

Lawrence Berkeley National Laboratory

LBL Publications

Title

Connecting the Elementary Reaction Pathways of Criegee Intermediates to the Chemical Erosion of Squalene Interfaces during Ozonolysis

Permalink

<https://escholarship.org/uc/item/4rx0s9zk>

Journal

Environmental Science and Technology, 51(23)

ISSN

0013-936X

Authors

Heine, Nadja

Houle, Frances A

Wilson, Kevin R

Publication Date

2017-12-05

DOI

10.1021/acs.est.7b04197

Peer reviewed

1 **Connecting the Elementary Reaction Pathways of Criegee**
2 **Intermediates to the Chemical Erosion of Squalene**
3 **Interfaces during Ozonolysis**

4 Nadja Heine, Frances A. Houle,* and Kevin R. Wilson*

5 Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California

6 94720, United States

7 *E-mail: krwilson@lbl.gov, fahoule@lbl.gov

8 Criegee Intermediates (CI), formed in alkene ozonolysis, are central for controlling the multiphase
9 chemistry of organic molecules in both indoor and outdoor environments. Here we examine the
10 heterogeneous ozonolysis of squalene, a key species in indoor air chemistry. Aerosol mass
11 spectrometry is used to investigate how the ozone (O₃) concentration, relative humidity (RH) and
12 particle size control reaction rates and mechanisms. Although the reaction rate is found to be
13 independent of RH, the reaction products and particle size depend upon H₂O. Under dry conditions
14 (RH =3%) the reaction produces high molecular weight secondary ozonides (SOZ), which are
15 known skin irritants, and a modest change in particle size. Increasing the RH reduces the aerosol
16 size by 30%, while producing mainly volatile aldehyde products; increasing potential respiratory
17 exposure. Chemical kinetics simulations link the elementary reactions steps of CI to the observed
18 kinetics, product distributions and changes in particle size. The simulations reveal that ozonolysis
19 occurs near the surface, and is O₃ transport limited. The observed secondary ozonides are
20 consistent with the formation of mainly secondary CI, in contrast to gas phase ozonolysis
21 mechanisms.

22

23

24

25

26

27

28

29 Introduction

30 Accurately predicting molecular weight growth and decomposition of products formed
31 during the oxidation of organic material requires understanding how the reaction pathways of
32 transient intermediates such as free radicals or Criegee intermediates (CI) generate multiphase
33 reaction products. CI produced from the ozonolysis of terpenes build molecular weight by forming
34 condensable vapors and organic aerosol in the troposphere.^{1, 2} On indoor surfaces, thin films of
35 skin lipids (e.g. squalene, unsaturated acids) contain reactive C=C bonds that are oxidized by
36 ozone, producing both gas and condensed phase reaction products.³⁻⁶ Here we examine the
37 ozonolysis of liquid squalene aerosol in an effort to elucidate how CI reaction steps control product
38 formation on model indoor interfaces.

39 Understanding and improving indoor air quality is important,⁷ especially as people spend
40 a significant fraction of their daily life inside (over 90%).⁸ In contrast to the extensive research
41 devoted to the health effects of outdoor air pollution, significantly less is known about the impact
42 of indoor air quality. A prevalent indoor oxidant, ozone (O₃), readily reacts with unsaturated
43 organic molecules in the gas phase and on surfaces such as skin.^{4, 9} Reactions with O₃ can produce
44 harmful substances and increase the quantity of volatile organic compounds (VOC), with
45 associated impacts on the respiratory system. High indoor concentrations of VOCs are mainly the
46 consequence of large surface areas and diverse sources, such as cleaning products, cooking and
47 occupants, which are concentrated in small enclosures often with limited air exchange.^{10, 11}

48 Skin lipids on indoor surfaces are typically emitted via desquamation from skin and hair,
49 or from clothes³ at a rate of 30–90 mg of skin flakes/h.¹² Squalene (Sqe) represents one of the most
50 abundant unsaturated constituents of the human sebum ($\leq 12\%$).¹³ Its six double bonds make Sqe

51 highly reactive towards ozone. As a result, significant effort has been devoted to identifying the
52 volatile and semi-volatile oxidation products formed in Sqe ozonolysis (e.g. in chamber studies,⁵
53 an aircraft cabin,¹⁴ class rooms¹⁵ and office environments¹⁶). A study by Lakey *et al.* explored how
54 semi-volatile and low volatile reaction products diffuse through skin layers and enter the
55 bloodstream.¹⁷ In laboratory experiments, Zhou *et al.* quantified some of the condensed phase
56 products of Sqe ozonolysis and found evidence that the relative humidity (RH) played a large role
57 in the reaction mechanism.⁶ These studies clearly show that distribution of products remaining on
58 the skin versus those that are in the gas phase can vary greatly (along with potential health effects)
59 and will depend upon the changes in the indoor environment (RH, O₃ concentration [O₃], air
60 exchange rate, etc.).

61 The objective of this study is to develop a quantitative description of reactive uptake of
62 ozone onto Sqe gas-liquid interfaces. Here the squalene surface is in the form of an aerosol, such
63 as would occur from cooking with oil,¹⁸ rather than a film on an indoor surface (e.g. skin, window
64 or tabletop). Submicron particles are used to take full advantage of advanced aerosol mass
65 spectrometry and mobility sizing techniques to measure the real-time evolution of reactants and
66 products, enabling closer examination of how their formation connects to the chemical erosion of
67 the interface. Our objective is to use these measurements to develop a predictive, quantitative
68 kinetic model of the multiphase chemistry that in turn can be adapted to any sample configuration
69 (aerosol or monolayer). We focus on how the elementary reaction pathways of CI depend upon
70 relative humidity and ozone concentration, and how these pathways produce both gas and
71 condensed phase reaction products. Furthermore, we explore the origin of the large discrepancy in
72 reported uptake coefficients which range from 10⁻³ to 10⁻⁶ ^{6, 19-23}, and discuss impacts of the
73 reactions and conditions on indoor air quality and health.

74 Methods

75 **Experiment.** The heterogeneous reaction of ozone with Sqs is measured in an aerosol flowtube
76 reactor. Polydisperse Sqs particles with a log-normal size distribution with a mean surface-
77 weighted diameter of $\sim 250 \pm 40$ nm are generated from heated liquid Sqs ($T = 145^\circ\text{C}$) in a tube
78 furnace. Particles are entrained in a 300 sccm flow of N_2 and passed through an activated charcoal
79 denuder in order to remove gas phase components. For monodisperse measurements, the aerosol
80 flow is size-selected with a TSI Electrostatic Classifier (3080L). The aerosol flow is then mixed
81 with 10% O_2 , and variable amounts of dry and humidified N_2 (RH) as well as O_3 (0-4 ppm),
82 yielding a total flowrate of 1 lpm. The gas/particle mix is introduced into the flow reactor with a
83 residence time of 37 s.²⁴ Ozone is produced by a corona discharge generator and measured with
84 an ozone monitor (2B Technology 106-L). The flow exiting the reactor is analyzed by a second
85 TSI Electrostatic Classifier coupled with a butanol TSI Condensation Particle Counter (3772) and
86 a homebuilt vacuum ultraviolet aerosol mass spectrometer (VUV-AMS). For analysis of the
87 heterogeneous kinetics and product formation, the aerosol is thermally vaporized followed by
88 photoionization using 10.2 eV VUV radiation at the Chemical Dynamics Beamline (Advanced
89 Light Source, Berkeley CA.)²⁵ Using mass spectral intensities to determine reaction product
90 populations is difficult due to uncertainties in cross sections and ion fragmentation. Thus,
91 comparisons between model and measured reaction products are expected to capture only the
92 product kinetic evolution vs. ozone exposure and RH rather than absolute product abundance.

93 The main experimental observables are the reactive decay of squalene exposed to ozone as
94 a function of particle size and relative humidity, the formation kinetics of the major reaction
95 products, and changes in particle size. These form the data set against which the mechanistic model
96 description of the heterogeneous reaction, described below, is developed and evaluated.

97 **Simulation methodology.** Kinetic modeling of the experimental results is conducted using
98 Kinetiscope,²⁶ which uses stochastic algorithms to propagate sets of elementary reactions. As
99 described in previous publications on heterogeneous aerosol chemistry,²⁷⁻²⁹ the aerosol is
100 represented as a single instantaneously mixed volume, which is a valid assumption for reactions
101 on particles that are well-mixed relative to the heterogeneous gas-aerosol collision frequency.³⁰ To
102 properly account for surface to volume scaling when the aerosol volume changes dynamically
103 during the reaction, the aerosol is represented by a 1 nm x 1 nm x $R/3$ nm rectangular volume
104 where R is the measured experimental aerosol radius.²⁹ O_3 adsorption occurs only in a 1 nm thick
105 portion of the 1 nm² surface region, rather than throughout the entire volume of the aerosol. Within
106 this subvolume it is assumed that each Sqe molecule provides 1 adsorption site for gaseous O_3 ,
107 and this number of sites is held constant as the reaction proceeds. Because the single compartment
108 model used in this work involves surface reactions as well as bulk reactions, all reaction rates are
109 expressed in per unit volume form, since it is not possible to mix 2- and 3- dimensional kinetics
110 using the stochastic algorithm in its current form. Description of a surface reaction in terms of a
111 volume is not a drastic assumption for liquids and soft solids since the outer surfaces are diffuse.

112 **Construction of the reaction mechanism.** As will be detailed below, the model incorporates three
113 main processes: **1)** ozone adsorption, **2)** condensed phase reactions within the particle, and **3)**
114 evaporation of volatile reaction products.

115 **Ozone adsorption kinetics.** The pseudo-first order rate constant of ozone adsorption on the
116 aerosol surface is,

117
$$[O_3] \cdot Z \cdot S, \tag{1}$$

118 where $[O_3]$ is the average gas phase ozone concentration in the experiment, S is the sticking
119 coefficient, and Z is the ozone collision frequency, given by: $\sigma \cdot v$, with σ as collision cross section
120 ($1 \times 1 \text{ nm}^2$), and v the mean speed of ozone (390.29 m/s). A value of $S = 1.96 \cdot 10^{-4}$ was measured
121 previously for ozone sticking on submicron carbonaceous particles.³¹ To achieve model agreement
122 with the experimental data a slightly smaller value is needed ($1.8 \cdot 10^{-4}$), which appears reasonable
123 given our estimated error in previous experiments and the expected differences between sticking
124 on the squalene surface vs. a carbonaceous particle. This single value of S , originally obtained
125 using a single data set was found to accurately represent the global data set (i.e. squalene decay
126 kinetics vs. particle size). As discussed below, we evaluated the possibility that the ozonolysis
127 reaction occurs through the entire volume of the particle. In this case, the rate would not be
128 governed by the surface collision frequency but rather by the Henry's Law solubility of O_3 .

129 **Construction of the ozonolysis reaction scheme.** The ozonolysis mechanism of Sqe used for the
130 simulations was previously reported, and is shown schematically in Figure 1.^{6, 20, 32} The rate
131 constants are shown in Table 1. It is preferable to use condensed phase rate coefficients but
132 unfortunately for many reactions studied here they are not available. For the model gas-phase rate
133 constants are used as reasonable starting points since energy barriers for many reactions should be
134 similar in both phases. The mechanism has three main parts: 1) the formation of the primary
135 ozonide (POZ, **R1**), followed by 2) dissociation of the POZ into a ketone or aldehyde and CI (**R1**),
136 and 3) subsequent reactions of the CI (**R2-R6**).

137 Formation of the POZ is multigenerational, since a single squalene molecule (with six
138 double bonds) can undergo repeated **R1** reactions with O_3 . The POZ is transient, and the rate
139 coefficient is for a composite step that forms either a primary or a secondary CI. For simplicity,
140 we use the same rate coefficients for each generation in the reaction mechanism. We assume that

141 each double bond is equally reactive, and the literature rate coefficient for the overall reaction (e.g.
142 Sqe + O₃) is divided by the number of double bonds (the statistical factor) to obtain the rate
143 coefficient for each. This appears to be a reasonable approximation for this study, which is mainly
144 focused on the formation pathways of the first and second generation reaction products. Reactions
145 at each unique double bond location are tracked explicitly since the reaction products and the CI
146 that are formed in step **R1** depend upon where the reaction with ozone occurs. Additional model
147 details can be found in the Supporting Information (SI).

148 Once formed, the main reaction pathways of CI are: (**R2**) reaction with water to form
149 carbonyls, (**R3**) reaction with carbonyls to form secondary ozonides (SOZ), (**R4**) unimolecular
150 rearrangement, and (**R6**) reaction with ozone to form a carbonyl.

151 As seen in the experiments described below, water plays a central role both in the specific
152 products that remain in the particle and those that are released to the gas phase (inferred via mass
153 loss from the aerosol). **R2** and **R3** are competitive sinks for the CI, depending directly and
154 indirectly on water, and producing the observed carbonyl and SOZ products. The rate coefficient
155 used for **R2** is taken from a previous gas phase measurement of CI + H₂O.³³ **R2** is assumed to
156 occur in the bulk of the aerosol so its overall rate is also governed by RH in the reaction and by
157 the Henrys law constant for H₂O in an organic solvent (Table 1).

158 To our knowledge, the only coefficients for **R3** (k_{CO}) are for the simplest gas phase CI
159 (formaldehyde oxide) reacting with either acetone ($k_{CO}=2.3\pm0.3\cdot10^{-13}$ cm³ molec.⁻¹ s⁻¹) or
160 acetaldehyde ($k_{CO}=9.5\pm0.7\cdot10^{-13}$ cm³ molec.⁻¹ s⁻¹).³⁴ Unfortunately, these gas phase CI + carbonyl
161 rate coefficients produced simulation results that are not in agreement with observations,
162 suggesting that entropic factors are significant. Specifically, **R3** (i.e. CI + carbonyl) was predicted

163 to be the dominant sink for the CI, producing large quantities of SOZ at RH = 60% and substantial
164 aerosol growth under dry conditions. Neither is consistent with experimental measurement of the
165 products and aerosol size. Therefore, we treated k_{CO} as the only adjustable parameter in the model.
166 An estimate for it was made by varying k_{CO} until the RH dependence of the carbonyl and SOZ
167 product concentrations could be reasonably reproduced. k_{CO} was optimized at
168 $1.33 \cdot 10^{-18} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ for species that form and immediately react within the same solvent
169 cage, and $6.7 \cdot 10^{-19} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$ for all other combinations. That these values are so small
170 relative to the gas phase is not surprising since the cage effect on recombination rate coefficients
171 is well known. The factor of ~ 2 difference between the intra-cage and extra-cage reaction
172 coefficients has been observed in other systems. For example the recombination rate coefficient of
173 newly formed acetyl peroxide radicals in octadecane is approximately double the value obtained
174 when one of the radical species leaves the solvent cage and reacts later.³⁵

175 The rate constant for CI + O₃ (**R6**) is taken from Veerecken *et al.* and is based on coupled
176 cluster calculations in combination with theoretical kinetic predictions of the rate coefficients.³⁶

177 The unimolecular reactions of the CI include isomerization to acids (**R4a**) or α -
178 hydroxyketones (**R4b**), and 1,4 H-shifts (**R5**). The rate coefficient for isomerization (**R4**) is
179 assumed to be equal to that for the decomposition of CIs in the gas phase. In the gas phase, an
180 excited acid intermediate forms and rapidly eliminates CO₂, forming a new C=C bond that can
181 react further with O₃. In the condensed phase, however, this intermediate is collisionally stabilized
182 to form an acid product. Literature values for CI isomerization range from 1.5 to 305 s⁻¹.^{37, 38} Here,
183 5 s⁻¹ is used for the simulations. A sensitivity test (Figure S1) shows that this isomerization rate is
184 too slow to be kinetically competitive with the bimolecular reaction **R2** when the RH is elevated.
185 The hydride shift reaction **R5** has been observed in the gas phase^{37, 39} and its importance in the

186 condensed phase reactions is uncertain as will be discussed below in the context of the
187 experimentally observed reaction products.

188

189 **Evaporation.** Evaporation is considered to be an irreversible desorption step from the surface of
190 the particle. Repartitioning of gas phase products that have undergone further reaction are
191 neglected, since C=C bond scission favored under wet conditions will form products that remain
192 in the gas phase. Evaporation rate constants, k_{evap} , were calculated using the formulation reported
193 in Wiegel *et al.*^{27,40} (see also Equation (2) in the SI), and depend upon the geometry of the particle
194 and the saturation vapor pressure (p_{sat}) of the corresponding species.⁴¹ If available, measured vapor
195 pressures are used. If they are not, p_{sat} are computed (see Table S1) using group contribution
196 methods (i.e. EVAPORATION),⁴² and are reasonably consistent with previous estimates
197 employing a different software package.¹⁷ Uncertainties in the estimated vapor pressures are
198 evaluated as shown in Figure S2. The aerosol volume is obtained from the simulation compartment
199 volume, which is calculated from the instantaneous populations and densities of all condensed
200 phase species. As species evaporate from the aerosol, the volume dynamically decreases, leading
201 to increases in concentrations and reaction rates. An increase or decrease of k_{evap} by a factor of 10
202 has a negligible effect on the predicted reaction kinetics and volume change of the particle.

203 Results and Discussion

204 In this section we examine the experimental and simulated decay of Sqe to elucidate where the
205 reaction occurs (heterogeneous vs. bulk) and whether ozone uptake is transport or reaction limited.
206 We identify the major reaction products, their kinetic evolution and RH dependence. This provides
207 the basis for understanding which key reaction pathways are active and why. Finally, we discuss
208 implications of the results for indoor air chemistry.

209 **Heterogeneous kinetics of squalene ozonolysis.** Shown in Figure 2a is the measured decay of
210 Sqe as a function of ozone exposure and RH, determined using the parent molecular ion (at m/z
211 =410) in the aerosol mass spectrum (Figure 3) as a function of ozone exposure. The observed
212 decays are nearly exponential and independent of RH. Also shown in Figure 2a is the simulated
213 decay of Sqe at all four RHs, which agree with experiment and depend only on the average ozone
214 concentration of the particular experiment. Although recent work has shown compelling evidence
215 that O_3 reacts within the first 1-2 nm of a squalene surface,¹⁹ we have nevertheless considered two
216 different simulation scenarios to examine the (i) surface vs (ii) bulk reactivity of O_3 .

217 As described earlier, two elementary steps are used to describe the reaction of O_3 with Sqe.
218 In the simulation, ozone first adsorbs to the squalene surface (described by Equation (1)) after
219 which it reacts with Sqe (**R1**, Figure 1). There are two previously reported values for the rate
220 coefficient for the Sqe + O_3 reaction that differ by a factor of 100: one for Sqe + O_3 in a dilute
221 solution of chloroform ($1.25 \cdot 10^{-15} \text{ cm}^3 \text{ s}^{-1}$)⁴³ and the other is estimated from O_3 transmission
222 measurements through a thin squalene coating ($1.21 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$).¹⁹ To determine which is
223 correct, we have compared experimental values for the phenomenological rate coefficients (k_{obs})
224 calculated from an exponential fit of the measured decay of Sqe (as a function of aerosol size) to
225 those for simulated decays as shown in Figure 2c at RH=3%. The model used a Sqe + O_3 rate
226 coefficient of $1.25 \cdot 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (k_1 , Scenario 1) or $1.21 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (k_2 , Scenario 2). For both
227 simulation and experiment the aerosol size ranged from 71 to 530 nm. For diameters between 200
228 and 500 nm both model Scenarios predict nearly identical results, despite the factor of 100
229 difference in Sqe + O_3 rate coefficient. It is only for experiments on smaller particles that a
230 difference between Scenario 1 and 2 appears, indicating that neither Scenario completely
231 reproduces the entire data set. It is interesting to note that although there is an increase at smaller

232 sizes, k_{obs} does not strictly follow the inverse radius scaling expected for a reaction localized at the
233 surface, suggesting a more complex relationship. It appears that the observed decay of squalene is
234 not simply controlled by the Sqe + O₃ rate coefficient but rather that it is the adsorption rate of O₃
235 on the surface that is limiting (i.e. gas phase transport limited).

236 We examined the possibility that the O₃ + Sqe reaction occurs within the volume of the
237 aerosol rather than at its surface. In this case [O₃] would be governed by its Henry's law constant
238 rather than a transient surface population. Details of this kinetic description are given in the SI.
239 Figure 2b compares the experimental Sqe decay with the simulated surface and bulk reaction
240 predictions. Both bulk Scenarios predict a much slower consumption rate of Sqe than is observed
241 by experiment or in the surface Scenarios. This result further confirms the previously determined
242 short reactive-diffusive lengths (~1 nm) of ozone in Sqe.¹⁹

243

244 **Reaction products.** Reaction products are formed according to the mechanism in Figure 1. The
245 exact distribution of products is governed by the location (i.e., which C=C bond) of the initial
246 ozone attack. Squalene has six double bonds, and because of symmetry there are only three unique
247 reactive sites for the formation and decomposition of the POZ. If the POZ decomposes into a
248 primary CI (p-CI, **R1** Figure 1) then its co-product will be a ketone. Thus there are three unique
249 p-CI that could form with carbon lengths of C₂₇, C₂₂ and C₁₇ as shown in Figure S3. The ketone
250 coproducts of these CI have corresponding carbon numbers of C₃ (acetone), C₈ and C₁₃,
251 respectively. Alternatively, the POZ could form a secondary CI (s-CI) and an aldehyde. In this
252 case, reaction at the three double bonds will produce smaller s-CI with carbon lengths of C₃, C₈
253 and C₁₃. The aldehyde co-products have corresponding carbon numbers of C₂₇, C₂₂, and C₁₇,
254 respectively (see Figure S4). Thus, the chemistry of squalene will be controlled in large part by

255 how the POZ decomposes to form p- and/or s-CI, with the corresponding small carbon number
256 ketones and/or larger molecular weight aldehydes.

257 Figure 3 shows aerosol mass spectra (MS) of the ozonolysis products as function of RH.
258 These spectra are all recorded after approximately 50% of the S_qe in the aerosol has been
259 consumed. Peaks corresponding to pure squalene have been removed by subtracting the unreacted
260 squalene mass spectrum. Analysis of the lower mass range ($m/z < 150$) in Figure 3 is challenging,
261 since it is difficult to distinguish small molecular weight reaction products from fragment ions
262 produced by dissociative photoionization of larger species. Products in this mass region will most
263 likely evaporate from the aerosol, and thus be underrepresented. Thus, we focus on explaining the
264 kinetics of the main SOZ and aldehyde products.

265 The product distribution is a sensitive function of relative humidity as expected from the
266 mechanism in Figure 1. The spectrum recorded at the lowest humidity (3% RH, Figure 3a) shows
267 a series of peaks at masses larger than unreacted squalene ($m/z = 410$), which can be easily assigned
268 to SOZs. The highest intensity SOZ appears at $m/z = 458$ and is assigned to the C₃₀ SOZ. The other
269 SOZ's are observed at $m/z = 322.25$, 390.31 , 526.43 and 594.50 and are assigned to C₂₀, C₂₅, C₃₅
270 and C₄₀ SOZ's, respectively.

271 The observed pattern of SOZ's (C₂₀, C₂₅, C₃₀, C₃₅, C₄₀) reveals key details about the reaction
272 mechanism. Most of the C₃₀ SOZ likely forms inside a solvent cage by the reaction of a CI with its
273 coproduct carbonyl; both originating from a common POZ. This reaction requires a simple
274 molecular rotation of the CI relative to the carbonyl co-product. If the CI and its carbonyl co-
275 product escape the solvent cage before reacting, then a much larger array of possible SOZ's can
276 form. As shown in Figure S5 and Table S2, there are 15 possible SOZ's that could form from all
277 of the potential reactive combinations of p- and s-CI with ketones and aldehydes. These are C₆,

278 C₁₁, C₁₆, C₂₀, C₂₁, C₂₅, C₂₆, C₃₀, C₃₄, C₃₅, C₃₉, C₄₀, C₄₄, C₄₉, and C₅₄. Only a small subset of these
279 SOZ possibilities are observed in the experiment; C₂₀, C₂₅, C₃₀, C₃₅, and C₄₀. This can only be
280 explained if the POZ that is formed decomposes exclusively into either a p-CI and a ketone or a s-
281 CI and an aldehyde as shown in Figure S6 and Table S2. Analysis of the changes in aerosol volume
282 indicate that Sqe ozonolysis forms mainly s-CI and aldehydes as will be demonstrated below.

283 As the relative humidity increases, the SOZ products decrease, vanishing completely at RH
284 = 60%. Since SOZ's (**R3**, Figure 1) are formed by the reaction of the CI with a carbonyl, this
285 indicates that formation of a CI dominates, and the observed trend in yield of the SOZ's with RH
286 is controlled by the competing loss reaction of CI with water (i.e. **R2**).

287 There are three other main product peaks at masses less than Sqe. These peaks correspond
288 to C₁₇-trienal (*m/z* 248.2), C₂₂-tetraenal (*m/z* 316.3), and C₂₇-pentaenal (*m/z* 384.3). These carbonyl
289 species appear under dry conditions, and increasing the RH doubles their intensity. This can be
290 explained qualitatively as being due to the CI + H₂O reaction that inhibits SOZ formation.

291 Carboxylic acids might be formed by the isomerization of p-CIs (**R4a**) with carbon
292 numbers of 17 (*m/z*= 264.4), 22 (*m/z*= 332.5), and 27 (*m/z*= 400.6). There are peaks in the mass
293 spectra consistent with these products, although at very low intensity. As found in previous studies,
294 these peaks decrease with increasing RH.⁶ The C₄ species levulinic and succinic acid, formed from
295 sequential reactions of Sqe with ozone, were recently identified as main products in a monolayer
296 study.⁶ These products cannot be definitively observed here; if present the peaks are small and
297 appear in a congested region of the mass spectrum. The lack of strong carboxylic acid signals is
298 consistent with product trends with RH that suggest only s-CI is formed in significant quantities.
299 It should be noted, however, that the differences in measured acid concentration between this and
300 previous studies may originate from the different ionization sources used, since DART mass

301 spectrometry, employed by Zhou *et al.*⁶, is known to have very high ionization sensitivity towards
302 acids.

303 Typical products from OH reactions, such as alcohols,⁴⁴ are not observed. This suggests
304 that under our reaction conditions OH formation from the 1,4 H-shift, observed in the gas phase,
305 is a minor pathway, and therefore is not included in the simulations. However, it may be important
306 under typical indoor air conditions where chemistry can occur over longer timescales and at lower
307 [O₃], which can alter the relative importance of unimolecular vs. bimolecular pathways.

308 While the reactive decay of Sqe is observed to be independent of RH (Figure 2a), the SOZ,
309 C₂₇ aldehyde products and aerosol diameter exhibit a substantial dependence on water (Figure 4).
310 At low RH (3%) there is a minimal loss of mass from the aerosol, resulting in shrinking of its
311 diameter by 5%. As the RH is increased to 60% the diameter is observed to decrease by ~30%,
312 indicating the formation of substantial quantities of gas phase reaction products. This decrease in
313 aerosol diameter with RH is accompanied by similar decreases in the quantity of the particle phase
314 C₃₀ SOZ and C₂₇ aldehyde products. When RH increases from 3 to 60%, the aldehyde increases
315 by about 3x. The C₃₀ SOZ exhibits the opposite behavior, a ~3x reduction in intensity occurs on
316 going from RH = 3% to 60%. Together these observations show that there are substantial changes
317 in the multiphase ozonolysis products of squalene driven mainly by the water content in the reactor.
318 Lower molecular weight carbonyls form under wet conditions and the higher mass forms SOZ
319 under dry conditions.

320 Simulation results are compared to experiment in Figure 4. Overall, the agreement for C₂₇
321 formation and decay and particle size changes in Figures 4a and 4b is reasonable. The model
322 predicted intensities of 30% SOZ and 70% carbonyls at 30% RH (Figure S7) are reasonable within
323 experimental uncertainty, compared to recent velocity map imaging experiments, which measured

324 values of 15% and 85%, respectively.²⁰ It is clear from Figure 4c, however, that the simulation
325 does not predict the relative humidity dependence of C₃₀ SOZ formation above an RH of 3%,
326 indicating that the mechanism is incomplete.

327 Several previous studies have examined the lifetime of Sqe in the presence of O₃ under a
328 variety of conditions.^{6, 19, 20, 22, 23, 32} These studies report a wide range of uptake coefficients, that
329 depend on experimental conditions (e.g. RH, concentration and phase state of Sqe, etc.). In light
330 of our results, measured uptake coefficients are an aggregate of two elementary steps (adsorption
331 and reaction). The adsorption rate is controlled by site concentration, collision frequency and
332 sticking probability. The adsorption site density will vary from experiment to experiment
333 depending on, for example, whether bulk liquid, dispersed droplets on a support, or a thin uniform
334 film is used. Thus one could imagine determining uptake coefficients in two very different kinetic
335 regimes where: 1) O₃ adsorption *is not* the limiting step, i.e. the reaction is relatively slow, and 2)
336 where O₃ adsorption *is* limiting due to low [O₃] or adsorption sites or both. The applicable kinetic
337 regime for the experiment will determine the overall consumption rate of Sqe and hence the uptake
338 coefficient. Furthermore, the substantial change in aerosol size under wet conditions can
339 complicate the determination of uptake coefficients, which scale as the inverse square of the
340 diameter.

341 **Branching Ratio Primary vs. Secondary CI.** As described above, the pattern of SOZ's
342 observed in the experiment is consistent with forming mainly p-CI or s-CI rather than the gas phase
343 POZ decomposition branching ratio (BR) of p-CI:s-CI = 53.5:46.5.⁴⁵ Using this gas phase
344 branching ratio would produce a much larger array of possible SOZ as shown in Table S2 and
345 Figure S5. For example, equal quantities of p- and s-CI should produce significant numbers of C₂₁,
346 C₃₉, C₄₄, C₄₉, and C₅₄ SOZ products (see Table S2), which are not observed in the experiment.

347 Based on these experimental findings we performed simulations to test sensitivities to two
348 different BRs for p- and s-CI formation (Figure 5). The solid lines are for a BR of p-CI:s-CI =
349 10:90, which provides the best description of the experimental results. The dashed lines are for a
350 BR of p-CI:s-CI = 50:50. It is clear that there is too much mass loss from the aerosol when p- and
351 s-CI are formed with equal probability. In addition the aerosol size exhibits only a very weak RH
352 dependence with the 50:50 assumption, which is inconsistent with observation. *Why* the selectivity
353 in condensed phase is so different from that found in the gas phase is not clear; this finding would
354 benefit from further theoretical and experimental investigations.

355 The enhanced mass loss from the aerosol predicted when significant quantities of p-CI are
356 formed is due to the evaporation of the small ketone (C₃, C₈, C₁₃) co-product. Since this step doesn't
357 involve water, rapid chemical erosion via p-CI formation would be predicted even under dry
358 conditions. Although the reaction of the p-CI with water (**R2**) will form the observed C₂₇, C₂₂,
359 and C₁₇ aldehydes, these species do not exhibit the sensitivity to RH that is observed in the
360 experiment (Figure 5b). Thus the weak RH dependence observed in the 50:50 scenario originates
361 solely from reactions involving s-CI.

362 The simulations that are most consistent with experiment indicate that s-CI are formed at
363 least 10 times faster than p-CI. This means that the most important CI's for squalene ozonolysis
364 have small carbon numbers: C₃, C₈, and C₁₃. According to **R1**, the corresponding coproducts of
365 these s-CI are the C₂₇, C₂₂, and C₁₇ aldehydes. These are the main aldehydes observed in the
366 experiment and they are present even under dry conditions since they originate directly from the
367 POZ decomposition. As the RH is raised, the reaction rate of C₃, C₈, and C₁₃ s-CI with water (**R2**)
368 increases, forming the C₃, C₈, and C₁₃ ketones, which are volatile and evaporate from the aerosol.
369 This explains the experimental observation that chemical erosion of the aerosol depends upon

370 water. This scenario also accounts for the changes in product distribution as a function of RH. At
371 low RH, the C₃, C₈, and C₁₃ s-CI mainly react with C₂₇, C₂₂, and C₁₇ aldehydes to form the observed
372 distribution of C₂₀, C₂₅, C₃₀, C₃₅, C₄₀ SOZ. At low RH, reaction with s-CI is the main sink for these
373 aldehydes (i.e. via **R3**). As the RH is raised the s-CI no longer react only with the C₂₇, C₂₂, and C₁₇
374 aldehydes but rather increasingly react with water (**R2**), which explains why the experimental
375 observed product distributions shift from SOZ to aldehydes as the availability of water increases.

376 In summary, using the rate coefficients and branching ratios for p-CI:s-CI described above,
377 the simulation can reproduce most of the experimental data. However, the loss of SOZ with
378 increasing RH remains under-predicted. This suggests that there are missing sink reaction
379 pathways for the SOZ not currently captured by **R1-R6**. We measured the hydrolysis rate of the
380 SOZ's, and detected little if any reaction over time scale of the experiment (37s) (see Figure S8).
381 Additional possibilities for the difference between simulated and experimental SOZ concentrations
382 vs O₃ exposure include: 1) SOZ reactions with H₂O₂ formed in **R2** 2) other radical forming
383 unimolecular decomposition pathways of SOZ⁴⁶ and 3) CI reactions with acids, which would
384 indirectly control the quantity of SOZ formed. To improve the agreement between the experiment
385 and the model, further work is needed to better understand the transformation chemistry of SOZ
386 particularly under conditions that replicate indoor environments.

387 **Implications for indoor air quality.** In an indoor environment S_qe, which is one of the main
388 organic contaminants present, has shown to be a major ozone sink and one of the main ozone
389 scavengers on human surfaces.⁵ The oxidation products influence air quality and occupant health,
390 as they can act as skin and/or respiratory irritants. Gaining better mechanistic insight is therefore
391 crucial for improving indoor air quality. Our study seeks to develop a detailed molecular-level
392 understanding of the mechanistic pathways of the CI and their sensitivity to reaction conditions.

393 We found that the decomposition of the POZ predominantly leads to the formation of small
394 secondary CI, which furthermore form ketones or isomerize to α -hydroxy ketones. α -hydroxy
395 ketones have been found in indoor measurements of gas phase species to be among the major
396 volatile primary products.⁵ In a second generation ozonolysis step they can form dicarbonyl
397 compounds, which are respiratory irritants⁴⁷ and may cause DNA damage.⁴⁸

398 The formation of ketones is enhanced with increasing relative humidity and results in
399 chemical erosion of the Sqe aerosol or surface. Under dry conditions the lifetime of a CI is about
400 7 s (Figure S9), whereas in the presence of water, CI instantly reacts to form reaction products
401 with high volatility. Given the high concentration of Sqe, its ozonolysis products may make up a
402 dominant part of indoor VOCs, particularly under humid conditions. If these are formed on the
403 body envelope, the concentration of potentially harmful VOCs is increased by 1.2 to 2.5 times in
404 our breathing zone compared to room levels.⁵

405 Our finding that the reaction of ozone occurs rapidly on the aerosol surface and therefore
406 is transport limited may explain the wide range of reported uptake coefficients. Understanding
407 how the ozone uptake to Sqe surfaces depends on varying conditions is particularly vital for
408 improving comprehensive indoor air models, and predicting the proportions of gas phase and
409 surface-bound products that may impact occupant health.

410 **Supporting Information.** The Supporting Information is available free of charge on the ACS
411 Publications website at DOI:

412 Ozone adsorption kinetics; evaporation description; Mass, compound names, density and
413 saturation vapor pressures of all modeled compounds; Model sensitivity tests for
414 isomerization and evaporation; Bulk reaction model scenario; Primary CI and
415 corresponding ketones; Secondary CI and corresponding aldehydes; SOZ formation

416 patterns; Total SOZ and Carbonyls; SOZ intensity under dry and humid conditions;
417 Lifetime of CI.

418 **Acknowledgments.**

419 This work is supported by the Department of Energy, Office of Science, Office of Basic Energy
420 Sciences, Chemical Sciences, Geosciences, and Biosciences Division, in the Gas Phase Chemical
421 Physics Program under Contract No. DE-AC02-05CH11231. This research used the Advanced
422 Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-
423 05CH11231. N.H. thanks the Alexander-von-Humboldt Foundation for a post-doctoral research
424 fellowship. The authors thank Michael Jacobs (Lawrence Berkeley National Laboratory and UC
425 Berkeley Department of Chemistry) for conducting the secondary ozonide hydrolysis
426 measurements.

427

428 **Corresponding Authors**

429 Kevin R. Wilson, 510-495-2474, krwilson@lbl.gov

430 Frances A. Houle, 510-495-8135, fahoule@lbl.gov

431 **Reference**

- 432 1. Donahue, N. M.; Tischuk, J. E.; Marquis, B. J.; Huff Hartz, K. E., Secondary organic
433 aerosol from limona ketone: insights into terpene ozonolysis via synthesis of key intermediates.
434 *PCCP* **2007**, *9* (23), 2991.
- 435 2. Presto, A. A.; Huff Hartz, K. E.; Donahue, N. M., Secondary Organic Aerosol Production
436 from Terpene Ozonolysis. 1. Effect of UV Radiation. *Environ. Sci. Technol.* **2005**, *39* (18), 7036.
- 437 3. Weschler, C. J., Roles of the human occupant in indoor chemistry. *Indoor Air* **2016**, *26* (1),
438 6.
- 439 4. Weschler, C. J., Ozone in Indoor Environments: Concentration and Chemistry. *Indoor Air*
440 **2000**, *10* (4), 269.
- 441 5. Wisthaler, A.; Weschler, C. J., Reactions of ozone with human skin lipids: sources of
442 carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air. *Proc. Natl. Acad. Sci. U. S. A.* **2010**,
443 *107* (15), 6568.
- 444 6. Zhou, S.; Forbes, M. W.; Abbatt, J. P. D., Kinetics and Products from Heterogeneous
445 Oxidation of Squalene with Ozone. *Environ. Sci. Technol.* **2016**, *50* (21), 11688.

- 446 7. Morrison, G., Recent Advances in Indoor Chemistry. *Current Sustainable/Renewable*
447 *Energy Reports* **2015**, 2 (2), 33.
- 448 8. Klepeis, N. E.; Nelson, W. C.; Ott, W. R.; Robinson, J. P.; Tsang, A. M.; Switzer, P.; Behar,
449 J. V.; Hern, S. C.; Engelmann, W. H., The National Human Activity Pattern Survey (NHAPS): a
450 resource for assessing exposure to environmental pollutants. *J. Expo. Anal. Environ. Epidemiol.*
451 **2001**, 11 (3), 231.
- 452 9. Weschler, C. J.; Shields, H. C., Potential reactions among indoor pollutants. *Atmos.*
453 *Environ.* **1997**, 31 (21), 3487.
- 454 10. Gómez Alvarez, E.; Amedro, D.; Afif, C.; Gligorovski, S.; Schoemaeker, C.; Fittschen,
455 C.; Doussin, J.-F.; Wortham, H., Unexpectedly high indoor hydroxyl radical concentrations
456 associated with nitrous acid. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, 110 (33), 13294.
- 457 11. Weschler, C. J.; Shields, H. C., Production of the Hydroxyl Radical in Indoor Air. *Environ.*
458 *Sci. Technol.* **1996**, 30 (11), 3250.
- 459 12. Milstone, L. M., Epidermal desquamation. *J. Dermatol. Sci.* **2004**, 36 (3), 131.
- 460 13. Picardo, M.; Ottaviani, M.; Camera, E.; Mastrofrancesco, A., Sebaceous gland lipids.
461 *Dermato-endocrinology* **2009**, 1 (2), 68.
- 462 14. Coleman, B. K.; Destailats, H.; Hodgson, A. T.; Nazaroff, W. W., Ozone consumption
463 and volatile byproduct formation from surface reactions with aircraft cabin materials and clothing
464 fabrics. *Atmos. Environ.* **2008**, 42 (4), 642.
- 465 15. Liu, S.; Thompson, S. L.; Stark, H.; Ziemann, P. J.; Jimenez, J. L., Gas-Phase Carboxylic
466 Acids in a University Classroom: Abundance, Variability, and Sources. *Environ. Sci. Technol.*
467 **2017**, 51 (10), 5454.
- 468 16. Fadeyi, M. O.; Weschler, C. J.; Tham, K. W.; Wu, W. Y.; Sultan, Z. M., Impact of human
469 presence on secondary organic aerosols derived from ozone-initiated chemistry in a simulated
470 office environment. *Environ. Sci. Technol.* **2013**, 47 (8), 3933.
- 471 17. Lakey, P. S. J.; Wisthaler, A.; Berkemeier, T.; Mikoviny, T.; Pöschl, U.; Shiraiwa, M.,
472 Chemical kinetics of multiphase reactions between ozone and human skin lipids: Implications for
473 indoor air quality and health effects. *Indoor Air* **2016**, 27 (4), 816.
- 474 18. Kalogeropoulos, N.; Andrikopoulos, N. K., Squalene in oils and fats from domestic and
475 commercial fryings of potatoes. *Int. J. Food Sci. Nutr.* **2004**, 55 (2), 125.
- 476 19. Lee, L.; Wilson, K., The Reactive–Diffusive Length of OH and Ozone in Model Organic
477 Aerosols. *J. Phys. Chem. A* **2016**, 120 (34), 6800.
- 478 20. Jacobs, M. I.; Xu, B.; Kostko, O.; Heine, N.; Ahmed, M.; Wilson, K. R., Probing the
479 Heterogeneous Ozonolysis of Squalene Nanoparticles by Photoemission. *J. Phys. Chem. A* **2016**,
480 120 (43), 8645.
- 481 21. Petrick, L.; Dubowski, Y., Heterogeneous oxidation of squalene film by ozone under
482 various indoor conditions. *Indoor Air* **2009**, 19 (5), 381.
- 483 22. Wells, J.; Morrison, G.; Coleman, B., Kinetics and Reaction Products of Ozone and
484 Surface-Bound Squalene. *J. ASTM Int.* **2008**, 5 (7), 12.
- 485 23. Fu, D.; Leng, C.; Kelley, J.; Zeng, G.; Zhang, Y.; Liu, Y., ATR-IR study of ozone initiated
486 heterogeneous oxidation of squalene in an indoor environment. *Environ. Sci. Technol.* **2013**, 47
487 (18), 10611.
- 488 24. Smith, J. D.; Kroll, J. H.; Cappa, C. D.; Che, D. L.; Liu, C. L.; Ahmed, M.; Leone, S. R.;
489 Worsnop, D. R.; Wilson, K. R., The heterogeneous reaction of hydroxyl radicals with sub-micron
490 squalane particles: a model system for understanding the oxidative aging of ambient aerosols.
491 *Atmos. Chem. Phys.* **2009**, 9 (9), 3209.

- 492 25. Gloaguen, E.; Mysak, E. R.; Leone, S. R.; Ahmed, M.; Wilson, K. R., Investigating the
493 chemical composition of mixed organic–inorganic particles by “soft” vacuum ultraviolet
494 photoionization: The reaction of ozone with anthracene on sodium chloride particles. *Int. J. Mass*
495 *spectrom.* **2006**, *258* (1–3), 74.
- 496 26. Hinsberg, W. D., Houle, F. A. Kinetiscope a stochastic kinetics simulator. Available under
497 a no-cost license from www.hinsberg.net/kinetiscope.
- 498 27. Wiegel, A. A.; Wilson, K. R.; Hinsberg, W. D.; Houle, F. A., Stochastic methods for
499 aerosol chemistry: a compact molecular description of functionalization and fragmentation in the
500 heterogeneous oxidation of squalane aerosol by OH radicals. *Phys. Chem. Chem. Phys.* **2015**, *17*
501 (6), 4398.
- 502 28. Richards-Henderson, N. K.; Goldstein, A. H.; Wilson, K. R., Sulfur Dioxide Accelerates
503 the Heterogeneous Oxidation Rate of Organic Aerosol by Hydroxyl Radicals. *Environ. Sci.*
504 *Technol.* **2016**, *50* (7), 3554.
- 505 29. Liu, M. J.; Wiegel, A. A.; Wilson, K. R.; Houle, F. A., Aerosol Fragmentation Driven by
506 Coupling of Acid-Base and Free Radical Chemistry in the Heterogeneous Oxidation of Aqueous
507 Citric Acid by OH Radicals. *J. Phys. Chem. A* **2017**, *121* (31), 5856.
- 508 30. Houle, F. A.; Hinsberg, W. D.; Wilson, K. R., Oxidation of a model alkane aerosol by OH
509 radical: the emergent nature of reactive uptake. *PCCP* **2015**, *17* (6), 4412.
- 510 31. Fendel, W.; Matter, D.; Burtscher, H.; Schmidt-Ott, A., Interaction between carbon or iron
511 aerosol particles and ozone. *Atmos. Environ.* **1995**, *29* (9), 967.
- 512 32. Petrick, L.; Dubowski, Y., Heterogeneous oxidation of squalene film by ozone under
513 various indoor conditions. *Indoor Air* **2009**, *19* (5), 381.
- 514 33. Taatjes, C. A.; Welz, O.; Eskola, A. J.; Savee, J. D.; Scheer, A. M.; Shallcross, D. E.;
515 Rotavera, B.; Lee, E. P. F.; Dyke, J. M.; Mok, D. K. W.; Osborn, D. L.; Percival, C. J., Direct
516 Measurements of Conformer-Dependent Reactivity of the Criegee Intermediate CH₃CHOO.
517 *Science* **2013**, *340* (6129), 177.
- 518 34. Taatjes, C. A.; Welz, O.; Eskola, A. J.; Savee, J. D.; Osborn, D. L.; Lee, E. P. F.; Dyke, J.
519 M.; Mok, D. W. K.; Shallcross, D. E.; Percival, C. J., Direct measurement of Criegee intermediate
520 (CH₂OO) reactions with acetone, acetaldehyde, and hexafluoroacetone. *PCCP* **2012**, *14* (30),
521 10391.
- 522 35. Pryor, W. A.; Smith, K., Reactions of Radicals. 25. Viscosity Dependence on Bond
523 Homolysis - A Qualitative and Semiquantitative Test for Cage Return. *J. Am. Chem. Soc.* **1970**, *92*
524 (18), 5403.
- 525 36. Vereecken, L.; Harder, H.; Novelli, A., The reactions of Criegee intermediates with
526 alkenes, ozone, and carbonyl oxides. *PCCP* **2014**, *16* (9), 4039.
- 527 37. Berndt, T.; Jokinen, T.; Mauldin, R. L.; Petäjä, T.; Herrmann, H.; Junninen, H.; Paasonen,
528 P.; Worsnop, D. R.; Sipilä, M., Gas-Phase Ozonolysis of Selected Olefins: The Yield of Stabilized
529 Criegee Intermediate and the Reactivity toward SO₂. *J. Phys. Chem. Lett.* **2012**, *3* (19), 2892.
- 530 38. Chhantyal-Pun, R.; Welz, O.; Savee, J. D.; Eskola, A. J.; Lee, E. P. F.; Blacker, L.; Hill,
531 H. R.; Ashcroft, M.; Khan, M. A. H.; Lloyd-Jones, G. C.; Evans, L.; Rotavera, B.; Huang, H.;
532 Osborn, D. L.; Mok, D. K. W.; Dyke, J. M.; Shallcross, D. E.; Percival, C. J.; Orr-Ewing, A. J.;
533 Taatjes, C. A., Direct Measurements of Unimolecular and Bimolecular Reaction Kinetics of the
534 Criegee Intermediate (CH₃)₂COO. *J. Phys. Chem. A* **2017**, *121* (1), 4.
- 535 39. Kurtén, T.; Rissanen, M. P.; Mackeprang, K.; Thornton, J. A.; Hyttinen, N.; Jørgensen, S.;
536 Ehn, M.; Kjaergaard, H. G., Computational Study of Hydrogen Shifts and Ring-Opening
537 Mechanisms in α -Pinene Ozonolysis Products. *J. Phys. Chem. A* **2015**, *119* (46), 11366.

- 538 40. Wiegel, A. A.; Liu, M. J.; Hinsberg, W. D.; Wilson, K. R.; Houle, F. A., Diffusive
539 confinement of free radical intermediates in the OH radical oxidation of semisolid aerosols. *PCCP*
540 **2017**, *19* (9), 6814.
- 541 41. Rembaum, A.; Szwarc, M., O-O Bond Dissociation Energies in Propionyl and Butyryl
542 Peroxides. *J. Chem. Phys.* **1955**, *23* (5), 909.
- 543 42. Compernelle, S.; Ceulemans, K.; Müller, J. F., EVAPORATION: a new vapour pressure
544 estimation method for organic molecules including non-additivity and intramolecular interactions.
545 *Atmos. Chem. Phys.* **2011**, *11* (18), 9431.
- 546 43. Razumovskii, S. D.; Lisitsyn, D. M., Reactions of ozone with double bonds in polymer and
547 biosystem chemistry. *Polymer Science Series A* **2008**, *50* (12), 1187.
- 548 44. Nah, T.; Zhang, H.; Worton, D. R.; Ruehl, C. R.; Kirk, B. B.; Goldstein, A. H.; Leone, S.
549 R.; Wilson, K. R., Isomeric product detection in the heterogeneous reaction of hydroxyl radicals
550 with aerosol composed of branched and linear unsaturated organic molecules. *J. Phys. Chem. A*
551 **2014**, *118* (49), 11555.
- 552 45. Richters, S.; Herrmann, H.; Berndt, T., Different Pathways of the Formation of Highly
553 Oxidized Multifunctional Organic Compounds (HOMs) from the Gas-Phase Ozonolysis of β -
554 Caryophyllene. *Atmospheric Chemistry and Physics Discussions* **2016**, *16*, 1.
- 555 46. Ellis, S. R.; Pham, H. T.; in het Panhuis, M.; Trevitt, A. J.; Mitchell, T. W.; Blanksby, S.
556 J., Radical Generation from the Gas-Phase Activation of Ionized Lipid Ozonides. *J. Am. Soc. Mass.*
557 *Spectrom.* **2017**, *28* (7), 1345.
- 558 47. Anderson, S. E.; Wells, J. R.; Fedorowicz, A.; Butterworth, L. F.; Meade, B. J.; Munson,
559 A. E., Evaluation of the Contact and Respiratory Sensitization Potential of Volatile Organic
560 Compounds Generated by Simulated Indoor Air Chemistry. *Toxicol. Sci.* **2007**, *97* (2), 355.
- 561 48. Roberts, M. J.; Wondrak, G. T.; Laurean, D. C.; Jacobson, M. K.; Jacobson, E. L., DNA
562 damage by carbonyl stress in human skin cells. *Mutation Research/Fundamental and Molecular*
563 *Mechanisms of Mutagenesis* **2003**, *522* (1–2), 45.
- 564 49. Kirschenbaum, L. J.; Rueckberg, B., A Correlation of the Solubility of Water in
565 Hydrocarbons as a Function of Temperature Based on the Corresponding Vapor Pressure of Pure
566 Water. *Chem. Sci. J.* **2013**, *2013* (CSJ-101), 1.

567 **Figure Captions**

568 **Figure 1.** Generalized reaction scheme for the oxidation of unsaturated hydrocarbons by O₃.

569 **Figure 2.** a) Reactive decay of 300 nm size-selected Sqe aerosol (inferred from the intensity of the
570 peak at m/z 410.39) for RH = 3, 20, 40 and 60% with simulation results; b) simulated reactive
571 decay for two different k scenarios compared to experimental decay of Sqe (see Supplemental
572 Information); c) Comparison of measured (filled red points) and simulated (green and blue circles,
573 dashed lines) results, which evaluate sensitivity of the Sqe + O₃ rate coefficient. Red corresponds

574 to $k_1 = 1.25 \cdot 10^{-15} \text{ cm}^3 \text{ s}^{-1}$, green to $k_2 = 1.21 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.^{19, 43} Error bars in a and b are the standard
575 deviation of the measured ion signal about its average.

576 **Figure 3.** 10.2 eV photoionization mass spectra recorded for polydisperse Sqe aerosol at a) RH =
577 3, b) 30 and c) 60%. For clarity only normalized difference MS are displayed, original spectra are
578 shown in the SI (Figure S4).

579 **Figure 4.** Overlay of experimental measurements of 300 nm size-selected Sqe aerosol, after
580 reactive uptake of ozone at different RH (3% to 60%), with simulation results. The same trends
581 are observed for all measured particle diameters and polydispers aerosol (SI). a) Change of particle
582 diameter; b) kinetic evolution of the secondary ozonide with the highest abundancy (m/z 458.38);
583 c) kinetic evolution of C27 pentaenal (m/z 384.34). The error bars in a are estimated from the
584 SMPS bin width and replicate measurements. The error bars in b and c are estimated using the
585 standard deviation of the measured ion signal about its average.

586 **Figure 5.** Sensitivity test for different branching ratios of **R1**. Solid lines represent a 1:10
587 primary:secondary CI ratio, dashed lines are model results for a 1:1 ratio. a) Particle diameter
588 change as function of RH. b) Maximum intensity of C27 (blue triangles) and SOZ (green circles)
589 as function of RH.

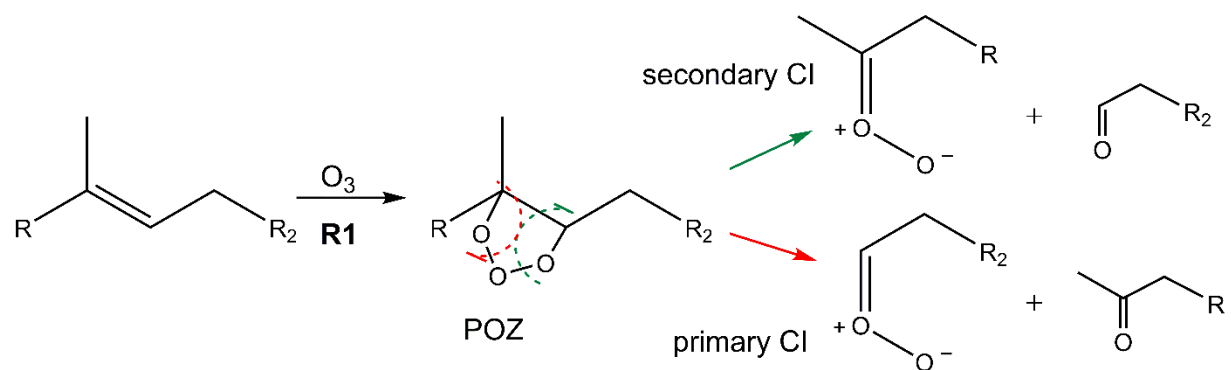
590

591 Table 1. Reaction Scheme and Rate Constants for Stochastic Simulations.^{a)}

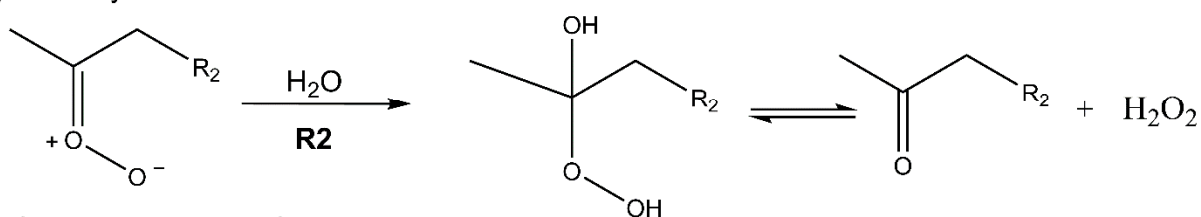
No.	Reaction step	Rate constant	Notes
	$O_3_{\text{gas}} \rightarrow O_3_{\text{adsorbed}}$	1.97 s^{-1}	b)
R1	$S_{\text{qe}} + O_3 \rightarrow \text{s/p-CI} + \text{R=O}$	$1.25 \cdot 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	c),d)
R2	$\text{CI} + \text{H}_2\text{O} \rightarrow \text{R=O} + \text{H}_2\text{O}_2$	5.14 s^{-1}	e)
R3	$\text{CI} + \text{R=O} \rightarrow \text{SOZ}$	$6.7 \cdot 10^{-19}, 1.3 \cdot 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	f)
R4	$\text{CI} \rightarrow \text{R(O)OH}, \text{HOR=O}$	5 s^{-1}	Ref. ³⁷
R6	$\text{CI} + O_3 \rightarrow \text{R=O}$	$4 \cdot 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Ref. ³⁶

592 ^{a)} **R5** was not considered in the model (see text for details). ^{b)} Rate coefficient depends on particle diameter (d) and
593 average $[O_3]$; here: $d=300 \text{ nm}$, $[O_3]=2.81 \cdot 10^{13} \text{ molecules cm}^{-3}$. ^{c)} Either a pair of aldehyde and secondary Criegee
594 intermediate (sCI) or ketone and primary CI (pCI) can be formed. See Computational Details and Results and
595 Discussion for details on branching ratios. ^{d)} Experimental second-order rate constant taken from Ref. ⁴³. ^{e)} Treated as
596 pseudo first order where $[\text{H}_2\text{O}] = 3\text{-}60\%$ (shown for 0%), $k = 1 \cdot 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (from Ref. ³³) and the
597 dimensionless Henry's law constant is $2.6 \cdot 10^{-2}$, which applies to solubility of water in aliphatic compounds with
598 comparable viscosity.⁴⁹ ^{f)} Constrained by calculation and experiment, corrected for solvent-cage effects and optimized
599 to multiple experimental data sets (see text for details).

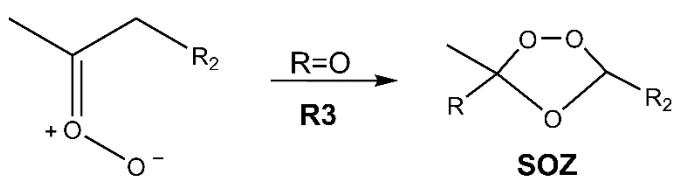
600



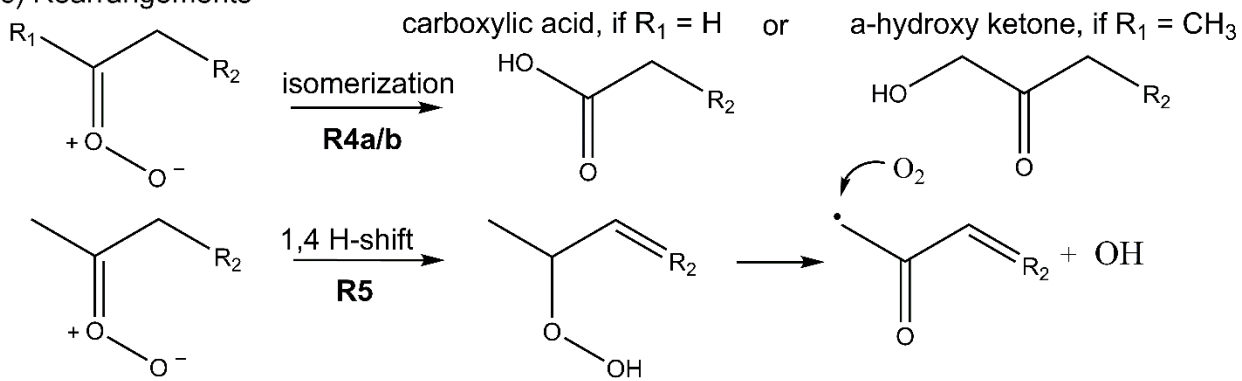
a) Carbonyl formation



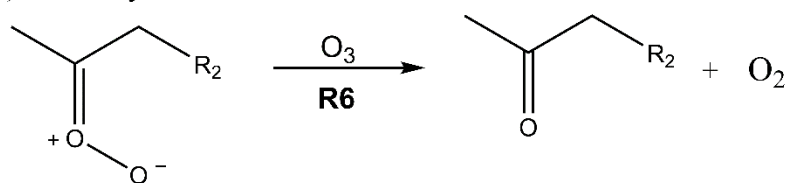
b) Secondary ozonide formation

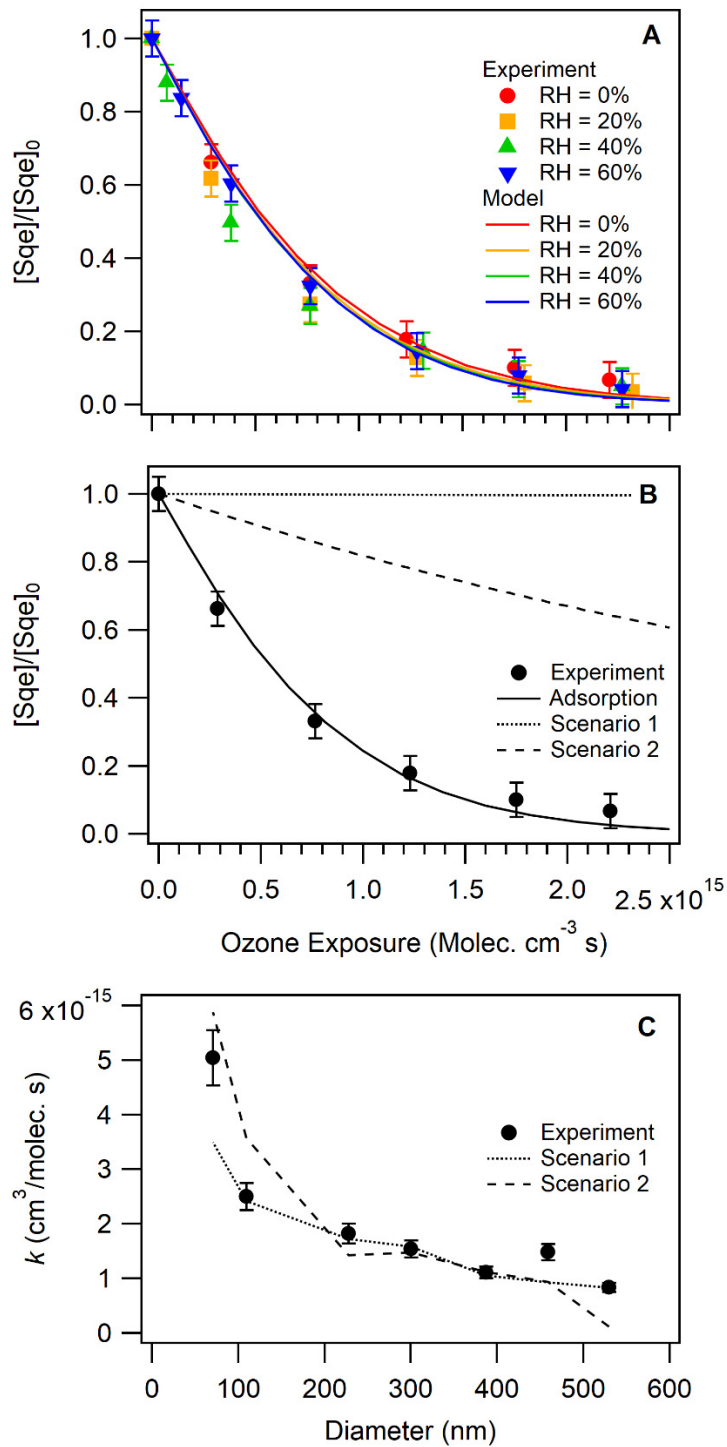


c) Rearrangements



d) Carbonyl formation II





603

604

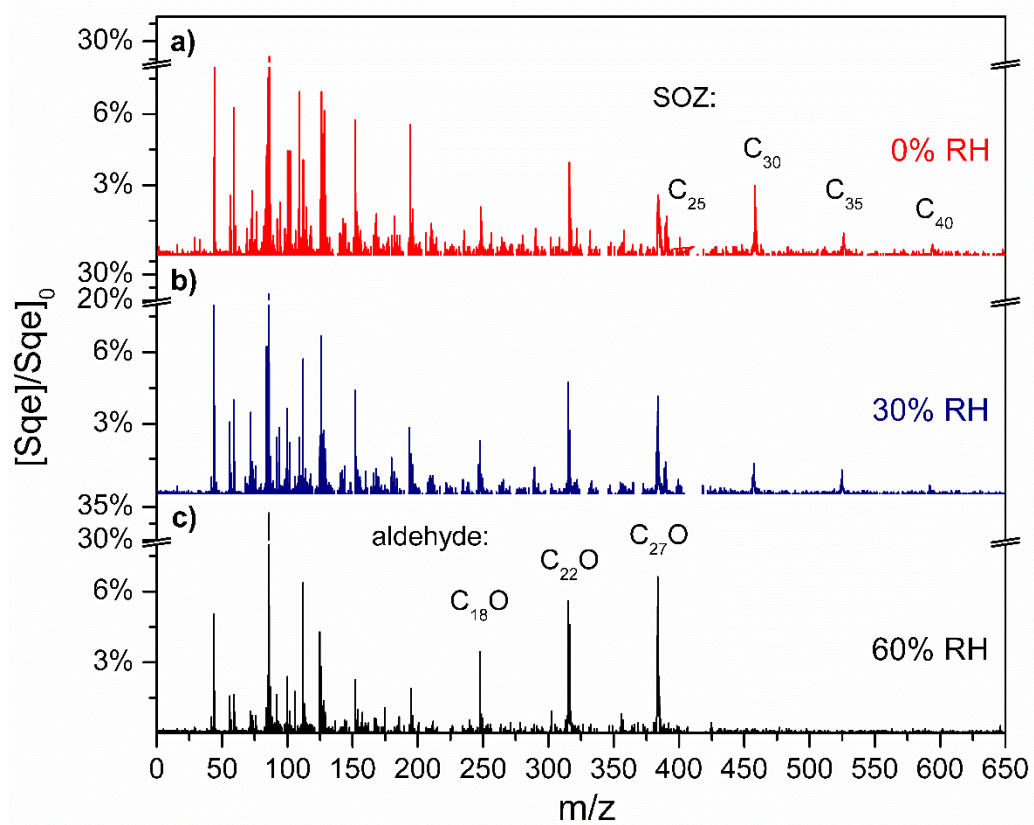
Figure 2

605
606

607

608

609



610
611

Figure 3

612
613
614
615
616
617

618
619
620
621

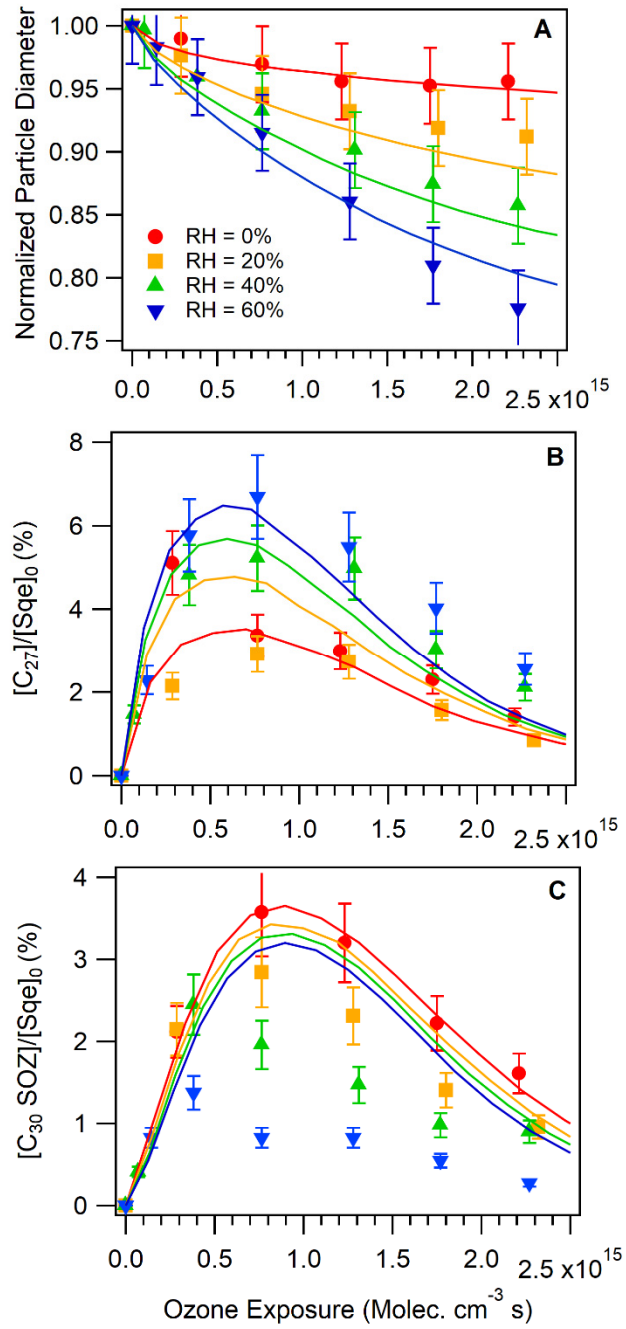
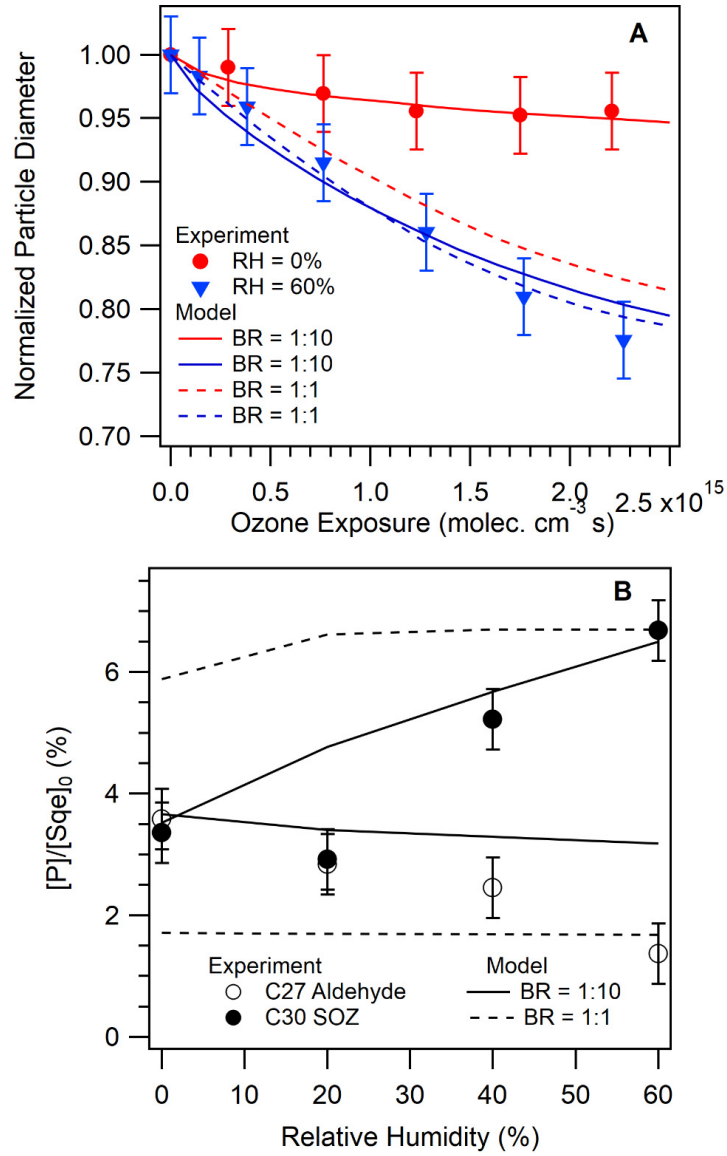


Figure 4

622
623
624
625
626
627
628

629
630
631
632

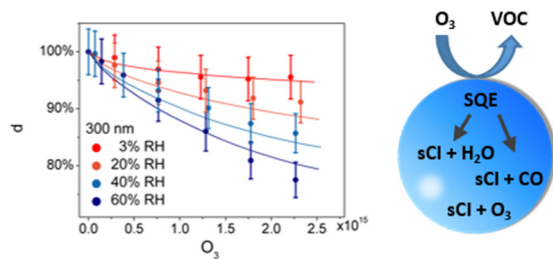


633
634
635
636
637
638
639
640
641
642
643

Figure 5

644
645
646
647
648
649
650

Table of Contents Graphic



651