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Atmospheric photochemistry at a fatty acid-coated air-water interface

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Title: Atmospheric photochemistry at a fatty acid coated air/water interface

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Abstract: While fatty acids are believed to be photochemically inert in the actinic region, complex volatile organic compounds (VOCs) are produced during illumination of an air-water interface coated solely with a monolayer of carboxylic acid, in the absence of any added photosensitizer. When aqueous solutions containing nonanoic acid (NA) at bulk concentrations that give rise to just over monolayer NA coverage are illuminated with actinic radiation, saturated and unsaturated aldehydes are seen in the gas phase and more highly oxygenated products appear in the aqueous phase. This chemistry is similar to that seen in the presence of known photosensitizers, and is probably initiated by triplet state NA molecules excited by direct absorption of actinic light at the water surface. As fatty acids covered interfaces are ubiquitous in the environment (aerosols and ground surfaces), such photochemical processing will have a significant impact on local ozone and particle formation.

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One Sentence Summary: When present at almost monolayer coatings at the air-water interface, fatty acids exhibit a weak UV-visible absorption which, under actinic radiation, triggers radical chemistry leading to the formation of atmospherically reactive species, including unsaturated compounds, but also to low volatility compounds, including dimers, influencing the reactivity of both gas and particulate condensed phase.

~~Main Text:~~ Over the past 20 years, interfacial processes have become increasingly of interest in the field of atmospheric chemistry (1), with many studies showing that environmental surfaces display specific chemistry and photochemistry, enhancing certain reactions and acting as reactive sinks or sources for various atmospherically relevant species (2-5). Many molecules display a free energy minimum at the air-water interface (6-9), making it a favored venue for compound accumulation and reaction. Indeed, surface active molecules have been shown to

undergo specific photochemistry at the air-water interface; for example dimers of 2-oxooctanoic acid are formed there in addition to the expected fragmentation pathways (10). Of importance in the environment, the sea-Surface MicroLayer (SML) is mainly composed of surface active, biogenically-derived organics. Recent measurements of the gas phase above irradiated SML surfaces, or simple organic-coated aqueous samples containing natural photosensitizers, have revealed the photochemical formation of a wide variety of functionalized VOCs (11, 12). Such novel surface photosensitized chemistry could constitute a significant abiotic source of VOCs to the marine boundary layer; it is therefore important to fully understand the production mechanisms. Here we show that complex VOCs may also be produced without an added photosensitizer from an illuminated simple organic acid, which does not absorb actinic light in dilute solutions, but exhibits a totally different behavior once present as coating at the air/water interface.

Nonanoic acid (NA) is a highly surface-active simple organic fatty acid, representative of many biogenic compounds present in the SML. In the gas phase and at its solubility limit in aqueous solution, it does not absorb UV-visible radiation in the actinic region (that is, at wavelengths longer than ~ 280 nm). Surprisingly, when a 15 mL quartz reactor was filled halfway with a 2 mM aqueous solution of NA, a concentration giving rise to just over a monolayer, and irradiated for 1 hour with a Xenon arc lamp, prompt formation of gas-phase saturated and unsaturated C₉ and C₈ aldehydes was observed. [FigureFig. 1](#) displays this remarkable result. In addition to the aldehydes, a wide variety of (mostly oxygenated) photoproducts was detected in both gas and condensed phases; these are listed in Table S1.

The influence of oxygen on the product distributions is displayed for the gas and solution phase in [FigureFig. 2](#), by comparing the ratios of net production of some of the observed products obtained in an atmosphere of N₂ versus under air. Saturated and unsaturated aldehydes and ketones (\leq C₉) are observed in both phases. In the condensed phase, C₉ products with three or

more oxygen atoms, tentatively identified as NA bearing additional hydroxyl and/or carbonyl functions, were also detected. These are clearly favored when oxygen is more abundant. On the contrary, alkenes, such as C_4H_8 and C_5H_{10} , were detected in the gas phase and were favored in the absence of oxygen. Additionally, $C_{18}H_{34}O_4$, the covalently bonded dimer of the parent acid, was observed in the condensed phase and favored in an oxygen poor environment.

The inset of [Figure Fig. 2](#) further illustrates the surface-specific nature of the chemistry. For some experiments, the quartz reactor was filled completely to eliminate the air-water interface exposed to light. The enrichment observed in the experiment with an irradiated surface (defined as the ratio of the net production with irradiated surface over the production without irradiated surface) clearly demonstrates that both the $C_{18}H_{34}O_4$ product and the C_9 saturated monocarbonyl compound ($C_9H_{18}O$) are formed only when there is an interface present in the absence of oxygen. This result also shows that reactions taking place on the quartz surfaces of the reactor are not responsible for the observations.

The results outlined above are consistent with an interface-specific radical-initiated reaction, with a mechanism similar to those we have previously reported for reactions initiated by a known photosensitizer (11-13). The significant and surprising finding here is that there is no added photosensitizing agent to initiate the chemistry. Of course, this immediately suggests that an impurity is responsible. HPLC-MS analysis of the NA samples gave no detectable aldehyde impurities. When a higher purity grade (99.5%) of NA was used, no significant difference in the products was observed upon irradiation (See Fig. S1). Likewise, Inductively Coupled Plasma (ICP) analysis of the 97% purity NA (described in the SM) shows that photoactive transition metals, in particular Fe and Cu, are not responsible for initiating this chemistry. The experiments were repeated using a Pyrex filter with a 50% transmittance cut-off of 315 nm. Although the total amount of product formation after 1 hour of irradiation was smaller than without the filter, by extending the irradiation time to 5 hours, most of the previously detected

products were observed with intensities comparable to those obtained after 1 hour without the optical filter (shown in [FigureFig. S2](#)). These tests lead us to conclude that nonanoic acid is somehow itself responsible for the observed photochemistry.

Such photochemistry has not been reported previously and dilute aqueous solutions of NA do not absorb in the near UV range. However, the UV-vis absorption spectra of neat or concentrated solutions of NA reveal an interesting feature. Figure S3 shows that in addition to the main absorption band of NA, centered as expected at 212 nm (*14*), a second very weak absorption band is seen. This is centered at 270 nm and extends to about 330 nm, growing linearly in intensity with increasing [NA]. Such weak absorption bands centered around 270 nm have been observed previously for a series of neat small aliphatic carboxylic acids (*15*). Although the acid anhydride is expected to absorb in this region (*16*), it seems highly unlikely that this species would be found in aqueous solution. If instead there is a very weakly-absorbing reactive state of the acid, favored at the interface, its existence could explain the initiation of photochemistry seen here. [FigureFig. S4](#) illustrates the overlap between the absorption of neat NA and the solar spectrum at Earth's surface.

Indeed, quantum chemical calculations, described fully in the SM, carried out on propionic acid using density-functional theory at the B3LYP 6-311+G(2df, 2p) level, indicate the presence of a triplet state lying at 402 kJ/mol above the ground state, whose Franck-Condon maximum is predicted to be at 443 kJ/mol (i.e. 270 nm). Although direct absorption to a triplet is expected to be weak, in the present 2 mM NA experiments the acid is quite concentrated at the water surface, as indicated in the adsorption isotherm displayed in [FigureFig. S5](#). With a monolayer coating indicated to form near 0.6 mM, the 2 mM solutions will exhibit multilayers of NA at the surface, perhaps giving rise to light absorption similar to that given by a neat solution of NA.

If a triplet state is responsible for initiating the surface photochemistry, one can imagine several possible initiation steps. The direct photochemistry of carboxylic acids in the 200-260 nm range can lead to a photolytic cleavage following a Norrish type I reaction, giving rise to the formation of radicals. If the triplet state reacts similarly, one might expect the products to include octyl radicals, but this cannot explain the formation of the observed dimers of NA or any of the observed C₉ compounds. Another possibility is the direct dissociation pathway that forms OH and nonyl radicals. Our quantum chemical calculations indicate that this channel is energetically possible for the triplet, being endothermic by 437 kJ/mol for the ground state species, so near thermoneutral for the triplet. If OH is formed, it is expected to give a suite of products similar to what is observed, as shown by experiments using H₂O₂ as a photoinitiator and displayed as [FigureFig. S6](#). The acyl radical could abstract a hydrogen from an adjacent acid to form the C₉ saturated aldehyde and an acid radical; this reaction is predicted to be only weakly endothermic (~ 6 kJ/mol) for the C₃ system and so may represent a formation route to the C₉ saturated aldehyde.

An alternative (or parallel) reaction initiation could involve the excited triplet acid acting as a "traditional" triplet photosensitizer: abstracting a hydrogen from an adjacent acid molecule to form a diol radical and an acid radical. This "intermolecular Norrish type II" reaction is predicted to be energetically feasible (exothermic by ~61 kJ/mol), with a low transition state energy (see SM for details). The formation of a diol radical may explain the formation of both the C₉ carbonyls, nonanal and nonenal, via diol dehydration in the water-poor organic surface layer.

Both initiation mechanisms appear to compete with classical hydrogen abstraction initiated by OH radicals. Indeed, the experiments performed in the presence of H₂O₂ in the aqueous phase also show the formation of C₉ carbonyls (Fig S6) whose formation can only be explained by these newly proposed chemistries. A general mechanism for the NA photosensitized

degradation follows that proposed for octanol at the air-water interface (13). As illustrated in [Figure Fig. 3](#), after H-abstraction from the acid (by an excited triplet acid, or by OH or an organic radical) two fates for the resulting C₉ acid radical are expected: the addition of molecular oxygen and radical-radical recombination. Oxygen addition, followed by disproportionation and decomposition, is expected to be favored in the presence of O₂. This pathway is in competition with radical recombination and other radical-radical reactions, expected if there is a high concentration of radicals and/or the availability of O₂ is reduced. The latter pathway readily explains the greatly enhanced appearance of NA dimer recombination products in the N₂-only experiments. This type of radical recombination, which is fast, has been observed previously in photosensitized reactions in aerosols (17) and at the air-water surface (9,12), but occurs only where high radical concentrations are achieved (18). The presence of such recombination products highlights some features of the surface active enhanced concentration at the air/water interface, which could also then favor disproportionation reactions (19), explaining the formation of nonenoic acid.

In conclusion, we report the photochemical production of functionalized and unsaturated compounds at a nonanoic acid-coated air/water interface in the absence of any known photosensitizer. This photochemistry may indicate the involvement of a triplet state common to all carboxylic acid molecules, accessible following light absorption in the environmentally relevant 280-330 nm UV region. The weak absorption to this state suggests that accessing the triplet is only possible for concentrated solutions of NA, such as exist for multilayers of surface-active acids at the air/water interface and could be particularly relevant for longer-chain acids (20). Reaction could be initiated by dissociation of this excited state, producing radicals, or by the formation of a diol radical following reaction of an excited state fatty acid with an adjacent molecule.

As fatty acid covered surfaces are ubiquitous, the photochemical production of gas phase unsaturated and functionalized compounds will impact the local oxidative capacity of the atmosphere and will lead to secondary aerosol formation. This interfacial photochemistry may exert a very large impact, especially if it is general that the mere presence of a surface layer of a carboxylic acid can trigger it at ocean surfaces, cloud droplets and the surface of evanescent aerosol particles.

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Fig. 1. Mass spectrometry time traces (using NO⁺ ionization) of the C₉ unsaturated (blue) and C₈ saturated (red) and unsaturated (black) aldehydes observed in the gas phase during illumination of the NA-coated water surface. The inset shows the first order derivatives of the first 28 minutes of irradiation, showing the different slopes for each compound (see also SM).

Fig. 2. Comparison of the enrichment of the net production of selected compounds in the condensed phase and the gas phase under N₂ compared to the production in air. The inset shows the enrichment of the net production in the condensed phase when an irradiated surface is present compared to a bulk irradiated only experiment, under air and N₂. Errors reflect the analytical uncertainties (condensed phase) or repeatability between experiments (gas phase). *Detected as PFBHA derivatives. #Identified as ketone due to NO⁺ adduct.

Fig. 3. Reaction mechanisms for nonanoic acid following its excitation to the triplet state.

Supplementary Materials:

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Materials and Methods

Tables S1 to S3

Figs. S1 to S5

References (21-26)

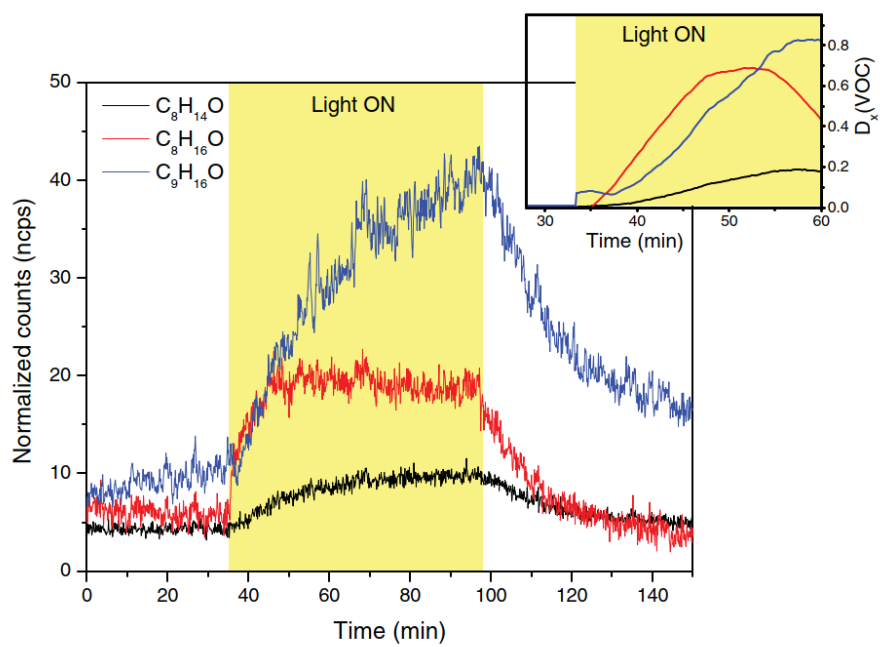
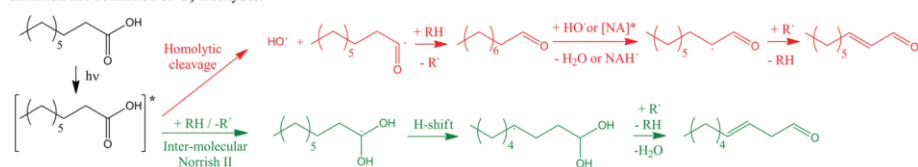


Fig. 1

Initiation and formation of C₉ aldehydes:



HO• or [NA]* can react with NA according to:

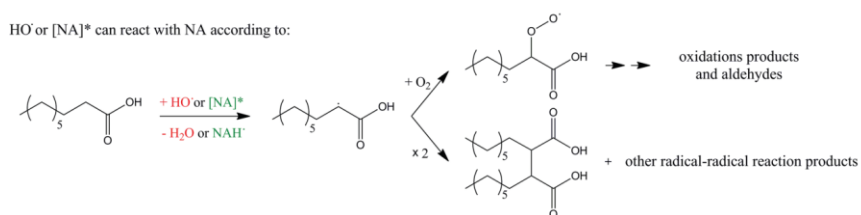


Fig. 3