

Anthropogenic Impacts on the Atmosphere

Stability of Monoterpene-Derived #-Hydroxyalkyl-Hydroperoxides in Aqueous Organic Media – Relevance to the Fate of Hydroperoxides in Aerosol Particle Phases

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Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.9b07497 • Publication Date (Web): 04 Mar 2020Downloaded from pubs.acs.org on March 5, 2020**Just Accepted**

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1 **Stability of Monoterpene-Derived α -Hydroxyalkyl-**
2 **Hydroperoxides in Aqueous Organic Media – Relevance to**
3 **the Fate of Hydroperoxides in Aerosol Particle Phases**

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12
13 **ABSTRACT** – The α -hydroxyalkyl-hydroperoxides [R-(H)C(-OH)(-OOH), α -HH] produced in the
14 ozonolysis of unsaturated organic compounds may contribute to SOA aging. α -HHs inherent
15 instability, however, hampers their detection and a positive assessment of their actual role.
16 Here we report, for the first time, the rates and products of the decomposition of the α -HHs
17 generated in the ozonolysis of atmospherically important monoterpenes α -pinene (α -P), *d*-
18 limonene (*d*-L), γ -terpinene (γ -Tn) and α -terpineol (α -Tp) in water:acetonitrile (W:AN)
19 mixtures. We detect α -HHs and multifunctional decomposition products as chloride-adducts
20 by online electrospray ionization mass spectrometry. Experiments involving D₂O and H₂¹⁸O
21 instead of H₂¹⁶O, and an OH-radical scavenger show that α -HHs decompose into *gem*-diols +
22 H₂O₂ rather than free radicals. α -HHs decay mono- or bi-exponentially depending on
23 molecular structure and solvent composition. *e*-fold times, $\tau_{1/e}$, in water-rich solvent mixtures
24 range from $\tau_{1/e}$ = 15-45 min for monoterpene-derived α -HHs to $\tau_{1/e}$ > 10³ min for the α -Tp-

25 derived α -HH. All $\tau_{1/e}$'s dramatically increase in < 20 % (v:v) water. Decay rates of the α -Tp-
26 derived α -HH in pure water increase at lower pH ($2.3 \leq \text{pH} \leq 3.3$). The hydroperoxides
27 detected in day-old SOA samples may reflect their increased stability in water-poor media
28 and/or the slow decomposition of α -HHs from functionalized terpenes.

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30

31 INTRODUCTION

32 The detection of extremely low-volatility organic compounds (ELVOCs)¹⁻³ has gone a long
33 way to explaining how biogenic volatile organic compounds (VOCs) contribute to the
34 formation of secondary organic aerosol (SOA).^{4, 5} ELVOCs are mostly produced during the
35 ozonolysis of monoterpenes (C₁₀H₁₆), particularly those containing endocyclic double bonds
36 such as α -pinene (see Scheme 1),^{2, 6} and condense as nanoparticles. High-resolution chemical
37 ionization mass spectrometry reveals that α -pinene ELVOCs consist of highly oxidized
38 monomeric C_{x=8-10}H_{y=12-16}O_{z=6-12} and dimeric C_{x=17-20}H_{y=26-32}O_{z=8-18} species.^{1, 3} The mechanism of
39 ELVOCs formation proceeds via Criegee intermediates (CIs) that isomerize, fragment or
40 undergo reactions with hydroxylic species such acids, alcohols and water.⁷⁻¹⁰ The
41 fragmentation of CIs produces alkylperoxyl (R'OO·) radicals that undergo fast intramolecular
42 H-transfers into hydroperoxides and second generation R''OO· radicals.^{11, 12} The latter
43 propagate an autoxidation mechanism that produces ELVOCs possessing multiple
44 hydroperoxide functionalities and elevated O/C ratios.¹³⁻¹⁵ CIs also react with water yielding
45 α -hydroxyalkyl-hydroperoxides (R-(H)C(-OOH)(-OH), α -HHs).^{7, 14}

46 Hydroperoxides as a class are thermally unstable,¹⁶⁻¹⁸ and decompose into RO· and HO·
47 radicals via O-O homolysis.^{19, 20} On this basis, it was hypothesized that they would trigger SOA
48 aging via free radical reactions under atmospheric conditions. Previous kinetic studies,
49 however, show that alkyl hydroperoxides in dilute solutions decompose at high temperatures,
50 having $\tau_{1/2} = 10$ h half-lives above 130 °C.¹⁸ The unidentified (hydro)peroxide functionalities
51 contained in the highly oxygenated molecules (HOMs) produced in the ozonolysis of α -pinene
52 (quantified by iodometry)²¹, however, decompose (into unidentified products) in tens of
53 minutes at ambient temperature.²²

54 Clearly, a better understanding of the factors that control the stabilities of
55 hydroperoxides, and the identity of their decomposition products in condensed phases will

56 help assess their actual role in SOA chemistry and, as potential sources of reactive oxygen
57 species (ROS), the toxicity of ambient particulate matter.²³ Here, we investigate the products
58 and decomposition rates of four atmospherically relevant monoterpene-derived α -HHs in
59 aqueous organic solutions at ambient temperature for the first time. Since α -HHs are the least
60 stable hydroperoxides,¹⁸ their lifetimes should provide a lower bound to the lifetimes of
61 hydroperoxides, and insights into structural and matrix effects on α -HHs persistence.

62 Recently, we found that the α -HHs generated from the ozonolysis of the sesquiterpene
63 β -caryophyllene in water:acetonitrile (W:AN) mixtures containing NaCl (an inert cosolute that
64 does not react with O_3 during our experiments) could be detected as chloride-adducts by
65 electrospray ionization mass spectrometry (ESI-MS).^{24, 25} The same study showed that α -HHs
66 decay in a couple of hours in $\geq 20\%$ (v:v) water mixtures, but persist longer than a day in < 10
67 vol % water.²⁵ The goal of the present study is to investigate the effects of chemical structure
68 and other functional groups on the stability of α -HHs. This information may help evaluate the
69 fate of atmospherically relevant α -HHs in general. Here we report the rates of decomposition
70 of α -HHs produced in the ozonolysis of α -pinene (α -P), *d*-limonene (*d*-L), γ -terpinene (γ -Tn),
71 and α -terpineol (α -Tp) (Scheme 1) in W:AN mixtures of variable composition. Our study
72 focuses on α -P as the most abundant biogenic monoterpene, whose global annual emissions
73 (66.1 Tg) vastly exceed those of related β -pinene (18.9 Tg) and limonene (11.4 Tg).²⁶ We take
74 advantage of the high solubility of α -Tp in pure water to investigate the effects of pH on α -
75 HH decay rates. The main findings are that in aqueous organic media monoterpene α -HHs
76 decompose into hydrogen peroxide plus aldehydes rather than free radicals in tens of
77 minutes, with *e*-fold decay times, $\tau_{1/e}$, that depend sensitively on water content and the
78 presence of substituents. The fact that $\tau_{1/e}$'s depend non-linearly on water content for all
79 tested terpenes, strongly suggest that similar behaviors should be expected for the α -HHs
80 produced in aqueous media in the atmosphere. We found that the decomposition of the α -

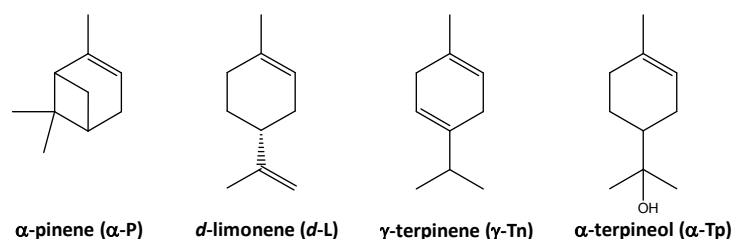
81 Tp-derived α -HH in water is accelerated at lower pH in the range of acidities prevalent in cloud
82 water and aqueous aerosols. The main finding, however, is that hydroperoxides and α -
83 hydroxyalkyl-hydroperoxides may not produce reactive free radicals by thermal^{16, 27-29} or
84 photochemical O-O homolysis under atmospheric conditions.³⁰ Among organic peroxides,
85 only diacyl peroxides could appreciably decompose into free radicals at ambient
86 temperatures.^{18, 31}

87

88

Scheme 1. Chemical Structures of the Monoterpenes Used in the Present Study

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92 EXPERIMENTAL SECTION

93 Figure S1 shows a schematic diagram of our experimental procedure for preparing α -HHs
94 in solution.²⁴ Monoterpenes ($C_{10}H_{16}$, MW 136.13) or α -Tp ($C_{10}H_{16}OH$, MW 154.14) and NaCl
95 were dissolved in 10 mL of W:AN mixtures (10, 20, 30, 40, 50, 60 vol % W for α -P, 20, 50 vol %
96 W for *d*-L, 20, 50 vol % W for γ -Tn, and 50, 100 vol % W for α -Tp) in a glass vial (25 mL). Note
97 that the low solubilities of α -P (0.018 mM)³² and other monoterpenes (except for α -Tp)
98 preclude these studies in neat water. We use W:AN mixtures as surrogates of environmental
99 aqueous SOA due to AN polarity and low reactivity toward O_3 and free radicals (SOA produced
100 from the ozonolysis of α -pinene mainly consists of mixtures of polar hydrophilic species, such
101 as di-carboxylic acids and esters, as well as some high-molecular weight HOMs).³³ O_3 solutions
102 were prepared separately by sparging 10 mL of the same W:AN mixtures in a 25 mL vial with
103 $O_3(g)$ from a commercial ozonizer (KSQ-050, Kotohira, Japan) fed with ultrahigh purity $O_2(g)$

104 (> 99.999%). The ozonizer output gases were carried to the vial using Teflon tubing (3 mm ID)
105 at 1 L/min flow rate (set by a digital mass flow controller) for 5~20 seconds. O₃ concentrations
106 in the sparged solutions, [O₃(sol)], were determined by UV-Vis spectroscopy (Agilent 8453)
107 based on the reported O₃ molar extinction coefficient in the near-UV: $\epsilon_{258\text{nm}} = 3840 \text{ M}^{-1} \text{ cm}^{-1}$
108 in water,³⁴ which is expected to be largely unaffected by the presence of AN.³⁵ Reactions were
109 initiated by mixing terpene and ozone solutions (2.5 mL each) in a glass syringe (5 mL) covered
110 with aluminum foil to avoid the photo-degradation. To minimize unwanted secondary
111 reactions, terpene concentrations were always in excess: $[\text{terpene}]_0/[\text{O}_3(\text{sol})]_0 > 15$. These
112 mixtures were immediately injected (at 100 $\mu\text{L min}^{-1}$ by a syringe-pump, Harvard apparatus)
113 into an ESI mass spectrometer (Agilent 6130 Quadrupole LC/MS Electrospray System at NIES,
114 at Tsukuba). The pH of solutions was measured with a calibrated pH meter (LAQUA F-74,
115 Horiba) before experiments. The evolution of α -HHs and other species were followed by ESI-
116 MS as a function of time, recorded with a digital stopwatch.

117 The prominent feature of our experiments is that the presence of sub-millimolar NaCl
118 allows us to detect by online ESI-MS, and unambiguously establish the molecular mass of α -
119 HHs and other multifunctional species (such as those containing -OOH, -OH and -C=O groups)
120 as chloride adducts without further manipulation.^{7, 36-42} We verified that the monofunctional
121 *tert*-butyl hydroperoxide (TBHP), cumene hydroperoxide (CHP) as well as difunctional 1,6-
122 hexanediol do not produce detectable Cl⁻-adducts in the presence of NaCl. The implication is
123 that species should contain at least three functional groups to be detected as a Cl⁻-adduct by
124 ESI-MS. Chloride-adducts characteristically appear as 3:1 doublets at $m/z = M + 35 (+ 37)$ in
125 the mass spectra.^{7-10, 43, 44} We verified that Cl⁻ is inert toward O₃ ($k \approx 1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) in the
126 time scale of our experiments.³⁶

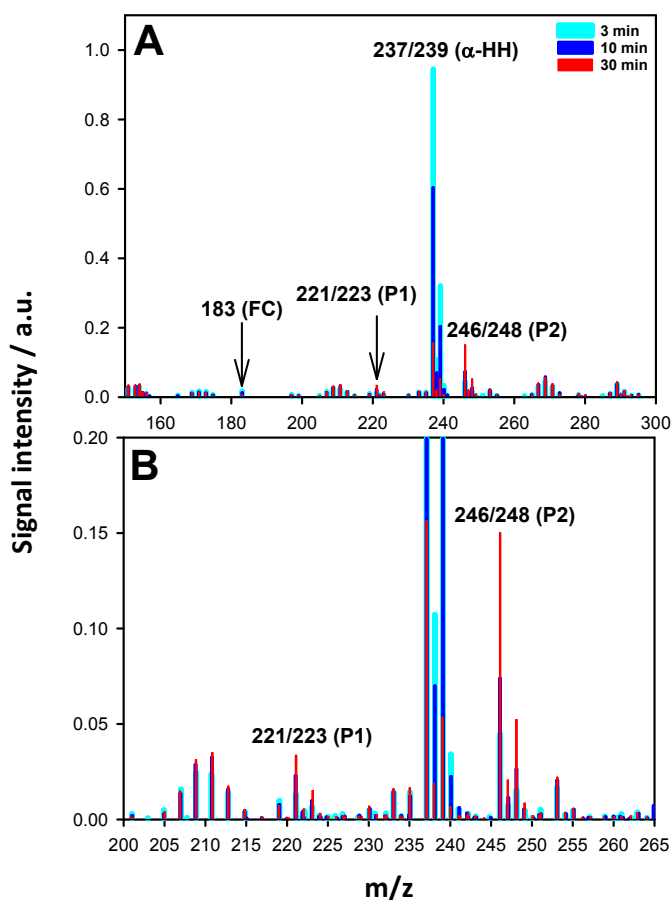
127 The ESI mass spectrometer was operated as follows: nitrogen drying gas flow rate: 12 L min⁻¹
128 ¹; nitrogen drying gas temperature: 340 °C; inlet voltage: + 3.5 kV relative to ground;

129 fragmentor voltage: 60 V. All solutions were prepared in ultrapure water (Resistivity ≥ 18.2
130 $M\Omega$ cm at 298 K) from a Millipore Milli-Q water purification system and used within a day.
131 Chemicals: (-)- α -pinene ($\geq 95\%$, Wako or $\geq 99\%$ Sigma-Aldrich), *d*-limonene ($> 99.0\%$, Tokyo
132 Chemical Industry), γ -terpinene ($> 95.0\%$, Tokyo Chemical Industry), α -terpineol ($> 97.0\%$,
133 Tokyo Chemical Industry), *tert*-butyl hydroperoxide (70 wt. %, Sigma-Aldrich), cumene
134 hydroperoxide ($> 80\%$, Tokyo Chemical Industry), 1,6-hexanediol ($> 97\%$, Tokyo Chemical
135 Industry), acetonitrile ($\geq 99.8\%$, Wako), tetrahydrofuran ($\geq 99.8\%$, stabilizer free, Wako), D_2O
136 (> 99.9 atom % D, Sigma-Aldrich), $H_2^{18}O$ ($\geq 97\%$, Cambridge Isotope Laboratories), NaCl (\geq
137 99.999% , Sigma-Aldrich) and HCl (37 %, ACS reagent, Sigma-Aldrich) were used as received.

138 RESULTS AND DISCUSSION

139 Products of the Ozonolysis of α -Pinene in Water:Acetonitrile Mixtures

140 The products of the ozonolysis of α -P appear as negative ions in the online ESI mass spectra
141 of (1 mM α -P + 0.2 mM NaCl + $[O_3]_0 = 0.03$ mM) solutions in W:AN (50:50 v:v; $[H_2O] = 27.8$ M)
142 mixtures (Fig. 1).



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144

145 **Figure 1** – A) Negative ion ESI mass spectra of (1 mM α -pinene + 0.2 mM NaCl + $[\text{O}_3]_0 = 0.03$ mM) in W:AN
 146 (50:50 by volume) at various times. B) Zooming-in on later-generated products. P1 and P2 correspond to
 147 the chloride-adducts of a gem-diol and a hydroperoxide-cyanohydrin, respectively. FC stands for
 148 functionalized carboxylate. See the text for details.

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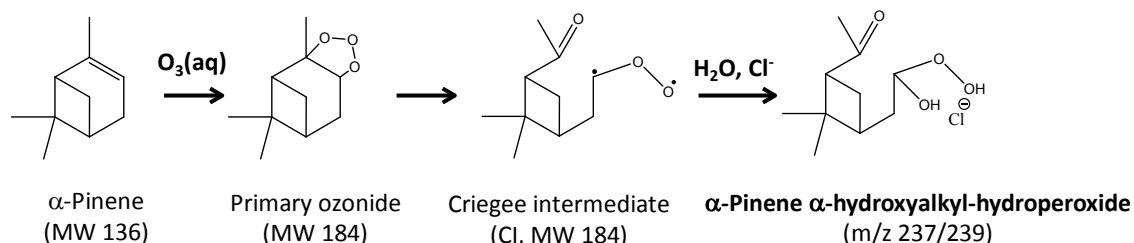
150 O_3 should be consumed by excess α -P in a few milliseconds upon mixing 2.5 mL each of
 151 the (2 mM α -P + 0.4 mM NaCl) and 0.06 mM O_3 solutions. Our estimate is based on assuming
 152 that the reaction rate constants in the gas and liquid phases have similar values, i.e.: $k(\alpha\text{-P} +$
 153 $\text{O}_3)_{\text{liquid}} \approx 6.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, from $k(\alpha\text{-P} + \text{O}_3)_{\text{gas}} = 1.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁴⁵ Hence, O_3
 154 should decay within $\tau_{1/e} \sim 17$ milliseconds in $[\alpha\text{-P}] = 1$ mM solutions. Based on previous
 155 studies,⁴⁶ we propose that O_3 adds to the α -P C=C double bond producing a primary ozonide,^{7,}
 156 ⁴⁷ which opens up into a carbonyl and (in condensed phases) a stabilized Cl (Scheme 2). The
 157 Cl is expected to rapidly isomerize into a functionalized carboxylic acid (detected as a

158 carboxylate, m/z 183) or competitively add water to produce a α -hydroxyalkyl-hydroperoxide
 159 (α -HH) (Scheme 2).⁴⁸

160

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Scheme 2. Mechanism of α -Pinene Ozonolysis in Aqueous Phases ^a



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163

^a Shown are what we consider the most likely structural isomers.

164

165 The intense peaks at m/z 237/239 are therefore assigned to the chloride-adducts of the
 166 α -HH: $237/239 = 136 (\alpha\text{-P}) + 48 (\text{O}_3) + 18 (\text{H}_2\text{O}) + 35/37 (\text{Cl})$, in line with previous experiments
 167 from our laboratory.⁴⁴ The substitution of D_2O and H_2^{18}O for H_2^{16}O and the addition of an OH-
 168 radical scavenger support the assigned stoichiometries (see below). Establishing their
 169 molecular structures would require tandem mass spectrometric studies. The presence of
 170 chloride in the m/z 237/239 and other species is revealed by the characteristic 3-to-1 ratio of
 171 237/239 signal intensities, which corresponds to the ratio of natural abundance $^{35}\text{Cl}/^{37}\text{Cl}$
 172 chlorine isotopes. We also detect species at m/z 221/223 (P1) and 246/248 (P2) (see below)
 173 at longer reaction times (Fig. 1B). Qualitatively similar results were obtained in the ozonolysis
 174 of the monoterpenes *d*-L and γ -Tn (see Figs. S2-S6, Schemes S1 and S2). It should be
 175 emphasized that the absence of commercially available samples of α -HH and the products of
 176 its decomposition precluded determining their relative response factors and, hence,
 177 establishing mass balances from measured mass signal intensities.

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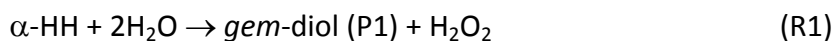
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We verified that the presence of 100 mM tetrahydrofuran (THF) (an efficient OH-radical
 scavenger, $k_{\text{OH}+\text{THF}} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)⁴⁹ in reaction mixtures has negligible effects on the extent
 of reaction or the products distribution: the same product signals appear at m/z 237/239 (α -

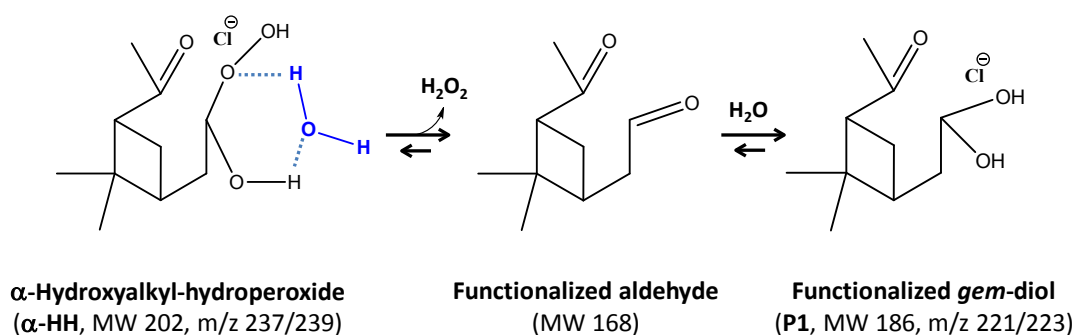
181 HH), m/z 221/223 (P1) and 246/248 (P2) (Fig. S7). This finding excludes the significant
 182 participation of OH-radicals in the formation or destruction of these species.⁵⁰

183 Products of the Ozonolysis of α -Pinene in D_2O :Acetonitrile and $H_2^{18}O$:Acetonitrile Mixtures

184 The shifts of mass signals in D_2O :AN and $H_2^{18}O$:AN solutions are consistent with the
 185 proposed mechanism of α -HH formation (Scheme 2) and decomposition (Scheme 3). The fact
 186 that the $m/z = 237/239$ signals shift by + 2 mass units to m/z 239/241 in both D_2O :AN and
 187 $H_2^{18}O$:AN (Figs. S8 and S9) confirms the participation of one water molecule in the formation
 188 of the α -HH. A second water molecule substitutes an $-O-H$ group for the $-O-O-H$ functionality
 189 by eliminating H_2O_2 and producing an aldehyde whose *gem*-diol can exchange two O-atoms
 190 via a *keto* \rightleftharpoons *gem*-diol equilibrium (Scheme 3). This is confirmed by the finding that the P1
 191 (m/z 221/223) signals shift by + 2 Da to m/z 223/225 in D_2O :AN (Fig. S8), and by + 4 Da to m/z
 192 225/227 in $H_2^{18}O$:AN (Fig. S9). We infer that α -HH decomposes by reacting with water via
 193 reaction R1,



196 **Scheme 3. Mechanism of α -Pinene α -Hydroxyalkyl-Hydroperoxide Reaction with Water ^a**



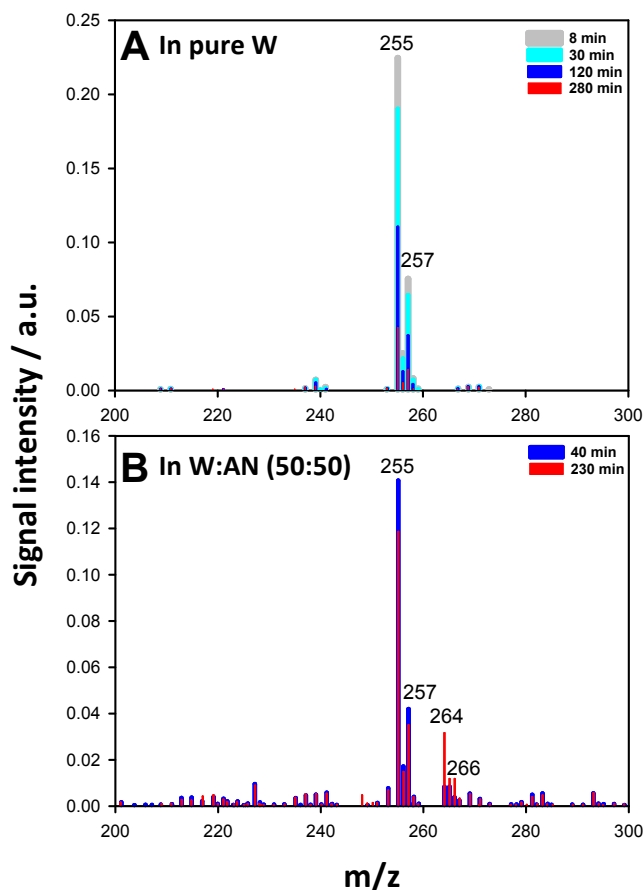
201 ^a Shown are what we consider the most likely among isomers.

202 The P2 m/z 246/248 even mass signals clearly correspond to a species containing one N-
 203 atom. The molecular formula of P2 corresponds to the chloride-adduct of the cyanohydrin

203 resulting from the addition of HCN (an impurity from the partial hydrolysis of AN in W:AN
204 mixtures) to an intermediate species derived from a fast Cl isomerization channel:^{51, 52} $m/z =$
205 $136 (\alpha\text{-P}) + 48 (\text{O}_3) + 27 (\text{HCN}) + 35/37 (\text{Cl}^-) = 246/248$. We tentatively assign to such
206 intermediate a vinyl-hydroperoxide (Scheme S3). The putative vinyl-hydroperoxide
207 intermediate, by having a single -OOH group (such as TBHP and CHP, see above), is not
208 expected to form a Cl-adduct. The reasoning behind this assignment is that the delayed
209 formation of P2 (see Figs. 1 B and 3) implies that HCN does not compete with water for the
210 Cl, but rather reacts with a species simultaneously produced with the formation of the α -HH
211 (Scheme S3). A P2 cyanohydrin containing -OH and -OOH groups that can exchange protons
212 for deuterons accounts for the +2 Da shifts undergone by the 246/248 signals in D₂O:AN (Fig.
213 S8). The +2 Da shifts in H₂¹⁸O:AN mixtures are tentatively ascribed to O-atom exchange
214 between H₂¹⁸O and the carbonyl O-atom of the vinyl-hydroperoxide (Fig. S9). We note that
215 HCN does not add to the carbonyl group of the α -HH (a reaction that would have produced a
216 species appearing at m/z 264/268), possibly because the carbonyl is blocked by
217 intramolecular hydrogen bonding with the -C(-OH)(-OOH) group.

218 **Products of the Ozonolysis of α -Terpineol in Water and Water:Acetonitrile Mixtures**

219 Negative ion mass spectra as functions of time in the ozonolysis of (α -Tp + NaCl) in 100%
220 W and W:AN (50:50) mixtures are shown in Fig. 2. The intense peaks at m/z 255/257 are
221 ascribed to the chloride-adducts of the α -Tp α -HH: $255/257 = 154 (\alpha\text{-Tp}) + 48 (\text{O}_3) + 18 (\text{H}_2\text{O})$
222 $+ 35/37 (\text{Cl}^-)$ (Scheme 4), in line with results for the ozonolysis of α -Tp at the air-water
223 interface.⁵³ The presence of a hydroperoxide-cyanohydrin, detected as a chloride-adduct at
224 $m/z = 264/266 = 154 (\alpha\text{-Tp}) + 48 (\text{O}_3) + 27 (\text{HCN}) + 35/37 (\text{Cl}^-)$, in W:AN (50:50) (Fig. 2B), and
225 its absence in pure W (Fig. 2A) confirms that HCN originates from the partial hydrolysis of AN
226 in W:AN mixtures.



227

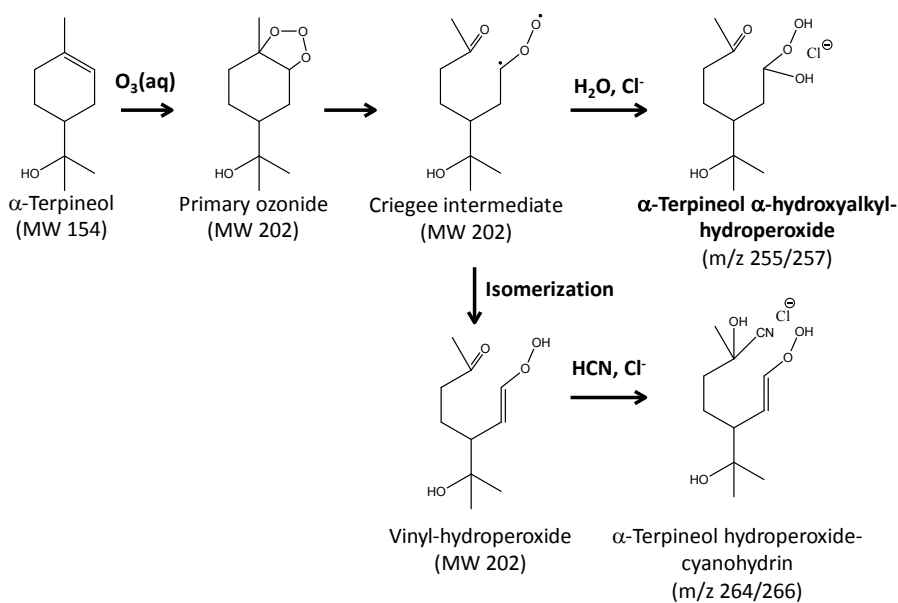
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229 **Figure 2** – A) Negative ion mass spectra of 1 mM α -terpineol + 0.2 mM NaCl + $[O_3]_0 \approx 0.04$ mM in neat
 230 water, B) in a W:AN (50:50) mixture, at various times.

231

232

Scheme 4. Mechanism of the Ozonolysis of α -Terpineol in Water:Acetonitrile ^a



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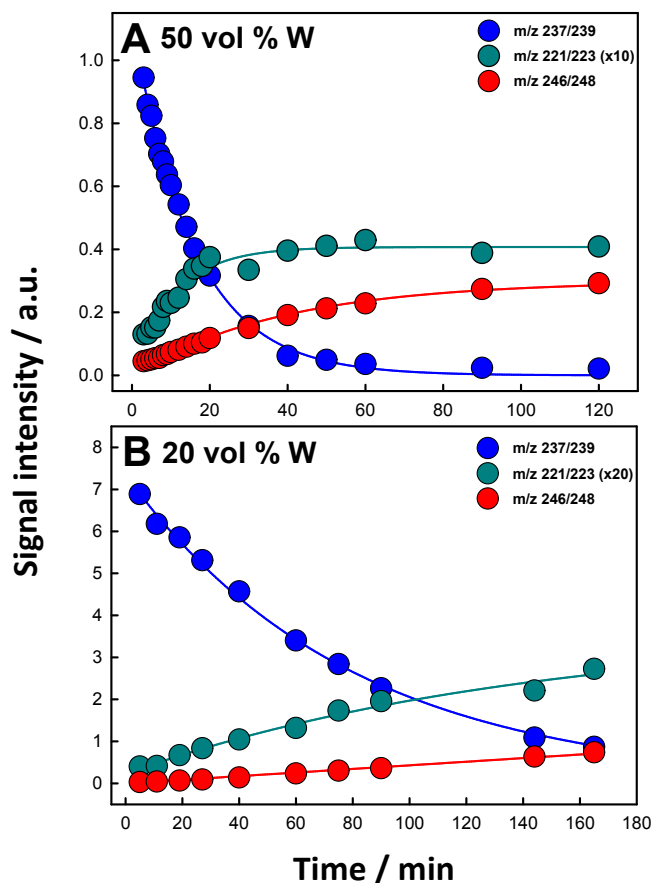
234 ^a Shown are what we consider the most likely among isomers

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236 **Kinetic Experiments**

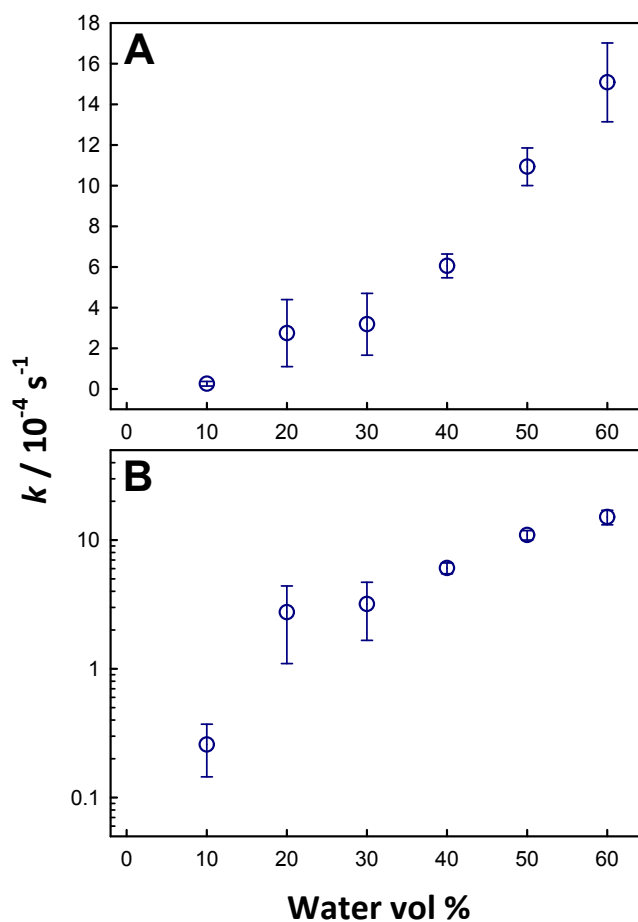
237 The temporal profiles of the detected products of α -P ozonolysis, namely the α -HH (m/z
238 237/239), P1 (m/z 221/223) and P2 (m/z 246/248), in W:AN (50:50, [W] = 27.8 M and 20:80,
239 [W] = 11.1 M) are shown in Figures 3 A and B. In both mixtures, α -HH (m/z 237/239) signals
240 decay as single-exponentials (see below) with rate coefficients: $k_1(20:80) = (2.7 \pm 1.7) \times 10^{-4}$
241 s^{-1} and $k_1(50:50) = (1.1 \pm 0.1) \times 10^{-3} s^{-1}$, the averages of four independent runs. These k_1 values
242 correspond to $\tau_{1/e} = 62$ min and 15 min, respectively. The rate coefficients determined in the
243 present study are summarized in Table 1. In similar experiments, we had found that the α -HH
244 from the ozonolysis of β -caryophyllene (50:50) mixtures decayed in $\tau_{1/e} = 52$ min.²⁵ Inspection
245 of the data in Table 1 and Figure 4 shows that the decay of α -P α -HH becomes significantly
246 slower in solvent mixtures of lower water content. The dependence of k_1 on water content,
247 however, is not linear as it would be expected from water as a reactant in R1. Remarkably,
248 while $\tau_{1/e} = 52$ min in 30% water slightly increases to $\tau_{1/e} = 62$ min in 20% water, the decay of
249 α -HH in 10% water is dramatically different. In the 10% water mixture, α -HH decays by $\sim 35\%$
250 in the first 15 min followed by a much slower decay that extends for hours (Figure S11).

251 It should be realized that if water molecules were homogeneously mixed at the molecular
252 level, the decay of α -HH would be single-exponential function because water participates as
253 a reagent in both the consecutive reactions in Scheme 3. The decay of α -HH signal intensities
254 (S) in (10:90) mixtures is well represented by a bi-exponential function: $S = S_{01} \exp(-k_1 t) + S_{02}$
255 $\exp(-k_2 t)$ (Fig. S11), with $\tau_{1/e} = 1/k_2 = 641$ min (Table 1). The observed fast and slow regimes
256 may be indicative of the availability of water to α -HHs in W:AN water-rich and water-poor
257 domains of molecular dimensions (see below). The α -HHs from *d*-L and β -caryophyllene
258 display a similar behavior in (20:80) and (10:90) mixtures.²⁵



259
260 **Figure 3** – Temporal profiles of the chloride-adducts of the products of α -pinene ozonolysis of (1 mM α -
261 pinene, 1 mM NaCl, $[O_3]_0 = 0.05$ mM) in **A**: (50:50), **B**: (20:80) W:AN mixtures. Blue: α -HH (m/z 237/239);
262 dark cyan: P1 (m/z 221/223); red: P2 (m/z 246/248). P1 signal intensities were multiplied by 10 (A) and 20
263 (B), respectively. Lines correspond to fitting signal intensities (S) vs time with: $S = S_0 \exp(-k_1 t)$ or $S = S_{\max} [1 -$
264 $\exp(-kt)]$ functions. See text for details.

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266

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268 **Figure 4** – A) First-order rate coefficients k_1 of the decay of the chloride-adduct of α -pinene α -HH (m/z
269 237/239) in W:AN mixtures as a function of water volume, at 298 ± 3 K. Data from Table 1. k_1 values
270 derived by fitting α -HH signal intensities (S) vs time with: $S = S_0 \exp(-k_1 t)$, except in the case of the 10 %
271 W mixture where the plotted value is k_2 from: $S = S_{01} \exp(-k_1 t) + S_{02} \exp(-k_2 t)$, fits. See text for details.
272 Error bars are derived from 3-4 independent measurements. B) The semi-log plot shows the dramatic
273 increase of α -HH persistence in 10 % W.

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Table 1- Rate Coefficients of α -HHs Decay in Water:Acetonitrile Mixtures vs Water vol % at 298 ± 3 K

280

Terpene	Water (volume %)	k (10^{-4} s^{-1}) ^a	$\tau_{1/e}$ (minutes)
α -Pinene	10	$0.26 \pm 0.11^*$	641
	20	2.7 ± 1.7	62
	30	3.2 ± 1.5	52
	40	6.1 ± 0.6	27
	50	11 ± 1	15
	60	12 ± 2	14
<i>d</i> -Limonene	20	$1.3 \pm 1.0^*$	128
	50	12 ± 3	14
γ -Terpinene	20	0.48 ± 0.29	347
	50	3.7 ± 1.5	45
α -Terpineol	50	0.16 ± 0.01	1042
	100	1.3 ± 0.4	128
	100 ^b	1.0 ± 0.1	167
β -Caryophyllene ^c	10	$0.031 \pm 0.002^*$	5376
	20	1.4 ± 0.6	119
	30	1.4 ± 0.2	119
	40	1.7 ± 0.4	98
	50	3.2 ± 0.7	52

284

295 ^aRate coefficients are k_1 values derived from experimental α -HH signal intensities (S) fits by single-
 296 exponential decay functions: $S = S_{01} \exp(-k_1 t)$ functions ($\tau_{1/e} = 1/k_1$), except those marked with an asterisk
 297 (*), which correspond to k_2 for the slower component of the observed bi-exponential decays: $S = S_{01} \exp(-$
 298 $k_1 t) + S_{02} \exp(-k_2 t)$ ($\tau_{1/e} = 1/k_2$) ^b In the presence of $1 \mu\text{M FeCl}_2$. ^c From reference 25. See text for details.

299

300 We also analyzed the rise of product signal intensities with time. The evolution of P1 (m/z
 301 221/223) signal intensities with time (Fig. 3) in α -P experiments is well fitted by: $S = S_{\text{max}} [1-$
 302 $\exp(-k_{P1} t)]$ functions. Four independent measurements led to $k_{P1} = (1.6 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ in
 303 (50:50) mixtures, and $k_{P1} (2.0 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$, in (20:80) mixtures. These values compare well
 304 with the $k_1 = (1.1 \pm 0.1) \times 10^{-3}$ and $(2.7 \pm 1.7) \times 10^{-4} \text{ s}^{-1}$ values for α -HH decays in the same
 305 mixtures, confirming that P1 is a direct product of α -HH decomposition. Based on this result
 306 and the P1 mass shifts in $\text{D}_2\text{O:AN}$ and $\text{H}_2^{18}\text{O:AN}$ experiments, we assign P1 to the [1-(3-(2,2-

307 dihydroxyethyl)-2,2-dimethylcyclobutyl) ethenone] *gem*-diol produced from the substitution
308 of an -OH for the -OOH group in α -HH (Scheme 3). Because α -HH signals decay to zero in all
309 cases, except in 10% water, the equilibrium: α -HH = P1 + H₂O₂, is fully shifted to the products
310 side (Scheme 3).⁵⁴ In contrast, the rise P2 (m/z 246/248) signal intensities in (50:50) mixtures:
311 $S = S_{\max} [1 - \exp(-k_{p2}t)]$, corresponds to $k_{p2} = (4.2 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$. This value is about four times
312 smaller than k_1 indicating that P2 is not a product of α -HH decomposition (Scheme 4).

313 To recapitulate, the data of Table 1 reveal that in (50:50) mixtures the α -HHs from α -P
314 and *d*-L decompose into H₂O₂ at comparable rates, which are ~3 times faster than the α -HH
315 from γ -Tn, and ~70 times faster than that from α -Tp. Decay rates markedly increase in a non-
316 linear manner with water content. The α -HH from α -P, the most abundant biogenic
317 monoterpene in the atmosphere, lasts from tens of minutes in > 20% water mixtures to ~9
318 hours in \leq 10% water. Below we show that the rapid conversion of α -HH to H₂O₂ in SOA under
319 atmospheric conditions may preempt its decomposition into free radicals via solar
320 photolysis^{22, 55} or catalyzed by transition metal ions.^{29, 30}

321 We analyze the physicochemical underpinnings of these findings, and their potential
322 implications for the fate and quantification of hydroperoxides in SOA. In the case of α -P, the
323 strong non-linear dependence on water content of the rate constants (k_1 or k_2 , see above) for
324 the α -HH + H₂O reaction (Fig. 4) implies that H₂O is not directly accessible to the α -HH in these
325 solvent mixtures. We had observed a similar non-linear behavior in the decay of the α -HH
326 produced from the ozonolysis of β -caryophyllene.^{25, 56} We propose that this is evidence that
327 α -HHs are produced in discrete domains where water accessibility depends on their structure
328 and water exchange dynamics, rather than in homogeneous media.

329 These domains are generally present in mixtures of water with miscible organic
330 solvents.⁵⁷⁻⁵⁹ This is substantiated by small-angle neutron and dynamic light scattering
331 experiments detect short-lived (< 50 ps), short-ranged (~1 nm) concentration fluctuations in

332 most water-hydrotrope mixtures,⁵⁸⁻⁶⁰ and with recent reactivity and selectivity studies of
333 reactions in these media.^{57, 59} A recent soft X-ray absorption spectroscopic study of W:AN
334 mixtures presented evidence of microheterogeneity.⁶¹ Ab-initio quantum chemical inner-
335 shell calculations suggested that the three distinct regions observed in these mixtures result
336 from the interplay of hydrogen bonding and dipolar interactions between water and
337 acetonitrile molecules.⁶¹ Notably, the discontinuity observed at ≈ 13 vol % W (molar fraction
338 of water $x_w = 0.3$) was ascribed to a transition between phases mainly containing AN-rich large
339 W_nAN_m clusters below $x_w = 0.3$ and smaller clusters held by dipolar interactions above $x_w =$
340 0.3 .⁶¹ We believe that the dramatic increase of α -HH persistence below 20 vol % W is
341 associated with such phase-transition. Additional evidence is provided by the non-linear
342 dependences of the intensity, peak emission wavelength, and decay lifetime of 7-cyanoindole
343 fluorescence in W:AN and other eight W:hydrotrope mixtures as functions of water molar
344 fraction.⁶² The fact that 7-cyanoindole fluorescence in W:AN decayed as a single exponential
345 in the 2-12 ns range, indicated that 7-cyanoindole fluoresced while embedded in the most
346 abundant W_nAN_m clusters of the (n, m) distribution.

347 Against this backdrop, our results suggest that α -HHs (reaction R1) are generated in situ
348 from the ozonolysis of monoterpenes embedded in W_nAN_m clusters rather than dissolved in
349 molecularly homogeneous solutions. The accessibility of H_2O to α -HHs should depend on the
350 composition and rearrangement dynamics of W_nAN_m clusters rather than on the macroscopic
351 concentration of water. In such scenario, the limited rapid initial decay of α -HHs followed by
352 a much slower process in (10:90) mixtures may reflect the (n, m) distribution of W_nAN_m
353 clusters. In (10:90) mixtures, only a few clusters would contain a significant number of water
354 molecules, those accounting for the fast α -HH decay. Since microheterogeneity should be a
355 general phenomenon in “internally mixed” aqueous organic mixtures, we suggest that the
356 existence of inhomogeneities at the molecular level, as distinct from mesoscopic

357 segregation,⁶³⁻⁶⁵ could play unanticipated roles in atmospheric aqueous media.⁵⁶

358 The relatively short lifetimes of the α -HHs derived from the ozonolysis of monoterpenes
 359 relative to the dramatic persistence of the α -HH derived from α -Tp (Table 1 and Fig. S12) is
 360 another unanticipated outcome, because it is difficult to envision a long-range intramolecular
 361 effect (through four bonds) of the -OH group on the reactivity of the R-(H)C(-OH)(-OOH)
 362 group. Even in pure W, the α -Tp-derived α -HH survives for over 2 hours. One possibility is
 363 that water molecules bridge -OH and -OOH groups via extended hydrogen-bonding, thereby
 364 blocking the formation of the six-membered transition state for α -HH decomposition into
 365 aldehyde + H₂O₂ (Scheme 1). Another possibility involves an orientation effect whereby the
 366 polar exo-OH group of α -Tp forces the hydrophobic backbone containing the endo C=C bond
 367 (and, as a result the R-(H)C(-OOH)(-OH) group) to AN-rich cluster cores in W:AN mixtures.⁶¹

368 pH Effects on the Decay Rates of α -Tp-derived α -HH in Pure Water

369 Finally, we investigated the pH dependence (in the pH = 2.3 to 3.3 range, adjusted by HCl
 370 additions) on the kinetics of decomposition of α -Tp-derived α -HH in pure water. The results
 371 are shown in Table 2.

372 **Table 2- Rate Coefficients of α -Tp-derived α -HHs Decay in Water vs pH at $[\alpha\text{-Tp}]_0 = 1$**
 373 **mM, $[\text{O}_3]_0 = 0.06$ mM at 298 ± 3 K.**

α -Terpineol	pH	k_1 (10^{-4} s^{-1})	$\tau_{1/e}$ (minutes) ^a
	2.3	8.7 ± 1.0	19
	2.6	4.4 ± 0.5	38
	3.0	3.0 ± 0.2	56
	3.3	2.5 ± 0.2	66
	6.1 (as is)	1.3 ± 0.4	128

377 ^a $\tau_{1/e} = 1/k_1$

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379 It is apparent that decomposition rates are accelerated at lower pH, implying an acid-

380 catalyzed reaction. This is an important effect, considering that ambient cloud water and
381 aqueous aerosols are more acidic than previously assumed.⁶⁶⁻⁶⁸ This finding is in contrast with
382 the opposite pH effect reported for the decomposition of α -acyloxyalkyl-hydroperoxides,
383 produced from α -P's CIs reactions with pinonic and adipic acids.⁴⁰ Zhao et al. reported the
384 linear increase in the first-order decay rate coefficient as pH increased from 3.5 to 5.1, which
385 is consistent with an OH^- catalyzed decomposition.⁴⁰ The different behaviors may be ascribed
386 to the key role played by the α -OH group in $\text{R}(-\text{H})(-\text{OH})(-\text{OOH})$ decomposition, which is absent
387 in α -acyloxyalkyl-hydroperoxides $\text{R}(-\text{H})(-\text{OR}')(-\text{OOH})$.

388 **Atmospheric Implications**

389 The fast decomposition of monoterpene-derived α -HHs, e.g., $\tau_{1/e} \sim 15$ min in 50 vol %
390 water, suggests that significant losses may occur prior to off-line chemical analyses of SOA
391 samples whether collected in the field or synthesized in the laboratory.^{39, 40, 69} We suggest
392 that discordant results obtained under otherwise similar conditions could be due to variations
393 of depending on relative humidity or water content, to the non-linear dependence of k_1 on
394 water content, and to the onset of the much slower component of bi-exponential decays in <
395 20% water media.

396 Regarding the role of α -HHs in SOA aging, our findings reveal that their decomposition
397 does not yield free radicals but H_2O_2 via reaction R1. R1 preserves the peroxide content and,
398 therefore, the potential toxicity of SOA.^{50, 70, 71} Regarding the putative role of free radicals in
399 SOA aging from the decomposition of RC-OOH hydroperoxides, we point out that thermal
400 decomposition studies in dilute solutions have shown that the homolysis of RO-OH bonds
401 proceeds with $\tau_{1/2} = 10$ h half-lives at temperatures above 130 °C.¹⁸ In other words, neither RC-
402 OOH hydroperoxides nor $\text{R}(-\text{H})\text{C}(-\text{OH})(-\text{OOH})$ α -hydroxyalkyl-hydroperoxides could
403 conceivably produce free radicals in SOA at ambient temperatures. On the other hand, UV-
404 visible spectra of 1 mM β -caryophyllene in W:AN (50:50) before and after ozonolysis (Fig. S13)

405 show that the peak absorption of reaction products occurs at ~ 280 nm, which corresponds to
406 carbonyl chromophores. Thus, the solar photolysis of α -HHs and their products will be
407 dominated by carbonyl rather than peroxide photochemistry.^{22, 72}

408 Fenton-like chemistry is expected to take place in hours rather than in tens of minutes
409 under typical conditions.^{22, 55} From representative values of $[\text{Fe}^{2+}] \sim 10^{-7}$ M, $[\text{ROOH}] \sim 10^{-6}$ M
410 in aqueous aerosol/cloud droplets,^{30, 54} and $k(\text{Fe}^{2+} + \text{ROOH}) \sim 20 \text{ M}^{-1} \text{ s}^{-1}$,²⁹ we estimate $\tau_{1/e} >$
411 14 h for Fenton-like α -HHs decompositions, which is much longer than the $\tau_{1/e} < 1$ h values
412 derived from the data of Table 1. We confirmed the slowness of Fenton-like chemistry in the
413 timeframe of our experiments by showing that the presence of catalytic concentrations of
414 Fe^{2+} did not even accelerate the slow decay of the α -HH derived from the ozonolysis of (1 mM
415 α -Tp + 0.2 mM NaCl + 1 μM FeCl_2) in neat water (Table 1).

416 In summary, we found that the α -HHs derived from the ozonolysis of atmospherically
417 important monoterpenes react with water to produce (*gem*-diols + H_2O_2) rather than free
418 radicals. α -HHs decay mono- or bi-exponentially depending on both molecular structure and
419 solvent composition. $\tau_{1/e}$ in water-rich solvent mixtures range from $\tau_{1/e} = 15$ -45 min for
420 monoterpene-derived α -HHs to $\tau_{1/e} > 10^3$ min for the α -Tp-derived α -HH. Remarkably, all
421 $\tau_{1/e}$'s dramatically increase in < 20 % (v:v) water. The decomposition of the α -Tp-derived α -
422 HH in pure water is accelerated at lower pH in the pH 2.3 to 3.3 range. The residual
423 hydroperoxides detected in day-old SOA samples may reflect the slower components of bi-
424 exponential decays in water-poor media and/or the slow decomposition of α -HHs from
425 functionalized terpenes.

426

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435 **Acknowledgements**

436 S. E. is grateful to the JSPS KAKENHI grant number 19H01154. A.J.C. acknowledges support
437 from the National Science Foundation USA, Grant AGS-1744353.

438 **SUPPORTING INFORMATION**

439 Additional experimental data.

440 **Author Contributions**

441 S.E. designed research; J.Q., Z.L. and S.E. performed experiments; S.E. contributed new
442 reagents/analytic tools; All authors analyzed data and wrote the paper.

443

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