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Reactions of Criegee Intermediates with Alcohols at Air-Aqueous Interfaces

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ABSTRACT –

The fate of Criegee intermediates (CIs) from the gas-phase ozonolysis of unsaturated organic compounds in the troposphere is largely controlled by their reactions with water vapor. We recently found that against all expectations carboxylic acids compete at millimolar concentrations with water for CIs at the air-liquid interface of aqueous organic media. This outcome is consistent with both the low water concentration in the outermost interfacial layers and the enrichment of the competing acids therein. Here we show, via on-line electrospray mass spectrometric detection, that CIs generated in situ in the fast ozonolysis of sesquiterpenes ($C_{15}H_{24}$) on the surface of water:acetonitrile microjets react with $n \geq 4$ linear alcohols $C_nH_{2n+1}OH$ to produce high molecular weight C_{n+15} ethers in one-step. The OH-group of 1-octanol proved to be ~ 25 times less reactive than that of n-octanoic towards CIs at the same bulk molar concentration, revealing that the reactivity of hydroxylic species both depends on acidities and interfacial affinities. CIs interfacial reactions with surface-active hydroxylic species, by bypassing water, represent shortcuts to molecular complexity in atmospheric aerosols.

INTRODUCTION

Ozonolysis of unsaturated hydrocarbons (such as those from massive biogenic terpene emissions) is the leading source of Criegee intermediates (CIs)¹ in the atmosphere. CIs have a major role in atmospheric HOx cycling and in particle formation, particularly over forests.²⁻¹¹ Unsaturated hydrocarbons are also deemed to be reactively uptaken on the surface of acidic aerosols and leaf films,¹²⁻¹⁴ where they would react with O₃(g) to generate CIs therein.¹⁵⁻¹⁶ The fate of the CIs generated on the surface of aqueous organic aerosols, however, is not known. Theoretical calculations predicted that the reaction of the smallest CI (CH₂OO) with water molecules at the air-water interface would proceed ~ 10² - 10³ faster than in the gas-phase.¹⁷ In this regard, we recently found that in the outermost interfacial layers of water/acetonitrile mixtures, as surrogates of aqueous organic aerosol media, long-chain carboxylic acids at millimolar concentrations compete with (H₂O)_n for CIs.¹⁸ We ascribed this finding to the low water concentrations prevalent in the outermost interfacial layers of such mixtures, and to the surface enrichment of the more hydrophobic carboxylic acids. We also found that surface-active *cis*-pinonic acid (CPA), a major product of the ozonolysis of biogenic monoterpenes, is a particularly reactive scavenger of CIs on aqueous surfaces, due to its peculiar molecular geometry that places the reactive hydroxylic – C(O)-OH group close to the interface.¹⁹ Our findings are the more remarkable because in the gas-phase CH₂OO reacts with (H₂O)₂ and C₁-C₂ carboxylic acids at large rate constant ~10⁻¹¹ and ~10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ respectively.²⁰⁻²² The fact that CIs react with organic hydroxylic species in competition with water at air-aqueous interfaces bears directly on the mechanism of organic aerosol accretion and growth, because it amounts to a one-step polymerization process involving large molecules that has not been hitherto considered in chemical models

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3 of secondary organic aerosol formation.²³
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6 Here we report the first direct detection of intermediates and products from
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8 atmospherically relevant alcohols $C_nH_{2n+1}OH$ ($n = 1-8$) reactions with CIs generated on fresh
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10 surfaces of β -caryophyllene (β -C) and α -humulene (α -H) solutions in acetonitrile (AN):water
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12 (W) exposed to $O_3(g)$ for $\sim 10 \mu s$. Long-chain alcohols are ubiquitous surfactants found in a
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14 variety of atmospheric aerosol and sea-surface microlayers²⁴⁻²⁸ and, therefore, their
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16 reactions with CIs will contribute to the formation and augmentation of the chemical
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18 complexity of atmospheric particles and organic microfilms.
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20 21 22 23 **EXPERIMENTAL SECTION**

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25 The experimental setup is essentially the same as that reported elsewhere.^{18, 29} A brief
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27 description follows. We inject [sesquiterpene (β -C or α -H) + alcohol + NaCl] solutions in
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29 acetonitrile:water (AN:W = 4:1 = vol:vol) as microjets into the spraying chamber of an
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31 electrospray mass spectrometer (ES-MS, Agilent 6130 Quadrupole LC/MS Electrospray
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33 System at NIES, Japan) flushed with $N_2(g)$ at 1 atm, 298 K. We chose sesquiterpenes as in
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35 situ sources of CIs due to their high reactivity toward $O_3(g)$,³⁰ which makes them compatible
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37 with the short $\tau_R \sim 10 \mu s$ contact times of our experiments.³¹⁻³³ We use a AN:W solvent
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39 mixture as surrogate of atmospheric aqueous organic aerosols because the composition of
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41 its interfacial layers is well characterized by both theory and experiments.³⁴⁻³⁵ Microjets are
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43 exposed to an orthogonal $O_3(g)$ beam (Fig. 1).
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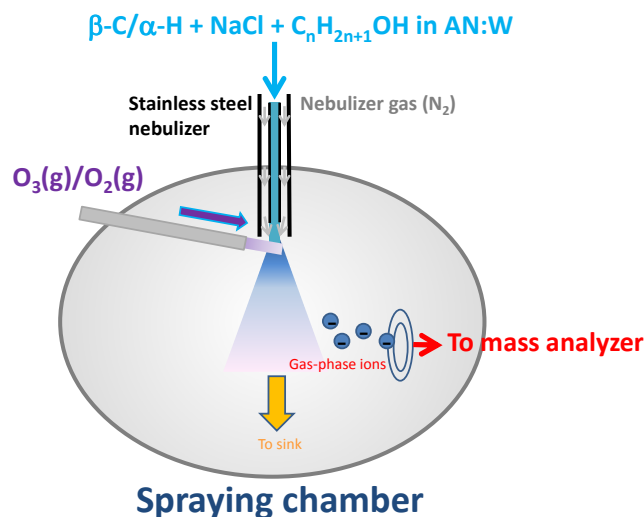


Figure 1 – Schematic diagram of the experimental setup. β -C, α -H, AN and W stand for β -caryophyllene, α -humulene, acetonitrile and water, respectively.

AN:W solutions are pumped (at $100 \mu L \text{ min}^{-1}$) into the spraying chamber through a grounded stainless steel needle ($100 \mu m$ bore) coaxial with a sheath issuing nebulizer $N_2(g)$ at high velocity v_g ($\sim 160 \text{ meter sec}^{-1}$).³⁶ The species detected by ES mass spectrometry are produced in $O_3(g)$ reactive collisions with the surface of the microjets as they emerge from the grounded nozzle.³¹ Previous experiments in our laboratory have demonstrated that mass spectral signal intensities are proportional to interfacial ion populations.^{31-32, 36} We have shown that mass spectra: (1) are not affected by the weak local electric fields at the tip of the grounded nozzle,³⁷⁻³⁸ (2) correspond to species generated by reactions taking place in the outermost interfacial layers of the microjets.^{29, 31-32, 39-40} The limited exposures of microjets to $O_3(g)$ during the short contact times of our experiments: $E = [O_3(g)] \times \tau_R \leq 2.4 \times 10^{11} \text{ molecules cm}^{-3} \text{ s}$, enables us to monitor the earliest reactive events undergone by the CIs generated right at the liquid surface. Note that in our experiments the addition of NaCl lets us detect neutral species as negatively charged chloride-adducts, which are

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3 unambiguously identified by the characteristic $M/M+2 = 3/1$ signal ratios arising from
4 natural abundance $^{35}\text{Cl}:^{37}\text{Cl}::0.75:0.25$ isotopes. We verified that chloride is inert towards
5 $\text{O}_3(\text{g})$ under present conditions.⁴¹⁻⁴² Further experimental details can be found in previous
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10 publications.^{18, 29, 32-33, 36, 40, 43}

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12 Ozone was generated by flowing ultrapure $\text{O}_2(\text{g})$ (> 99.999%) through a silent discharge
13 ozonizer (KSQ-050, Kotohira, Japan) and quantified by online absorption spectrophotometry
14 at 250 or 300 nm (Agilent 8453) prior to entering the reaction chamber. The reported $[\text{O}_3(\text{g})]$
15
16 correspond to the concentrations sensed by the microjets, which are ~12 times smaller than
17 the $[\text{O}_3(\text{g})]$ determined by spectrophotometry due to dilution by the drying N_2 gas-flow.
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19 Conditions in the present experiments were: drying N_2 gas-flow rate: 12 L min^{-1} ; drying N_2
20 gas temperature: $340 \text{ }^\circ\text{C}$; inlet electric potential: + 3.5 kV relative to ground; fragmentor
21 polarization: 60 V. All solutions were prepared in Milli-Q water (Resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$)
22 and used within 48 h. β -caryophyllene ($\geq 98.5 \%$, Sigma-Aldrich), α -humulene ($\geq 96.0 \%$,
23 Sigma-Aldrich), methanol ($\geq 99.9 \%$, Sigma-Aldrich), ethanol ($\geq 99.5 \%$, Wako), 1-propanol (\geq
24 99.7% , Wako), 1-butanol ($\geq 99.9 \%$, Sigma-Aldrich), 1-pentanol ($\geq 99 \%$, Sigma-Aldrich),
25 1-hexanol ($\geq 97 \%$, Wako), 1-heptanol ($\geq 98 \%$, Wako), 1-octanol ($\geq 99 \%$, Sigma-Aldrich),
26 n-octanoic acid ($\geq 97 \%$, Wako), acetonitrile ($\geq 99.8 \%$, Wako), D_2O (99.9 atom % D,
27 Sigma-Aldrich), H_2^{18}O (97%, Santa Cruz Isotope), and NaCl ($\geq 99.999 \%$, Sigma-Aldrich) were
28 used as received.
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47 RESULTS AND DISCUSSION

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49 Fig. 2 shows negative ion electrospray mass spectrum of [1 mM β -C + 0.2 mM NaCl + 100
50 mM 1-octanol] in AN:W (4:1=vol:vol) microjets in the absence and presence of $\text{O}_3(\text{g})$.
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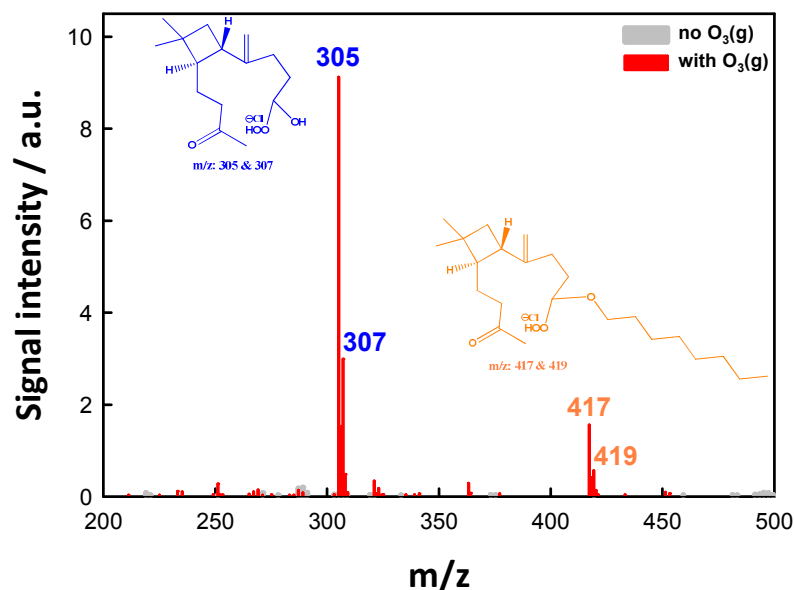
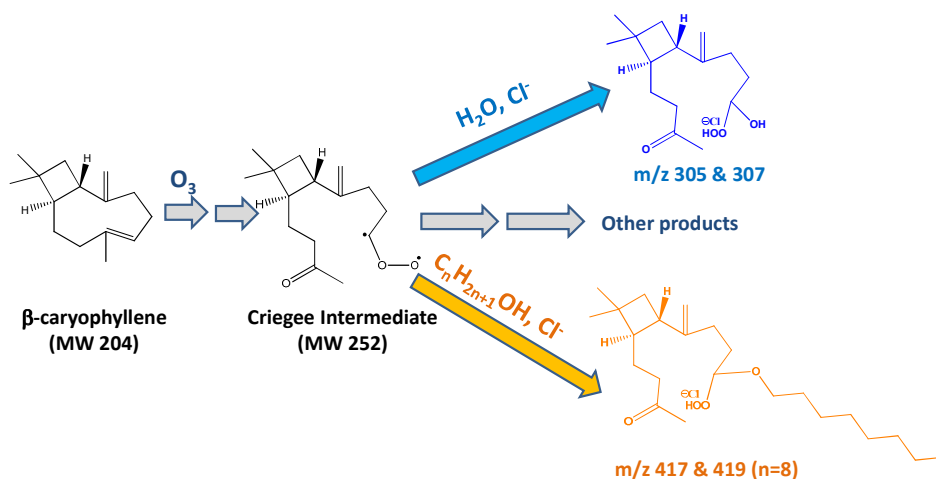


Figure 2 – Negative ion electrospray mass spectra of [1 mM β -C + 0.2 mM NaCl + 100 mM 1-octanol] in AN:W (4:1=vol:vol) microjets before (gray) and after (red) being exposed to $O_3(g)$ ($E = 4.1 \times 10^{10}$ molecules cm^{-3} s) in 1 atm $N_2(g)$ at 298 K. The m/z 305;307 and 417;419 signals correspond to chloride-adducts of C_{15} α -hydroxy-hydroperoxides and C_{23} α -alkoxy-hydroperoxides, respectively. We show the representative structures of possible isomers. See text for details.

In the presence of $O_3(g)$, intense peaks appear at m/z 305;307 and 417;419 in $M/M+2 = 3/1 = {}^{35}Cl/{}^{37}Cl$ ratios (Fig. 2). We had found that the ozonolysis of β -C on AN:W surfaces proceeds ~ 20 times faster than in the bulk liquid saturated with ozone,³⁰ and orders of magnitude faster than in the gas-phase.^{10, 44} We confirmed that 1-octanol is inert toward $O_3(g)$ under present conditions (Fig. S1), in accordance with the negligibly small rate constant: $k_{O_3+1-octanol} \leq 0.8 \text{ M}^{-1} \text{ s}^{-1}$ in bulk water.⁴⁵ The m/z 305;307 signals correspond to species resulting from the addition of O_3 (+ 48) to a β -C (MW = 204) endo C=C bond,^{10, 30} followed by the addition of H_2O (+ 18) and detected as chloride-adducts: 305 (307) = 204 + 48 + 18 + 35 (37).¹⁸ Our observation that (neutral) hydroperoxides form detectable chloride-adducts is in line with the reported strong affinity of chloride for such species.^{7, 46-47}

The m/z 417;419 signals correspond to the products of 1-octanol (MW = 130) addition to CIs: 417 (419) = $204 + 48 + 130 + 35$ (37) (Scheme 1).



SCHEME 1: Reaction mechanism of β -caryophyllene's Criegee intermediate + n -alkanols at air-aqueous interfaces. Here we show representative structures among possible isomers.

Thus, the m/z 417;419 signals are assigned to the α -alkoxy-hydroperoxides (C_{23} ethers) produced from CIs reactions with 1-octanol (Scheme 1). As mentioned above, we recently found that carboxylic acids R_n-COOH ($n \geq 4$) and a surface-active C_{10} keto-carboxylic acid at mM concentrations are able to compete with interfacial water molecules for the CIs derived from the ozonolysis of β -C or α -H on the surface of AN:W.¹⁸⁻¹⁹ Here we find that 1-octanol also competes with interfacial water for CIs to generate a higher mass product (MW 382, detected as m/z 417 and 419) than the m/z = 305 α -hydroxy-hydroperoxides resulting from CIs reactions with $(H_2O)_n$. Similarly, in experiments involving shorter-chain alcohols at the same molar concentrations (Figs. S2 and S3), we detect smaller signals at m/z = $204 + 48 + MW(R_nH_{2n+1}OH, 4 \leq n \leq 7) + 35(37)$ where signal intensity decreases as n decreases (see below). The formation of α -alkoxy-hydroperoxides from CIs reactions with alcohols is consistent with reports on ozonolyses in the gas and bulk liquid phases.^{5, 48-52,53} To our knowledge, this is the first-time report that α -alkoxy-hydroperoxides are produced from CIs reactions with alcohols in the presence of excess water at air-aqueous interfaces. Our

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3 results suggest the involvement of *interfacial* Cls chemistry in the prompt generation of
4 molecular complexity on aqueous organic surfaces. Note that α -hydroxy-hydroperoxides
5 and α -alkoxy-hydroperoxides are much less volatile than their precursors, and can further
6 extend this process into even less volatile species via free radical polymerizations upon
7 thermal or photochemical O-OH bond dissociation,⁵⁴⁻⁵⁵ or by addition to Cls.^{3, 23} Peaks at m/z
8 305;307 and 417;419 appear both in the ozonolysis of β -C and α -H in the presence of
9 1-octanol (Fig. S4), thereby implying that Cls generated in situ will generally react with
10 long-chain alcohols on aqueous organic surfaces.⁵⁶⁻⁵⁹

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12 Additional evidence on the identity and mechanisms of formation of the observed
13 products was obtained from negative ion electrospray mass spectrometry of [β -C + NaCl +
14 1-octanol] in AN:D₂O (Fig. 3A) and AN:H₂¹⁸O (Fig. 3B) microjets in the absence and presence
15 of O₃(g).
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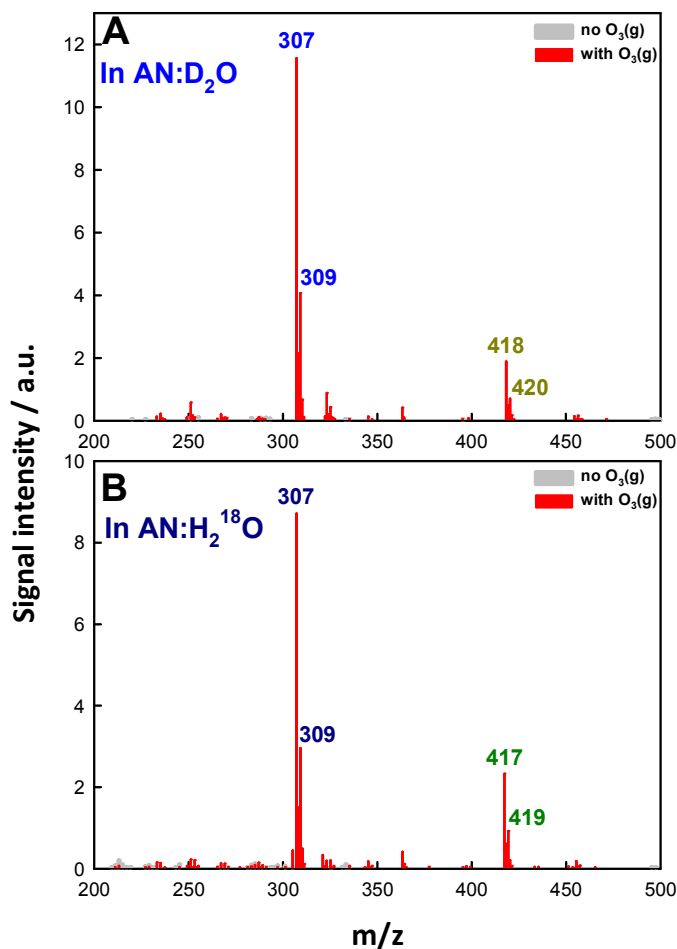


Figure 3 –Negative ion electrospray mass spectra of: (A) [1 mM β -C + 1 mM NaCl + 100 mM 1-octanol] in AN:D₂O (4:1=vol:vol) microjets, (B) [1 mM β -C + 1.3 mM NaCl + 100 mM 1-octanol] in AN:H₂¹⁸O (4:1=vol:vol) microjets before (gray) and after (red) being exposed to O₃(g) ($E = 1.4 \times 10^{11}$ molecules cm⁻³ s).

It is apparent that the $m/z = 305;307$ product signals shift by +2 mass units into $307;309$ signals in both AN:D₂O and AN:H₂¹⁸O (Fig. 3), in accordance with the formation of α -hydroxy-hydroperoxides possessing two exchangeable hydroxylic H-atoms via the incorporation of a single water molecule (Scheme 1).¹⁸ The observation that the $m/z = 417;419$ product signals shift by +1 mass unit into $418;420$ signals in AN:D₂O (Fig. 3A), but do not shift in AN:H₂¹⁸O (Fig. 3B) is consistent with the formation of α -alkoxy-hydroperoxides

(ethers) having a single exchangeable (OO)-H atom (see Scheme 1).

Since the hydrophobic C₂₃-ether products (MW 382, detected as m/z 417 and 419) still have one (in the case of β-C) and two (for α-H) C=C double bond(s), they would be further ozonolyzed leading to higher O/C ratio products.¹⁸ Ethers possessing hydroperoxide -OOH groups could propagate further polymerizations, as indicated above.^{3, 7, 51, 60} Such processes are deemed to contribute to the formation of the exceedingly low-volatility organic compounds (ELVOCs) detected in recent field studies of tropospheric aerosols.^{23, 53, 61-62} Related high molecular weight species were also observed as major products in aerosols produced in the laboratory via α-pinene ozonolysis, and in aerosols collected over boreal forests.^{50, 53}

Fig. 4 shows electrospray mass spectral signals acquired from [1 mM β-C + 0.2 mM NaCl + 100 mM 1-octanol] in AN:W (4:1) microjets exposed to gaseous O₃/O₂ mixtures as functions of O₃(g) exposure.

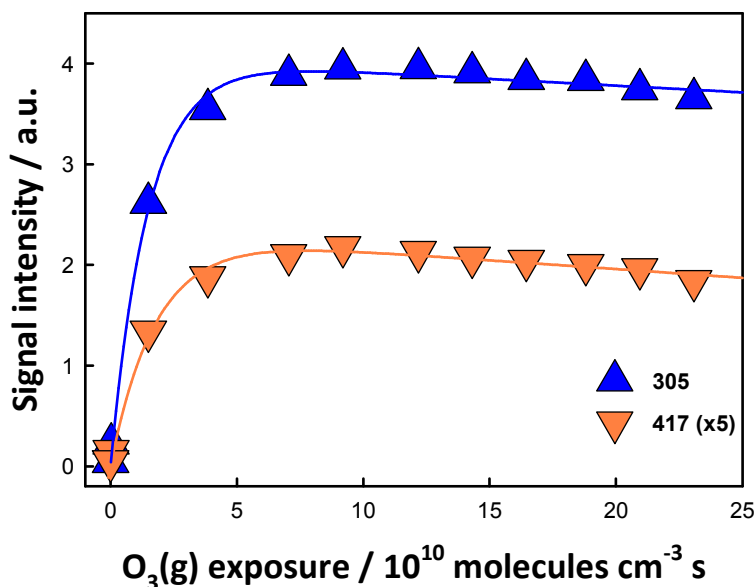


Figure 4 - Mass spectral signal intensities from [1 mM β-C + 0.2 mM NaCl + 100 mM 1-octanol] in AN:W

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3 (4:1=vol:vol) microjets exposed to $O_3(g)$ as functions of $O_3(g)$ exposure (in 10^{10} molecules cm^{-3} s). Plotted
4 m/z 417 signal intensities are fivefold larger than actual values. The lines correspond to double
5 exponential growth function regressions.
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9 Both signals display non-zero initial slopes, as expected from early products generated
10 within the first microseconds. The decline of $m/z = 305$ and 417 signals above $E \sim 1 \times 10^{11}$
11 molecules cm^{-3} s implies that at that point unsaturated products begin to compete for ozone
12 with partially depleted reactant sesquiterpenes in interfacial layers.^{18, 63-64} This in turn
13 implies that interfacial ozonolysis is faster than sesquiterpene diffusion from the bulk
14 solution into interfacial layers. The key finding is that CIs react competitively with 1-octanol
15 and interfacial $(H_2O)_n$ at significantly dissimilar bulk concentration ratios: $[1\text{-octanol}]/[H_2O] =$
16 $100 \text{ mM}/23 \text{ M} \sim 10^{-2}$ (molar fraction of H_2O : $mf_W = 0.42$, in 4:1::AN:W).
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26 We found that the reactivity of alcohols $C_nH_{2n+1}OH$ vs. H_2O towards sesquiterpene CIs at
27 the air-aqueous interface is a strongly increasing function of n . We quantified the
28 competition between $C_nH_{2n+1}OH$ vs. H_2O by the ratio of the mass spectral signal intensities:
29 $m/z = X = 204 + 48 + MW(C_nH_{2n+1}OH) + 35/37$, of the C_{15+n} ether products of $C_nH_{2n+1}OH$
30 reactions with CIs vs. over the m/z 305 signal intensity of the product of CIs reaction with
31 H_2O : $X/305$ and $\ln(X/305)$ as a function of n at constant $O_3(g)$ exposure (Fig. 5).
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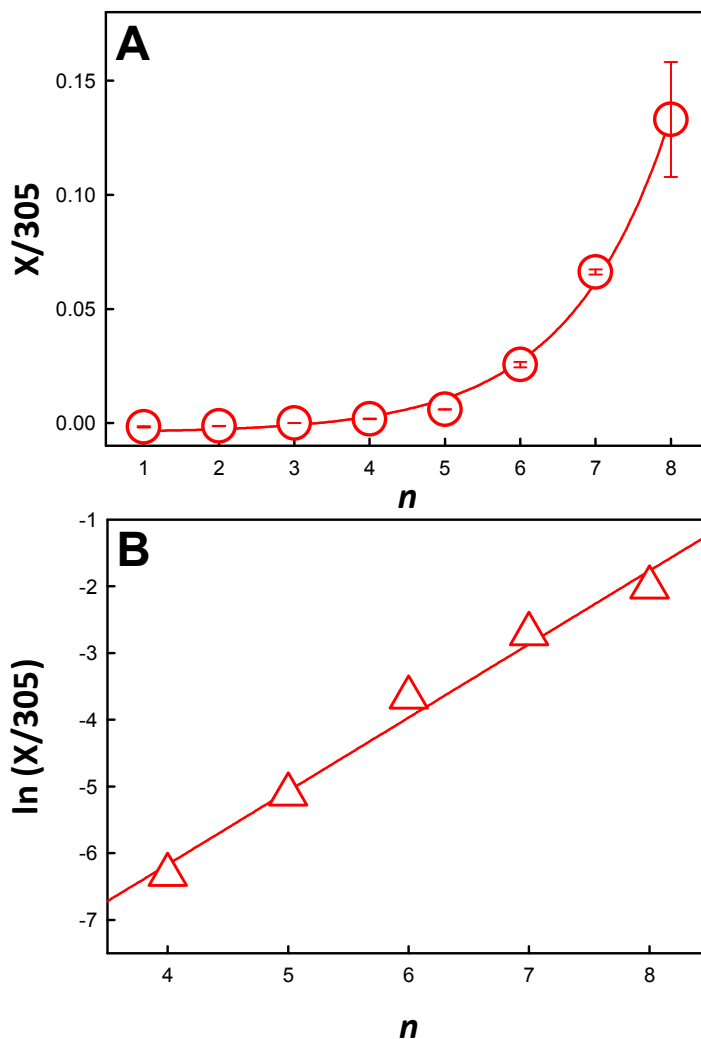


Figure 5 – A) The X/305 ratio of signal intensities and B) $\ln(X/305)$ from [1 mM β -C + 0.2 mM NaCl + 100 mM $C_nH_{2n+1}OH$] in AN:W (4:1 = vol:vol) microjets exposed to $O_3(g)$ ($E \approx 1.4 \times 10^{11}$ molecules cm^{-3} s) as a function of n . $X = 319, 333, 347, 361, 375, 389, 403,$ and 417 for $n = 1, 2, 3, 4, 5, 6, 7,$ and $8,$ respectively. Error bars are derived from duplicate measurements. The line corresponds to a single exponential growth function regression.

The fact that the X/305 ratio is a strongly increasing function of n is consistent with the larger propensity of the longer alkyl chain alcohols for interfacial layers,⁶⁵⁻⁶⁶ and represent direct evidence that our experiments indeed probe interfacial events. The small $n \leq 3$ alcohols in fact did not generate detectable X signals (i.e., within background noise levels).

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3 Our results evoke a recent heterodyne-detected vibrational sum frequency generation
4 (HD-VSFG) study, which revealed that whereas $C_nH_{2n+1}OH$ ($n < 4$) do not affect the structure
5 and orientation of water at the air-water interface, the longer chain $C_nH_{2n+1}OH$ ($n > 4$)
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10 alcohols enhance H-bonding and force H_2O molecules to point their H-atoms to the
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12 gas-phase.⁶⁶ Recently, Walz et al. showed, by using X-ray photoelectron spectroscopy (XPS),
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14 that $C_nH_{2n+1}OH$ interfacial affinities exponentially increase as a function of n . They reported
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16 free energies of $C_nH_{2n+1}OH$ adsorption to the air-water interface $\Delta G_{Ads}(n)$, which range from
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18 -15 to -19 kJ mol^{-1} for $n = 4$ to 6, respectively.⁶⁵ Similarly, we recently determined that the
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20 stabilization energy of R_n-COOH (n -alkanoic acids, $2 \leq n \leq 7$) at the air-water interface
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22 increases by $\approx -0.8 \text{ kJ mol}^{-1}$ per additional $-CH_2-$ group.³²
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25 However, the gas-phase acidity of alcohols also increases exponentially with n (see
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27 below).⁶⁷⁻⁶⁸ In this regard, we found that the X/305 values in Fig. 5 are ~ 20 times smaller
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29 than those we previously reported for the corresponding products of Cls + R_n-COOH
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31 reactions on a molecular basis.¹⁸ This effect is clearly apparent in Fig. 6, which shows
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33 negative ion electrospray mass spectra of [1 mM β -C + 0.2 mM NaCl + 100 mM 1-octanol +
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35 100 mM n -octanoic acid (OA, MW 144)] in AN:W (4:1=vol:vol) microjets in the absence and
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37 presence of $O_3(g)$.
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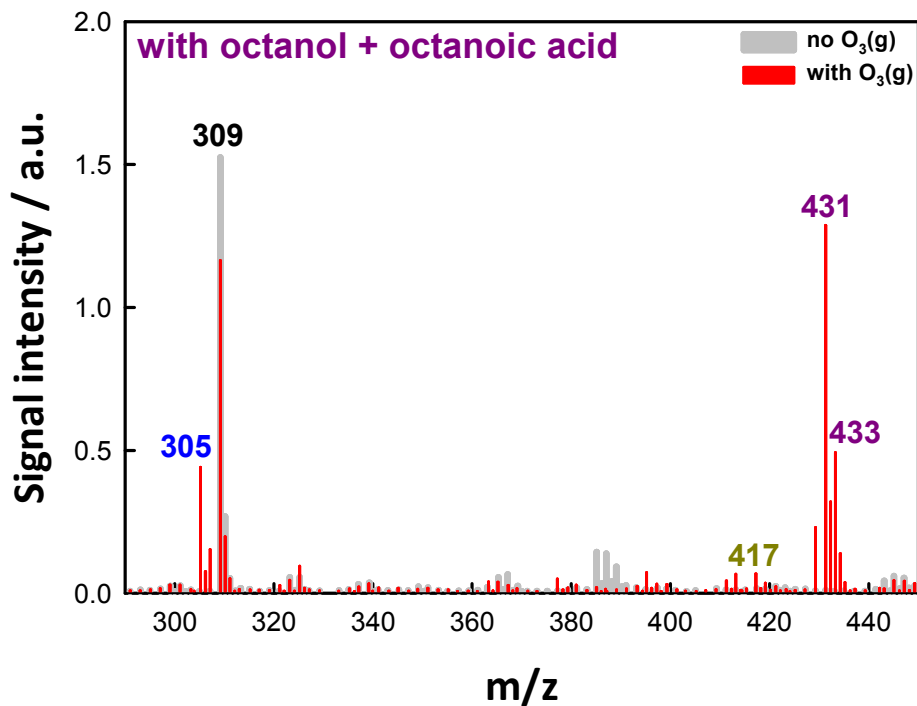


Figure 6 – Negative ion electrospray mass spectra of [1 mM β -C + 0.2 mM NaCl + 100 mM 1-octanol + 100 mM n-octanoic acid] in AN:W (4:1=vol:vol) microjets before (gray) and after (red) being exposed to O₃(g) ($E = 2.3 \times 10^{11}$ molecules cm⁻³ s) in 1 atm N₂(g) at 298 K. The m/z 309 and 431;433 signals correspond to Na(OA)₂⁻ and α -acyloxy-hydroperoxides (C₂₃ esters) from the Cls + OA reaction, respectively. See text for details.

The peaks at m/z 431 and 433 correspond to C₂₃ esters produced from OA addition to Cls: 431 (433) = 204 + 48 + 144 + 35 (37).¹⁸ Note that OA is inert toward O₃(g) in the absence of Cls.⁴⁰ The observation that signal intensities at m/z 417 (and 419) from 1-octanol are ~25 times smaller than those at m/z 431 (and 433) from OA at [1-octanol] = [OA] = 100 mM reveals that 1-octanol is much less reactive than OA toward Cls, although both species are expected to have similar affinities for aqueous surfaces.^{25, 32, 43, 69-70} The C₂₃ ethers and esters produced in each case, by having similar mass and structures (see Scheme 1), are also expected to have similar interfacial affinities. Thus, the dissimilar mass spectral signal intensities in Fig. 6 are bona fide representations of the relative reactivities of n-alkanols vs

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4 n-alkanoic acids homologues toward Cls, and highlight the role of acidity in these processes.
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6 This finding is in line with gas-phase reaction rate constants of Cls + HCOOH/CH₃COOH,
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8 which approach collisionally controlled values: $k \geq 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,²² vs. the much
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10 smaller values for Cls + methanol/2-propanol.^{48, 50, 68} Tobias and Ziemann have reported that
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12 rate constants of gas-phase C₁₃ Cls reactions with various species increase in the order:
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14 water < methanol < 2-propanol < formaldehyde < formic acid < heptanoic acid, over a 10⁴
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16 range.⁶⁸ Remarkably, the reactivity of Cls toward these hydroxylic compounds is not
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18 determined by their O-H bond dissociation energies but correlates with their gas-phase
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20 acidities, thereby suggesting polar transition states involving zwitterionic Cls.⁶⁸ Our results
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22 are in excellent accordance with Tobias and Ziemann's findings, and strongly suggests that
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24 Cls reactions with hydroxylic compounds at gas-aqueous interfaces proceed by a similar
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26 mechanism. This is confirmed by Fig. 7, where we plotted $\ln(X/305)$ vs. gas-phase $\Delta G_{\text{acidity}}$
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28 values for C_nH_{2n+1}OH (n ≥ 4) alcohols. Recall that gas-phase acidity is the negative of the
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30 Gibbs free energy associated with deprotonation, i.e., the smaller absolute $\Delta G_{\text{acidity}}$ values
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32 correspond to the more acidic species. The exponential dependence of X with gas-phase
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34 $\Delta G_{\text{acidity}}$ values for C_nH_{2n+1}OH (n =1-8), which range from 1563 kJ mol⁻¹ (n=1) to 1525 kJ mol⁻¹
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36 (n=8), is consistent with Tobias and Ziemann's findings and suggest similar reaction media in
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38 both cases, supporting our argument that the low water density at air-aqueous interfaces is
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40 a key factor underlying our observations.⁶⁸ From this perspective, the results of Fig. 6 are
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42 consistent with the smaller gas-phase $\Delta G_{\text{acidity}}$ values for the n-alkanoic acids vs those for the
43
44 n-alkanols: $\Delta G_{\text{acidity}} = 1429 \text{ kJ mol}^{-1}$ (n=1) to 1418 kJ mol^{-1} (n=6) for R_n-COOH.^{67, 68, 71}
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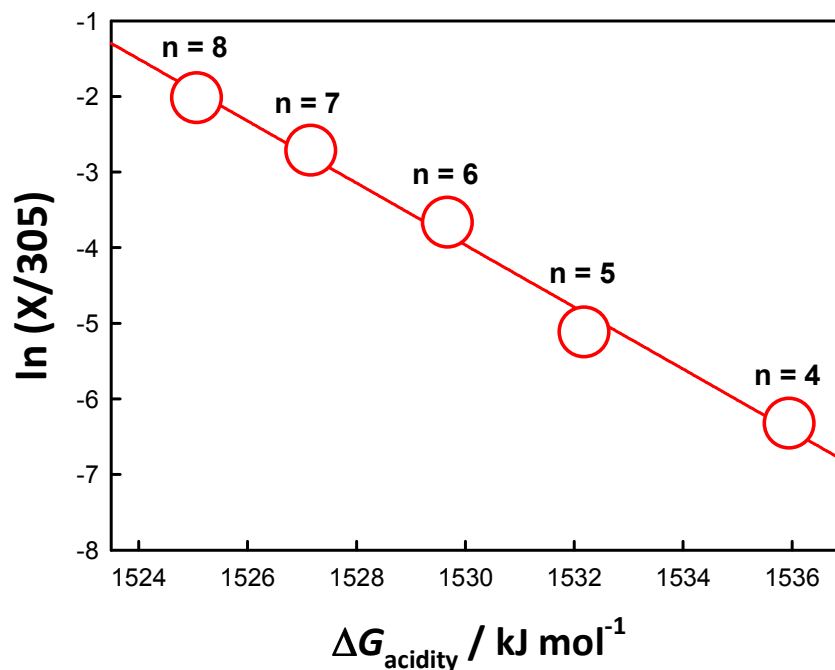


Figure 7 – A $\ln (X/305)$ plot from [1 mM β -C + 0.2 mM NaCl + 100 mM $C_nH_{2n+1}OH$ ($n \geq 4$)] in AN:W (4:1 = vol:vol) microjets exposed to $O_3(g)$ ($E \approx 1.4 \times 10^{11}$ molecules cm^{-3} s) as a function of gas-phase $\Delta G_{\text{acidity}}$ values from Ref 67.

Thus, the significant $\Delta G_{\text{acidity}}$ differences (≥ 100 kJ mol^{-1}) between alcohols vs. carboxylic acids is what determines their relative reactivities towards Cls. Therefore, both the increasing interfacial affinities and acidities of the larger $C_nH_{2n+1}OH$ mostly contribute to the strong X/305 vs. n dependence in Fig. 5.

Our experiments simulate a rapid ozonolysis process in which $O_3(g)$ initially sticks to the surface of aqueous organic aerosols in the presence of unsaturated hydrocarbons and ubiquitous alcohols. We found that the heterogenous ozonolysis of a solution of sesquiterpenes plus n -alkanols in AN:W leads to higher mass products, such as α -hydroxy-hydroperoxides and α -alkoxy-hydroperoxides (C_{15+n} ethers). Since long-chain alcohols are ubiquitous amphiphilic species found in atmospheric aerosols and sea-surface microlayers,²⁴⁻²⁸ the interfacial chemistry on Cls involving alcohols would contribute to the

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3 growth/augmentation of atmospheric particles and to the formation of increasingly complex
4 organic microfilms.
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8 9 10 **Conclusion**

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12 Our experiments show that Criegee intermediates produced in the ozonolysis of
13 sesquiterpenes in the interfacial layers of aqueous organic media react with long-chain
14 $C_nH_{2n+1}OH$ ($n \geq 4$) alkanols to produce high mass species (C_{15+n} ethers). Our results suggest
15 that the reduced water concentration in interfacial layers relative to the bulk liquid makes
16 amphiphilic components of aqueous organic aerosol competitive substrates for Criegee
17 intermediates generated therein. The CIs chemistry we observe on aqueous organic surfaces
18 provides direct pathways to exceedingly low-volatility organic compounds (ELVOCs). From
19 this perspective, our findings provide new insights into how to narrow down the mismatch
20 between field observations and atmospheric model calculations regarding the evolution of
21 chemical complexity in organic aerosols. We found that among C_n hydroxylic molecules,
22 alcohols are significantly less reactive than carboxylic acids towards CIs, and show that their
23 reactivities depend both on interfacial affinities and gas-phase acidities.
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40 **SUPPORTING INFORMATION**

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42 Additional experimental data. This material is available free of charge via the Internet.
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47 **Author Contributions**

48
49 S.E. designed and performed research; S.E and A.J.C. analyzed data and wrote the paper.
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52

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REFERENCES

1. Criegee, R., Mechanism of Ozonolysis. *Angew. Chem. Internat. Edit.* **1975**, *14*, 745-752.
2. Hatakeyama, S.; Akimoto, H., Reactions of Criegee Intermediates in the Gas-Phase. *Res. Chem. Intermed.* **1994**, *20*, 503-524.
3. Sakamoto, Y.; Yajima, R.; Inomata, S.; Hirokawa, J., Water Vapour Effects on Secondary Organic Aerosol Formation in Isoprene Ozonolysis. *Phys. Chem. Chem. Phys.* **2017**, *19*, 3165-3175.
4. Nguyen, T. B., et al., Atmospheric Fates of Criegee Intermediates in the Ozonolysis of Isoprene. *Phys. Chem. Chem. Phys.* **2016**, *18*, 10241-10254.
5. Yao, L.; Ma, Y.; Wang, L.; Zheng, J.; Khalizov, A.; Chen, M. D.; Zhou, Y. Y.; Qi, L.; Cui, F. P., Role of Stabilized Criegee Intermediate in Secondary Organic Aerosol Formation from the Ozonolysis of Alpha-Cedrene. *Atmos. Environ.* **2014**, *94*, 448-457.
6. Taatjes, C. A.; Shallcross, D. E.; Percival, C. J., Research Frontiers in the Chemistry of Criegee Intermediates and Tropospheric Ozonolysis. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1704-1718.
7. Sakamoto, Y.; Inomata, S.; Hirokawa, J., Oligomerization Reaction of the Criegee Intermediate Leads to Secondary Organic Aerosol Formation in Ethylene Ozonolysis. *J. Phys. Chem. A* **2013**, *117*, 12912-12921.
8. Mauldin, R. L.; Berndt, T.; Sipila, M.; Paasonen, P.; Petaja, T.; Kim, S.; Kurten, T.; Stratmann, F.; Kerminen, V. M.; Kulmala, M., A New Atmospherically Relevant Oxidant of Sulphur Dioxide. *Nature* **2012**, *488*, 193-196.
9. Beck, M.; Winterhalter, R.; Herrmann, F.; Moortgat, G. K., The Gas-Phase Ozonolysis of Alpha-Humulene. *Phys. Chem. Chem. Phys.* **2011**, *13*, 10970-11001.
10. Winterhalter, R.; Herrmann, F.; Kanawati, B.; Nguyen, T. L.; Peeters, J.; Vereecken, L.; Moortgat, G. K., The Gas-Phase Ozonolysis of Beta-Caryophyllene (C₁₅H₂₄). Part I: An Experimental Study. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4152-4172.
11. Huang, H. L.; Chao, W.; Lin, J. J. M., Kinetics of a Criegee Intermediate That Would Survive High Humidity and May Oxidize Atmospheric So₂. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 10857-10862.
12. Matsuoka, K.; Sakamoto, Y.; Hama, T.; Kajii, Y.; Enami, S., Reactive Uptake of Gaseous Sesquiterpenes on Aqueous Surfaces. *J. Phys. Chem. A* **2017**, *121*, 810-818.
13. Enami, S.; Mishra, H.; Hoffmann, M. R.; Colussi, A. J., Protonation and Oligomerization of Gaseous Isoprene on Mildly Acidic Surfaces: Implications for Atmospheric Chemistry. *J. Phys.*

1
2
3 *Chem. A* **2012**, *116*, 6027-6032.

4 14. Enami, S.; Hoffmann, M. R.; Colussi, A. J., Dry Deposition of Biogenic Terpenes via Cationic
5 Oligomerization on Environmental Aqueous Surfaces. *J. Phys. Chem. Lett.* **2012**, *3*, 3102-3108.

6 15. Spielmann, F.; Langebner, S.; Ghirardo, A.; Hansel, A.; Schnitzler, J. P.; Wohlfahrt, G.,
7 Isoprene and Alpha-Pinene Deposition to Grassland Mesocosms. *Plant Soil* **2017**, *410*, 313-322.

8 16. Potier, E.; Loubet, B.; Durand, B.; Flura, D.; Bourdat-Deschamps, M.; Ciuraru, R.; Ogée, J.,
9 Chemical Reaction Rates of Ozone in Water Infusions of Wheat, Beech, Oak and Pine Leaves of
10 Different Ages. *Atmos. Environ.* **2017**, *151*, 176-187.

11 17. Zhu, C. Q.; Kumar, M.; Zhong, J.; Li, L.; Francisco, J. S.; Zeng, X. C., New Mechanistic
12 Pathways for Criegee-Water Chemistry at the Air/Water Interface. *J. Am. Chem. Soc.* **2016**, *138*,
13 11164-11169.

14 18. Enami, S.; Colussi, A. J., Criegee Chemistry on Aqueous Organic Surfaces. *J. Phys. Chem.*
15 *Lett.* **2017**, *8*, 1615-1623.

16 19. Enami, S.; Colussi, A. J., Efficient Scavenging of Criegee Intermediates on Water by
17 Surface-Active Cis-Pinonic Acid. *Phys. Chem. Chem. Phys.* **2017**, DOI: 10.1039/C7CP03869K.

18 20. Long, B.; Bao, J. L.; Truhlar, D. G., Atmospheric Chemistry of Criegee Intermediates:
19 Unimolecular Reactions and Reactions with Water. *J. Am. Chem. Soc.* **2016**, *138*, 14409-14422.

20 21. Lee, Y. P., Perspective: Spectroscopy and Kinetics of Small Gaseous Criegee Intermediates. *J.*
21 *Chem. Phys.* **2015**, *143*, 020901.

22 22. Welz, O., et al., Rate Coefficients of C1 and C2 Criegee Intermediate Reactions with Formic
23 and Acetic Acid near the Collision Limit: Direct Kinetics Measurements and Atmospheric
24 Implications. *Angew. Chem. Int. Edit.* **2014**, *53*, 4547-4550.

25 23. Barsanti, K. C.; Kroll, J. H.; Thornton, J. A., Formation of Low-Volatility Organic Compounds
26 in the Atmosphere: Recent Advancements and Insights. *J. Phys. Chem. Lett.* **2017**, *8*, 1503-1511.

27 24. Donaldson, D. J.; Vaida, V., The Influence of Organic Films at the Air-Aqueous Boundary on
28 Atmospheric Processes. *Chem. Rev.* **2006**, *106*, 1445-1461.

29 25. Gilman, J. B.; Eliason, T. L.; Fast, A.; Vaida, V., Selectivity and Stability of Organic Films at
30 the Air-Aqueous Interface. *J. Colloid Interface Sci.* **2004**, *280*, 234-243.

31 26. Fu, P. Q.; Kawamura, K.; Okuzawa, K.; Aggarwal, S. G.; Wang, G. H.; Kanaya, Y.; Wang, Z. F.,
32 Organic Molecular Compositions and Temporal Variations of Summertime Mountain Aerosols
33 over Mt. Tai, North China Plain. *J. Geophys. Res. Atmos.* **2008**, *113*, D19107.

34 27. Donaldson, D. J.; George, C., Sea-Surface Chemistry and Its Impact on the Marine Boundary
35 Layer. *Environ. Sci. Technol.* **2012**, *46*, 10385-10389.

36 28. Donaldson, D. J.; Valsaraj, K. T., Adsorption and Reaction of Trace Gas-Phase Organic
37 Compounds on Atmospheric Water Film Surfaces: A Critical Review. *Environ. Sci. Technol.* **2010**,
38 *44*, 865-873.

39 29. Enami, S.; Sakamoto, Y.; Colussi, A. J., Fenton Chemistry at Aqueous Interfaces. *Proc. Natl.*
40 *Acad. Sci. U. S. A.* **2014**, *111*, 623-628.

- 1
2
3 30. Enami, S.; Hoffmann, M. R.; Colussi, A. J., Prompt Formation of Organic Acids in Pulse
4 Ozonation of Terpenes on Aqueous Surfaces. *J. Phys. Chem. Lett.* **2010**, *1*, 2374-2379.
5
6 31. Enami, S.; Colussi, A. J., Long-Range Hofmeister Effects of Anionic and Cationic
7 Amphiphiles. *J. Phys. Chem. B* **2013**, *117*, 6276-6281.
8
9 32. Enami, S.; Fujii, T.; Sakamoto, Y.; Hama, T.; Kajii, Y., Carboxylate Ion Availability at the
10 Air-Water Interface. *J. Phys. Chem. A* **2016**, *120*, 9224-9234.
11
12 33. Enami, S.; Hoffmann, M. R.; Colussi, A. J., Proton Availability at the Air/Water Interface. *J.*
13 *Phys. Chem. Lett.* **2010**, *1*, 1599-1604.
14
15 34. Perrine, K. A.; Van Spyk, M. H.; Margarella, A. M.; Winter, B.; Faubel, M.; Bluhm, H.;
16 Hemminger, J. C., Characterization of the Acetonitrile Aqueous Solution/Vapor Interface by
17 Liquid-Jet X-Ray Photoelectron Spectroscopy. *J. Phys. Chem. C* **2014**, *118*, 29378-29388.
18
19 35. Makowski, M. J.; Stern, A. C.; Hemminger, J. C.; Tobias, D. J., Orientation and Structure of
20 Acetonitrile in Water at the Liquid-Vapor Interface: A Molecular Dynamics Simulation Study. *J.*
21 *Phys. Chem. C* **2016**, *120*, 17555-17563.
22
23 36. Enami, S.; Colussi, A. J., Long-Range Specific Ion-Ion Interactions in Hydrogen-Bonded
24 Liquid Films. *J. Chem. Phys.* **2013**, *138*, 184706.
25
26 37. Enami, S.; Vecitis, C. D.; Cheng, J.; Hoffmann, M. R.; Colussi, A. J., Electrospray Mass
27 Spectrometric Detection of Products and Short-Lived Intermediates in Aqueous Aerosol
28 Microdroplets Exposed to a Reactive Gas. *J. Phys. Chem. A* **2007**, *111*, 13032-13037.
29
30 38. Enami, S.; Hoffmann, M. R.; Colussi, A. J., How Phenol and Alpha-Tocopherol React with
31 Ambient Ozone at Gas/Liquid Interfaces. *J. Phys. Chem. A* **2009**, *113*, 7002-7010.
32
33 39. Enami, S.; Hoffmann, M. R.; Colussi, A. J., Extensive H-Atom Abstraction from Benzoate by
34 OH-Radicals at the Air-Water Interface. *Phys. Chem. Chem. Phys.* **2016**, *18*, 31505-31512.
35
36 40. Enami, S.; Hoffmann, M. R.; Colussi, A. J., In Situ Mass Spectrometric Detection of
37 Interfacial Intermediates in the Oxidation of RCOOH(aq) by Gas-Phase OH-Radicals. *J. Phys.*
38 *Chem. A* **2014**, *118*, 4130-4137.
39
40 41. Hoigne, J.; Bader, H.; Haag, W. R.; Staehelin, J., Rate Constants of Reactions of Ozone with
42 Organic and Inorganic-Compounds in Water 3. Inorganic-Compounds and Radicals. *Water Res.*
43 **1985**, *19*, 993-1004.
44
45 42. Enami, S.; Vecitis, C. D.; Cheng, J.; Hoffmann, M. R.; Colussi, A. J., Global Inorganic Source
46 of Atmospheric Bromine. *J. Phys. Chem. A* **2007**, *111*, 8749-8752.
47
48 43. Enami, S.; Sakamoto, Y., OH-Radical Oxidation of Surface-Active Cis-Pinonic Acid at the Air-
49 Water Interface. *J. Phys. Chem. A* **2016**, *120*, 3578-3587.
50
51 44. Ghalaieny, M.; Bacak, A.; McGillen, M.; Martin, D.; Knights, A. V.; O'Doherty, S.; Shallcross,
52 D. E.; Percival, C. J., Determination of Gas-Phase Ozonolysis Rate Coefficients of a Number of
53 Sesquiterpenes at Elevated Temperatures Using the Relative Rate Method. *Phys. Chem. Chem.*
54 *Phys.* **2012**, *14*, 6596-6602.
55
56 45. Hoigne, J.; Bader, H., Rate Constants of Reactions of Ozone with Organic and
57
58
59
60

1
2
3 Inorganic-Compounds in Water .1. Non-Dissociating Organic-Compounds. *Water Res.* **1983**, *17*,
4 173-183.

5
6 46. Larson, J. W.; McMahon, T. B., Fluoride and Chloride Affinities of Main Group Oxides,
7 Fluorides, Oxofluorides, and Alkyls. Quantitative Scales of Lewis Acidities from Ion Cyclotron
8 Resonance Halide-Exchange Equilibria. *J. Am. Chem. Soc.* **1985**, *107*, 766-773.

9
10 47. Bohringer, H.; Fahey, D. W.; Fehsenfeld, F. C.; Ferguson, E. E., Bond-Energies of the
11 Molecules H₂O, SO₂, H₂O₂, and HCl to Various Atmospheric Negative-Ions. *J. Chem. Phys.* **1984**,
12 *81*, 2805-2810.

13
14 48. Neeb, P.; Horie, O.; Moortgat, G. K., Gas-Phase Ozonolysis of Ethene in the Presence of
15 Hydroxylic Compounds. *Int. J. Chem. Kinet.* **1996**, *28*, 721-730.

16
17 49. Witkowski, B.; Gierczak, T., Analysis of α -Acyloxyhydroperoxy Aldehydes with Electrospray
18 Ionization-Tandem Mass Spectrometry (ESI-MSn). *J. Mass Spectrom.* **2013**, *48*, 79-88.

19
20 50. Lee, S.; Kamens, R. M., Particle Nucleation from the Reaction of Alpha-Pinene and O₃. *Atmos.*
21 *Environ.* **2005**, *39*, 6822-6832.

22
23 51. Wang, M. Y.; Yao, L.; Zheng, J.; Wang, X. K.; Chen, J. M.; Yang, X.; Worsnop, D. R.; Donahue,
24 N. M.; Wang, L., Reactions of Atmospheric Particulate Stabilized Criegee Intermediates Lead to
25 High-Molecular-Weight Aerosol Components. *Environ. Sci. Technol.* **2016**, *50*, 5702-5710.

26
27 52. Witkowski, B.; Gierczak, T., Early Stage Composition of SOA Produced by
28 Alpha-Pinene/Ozone Reaction: Alpha-Acyloxyhydroperoxy Aldehydes and Acidic Dimers. *Atmos.*
29 *Environ.* **2014**, *95*, 59-70.

30
31 53. Kristensen, K.; Watne, Å. K.; Hammes, J.; Lutz, A.; Petäjä, T.; Hallquist, M.; Bilde, M.;
32 Glasius, M., High-Molecular Weight Dimer Esters Are Major Products in Aerosols from α -Pinene
33 Ozonolysis and the Boreal Forest. *Environ. Sci. Technol. Lett.* **2016**, *3*, 280-285.

34
35 54. Tong, H.; Arangio, A. M.; Lakey, P. S. J.; Berkemeier, T.; Liu, F.; Kampf, C. J.; Brune, W. H.;
36 Pöschl, U.; Shiraiwa, M., Hydroxyl Radicals from Secondary Organic Aerosol Decomposition in
37 Water. *Atmos. Chem. Phys.* **2016**, *16*, 1761-1771.

38
39 55. Vidrio, E.; Phuah, C. H.; Dillner, A. M.; Anastasio, C., Generation of Hydroxyl Radicals from
40 Ambient Fine Particles in a Surrogate Lung Fluid Solution. *Environ. Sci. Technol.* **2009**, *43*,
41 922-927.

42
43 56. Ruehl, C. R.; Wilson, K. R., Surface Organic Mono Layers Control the Hygroscopic Growth of
44 Submicrometer Particles at High Relative Humidity. *J. Phys. Chem. A* **2014**, *118*, 3952-3966.

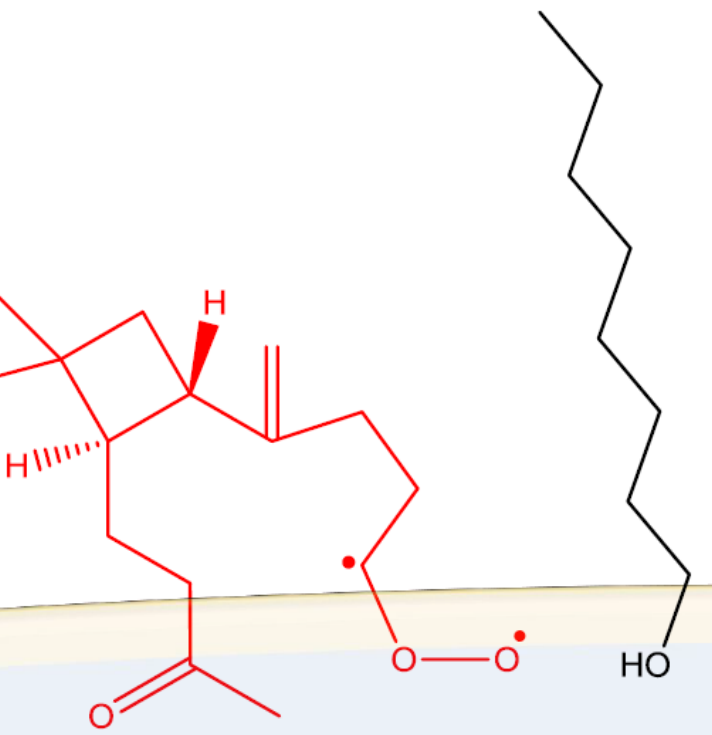
45
46 57. Müller, L.; Reinnig, M. C.; Naumann, K. H.; Saathoff, H.; Mentel, T. F.; Donahue, N. M.;
47 Hoffmann, T., Formation of 3-Methyl-1,2,3-Butanetricarboxylic Acid via Gas Phase Oxidation of
48 Pinonic Acid - A Mass Spectrometric Study of SOA Aging. *Atmos. Chem. Phys.* **2012**, *12*,
49 1483-1496.

50
51 58. Cheng, Y.; Brook, J. R.; Li, S. M.; Leithead, A., Seasonal Variation in the Biogenic Secondary
52 Organic Aerosol Tracer Cis-Pinonic Acid: Enhancement Due to Emissions from Regional and Local
53 Biomass Burning. *Atmos. Environ.* **2011**, *45*, 7105-7112.

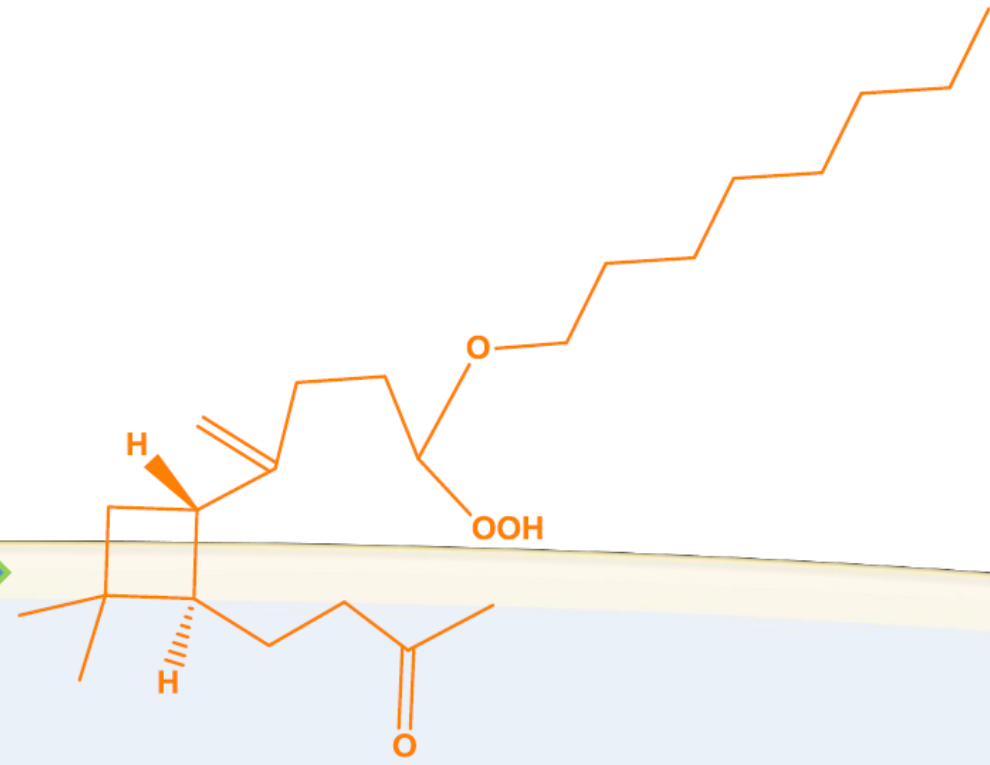
- 1
2
3 59. Zhang, Y. Y.; Muller, L.; Winterhalter, R.; Moortgat, G. K.; Hoffmann, T.; Poschl, U., Seasonal
4 Cycle and Temperature Dependence of Pinene Oxidation Products, Dicarboxylic Acids and
5 Nitrophenols in Fine and Coarse Air Particulate Matter. *Atmos. Chem. Phys.* **2010**, *10*, 7859-7873.
6
7 60. Riva, M.; Budisulistiorini, S. H.; Zhang, Z.; Gold, A.; Thornton, J. A.; Turpin, B. J.; Surratt, J.
8 D., Multiphase Reactivity of Gaseous Hydroperoxide Oligomers Produced from Isoprene
9 Ozonolysis in the Presence of Acidified Aerosols. *Atmos. Environ.* **2017**, *152*, 314-322.
10
11 61. Ehn, M., et al., A Large Source of Low-Volatility Secondary Organic Aerosol. *Nature* **2014**,
12 *506*, 476-479.
13
14 62. Riccobono, F., et al., Oxidation Products of Biogenic Emissions Contribute to Nucleation of
15 Atmospheric Particles. *Science* **2014**, *344*, 717-721.
16
17 63. Kjaergaard, H. G.; Kurten, T.; Nielsen, L. B.; Jorgensen, S.; Wennberg, P. O., Criegee
18 Intermediates React with Ozone. *J. Phys. Chem. Lett.* **2013**, *4*, 2525-2529.
19
20 64. Vereecken, L.; Harder, H.; Novelli, A., The Reactions of Criegee Intermediates with Alkenes,
21 Ozone, and Carbonyl Oxides. *Phys. Chem. Chem. Phys.* **2014**, *16*, 4039-4049.
22
23 65. Walz, M. M.; Werner, J.; Ekholm, V.; Prisle, N. L.; Ohrwall, G.; Bjorneholm, O., Alcohols at
24 the Aqueous Surface: Chain Length and Isomer Effects. *Phys. Chem. Chem. Phys.* **2016**, *18*,
25 6648-6656.
26
27 66. Mondal, J. A.; Namboodiri, V.; Mathi, P.; Singh, A. K., Alkyl Chain Length Dependent
28 Structural and Orientational Transformations of Water at Alcohol-Water Interfaces and Its
29 Relevance to Atmospheric Aerosols. *J. Phys. Chem. Lett.* **2017**, *8*, 1637-1644.
30
31 67. Boand, G.; Houriet, R.; Gaumann, T., Gas-Phase Acidity of Aliphatic-Alcohols. *J. Am. Chem*
32 *Soc.* **1983**, *105*, 2203-2206.
33
34 68. Tobias, H. J.; Ziemann, P. J., Kinetics of the Gas-Phase Reactions of Alcohols, Aldehydes,
35 Carboxylic Acids, and Water with the C13 Stabilized Criegee Intermediate Formed from
36 Ozonolysis of 1-Tetradecene. *J. Phys. Chem. A* **2001**, *105*, 6129-6135.
37
38 69. Donaldson, D. J.; Anderson, D., Adsorption of Atmospheric Gases at the Air-Water Interface.
39 2. C-1-C-4 Alcohols, Acids, and Acetone. *J. Phys. Chem. A* **1999**, *103*, 871-876.
40
41 70. Houriez, C.; Meot-Ner, M.; Masella, M., Simulated Solvation of Organic Ions II: Study of
42 Linear Alkylated Carboxylate Ions in Water Nanodrops and in Liquid Water. Propensity for
43 Air/Water Interface and Convergence to Bulk Solvation Properties. *J. Phys. Chem. B* **2015**, *119*,
44 12094-12107.
45
46 71. Caldwell, G.; Renneboog, R.; Kebarle, P., Gas-Phase Acidities of Aliphatic Carboxylic-Acids,
47 Based on Measurements of Proton-Transfer Equilibria. *Can. J. Chem.* **1989**, *67*, 611-618.
48
49
50
51
52
53
54
55
56
57
58
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60

1
2
3
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n-Alkanols



Criegee Intermediates



*C*_{15+n} Ethers