

The influence of molecular structure and aerosol phase on the heterogeneous oxidation of normal and branched alkanes by OH

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ABSTRACT:

Insight into the influence of molecular structure and thermodynamic phase on the chemical mechanisms of hydroxyl radical-initiated heterogeneous oxidation is obtained by identifying reaction products of submicron particles composed of either *n*-octacosane (C₂₈H₅₈, a linear alkane) or squalane (C₃₀H₆₂, a highly branched alkane) and OH. A common pattern is observed in the positional isomers of octacosanone and octacosanol, with functionalization enhanced towards the end of the molecule. This suggests that relatively large linear alkanes are structured in submicron particles such that their ends are oriented towards the surface. For squalane, positional isomers of first-generation ketones and alcohols also form in distinct patterns. Ketones are favored on carbons adjacent to tertiary carbons, while hydroxyl groups are primarily found on tertiary carbons but also tend to form towards the end of the molecule. Some first-generation products, viz., hydroxycarbonyls and diols, contain two oxygen atoms. These results suggest that alkoxy radicals are important intermediates and undergo both intramolecular (isomerization) and intermolecular (chain propagation) hydrogen abstraction reactions. Oxidation products with carbon numbers less than the parent alkane are observed to a much greater extent for squalane than for *n*-octacosane oxidation and can be explained by the preferential cleavage of bonds involving tertiary carbons.

32 1. Introduction

33 The heterogeneous oxidation of atmospheric organic aerosols can transform particulate
34 properties with a direct influence on climate, human health and visibility. Previous work has
35 attempted to estimate the relative importance of different oxidation pathways by distilling the
36 complex chemistry involving free radical intermediates into two generalized reaction pathways,
37 termed functionalization and fragmentation. Functionalization occurs when an oxygenated
38 functional group is added to a molecule, leaving the carbon skeleton intact. Alternatively,
39 fragmentation involves C–C bond cleavage and produces two oxidation products with smaller
40 carbon numbers than the reactant. The ability to predict secondary organic aerosol (SOA) yields,
41 and thus ambient SOA concentrations, is very sensitive to the assumed “branching ratio”
42 between functionalization and fragmentation. This is because functionalization produces less
43 volatile compounds and increases particulate mass, while fragmentation typically forms more
44 volatile products that can evaporate and thereby decrease particulate mass. A third general type
45 of pathway, oligomerization, reduces average volatility and increases carbon number, and is thus
46 similar to functionalization in its impact on organic aerosol formation and aging. The potential
47 utility of representing aerosol formation and aging chemistry in models using these “generalized
48 reaction pathways” relies on developing parameterizations that are experimentally validated
49 through detailed measurements of oxidation products.

50 Much more is known about the chemistry of free radical-induced hydrocarbon oxidation
51 in the gas phase than in the condensed phase.¹ Gas-phase mechanisms and product branching
52 ratios are often used as a starting point (including in this study) when investigating
53 heterogeneous oxidation, in an effort to identify key similarities and/or differences between
54 heterogeneous and gas-phase oxidation rates and mechanisms. The reaction between a saturated

55 organic molecule and OH begins with the abstraction of a hydrogen atom to form an alkyl
56 radical, which in the presence of O₂, forms a peroxy radical as shown in Fig. 1a. In the absence
57 of NO and HO₂, peroxy radicals undergo self-reactions following one of two general pathways,
58 which form stable products and/or alkoxy radicals. The pathway that forms stable products in the
59 condensed phase includes (at least) two specific mechanisms. Peroxy radicals can react via the
60 Russell mechanism to form a carbonyl-containing compound (either an aldehyde or a ketone),
61 and an alcohol, with O₂ formed as a co-product.² The self reaction can also proceed via the
62 Bennett-Summers mechanism to form two carbonyls and H₂O₂.³ Alternatively, two alkoxy
63 radical intermediates and O₂ can be formed via self-reaction, opening up a variety of possible
64 subsequent reaction pathways.

65 Gas phase alkoxy radicals, under atmospheric conditions, react in one of three ways:⁴
66 hydrogen abstraction, decomposition by β-scission, and ketone formation via reaction with O₂
67 (Fig. 1b). Intramolecular hydrogen abstraction results by isomerization; intermolecular hydrogen
68 abstraction leading to chain propagation is also possible, perhaps even more so in the condensed
69 phase where concentrations are locally very high. Isomerization proceeds most rapidly via a 1,5
70 H shift (i.e., abstraction of a H atom from the δ-C atom) through a relatively low-strain six-
71 member cyclic transition state. Evidence for this pathway in the gas phase includes observations
72 of pentanone isomers formed from the photooxidation of pentane.⁵ Similar observations of
73 hexane photooxidation products indicate that 1,4 H shifts (involving five-membered cyclic
74 transition states) are of negligible importance relative to 1,5 H shifts.⁶ Photooxidation
75 experiments on larger gas-phase *n*-alkanes have shown that isomerization reactions increase in
76 importance (and that of scission reactions decreases) with carbon chain length.^{7, 8} It remains
77 unclear how these detailed gas phase mechanisms, formulated for relatively small molecules, can

78 be applied to heterogeneous free radical oxidation of larger organic molecules in aerosol
79 particles.

80 Early studies of heterogeneous chemistry focused on inorganic compounds, and some of
81 the first identified atmospherically-relevant reactions involve nitrogen and/or chlorine containing
82 compounds on sea salt aerosol⁹ or in polar stratospheric clouds.¹⁰ Recently, heterogeneous
83 oxidation of organic aerosols (OA) has received increased attention.^{11, 12, 13} Most studies have
84 shown that heterogeneous oxidation of organic compounds is about as efficient as gas-phase
85 oxidation, assuming there is sufficient time for gas-phase oxidants to diffuse to the surfaces of
86 condensed phases. The heterogeneous rate is typically expressed as an uptake coefficient or
87 reaction probability (γ), which is the fraction of collisions between gas-phase oxidants and a
88 condensed phase, or a specific condensed-phase molecule, that result in a reaction. One of the
89 most important of these gas phase oxidants is the hydroxyl (OH) radical, and OH uptake
90 coefficients (γ^{OH}) have been reported both for films and microscopic particles. For example, γ^{OH}
91 = 0.34 was measured for thin paraffin wax films¹⁴ and $\gamma^{\text{OH}} > 0.2$ for hexanol adsorbed onto water
92 ice surfaces¹⁵, based on gas-phase OH decay. More recently, OH uptake coefficients based on
93 measured particle-phase decay of specific compounds ranging from 0.37 to 0.51 were reported
94 for more oxygenated single-component organic particles such as citric acid,¹⁶ and values
95 between 0.77 and 1.04 for erythritol and levoglucosan,¹⁷ palmitic acid,¹⁸ and hexacosane
96 particles.¹⁹ Larger γ^{OH} values of 1.3²⁰ and 2.0²¹ have been observed for free radical oxidation of
97 bis(2-ethylhexyl) sebacate particles in a flow tube. Observations of $\gamma^{\text{OH}} > 1$ indicate an important
98 role for secondary radical chain chemistry (although even when $\gamma^{\text{OH}} < 1$ such chain chemistry
99 may still be important). Values larger than 3 were observed for the reaction of squalane particles
100 with Cl atoms in the absence of O₂.²² Although these studies have provided much insight into

101 heterogeneous reaction rates, there are comparably fewer studies that have examined the
102 resulting distribution of oxidation products produced in these reactions. Such measurements are
103 essential to the identification of important heterogeneous reaction mechanisms.

104 Several previous studies have investigated the relative importance of functionalization
105 and fragmentation pathways in the oxidation of organic matter. In the gas phase, the
106 decomposition rate of alkoxy radicals (i.e., fragmentation) depends on the stability (i.e., the
107 ionization energy) of the alkyl radical created by the C-C bond scission.²³ While fragmentation
108 pathways are well-established in the gas-phase, previous studies have come to conflicting
109 conclusions about the relative importance of fragmentation in heterogeneous reactions. Some
110 studies have found that fragmentation is an important pathway leading to rapid carbon loss from
111 organic films^{24,25} or aerosol particles.¹⁸ Volatilization of oxidation products was observed to
112 decrease the volume of bis(2-ethylhexyl) sebacate (BES) aerosol by ~20% after ~2 OH
113 lifetimes.²⁰ This is in contrast to a study of NO₃-initiated oxidation of oleic acid (C₁₈) aerosol,
114 which observed no C₉ aldehyde formation (i.e., the fragmentation product expected based on the
115 position of the double bond in oleic acid). This indicates, for this system of liquid particles,
116 functionalization (e.g., the Russell mechanism) dominates the peroxy radical self-reaction.²⁶ This
117 agrees with a study of the NO₃-initiated oxidation of thin saturated hydrocarbon films, which
118 also resulted in minimal fragmentation.²⁷ Changes in particle phase may be playing a role in
119 these discrepancies, but it is currently not clear how important this effect might be.

120 Some previous work has identified specific products of radical-initiated heterogeneous
121 oxidation to reveal the importance (or lack thereof) of certain chemical mechanisms. For
122 example, a previous study of the heterogeneous oxidation of a hexadecane film by OH identified
123 all positional isomers of hexadecanone (i.e., functionalization products), as well as short-chain

124 aldehydes and carboxylic acids (i.e. fragmentation products).²⁸ However, no alcohol products
125 were detected, which was attributed to a small branching ratio to the Russell mechanism. An
126 excess of ketones relative to alcohols was observed during the heterogeneous radical-initiated
127 oxidation of dioctyl sebacate aerosol, suggesting an alternative pathway to the Russell
128 mechanism, such as the Bennett-Summers pathway or alkoxy radical formation.²⁹ On the other
129 hand, in a study of NO₃-initiated oxidation of oleic acid (C₁₈) particles found that the Russell
130 mechanism (i.e., functionalization) is dominant and that the branching ratio to form alkoxy
131 radicals (which can fragment) is of minimal importance.²⁶

132 In addition to investigations of the heterogeneous oxidation products of different model
133 compounds, the importance of aerosol phase (i.e., solid vs. liquid) has also been examined. The
134 Cl atom initiated oxidation of supercooled liquid and solid brassidic acid (C₂₂H₄₂O₂) particles,
135 revealed that liquid particles reacted slightly more rapidly. However, the volume of solid
136 particles decreased to a greater extent upon reaction, suggesting greater fragmentation and
137 subsequent evaporation than for liquid particles.³⁰ A similar increase in the production of volatile
138 gas phase molecules was observed for OH-initiated heterogeneous oxidation of solid steric acid
139 films relative to liquid BES films.²⁵

140 The two hydrocarbon precursors used in this work, squalane (a liquid branched alkane)
141 and octacosane (a solid normal alkane), are relatively non-volatile (boiling points of 176 and
142 343°C, respectively), and thus have been used in previous studies of particle-phase hydrocarbon
143 oxidation.^{31, 32, 33} Here these two compounds are used to explore how aerosol phase and/or
144 differences in molecular structure (i.e. branching of the carbon skeleton) alter the reaction
145 product distributions produced by heterogeneous oxidation. Previously, it was found that the
146 squalane + OH reaction could be well described by the multigenerational formation and

147 evolution of reaction products described as a Poisson distribution.³⁴ While these studies have
148 provided a general description of the reaction, finer details are needed to develop new molecular
149 and mechanistic insights into how functionalization and fragmentation pathways depend upon
150 molecular structure and/or aerosol phase.

151 Although previous work has focused broadly on describing how multiple generations of
152 reaction products evolve during heterogeneous oxidation, here we primarily focus on the
153 molecular and positional isomeric distribution of first generation oxidation products. Single-
154 component aerosols (either squalane or octacosane) are photo-oxidized in a flow tube reactor and
155 the reactions products are analyzed using two-dimensional gas chromatography coupled to mass
156 spectrometry. Analytes are ionized either with vacuum ultraviolet (VUV, 10.5 eV) photons or by
157 electron impact (EI, 70 eV). This approach provides a way to examine how the formation of
158 specific oxidation products depends upon aerosol phase and molecular branching structure.
159 Specifically we determine how the location of a carbon atom along the molecular backbone
160 relates to its propensity to functionalize (i.e., the distribution of positional isomers of
161 functionalization products). Furthermore, for fragmentation reactions, the most likely carbon-
162 carbon bonds to cleave are identified by examining the carbon number distribution of the
163 oxidation products. These results provide the molecular details to better refine heterogeneous
164 reaction mechanisms, which provide the fundamental basis for more realistic parameterizations
165 of functionalization and fragmentation pathways in organic aerosols.

166 2. Experimental

167 Pure hydrocarbon particles are formed via homogeneous nucleation using an oven heated
168 to 120-130 °C. The aerosol is then passed through an annular charcoal denuder to remove

169 residual gas phase species from the flow. The particles are then mixed with humidified N₂, O₂,
170 and O₃, and sent to a flow-tube reactor as described in detail in previous publications.^{31, 32} The
171 reactor is comprised of a 1.3m long, 2.5cm ID type-219 quartz tube, surrounded by mercury
172 lamps which produce light with a peak wavelength of 254 nm. O₃ is produced by passing O₂
173 through a corona discharge ozone generator. OH concentration is varied by changing the O₃
174 concentration in the reactor (maximum [O₃] was 1000 ppb). The relative humidity in the reactor
175 is kept at 30%, and the total flowrate at 1 lpm, resulting in an average residence time in the flow
176 tube of ~37s. With all the lights off (i.e., when OH exposure was zero), the octacosane and
177 squalane particles have concentrations of 11,000 and 6,500 μg m⁻³ and surface-weighted mean
178 diameters (D_{surf}) of 282 and 164 nm, respectively. Under these conditions, heterogeneous
179 processes (relative to gas phase oxidation) are expected to dominate, due to the high particle
180 loading and surface-to-volume ratios.¹¹

181 During flow tube experiments, samples are collected onto quartz filters (47 mm
182 Tissuquartz, Pall Life Science) which were pre-baked at 600 °C for at least 6 hours to remove
183 organic contaminants. Immediately before collection, gas-phase compounds are removed from
184 the samples by a charcoal denuder (8 in. 480-channel MAST Carbon). Samples are collected at
185 OH exposures ([OH] × time) ranging from 0 to 5.8×10^{12} molec cm⁻³ s, as determined by the
186 observed decay of the gas phase tracer hexane. The air volume sampled varies from 4.5 to 20 L,
187 to achieve filter concentrations of 1.1 to 3.7 μg C cm⁻². Filter punches (1.6 cm²) are thermally
188 desorbed at 320°C under helium using a thermal desorption system and autosampler (TDS3 &
189 TDSA2, Gerstel). Desorbed samples are focused at 20°C on a quartz wool liner in a cooled
190 injection system (CIS4, Gerstel) before they are introduced into a two-dimensional gas
191 chromatograph (GC×GC, Agilent 7890). All filters are analyzed using 70 eV electron impact

192 (EI) as an ionization source. A subset of these filters (for each parent compound, one at ~1 and
193 one at ~3 OH lifetimes) are analyzed using soft (10.5 eV) vacuum ultraviolet (VUV) photons at
194 the Advanced Light Source (ALS), Lawrence Berkeley Laboratory (extracted single-ion
195 chromatograms shown in Figs. S1-4). These measurements involve a custom modification of the
196 mass spectrometer ion source to facilitate direct coupling to the ALS.

197 For both VUV and EI ionization sources, comprehensive GC×GC analysis is performed
198 using a 60 m × 0.25 mm × 0.25 μm non-polar capillary column (Rxi-5Sil MS, Restek) for the
199 first-dimension separation (by volatility), and a medium-polarity second dimension column (1 m
200 × 0.25 mm × 0.25 μm, Rtx-200MS, Restek). A dual-stage thermal modulator (Zoex), consisting
201 of a guard column (1 m × 0.25 mm, Rxi, Restek) and with a modulation period of 2.4 s, is used
202 as the interface between the two columns. Mass spectra are obtained with a high-resolution
203 ($m/\Delta m = 4000$) time-of-flight mass spectrometer (HTOF, ToFWerK). An example EI
204 chromatogram is shown in Fig. 2. The VUV results, which feature a larger signal at the parent
205 m/z ratio and fewer ion fragment peaks (Fig. 3), are used to identify specific compounds,
206 including positional isomers, in the chromatogram. For the detection of alcohols and acids, all
207 filters are also subjected to *in situ* gas-phase derivatization facilitated by sweeping the headspace
208 of a vial filled with *N*-Methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) during the thermal
209 desorption cycle. Comparison of derivatized and underivatized chromatograms indicate that
210 tertiary alcohols dehydrated during desorption (i.e., before chromatography) and were detected
211 as alkenes. For example, tertiary “squalanols” ($C_{30}H_{62}O$) appear as derivatized alcohols
212 ($C_{33}H_{70}OSi$) when MSTFA was used, but as alkenes ($C_{30}H_{60}$) in the absence of MSTFA.
213 Dehydration of tertiary alcohols is confirmed with authentic standards of tertiary alcohols
214 including 3,7-dimethyl-3-octanol and 4-terpeneol.

215 The decay of both octacosane and squalane are quantified both by the total EI signal and
216 the 12 most prominent $C_nH_{2n+1}^+$ EI fragments. The decay constants (k_{parent}) obtained from
217 exponential fits to the decay of octacosane or squalane are used to compute uptake coefficients
218 (γ_{parent}^{OH}), by normalizing the rate of parent decay to the OH-particle collision rate,³² while
219 correcting for the limitations to reaction rate due to gas-phase diffusion of OH to the particle
220 surface.³⁵ Kinetic lifetimes (τ) are computed using the first-order decay constants of squalane or
221 octacosane (i.e. $\tau = k_{parent}^{-1}$). Analytical standards are not available for the early oxidation
222 products of squalane and octacosane, thus adding to the uncertainty in their quantification. In
223 most GC systems (including ours), the response factors tend to decrease with both decreasing
224 volatility and increasing polarity. As an upper limit for the response factor, deuterated *n*-alkanes
225 are used to correct for the volatility response. As a lower limit, we also account for the polarity
226 by multiplying the upper limit response factor by the ratio of the response of anthraquinone to *n*-
227 eicosane, two deuterated internal standards with similar volatilities but different polarities. This
228 is considered a lower limit since the difference in both the number of O atoms and O:C ratio is
229 greater between anthraquinone and eicosane than it is between first-generation oxidation
230 products and squalane/octacosane. Authentic standards for several octadecanone isomers (2-, 3-,
231 5-, and 9-octadecanone) are used to correct the response factors for equivalent octacosanone
232 isomers. Standards of 2- and 3-tridecanone as well as tridecanal are used to correct the response
233 factors of aldehydes relative to ketones.

234 3. Results and Discussion

235 In Section 3.1 the oxidation kinetics of octacosane and squalane will be presented and
236 compared. Oxidation product identification for octacosane and squalane are detailed in sections

237 3.2 and 3.3, respectively. These final two sections are further subdivided into functionalization
238 (3.n.1) and fragmentation (3.n.2) products.

239 3.1 Oxidation Kinetics

240 The total octacosane EI signal decays with OH exposure, with an average first-order
241 decay constant of $4.2 \pm 2.2 \times 10^{-13} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Fig. 4a, uncertainty indicates 90% confidence
242 intervals of the exponential fit). All individual $\text{C}_n\text{H}_{2n+1}^+$ EI fragments are within this uncertainty
243 range, which is equivalent to an uptake coefficient of 0.18 ± 0.11 . Squalane decreases with OH
244 exposure, with a decay constant of $1.6 \pm 0.4 \times 10^{-12} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Fig. 4b). This yields an
245 uptake coefficient of 0.36 ± 0.11 , indicating that squalane is oxidized twice as quickly as
246 octacosane. This value is slightly larger than the previously reported value of 0.30 ± 0.07 ,³² and
247 the larger uncertainty for the measurement reported here arises from the relatively few (six) data
248 points used to calculate the squalane decay.

249 Possible explanations for the larger γ^{OH} for squalane than octacosane can be understood
250 by comparing the timescales of the different processes that influence the oxidation kinetics under
251 the conditions of this reaction. The self-diffusion coefficient of squalane is $7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$,³⁶
252 which (for a 164 nm particle) is equivalent to a mixing timescale of 10^{-5} s .²⁶ The timescale for
253 the reactive loss of squalane to OH radicals (i.e., the ratio of the squalane decay constant to the
254 average [OH] in the reactor) is approximately 20 s.²⁶ Because the timescale for diffusion in the
255 squalane particle is a factor of $\sim 2 \times 10^5$ shorter than that of the reaction timescale, it can be
256 assumed that unreacted squalane is continuously replenished at the surface of these microscopic
257 particles. In contrast, diffusion coefficients for semi-solids and solids are expected to be below
258 $10^{-10} \text{ cm}^2 \text{ s}^{-1}$,³⁷ and therefore the timescale of mixing in solid octacosane particles will be much

259 closer to the reaction timescale. This suggests that the diffusion of unreacted material to the
260 particle surface may limit the overall rate at which octacosane reacts with OH. A more subtle
261 difference in the decay of the parent ion signals is consistent with this difference in phase. The
262 squalane decay is better described as single exponential (Fig. 4b), whereas octacosane appears to
263 react more quickly during the first oxidation lifetime and then more slowly as oxidation proceeds
264 (Fig. 4a). This could be consistent with a kinetic delay associated with surface replenishing of
265 octacosane molecules.

266 In addition to differences in phase, the more rapid heterogeneous oxidation of squalane
267 relative to *n*-octacosane could also be due to more rapid hydrogen abstraction from the tertiary
268 carbons present in squalane (*n*-octacosane, a linear alkane, has no tertiary carbons, while
269 squalane has six). Previous studies of the reactivity of different carbon atoms (primary,
270 secondary, and tertiary) for gas phase hydrocarbons are summarized in so-called Structure
271 Reactivity Relationships (SRR), and indicate that tertiary carbons are more reactive than
272 secondary or primary carbons.³⁸ A previous investigation into the heterogeneous oxidation of
273 motor oil using similar analytical techniques concluded that this enhanced reactivity associated
274 with tertiary carbons (i.e., branching in the carbon backbone) is more pronounced in
275 heterogeneous oxidation than it is in the gas phase.³⁹

276 3.2 Octacosane

277 3.2.1 Functionalization products

278 The majority of the observed octacosane oxidation products are the result of
279 functionalization reactions, including C₂₈H₅₆O compounds (i.e., various octacosanone isomers
280 and octacosanal). The sum of the concentrations of C₂₈H₅₆O isomers reaches a maximum value

281 of $45 \pm 18 \mu\text{g m}^{-3}$ at an OH exposure of $1.2 \times 10^{12} \text{ molec cm}^{-3} \text{ s}$ (approximately 0.5 lifetimes).
282 Similar concentrations of $\text{C}_{28}\text{H}_{58}\text{O}$ compounds (i.e., octacosanols) are observed. The observed
283 fragmentation products (with carbon numbers less than 28) are minor in comparison, with a
284 maximum uncertainty range of less than $5 \mu\text{g m}^{-3}$ (Fig. 4a).

285 All single-carbonyl compounds (octacosanal and 2- through 14-octacosanone) are
286 detected and chromatographic separation is achieved for all these isomers up to 8-octacosanone.
287 The total EI signal intensity could not be used to individually quantify the 9- through 14-
288 octacosanone isomers since they co-elute. The closer the carbonyl is to the end of the molecule,
289 the greater the GC retention time, with relatively large gaps between 2-, 3-, and 4-octacosanone,
290 but smaller gaps between subsequent octacosanone isomers (Fig. S1). This is in agreement with a
291 previous GC/MS analysis of heterogeneous oxidation of hexadecane films by OH,²⁸ as well as
292 the analysis of an isotopic mixture of authentic octadecanone standards.

293 Shown in Fig. 5a is the distribution of octacosanone isomers, which reveals a clear
294 enhancement in the formation of the carbonyl group towards the terminus of the molecule. While
295 the ketone groups formed at carbon positions greater than 5 are formed with similar yields, 5-, 4-
296 , 3-, and 2-octacosanone are enriched relative to the more interior ketones by factors of 1.5, 2.2,
297 4.8, and 10, respectively (Fig. 5a). The yield of octacosanal is smaller than that of the interior
298 ketones. A similar pattern is observed for the positional isomers of octacosanol as shown in Fig.
299 5b.

300 Previous studies of the reactivity of different carbon atoms (primary, secondary, and
301 tertiary) for gas phase hydrocarbons are summarized in SRR predictions,³⁸ shown explicitly in
302 Figs. 5a and b. The rate of hydrogen abstraction from terminal carbons is expected to occur ten

303 times more slowly than from more interior carbons, which helps explain the observed low yields
304 of octacosanal and *n*-octacosanol. SRR, however, also predicts that the hydrogen abstraction rate
305 from the secondary carbon atoms adjacent to terminal carbons should occur about 20% more
306 slowly than from those carbon atoms located towards the interior of the molecule. This is in
307 contrast to the observed isomer distribution, which exhibits a pattern nearly opposite of that
308 predicted by SRR. This suggests that more subtle features of the aerosol (e.g., phase or molecular
309 orientation at the particle surface) are playing a more dominant role in the reaction than
310 differences in the reactivity of individual carbon atoms within the molecule.

311 One explanation for the positional isomer pattern is that octacosane molecules at the
312 interface are preferentially oriented with their carbon backbones normal to the aerosol surface.
313 This is consistent with “surface freezing” of *n*-alkanes, in which these hydrocarbon molecules
314 adopt more ordered configurations at the interface.⁴⁰ Furthermore, molecular dynamics
315 simulations show that the terminal carbons of liquid *n*-alkanes are enhanced at the interface.^{41,42}
316 Such a surface orientation would lead to an enhanced encounter frequency of an OH radical with
317 the terminal carbons of *n*-octacosane and is consistent with the observed carbonyl and alcohol
318 isomer distributions, shown in Fig. 5.

319 3.2.2 Fragmentation products

320 Analysis of the chromatogram shown in Fig. 2 reveals very low yields of octacosane-
321 derived fragmentation products (i.e., formed by breaking C-C bonds). As shown in Fig. 6,
322 several *n*-alkanoic acids up to octacosanoic (C₂₈) acid are detected at concentrations of ~1 μg m⁻³.
323 ³. At low OH exposures, *n*-alkanoic acid concentrations increase for carbon numbers larger than
324 22. Hexacosanoic (C₂₆) acid is formed in the largest relative yield, suggesting that breaking the
325 second C-C bond is more favorable than the terminal C-C bond. At higher OH exposures, a

326 preference for even-numbered acids provides further evidence for enhanced cleavage of the
327 second (relative to the terminal) C-C bond. Octacosanoic acid is the most prevalent acid at higher
328 OH exposures, suggesting that it is formed as a second- or higher-generation product.
329 Conversion of aldehydes to acids during the heterogeneous oxidation of thin films has previously
330 been observed,²⁵ which could explain the increase in the relative importance of octacosanoic acid
331 at higher OH exposures.

332 Octacosane fragmentation reactions can explain only a small part of the rapid decrease in
333 the volume of octacosane particles measured by the SMPS (54% over ~1 oxidation lifetime, Fig.
334 4a). Alternatively, most of the SMPS volume decrease could be related to a decrease in mobility
335 diameter associated with a particle shape or density change induced by oxidation. A decrease in
336 the shape factor from an initial value of 1.3 to 1 would explain the entirety of this 54% decrease
337 in volume. Thus, while alkanolic acid fragmentation products are observed (Fig. 6), and
338 fragmentation reactions have been observed in other studies of solid hydrocarbons,^{24, 30, 25} C-C
339 bond scission is much less significant for octacosane relative to squalane (discussed below).

340 3.3 Squalane

341 3.3.1 Functionalization products

342 The observed concentrations of squalane oxidation products are much higher than those
343 of octacosane at a given oxidation lifetime. The sum of “squalanone” (2,6,10,15,19,23-
344 hexamethyltetracosan-*n*-one) concentrations reaches a maximum of $297 \pm 120 \mu\text{g m}^{-3}$ after an
345 OH exposure of $5.5 \times 10^{11} \text{ molec cm}^{-3} \text{ s}$ (approximately 0.9 lifetimes), as shown in Fig. 4b.
346 Using the VUV chromatograms for individual $\text{C}_n\text{H}_{2n+1}\text{O}^+$ ion fragments, six squalanone isomers
347 are isolated, with the two remaining isomers (9- and 12-squalanone) co-eluting (Fig. S3). Similar

348 concentrations and kinetics are observed for squalanol, with twelve positional isomers isolated
349 by VUV-MS (Fig. S4).

350 As shown in Fig. 7a, carbonyls on carbon atoms adjacent to tertiary carbons are formed
351 in the highest abundance. The EI signal for these “ α -carbonyls” is about five times larger than for
352 the “ β -carbonyls” (i.e., carbonyls on atoms separated from tertiary carbons by one intermediate
353 carbon). Standards for branched ketone isomers are not available, and therefore the assessment
354 of this ketone isomer pattern is not as quantitative as the octacosanone isomer pattern discussed
355 above. However, the similarity in total EI signal with those of individual fragment ions (e.g.,
356 $C_4H_9^+$, the formation of which would not be expected to depend strongly on the location of a
357 single carbonyl group on a C_{30} compound) provides additional confidence in our observation that
358 α -carbonyls are enriched relative to β -carbonyls. As with the sum of these compounds, the
359 individual ketone isomers reach a maximum at an OH exposure of 5.5×10^{11} molec cm^{-3} s (i.e.,
360 ~ 0.9 lifetimes, Fig. 4b), indicating that these species are first generation oxidation products.

361 SRR predicts that H-abstraction should be equally rapid for the α - and β -carbons of
362 squalane (Fig. 7a), since they are both secondary.³⁸ This suggests that the observed enrichment
363 of the α - over the β -carbonyls is due to differences in the subsequent chemistry of the peroxy or
364 alkoxy radicals formed at these different carbon sites. Peroxy radicals formed at these α - and β -
365 positions can both form carbonyls via the Russell mechanism. If these peroxy radicals are
366 converted to alkoxy radicals, however, they can abstract a hydrogen from either the same
367 molecule (isomerization) or another molecule (chain propagation), which converts the alkoxy
368 radical into a hydroxyl group (Fig. 1b). Because isomerization generally involves a six-
369 membered cyclic transition state, β -alkoxy radicals have more hydrogen atoms available for
370 abstraction than α -alkoxy radicals, as shown in Fig. 8. It is therefore likely that this pathway is

371 enhanced for β -carbons, resulting in less efficient ketone formation at these sites. Further
372 evidence for this pathway is observed in the kinetic evolution of multi-functional products with
373 two oxygen atoms, discussed below. A difference in the O_2 reactivity of these isomers is much
374 less likely, and while fragmentation is an important pathway for these squalane oxidation
375 experiments (if only at higher OH exposures), it would tend to suppress squalanone formation at
376 the α -carbons. It is also possible that β -alkoxy radicals more readily abstract H atoms from other
377 molecules, as this would also inhibit squalanone formation at β -carbons. We conclude that the
378 distribution of first-generation ketones in radical-initiated squalane oxidation is not controlled
379 solely by rate of H abstraction but is also governed, in part, by intra- and/or intermolecular
380 hydrogen abstraction pathways via alkoxy radical intermediates.

381 In contrast to the linear alkane, the distribution of squalanol isomers (Fig. 7b) is different
382 than what is observed for squalanones. The preference for α - over β -carbons for hydroxyl
383 functionalization is much less pronounced. The most prevalent isomers, 2-, 6-, and 10-squalanol,
384 can be explained by more rapid initial H abstraction rates from these tertiary carbons consistent
385 with SRR predictions shown in Fig. 7b. There is also, however, an overall enrichment in alcohol
386 functional groups formed toward the end of the molecule, which is not captured by SRR
387 calculations. The origin of this enrichment is currently unknown, but could be due to the
388 branching ratio of intra- to intermolecular H abstraction by alkoxy intermediates (Fig. 1b). If
389 alkoxy radicals towards the end of the molecule are more exposed to other molecules, they might
390 be more likely to undergo intermolecular H abstraction, yielding squalanols. More interior
391 alkoxy radicals may instead be more likely to undergo intramolecular H abstraction, which
392 would lead to multi-functional compounds, discussed below.

393 Several products containing two oxygenated functional groups are also detected. The
394 identification of the parent ion in the VUV mass spectra, combined with both GC retention
395 times, allows these compounds to be classified into three groups: $C_{30}H_{62}O_2$ (“squaladiols”),
396 $C_{30}H_{60}O_2$ (“hydroxysqualanones”), and $C_{30}H_{58}O_2$ (“squaladiones”). The first two groups do not
397 include alkanolic acids, which have distinct mass spectra. Figure 9 depicts the kinetic evolution of
398 these three groups. All squaladiones (two carbonyl groups) compounds are second- or higher-
399 generation products and are thus formed via multiple reactions with OH (Fig. 9c). Most
400 squaladiols (two OH groups, Fig. 9a) and approximately half the hydroxysqualanones (Fig. 9b),
401 however, have a kinetic evolution that is consistent with first generation products. The formation
402 of two oxygenated functional groups by a single OH reactive collision can occur via
403 isomerization (discussed above). Thus the presence and kinetic evolution of these species
404 supports the interpretation that intramolecular hydrogen abstraction by alkoxy radicals is an
405 important pathway during the heterogeneous oxidation of squalane. As suggested by Fig. 7b,
406 alkoxy radicals formed on terminal carbon atoms are more likely to abstract a hydrogen atom
407 from a neighboring molecule, implying that these first-generation bi-functional compounds are
408 produced predominantly from alkoxy radicals centered on interior carbons.

409 3.3.2 Fragmentation products

410 In contrast to octacosane, significant quantities of squalane fragmentation products (i.e.,
411 particle-phase molecules containing less than 30 carbon atoms) are formed during the reaction.
412 The sum of the concentrations of these compounds is $154 \pm 71 \mu\text{g m}^{-3}$ at ~ 0.9 lifetimes (Fig. 4b),
413 which is approximately half the quantity of first-generation carbonyl functionalization ($C_{30}H_{60}O$)
414 products. As shown in Fig. 10, identified fragmentation products in non-derivatized samples
415 include 33 carbonyls ($C_nH_{2n}O$), 32 lactones ($C_nH_{2n-2}O_2$), 57 alcohols (detected as C_nH_{2n}), and 40

416 hydroxycarbonyls (detected as $C_nH_{2n-2}O$). These classifications are based upon knowledge of
417 exact parent molar masses and 2nd dimension (polarity) GC retention times. The most common
418 carbon number of the fragmentation products is 24 (this was true of several compound classes).
419 Other prevalent carbon numbers, in order of decreasing abundance, are 19, 22, 13, 11, and 17
420 (Fig. 10a). Assuming that only one C–C bond is broken in these reactions, this indicates that
421 bonds involving tertiary carbons are the most likely to be cleaved.

422 This analysis does not detect molecules with fewer than ~8 carbon atoms, although the
423 decrease in squalane particle volume limits the yield of such species to < 7% at one lifetime.
424 Previous studies of the squalane system conducted by our group have found that at low OH
425 exposures, oxidation is dominated by functionalization, while fragmentation becomes
426 increasingly important as OH exposure increases, equaling functionalization after approximately
427 3 squalane oxidation lifetimes.^{31, 34} Most of the products measured here reach their maxima
428 between 1 and 2 kinetic lifetimes, and thus the 2:1 functionalization:fragmentation branching
429 ratio of this study is consistent with previous work. The lack of fragmentation in linear
430 octacosane (Fig. 6a), along with the strong preference for squalane fragmentation products
431 formed via cleavage of a C-C bond involving a tertiary carbon (Fig. 10a), suggests that the
432 heterogeneous functionalization:fragmentation branching ratio depends strongly on the amount
433 of branching in the parent hydrocarbon. Lower aerosol yields have been observed for branched
434 alkanes in the gas phase, which is also likely due to enhanced fragmentation relative to linear
435 alkanes.⁴³

436 The observation that the bonds in squalane most susceptible to cleavage involve tertiary
437 carbons is expected, since β -scission of an alkoxy radical produces an alkyl radical (Fig. 1b) and
438 an α -alkoxy radical would produce a more stable secondary alkyl radical. This preference is not

439 reflected in the squalanone isomer pattern because a preference for fragmentation of α - over β -
440 alkoxy radicals would, for functionalization products, tend to favor formation of β - over α -
441 ketones. This is likely due to the relatively low OH exposures examined in this study, under
442 which functionalization dominates fragmentation. It is quite possible that at higher OH exposure
443 (i.e., higher generations), the fragmentation pathway (i.e., β -scission) will have similar or even
444 greater influence than functionalization pathways (i.e., isomerization vs. reaction with O_2) on the
445 isomeric distribution of squalane heterogeneous oxidation products.

446 The temporal evolution of the fragmentation product classes is consistent with previous
447 studies of this system. OH-initiated heterogeneous oxidation of squalane tends to add an average
448 of one O atom per molecule for each squalane oxidation lifetime.³² Thus, it is expected that
449 carbonyl ($C_nH_{2n}O$) compounds and alcohols (detected as C_nH_{2n}) are first-generation products
450 (Fig. 10b). Two other classes, $C_nH_{2n-2}O_2$ (here called “lactones” based on similarities to
451 compounds in EI-MS libraries) and hydroxycarbonyls (detected as $C_nH_{2n-2}O$), both peak at
452 higher OH exposures, suggesting that they originate from second- or higher-generation products.

453 4. Conclusions

454 The OH-initiated heterogeneous oxidation of squalane aerosol is approximately two times
455 faster than for octacosane (uptake coefficients of 0.41 ± 0.11 and 0.18 ± 0.11 , respectively). This
456 is likely due at least in part to the differences in the aerosol phase. Squalane is a liquid at room
457 temperature, and thus unreacted squalane is likely rapidly replenished at the surface of these
458 particles. In contrast, octacosane is a solid, and thus diffusion of molecules from the interior to
459 the surface is expected to be many orders of magnitude slower. Although octacosane reacts more
460 slowly than squalane, the octacosane volume determined from measured particle mobility

461 diameter (assuming spherical particles) decreased much more rapidly than for squalane particles
462 (54% vs. 7% over one oxidation lifetime). While this could partially be caused by evaporation of
463 fragmentation products, it is likely largely due to an increase in density and/or a decrease in
464 particle shape factor for the aerosol as it is oxidized.

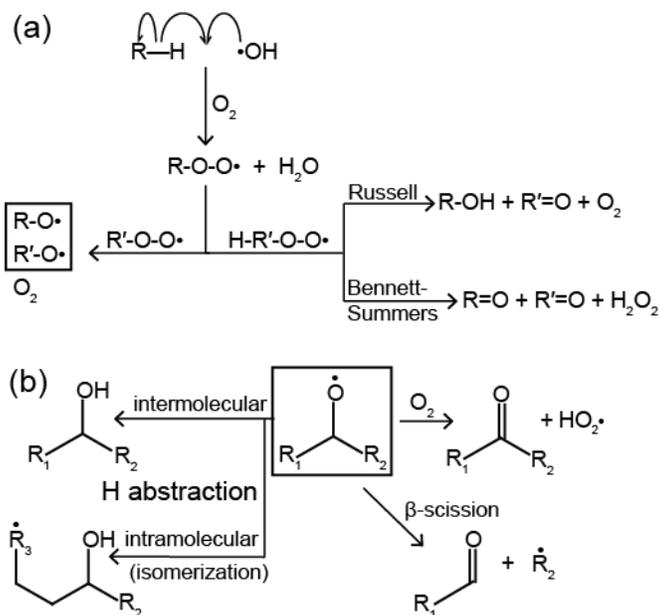
465 The influence of the phase of the particle is observed in the distribution of octacosanone
466 and octacosanol positional isomers, which are the most prominent first-generation products
467 observed during octacosane oxidation. All functionalization of interior carbons (i.e., 6- through
468 14-octacosanone/ol) occurs with similar albeit small yields. The ketones and alcohols formed at
469 the end of the molecule, however, are enriched compared to these interior isomers, with the
470 yields of 5-, 4-, 3-, and 2-octacosanone higher by factors of 1.5, 2.2, 4.8, and 10, respectively.
471 This product distribution is consistent with so-called “surface freezing” of linear alkanes where
472 the molecules are preferentially oriented normal to the surface in microscopic particles.

473 Squalanone isomers with carbonyl groups located adjacent to tertiary carbons are ~5
474 times enriched relative to those with carbonyl carbons not directly bound to tertiary carbons.
475 Since the initial hydrogen abstraction step is not expected to occur more rapidly for these “ α -
476 carbons,” this preference is likely due to more efficient hydrogen abstraction by β -alkoxy
477 radicals compared to α -alkoxy radicals. This hydrogen abstraction is either intra- (i.e.,
478 isomerization) or intermolecular (i.e. chain propagation). As both these pathways compete with
479 the reaction of alkoxy radicals with O₂ to form a ketone, it could explain the observed preference
480 for α -ketones. Further evidence for the importance of isomerization reactions in this system is
481 observed by oxidation products containing two oxygen atoms, some of which were second-
482 generation products but others, containing hydroxyl groups, were formed after a single reaction
483 with OH.

484 Finally, substantial abundances of fragmentation products are observed for squalane, but
485 are much less prevalent for octacosane particles. The only octacosane-derived fragmentation
486 products observed are *n*-carboxylic acids, exhibiting an even-number preference suggesting that
487 cleavage of the second C-C bond is more favorable than the terminal C-C bond. The majority of
488 squalane fragmentation products are formed by cleaving C-C bonds involving tertiary carbons. It
489 is therefore likely that the lack of such carbons (i.e., branching points) in *n*-octacosane is at least
490 partially responsible for the small quantity of observed fragmentation products. This work
491 begins to unravel the complex interplay of molecular structure and particle phase in the
492 heterogeneous oxidation of organic aerosol by OH.

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500 Figure 1. The OH-initiated hydrocarbon oxidation mechanism in the absence of NO_x . Alkoxy

501 radicals are indicated by boxes. (a) Hydrogen abstraction followed by rapid reaction with O_2

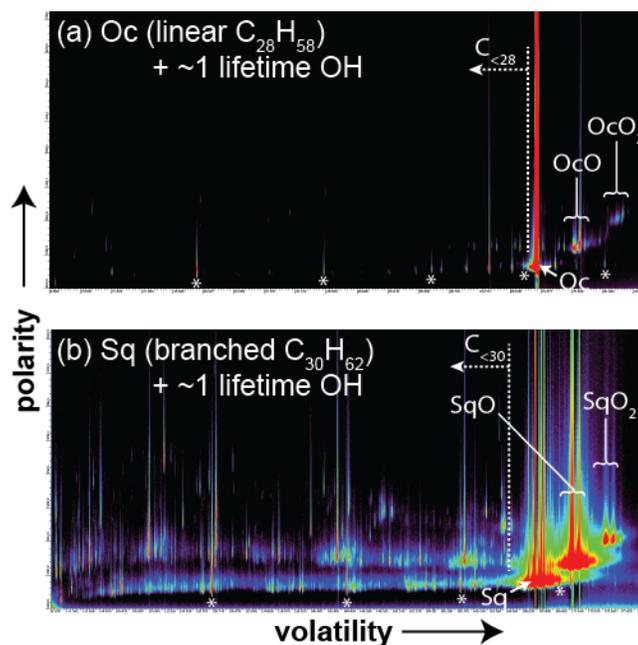
502 produces a peroxy radical, which can react with another peroxy radical either to form an alcohol

503 and a ketone (the Russell mechanism) or two ketones (the Bennett-Summers mechanism), or

504 form two alkoxy radicals. (b) Alkoxy radicals decompose either via H-abstraction (which can be

505 inter- or intramolecular), undergo β -scission, or react with O_2 to form a ketone.

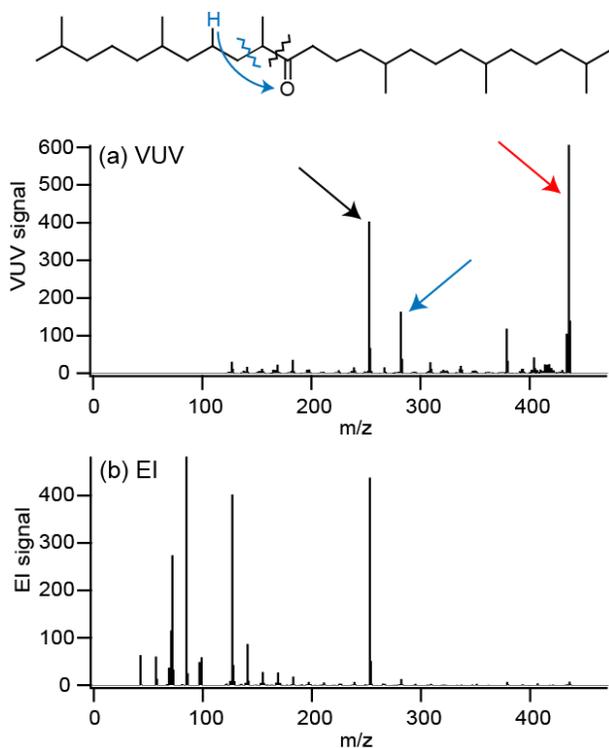
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509 Figure 2. GC×GC EI chromatograms of (a) octacosane (Oc) and (b) squalane (Sq) particles after
 510 ~1 oxidation lifetime (OH exposures of 2.7×10^{12} and 5.7×10^{11} molec cm⁻³ s, respectively).
 511 Internal standards are labeled “*”, and the vertical dotted line separates products that formed via
 512 C-C bond scission of the parent (i.e., fragmentation products, to the left) from those that did not
 513 (i.e., functionalization products, to the right). Regions with one (OcO, SqO) and two (OcO₂,
 514 SqO₂) carbonyl groups added to parent compound are indicated.

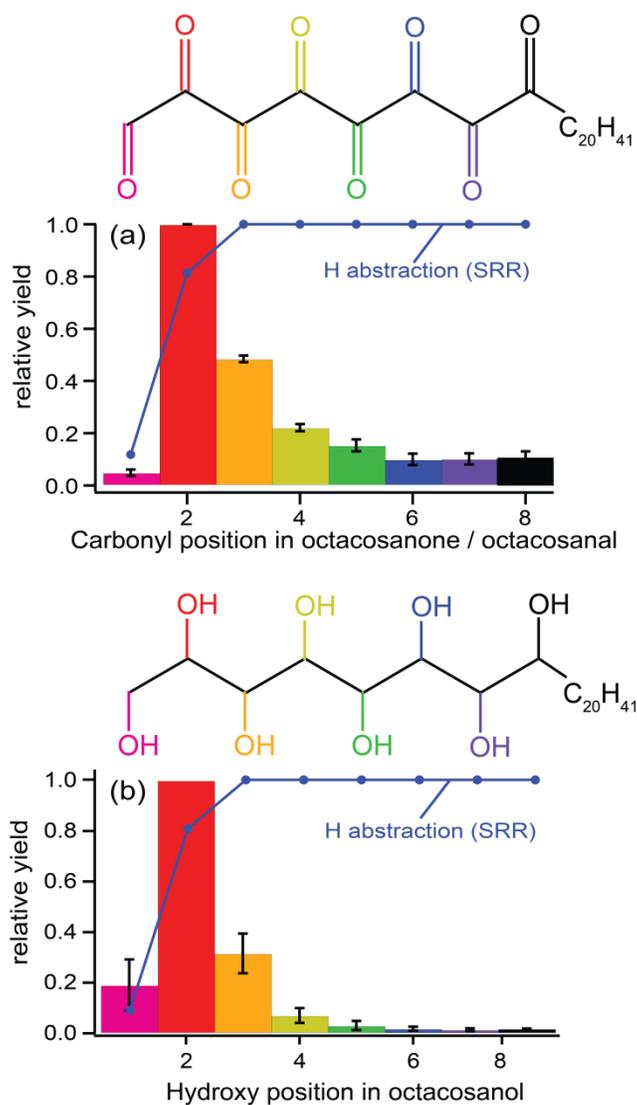
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517 Figure 3. Comparison of mass spectra for squalan-11-one, a first-generation product of the
 518 squalane + OH reaction. (a) VUV (10.5 eV, i.e., soft) ionization. A large signal is seen for the
 519 parent ion ($m/z=436$, red), and relatively few fragments are seen, including an acylium ion
 520 (black) and a McLafferty rearrangement product (blue). (b) EI (70 eV, i.e., hard) ionization.
 521 Essentially no parent ion is observed, and most of the signal is on much smaller mass fragments
 522 that provide less information on the molecular structure.

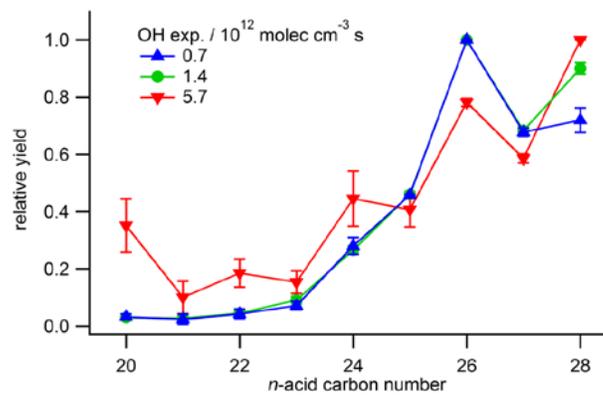
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533 Figure 5. Distribution of positional isomers of octacosane functionalization products. The blue
 534 line shows structure-reactivity relationship (SRR) predictions for gas-phase H abstraction.³⁸ (a)
 535 Octacosanone and octacosanal isomers. (b) Octacosanol isomers.

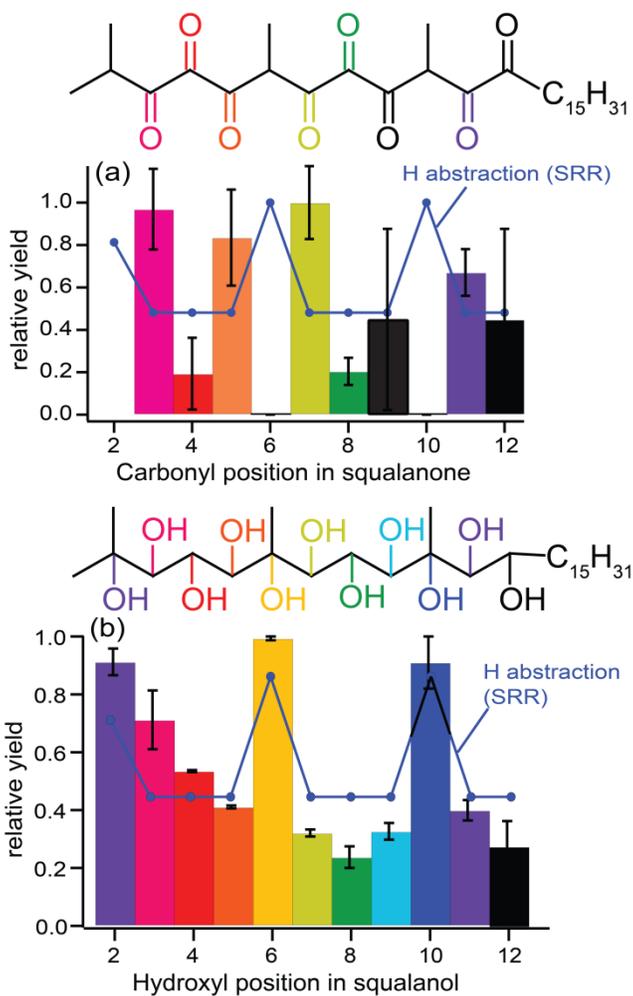
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538 Figure 6. Distribution of n -alkanoic acids in octacosane particles after exposure to gas-phase OH
539 radicals. Error bars indicate the difference in quantifications based on total EI signal and +117
540 ion.

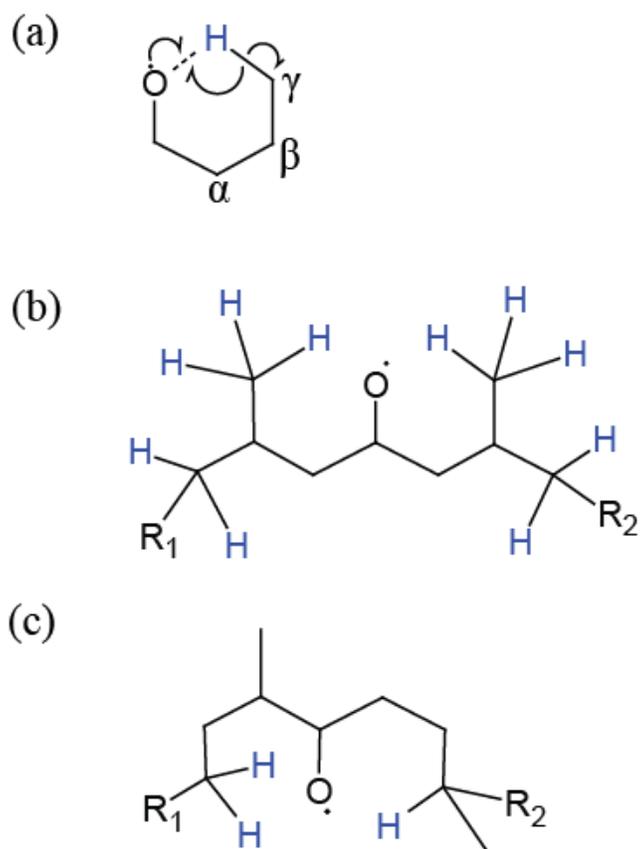
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543 Figure 7. Distribution of positional isomers of squalane functionalization products. The blue line
 544 depicts structure-reactivity relationship (SRR) predictions for gas-phase H abstraction.³⁸ (a)
 545 Squalanone (2,6,10,15,19,23-hexamethyl-tetracosanone) isomers. (b) Squalanol
 546 (2,6,10,15,19,23-hexamethyl-tetracosanol) isomers.

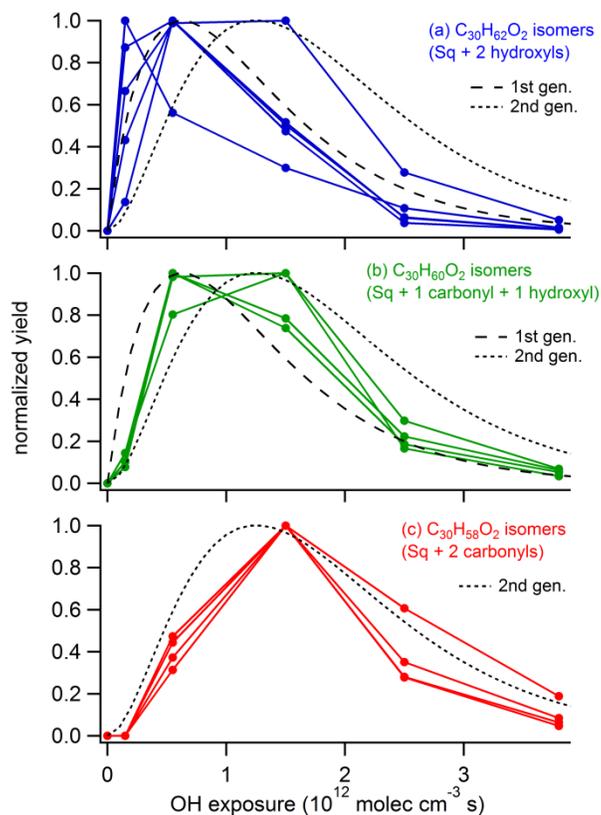
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549 Figure 8. Reaction of alkoxy radicals via isomerization (a), with potential hydrogen atoms to
 550 abstract in blue for (b) β - and (c) α -alkoxy radicals.

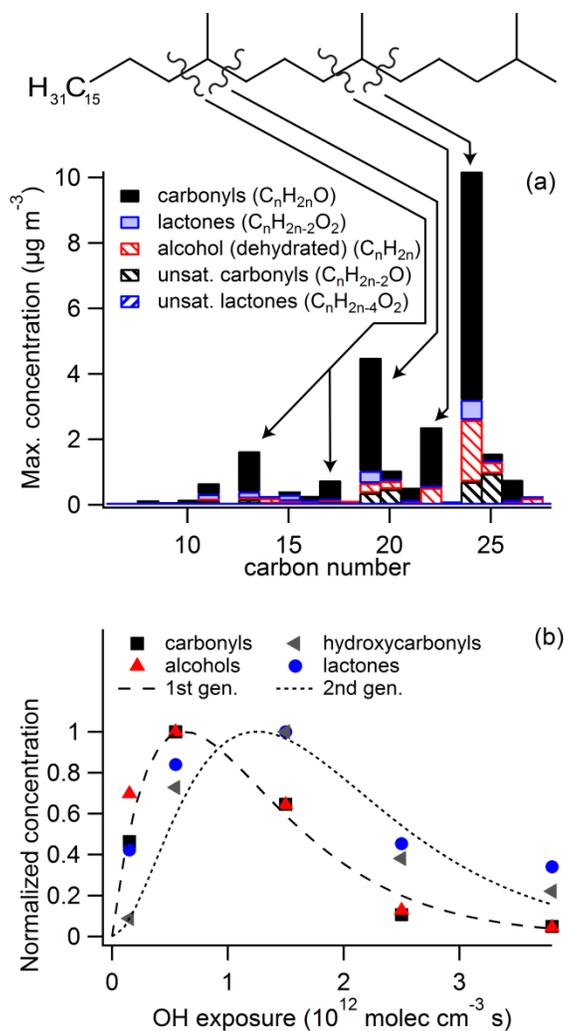
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553 Figure 9. Normalized yields of $C_{30}H_nO_2$ products (squalane precursor) vs. OH exposure. The
 554 dashed lines show the predicted kinetic evolution of first (dashed line) and second (dotted line)
 555 generation products.³⁴ (a) 5 squaladiol isomers. (b) 4 hydroxysqualanol isomers. (c) 4
 556 squaladienes isomers. See text for full compound names.

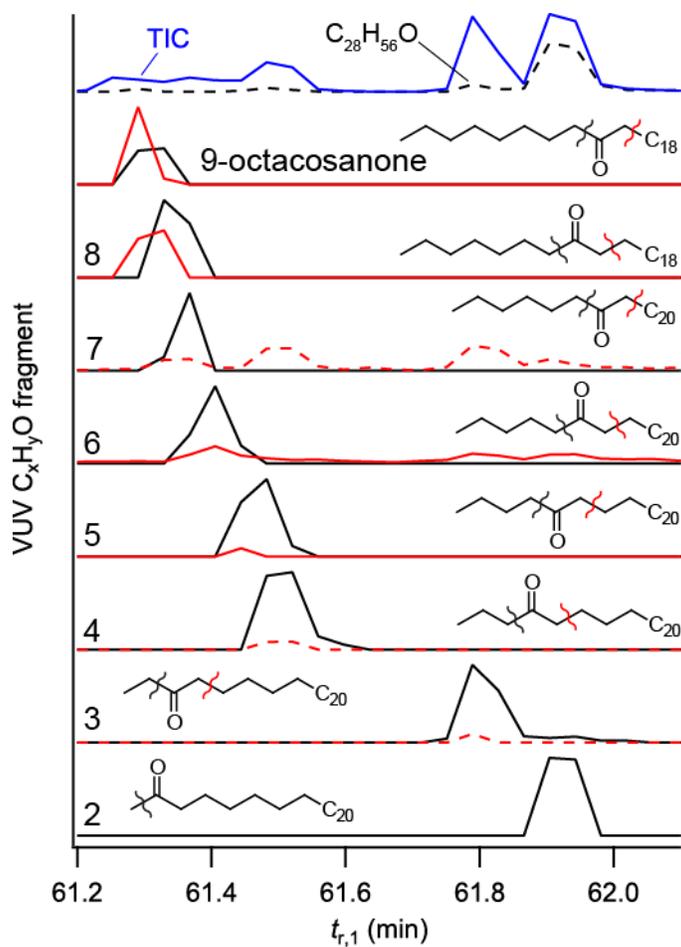
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559 Figure 10. Squalane fragmentation products as a function of: (a) carbon number and (b) OH
 560 exposure with dashed lines showing the kinetic evolution of first and second generation
 561 products.³⁴ Shown above the figure is a schematic of the C-C bonds in squalane that are most
 562 likely to undergo scission.

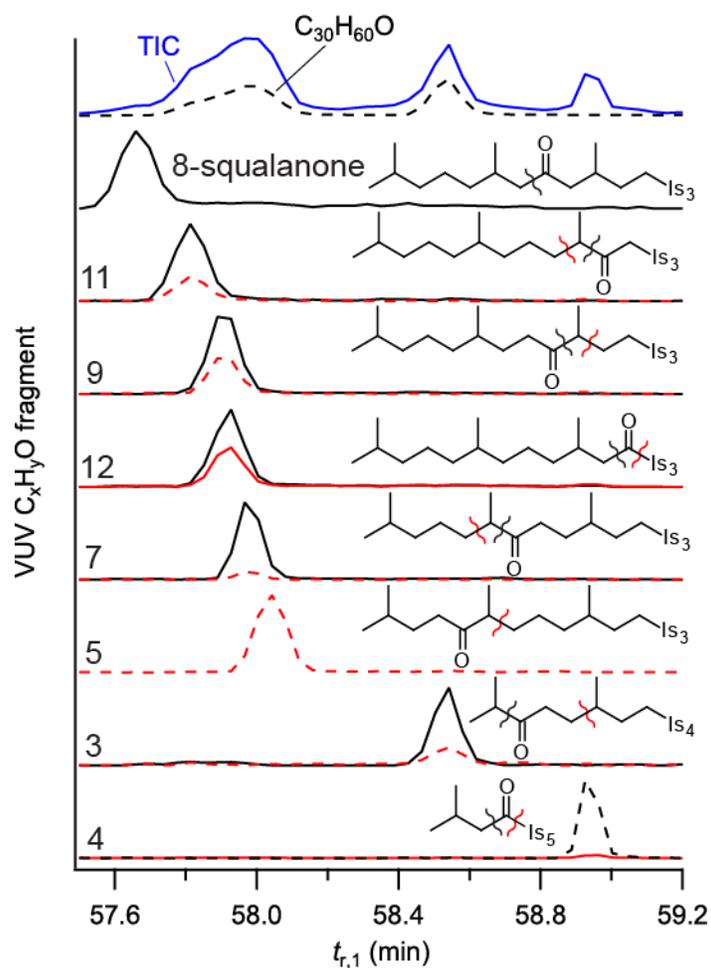
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565 Figure S1. Separation of octacosanone isomers using single-ion VUV chromatograms. Dotted
 566 lines indicate a transfer of a hydrogen atom across the C-C bond scission (i.e., a McLafferty
 567 rearrangement). The total ion chromatogram (TIC) is of the octacosanone region of the GC×GC
 568 chromatogram, and $C_{28}H_{56}O$ is the parent ion.

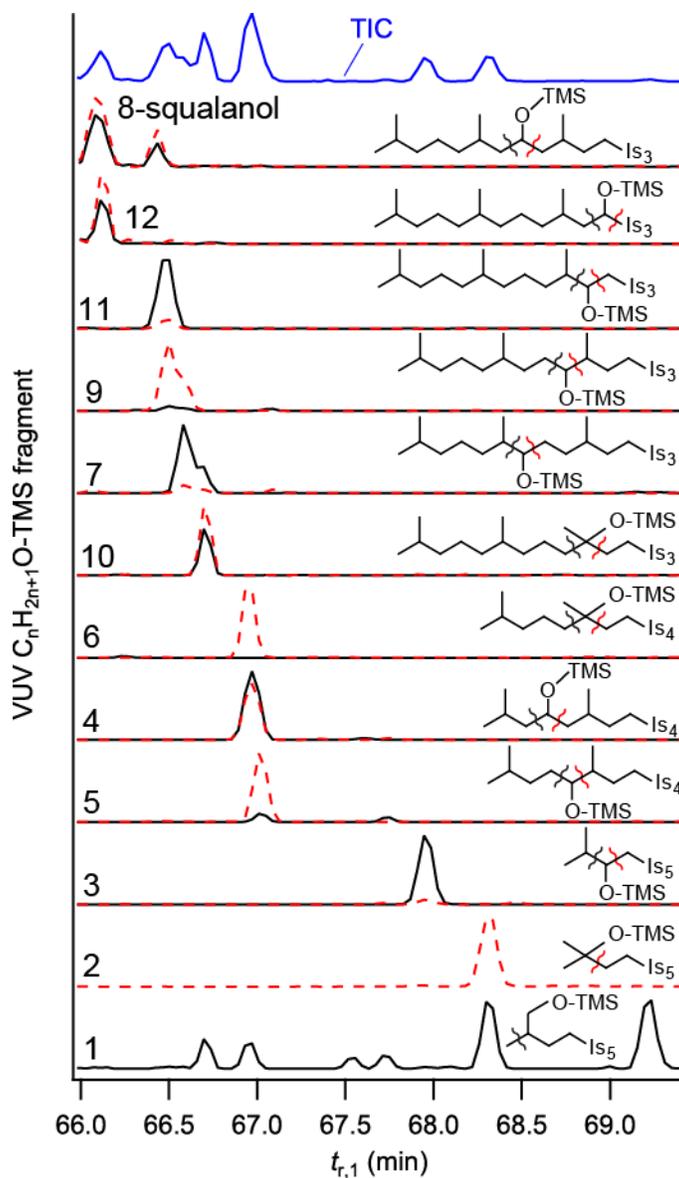
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571 Figure S2. Separation of “squalanone” (2,6,10,15,19,23-hexamethyltetracosanone) isomers using
 572 single-ion VUV chromatograms. Dotted lines indicate a transfer of a hydrogen atom across the
 573 C-C bond scission (i.e., a McLafferty rearrangement). The TIC is of the squalanone region of the
 574 GC×GC chromatogram, and $C_{30}H_{60}O$ is the parent ion. “Is” indicates a C_5H_8 (“isoprene”) unit.

575



582

583 Figure S4. Separation of “squalanol” (2,6,10,15,19,23-hexamethyltetracosanol) isomers using
 584 single-ion VUV chromatograms w/MSTFA derivatization (which replaces –OH groups with –O-
 585 TMS). In VUV, fragmentation tends to break either C-C bond involving the functionalized
 586 carbon atom. The TIC is of the squalanol region of the GC×GC chromatogram. “Is” indicates a
 587 C₅H₈ (“isoprene”) unit.

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