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1 Mechanistic insights on the photosensitized
2 chemistry of a fatty acid at the air/water interface

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15 KEYWORDS Photochemical reactions, surface microlayer, air/sea interface, photosensitized
16 reactions, 4-benzoyl-benzoic acid, nonanoic acid

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19 Interfaces are ubiquitous in the environment and many atmospheric key processes, such as gas
20 deposition, aerosol and cloud formation are, at one stage or another, strongly impacted by
21 physical and chemical processes occurring at interfaces. Here, the photo-induced chemistry of an
22 air/water interface coated with nonanoic acid - a fatty acid surfactant we use as a proxy for
23 chemically complex natural aqueous surface microlayers - was investigated as a source of
24 volatile and semi-volatile reactive organic species. The carboxylic acid coating significantly
25 increased the propensity of photosensitizers, chosen to mimic those observed in real
26 environmental waters, to partition to the interface and enhance reactivity there. Photochemical
27 formation of functionalized and unsaturated compounds was systematically observed upon
28 irradiation of these coated surfaces. The role of a coated interface appears to be critical in
29 providing a concentrated medium allowing radical-radical reactions to occur in parallel with
30 molecular oxygen additions. Mechanistic insights are provided from extensive analysis of
31 products observed in both gas and aqueous phases by on-line SRI-ToF-MS and off-line
32 UPLC/(±)HESI-HRMS, respectively.

33

34 **Introduction**

35 The air/water interface is perhaps the most widespread surface in Earth's environment. Cloud
36 droplets, lakes, seas and oceans all exhibit very large surfaces that play a crucial role in the
37 exchange of matter between the hydrosphere and the atmosphere. The understanding of the
38 specific processes occurring at such interfaces is thus of importance from an atmospheric point
39 of view. Environmental air/water interfaces often show the presence of surfactants, which are

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40 known to impact the physical processes there. For instance, the transfer between the aqueous
41 phase and the gas phase is restrained in the presence of an insoluble organic coating, which is
42 able to inhibit both water evaporation and solubilization of trace gases.¹ Moreover, organic
43 coated air/water interfaces are expected to increase the surface concentrations of a variety of
44 hydrophobic compounds, possibly impacting their phase transfers.¹ These coated interfaces can
45 also play a role in the removal of atmospheric gases. For example, dry deposition on organic
46 coated water surfaces is suspected to constitute an important sink for ozone in the marine
47 boundary layer, both through its reactivity with the components of the coating material and
48 through increased solubility in this thin organic layer.^{1,2} These air/water surfaces are furthermore
49 exposed to solar light for much of the time and specific photochemical processes are therefore
50 expected to occur there.^{3,4} One interface of particular interest is the sea Surface MicroLayer
51 (sea-SML), defined as the uppermost 1 μm to 1 mm of the surface of the ocean, which is mainly
52 composed of biogenic organics species such as lipids, hydrocarbons, proteins or polysaccharides.
53 It was shown that light absorbing compounds, such as the natural Chromophoric Dissolved
54 Organic Matter (CDOM), are more concentrated in the sea-SML than in the bulk water^{5,6} and
55 therefore it has been speculated that photosensitized reactions could be particularly important in
56 this region, although these processes are still poorly understood and neglected in atmospheric
57 models.^{3,7,8} Contrary to what was previously thought, the SML is widespread over the sea
58 surface and stable under wind speeds up to 6.6 m s^{-1} .⁹ Evidence also shows rapid reformation,
59 within minutes, of the perturbed SML.¹⁰ In direct contact with the atmosphere, the role the SML
60 plays in the physical and chemical regulation of emission and uptake of volatile organic
61 compounds (VOCs) and trace gases is still to be clarified.¹¹ Light absorbing species within the
62 SML can participate in heterogeneous light-induced or light-enhanced reactions with trace gases

63 at the interface, as has been shown for NO₂ reacting with humic acids or for ozone with
64 chlorophyll.^{12,13} These photochemical reactions can also be a source of gaseous reactive species,
65 as demonstrated for the light induced release of volatile halogen radicals above organic films.¹⁴
66 ¹⁵ In another context, the SML sampled in a commercial rice field, highly enriched in pesticides
67 with concentrations up to 10⁵ times higher than in the subsurface waters, showed an enhanced
68 degradation for the pesticide thiobencarb compared to the sampled subsurface water.¹⁶ Organic
69 coatings can thus have significant impacts on the interfacial processes compared to pure water
70 surfaces, particularly if photosensitizers show a propensity to partition to this organic layer.

71 Recently, spectrometric measurements of the gas phase above an irradiated real sea-SML
72 sample or synthetic nonanoic acid SML enriched with humic acids, showed the formation of a
73 wide variety of functionalized VOCs.^{17, 18} The photosensitized formation of unsaturated
74 compounds from a synthetic 1-octanol interfacial layer was also evidenced.¹⁹ These surface
75 photochemical pathways could constitute a still unaccounted for abiotic source of VOCs in the
76 marine boundary layer and in all atmospheric environments where large air/water interfaces are
77 present. In particular the fate of common organic acids, who are relatively unreactive in the gas-
78 phase,²⁰ could present an ubiquitous photochemical substrate and a source of VOCs in the SML,
79 where such photochemical reactions would compete with *e.g.* oxidation by hydroxyl radicals.
80 Nevertheless, the chemical formation routes of these VOCs are still poorly understood as well as
81 the role of the organic coating on the concentration of photosensitizers at the interface.

82 This work presents the study of photochemical reactions in a synthetic SML, composed of a
83 saturated carboxylic acid, nonanoic acid (NA), in the presence of known photosensitizers (4-
84 benzoylbenzoic acid and imidazole-2-carboxaldehyde). It focuses on the fundamental processes
85 leading to the formation of functionalized and unsaturated compounds in the gas and condensed

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86 bulk phases. UV-vis spectroscopy and surface fluorescence experiments were performed to
87 elucidate the behavior of the photosensitizer at the coated interface. Photoproducts were
88 observed in parallel in the gas phase by on-line mass spectrometry and in the aqueous phase by
89 off-line liquid chromatography coupled to high resolution mass spectrometry. Chemical
90 mechanisms which explain the observed product distributions are proposed and discussed in
91 detail.

92 **Experimental section**

93 **Materials.** All chemicals were used as received, without further purification. Further details can
94 be found in the Supplementary Information.

95 **UV-vis spectroscopy.** UV-vis spectra were acquired on a Cary 60 UV-Vis spectrophotometer
96 (Agilent Technologies) using 1 cm quartz cuvettes. The absorption spectra of a 0.2 mM 4-
97 benzoylbenzoic acid (4-BBA) aqueous solution at pH=7.0 and of neat NA were first recorded.
98 Next, 5 mL of the 4-BBA aqueous solution was mixed with 5 mL of neat NA. The biphasic
99 system was separated by centrifugation at 4500 rpm for 2 minutes with Fisher Bioblock
100 Scientific Sigma centrifuge using a 15 mL Eppendorf centrifuge tube. Final UV-vis spectra of
101 both phases were recorded separately. A similar experiment was performed without 4-BBA in
102 the aqueous phase to check for changes in the NA spectrum due to the presence of dissolved
103 water.

104 **Glancing angle laser induced fluorescence.** Fluorescence of imidazole-2-carboxaldehyde (IC)
105 at the air-water interface has been studied by Glancing Angle Laser-Induced Fluorescence
106 (GALIF). A detailed description of this method has been given elsewhere.^{21, 22} Fluorescence at
107 the air-aqueous interface was induced using the unfocussed output of a Nd:YAG-pumped Optical
108 Parametric Oscillator (OPO) set at 285 nm, with ~ 2 mJ per 5 ns pulse. The laser beam impinged

109 the liquid sample surface at an angle $>85^\circ$ from the surface normal. The fluorescence emission
110 signal was collected using a liquid light guide suspended ~ 6 mm above the impinging laser beam
111 and transmitted through a monochromator to a photomultiplier tube. More details about
112 experimental protocols, signal treatment and surface adsorption isotherm measurements are
113 provided in the Supporting Information.

114 **Laser flash photolysis experiments.** Transient absorption experiments were carried out using
115 the fourth harmonic (266 nm) of a Quanta Ray GCR 130-01 Nd:YAG laser, exciting the sample
116 in a right-angle geometry with respect to the monitoring light beam. The single pulses were ca. 9
117 ns in duration, with an energy of ~ 40 mJ/pulse. Individual cuvette samples (~ 3.5 mL volume)
118 were used for a maximum of two consecutive laser shots in order to avoid possible substrate
119 degradation. The transient absorption at a pre-selected wavelength was monitored by a detection
120 system consisting of a pulsed Xenon lamp (150 W), monochromator and a photomultiplier
121 (1P28). A spectrometer control unit was used for synchronising the pulsed light source and
122 programmable shutters with the laser output. The signal from the photomultiplier was digitized
123 by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic
124 spectrometer workstation was used to analyse the digitized signal. Stock solutions of NA and 4-
125 BBA were prepared in Milli-Q water and mixed in an appropriate volume to obtain the desired
126 concentrations just before each Laser Flash Photolysis (LFP) experiment. The second-order rate
127 constant for the quenching of triplet state 4-BBA (4-BBA*) in the presence of NA was obtained
128 from the slope of the best-fit linear correlation between the pseudo-first-order decay constant of
129 4-BBA* monitored at 540 nm vs. concentration of NA in aqueous solution. All experiments were
130 performed at ambient temperature (295 ± 2 K) in aerated solutions.

131 **Quartz cell experiments – Gas phase analysis.** The experiments were performed using a 5 cm
132 path length, 2 cm id, 14 mL cylindrical quartz cell with a gas inlet near each end (Starna, UK) 13
133 cm away from the output lens of a Xenon lamp (150 W Xe, LOT-QuantumDesign, France). The
134 lamp was equipped with a 1 cm water filter in front of the reaction cell to avoid excessive
135 heating. The cell was half-filled with 7 mL of the aqueous phase under study (pure water or an
136 aqueous 0.1 mM 4-BBA solution) in order to maximize the surface to volume ratio (1.4 cm^{-1}). A
137 theoretical concentration of 2 mM of NA was achieved by the addition of 2.5 μL of neat NA.
138 The solution was then slightly stirred to promote NA spreading over the surface and was left to
139 sit for 20 minutes in the dark before starting the irradiation. A gas flow at a flow rate of 200
140 sccm (standard cubic centimeter per minute) was continuously introduced into the cell, with 80
141 sccm of the outgoing gas flow sampled for analysis by a Switchable Reagent Ion-Time of Flight-
142 Mass Spectrometer (8000 SRI-ToF-MS, Ionicon Analytik GmbH, Innsbruck, Austria). The
143 experiments were performed either under purified compressed dry air (DF Ultrafilter,
144 Donaldson, USA) or dry nitrogen. For the experiments performed under nitrogen, the aqueous
145 solution was deoxygenated before NA addition by bubbling nitrogen for 25 min.

146 The analysis of the gas phase products was performed using both H_3O^+ and NO^+ ionization
147 modes to provide information about the product functionalities.²³⁻²⁶ Ions used for identification
148 of functional groups in the NO^+ mode are listed in Table S2 (Supporting Information). Only
149 qualitative results and normalized signals are discussed for the NO^+ reagent mode as reaction
150 rates for most of the products with NO^+ are unknown. Fragmentation patterns for the main
151 products under our experimental conditions were carefully assessed using liquid standards
152 diluted in 7 mL of water in the reactor and analyzed under the same conditions as the samples, as
153 shown Table S3 (Supporting Information). Concentrations were theoretically determined from

154 the spectra taken in H_3O^+ ionization mode, corrected for the reaction branching ratios when these
155 were known. The global uncertainty on the absolute concentrations can be estimated to be about
156 40 %.²⁷ Background spectra were taken before each experiment above pure water, before adding
157 the surfactant and an eventual photosensitizer. The error bars reported represent the standard
158 deviation on repeated experiments ($n \geq 2$). More analytical details are provided in the Supporting
159 Information.

160 **Quartz cell experiments – Aqueous phase analysis.** The experiments were performed using a
161 similar setup as for the gas phase products analysis. The cell was first filled with 11 mL of the
162 aqueous phase under study (pure water or an aqueous 0.1 mM 4-BBA solution) and 3.8 μL of
163 NA was added to achieve a theoretical concentration of 2 mM. The solution was then slightly
164 stirred to promote NA spreading over the surface and was left to sit a few minutes in the dark
165 before a first sampling of 4 mL of the solution. The remaining 7 mL filled the cell halfway. A
166 fixed irradiation time of 1 hour was used for all the experiments. After irradiation, the solution
167 was stirred again for a few minutes in the dark before a second 4 mL sampling. The cell was
168 hermetically closed during irradiation. Sampling was performed using a glass syringe through a
169 septum before and after irradiation. The experiments were carried out either under air or under
170 nitrogen. For the experiments performed under nitrogen, the aqueous solution was deoxygenated
171 before NA addition by bubbling with N_2 for 25 min. The empty volume of the cell was purged
172 before hermetical closing.

173 Aliquots of 500 μL of each aqueous sample were diluted adding 500 μL of a 1:1, v:v,
174 water:acetonitrile mixture. Next, 200 μL of each sample was derivatized for specific carbonyl
175 compounds detection adding 800 μL of a 1 mg mL^{-1} PFBHA solution and leaving the obtained
176 mixture at room temperature for 24 hours before analysis. Further details about the PFBHA

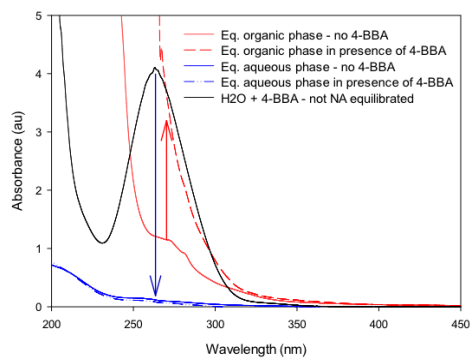
177 derivatization process are given in the Supporting Information. Each dilution, derivatization and
178 analysis was performed three times. All samples were analyzed by reversed phase
179 UltraPerformance Liquid Chromatography coupled to a Q Exactive™ High Resolution Mass
180 Spectrometer through Heated Electrospray Ionization [UPLC/(±)HESI-HRMS, Thermo
181 Scientific, USA]. A water/acetonitrile solvent gradient was applied. The mass spectrometer was
182 operated in the negative ionization mode for the analysis of the non derivatized samples and in
183 the positive ionization mode for the analysis of the derivatized ones. Reported signal intensities
184 correspond to the total areas of the chromatographic peaks determined from the extracted ion
185 chromatograms of the identified quasi-molecular ions. The analytical uncertainties were
186 determined over the whole experimental period as the relative standard deviation on two series of
187 standard injection: 8% for the non derivatized standard (negative ionization mode) and 23% for
188 the derivatized standard (positive ionization mode). These standard deviation values are reported
189 on the bar graphs. The standard deviation over the three replicates performed for each sample is
190 reported only if it is above this overall experimental period standard deviation. Details about
191 ionization conditions, calibration and data acquisition and processing are provided in the
192 Supporting Information.

193

194 **Results and discussion**

195 **Photosensitizer enrichment at the air-water interface.** The propensity of a photosensitizer to
196 partition to the surface in the presence of an organic surfactant was investigated using UV-vis
197 spectroscopy and Glancing Angle Laser Induced Fluorescence spectroscopy. Two well-known
198 efficient photosensitizers were used, 4-benzoylbenzoic acid (4-BBA)²⁸⁻³⁰ and 2-imidazole-
199 carboxaldehyde (IC)^{31,32} which are both aromatics possessing a carbonyl function and therefore

200 appropriate as a proxy for CDOM.³³ IC, which is formed in situ in aerosols, can induce aerosol
201 growth³¹ and has recently been observed in aerosol particles in the field.³⁴ Firstly, the UV-vis
202 absorption spectrum of an aqueous solution of 4-BBA at pH 7 was recorded, as shown in Figure
203 1 (black). Neat nonanoic acid was then added to this solution and aqueous and organic phases
204 were separated by centrifugation. The absorption spectrum of each phase was registered
205 separately, and displayed in Figure 1 (dashed lines). Changes in the absorption spectrum of the
206 two phases show an almost quantitative removal of 4-BBA from the aqueous phase. Indeed,
207 approximately 98% of the 4-BBA migrated from the aqueous phase into the organic phase after
208 seconds of contact, suggesting that the partitioning of the photosensitizer towards the organic
209 layer is highly favored.

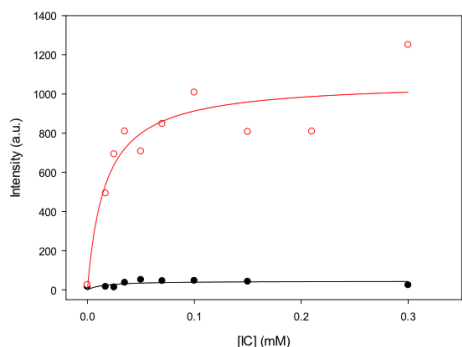


210
211 **Figure 1.** UV-vis spectra of aqueous and NA solutions before and after equilibration with the
212 other phase in the presence and absence of 4-BBA. Blue and red arrows show the change in the
213 absorption spectra for the aqueous phase and the organic phase respectively in presence of 4-
214 BBA. The black line shows the absorption spectrum of an aqueous solution of 4-BBA at 0.2
215 mM. The red lines show the absorption spectra of the organic phase after separation of the two
216 phases; the solid line when no 4-BBA was present in the system, the red dashed line when in

217 presence of 4-BBA. The blue lines show the absorption spectrum of the aqueous phase after
218 separation of the phases; the solid blue line when the system contained no 4-BBA, the blue
219 dashed line when 4-BBA was present in the system.

220 The GALIF measurements probed the fluorescence of IC at the surface of an aqueous solution as
221 a function of its solution concentration. The intensity of this IC surface fluorescence using pure
222 water as a substrate was compared with the IC surface fluorescence measured at the surface of a
223 1.5 mM solution of NA, This bulk concentration provides near-monolayer NA coverage at the
224 air-water interface.^{17,35} The adsorption isotherms of IC at the aqueous-air interface, derived from
225 these measurements and displayed in Figure 2, clearly show an enhanced fluorescence ($\times 50$) in
226 the presence of a NA coating at the surface, ~~demonstrating the propensity of the photosensitizer~~
227 ~~to partition to the organic surface layer. This difference in fluorescence can solely be attributed~~
228 ~~to changes in the surface concentration of IC demonstrating the propensity of the photosensitizer~~
229 ~~to partition to the organic surface layer, since (a) the bulk fluorescence yield of IC in nonanoic~~
230 ~~acid is lower than in pure water (Figure S1, Supporting Information) and (b) the enrichment of a~~
231 ~~compound at the surface seems to depend on its solubility in the monolayer.~~³⁵ This is in
232 agreement with the results obtained by Fu et al.¹⁹ that show enhanced fluorescence of IC in
233 presence of a near monolayer of 1-octanol. Both spectroscopic techniques confirm the enhanced
234 concentration of the photosensitizers used here at the air/water interface in the presence of an
235 organic coating, leading very probably to an enhanced and specific photochemistry there.

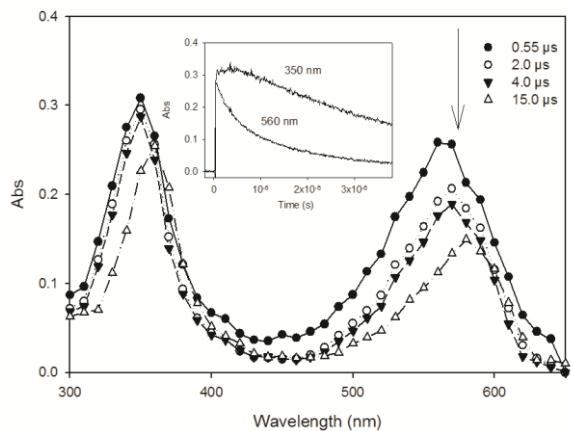
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236
 237 **Figure 2.** Fluorescence intensity ($\lambda=335$ nm) of IC at the air/water interface as a function of the
 238 bulk concentration of IC, measured at a pure water surface (●) and at a nonanoic acid coated
 239 surface (○). The solid lines show the fits to -Langmuir adsorption isotherms.

240 **Reaction rate between triplet state 4-BBA and NA.** LFP excitation of a 0.21 mM 4-BBA
 241 aqueous solution at pH 7.0 produces a transient absorption spectrum presenting two intense
 242 absorption peaks at 410 and 540 nm, illustrated in Figure S24 (Supplementary Information),
 243 which are attributed to the triplet state of 4-BBA (4-BBA*³⁶). The transient species decays
 244 uniformly with a pseudo-first order $k'_{540nm} = 4.76 \pm 0.11 \times 10^5 \text{ s}^{-1}$ and no residual absorbance was
 245 observed after about 5 μs . When dissolved in neat NA the transient spectrum of 4-BBA*
 246 presents two maxima at 350 nm and 560 nm, shown in Figure 3. After relaxation of the triplet
 247 state, approximately 2 μs after the laser impulse, two intense bands centered at 360 nm and at
 248 580 nm are observed. The absorption decay in this pure NA solution was followed at 560 nm and
 249 fitted well a double exponential equation, suggesting the presence of two different species. The
 250 first, short-lived species can be attributed to the excited state of 4-BBA. The second long-lived
 251 component may correspond to the ketyl radical of 4-BBA.^{37, 38} The formation of a ketyl radical

252 can be explained by electron or hydrogen transfer from organic molecules (i.e. NA), a process
253 which has previously been reported for other benzophenone derivatives.^{39, 40}

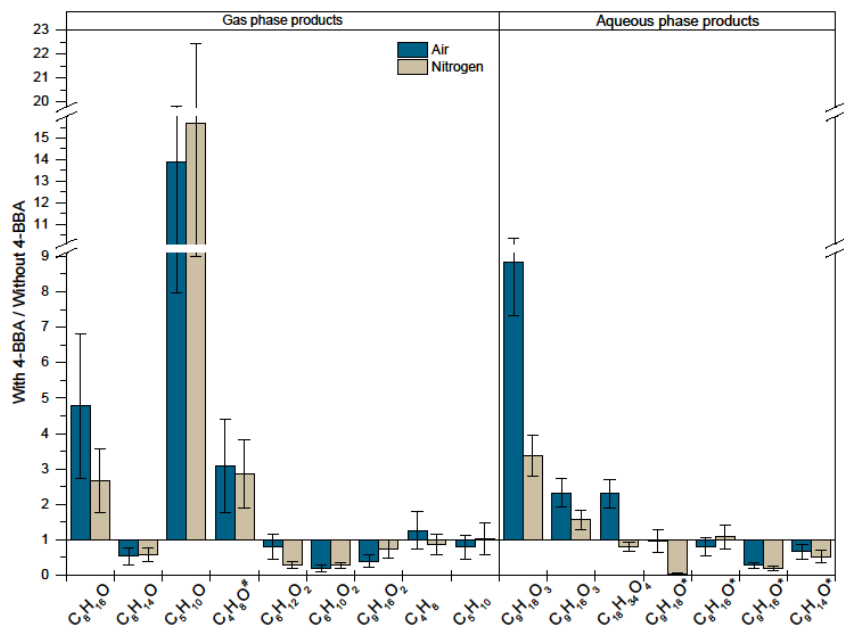


254
255 **Figure 3:** Time trend of the transient spectrum obtained upon laser-pulse excitation (266 nm,
256 ~40 mJ) of 0.21 mM 4-BBA in NA solution. The insert shows the time trend of the signals at
257 350 and 560 nm

258 Figure S32 (Supporting Information) reports the rate constant for the pseudo-first order decay of
259 4-BBA* followed at 540 nm as a function of NA concentration in an aqueous solution. The data
260 allows for the determination of the second-order rate constant for the quenching of the triplet
261 state by nonanoic acid $k_{4-BBA^*,NA} = 3.0 \pm 0.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is competitive with rate
262 constants reported for aliphatic carboxylic acids and hydroxyl radicals.⁴¹

263 **Surface microlayer photochemistry in the presence of 4-BBA.** The photo-induced chemistry
264 occurring at the air/water interface in the presence of NA as organic coating and 4-BBA as
265 photosensitizer was investigated. Gas-phase products were analyzed on-line while the analysis of
266 bulk condensed phase products was performed off-line, with and without selective derivatization

267 of carbonyl groups. Upon irradiation, the prompt formation of gas phase products was observed
268 (Figure S43, Supporting Information). Similarly, a wide variety of photoproducts was detected in
269 the condensed phase after 1 h of irradiation. A complete list of the detected compounds is
270 provided in Table S1 (Supporting Information). Nevertheless, it clearly appears that this large
271 variety of photo-products is formed upon irradiation in the presence and in the absence of 4-
272 BBA. The photochemistry of only NA in concentrated media, and more specifically at the
273 air/water interface, was recently evidenced and can explain these observations.⁴² However, here,
274 the detection of the NA-4-BBA recombination product ($C_{23}H_{28}O_5$) confirms the existence of
275 photo-induced reactions between the photosensitizer and the organic surfactant. The ratios of the
276 net productions for a selection of photo-products in the gas and condensed phase in the presence
277 and in the absence of 4-BBA are displayed in Figure 4. Net production signals observed for the
278 same series of products in both phases are shown in Figures S54 and S56 (Supporting
279 Information).



280
 281 **Figure 4:** Ratio of the signal detected in the presence of 4-BBA (0.2 mM) to the signal observed
 282 without 4-BBA for a series of selected photo-products in the gas phase and in the aqueous phase,
 283 for a 2 mM NA aqueous solution. Errors reflect the analytical uncertainties (condensed phase) or
 284 repeatability between experiments (gas phase). [#]Identified as ketone due to NO⁺ adduct.
 285 *Detected as PFBHA derivatives.

286
 287 Most of the observed photoproducts were oxygenated. Octanal (C₈H₁₆O) was one of the main
 288 products in both phases. Aldehydes and ketones (< C₉), including unsaturated and dicarbonyl
 289 compounds, were also detected. Octenal (C₈H₁₄O) was one of the main unsaturated oxygenated
 290 compounds observed. In the condensed phase, C₉ products with three or more oxygen atoms,
 291 such as C₉H₁₈O₃ and C₉H₁₆O₃, were also detected. These compounds can be tentatively identified

292 as NA bearing additional hydroxyl and/or carbonyl functions. They were not detected in the gas
293 phase, probably due to their low volatility. Small acids ($< C_9$) were detected in both phases but
294 only in rather low abundances. Some unsaturated acids were observed as well, the main one
295 being $C_9H_{16}O_2$, identified as nonenoic acid. Alkenes could not be evidenced in the condensed
296 phase due to the electrospray ionization limitation for non-polar compounds, but C_4H_8 and C_5H_{10}
297 were the most abundant unsaturated products detected in the gas phase. Additionally, compounds
298 bearing more than nine carbon atoms were observed in the condensed phase, such as $C_{18}H_{34}O_4$,
299 $C_{28}H_{22}O_6$ and $C_{23}H_{28}O_5$. These molecular formulae can be attributed to the dimer of NA, the
300 dimer of 4-BBA and, as already mentioned, the combination of NA and 4-BBA, respectively.
301 Experiments performed using IC as the photosensitizer showed overall a very similar pattern of
302 product formation, but with lower intensities for the products, probably due to the lower quantum
303 yield of the triplet state of IC compared to 4-BBA. Figure S76, Supporting Information displays
304 details of these results.

305 Interestingly, the formation of certain products is favored in the presence of 4-BBA while the
306 formation of others is hindered, as shown in Figure 4. Enhanced production is observed in the
307 presence of 4-BBA for some oxidized and saturated compounds, such as the $C < 9$ aldehydes
308 ($C_8H_{16}O$, $C_5H_{10}O$, C_4H_8O) and various C_9 oxidation products ($C_9H_{18}O_3$ and $C_9H_{16}O_3$). Photo-
309 products hindered in the presence of 4-BBA are the C_9 carbonyls, nonanal and nonenal, and in a
310 more general way the compounds presenting a C-C double bond. Very similar observations arose
311 from experiments performed in the presence and in the absence of H_2O_2 as photo-initiator, as can
312 be seen in Figure S87 (Supporting Information),⁴² hydroxyl radicals being also able to react
313 quickly with C-C double bonds leading to functionalization and fragmentation⁴³. Competition for
314 H abstraction between 4-BBA* and NA* could contribute to the fact that saturated and

315 unsaturated C₉ aldehydes, expected to be specific to the reactivity of NA alone photochemistry in
316 concentrated media, are hindered in the presence of 4-BBA.⁴²
317 Triplet state 4-BBA can react with organics such as NA through H-abstraction, to initiate radical
318 chemistry,^{44, 45} a pathway supported by the similarity between the series of products observed in
319 these experiments with those obtained using H₂O₂ as photo-initiator.⁴² The hydroxyl radical
320 generated by H₂O₂ photolysis upon irradiation is expected to react with NA only via H-
321 abstraction. Recently Rossignol et al.⁴² have demonstrated that radical-initiated photochemistry
322 of aqueous solutions containing only NA readily occurs, and suggested that this is initiated by
323 the formation of an NA excited state, followed either by H-abstraction from another NA
324 molecule or by a homolytic cleavage releasing a hydroxyl radical. If this hypothesis is true, the
325 formation of C₉ aldehydes would be specific to the photochemistry of NA alone, as these
326 compounds are formed directly from the excited state of NA. The results detailed here suggest
327 that in the presence of 4-BBA (or H₂O₂), a competition between the photochemistry of NA-only
328 chemistry and “traditional” H-abstraction by an excited photosensitizer occurs, with the products
329 derived from the NA radical formed after H-abstraction on the carbon chain being favored, and
330 those derived directly from the NA excited state hindered.

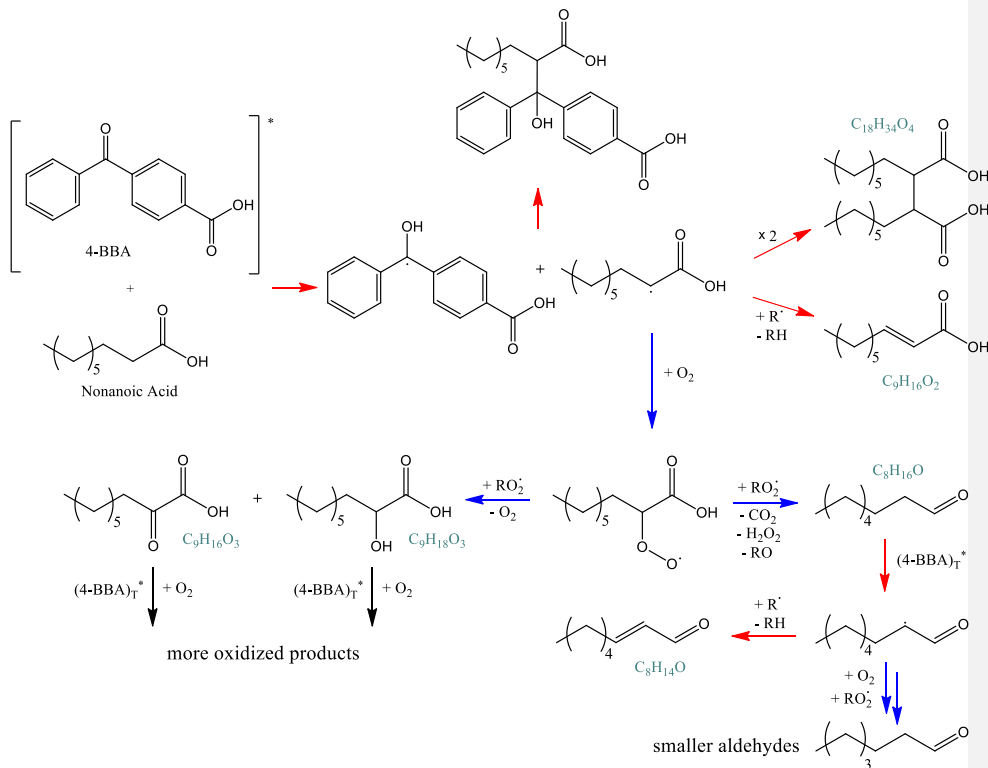
331 In order to investigate the role of oxygen in this chemistry, all the experiments were repeated
332 under nitrogen using deoxygenated solutions. The net production of the same selection of
333 compounds under these two conditions is compared Figures ~~S54~~ and ~~S65~~ (Supporting
334 Information) and Figure 4 compares the ratios of the signals obtained under these two conditions.
335 The highly oxygenated C₉ products are clearly favored when oxygen is more abundant (e.g.
336 C₉H₁₈O₃ and C₉H₁₆O₃). While on the other hand, the dimers (e.g. C₁₈H₃₄O₄) as well as the
337 unsaturated C₉ acid (C₉H₁₆O₂) appear to be favored in an oxygen-poor environment. The

338 formation of alkenes also seems to be favored under nitrogen. The influence of oxygen is less
339 clear for the carbonyl compounds and in particular for those bearing an unsaturation, as
340 illustrated for octenal.

341 From these observations a general mechanism of the photosensitized degradation of NA may
342 be derived; this is given in Figure 5. After the initial H-abstraction by the excited state of the
343 photosensitizer, two pathways are expected: the addition of molecular oxygen or radical-radical
344 reactions. The latter explains the formation of NA dimers, but also the formation of the observed
345 NA-4-BBA and 4-BBA-4-BBA recombination products. This type of fast radical recombination,
346 has been observed previously in photosensitized reactions in aerosols,³¹ but occurs only where
347 high radical concentrations are achieved.⁴⁶ The presence of such recombination products thus
348 highlights some particular features of the enhanced concentration at the air/water interface. This
349 surface enhanced concentration can also favor radical-radical disproportionation reactions,¹⁹
350 explaining the formation of nonenoic acid and possibly of other unsaturated compounds.
351 Molecular oxygen addition is not expected to be specific to the interface, as oxygen readily
352 dissolves in bulk water, where similar chemistry, leading to the formation of a peroxy radical,
353 has been reported.⁴⁷ This peroxy radical is then expected either to fragment, leading to the
354 formation of octanal, or to evolve toward hydroxyl or carbonyl functions. These products can
355 then undergo similar processes as the initial NA molecules, leading to the formation of second
356 generation products. The competition between radical-radical reactions promoted at the interface
357 and oxygen addition appears thus to play a key role in the distribution of the products. This is
358 highlighted by the fact that recombination and disproportionation products were observed to be
359 favored in an oxygen-poor environment. Considering the proposed mechanism, the formation of
360 unsaturated aldehydes, apparently not impacted by the presence of oxygen, also underlines this

361 competition; while oxygen is required to form the saturated aldehyde on which H-abstraction can
362 then occur, disproportionation reactions leading to the unsaturated aldehyde is favored under
363 nitrogen.

364 Alkenes, which are not mentioned on the proposed mechanism, could arise from the photolytic
365 cleavage of the carbonyl compounds, but this does not strictly match the observations, as the
366 formation of the main alkenes observed, butene and pentene, appears to be favored under
367 nitrogen (Figure S54, Supporting Information). Another pathway could invoke the cyclization of
368 the NA radical leading to the formation of a C₅ or C₄ lactone and a related C₄ or C₅ alkyl radical
369 fragment, which ultimately gives rise to butene and pentene (Figure S98, Supporting
370 Information). This mechanism is in agreement with the observation that these products are
371 favored under nitrogen since the cyclization and disproportionation steps would both be in
372 competition with oxygen addition.



373
 374 **Figure 5.** Proposed mechanism for the photosensitized degradation of NA. Blue highlighted
 375 pathways are expected to be promoted under air and red highlighted pathways at the interface
 376 and under nitrogen. The products identified by their chemical formulas (grey) correspond to
 377 products shown in Figure 4.

378 In conclusion, this study relates the photochemical production of functionalized and
 379 unsaturated compounds at an air/water interface in the presence of a carboxylic acid, nonanoic
 380 acid, as surfactant. When a photosensitizer, such as 4-BBA or IC, is present in the aqueous
 381 solution, it will rapidly partition to the organic surface layer where it can induce radical reactions

382 through a hydrogen abstraction on a NA molecule, leading to the formation of a large variety of
383 compounds.

384 The photochemical production and the gas phase release of such unsaturated and
385 functionalized compounds will influence the oxidative capacity of the atmosphere and can lead
386 to secondary aerosol formation. This interfacial photochemistry has potentially a very large
387 impact, especially as both reactants, the photosensitizer and the substrate can be naturally present
388 at high concentrations at the surface, providing a very favorable venue for this new type of
389 photochemistry. Although the photochemistry triggered by the photosensitizer competes with the
390 photochemistry induced by a carboxylic acid at the surface layer, it is generally leading more
391 efficiently to oxidized products. Moreover, this photochemistry seems to occur with different
392 types of photosensitizers (4-BBA, IC, H₂O₂) and surfactant organic coatings (nonanoic acid,
393 octanol, heptanol), meaning that these photosensitized processes could be much more generally
394 occurring than previously thought. We expect that this chemistry will apply especially to ocean
395 surfaces, cloud droplets and evanescent atmospheric droplets, where organics are expected to be
396 enriched at the air interface.

397

398 ASSOCIATED CONTENT

399 **Supporting Information.** Experimental setup details, Tables S1-3 and Figures S1-98. This
400 material is available free of charge via the Internet at <http://pubs.acs.org>.

401

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415 **Notes**

416 The authors declare no competing financial interest.

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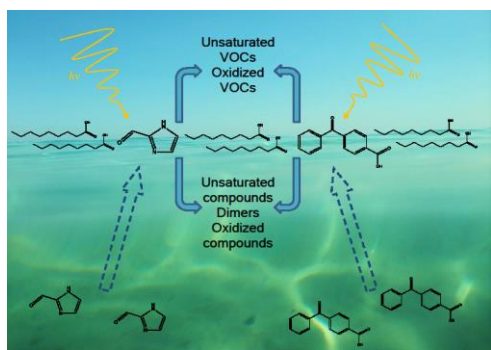
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