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1 Production of peroxy radicals from the
2 photochemical reaction of fatty acids at the air-water
3 interface

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7

8 ABSTRACT: Peroxy radicals are known for their role in tropospheric photochemistry as
9 intermediates in the oxidation of volatile organic compounds, leading to the formation of ozone
10 and organic nitrate compounds. Similarly, in the particle phase, peroxy radicals, considered a type
11 of reactive organic species (ROS), are also involved in many chemical transformations and
12 produce a consequential fraction of aerosols with an impact on health. Here, we show that peroxy
13 radicals are efficiently produced at the air/water interface upon irradiation of an organic film made
14 of a simple fatty acid (i.e., nonanoic acid). This source of peroxy radicals was quantified as 0.27
15 ppbv after interfacial titration of the peroxy radicals by nitric oxide in a photochemical flow
16 reactor. Using a combination of proton transfer reaction – time of flight – mass spectrometry (PTR-
17 ToF-MS) and ultrahigh performance liquid chromatography – heated electrospray ionization –
18 high resolution orbitrap – mass spectrometry (UHPLC-HESI-HR Orbitrap-MS), the products of

19 this photochemistry were identified in the presence and absence of NO. The amount of peroxy
20 radicals produced by this photochemistry was comparable to those measured in surface water, or
21 the ROS bounded to ambient secondary organic aerosols. Accordingly, the photochemistry of
22 surfactant at the air/water interface might play a significant role in the health impact of organic
23 aerosols.

24 **KEYWORDS** Peroxy radicals, Reactive oxygen species, nonanoic acid, photochemistry, air-
25 water interface.

26

27

28 1. INTRODUCTION

29 The oxidative capacity of the atmosphere is obviously gaining a lot of attention for its important
30 role in controlling air quality, but also through the production of ROS due to their effects on human
31 health¹. The broadened definition of ROS includes oxygen-derived free radicals such as peroxy
32 radicals (RO₂•)¹⁻⁴, which play a central role in the oxidation of volatile organic compounds
33 (VOCs). They can react with other radicals present in the atmosphere such as NO, NO₂, HO₂ or
34 other peroxy radicals⁵, and are therefore essential in the budget of tropospheric ozone via the
35 production of NO₂⁶. Although this production has been known for decades, recent measurements
36 of OH and HO₂ radicals have shown disagreements with modeled O₃ concentrations⁷⁻⁹. These
37 findings, together with subsequent investigations, pointed toward unknown reactions involving or
38 producing peroxy radicals as the reason for the difference between observed and modeled O₃ levels
39⁸⁻¹¹. Recent theoretical and experimental studies have now shown that peroxy radicals also play an
40 important role in the initiation of new particle formation via the production of highly oxygenated
41 organic molecules (HOMs)¹²⁻¹⁴.

42 Surface active compounds (i.e., surfactants) are omnipresent at air/water interfaces. In the
43 atmosphere, those surfaces are found on aerosol particles, lakes and oceans, which cover more
44 than 70% of the Earth¹⁵. Very recently, it has been shown that the surface propensity of these
45 surfactants in the sea surface microlayer (SML), which corresponds to the uppermost layer of
46 oceans, combined with the presence of photosensitizing compounds such as dissolved organic
47 matter, induce unique photochemical reactions with a significant effect on the climate. This impact
48 is materialized through their contribution to the formation of organic aerosols¹⁶⁻¹⁸, the abiotic
49 production of VOCs¹⁹⁻²⁴ or by acting as sinks for atmospheric gases such as O₃ and NO₂²⁵⁻²⁸. It
50 was also shown that even a simple monolayer of fatty acid (namely, nonanoic acid) at the air/water

51 interface can be photolyzed under actinic conditions, due to a slight red shift of its absorption
52 spectrum. Such an organic film, when exposed to light in the absence of any photosensitizer,
53 produces unsaturated and functionalized VOCs²³. The authors suggested that these VOCs arise
54 from complex chemistry involving the production of peroxy radicals at the air/water interface.

55 Here, we investigated this interfacial peroxy radical production by studying the chemistry of
56 nitric oxide, acting as a trap for radicals at the surface of the water. This chemistry is discussed in
57 association with the titration of RO₂^{*} radicals produced by the photochemistry of nonanoic acid.
58 Moreover, the VOCs produced were identified using a proton transfer reaction time-of-flight mass
59 spectrometer (PTR-ToF-MS). At the same time, the liquid phase composition was monitored using
60 ultra-high performance liquid chromatography coupled to a high-resolution mass spectrometer
61 (UHPLC-HR Orbitrap-MS).

62

63 2. EXPERIMENTAL SECTION

64 2.1. Photochemical reactor

65 The system used here is similar to the one deployed in our previous investigations^{20,23}. In short,
66 a cylindrical quartz reactor with a path length of 7 cm and an internal diameter of 1.6 cm was used
67 as a photochemical reactor (internal volume ~14 mL). It was typically half filled with pure water
68 with a mono to multilayer coverage of nonanoic acid. This reactor was then irradiated with a xenon
69 arc lamp (150 W, LOT-Quantum Design, France) placed at a distance of 13 cm from the
70 photochemical reactor to mimic the solar irradiation at the Earth's surface. To avoid excessive
71 heating of the reactor, a quartz water filter was placed in front of the lamp to remove infrared
72 irradiation. An additional Pyrex filter was used to eliminate the light in the UV region i.e.,
73 wavelengths lower than 290 nm. A total flow of 300 ml·min⁻¹ of a mixture of air and NO was

74 continuously flowing through the reactor and analyzed using a NO_x analyzer. Identification of
75 VOCs emitted in the gas phase was performed using commercial PTR-ToF-MS. Condensed phase
76 products were analyzed by means of UHPLC (±) HESI-Orbitrap-MS (Figure S1).

77 **2.2. Gas-phase measurements**

78 NO and NO₂ concentrations were monitored simultaneously using a chemiluminescence NO
79 detector (CLD 88p, Eco Physics, Switzerland) coupled to a photolytic converter (PLC 860, Eco
80 Physics, Switzerland), equipped with a metal halide discharge lamp converting NO₂ to NO prior
81 to the detection by the CLD. The NO₂ mixing ratios were corrected by the conversion factor of the
82 photolytic converter. With this instrument, a detection limit of 0.25 ppbv was achieved.

83 The photochemically produced VOCs, in presence or absence of NO, were monitored using a
84 selected reagent ion-proton transfer reaction time of flight mass spectrometer (SRI-PTR-ToF-MS
85 8000, Ionicon Analytik GmbH, Innsbruck, Austria) in H₃O⁺ and NO⁺ modes. Air was sampled at
86 a constant flow of 100 mL/min at an inlet temperature of 60°C for both ionization modes. For the
87 H₃O⁺ mode, a drift voltage of 500 V, a drift temperature of 60°C and a drift pressure of 2 mbar
88 were used, resulting in an E/N of about 125 Td. When NO⁺ mode was used, the settings led to a
89 low E/N of about 93 Td, which was suitable to detect nitrate organic compounds but not too low
90 to avoid water cluster formation ²⁹.

91 **2.3. Condensed-phase measurements**

92 The organic composition of the liquid phase was analyzed by ultra-high-performance liquid
93 chromatography (Dionex 3000, Thermo Scientific, USA) coupled to a high resolution Orbitrap
94 mass spectrometer (QExactive, Thermo Scientific, Germany). Analytes were separated on a
95 Waters Acquity HSS T3 column (1.8 μm, 2.1 x 100 mm) using acidified water (eluent A: 0.1%,
96 v/v, formic acid; Optima LC/MS, Fisher Scientific, USA) and acidified acetonitrile (eluent B:

97 0.1%, v/v, formic acid; Optima LC/MS, Fisher Scientific, USA) as the mobile phase. The
98 QExactive was equipped with a heated electrospray ionization source (HESI) used to apply a
99 voltage of -3.0 kV in negative mode and 3.2 kV in positive mode. The auxiliary gas flow rate was
100 set to 25 arbitrary units (a.u.) and the sheath gas flow rate to 42 a.u. A heater temperature of 250°C
101 and a capillary temperature of 350°C were used. The highest mass resolution of 140 000 at m/z
102 200 was used. A daily mass calibration was performed for the mass range of m/z 50-750 using a 2
103 mM of sodium acetate solution ²³.

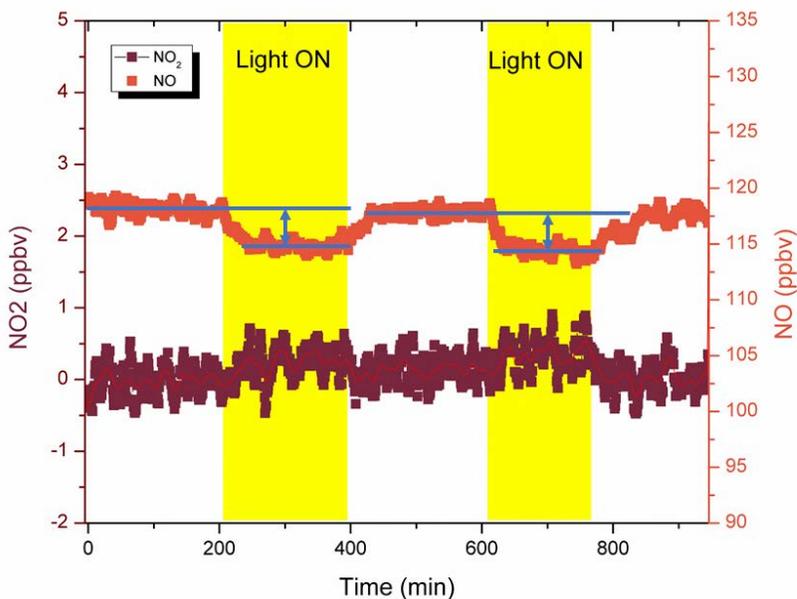
104 Each sample was divided into two aliquots; the first one was analyzed directly after filtration.
105 The second one underwent a derivatization process using an excess of a PFBHA (o-(2, 3, 4, 5, 6-
106 pentafluorobenzyl) hydroxylamine hydrochloride, Sigma Aldrich, ≥ 99.0%) in order to identify
107 the organic compounds containing carbonyl functional groups present in the sample ³⁰. For this,
108 200 μL of the sample was mixed with 800 μL of the PFBHA solution (1 mg/mL). The mixture was
109 left in darkness at room temperature for 24 h before analysis. Three replicates of direct and
110 derivatized analyses were assessed for each sample. Data processing and evaluation were
111 performed using XCalibur 2.2 (Thermo, USA). Formula assignment of the identified compounds
112 were achieved using a mass tolerance of 2 ppm.

113

114 3. RESULTS AND DISCUSSION

115 The production of peroxy radicals, as intermediates in the photochemistry of nonanoic acid, was
116 assessed by the reactive uptake of nitric oxide. Effectively, when the organic fatty acid film was
117 exposed to ~120 ppbv of NO in pure air, a decrease in the level of 1.1 ppbv NO was observed
118 solely when the system was irradiated (Figure 1). This decrease in the NO concentration is
119 understood as being induced by the conversion of NO by the peroxy radicals produced via the

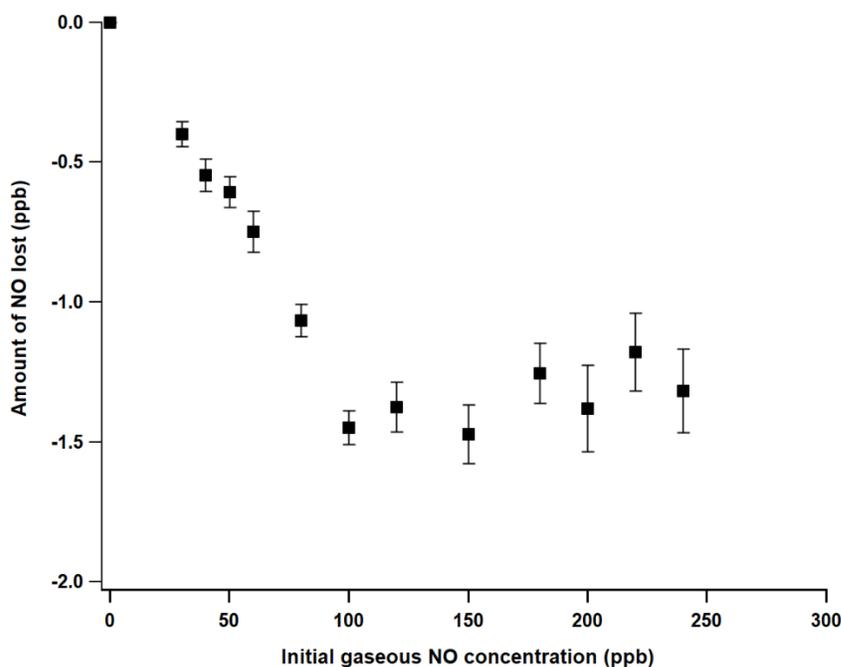
120 photochemical reaction of nonanoic acid, as described by Rossignol et al. ²³, with 1:1
121 stoichiometry. However, this NO conversion was accompanied by only a minimal increase in NO₂,
122 mostly within the noise of our detector.



123
124 **Figure 1.** NO concentration measured in the photochemical reactor when the reactor was
125 irradiated and under dark conditions.

126 Our experimental approach did not allow us to resolve the uptake kinetics of NO, but allowed the
127 determination at steady-state (which was established very rapidly, as shown in Figure 1) of the
128 amount of NO lost at the air/water interface due to the photochemical production of peroxy
129 radicals. The amount of NO lost depends on the initial gaseous NO concentration, as shown in
130 Figure 2. Therefore, to use this information quantitatively, we performed some experiments at
131 higher concentrations, i.e. 120 ppbv NO, where the reaction between RO₂ radicals and NO
132 dominates over the self-reaction and cross-reaction of peroxy radicals, as shown by the plateau in
133 Figure 2 above 100 ppb ^{31,32}. At low NO mixing ratios, i.e. between 30 and 80 ppbv, the loss
134 increased (almost linearly) and levelled off at a NO mixing ratio greater than 100 ppbv. In other

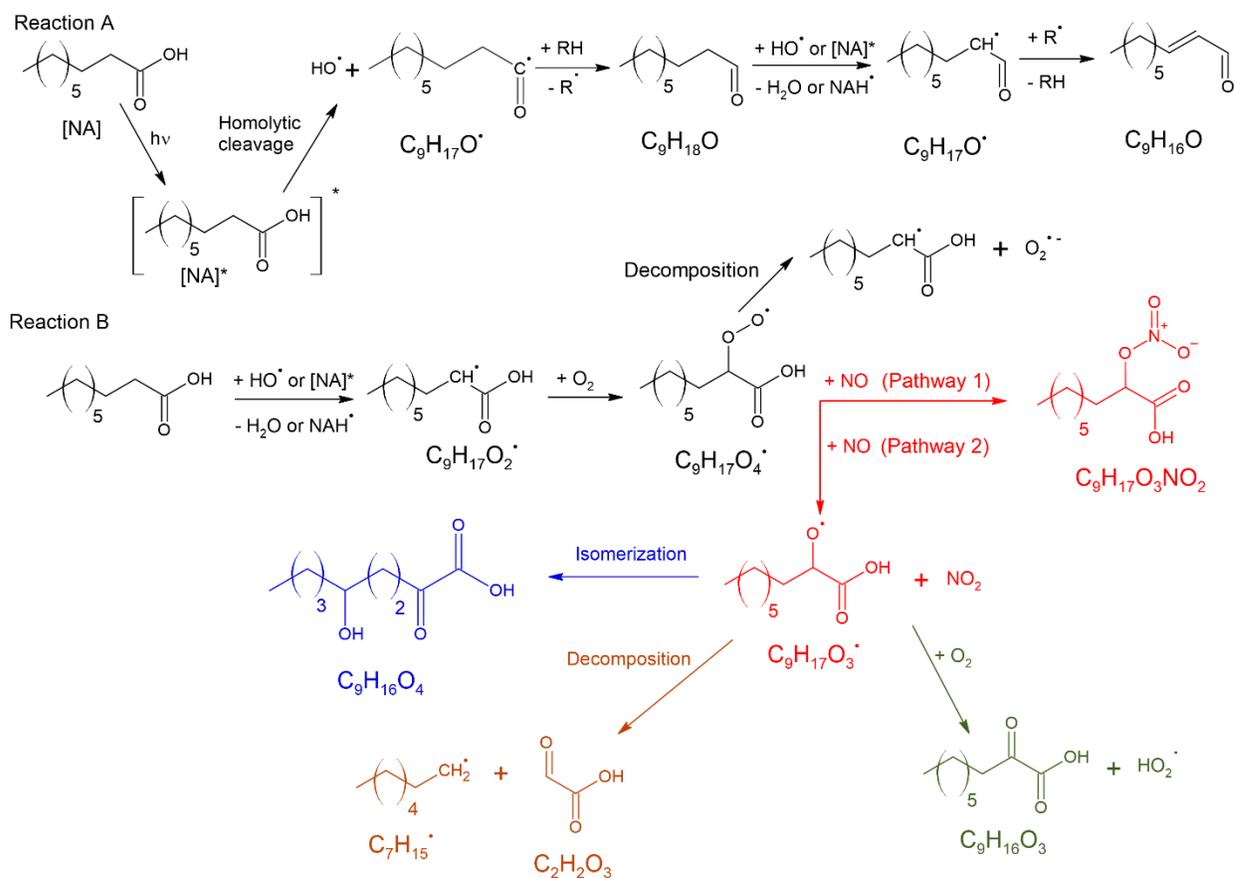
135 words, at concentrations lower than 100 ppbv, self- and cross-reactions of RO₂ are possible, while
136 at higher values, the NO – RO₂ reaction dominates. Therefore, a mixing ratio of 120 ppbv was
137 used in this study to quantitatively determine the amount of peroxy radicals produced by the
138 photochemistry of nonanoic acid.



139
140 **Figure 2.** The amount of NO lost during the photochemical reaction as a function of the initial
141 gaseous concentration of NO in the gas phase of the reactor.

142 In Figure 3, only two pathways from the mechanism suggested by Rossignol et al.²³ are
143 represented, due to their effect on peroxy radical formation and therefore on NO uptake on
144 irradiated nonanoic acid films. The first pathway produces a C₉-aldehyde (C₉H₁₆O) and OH
145 radicals as intermediates. Since it is well-known that NO can react with OH[•], any loss of NO due
146 to this reaction should be taken into account. We therefore studied the production of this C₉-
147 aldehyde, which is initiated by either homolytic cleavage or an inter-molecular Norrish II reaction
148 ²³. Homolytic cleavage (reaction A) produces OH radicals, which could abstract an H atom from

149 a saturated aldehyde ($C_9H_{18}O$) to produce an unsaturated aldehyde ($C_9H_{16}O$). In order to
150 investigate the possible reaction between NO and OH^\bullet , the products of the reaction involving OH^\bullet
151 radicals as a reagent were compared in the presence and absence of NO. An unsaturated C_9
152 aldehyde ($C_9H_{16}O$) was found to be present at similar amounts in both cases, as shown in Figure
153 4. As shown by reaction A in Figure 3, H abstraction from the saturated aldehyde can be done by
154 an excited nonanoic acid molecule $[NA]^*$ as well. $[NA]^*$ does not compete with OH radicals since,
155 according to a quantum chemical investigation into the photochemical reaction of nonanoic acid
156 at an air-water interface, dehydrogenation of the saturated aldehyde by an OH radical is easier than
157 that by an excited nonanoic acid molecule $[NA]^*$ ³³. Therefore, the formation of the unsaturated
158 aldehyde ($C_9H_{16}O$) is due to the reaction of OH radicals with the saturated aldehyde ($C_9H_{18}O$). As
159 shown in Figure 4, an unsaturated aldehyde is formed in the presence and absence of NO, which
160 means that, when NO is present, OH radicals do not react with NO but rather with the saturated
161 aldehyde ($C_9H_{18}O$) to produce the unsaturated aldehyde ($C_9H_{16}O$). Thus, the reaction between NO
162 and OH radicals does not compete with the one between NO and carboxyperoxy radicals
163 ($C_9H_{17}O_4^\bullet$).

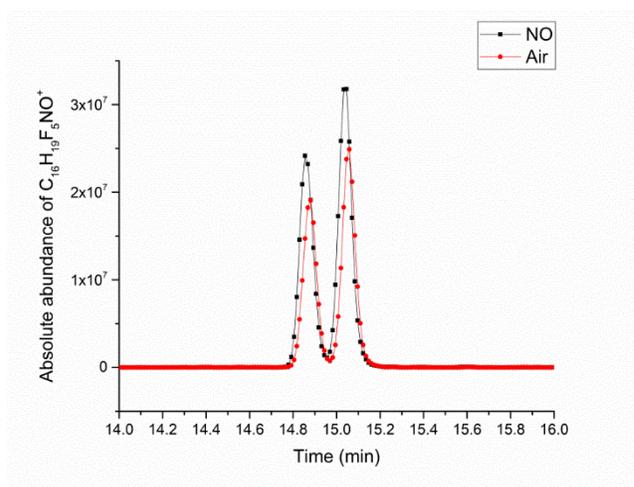


164

165 **Figure 3.** Photochemical mechanism of nonanoic acid (modified from ²³) with the possible
 166 reactions of the peroxy radical with NO. [NA] represents a nonanoic acid molecule, while [NA]*
 167 stands for a nonanoic acid molecule in the excited state. NAH• is a nonanoic acid molecule after
 168 the abstraction of one hydrogen atom from another molecule.

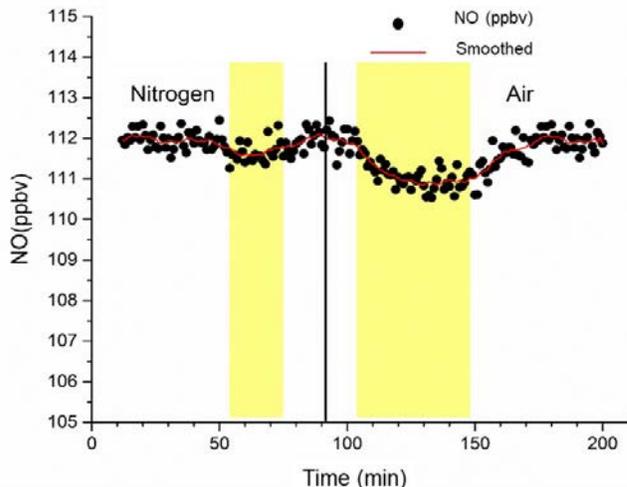
169 As shown by reaction B in Figure 3, the radical $C_9H_{17}O_2^\bullet$ reacts with oxygen to produce the
 170 carboxy peroxy radical ($C_9H_{17}O_4^\bullet$). As previously explained, the carboxy peroxy radical reacts
 171 with NO via two pathways, which leads to the decrease in the NO concentration. In the absence of
 172 oxygen, no peroxy radicals can be produced and the concentration of NO remains constant during
 173 the photochemical reaction. In order to validate the presence of peroxy radicals in this
 174 photochemical reaction, the same photochemical experiment was conducted in the absence of

175 oxygen, i.e., under pure nitrogen. The water was bubbled with a gentle nitrogen stream to remove
176 any dissolved oxygen, and therefore prevent the formation of peroxy radicals. Figure 5 shows the
177 changes in the amount of NO taken up when the reactor was irradiated (yellow highlight) under
178 nitrogen or air as the dilution gas. As highlighted by the smoothed red line, a very small decrease
179 of NO was observed when the reactor was irradiated under nitrogen. However, when air was
180 present in the reactor, more notable uptake of NO was clearly observed. The latter confirms the
181 role of oxygen, and possibly the formation of peroxy radicals, in NO uptake. The slight decrease
182 in the NO mixing ratio under nitrogen could be due to the presence of a small amount of oxygen
183 in the reactor or to the reaction of NO with OH^\bullet produced by the first reaction with nonanoic acid.



184
185 **Figure 4.** Chromatographic peaks corresponding to the derivatized ion of the aldehyde $\text{C}_9\text{H}_{16}\text{O}$

186 According to reaction B of the mechanism shown in Figure 3, the carboxy peroxy radical
187 ($\text{C}_9\text{H}_{17}\text{O}_4^\bullet$) may react with NO via two pathways, or decompose³⁴. The first one (pathway 1)
188 produces complex organic nitrate compounds ($\text{C}_9\text{H}_{17}\text{O}_3\text{NO}_2$), while the second one leads to an
189 alkoxy radical ($\text{C}_9\text{H}_{17}\text{O}_3^\bullet$) and NO_2 , which did not increase significantly here (Figure 1).



190

191 **Figure 5.** NO uptake under nitrogen flow on the left and air flow on the right.

192 However, we did not detect any organic nitrate compounds in the gas or in the liquid phases.

193 Previous studies on gaseous alkyl nitrate formation from the reactions of C₈ – C₁₄ n-alkanes with

194 OH radicals in the presence of NO showed that the branching ratios for the formation of secondary

195 alkyl nitrates are similar for all isomers of a particular carbon number; average values of alkyl

196 nitrate yields were 0.219 and 0.254 for reactions of n-octane and n-dodecane, respectively. The

197 alkyl nitrate yields increased to a plateau of 0.3 for alkyls of C₁₃ and C₁₄³⁵. Even though no studies

198 have been conducted to determine the direct effect of the presence of a carboxylic group adjacent

199 to a peroxy group, the absence of alkyl nitrate compounds in our experiments could be explained

200 by the presence of the carboxylic group, which has a double role in reducing the alkyl nitrate yield.

201 First, the presence of the carboxylic group may induce a net decrease in the yield of organic nitrate

202 by a factor of 3³⁶. In addition, the presence of a hydroxyl group on an adjacent carbon (β-

203 hydroxyperoxy) reduces the branching ratio by 46% compared to the branching ratio of an alkyl

204 peroxy radical. These authors related this to hydrogen bonding between the hydroxy and the

205 peroxy radical³⁷. Based on these two conclusions, organonitrate production from the carboxy

206 peroxy radical (C₉H₁₇O₄•) could be inhibited or at least reduced to very low concentrations. Since

207 the photochemical process studied in this work takes place at an air-water interface, the products
208 of this reaction are expected to be divided between the gas phase and the aqueous phase. Therefore,
209 the amounts of organonitrate present in the gas phase and the liquid phase were probably lower
210 than the limits of detection of the PTR-ToF-MS and the HESI-Orbitrap MS, which explains the
211 absence of any organonitrate compounds produced from the reaction of the carboxy peroxy radical
212 and NO.

213 The second pathway (pathway 2 in Figure 3) in the reaction of NO with the carboxy peroxy
214 radical was observed to be the major one, since the isomerization product ($C_9H_{16}O_4$) and the
215 oxidation product ($C_9H_{16}O_3$) of the alkoxy radical ($C_9H_{17}O_3^*$) were formed exclusively under NO
216 (Figure S3 and Figure S4). These isomerization and oxidation reactions are well-documented for
217 alkoxy radicals derived from linear and cyclic alkanes³⁸. To the best of our knowledge, no studies
218 have been conducted on carboxy alkoxy radicals. Nevertheless, our study showed the presence of
219 the isomerization product $C_9H_{16}O_4$ having, in addition to the carboxylic function, the same
220 functions as hydroxycarbonyls formed from the alkoxy radical isomerization reactions. This
221 compound is produced due to the formation of a six-membered ring (cf. SI)^{31,39}. The
222 decomposition product $C_2H_2O_3$ was not detected in the samples as a product of the reaction in the
223 presence of NO.

224 The detection of these products also demonstrates that the decomposition of peroxy radicals,
225 which produces O_2^{-34} , proceeds on time scales longer than the $RO_2 + NO$ reaction. In fact, such
226 unimolecular decomposition is enabled only for alcohols. In the case of carboxylic acids, the
227 peroxy group is only next to a CO_2H group and it appears that the peroxy radical is the more
228 electronegative substituent, leading to quite slow unimolecular decomposition.

229 **3.1. Environmental implications**

230 In order to compare our results with field results, it is important to correct the observed loss of
231 NO by the ratio between the real solar irradiation and the xenon lamp output in the range between
232 280 and 330 nm, where nonanoic acid absorbs light and reacts photochemically. Scaling down to
233 real actinic conditions (cf. SI), and using the actual flow conditions in our reactor, and finally
234 assuming that one NO titrates one peroxy radical, the aqueous steady-state formation rate R_f of
235 RO_2 can be approximated by the following equation:

$$236 \quad R_f \approx \frac{\Delta NO \times F_g}{V_{aq}} \quad \text{Eq. 1}$$

237 Where, ΔNO is the amount of NO lost (0.27 ppb), F_g the gas flow rate (300 mL min^{-1}) and finally
238 V_{aq} the liquid volume in which the reaction takes place. This volume can be defined by two limiting
239 cases, either the reaction takes place homogeneously in the aqueous volume of the reactor (7 mL)
240 or in an outer shell defined by the local surface enrichment and diffusion limitations which
241 thickness can estimate to be $100 \mu\text{m}$ similarly to the oceanic SML. Applying this equation to our
242 conditions leads to peroxy formation rates in the range from 8×10^{-12} to $5 \times 10^{-10} \text{ M s}^{-1}$. Interestingly,
243 those data compare favorably by those reported by Faust and Hoigné^{40,41} who reported midday
244 peroxy radical formation rates in the rate from 10^{-11} to $10^{-10} \text{ M s}^{-1}$.

245 To derive the steady-state concentration of these peroxy radicals, one can estimate that in the
246 environment their main loss corresponds to their second-order self-recombination reaction, which
247 proceeds with a rate constant of ca. $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ⁴². In this case, the steady-state concentration can
248 be calculated from:

$$249 \quad [ROO]_{ss} = \sqrt{\frac{R_f}{2 \times 10^7}} \quad \text{Eq. 2}$$

250 leading to concentrations in the range 6×10^{-10} - $6 \times 10^{-9} \text{ M}$. One could then speculate that if those
251 are in Henry's law equilibrium, then the concentration of peroxy radicals in the air aloft would be

252 in the range 0.006 – 0.06 ppb (assuming arbitrarily Henry’s law constant of 100 M atm⁻¹,
253 corresponding to the upper limit of reported values⁴³). Several studies have been conducted to
254 measure RO₂• radicals in the marine boundary layer ^{10,44-47}. In these studies, RO₂• radicals ranged
255 between 0.01 and 0.05 ppbv, depending on the season, the measurement location and the air
256 masses. Even though the values of this study are higher than those of previous work, the
257 photochemistry of surfactants could be an important source of peroxy radicals, which may
258 influence atmospheric chemistry models. As an example, Burkert et al. found that the atmospheric
259 model used to simulate the total amount of RO₂• shows a discrepancy with actual measurements.
260 Therefore, they suggested that the presence of reactive non-methane hydrocarbons, which are not
261 measured and included in the model, are responsible for this disagreement ²⁴.

262 The experiments described above were performed on bulk solutions, and cannot therefore be
263 applied to aerosols. Nevertheless, in an attempt to scale up the bulk concentrations given above
264 for peroxy radicals to dispersed ultrafine particles, by normalizing the surface-to-volume ratio of
265 our reactor to those of 200 nm diameter sized particle with an average loading of 15 µg m⁻³, ⁴⁸ we
266 obtain a ROS loading in the range of 0.14-1.4 ppb (hereby assuming that all peroxy radicals are
267 ROS in the condensed phase). This rough estimate is comparable to ambient particle-bound ROS
268 (PB-ROS) measured in different cities. The ambient ROS levels measured at a polluted urban site
269 in the UK varied between 0.098 and 0.59 ppbv of equivalent [H₂O₂] ⁴⁸. An average ROS
270 concentration of 0.2 ppbv of equivalent [H₂O₂] was found during a study in Rochester, New York,
271 USA in 2011 ⁴⁹, which is comparable in magnitude to the concentration of ROS found in our study.
272 Online measurements of PB-ROS in Beijing and Bern showed concentrations between 0.25 to 0.74
273 ppbv, and between 0.025 and 0.049 ppbv, respectively ⁵⁰. In addition, the authors found that PB-
274 ROS are correlated with the oxygenated organic fraction. They showed that this organic aerosol

275 fraction contributed to more than 60% of the total PB-ROS. Considering the fact that surfactants
276 are concentrated in the organic matrix of aerosol particles ¹⁵, this accordance in the results shows
277 the importance of the photochemistry of fatty acids studied here in terms of ROS production and
278 its effects on the atmosphere and human health.

279

280 4. CONCLUSION

281 In this work, the formation of peroxy radicals from the photochemistry of a nonanoic acid film
282 at an air/water interface was indirectly demonstrated. The study of the gas phase and liquid phase
283 products showed the absence of organic nitrate compounds because of the presence of the carboxyl
284 function in the nonanoic acid. On another hand, the reaction of peroxy radicals with NO led to the
285 formation of alkoxy radicals and subsequently new functionalized compounds formed by the
286 oxidation and isomerization of the alkoxy radical.

287 The total amount of peroxy radicals produced was assessed through a titration with nitric oxide
288 (NO). It was shown that the amount of peroxy radicals produced at the air/water interface coated
289 with a film of nonanoic acid is comparable to the concentration of peroxy radicals found in surface
290 water and is consistent with the fact that the SML is concentrated with organic compounds, i.e.
291 surfactants.

292 This study shows the importance of surfactant photochemistry in the oxidative capacity of the
293 atmosphere. Including the production of peroxy radicals from this photochemistry in atmospheric
294 models might explain the difference between the modeled and measured peroxy radicals in the
295 marine boundary layer.

296

297

298 ASSOCIATED CONTENT

299 **Supporting Information.** Determination of the peroxy radicals produced by the photochemical
300 reaction of the nonanoic acid monolayer, Figure S1-S4 and Scheme S1. This material is available
301 free of charge via the Internet at <http://pubs.acs.org>.

302

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307 **Present Address**

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309 Beirut, Lebanon.
310

311 **Author Contributions**

312 The manuscript was written with contributions from all authors. All authors have given approval
313 to the final version of the manuscript.

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319 **Notes**

320 The authors declare no competing financial interests.

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323 **Abbreviations**

324 ROS, Reactive Oxygen Species; VOCs, Volatile Organic Compounds; HOM, Highly Oxygenated
325 Organic Molecules; SML, Sea Surface Microlayer; PTR-ToF-MS, Proton Transfer Reaction Time-
326 of-Flight Mass Spectrometry; UHPLC-HR Orbitrap-MS, Ultra-high Performance Liquid
327 Chromatography High Resolution Mass Spectrometry; HESI, Heated Electrospray Ionization
328 Source; PFBHA, o-(2, 3, 4, 5, 6-pentafluorobenzyl) hydroxylamine; PB-ROS, Particle Bound
329 Reactive Oxygen Species

330

331

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