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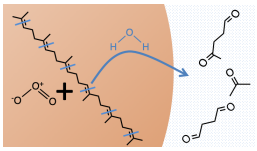

Heterogeneous Ozonolysis of Squalene: Gas-Phase Products Depend on Water Vapor Concentration

Caleb Arata[*†§], Nadja Heine[‡], Nijing Wang[¶], Pawel K. Misztal[§#], Pawel Wargocki[^], Gabriel Bekö[^], Jonathan Williams[¶], William W Nazaroff[‖], Kevin R. Wilson[‡], Allen H. Goldstein[§‖]

[†]Department of Chemistry, [§]Department of Environmental Science, Policy and Management, and [‖]Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720 United States

[‡]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[¶]Air Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany

[^]Department of Civil Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

[#] Now at: Department of Civil, Architectural and Environmental Engineering, The University of Texas at Austin, Austin, TX 78712

[*]Phone: 310 968 8331. Email: caleb.arata@berkeley.edu

Abstract

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

Introduction

People spend 90% of their lives indoors[1]. Each day, adult humans inhale 12-15 kg of air, making indoor air an important route of exposure to many chemicals, including volatile organic compounds (VOCs). People can be the dominant indoor VOC emission source in densely occupied spaces, and, in the presence of ozone (O_3), the oxidation of skin lipids adds ketones and aldehydes to the composition of indoor air[2–8].

Indoor O_3 concentrations are commonly 20-70% of outdoor levels, with the ratio depending on building air-change rate (ACR), type of ventilation system, and the nature of indoor surfaces[9]. Indoor air is estimated to contribute 25-60% of an individual's daily O_3 exposure.[10] In densely occupied spaces, occupants may be the dominant indoor sinks for O_3, mainly due to reactions with lipids on their skin, hair, and clothing.[11]

Squalene ($C_{30}H_{50}$) constitutes 10% of the mass of human skin lipids, and contributes 50% of the unsaturated carbon bonds.[12] When exposed to O_3, squalene is quickly oxidized to products that span a wide range of volatility; some products remain in the condensed phase while others become gaseous.[5]

Researchers have investigated effects of human occupancy on aircraft cabin air, considering that interior O_3 levels are sometimes elevated in airplanes.[13] Weschler et al. conducted experiments in a simulated aircraft cabin section and found that more than half of the observed oxidation products in the gas phase came from O_3 reacting with human skin lipids.[4]

Further work studied O_3 deposition on materials common to aircraft cabin interiors, finding that soiled clothing exposed to O_3 emits 6-methyl-5-hepten-2-one (6-MHO).[14,15] Surface bound squalene was found to have a high reaction probability with O_3, in the range of $0.5\text{-}1 \times 10^{-3}$, and reaction of ozone with squalene on soiled clothing has been shown to be mass-transport limited.[16–18] Both 4-oxopentanal (4-OPA) and 6-MHO are known respiratory irritants.[19,20] Acetone and 6-MHO are among the most prominent VOCs emitted from human skin.[21] While acetone is known to originate from a wide variety of sources, including breath, 6-MHO is thought to be specific to squalene oxidation. The high emission rate suggests that squalene oxidation contributes significantly to VOC emissions from human skin.

Heine et al. investigated the influence of RH on squalene ozonolysis using pure squalene particles in a flow-tube reactor.[22] They showed that water vapor concentration does not affect the rate of squalene ozonolysis, but does substantially change the product composition. Under dry conditions, as O_3 consumes squalene, secondary ozonide concentrations increase in the condensed phase and initial particle volume is reduced by 15%. At 60% RH, condensed-phase ozonolysis products shift from secondary ozonides to carbonyls, and particle volume is reduced by as much as 50%. Such losses of particle volume should correspond to an increase in gas-phase oxidation products.

For this study, we designed experiments specifically to observe the mass lost to the gas

phase and the products formed by O_3-squalene reactions as a function of RH, and to understand the implications for the fate of the Criegee intermediate on squalene particle surfaces and skin-oil coated clothing. Here, we investigate the gas-phase products from squalene particle ozonolysis in a flow tube reactor, and on skin-oil soiled shirts in a climate chamber. From the flow-tube experiments, we show that the RH dependent loss of particle diameter corresponds to an increase in gas-phase reaction products, consistent with the mechanism of water molecules promoting carbonyl formation from the Criegee intermediate under real world conditions. We discuss implications for product yields from skin oil ozonolysis indoors under varying RH conditions.

Experimental Methods

Squalene ozonolysis was carried out in a flow-tube reactor, as described in Heine et al.[22,23] Liquid squalene in a tube furnace was heated to 145 ºC, generating, by means of homogeneous nucleation, polydisperse particles with a mean surface-weighted diameter of 250 +/- 40 nm. A continuous flow of 300 standard cm^3 min^{-1} dry nitrogen (N_2) carried the particles from the furnace through a charcoal denuder to remove any gas-phase contamination. This flow was then combined with flows of oxygen (O_2), O_3, dry N_2, and humidified N_2 for a total flow of 1 L min^{-1}. Levels of O_2 were held at a constant 10%, while the flows of dry and humidified N_2 were varied to give a range of nearly 0% (< 3%) to 100% RH. This combined flow traversed the flow tube

reactor (130 cm long, 2.5 cm inner diameter) with a residence time of 37 s.[24] Ozone was produced by a corona discharge generator, and the concentrations of O_3 were in the range 0-4 ppm, giving O_3 exposures of 0-44 ppb h. The initial particle loading in the flow reactor was 1000 μg m^{-3}.

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

PTR-TOF-MS is a chemical ionization technique with minimal fragmentation using H_3O^+ as the primary reagent ion. PTR-TOF-MS has been previously used to detect gas-phase products of squalene ozonolysis.[2,4,5] For these experiments, the instrument was calibrated with a multicomponent VOC gas standard to ensure stability throughout the campaign. Of the compounds reported here, only acetone was determined using a direct calibration. All other compound concentrations were calculated using a default proton transfer reaction rate constant of 2.5×10^{-9} cm^3 s^{-1} for both the primary ion, H_3O^+, as well as for the first water cluster, $H_3O^+(H_2O)$. Direct calibration accuracies are estimated to be +/- 10%, whereas concentration

accuracies derived from the default rate constant are typically +/- 50%.[25] Increases in RH can cause increases in instrument sensitivities for certain compounds. However, these changes are typically a few percent, much lower than concentration differences reported in this work.[26,27]

Measurements of VOCs at each specified RH and O_3 exposure were made by allowing concentrations in the reactor to stabilize. Once stable, the particle flow was quickly replaced with a flow of N_2. After 2 min, 95% of the particles were removed from the reactor, and a background concentration was taken. To account for both compounds being desorbed from the flow-tube walls as well as compounds being produced by heterogeneous oxidation on the walls, O_3 flow was maintained during the background sampling procedure. The difference between the stable concentration and the background concentration was taken to be the gas-phase concentration attributable to squalene-particle ozonolysis. Tables S1–S5 show the concentrations for each species as measured from the flow tube, as well as the measured background.

An experiment to analyze emissions from skin-oil soiled clothing under varying conditions of RH and O_3 was performed as part of the Indoor Chemical Human Emissions and Reactivity (ICHEAR) project. Four identical T-shirts (100% cotton) were washed with fragrance-free detergent and tumble dried, before being worn by four people overnight (minimum of 8 h). The skin-oil soiled T-shirts were then placed inside a stainless-steel climate chamber (volume 26.8 m^3) ventilated with an air-change rate of 3.2 h^{-1}. Outdoor air was used for

ventilation. It was filtered using particle and activated carbon filters to avoid interference from outdoor VOCs, and conditioned to reach the required temperature and RH. Ozone was generated (Jelight Model 600 UV) in the HVAC system downstream of the activated carbon filter and continuously introduced into the chamber at levels between 95-100 ppb. The temperature inside the chamber was maintained at 27.4–28.3 °C during the experiment and the O_3 levels were monitored throughout. Four RH levels were established. The lowest RH levels (at the beginning and end of the experiment) were not controlled (humidifier off, no dehumidifying present), while the two higher RH levels were achieved by operating a steam humidifier in the HVAC system. The first three levels were maintained for 1.5-2 hours to allow steady-state conditions to be reached. The resulting average RH levels during these three periods were 26%, 41%, and 56%. The final, fourth, RH condition was a decay from 50% to 28% with the humidifier off. The average RH for this period was 33%.

A PTR-TOF-MS (8000, Ionicon Analytik GmbH Innsbruck, Austria) was deployed during ICHEAR to monitor VOCs produced from O_3 oxidation of skin oil. The operational conditions of the PTR-TOF-MS were drift tube pressure 2.2 mbar, temperature 60 °C and 137 Td (*E*/*N*). The 3.2-mm (1/8") Teflon inlet of the instrument was attached to the main exhaust duct of the chamber, approximately 1 m from the terminal through which the air was exhausted from the chamber and set to draw 100 mL min^{-1} (via a main high flow inlet of 7 L min^{-1}) continuously

143 into the mass spectrometer. Data reported for the skin-oil T-shirt experiment represent sample
144 time resolution of 20 s. Before putting T-shirts inside the chamber, a background level of the
145 empty chamber was established and maintained for 10 minutes. The measured background VOC
146 levels were subsequently subtracted from the VOC levels measured while the T-shirts were in
147 the chamber.

148 **Results and Discussion**

149 Figure 1 shows the chemical structures of squalene and selected gas-phase ozonolysis
150 products. The first-generation gas-phase products are acetone, 6-methyl-5-hepten-2-one (6-
151 MHO), and geranylacetone. Terminal oxidation products found in the gas phase, i.e. products
152 that are minimally reactive with O_3 because of their lack of carbon-carbon double bonds, are
153 acetone, 4-oxopentanal (4-OPA), and 1,4-butanedial (succinaldehyde). Scheme 1 shows a
154 simplified mechanism for alkenes reacting with O_3. In **R1**, O_3 adds across the double bond,
155 forming a primary ozonide (not shown), which quickly decomposes to one of two combinations
156 of carbonyl and Criegee intermediate. This reaction is fast and does not include water, so water
157 vapor concentration has no effect on the rate of alkene loss.[22] The Criegee intermediate produced
158 by **R1** is reactive, and can proceed through **R2** or **R3**, as well as through rearrangement or
159 reactions with carboxylic acids[28,29]. **R2** shows the Criegee intermediate reacting with water to

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

Figures 2A and 2B show the gas-phase concentration of geranylacetone and 6-MHO exiting the flow-tube reactor as a function of O_3 exposure and RH. Both compounds are primary products of squalene oxidation, and both have carbon-carbon double bonds that can further react with O_3. At all RH levels, geranylacetone production peaks at an O_3 exposure of 10 ppb h. Dry conditions yield 5 μg m^{-3} of geranylacetone, whereas more humid conditions (70% RH) enhance the concentration to 19 μg m^{-3}, an increase by almost 4×. More humid conditions, specifically RH of 30% and 50%, also show an increase in geranylacetone concentration compared to dry conditions. At exposures of 20 ppb h, the geranylacetone is fully consumed by ozonolysis and is not detected. Compared to other products measured, concentrations of geranylacetone are small. As a 13-carbon ketone, with a vapor pressure of 3.5 Pa at 298 K, most of the geranylacetone is expected to remain in the condensed phase.[6] Furthermore, there are fewer possible reaction pathways to produce geranylacetone than the other, shorter chain products. The low concentration measured in this study is consistent with a classroom study by Tang et al., where

both 6-MHO and 4-OPA were found at significantly higher concentrations than geranylacetone.[2]

The production of 6-MHO shows strong RH dependence. At all levels of O_3 exposure, an increase in RH leads to an increase in 6-MHO concentration. As 6-MHO is a primary product that can also be consumed, peak concentrations are found at the lower levels of O_3 exposure. At 70% RH and 12 ppb h of O_3 exposure, the detected concentration is 170 μg m^{-3}, 3 times the level of 6-MHO detected at the same O_3 exposure but under dry conditions. Unlike geranylacetone, 6-MHO is detected at even the highest levels of O_3 exposure tested, 30 ppb h. The 6-MHO species is used as a primary tracer compound for squalene oxidation, along with 4-OPA as a secondary tracer. The fact that 6-MHO is consumed at higher O_3 exposures, while 4-OPA is not, suggests that 6-MHO concentrations could be used as a proxy indicator for the age of oxidation products: at longer timescales, 6-MHO becomes depleted while 4-OPA does not.

Figures 3A-3C show the gas-phase concentrations as a function of O_3 exposure and RH of the three terminal products: acetone, 4-OPA, and 1,4-butanedial. At most levels of O_3 exposure, increasing RH produces increasing concentrations of acetone, again showing strong humidity dependence. At very low O_3 exposure (5-6 ppb h), 30% RH produces 32 μg m^{-3} of acetone, whereas 70% RH conditions give 77 μg m^{-3}, an increase by more than 2×. Under dry conditions, acetone increases to 100 μg m^{-3} at 12 ppb h exposure, and then does not increase with increasing O_3 exposure. As acetone does not have carbon-carbon double bonds, it does not react

196 significantly with O_3 and so increasing exposure is not expected to consume acetone. Under
197 higher RH conditions, the same leveling off is seen, but at higher concentrations. At 70% RH,
198 acetone concentrations begin to plateau at 20 ppb h exposure, at a concentration of 280 μg m^{-3}.
199 At O_3 exposures greater than 10 ppb h, increasing RH from 0% to 70% increases acetone
200 concentrations by a factor of 2.5 to 3.

201 Figure 3B shows the RH dependence of 4-OPA from the ozonolysis of squalene. A
202 minimum of two reactions involving O_3 are required to produce 4-OPA from squalene, so
203 concentrations are observed to increase later than the primary products, acetone and 6-MHO.
204 Despite being a terminal product, 4-OPA does not show the same leveling off behavior as
205 acetone. Under dry conditions, production stops increasing at 20 ppb h O_3 exposure, but under
206 high RH conditions no leveling off is seen; production of 4-OPA may increase past 30 ppb h
207 exposure. At O_3 exposures less than 12 ppb h, no RH dependence is seen, but production is also
208 small. At higher O_3 exposures, 4-OPA shows strong RH dependence, with a factor of 6 increase
209 in concentration between dry and humid conditions at 30 ppb h O_3 exposure. In both mixing ratio
210 and mass concentration, 4-OPA is the most abundant gas-phase product, with a peak
211 concentration of 600 μg m^{-3}. If each double bond in squalene proceeds through reaction **R2**, one
212 molecule of squalene would produce a single 1,4-butanedial molecule, two acetone molecules,
213 and four 4-OPA molecules. While the observed mixing ratios of terminal products do not follow

these stoichiometric ratios, the relatively large number of 4-OPA molecules that can be made from each squalene molecule help to explain why it is the most abundant gas-phase product.

Figure 3C shows the concentration of 1,4-butanedial as a function of RH and O_3 exposure. As a terminal product, abundance of this species increases with O_3 exposure, and, for some RH conditions, eventually levels off. As with 4-OPA, production of 1,4-butanedial requires a minimum of two ozonolysis reactions, so concentrations substantially increase at greater O_3 exposure. Production of 1,4-butanedial shows a more complicated relation to RH than other species. The lowest levels of production, across all O_3 exposures, are under the most humid conditions. The next lowest levels of production are under the driest conditions. Although it does not follow the pattern of the other species measured, 1,4-butanedial levels do show strong variability with RH. At 30 ppb h O_3 exposure, switching from 70% RH to 30% RH increases the concentration of 1,4-butanedial from 52 μg m^{-3} to 140 μg m^{-3}. This ~3× increase in production is in line with the 3-6× changes in production observed at different RH for other compounds. The fact that 1,4-butanedial production peaks at intermediate RH, and declines at low and high RH, suggests that water plays a more complicated role than depicted in Scheme 1. Specifically, reaction **R2** increases 1,4-butanedial production up to a point, and then facilitates other reactions that suppress production.

Wisthaler and Weschler (2010) observed 12 prominent VOCs from squalene ozonolysis,

including the five compounds already discussed.[5] When glass wool soiled with human skin oil was exposed to O_3 (0-75 ppb h), three species — 4-methyl-8-oxo-4-nonenal (4-MON), 4-methyl-4-octene-1,8-dial (4-MOD), and 1-hydroxy-6-methyl-5-hepten-2-one (OH-6MHO) — showed mixing ratios similar to the observed mixing ratios of 4-OPA and 1,4-butanedial. These species were also observed during ozonolysis of a pure squalene film; however, the mixing ratios for that experiment were not reported. In our work, all three compounds were detected (4-MON, 4-MOD, and OH-6MHO), but at very low concentrations, 2 μg m^{-3} or less. Possibly due to the low concentration of these species, a RH dependence isn't discernible.

Four other compounds identified by Wisthaler and Weschler (2010) — 1-hydroxypropan-2-one (hydroxyacetone), 4-oxobutanoic acid, and the isobaric compounds 5-hydroxy-4-oxopentanal and 4-oxopentanoic acid (levulinic acid) — are found in the present work at peak concentrations much lower than 6-MHO, acetone, 4-OPA, and 1,4-butanedial (5-15 μg m^{-3} versus 140-600 μg m^{-3}). All four compounds are terminal products; concentrations either increase or level off with increasing O_3 exposure, and none of the products show increasing production with increasing RH. Hydroxyacetone shows a muted response to changes in RH, as seen in Figure S6. Production is similar at 30% RH, 50% RH, and 70% RH, but increase by ~50-100% under dry conditions. Concentrations are modest, peaking at 15 μg m^{-3} under dry conditions and 30 ppb h O_3 exposure. Levulinic acid or 5-hydroxy-4-oxopentanal (or a

250 combination of the two) only shows a RH effect at the highest O_3 exposure. At 30 ppb h, 70%
251 RH yields 7 μg m^{-3} while 30% RH produces 15 μg m^{-3}, as seen in Figure S7. Figure S8 shows 4-
252 oxobutanoic acid production *decreasing* with increased RH. At 70% RH and 30 ppb h O_3
253 exposure, we observe 1 μg m^{-3}, whereas under dry conditions we measure 5 μg m^{-3}.
254 One fragmentation ion was produced in quantities comparable to those of the dominant
255 products, *m/z* 43.018 Da, $C_2H_3O^+$. This fragment is common to acetic acid and acetate esters, but
256 ions consistent with these parent masses were only found in low concentrations, so it is
257 unassigned.[30] The fragment was found at mixing ratios comparable to 1,4-butanedial, and shows
258 similar responses to RH.
259 To explore whether our gas-phase measurements agree with the amount of material lost
260 from the particle phase, we summed the amount of carbon detected in the gas-phase products at
261 different levels of RH. We used a carbon-balance approach to test whether the loss of material
262 from the particle phase could be accounted for by generation of gas-phase products. The
263 concentration of squalene entering the flow tube reactor was 1000 μg m^{-3}, corresponding to 880
264 μg m^{-3} of carbon. Converting the measurements in Figures 2-3 from μg m^{-3} to μg C m^{-3}, and
265 normalizing to the initial concentration of carbon entering the flow tube, gives the percent carbon
266 in the gas phase. (As with the reported concentrations, these measurements are accurate to +/-
267 50% for all species except for acetone, which is accurate to +/- 10% because it is directly

calibrated.) Figure 4 shows the percent carbon in the gas phase at 20 ppb h O_3 exposure. Note that only the dominant products are shown. Switching from 0% RH to 70% RH increases the proportion of carbon entering the gas phase from 21% to 65%, with increases in all dominant products except 1,4-butanedial. Assuming that an average of two molecules of oxidation products are generated for each molecule of ozone that reacts with squalene, this outcome corresponds to yields of between 42% and 130% for gas-phase oxidation products per molecule of ozone consumed. Even a moderate change, from dry conditions to 30% RH, increases the proportion of carbon entering the gas phase by 60%. The largest increases are seen in 4-OPA production.

Because the VUV-AMS only measures relative concentrations of species, there is no direct measurement of the amount of carbon present in the condensed phase. However, measurements of the change in particle volume can be used as a quantitative indicator for mass loss from the particle. Note that this approach ignores any mass gained by the addition of oxygen to condensed phase products of ozonolysis, as well as any difference in densities between squalene and condensed-phase reaction products. Despite these limitations, using this approach, there is a clear and strong correlation between the carbon detected in the gas phase and the volume lost from the particle, as shown in Figure 5. Under dry conditions, at all levels of O_3 exposure, ~20% of the particle volume is lost, and ~20% of the carbon from squalene is found in

286 the gas phase. At higher RH values, both the particle volume lost and the amount of carbon
287 entering the gas phase are more sensitive to O_3 exposure, as shown by the larger spread for these
288 humidified conditions. The highest RH level (70%) gives both the greatest particle volume loss
289 and the largest percent of carbon in the gas phase. Notwithstanding experimental uncertainties,
290 the evidence displayed in Figure 5 is consistent with expectations for the quantitative loss of
291 particle-phase carbon being balanced with increased abundances of gaseous carbon species.
292 Figures 6 and S9 show the measurements in chamber air of several pertinent VOCs along
293 with O_3 and RH. Four T-shirts were placed inside the measurement chamber at 10:25 with RH
294 maintained at ~26% for 1.5 h. Thereafter the RH was increased in a series of steps. The
295 previously identified squalene oxidation products (4-OPA, 1,4-butanedial, acetone, 6-MHO, and
296 geranylacetone) were observed to vary in response to the changing RH levels. Owing to the
297 working principle of the humidifier, the RH in the chamber fluctuated regularly within a 10%
298 range with a cycle of 38 minutes. In the data shown, primary unsaturated products and terminal
299 products all faithfully follow the RH variation, confirming the dependence of gas-phase squalene
300 ozonolysis products on RH, consistent with the flow-tube experiments. In accordance with
301 previous studies, 4-OPA was the most abundant product (especially at higher RH levels);
302 geranylacetone concentration was consistently the lowest among the quantified species.
303 In contrast with the flow-tube experiment, in which squalene particles were continuously

304 supplied, the skin-oil soiled T-shirts contained a limited amount of squalene that was
305 progressively consumed by O_3. Therefore, at any given RH, most of the compounds showed a
306 decreasing trend as the available squalene was depleted, except the first level where the lagging
307 terminal products still increase towards steady state. In particular, acetone clearly followed the
308 RH modulation while steadily decreasing as the experiment progressed. To better quantify the
309 relative yields of the VOCs as a function of RH, two pairs of RH levels were selected,
310 corresponding to points labeled 1-4 in Figure 6. As shown in Table 1, the concentration of 4-
311 OPA increased by 5.9 μg m^{-3} as the RH increased from 26% (point 1) to 44% (point 2). A
312 similar increase of 5.1 μg m^{-3} was seen in a second cycle as the RH changed from 46% (point 3)
313 to 59% (point 4). The other terminal products (1,4-butanedial, hydroxy acetone, 4-oxobutanoic
314 acid and 5-hydroxy-4-oxopentanal/levulinic acid) also showed slightly higher yields during the
315 first RH increase (point 1 to point 2). Although the level of the first-generation products
316 (acetone, 6-MHO and geranylacetone) tended to decrease with time, an increase was still
317 observed in the second step (points 3 and 4) when the RH increased from 46% to 59%. However,
318 unlike 4-OPA, the concentration changes were much lower than during the first RH increase
319 (points 1 and 2), as shown in Table 1. For 6-MHO and geranylacetone, additional oxidation by
320 O_3 could also be a contributing factor. Ozone removal was 3.4 ppb in the second RH step (46%
321 to 59%), compared to 2.9 ppb in the first step, indicating that more 6-MHO and geranylacetone

were produced and subsequently oxidized by O_3 at this stage. Significantly elevated 4-OPA concentrations after the second increase of RH further supports this explanation.

Effects of RH on squalene ozonolysis have been observed in prior studies. Petrick and Dubowski studied the condensed phase of squalene film oxidation while varying RH, finding that increased RH led to more ketone production.[31] They also note that RH did not influence reaction kinetics, a finding also reported by Fu et al.[32] Wang and Waring examined secondary organic aerosol formation from the ozonolysis of surface-film squalene at 21% RH and 51% RH.[33] At high O_3 exposures, they found that the higher RH increased the aerosol mass fraction (AMF) from squalene. This increase suggests that higher RH leads to more oxidation products entering the gas phase, where they then can condense onto airborne particles. Zhou et al. examined the RH dependence of squalene film oxidation on the condensed phase products, finding that increasing the RH increased the yield of lower molecular weight products and decreased the yield of higher molecular weight products.[34] Although not quantitatively comparable, these previous studies qualitatively agree that an increase in RH leads to an increase in volatile products from squalene ozonolysis.

Humidity is already known to be an important factor that can influence VOC emissions from materials, compete with VOCs for sorptive uptake, and influence how indoor air is perceived.[35–44] Humidity is also known to change the rate of uptake of O_3 on indoor surfaces, a

relationship that varies among common indoor materials.[45] Few studies have assessed how RH changes ozonolysis products and emission rates. Coleman et al. (2008) found that increasing RH from 10% to 50% doubled the emissions of most ozonolysis byproducts from a cotton surface, with nonanal and decanal emissions increasing by about 5×.[14] Gall et al. (2013) studied primary and secondary ozonolysis emissions from building materials, finding RH to have mixed effects.[46] Secondary emissions increased with RH for painted drywall, while emissions from carpet and ceiling tile did not. The present work contributes new knowledge, showing that RH can directly influence the products of squalene ozonolysis, providing an alternate route by which water vapor can increase VOC concentrations. At realistic indoor O_3 exposures, a change from 0% RH to 70% RH results in ~3 times the amount of carbon entering the gas phase. Squalene, with six carbon-carbon double bonds, is a model molecule to show this effect. Other unsaturated compounds, especially those with double bonds separating small moieties, may show similar behavior. The reactions shown in Scheme 1 are not specific to squalene, and so long as the carbonyls formed by reaction **R2** have sufficient volatility, increased production of gas-phase products are generally expected from increases in RH.

The effects seen in this study suggest that RH can significantly alter the gas-phase composition of indoor air. In high occupancy settings, skin-oil oxidation can be the dominant source of VOCs, and changes in RH can alter the strength of this source by as much as a factor

of 3.[4] In the flow-tube reactor, at the highest level of O_3 exposure and RH, the sum of the concentrations of dominant products was 940 μg m^{-3}, comparable to the 1000 μg m^{-3} of squalene entering the reactor. It should be noted that RH does not change the rate of squalene ozonolysis: at low RH, oxidized products are still being formed, but remain in the condensed phase. If that condensed phase is the skin surface, then the products might be taken up dermally, where they might influence health.[19,47] The large effect of RH on ozonolysis products from squalene, and the potential for the underlying mechanism to act on other alkenes, warrants further research on how humidity may modulate indoor reactive chemistry and its consequences.

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

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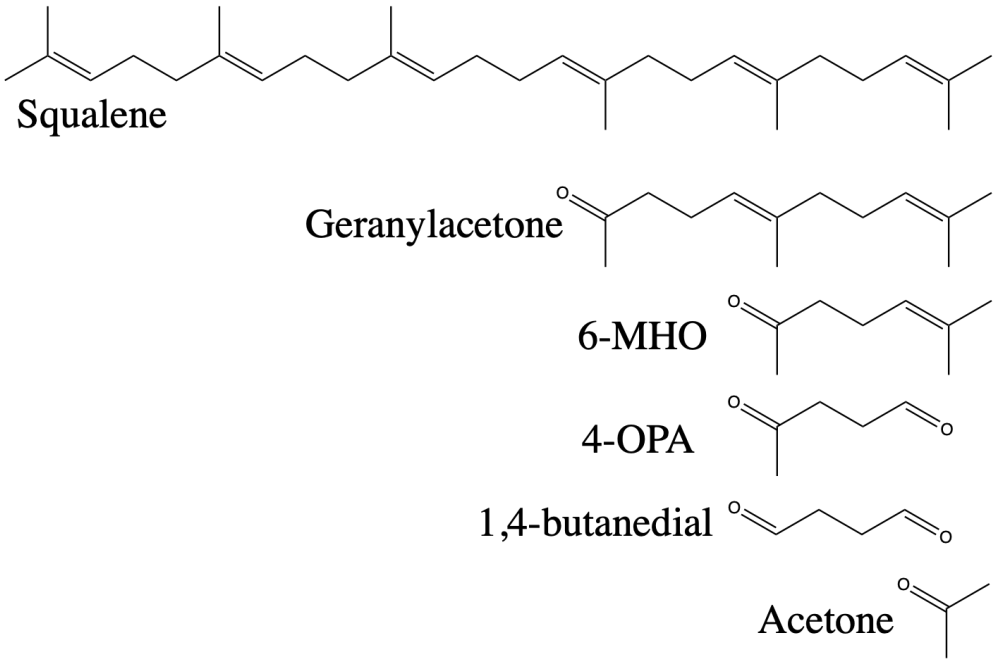
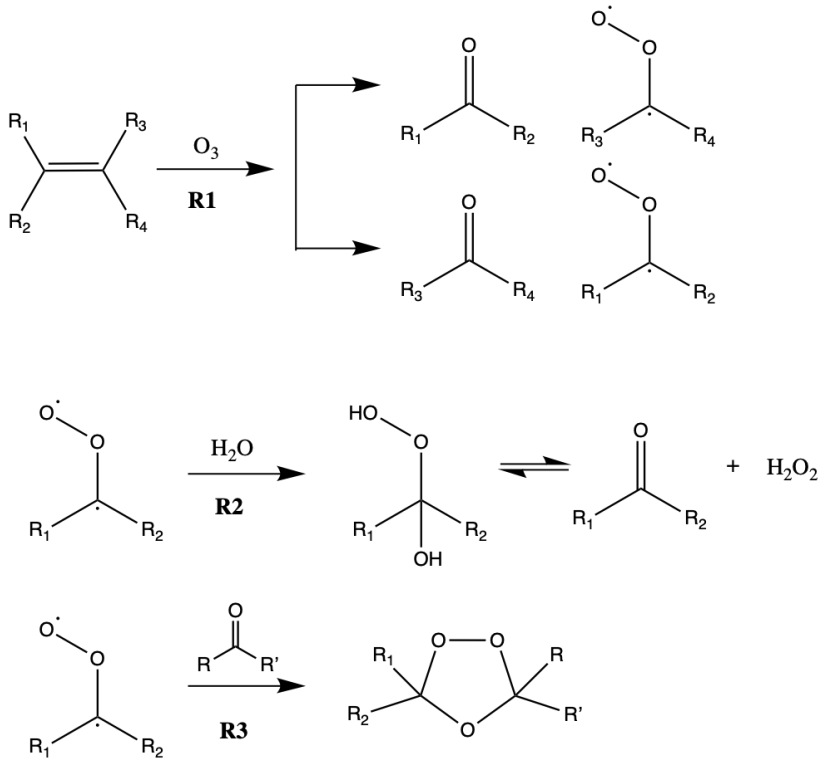


Figure 1: Chemical structure of squalene and selected squalene ozonolysis products

Scheme 1: Simplified Reaction Mechanism for Ozonolysis of Alkenes



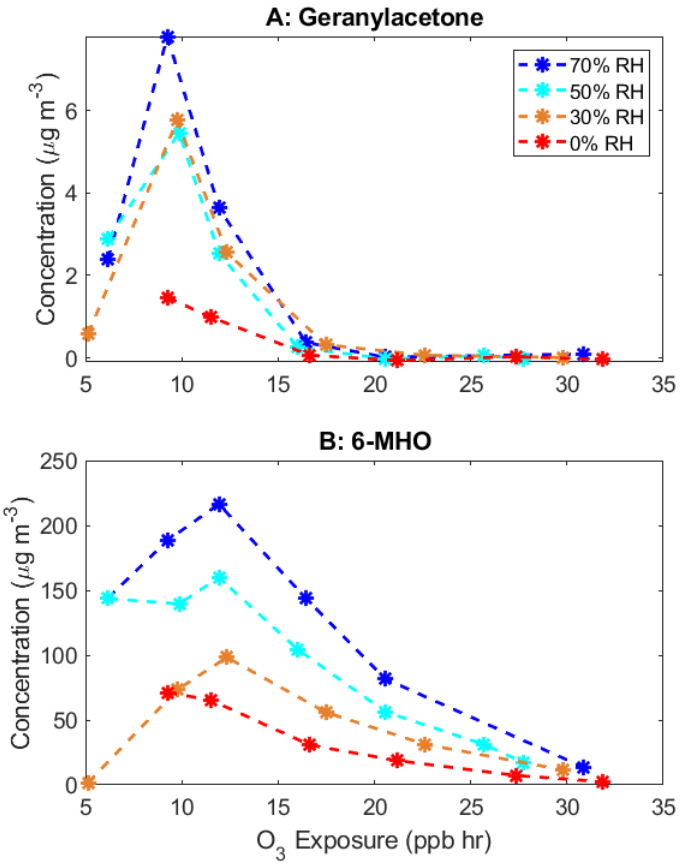


Figure 2: Primary unsaturated products from squalene ozonolysis as a function of humidity and O_3 exposure.

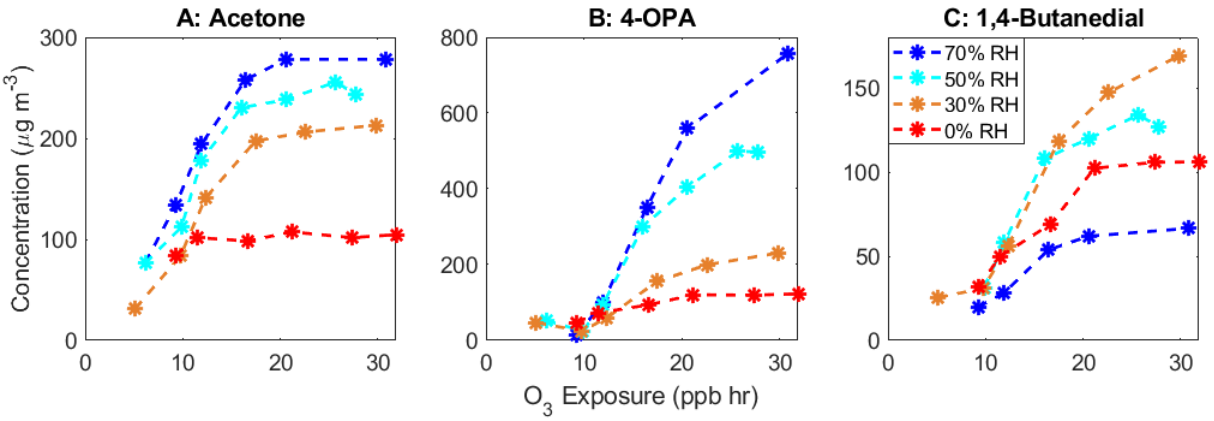


Figure 3: Terminal products from squalene ozonolysis as a function of humidity and O_3 exposure.

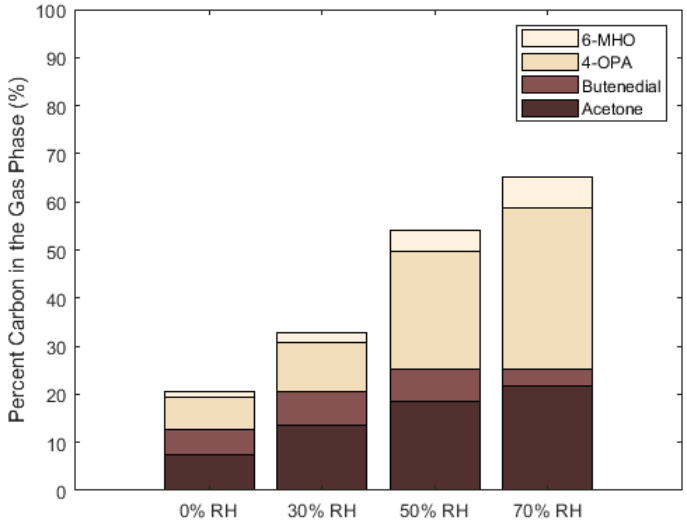


Figure 4: Percent of carbon in the gas phase at 20 ppb h O_3 exposure as a function of RH. Converting the measurements in Figures 2-3 from μg m^{-3} to μg C m^{-3}, and normalizing to the initial concentration of carbon entering the flow tube gives the percent carbon in the gas phase.

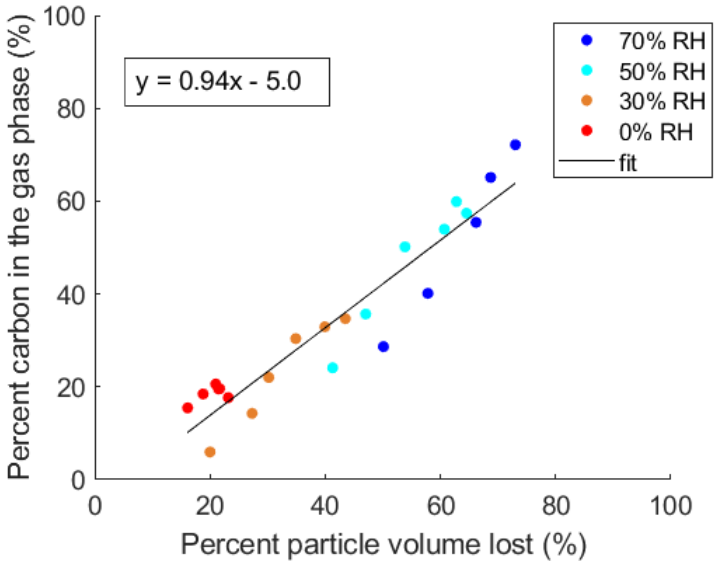


Figure 5: Percent carbon in the gas phase compared to the percent of particle volume lost for all RH and O_3 exposures.

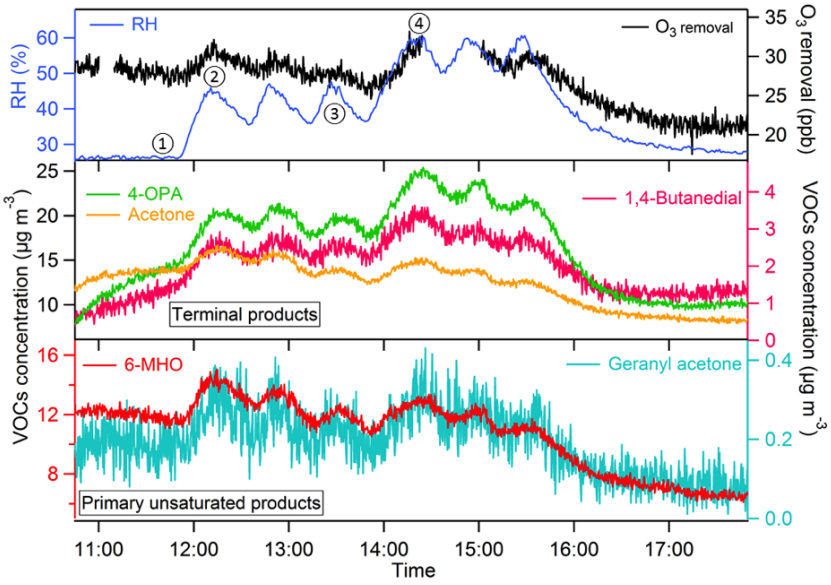


Figure 6: Time series of primary unsaturated products (lower panel) and terminal products (middle panel) with relative humidity and O_3 removal (upper panel) for clothing experiment (O_3 removal was obtained by subtracting measured O_3 level from the level of O_3 in supply air; the gap in the O_3 removal 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 (ΔVOCs, μg m^{-3}) due to relative humidity (RH) increase. Circled numbers refer to points in Figure 6.

RH (%)	ΔO_3 (ppb)	ΔVOCs (μg m^{-3})							
		acetone	4-OPA	6-MHO	geranyl acetone	1,4-butanedial	hydroxy acetone	4-oxobutanoic acid	5-hydroxy-4-oxopentanal
① 26 ② 44	2.90	2.17	5.91	2.54	0.117	1.14	1.28	0.340	0.339
③ 46 ④ 59	3.37	0.960	5.09	0.652	0.084	0.812	0.881	0.327	0.284