



Photosensitized Production of Atmospherically Reactive Organic Compounds at the Air/Aqueous Interface

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Supporting Information

ABSTRACT: We report on experiments that probe photosensitized chemistry at the air/water interface, a region that does not just connect the two phases but displays its own specific chemistry. Here, we follow reactions of octanol, a proxy for environmentally relevant soluble surfactants, initiated by an attack by triplet-state carbonyl compounds, which are themselves concentrated at the interface by the presence of this surfactant. Gas-phase products are determined using PTR-ToF-MS, and those remaining in the organic layer are determined by ATR-FTIR spectroscopy and HPLC-HRMS. We observe the photosensitized production of carboxylic acids as well as unsaturated and branched-chain oxygenated products, compounds that act as organic aerosol precursors and had been thought to be produced solely by biological activity. A mechanism that is consistent with the observations is detailed here, and the energetics of several key reactions are calculated using quantum chemical methods. The results suggest that the concentrating nature of the interface leads to its being a favorable venue for radical reactions yielding complex and functionalized products that themselves could initiate further secondary chemistry and new particle formation in the atmospheric environment.

Air/water interfaces are ubiquitous in the environment, with the air/sea interface being among the most obvious.¹ The air/water interface represents a unique environment for chemical reactions because the high surface energy of water means that many organic species are surface active having surface mole fractions greater than those in the bulk.^{1,2} This surface activity gives rise to a concentrating effect at the interface: reagents may be present there at much greater effective concentrations than in either the underlying water or overlying air bulk phases. Moreover, this concentrating effect may be enhanced if the presence of one compound at the interface increases the propensity of other compounds to reside there as well.¹ This effect is seen, for example, in the increased surface partitioning of

polycyclic aromatic hydrocarbons (PAHs) at the water surface when there is a near monolayer coating of 1-octanol present there.^{3–5} Organic coatings at the surface of aerosols, lakes, and oceans have been proposed to impact both atmospheric and prebiotic chemistries.^{1,6,7}

Such surface coatings, potentially as thin as a monolayer, may also provide a different reaction medium compared to bulk water, thus modifying reaction mechanisms, rates, and products,^{1,8–10} as shown for peptide bond formation.¹¹ Furthermore, specific chromophores concentrated within organic surface films could absorb actinic radiation and initiate photochemistry^{12,13} at the interface. This led to the investigation of photoenhanced uptake of NO₂ and O₃ at surfaces containing photoactive compounds, such as simple aromatic ketones or chlorophyll present at the air/sea interface.^{14,15} There is also a growing body of evidence that some aerosols contain strong light-absorbing compounds, such as humic-like substances,¹⁶ aromatic carbonyls, or in situ produced *N*-derivatized imidazoles,¹⁷ which can photosensitize reactions that give rise to secondary organic aerosol (SOA) formation and aging.¹⁸ In general, however, photochemistry at interfaces remains very poorly characterized, giving rise to potentially large uncertainties in our ability to simulate and predict both atmospheric processes and sea surface chemistry.¹⁹ In particular, there has been no attention paid to the impact of such specific chemistry on the photosensitized production of gaseous volatile organic compounds (VOCs) from aqueous surfaces, nor to the chemical signatures of the VOCs thus released. Although ozonolysis at (marine) environmental surfaces has been shown to produce a series of gaseous carbonyls and some unsaturated compounds, these carry only unsaturations already present in their parent molecules.²⁰ For the most part, the production of unsaturated compounds in the marine environment has been attributed solely to biological activity.

In the following, we challenge this viewpoint and show that trace amounts of photoactive agents concentrated at the air/water interface can give rise to a distinct interfacial chemistry

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producing unsaturated products from linear alkyl chains. We probed photochemistry by measuring the gas-phase products obtained from a radical reaction initiated at the octanol-coated air/water interface and comparing these to those from a reaction initiated in the same way but taking place in a bulk octanol environment. Trace quantities of a photosensitizer present at the interface (either imidazole 2-carboxaldehyde (IC) or 4-benzoylbenzoic acid (BBA)), when excited to the triplet state, initiated radical reactions by abstracting a H atom from 1-octanol molecules present in monolayer amounts, creating a C₈ alcohol radical. The ultimate gas-phase reaction products, which surprisingly include atmospherically reactive unsaturated and carbonyl-containing compounds, were detected using proton-transfer reaction time of flight mass spectrometry (PTR-ToF-MS). These products are compared to those obtained from the reaction initiated by either IC or BBA in a thin film of 1-octanol spread on a ZnSe crystal, measured by ATR-FTIR and HPLC-HESI/HRMS. Quantum chemical calculations are used to confirm the proposed reaction mechanisms.

To demonstrate the concentrating effect of an organic monolayer on the photosensitizers used here, Figure 1 displays

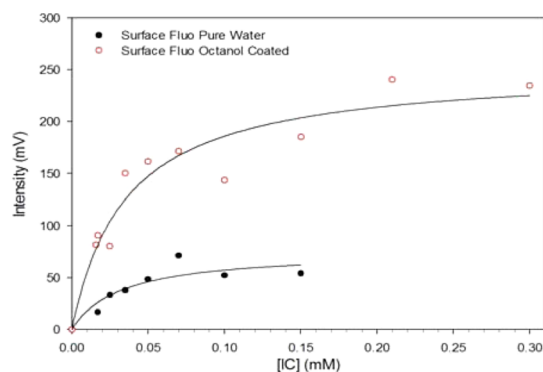


Figure 1. Fluorescence intensity of IC at the air/aqueous interface, measured at its maximum emission wavelength. Emission wavelength of 335 nm as a function of the concentration of photosensitizer (IC) in the bulk, measured at a pure water surface (●) and at a 1 mM octanol-coated surface (○). The solid lines show fits to Langmuir adsorption isotherms.

adsorption isotherms of IC at the air/aqueous interface, obtained from glancing-angle laser-induced fluorescence spectra. Although the bulk fluorescence of IC in octanol is about 5 times less intense than that in pure water, a clearly enhanced fluorescence of IC is observed at the surface of a 1 mM solution of 1-octanol, an aqueous concentration giving rise to near-monolayer coverage at the surface.⁵ It is clear that the surface concentration of the photosensitizer is enhanced in the presence of a 1-octanol coating, indicating an increased propensity to partition to the organic-coated interface. An enhanced presence of photosensitizer at the coated interface strongly suggests that photosensitized reactions may also be enhanced there.

To test this hypothesis, we measured the gas-phase products evolved following illumination of a cell containing an octanol-coated aqueous solution of BBA, which is also expected to show an enhanced concentration at an organic-coated aqueous interface. A quartz cell (2 cm diameter and 5 cm length) was half-filled with 7 mL of 18 MΩ deionized water with 0.1 mM BBA and 2.5 mM 1-octanol; this solution was continuously purged with 100 sccm of purified air. After a stabilization time, the cell was illuminated by a 150 W Xe lamp, simulating actinic solar radiation. As soon as the continuous illumination started, a

series of gas-phase compounds, including octanoic acid, octenoic acid, and several unsaturated C₆ and C₈ products, was observed by PTR-ToF-MS, as shown in Figure 2 and Table S1. Such

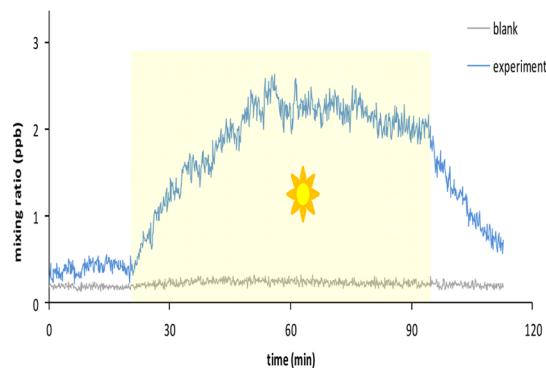


Figure 2. PTR-ToF-MS results from a typical irradiation experiment. The gas-phase concentration of 1-octenal is shown as a function of time following illumination (indicated by the yellow highlight). The gray line shows the result from a blank experiment, in which no BBA was present. The blue line displays the results seen when a solution containing water, 1-octanol, and BBA is illuminated.

gaseous products containing double bonds and/or carbonyl functions are rapidly produced and reach a steady state level after ~25 min. As soon as the light is switched off, the gas-phase concentrations of these compounds decrease swiftly and return to background levels after 20 min. The detected unsaturated species include hexenal (*m/z*, 99.080), octenal (*m/z*, 127.112), hexenoic acid (*m/z*, 115.075), octenoic acid (*m/z*, 143.107), and heptene (*m/z*, 99.117). These unsaturated compounds were about 14 times more plentiful in the gas phase than the C₆ and C₈ acids. Long carbon chain products (C₁₅, C₁₆) were also detected (Table S1). Control experiments indicated no formation of any gas-phase organic compounds in the dark or in the absence of the photosensitizer.

Because the gas-phase products seen with illumination (and reported in Table S1) appear to derive from 1-octanol, we carried out further experiments in which thin films of 1-octanol containing either IC or BBA were deposited on a ZnSe ATR crystal then irradiated with a UV lamp (20 W, 280–400 nm). The photochemical reaction was followed in time by monitoring changes in the FTIR spectrum. The reactions initiated by both photosensitizers show similar behavior. Net changes in the absorption spectra are shown in Figure 3 with peak assignments given in Table S2. Peaks assigned to 1-octanol diminished in intensity, as indicated by the negative-going peaks in the figure, appearing at 2958 cm⁻¹ (-CH₃ asymmetric stretching), 2926 cm⁻¹ (-CH₂ symmetric stretching), 2852 cm⁻¹ (-CH₂ asymmetric stretching), 1461 cm⁻¹ (-CH₃ bending mode), and 1061 cm⁻¹ (C-O stretching vibration).²¹ At the same time, product peaks appeared, indicative of branched aliphatic hydrocarbon components, for instance, the peak seen at 1108 cm⁻¹ corresponding to the bending vibration of a branched carbon backbone. The wide band appearing around 1380 cm⁻¹ splits into a doublet with peaks at 1388 and 1368 cm⁻¹, assigned to C-H bending from tertiary carbon.²² A broad product peak was also observed in the region of 1600–1750 cm⁻¹, which could be separated into four independent peaks centered at 1713, 1671, 1642, and 1611 cm⁻¹ using Gaussian fitting (OMNIC8.2, Thermo Scientific). The resulting fits are shown in Figure S1. The shoulder peak at 1713 cm⁻¹ is assigned to an absorption band

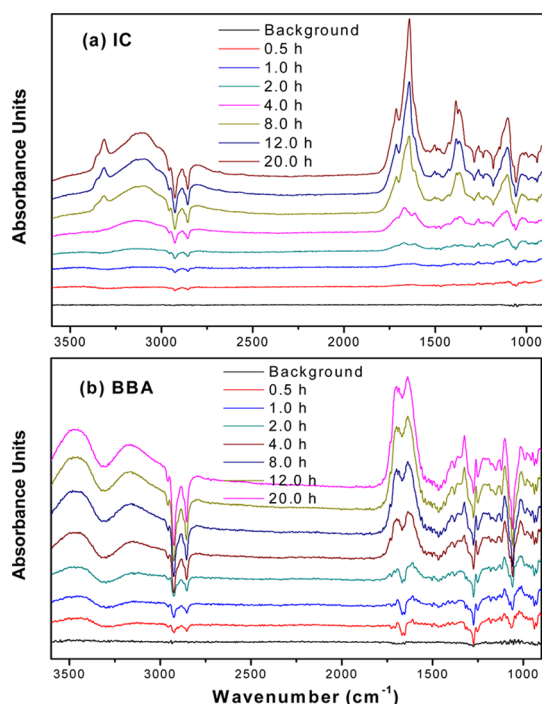


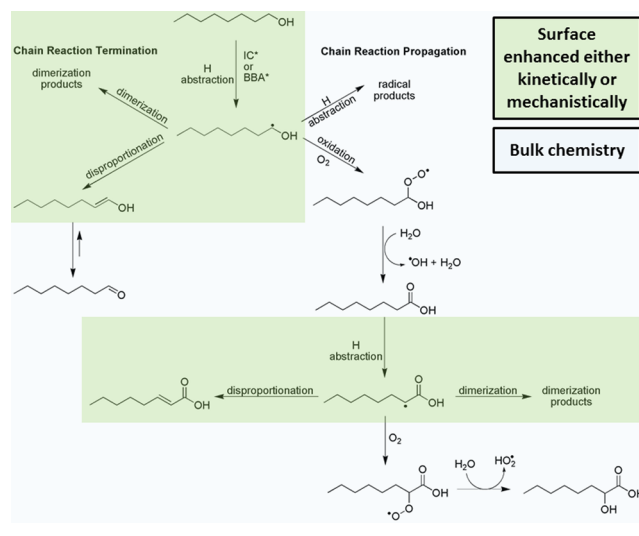
Figure 3. Time-resolved ATR-IR absorbance spectra: phototransformation of 1-octanol in the presence of (a) IC and (b) BBA under irradiation.

from C=O groups of carboxylic acids, supported by the observation of weak absorption bands at ~ 2680 and ~ 2558 cm^{-1} , assigned as the O–H stretching vibration of carboxylic acids.^{23,24} The peak at 1671 cm^{-1} was assigned to the C=O vibrations of unsaturated aldehyde structures, and the sharp peak at 1642 cm^{-1} was assigned to the C=C stretching of the same structure.

The FTIR results described above are consistent with the general picture obtained from the PTR-ToF-MS measurements: formation of branched and unsaturated functionalized compounds from 1-octanol following illumination. After the FTIR experiments, the products in the illuminated sample were identified using HPLC(-)HESI/HRMS. The major product seen was $\text{C}_8\text{H}_{16}\text{O}_3$ (m/z 159.103), attributed to hydroxyoctanoic acid. Five chromatographic peaks at this mass were observed (Figure S2), probably because of five different positions of the hydroxyl function on the carbon chain. This is in good agreement with the FTIR spectra (Figure 3) that show a new peak around 1700 cm^{-1} which could be assigned to the carbonyl region of the -COOH groups. Generally, the condensed-phase products detected here represent longer carbon chains ($\sim \text{C}_{22}$) than those identified by PTR-ToF-MS ($\sim \text{C}_{16}$). This points to different partitioning of the products: those with higher solubility or lower vapor pressure are trapped in the condensed phase, whereas those with significant volatility are more readily observed in the gas phase.²⁵

From this global picture of the products formed during the irradiation of an octanol layer in the presence of a photosensitizer, a general mechanism can be proposed, as illustrated in Scheme 1 and confirmed by the results of quantum chemical calculations (Tables S3 and S4). The first step is the known formation of the photosensitizer triplet state under irradiation.^{26,27} This energetic species can then abstract a H from 1-octanol to form a hydroxyoctyl radical, a process that is quite exothermic as estimated by the quantum calculations. This step

Scheme 1. Proposed Mechanisms for Photochemical Reactions at the Interface in the Presence of Octanol and a Photosensitizer, Highlighting the Specific Nature of the Surface Chemistry



could be kinetically enhanced at the interface because of the enhanced concentration of the photosensitizer there. Regeneration of the IC molecule is possible in the presence of O_2 via H abstraction to form HO_2 , another very exothermic process. Formation of condensed-phase HO_2/O_2^- was indeed observed by means of ESR, as shown in Figure S3. Characteristic peaks of HO_2/O_2^- were observed for 1-octanol mixed with BBA,^{28,29} and the signal intensity increased markedly with irradiation time. No such signals were observed in the dark.

The C_8 alcohol radical formed in the first reaction can suffer one of two probable fates: disproportionation or dimerization in the presence of another such radical and addition of O_2 , forming a peroxy-alcohol radical. Although both are strongly exothermic, we expect that the likelihood of the disproportionation will increase as the local concentration of radicals becomes large, e.g., under our conditions of continuous illumination with constant regeneration of the photosensitizer. The ready availability of O_2 from the gas phase will certainly help to promote the O_2 addition reaction at the air interface, giving a ready source of peroxy-alcohol radicals there.

The disproportionation of the hydroxyoctyl radical will yield as products an unsaturated product and the original alcohol. The location of the unsaturation will depend upon the location from which the H abstraction occurs. The formation of octanal from the α/β unsaturated alcohol is energetically favorable, providing a route to aldehyde products. Although elimination of HO_2 from the peroxy-alcohol could also give unsaturated or aldehyde products, this process is calculated to be quite endothermic, so it is likely to be very slow at room temperature. A more likely fate for α -peroxy-alcohol is carboxylic acid formation via elimination of OH, which is calculated to be exothermic. Although such four-membered ring reactions typically exhibit high activation barriers, the presence of a bridging water molecule has been shown in similar cases to lower considerably the transition state energy.³⁰ The ready availability of water molecules at the air/water interface is thus likely to play an important role in the acid formation reaction. Following the production of these first-generation products, similar radical reactions involving the daughter compounds may take place. For example, a disproportionation type reaction involving an octanoic acid

radical could yield the octenoic acid species observed here. Likewise, radical recombination without reaction will give branched compounds containing C₁₆ backbones, also observed here.

The similarity in the products observed from the 1-octanol film and the water surface experiments suggests that the latter take place in an octanol-rich region of the aqueous system. The strong partitioning of IC to the 1-octanol-coated interface that we observe here, in conjunction with the known surface-partitioning behavior of the alcohol, suggests that the initial radical formation takes place in the interface region, where both reagents are concentrated. Indeed, to be competitive with quenching of ³IC* by water,³¹ the first-order reaction rate of ³IC* with 1-octanol in bulk aqueous solution must be >6 × 10⁵ s⁻¹; with the concentration of 1-octanol used here, this implies a near-diffusion-limited reaction rate constant of 2.4 × 10⁸ M⁻¹ s⁻¹ for the H abstraction reaction. Although conceivable, this seems unphysically high for an atom transfer reaction between neutral species. The formation of acidic products requires the availability of O₂; it may be that the presence of water is also critical to lower the OH elimination barrier. The concentrations of both of these are high in the interface region.

The irradiation of an organic film in the presence of photosensitizers at the water surface clearly leads to release of VOCs to the gas phase without any gas-phase oxidants except molecular O₂ playing a role. The advantageous venue provided by the organic-coated water surface region can help promote photoinitiated radical chain reactions, including radical/radical, radical/molecule, or intramolecular rearrangement, to produce either another radical or molecule. The surface activity of the organic compounds involved in the interfacial photochemistry allows for their local concentrations to be greater than their bulk concentrations, increasing the probability of contact between reactive species. The presence at the interface of both gas-phase O₂ and aqueous-phase water allows these species to participate as well in the reaction in a facile manner. The work presented here demonstrates that an organic film at the top of an aqueous phase represents a favorable venue for photoinduced chemistry. Because aqueous surfaces coated with organic films are potentially widespread in the environment (oceans, lakes, wet aerosols, cloud droplets, etc.), it seems clear that such photochemistry has the potential to increase abiotic VOC emissions, including unsaturated VOC emissions, that can contribute to SOA formation. This process could be one of the missing sources of SOA in current modeling and could be consistent with a number of previously unexplained field study observations.^{19,25}

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details, characterization data, and results of quantum chemical calculations. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04051.

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Notes

The authors declare no competing financial interest.

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