73 coated clothing. Here, we investigate the gas-phase products from squalene particle ozonolysis in  
74 a flow tube reactor, and on skin-oil soiled shirts in a climate chamber. From the flow-tube  
75 experiments, we show that the RH dependent loss of particle diameter corresponds to an increase  
76 in gas-phase reaction products, consistent with the mechanism of water molecules promoting  
77 carbonyl formation from the Criegee intermediate under real world conditions. We discuss  
78 implications for product yields from skin oil ozonolysis indoors under varying RH conditions.

## 79 **Experimental Methods**

80 Squalene ozonolysis was carried out in a flow-tube reactor, as described in Heine et al.<sup>22,23</sup>  
81 Liquid squalene in a tube furnace was heated to 145 °C, generating, by means of homogeneous  
82 nucleation, polydisperse particles with a mean surface-weighted diameter of 250 +/- 40 nm. A  
83 continuous flow of 300 standard cm<sup>3</sup> min<sup>-1</sup> dry nitrogen (N<sub>2</sub>) carried the particles from the  
84 furnace through a charcoal denuder to remove any gas-phase contamination. This flow was then  
85 combined with flows of oxygen (O<sub>2</sub>), O<sub>3</sub>, dry N<sub>2</sub>, and humidified N<sub>2</sub> for a total flow of 1 L min<sup>-1</sup>.  
86 Levels of O<sub>2</sub> were held at a constant 10%, while the flows of dry and humidified N<sub>2</sub> were varied  
87 to give a range of nearly 0% (< 3%) to 100% RH. This combined flow traversed the flow tube  
88 reactor (130 cm long, 2.5 cm inner diameter) with a residence time of 37 s.<sup>24</sup> Ozone was  
89 produced by a corona discharge generator, and the concentrations of O<sub>3</sub> were in the range 0-4

90 ppm, giving O<sub>3</sub> exposures of 0-44 ppb h. The initial particle loading in the flow reactor was 1000  
91 μg m<sup>-3</sup>.

92           Upon leaving the flow-tube reactor, the outflow composition was measured by proton-  
93 transfer-reaction time-of-flight mass spectrometry (Ionicon PTR-TOF-MS 8000), an electrostatic  
94 classifier (TSI model 3080L) with a butanol-based condensation particle counter (TSI model  
95 3772), and a custom-built vacuum ultraviolet aerosol mass spectrometer (VUV-AMS). The  
96 particle size and composition measurements are described in Heine et al.<sup>22</sup>; the PTR-TOF-MS  
97 was used to measure speciated gas-phase VOC concentrations.

98           PTR-TOF-MS is a chemical ionization technique with minimal fragmentation using H<sub>3</sub>O<sup>+</sup>  
99 as the primary reagent ion. PTR-TOF-MS has been previously used to detect gas-phase products  
100 of squalene ozonolysis.<sup>2,4,5</sup> For these experiments, the instrument was calibrated with a  
101 multicomponent VOC gas standard to ensure stability throughout the campaign. Of the  
102 compounds reported here, only acetone was determined using a direct calibration. All other  
103 compound concentrations were calculated using a default proton transfer reaction rate constant of  
104  $2.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for both the primary ion, H<sub>3</sub>O<sup>+</sup>, as well as for the first water cluster,  
105 H<sub>3</sub>O<sup>+</sup>(H<sub>2</sub>O). Direct calibration accuracies are estimated to be +/- 10%, whereas concentration  
106 accuracies derived from the default rate constant are typically +/- 50%.<sup>25</sup> Increases in RH can

107 cause increases in instrument sensitivities for certain compounds. However, these changes are  
108 typically a few percent, much lower than concentration differences reported in this work.<sup>26,27</sup>

109         Measurements of VOCs at each specified RH and O<sub>3</sub> exposure were made by allowing  
110 concentrations in the reactor to stabilize. Once stable, the particle flow was quickly replaced with  
111 a flow of N<sub>2</sub>. After 2 min, 95% of the particles were removed from the reactor, and a background  
112 concentration was taken. To account for both compounds being desorbed from the flow-tube  
113 walls as well as compounds being produced by heterogeneous oxidation on the walls, O<sub>3</sub> flow  
114 was maintained during the background sampling procedure. The difference between the stable  
115 concentration and the background concentration was taken to be the gas-phase concentration  
116 attributable to squalene-particle ozonolysis. Tables S1–S5 show the concentrations for each  
117 species as measured from the flow tube, as well as the measured background.

118         An experiment to analyze emissions from skin-oil soiled clothing under varying  
119 conditions of RH and O<sub>3</sub> was performed as part of the Indoor Chemical Human Emissions and  
120 Reactivity (ICHEAR) project. Four identical T-shirts (100% cotton) were washed with  
121 fragrance-free detergent and tumble dried, before being worn by four people overnight  
122 (minimum of 8 h). The skin-oil soiled T-shirts were then placed inside a stainless-steel climate  
123 chamber (volume 26.8 m<sup>3</sup>) ventilated with an air-change rate of 3.2 h<sup>-1</sup>. Outdoor air was used for  
124 ventilation. It was filtered using particle and activated carbon filters to avoid interference from

125 outdoor VOCs, and conditioned to reach the required temperature and RH. Ozone was generated  
126 (Jelight Model 600 UV) in the HVAC system downstream of the activated carbon filter and  
127 continuously introduced into the chamber at levels between 95-100 ppb. The temperature inside  
128 the chamber was maintained at 27.4–28.3 °C during the experiment and the O<sub>3</sub> levels were  
129 monitored throughout. Four RH levels were established. The lowest RH levels (at the beginning  
130 and end of the experiment) were not controlled (humidifier off, no dehumidifying present), while  
131 the two higher RH levels were achieved by operating a steam humidifier in the HVAC system.  
132 The first three levels were maintained for 1.5-2 hours to allow steady-state conditions to be  
133 reached. The resulting average RH levels during these three periods were 26%, 41%, and 56%.  
134 The final, fourth, RH condition was a decay from 50% to 28% with the humidifier off. The  
135 average RH for this period was 33%.

136 A PTR-TOF-MS (8000, Ionicon Analytik GmbH Innsbruck, Austria) was deployed  
137 during ICHEAR to monitor VOCs produced from O<sub>3</sub> oxidation of skin oil. The operational  
138 conditions of the PTR-TOF-MS were drift tube pressure 2.2 mbar, temperature 60 °C and 137 Td  
139 (*E/N*). The 3.2-mm (1/8”) Teflon inlet of the instrument was attached to the main exhaust duct of  
140 the chamber, approximately 1 m from the terminal through which the air was exhausted from the  
141 chamber and set to draw 100 mL min<sup>-1</sup> (via a main high flow inlet of 7 L min<sup>-1</sup>) continuously  
142 into the mass spectrometer. Data reported for the skin-oil T-shirt experiment represent sample



143 time resolution of 20 s. Before putting T-shirts inside the chamber, a background level of the  
144 empty chamber was established and maintained for 10 minutes. The measured background VOC  
145 levels were subsequently subtracted from the VOC levels measured while the T-shirts were in  
146 the chamber.

## 147 **Results and Discussion**

148 Figure 1 shows the chemical structures of squalene and selected gas-phase ozonolysis  
149 products. The first-generation gas-phase products are acetone, 6-methyl-5-hepten-2-one (6-  
150 MHO), and geranylacetone. Terminal oxidation products found in the gas phase, i.e. products  
151 that are minimally reactive with O<sub>3</sub> because of their lack of carbon-carbon double bonds, are  
152 acetone, 4-oxopentanal (4-OPA), and 1,4-butanedial (succinaldehyde). Scheme 1 shows a  
153 simplified mechanism for alkenes reacting with O<sub>3</sub>. In **R1**, O<sub>3</sub> adds across the double bond,  
154 forming a primary ozonide (not shown), which quickly decomposes to one of two combinations  
155 of carbonyl and Criegee intermediate. This reaction is fast and does not include water, so water  
156 vapor concentration has no effect on the rate of alkene loss.<sup>22</sup> The Criegee intermediate produced  
157 by **R1** is reactive, and can proceed through **R2** or **R3**, as well as through rearrangement or  
158 reactions with carboxylic acids<sup>28,29</sup>. **R2** shows the Criegee intermediate reacting with water to  
159 form the  $\alpha$ -hydroxyhydroperoxide, which decomposes to a carbonyl and to hydrogen peroxide.

160 **R3** shows the Criegee intermediate reacting with another carbonyl to form a secondary ozonide.  
161 The carbonyl products are more volatile than their respective secondary ozonides; in the  
162 presence of water, **R2** occurs faster than **R3**, leading to greater release of reaction products to the  
163 gas phase and a concomitant shrinking of the particle.

164         Figures 2A and 2B show the gas-phase concentration of geranylacetone and 6-MHO  
165 exiting the flow-tube reactor as a function of O<sub>3</sub> exposure and RH. Both compounds are primary  
166 products of squalene oxidation, and both have carbon-carbon double bonds that can further react  
167 with O<sub>3</sub>. At all RH levels, geranylacetone production peaks at an O<sub>3</sub> exposure of 10 ppb h. Dry  
168 conditions yield 5 μg m<sup>-3</sup> of geranylacetone, whereas more humid conditions (70% RH) enhance  
169 the concentration to 19 μg m<sup>-3</sup>, an increase by almost 4×. More humid conditions, specifically  
170 RH of 30% and 50%, also show an increase in geranylacetone concentration compared to dry  
171 conditions. At exposures of 20 ppb h, the geranylacetone is fully consumed by ozonolysis and is  
172 not detected. Compared to other products measured, concentrations of geranylacetone are small.  
173 As a 13-carbon ketone, with a vapor pressure of 3.5 Pa at 298 K, most of the geranylacetone is  
174 expected to remain in the condensed phase.<sup>6</sup> Furthermore, there are fewer possible reaction  
175 pathways to produce geranylacetone than the other, shorter chain products. The low  
176 concentration measured in this study is consistent with a classroom study by Tang et al., where  
177 both 6-MHO and 4-OPA were found at significantly higher concentrations than geranylacetone.<sup>2</sup>

178           The production of 6-MHO shows strong RH dependence. At all levels of O<sub>3</sub> exposure, an  
179 increase in RH leads to an increase in 6-MHO concentration. As 6-MHO is a primary product  
180 that can also be consumed, peak concentrations are found at the lower levels of O<sub>3</sub> exposure. At  
181 70% RH and 12 ppb h of O<sub>3</sub> exposure, the detected concentration is 170 μg m<sup>-3</sup>, 3 times the level  
182 of 6-MHO detected at the same O<sub>3</sub> exposure but under dry conditions. Unlike geranylacetone, 6-  
183 MHO is detected at even the highest levels of O<sub>3</sub> exposure tested, 30 ppb h. The 6-MHO species  
184 is used as a primary tracer compound for squalene oxidation, along with 4-OPA as a secondary  
185 tracer. The fact that 6-MHO is consumed at higher O<sub>3</sub> exposures, while 4-OPA is not, suggests  
186 that 6-MHO concentrations could be used as a proxy indicator for the age of oxidation products:  
187 at longer timescales, 6-MHO becomes depleted while 4-OPA does not.

188           Figures 3A-3C show the gas-phase concentrations as a function of O<sub>3</sub> exposure and RH  
189 of the three terminal products: acetone, 4-OPA, and 1,4-butanediol. At most levels of O<sub>3</sub>  
190 exposure, increasing RH produces increasing concentrations of acetone, again showing strong  
191 humidity dependence. At very low O<sub>3</sub> exposure (5-6 ppb h), 30% RH produces 32 μg m<sup>-3</sup> of  
192 acetone, whereas 70% RH conditions give 77 μg m<sup>-3</sup>, an increase by more than 2×. Under dry  
193 conditions, acetone increases to 100 μg m<sup>-3</sup> at 12 ppb h exposure, and then does not increase with  
194 increasing O<sub>3</sub> exposure. As acetone does not have carbon-carbon double bonds, it does not react  
195 significantly with O<sub>3</sub> and so increasing exposure is not expected to consume acetone. Under

196 higher RH conditions, the same leveling off is seen, but at higher concentrations. At 70% RH,  
197 acetone concentrations begin to plateau at 20 ppb h exposure, at a concentration of 280  $\mu\text{g m}^{-3}$ .  
198 At  $\text{O}_3$  exposures greater than 10 ppb h, increasing RH from 0% to 70% increases acetone  
199 concentrations by a factor of 2.5 to 3.

200 Figure 3B shows the RH dependence of 4-OPA from the ozonolysis of squalene. A  
201 minimum of two reactions involving  $\text{O}_3$  are required to produce 4-OPA from squalene, so  
202 concentrations are observed to increase later than the primary products, acetone and 6-MHO.  
203 Despite being a terminal product, 4-OPA does not show the same leveling off behavior as  
204 acetone. Under dry conditions, production stops increasing at 20 ppb h  $\text{O}_3$  exposure, but under  
205 high RH conditions no leveling off is seen; production of 4-OPA may increase past 30 ppb h  
206 exposure. At  $\text{O}_3$  exposures less than 12 ppb h, no RH dependence is seen, but production is also  
207 small. At higher  $\text{O}_3$  exposures, 4-OPA shows strong RH dependence, with a factor of 6 increase  
208 in concentration between dry and humid conditions at 30 ppb h  $\text{O}_3$  exposure. In both mixing ratio  
209 and mass concentration, 4-OPA is the most abundant gas-phase product, with a peak  
210 concentration of 600  $\mu\text{g m}^{-3}$ . If each double bond in squalene proceeds through reaction **R2**, one  
211 molecule of squalene would produce a single 1,4-butanedial molecule, two acetone molecules,  
212 and four 4-OPA molecules. While the observed mixing ratios of terminal products do not follow  
213 these stoichiometric ratios, the relatively large number of 4-OPA molecules that can be made

214 from each squalene molecule help to explain why it is the most abundant gas-phase product.

215           Figure 3C shows the concentration of 1,4-butanedial as a function of RH and O<sub>3</sub>  
216 exposure. As a terminal product, abundance of this species increases with O<sub>3</sub> exposure, and, for  
217 some RH conditions, eventually levels off. As with 4-OPA, production of 1,4-butanedial requires  
218 a minimum of two ozonolysis reactions, so concentrations substantially increase at greater O<sub>3</sub>  
219 exposure. Production of 1,4-butanedial shows a more complicated relation to RH than other  
220 species. The lowest levels of production, across all O<sub>3</sub> exposures, are under the most humid  
221 conditions. The next lowest levels of production are under the driest conditions. Although it does  
222 not follow the pattern of the other species measured, 1,4-butanedial levels do show strong  
223 variability with RH. At 30 ppb h O<sub>3</sub> exposure, switching from 70% RH to 30% RH increases the  
224 concentration of 1,4-butanedial from 52 μg m<sup>-3</sup> to 140 μg m<sup>-3</sup>. This ~3× increase in production is  
225 in line with the 3-6× changes in production observed at different RH for other compounds. The  
226 fact that 1,4-butanedial production peaks at intermediate RH, and declines at low and high RH,  
227 suggests that water plays a more complicated role than depicted in Scheme 1. Specifically,  
228 reaction **R2** increases 1,4-butanedial production up to a point, and then facilitates other reactions  
229 that suppress production.

230           Wisthaler and Weschler (2010) observed 12 prominent VOCs from squalene ozonolysis,  
231 including the five compounds already discussed.<sup>5</sup> When glass wool soiled with human skin oil

232 was exposed to O<sub>3</sub> (0-75 ppb h), three species — 4-methyl-8-oxo-4-nonenal (4-MON), 4-methyl-  
233 4-octene-1,8-dial (4-MOD), and 1-hydroxy-6-methyl-5-hepten-2-one (OH-6MHO) — showed  
234 mixing ratios similar to the observed mixing ratios of 4-OPA and 1,4-butanediol. These species  
235 were also observed during ozonolysis of a pure squalene film; however, the mixing ratios for that  
236 experiment were not reported. In our work, all three compounds were detected (4-MON, 4-  
237 MOD, and OH-6MHO), but at very low concentrations, 2 µg m<sup>-3</sup> or less. Possibly due to the low  
238 concentration of these species, a RH dependence isn't discernible.

239 Four other compounds identified by Wisthaler and Weschler (2010) — 1-hydroxypropan-  
240 2-one (hydroxyacetone), 4-oxobutanoic acid, and the isobaric compounds 5-hydroxy-4-  
241 oxopentanal and 4-oxopentanoic acid (levulinic acid) — are found in the present work at peak  
242 concentrations much lower than 6-MHO, acetone, 4-OPA, and 1,4-butanediol (5-15 µg m<sup>-3</sup>  
243 versus 140-600 µg m<sup>-3</sup>). All four compounds are terminal products; concentrations either  
244 increase or level off with increasing O<sub>3</sub> exposure, and none of the products show increasing  
245 production with increasing RH. Hydroxyacetone shows a muted response to changes in RH, as  
246 seen in Figure S1. Production is similar at 30% RH, 50% RH, and 70% RH, but increase by ~50-  
247 100% under dry conditions. Concentrations are modest, peaking at 15 µg m<sup>-3</sup> under dry  
248 conditions and 30 ppb h O<sub>3</sub> exposure. Levulinic acid or 5-hydroxy-4-oxopentanal (or a  
249 combination of the two) only shows a RH effect at the highest O<sub>3</sub> exposure. At 30 ppb h, 70%

250 RH yields 7  $\mu\text{g m}^{-3}$  while 30% RH produces 15  $\mu\text{g m}^{-3}$ , as seen in Figure S2. Figure S3 shows 4-  
251 oxobutanoic acid production *decreasing* with increased RH. At 70% RH and 30 ppb h O<sub>3</sub>  
252 exposure, we observe 1  $\mu\text{g m}^{-3}$ , whereas under dry conditions we measure 5  $\mu\text{g m}^{-3}$ .

253 One fragmentation ion was produced in quantities comparable to those of the dominant  
254 products,  $m/z$  43.018 Da, C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>. This fragment is common to acetic acid and acetate esters, but  
255 ions consistent with these parent masses were only found in low concentrations, so it is  
256 unassigned.<sup>30</sup> The fragment was found at mixing ratios comparable to 1,4-butanediol, and shows  
257 similar responses to RH.

258 To explore whether our gas-phase measurements agree with the amount of material lost  
259 from the particle phase, we summed the amount of carbon detected in the gas-phase products at  
260 different levels of RH. We used a carbon-balance approach to test whether the loss of material  
261 from the particle phase could be accounted for by generation of gas-phase products. The  
262 concentration of squalene entering the flow tube reactor was 1000  $\mu\text{g m}^{-3}$ , corresponding to 880  
263  $\mu\text{g m}^{-3}$  of carbon. Converting the measurements in Figures 2-3 from  $\mu\text{g m}^{-3}$  to  $\mu\text{g C m}^{-3}$ , and  
264 normalizing to the initial concentration of carbon entering the flow tube, gives the percent carbon  
265 in the gas phase. (As with the reported concentrations, these measurements are accurate to +/-  
266 50% for all species except for acetone, which is accurate to +/- 10% because it is directly  
267 calibrated.) Figure 4 shows the percent carbon in the gas phase at 20 ppb h O<sub>3</sub> exposure. Note

268 that only the dominant products are shown. Switching from 0% RH to 70% RH increases the  
269 proportion of carbon entering the gas phase from 21% to 65%, with increases in all dominant  
270 products except 1,4-butanediol. Assuming that an average of two molecules of oxidation  
271 products are generated for each molecule of ozone that reacts with squalene, this outcome  
272 corresponds to yields of between 42% and 130% for gas-phase oxidation products per molecule  
273 of ozone consumed. Even a moderate change, from dry conditions to 30% RH, increases the  
274 proportion of carbon entering the gas phase by 60%. The largest increases are seen in 4-OPA  
275 production.

276         Because the VUV-AMS only measures relative concentrations of species, there is no  
277 direct measurement of the amount of carbon present in the condensed phase. However,  
278 measurements of the change in particle volume can be used as a quantitative indicator for mass  
279 loss from the particle. Note that this approach ignores any mass gained by the addition of oxygen  
280 to condensed phase products of ozonolysis, as well as any difference in densities between  
281 squalene and condensed-phase reaction products. Despite these limitations, using this approach,  
282 there is a clear and strong correlation between the carbon detected in the gas phase and the  
283 volume lost from the particle, as shown in Figure 5. Under dry conditions, at all levels of O<sub>3</sub>  
284 exposure, ~20% of the particle volume is lost, and ~20% of the carbon from squalene is found in  
285 the gas phase. At higher RH values, both the particle volume lost and the amount of carbon



286 entering the gas phase are more sensitive to O<sub>3</sub> exposure, as shown by the larger spread for these  
287 humidified conditions. The highest RH level (70%) gives both the greatest particle volume loss  
288 and the largest percent of carbon in the gas phase. Notwithstanding experimental uncertainties,  
289 the evidence displayed in Figure 5 is consistent with expectations for the quantitative loss of  
290 particle-phase carbon being balanced with increased abundances of gaseous carbon species.

291         Figures 6 and S4 show the measurements in chamber air of several pertinent VOCs along  
292 with O<sub>3</sub> and RH. Four T-shirts were placed inside the measurement chamber at 10:25 with RH  
293 maintained at ~26% for 1.5 h. Thereafter the RH was increased in a series of steps. The  
294 previously identified squalene oxidation products (4-OPA, 1,4-butanedial, acetone, 6-MHO, and  
295 geranylacetone) were observed to vary in response to the changing RH levels. Owing to the  
296 working principle of the humidifier, the RH in the chamber fluctuated regularly within a 10%  
297 range with a cycle of 38 minutes. In the data shown, primary unsaturated products and terminal  
298 products all faithfully follow the RH variation, confirming the dependence of gas-phase squalene  
299 ozonolysis products on RH, consistent with the flow-tube experiments. In accordance with  
300 previous studies, 4-OPA was the most abundant product (especially at higher RH levels);  
301 geranylacetone concentration was consistently the lowest among the quantified species.

302         In contrast with the flow-tube experiment, in which squalene particles were continuously  
303 supplied, the skin-oil soiled T-shirts contained a limited amount of squalene that was

304 progressively consumed by O<sub>3</sub>. Therefore, at any given RH, most of the compounds showed a  
305 decreasing trend as the available squalene was depleted, except the first level where the lagging  
306 terminal products still increase towards steady state. In particular, acetone clearly followed the  
307 RH modulation while steadily decreasing as the experiment progressed. To better quantify the  
308 relative yields of the VOCs as a function of RH, two pairs of RH levels were selected,  
309 corresponding to points labeled 1-4 in Figure 6. As shown in Table 1, the concentration of 4-  
310 OPA increased by 5.9 µg m<sup>-3</sup> as the RH increased from 26% (point 1) to 44% (point 2). A  
311 similar increase of 5.1 µg m<sup>-3</sup> was seen in a second cycle as the RH changed from 46% (point 3)  
312 to 59% (point 4). The other terminal products (1,4-butanedial, hydroxy acetone, 4-oxobutanoic  
313 acid and 5-hydroxy-4-oxopentanal/levulinic acid) also showed slightly higher yields during the  
314 first RH increase (point 1 to point 2). Although the level of the first-generation products  
315 (acetone, 6-MHO and geranylacetone) tended to decrease with time, an increase was still  
316 observed in the second step (points 3 and 4) when the RH increased from 46% to 59%. However,  
317 unlike 4-OPA, the concentration changes were much lower than during the first RH increase  
318 (points 1 and 2), as shown in Table 1. For 6-MHO and geranylacetone, additional oxidation by  
319 O<sub>3</sub> could also be a contributing factor. Ozone removal was 3.4 ppb in the second RH step (46%  
320 to 59%), compared to 2.9 ppb in the first step, indicating that more 6-MHO and geranylacetone  
321 were produced and subsequently oxidized by O<sub>3</sub> at this stage. Significantly elevated 4-OPA

322 concentrations after the second increase of RH further supports this explanation.

323           Effects of RH on squalene ozonolysis have been observed in prior studies. Petrick and  
324 Dubowski studied the condensed phase of squalene film oxidation while varying RH, finding  
325 that increased RH led to more ketone production.<sup>31</sup> They also note that RH did not influence  
326 reaction kinetics, a finding also reported by Fu et al.<sup>32</sup> Wang and Waring examined secondary  
327 organic aerosol formation from the ozonolysis of surface-film squalene at 21% RH and 51%  
328 RH.<sup>33</sup> At high O<sub>3</sub> exposures, they found that the higher RH increased the aerosol mass fraction  
329 (AMF) from squalene. This increase suggests that higher RH leads to more oxidation products  
330 entering the gas phase, where they then can condense onto airborne particles. Zhou et al.  
331 examined the RH dependence of squalene film oxidation on the condensed phase products,  
332 finding that increasing the RH increased the yield of lower molecular weight products and  
333 decreased the yield of higher molecular weight products.<sup>34</sup> Although not quantitatively  
334 comparable, these previous studies qualitatively agree that an increase in RH leads to an increase  
335 in volatile products from squalene ozonolysis.

336           Humidity is already known to be an important factor that can influence VOC emissions  
337 from materials, compete with VOCs for sorptive uptake, and influence how indoor air is  
338 perceived.<sup>35–44</sup> Humidity is also known to change the rate of uptake of O<sub>3</sub> on indoor surfaces, a  
339 relationship that varies among common indoor materials.<sup>45</sup> Few studies have assessed how RH

340 changes ozonolysis products and emission rates. Coleman et al. (2008) found that increasing RH  
341 from 10% to 50% doubled the emissions of most ozonolysis byproducts from a cotton surface,  
342 with nonanal and decanal emissions increasing by about 5×.<sup>14</sup> Gall et al. (2013) studied primary  
343 and secondary ozonolysis emissions from building materials, finding RH to have mixed effects.<sup>46</sup>  
344 Secondary emissions increased with RH for painted drywall, while emissions from carpet and  
345 ceiling tile did not. The present work contributes new knowledge, showing that RH can directly  
346 influence the products of squalene ozonolysis, providing an alternate route by which water vapor  
347 can increase VOC concentrations. At realistic indoor O<sub>3</sub> exposures, a change from 0% RH to  
348 70% RH results in ~3 times the amount of carbon entering the gas phase. Squalene, with six  
349 carbon-carbon double bonds, is a model molecule to show this effect. Other unsaturated  
350 compounds, especially those with double bonds separating small moieties, may show similar  
351 behavior. The reactions shown in Scheme 1 are not specific to squalene, and so long as the  
352 carbonyls formed by reaction **R2** have sufficient volatility, increased production of gas-phase  
353 products are generally expected from increases in RH.

354       The effects seen in this study suggest that RH can significantly alter the gas-phase  
355 composition of indoor air. In high occupancy settings, skin-oil oxidation can be the dominant  
356 source of VOCs, and changes in RH can alter the strength of this source by as much as a factor  
357 of 3.4 In the flow-tube reactor, at the highest level of O<sub>3</sub> exposure and RH, the sum of the

358 concentrations of dominant products was  $940 \mu\text{g m}^{-3}$ , comparable to the  $1000 \mu\text{g m}^{-3}$  of squalene  
359 entering the reactor. It should be noted that RH does not change the rate of squalene ozonolysis:  
360 at low RH, oxidized products are still being formed, but remain in the condensed phase. If that  
361 condensed phase is the skin surface, then the products might be taken up dermally, where they  
362 might influence health.<sup>19,47</sup> The large effect of RH on ozonolysis products from squalene, and the  
363 potential for the underlying mechanism to act on other alkenes, warrants further research on how  
364 humidity may modulate indoor reactive chemistry and its consequences.

365

366 **Supporting Information.** Tables of raw and background concentrations of species measured for  
367 this study. Figures for species not seen in large quantities.

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## 379 **References**

- 380 (1) Klepeis, N. E.; Nelson, W. C.; Ott, W. R.; Robinson, J. P.; Tsang, A. M.; Switzer, P.;  
381 Behar, J. V.; Hern, S. C.; Engelmann, W. H. The National Human Activity Pattern Survey  
382 (NHAPS): A Resource for Assessing Exposure to Environmental Pollutants. *J. Exposure*  
383 *Anal. Environ. Epidemiol.* **2001**, *11*, 231–252.
- 384 (2) Tang, X.; Misztal, P. K.; Nazaroff, W. W.; Goldstein, A. H. Volatile Organic Compound  
385 Emissions from Humans Indoors. *Environ. Sci. Technol.* **2016**, *50*, 12686–12694.
- 386 (3) Weschler, C. J. Roles of the human occupant in indoor chemistry. *Indoor Air* **2016**, *26*, 6–  
387 24.
- 388 (4) Weschler, C. J.; Wisthaler, A.; Cowlin, S.; Tamás, G.; Strøm-Tejsen, P.; Hodgson, A. T.;  
389 Destailats, H.; Herrington, J.; Zhang, J.; Nazaroff, W. W. Ozone-Initiated Chemistry in  
390 an Occupied Simulated Aircraft Cabin. *Environ. Sci. Technol.* **2007**, *41*, 6177–6184.
- 391 (5) Wisthaler, A.; Weschler, C. J. Reactions of ozone with human skin lipids: Sources of  
392 carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. *Proc. Natl. Acad. Sci.* **2010**,  
393 *107*, 6568–6575.
- 394 (6) Lakey, P. S. J.; Wisthaler, A.; Berkemeier, T.; Mikoviny, T.; Pöschl, U.; Shiraiwa, M.  
395 Chemical kinetics of multiphase reactions between ozone and human skin lipids:  
396 implications for indoor air quality and health effects. *Indoor Air* **2017**, *27*, 816–828.

- 397 (7) Lakey, P. S. J.; Morrison, G. C.; Won, Y.; Parry, K. M.; von Domaros, M.; Tobias, D. J.;  
398 Rim, D.; Shiraiwa, M. The impact of clothing on ozone and squalene ozonolysis products  
399 in indoor environments. *Commun. Chem.* **2019**, *2*, 56.
- 400 (8) Kruza, M.; Carslaw, N. How do breath and skin emissions impact indoor air chemistry?  
401 *Indoor Air* **2019**, *29*, 369–379.
- 402 (9) Weschler, C. J. Ozone in indoor environments: Concentration and chemistry. *Indoor Air*  
403 **2000**, *10*, 269–288.
- 404 (10) Weschler, C. J. Ozone’s Impact on Public Health: Contributions from Indoor Exposures to  
405 Ozone and Products of Ozone-Initiated Chemistry. *Environ. Health Perspect.* **2006**, *114*,  
406 1489–1496.
- 407 (11) Fischer, A.; Ljungström, E.; Langer, S. Ozone removal by occupants in a classroom.  
408 *Atmos. Environ.* **2013**, *81*, 11–17.
- 409 (12) Nicolaidis, N. Skin Lipids: Their Biochemical Uniqueness. *Science.* **1974**, *186*, 19–26.
- 410 (13) Bhangar, S.; Cowlin, S. C.; Singer, B. C.; Sextro, R. G.; Nazaroff, W. W. Ozone Levels in  
411 Passenger Cabins of Commercial Aircraft on North American and Transoceanic Routes.  
412 *Environ. Sci. Technol.* **2008**, *42*, 3938–3943.
- 413 (14) Coleman, B. K.; Destailats, H.; Hodgson, A. T.; Nazaroff, W. W. Ozone consumption  
414 and volatile byproduct formation from surface reactions with aircraft cabin materials and  
415 clothing fabrics. *Atmos. Environ.* **2008**, *42*, 642–654.
- 416 (15) Wisthaler, A.; Tamás, G.; Wyon, D. P.; Strøm-Tejsen, P.; Space, D.; Beauchamp, J.;  
417 Hansel, A.; Märk, T. D.; Weschler, C. J. Products of Ozone-Initiated Chemistry in a  
418 Simulated Aircraft Environment. *Environ. Sci. Technol.* **2005**, *39*, 4823–4832.

- 419 (16) Wells, J. R.; Morrison, G. C.; Coleman, B. K. Kinetics and Reaction Products of Ozone  
420 and Surface-Bound Squalene. *J. ASTM Int.* **2008**, *5*, 101629.
- 421 (17) Jacobs, M. I.; Xu, B.; Kostko, O.; Heine, N.; Ahmed, M.; Wilson, K. R. Probing the  
422 Heterogeneous Ozonolysis of Squalene Nanoparticles by Photoemission. *J. Phys. Chem. A*  
423 **2016**, *120*, 8645–8656.
- 424 (18) Salvador, C. M.; Bekö, G.; Weschler, C. J.; Morrison, G.; Le Breton, M.; Hallquist, M.;  
425 Ekberg, L.; Langer, S. Indoor ozone/human chemistry and ventilation strategies. *Indoor*  
426 *Air* **2019**, *29*, 913–925.
- 427 (19) Anderson, S. E.; Franko, J.; Jackson, L. G.; Wells, J. R.; Ham, J. E.; Meade, B. J. Irritancy  
428 and Allergic Responses Induced by Exposure to the Indoor Air Chemical 4-Oxopentanal.  
429 *Toxicol. Sci.* **2012**, *127*, 371–381.
- 430 (20) Wolkoff, P.; Larsen, S. T.; Hammer, M.; Kofoed-Sørensen, V.; Clausen, P. A.; Nielsen,  
431 G. D. Human reference values for acute airway effects of five common ozone-initiated  
432 terpene reaction products in indoor air. *Toxicol. Lett.* **2013**, *216*, 54–64.
- 433 (21) Mochalski, P.; King, J.; Unterkofler, K.; Hinterhuber, H.; Amann, A. Emission rates of  
434 selected volatile organic compounds from skin of healthy volunteers. *J. Chromatogr. B.*  
435 **2014**, *959*, 62–70.
- 436 (22) Heine, N.; Houle, F. A.; Wilson, K. R. Connecting the Elementary Reaction Pathways of  
437 Criegee Intermediates to the Chemical Erosion of Squalene Interfaces during Ozonolysis.  
438 *Environ. Sci. Technol.* **2017**, *51*, 13740–13748.
- 439 (23) Heine, N.; Arata, C.; Goldstein, A. H.; Houle, F. A.; Wilson, K. R. Multiphase  
440 Mechanism for the Production of Sulfuric Acid from SO<sub>2</sub> by Criegee Intermediates



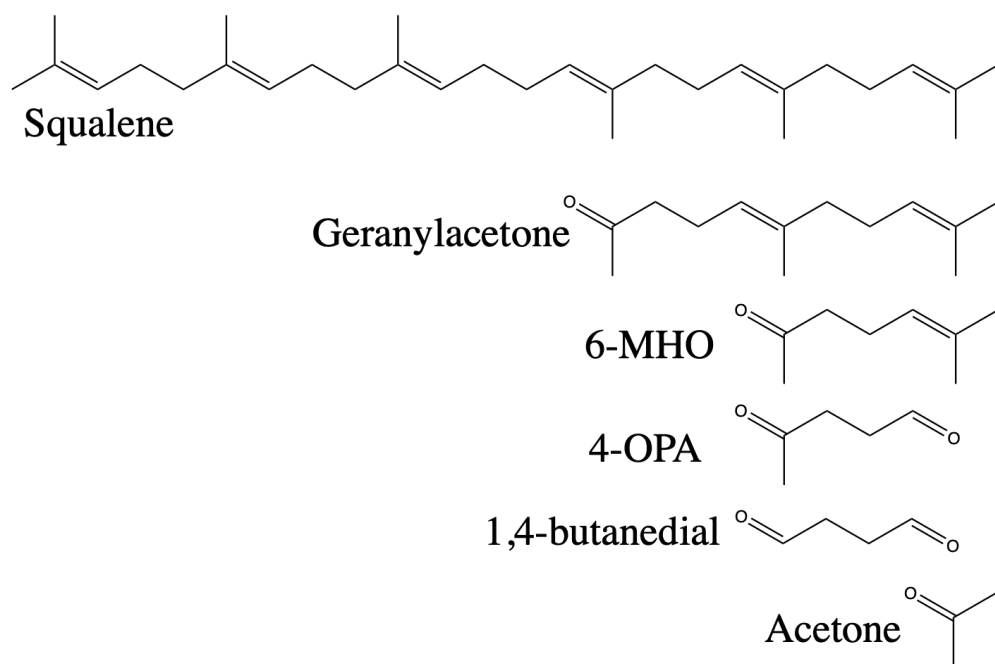
- 441 Formed during the Heterogeneous Reaction of Ozone with Squalene. *J. Phys. Chem. Lett.*  
442 **2018**, *9*, 3504–3510.
- 443 (24) Smith, J. D.; Kroll, J. H.; Cappa, C. D.; Che, D. L.; Liu, C. L.; Ahmed, M.; Leone, S. R.;  
444 Worsnop, D. R.; Wilson, K. R. The heterogeneous reaction of hydroxyl radicals with sub-  
445 micron squalane particles: a model system for understanding the oxidative aging of  
446 ambient aerosols. *Atmos. Chem. Phys* **2009**, *9*, 3209–3222.
- 447 (25) Zhao, J.; Zhang, R. Proton transfer reaction rate constants between hydronium ion ( $\text{H}_3\text{O}^+$ )  
448 and volatile organic compounds. *Atmos. Environ.* **2004**, *38*, 2177–2185.
- 449 (26) Kari, E.; Miettinen, P.; Yli-Pirilä, P.; Virtanen, A.; Faiola, C. L. PTR-ToF-MS product ion  
450 distributions and humidity-dependence of biogenic volatile organic compounds. *Int. J.*  
451 *Mass Spectrom.* **2018**, *430*, 87–97.
- 452 (27) Vlasenko, A.; MacDonald, A. M.; Sjostedt, S. J.; Abbatt, J. P. D. Formaldehyde  
453 measurements by proton transfer reaction - mass spectrometry (PTR-MS): correction for  
454 humidity effects. *Atmos. Meas. Tech.* **2010**, *3*, 1055–1062.
- 455 (28) Zhou, S.; Joudan, S.; Forbes, M. W.; Zhou, Z.; Abbatt, J. P. D. Reaction of Condensed-  
456 Phase Criegee Intermediates with Carboxylic Acids and Perfluoroalkyl Carboxylic Acids.  
457 *Environ. Sci. Technol. Lett.* **2019**, *6*, 243–250.
- 458 (29) Zhao, R.; Kenseth, C. M.; Huang, Y.; Dalleska, N. F.; Kuang, X. M.; Chen, J.; Paulson, S.  
459 E.; Seinfeld, J. H. Rapid Aqueous-Phase Hydrolysis of Ester Hydroperoxides Arising  
460 from Criegee Intermediates and Organic Acids. *J. Phys. Chem. A* **2018**, *122*, 5190–5201.
- 461 (30) Pagonis, D.; Sekimoto, K.; de Gouw, J. A Library of Proton-Transfer Reactions of  $\text{H}_3\text{O}^+$   
462 Ions Used for Trace Gas Detection. *J. Am. Soc. Mass Spectrom.* **2019**, *30*, 1330–1335.

- 463 (31) Petrick, L.; Dubowski, Y. Heterogeneous oxidation of squalene film by ozone under  
464 various indoor conditions. *Indoor Air* **2009**, *19*, 381–391.
- 465 (32) Fu, D.; Leng, C.; Kelley, J.; Zeng, G.; Zhang, Y.; Liu, Y. ATR-IR Study of Ozone  
466 Initiated Heterogeneous Oxidation of Squalene in an Indoor Environment. *Environ. Sci.*  
467 *Technol.* **2013**, *47*, 10611–10618.
- 468 (33) Wang, C.; Waring, M. S. Secondary organic aerosol formation initiated from reactions  
469 between ozone and surface-sorbed squalene. *Atmos. Environ.* **2014**, *84*, 222–229.
- 470 (34) Zhou, S.; Forbes, M. W.; Abbatt, J. P. D. Kinetics and Products from Heterogeneous  
471 Oxidation of Squalene with Ozone. *Environ. Sci. Technol.* **2016**, *50*, 11688–11697.
- 472 (35) Markowicz, P.; Larsson, L. Influence of relative humidity on VOC concentrations in  
473 indoor air. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5772–5779.
- 474 (36) Andersen, I.; Lundqvist, G. R.; Møhlave, L. Indoor Air Pollution Due to Chipboard Used  
475 as a Construction Material. *Atmos. Environ.* **1975**, *9*, 1121–1127.
- 476 (37) Fang, L.; Clausen, G.; Fanger, P. O. Impact of temperature and humidity on chemical and  
477 sensory emissions from building materials. *Indoor Air* **1999**, *9*, 193–201.
- 478 (38) Huang, H.; Haghghat, F.; Blondeau, P. Volatile organic compound (VOC) adsorption on  
479 material: influence of gas phase concentration, relative humidity and VOC type. *Indoor*  
480 *Air* **2006**, *16*, 236–247.
- 481 (39) Huang, S.; Xiong, J.; Cai, C.; Xu, W.; Zhang, Y. Influence of humidity on the initial  
482 emittable concentration of formaldehyde and hexaldehyde in building materials:  
483 experimental observation and correlation. *Sci. Rep.* **2016**, *6*, 23388.
- 484 (40) Liang, W.; Yang, S.; Yang, X. Long-Term Formaldehyde Emissions from Medium-

- 485 Density Fiberboard in a Full-Scale Experimental Room: Emission Characteristics and the  
486 Effects of Temperature and Humidity. *Environ. Sci. Technol.* **2015**, *49*, 10349–10356.
- 487 (41) Parthasarathy, S.; Maddalena, R. L.; Russell, M. L.; Apte, M. G. Effect of Temperature  
488 and Humidity on Formaldehyde Emissions in Temporary Housing Units. *J. Air Waste*  
489 *Manag. Assoc.* **2011**, *61*, 689–695.
- 490 (42) Sidheswaran, M.; Chen, W.; Chang, A.; Miller, R.; Cohn, S.; Sullivan, D.; Fisk, W. J.;  
491 Kumagai, K.; Destailats, H. Formaldehyde Emissions from Ventilation Filters under  
492 Different Relative Humidity Conditions. *Environ. Sci. Technol.* **2013**, *47*, 5336–5343.
- 493 (43) Xu, J.; Zhang, J. S. An experimental study of relative humidity effect on VOCs' effective  
494 diffusion coefficient and partition coefficient in a porous medium. *Build. Environ.* **2011**,  
495 *46*, 1785–1796.
- 496 (44) Won, D.; Corsi, R. L.; Rynes, M. Sorptive interactions between VOCs and indoor  
497 materials. *Indoor Air* **2001**, *11*, 246–256.
- 498 (45) Shen, J.; Gao, Z. Ozone removal on building material surface: A literature review. *Build.*  
499 *Environ.* **2018**, *134*, 205–217.
- 500 (46) Gall, E.; Darling, E.; Siegel, J. A.; Morrison, G. C.; Corsi, R. L. Evaluation of three  
501 common green building materials for ozone removal, and primary and secondary  
502 emissions of aldehydes. *Atmos. Environ.* **2013**, *77*, 910–918.
- 503 (47) Anderson SE, Franko J, Jackson LG, Wells J, Ham JE, Meade B. Irritancy and allergic  
504 responses induced by exposure to the indoor air chemical 4-oxopentanal. *Toxicol Sci.*  
505 **2012**, *127*, 371–381.
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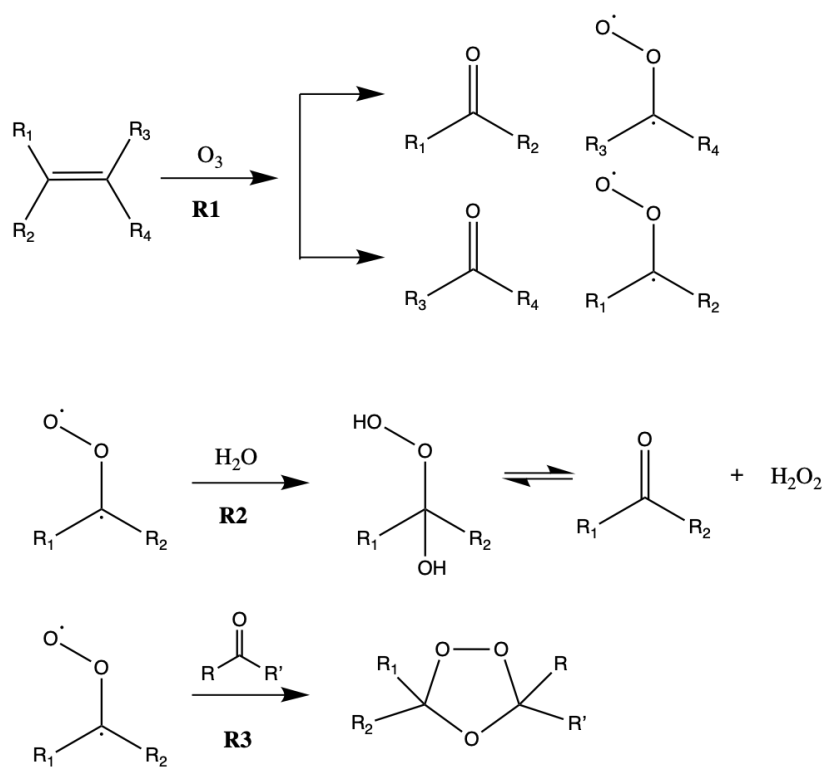
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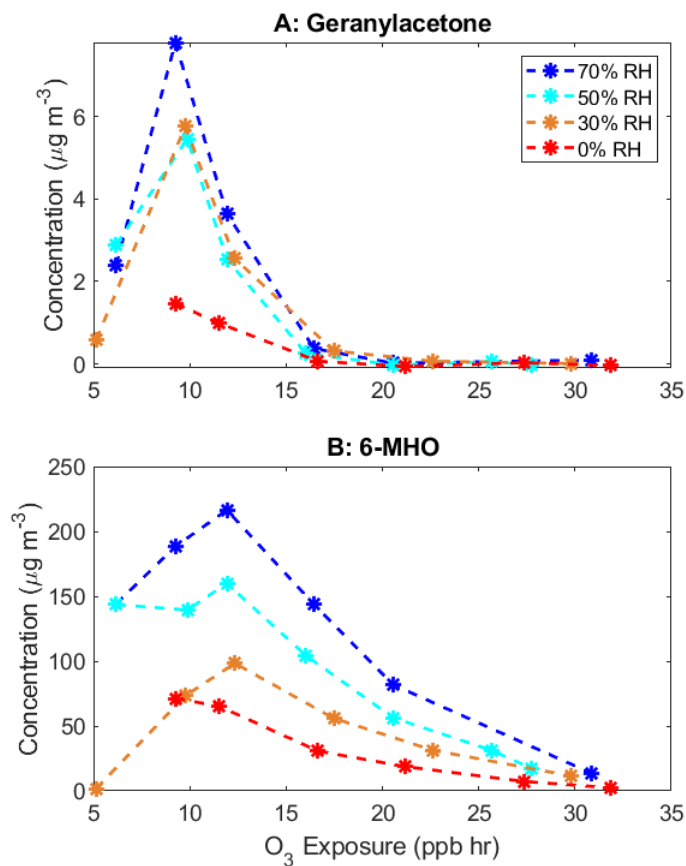
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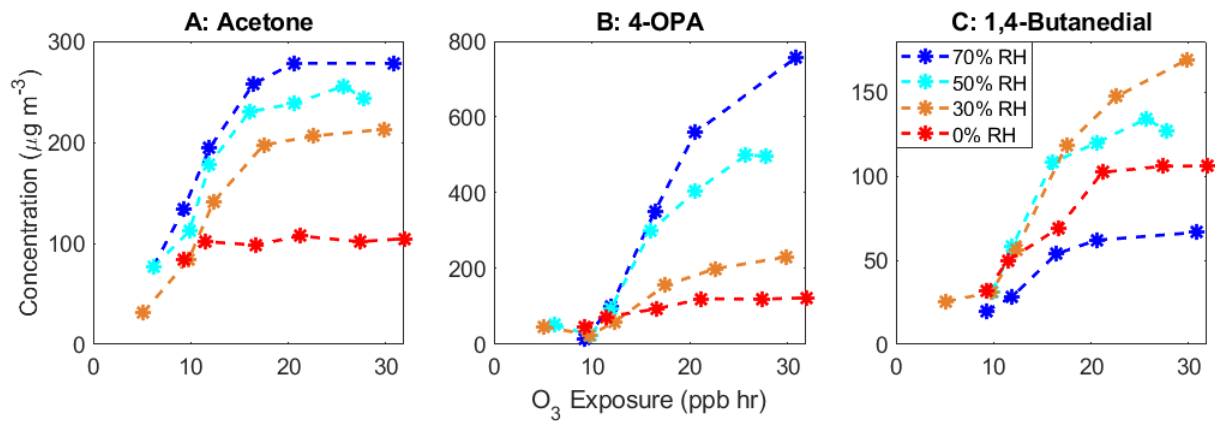
**Figure 1:** Chemical structure of squalene and selected squalene ozonolysis products

Scheme 1: Simplified Reaction Mechanism for Ozonolysis of Alkenes



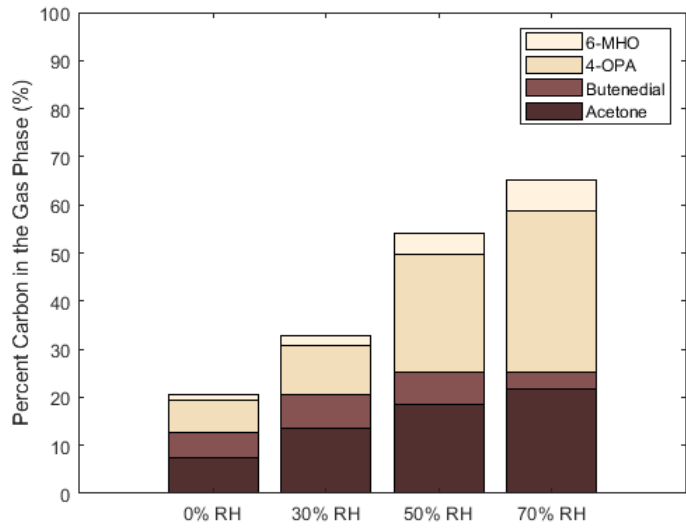


**Figure 2:** Primary unsaturated products from squalene ozonolysis as a function of humidity and  $\text{O}_3$  exposure.

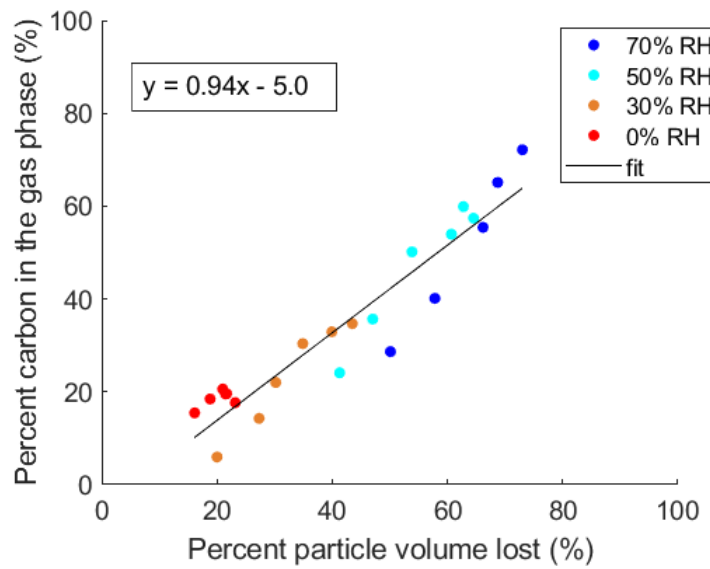


**Figure 3:** Terminal products from squalene ozonolysis as a function of humidity and  $O_3$  exposure.

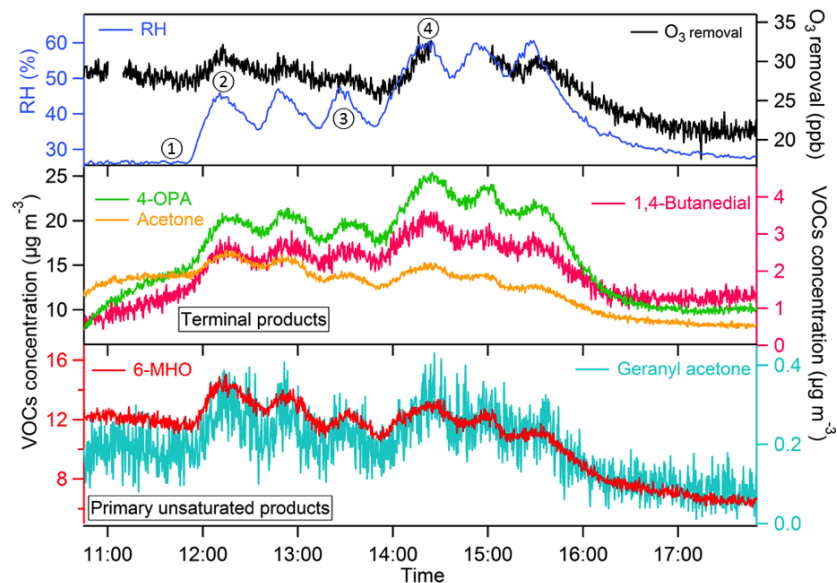




**Figure 4:** Percent of carbon in the gas phase at 20 ppb h O<sub>3</sub> exposure as a function of RH. Converting the measurements in Figures 2-3 from  $\mu\text{g m}^{-3}$  to  $\mu\text{g C m}^{-3}$ , and normalizing to the initial concentration of carbon entering the flow tube gives the percent carbon in the gas phase.



**Figure 5:** Percent carbon in the gas phase compared to the percent of particle volume lost for all RH and O<sub>3</sub> exposures.



**Figure 6:** Time series of primary unsaturated products (lower panel) and terminal products (middle panel) with relative humidity and  $O_3$  removal (upper panel) for clothing experiment ( $O_3$  removal was obtained by subtracting measured  $O_3$  level from the level of  $O_3$  in supply air; the gap in the  $O_3$  removal curve is due to the measurement of  $O_3$  level in supply air). Circled numbers in the top panel refer to conditions referenced in Table 1.

**Table 1:** The concentration change of squalene oxidation products ( $\Delta\text{VOCs}$ ,  $\mu\text{g m}^{-3}$ ) due to relative humidity (RH) increase. Circled numbers refer to points in Figure 6.

RH (%)	$\Delta\text{O}_3$ (ppb)	$\Delta\text{VOCs}$ ( $\mu\text{g m}^{-3}$ )							
		acetone	4-OPA	6-MHO	geranyl acetone	1,4- butanediol	hydroxy acetone	4-oxobutanoic acid	5-hydroxy-4- oxopentanal
① 26	② 2.90	2.17	5.91	2.54	0.117	1.14	1.28	0.340	0.339
44	③ 46	0.960	5.09	0.652	0.084	0.812	0.881	0.327	0.284
59	④ 59								

## Heterogeneous Ozonolysis of Squalene: Gas-Phase Products Depend on Water Vapor Concentration

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### **Supporting Information**

Pages S1-S8

Tables S1-S5

Figures S1-S4

**Table S1:** Geranyl acetone concentration data used to calculate production from ozonolysis. Once concentrations were stable in the flow tube reactor, a ‘Raw’ measurement was taken. Shortly after, the particle flow was replaced with a flow of N<sub>2</sub>, and squalene particles were removed from the flow tube reactor, allowing for a background measurement. Background measurements were taken 2 min after the particle flow was removed, when 95% of particles are removed from the flow tube.

RH (%)	O <sub>3</sub> Exposure (ppb h)	Background ( $\mu\text{g m}^{-3}$ )	Raw ( $\mu\text{g m}^{-3}$ )	Difference ( $\mu\text{g m}^{-3}$ )
0	9	9	14	5
0	12	1	4	3
0	17	0	0	0
0	21	0	0	0
0	27	0	0	0
0	32	0	0	0
30	5	69	70	1
30	10	22	37	15
30	12	3	10	7
30	17	0	1	1
30	23	0	0	0
30	30	0	0	0
50	6	149	160	11
50	10	20	34	14
50	12	3	9	6
50	16	0	1	1
50	21	0	0	0
50	26	0	0	0
50	28	0	0	0
70	6	118	127	9
70	9	24	43	19
70	12	3	12	9
70	16	0	1	1
70	21	0	0	0
70	31	0	0	0

**Table S2:** 6-MHO concentration data used to calculate production from ozonolysis. Once concentrations were stable in the flow tube reactor, a ‘Raw’ measurement was taken. Shortly after, the particle flow was replaced with a flow of N<sub>2</sub>, and squalene particles were removed from the flow tube reactor, allowing for a background measurement. Background measurements were taken 2 min after the particle flow was removed, when 95% of particles are removed from the flow tube.

RH (%)	O <sub>3</sub> Exposure (ppb h)	Background ( $\mu\text{g m}^{-3}$ )	Raw ( $\mu\text{g m}^{-3}$ )	Difference ( $\mu\text{g m}^{-3}$ )
0	9	36	94	57
0	12	15	69	52
0	17	7	31	25
0	21	2	18	15
0	27	1	7	6
0	32	1	3	2
30	5	151	152	1
30	10	112	172	59
30	12	51	132	79
30	17	12	58	45
30	23	6	31	25
30	30	3	13	9
50	6	290	401	115
50	10	105	218	112
50	12	41	169	128
50	16	6	90	83
50	21	2	47	45
50	26	1	27	25
50	28	1	15	14
70	6	240	355	115
70	9	109	260	151
70	12	42	216	173
70	16	6	121	115
70	21	2	68	65
70	31	2	12	11

**Table S3:** 4-OPA concentration data used to calculate production from ozonolysis. Once concentrations were stable in the flow tube reactor, a ‘Raw’ measurement was taken. Shortly after, the particle flow was replaced with a flow of N<sub>2</sub>, and squalene particles were removed from the flow tube reactor, allowing for a background measurement. Background measurements were taken 2 min after the particle flow was removed, when 95% of particles are removed from the flow tube.

RH (%)	O <sub>3</sub> Exposure (ppb h)	Background ( $\mu\text{g m}^{-3}$ )	Raw ( $\mu\text{g m}^{-3}$ )	Difference ( $\mu\text{g m}^{-3}$ )
0	9	148	185	38
0	12	147	205	58
0	17	134	209	75
0	21	105	202	96
0	27	96	192	95
0	32	101	199	98
30	5	191	229	38
30	10	335	353	19
30	12	378	425	47
30	17	368	492	125
30	23	344	502	160
30	30	337	522	184
50	6	848	887	42
50	10	579	601	20
50	12	712	785	75
50	16	676	917	240
50	21	626	950	323
50	26	618	1020	399
50	28	640	1038	398
70	9	857	871	11
70	12	1083	1165	79
70	16	1233	1516	282
70	21	1179	1630	447
70	31	1136	1734	606

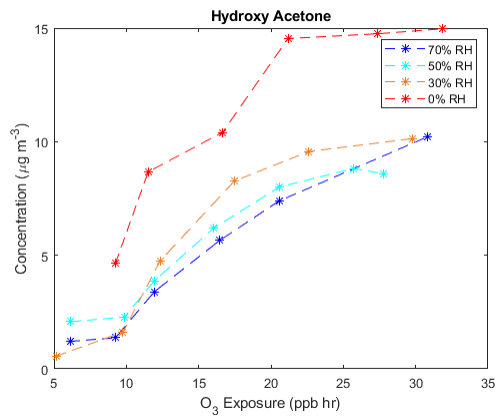
**Table S4:** 1,4-butanediol concentration data used to calculate production from ozonolysis. Once concentrations were stable in the flow tube reactor, a ‘Raw’ measurement was taken. Shortly after, the particle flow was replaced with a flow of N<sub>2</sub>, and squalene particles were removed from the flow tube reactor, allowing for a background measurement. Background measurements were taken 2 min after the particle flow was removed, when 95% of particles are removed from the flow tube.

RH (%)	O <sub>3</sub> Exposure (ppb h)	Background ( $\mu\text{g m}^{-3}$ )	Raw ( $\mu\text{g m}^{-3}$ )	Difference ( $\mu\text{g m}^{-3}$ )
0	9	81	106	25
0	12	87	126	40
0	17	88	143	55
0	21	67	150	82
0	27	57	142	85
0	32	57	143	85
30	5	66	87	20
30	10	112	135	25
30	12	122	166	45
30	17	110	205	95
30	23	100	218	118
30	30	92	229	135
50	10	153	178	25
50	12	161	207	46
50	16	152	238	86
50	21	146	242	96
50	26	149	257	107
50	28	159	260	101
70	9	189	206	16
70	12	223	246	23
70	16	254	297	43
70	21	239	289	50
70	31	257	309	53

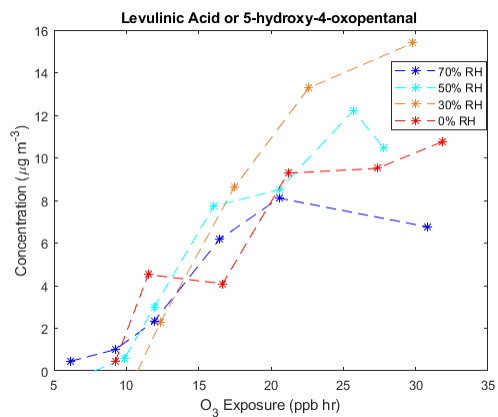


**Table S5:** Acetone concentration data used to calculate production from ozonolysis. Once concentrations were stable in the flow tube reactor, a ‘Raw’ measurement was taken. Shortly after, the particle flow was replaced with a flow of N<sub>2</sub>, and squalene particles were removed from the flow tube reactor, allowing for a background measurement. Background measurements were taken 2 min after the particle flow was removed, when 95% of particles are removed from the flow tube.

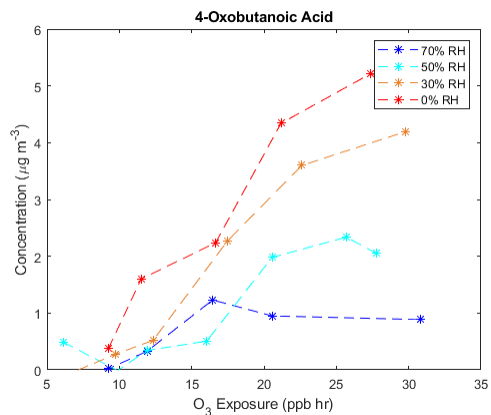
RH (%)	O <sub>3</sub> Exposure (ppb h)	Background ( $\mu\text{g m}^{-3}$ )	Raw ( $\mu\text{g m}^{-3}$ )	Difference ( $\mu\text{g m}^{-3}$ )
0	9	81	167	84
0	12	71	173	102
0	17	71	169	98
0	21	57	165	107
0	27	52	154	102
0	32	52	158	105
30	5	105	137	32
30	10	142	227	84
30	12	123	267	141
30	17	92	293	197
30	23	81	289	206
30	30	75	288	213
50	6	163	240	77
50	10	135	249	112
50	12	110	289	178
50	16	71	301	230
50	21	62	302	238
50	26	60	319	256
50	28	62	307	243
70	6	137	216	77
70	9	158	293	133
70	12	142	337	194
70	16	122	381	258
70	21	149	428	278
70	31	184	459	278



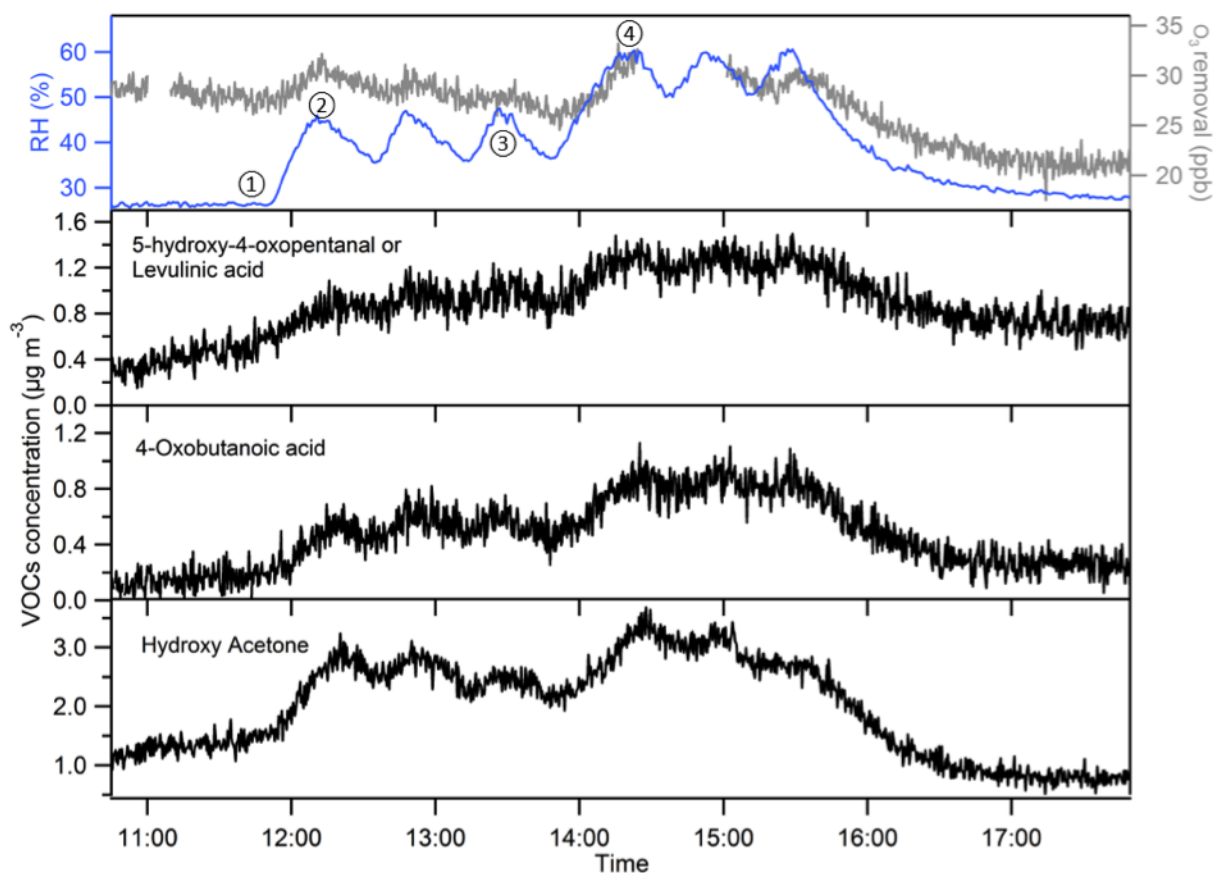
**Figure S1:** Hydroxy acetone concentration as a function of humidity and O<sub>3</sub> exposure.



**Figure S2:** 5-hydroxy-4-oxopentanal and levulinic acid concentration as a function of humidity and O<sub>3</sub> exposure.



**Figure S3:** 4-oxopentanoic acid concentration as a function of humidity and O<sub>3</sub> exposure.



**Figure S4:** Time series of other squalene oxidation products with relative humidity and  $O_3$  removal (upper panel) for the clothing experiment ( $O_3$  removal is the difference between  $O_3$  measured in supply air and the chamber; the data gap is due to the supply air measurement).