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Photoinduced oxidation reactions at the air–water interface.

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ABSTRACT: Chemistry on water is a fascinating area of research. The surface of water and the interfaces between water and air or hydrophobic media represent asymmetric environments with unique properties that lead to unexpected solvation effects on chemical and photochemical processes. Indeed, the features of interfacial reactions differ, often drastically, from those of bulk-phase reactions. In this perspective, we focus on photoinduced oxidation reactions, which have attracted enormous interest in recent years because of their implications in many areas of chemistry, including atmospheric and environmental chemistry, biology, electrochemistry, and solar energy conversion. We have chosen a few representative examples of photoinduced oxidation reactions to focus on in this perspective. Although most of these examples are taken from the field of atmospheric chemistry, they were selected because of their broad relevance to other areas. First, we outline a series of processes whose photochemistry generates hydroxyl radicals. These OH precursors include reactive oxygen species, reactive nitrogen species, and sulfur dioxide. Second, we discuss processes involving the photooxidation of organic species, either directly or via photosensitization. The photochemistry of pyruvic acid and fatty acid, two examples that demonstrate the complexity and versatility of this kind of chemistry, is described. Finally, we discuss the physicochemical factors that can be invoked to explain the kinetics and thermodynamics of photoinduced oxidation reactions at aqueous interfaces and analyze a number of challenges that need to be addressed in future studies.

1. INTRODUCTION

Chemical processes are sensitive to the molecular environments where they take place, including the solvent, the protein active site, or the surface of a material. The environment influences the relative stability of the species along the reaction path. In the case of liquids, the solvation power and the nature of the reaction system determine how different species are stabilized, and the differential stability may retard or accelerate the reaction process. Moreover, environmental factors can also modify the regioselectivity or stereoselectivity, the endo/exothermicity, or even the mechanism.¹

When reactions occur at the surface of liquid water or at the interface of liquid water with a hydrophobic medium, the asymmetry of the interface, the presence of free water OH-groups, and the distinctive properties of interfacial water often lead to unexpected solvation effects on chemical reactions, and the resulting properties are not necessarily intermediate between the two bulk phases.² For instance, a variety of thermal reactions occurring at aqueous interfaces have been found to be significantly accelerated compared to the bulk reactions; this effect is referred to as “on-water catalysis.”³ The reaction rate acceleration can stem from an increase in reactant concentration (molecular crowding) or the stabilization of a transition state (or a combination of both); however, a full understanding of this mechanism remains lacking. The enhancement of redox reactions has been broadly studied in this context, with

prominent examples including H-abstraction by OH,⁴ ozonolysis⁵⁻¹¹ and ozonations,¹² Fenton and Fenton-like reactions,¹³ Dakin and Baeyer–Villiger oxidations,¹⁴ halide anion oxidation by OH and O₃,¹⁵ and the spontaneous formation of hydrogen peroxide¹⁴ and spontaneous reduction of organic molecules¹⁶ at the neat water surface.

This Perspective deals with the special case of photoinduced oxidation reactions at aqueous interfaces. Photoredox chemistry covers a broad range of processes with great atmospheric and environmental relevance.^{17,18} These processes are also key in the fast-developing field of photocatalysis,¹⁹ which in a non-restrictive sense connects multiple disciplines such as synthetic organic chemistry to biochemistry, electrochemistry, water purification technologies, and solar energy conversion. A review of the literature related to all these fields obviously goes beyond the scope of the present report; however, the roles of liquid water interfaces in reaction kinetics, dynamics, and thermodynamics are highly relevant in all the above fields.

In the atmosphere, gas-phase photochemistry is fundamentally associated with photooxidation by OH radicals and other reactive oxygen species (ROS).^{20,21} The main source of tropospheric OH is the photolysis of ozone via the absorption of ultraviolet (UV) light in the presence of water vapor, although several other routes can lead, directly or indirectly, to the formation of OH radicals.²² ROS react with other compounds to initiate and propagate most tropospheric

chemical reactions. A **simplified** scheme illustrating the complexity of the tropospheric chemistry of ROS in the gas phase is shown in Fig. 1. **It shows the set of coupled reactions that constitute the sources and sinks of reactive oxygen species and the crucial role played by ozone and hydroxyl radicals.** On the other hand, the aqueous-phase chemistry of ROS is of cross-cutting importance in biology, environmental science, and water treatment, for instance.²³

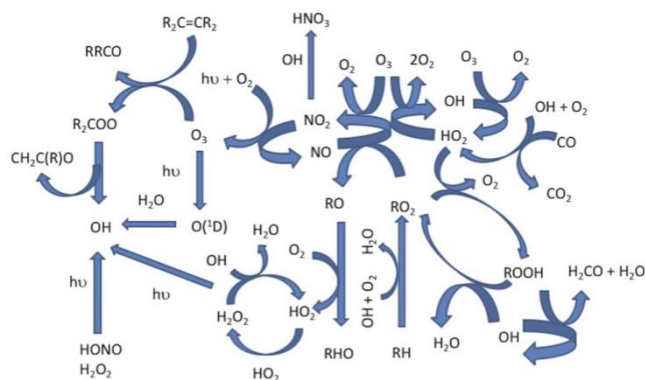


Figure 1. Gas-phase atmospheric reactions involving reactive oxygen species (ROS). Reproduced with permission from Ref. ²³

Interest in the direct photochemistry of organic compounds in the atmosphere has grown significantly in recent years in parallel with the development of photocatalysis. Most compounds directly emitted to the atmosphere (e.g., saturated hydrocarbons, monoterpenes, and alcohols) do not absorb sunlight available in the troposphere (i.e., beyond the cutoff of 290 nm) and therefore do not undergo significant direct photochemical reactions. However, their oxidation products can be photochemically active. For instance, methylhydroperoxide (CH_3OOH), is an important trace gas in Earth's atmosphere that is mainly produced by the oxidation of methane, the ozonolysis of alkenes, and biomass burning. CH_3OOH has an electronic transition band that is centered at 200 nm but extends beyond the tropospheric cutoff, leading to photodissociation into OH and CH_3O radicals; the latter can react with O_2 to form HO_2 and formaldehyde.^{24,25} Other species produced via the oxidation of primary organic compounds [e.g., pyruvic acid (PYA) and certain imidazole derivatives] and compounds emitted to the atmosphere through combustion processes (e.g., polycyclic aromatic hydrocarbons and aromatic ketones) are also photoactive. The excited states of these species can initiate chemical processes through interactions with other organic compounds that are not themselves photoactive. In these photoinduced processes, a chromophore called a photosensitizer absorbs light and transfers the excess energy to a nearby molecule that is not naturally photoactive, eventually initiating the oxidation chain. Commonly, the photosensitizer absorbs light to a singlet excited state, which then evolves to a triplet state via intersystem crossing (ISC) with a large quantum yield. The higher lifetime of the triplet compared to the singlet facilitates encounters and reaction with other molecules. Overall, two main types of photosensitization processes occur in the atmosphere¹⁸ depending on how the excited photosensitizer is quenched. The quencher can be an organic molecule (Type I) or triplet oxygen (Type II), as shown in Fig. 2. In the first case, an electron-transfer or H-abstraction reaction

results in the creation of a new organic radical that propagates the oxidation process. In the second case, the photosensitizer reacts with $^3\text{O}_2$, either by transferring the excess energy to form the reactive excited singlet $^1\text{O}_2$ or by electron transfer to form the superoxide anion O_2^- . In principle and according to the IUPAC definition, a photosensitization process is one in which the photosensitizer is not consumed in the reaction. From this point of view, photosensitization and photocatalysis can be considered synonyms. However, there are processes in which the photosensitizer molecule is also a reactant; in such a case, the molecule is referred to as a photoinitiator.

While all the above processes can occur in the gas phase, the importance of multiphase chemistry involving surfaces and interfaces of different natures (e.g., mineral dust, liquid water and ice surfaces, aerosols, and urban surfaces) has also been established.^{17,18,26,27} This Perspective first presents some studies that found enhancements in these photoinduced processes at the air–water interface, which is illustrated by some selected examples. We then discuss the different factors that can lead to modifications of the reaction properties. Finally, we present some perspectives in the field.

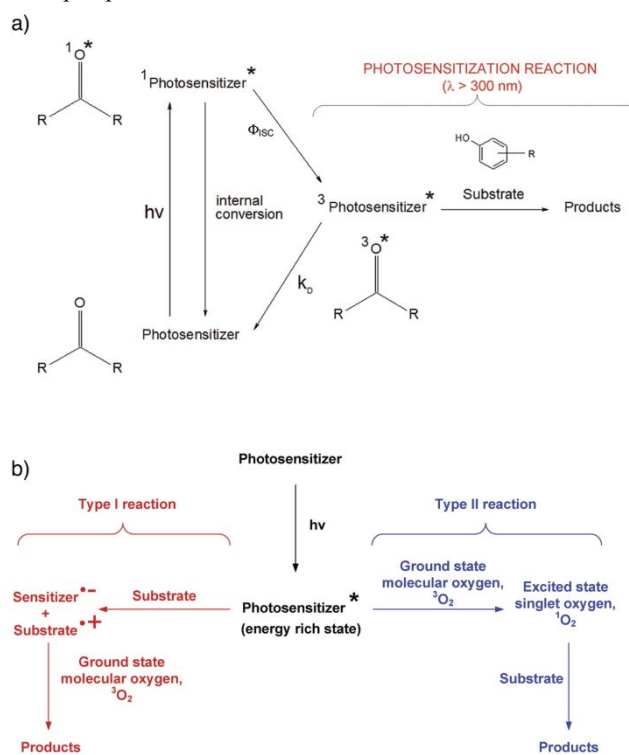


Figure 2. (a) Schematic representation of a Type I sensitization process involving the degradation of phenols via a reaction with an excited carbonyl compound as photosensitizer. (b) Comparison of Type I and Type II photosensitization processes. Reproduced with permission from Ref. ¹⁸

2. PHOTOCHEMISTRY OF OH PRECURSORS

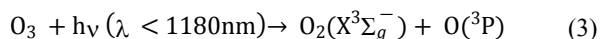
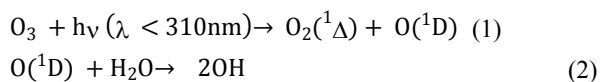
In this section, we present a few select examples to describe the photochemistry of simple precursors that generate OH radicals (and possibly other ROS), which then trigger the oxidation of more complex compounds present in the environment. These reaction pathways are key in atmospheric

and environmental chemistry, and the examples given below refer essentially to these fields. The production of OH originates from the direct photolysis of the precursor (hydroperoxides, HNO₃) or from hydrogen abstraction from water molecules, either by an appropriate precursor excited state (SO₂^{*}, NO₂^{*}) or one of its photolytic products (O₃).

2.1 ROS

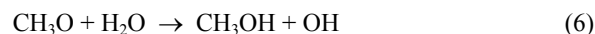
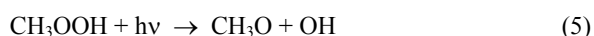
Ozone, hydrogen peroxide, and methyl hydroperoxide are among the main ROS.²³ They are strong oxidants with relevance in atmospheric chemistry, biological processes, and wastewater treatment in peroxone chemistry.^{17,21,23,24,28-37} In the stratosphere, ozone absorbs solar radiation, protecting living organisms from harmful UV radiation; in the troposphere, ozone acts as a greenhouse gas and a pollutant, damaging the respiratory tissues of animals.³⁸ Hydrogen peroxide and methyl hydroperoxide are prototypical hydroperoxides that are mainly formed via the self-reaction of HO₂ radicals and the oxidation of methane, respectively.^{24,25,39} These hydroperoxides are reservoirs of hydroxyl radicals and are found in rainwater and aerosols.⁴⁰⁻⁴²

One of the main roles of tropospheric ozone is to serve as an important source of hydroxyl radicals. Ozone photolysis produces O(¹D), which reacts with water vapor to form two OH radicals [Reactions (1) and (2)].⁴³ In the gas phase, the measured photolysis rate constant for these reactions is $3.8 \times 10^{-5} \text{ s}^{-1}$,⁴⁴ while calculations produced a value of $3.2 \times 10^{-5} \text{ s}^{-1}$.⁴⁵ It should be noted that both of these values assume sunlight actinic flux, as will be considered from now on in this work.



Anglada and co-workers^{27,45} carried out QM/MM-MD (Quantum Mechanics/Molecular Mechanics – Molecular Dynamics) simulations to investigate the spectrum of ozone at the air–water interface and found a red shift and shape broadening compared to the gas phase. They also predicted the photolysis rate constant to be one order of magnitude greater at the interface than in the gas phase ($1.1\text{--}7.6 \times 10^{-4} \text{ s}^{-1}$) when the contribution of Reaction (3) was taken into account.⁴⁵ Moreover, simulations⁴⁵⁻⁴⁷ have shown that ozone pile up at the air–water interface. For instance, for a typical gas phase concentration of $7.5 \times 10^{11} \text{ molecules}\cdot\text{cm}^{-3}$, an average concentration of $9.6 \times 10^{12} \text{ molecules}\cdot\text{cm}^{-3}$ in the interfacial layer is estimated. This corresponds to a predicted increase of approximately four orders of magnitude in the rate of OH radical formation at the interface, which has important atmospheric implications.⁴⁵

In contrast to ozone, the photolytic process of hydroperoxides (Reactions 4 and 5) produces OH radicals directly. In the case of alkyl derivatives like CH₃OOH, OH radicals are also produced by the reaction of alkoxy radicals with water (Reaction 6).



The absorption cross-sections and quantum yields of H₂O₂ and CH₃OOH have been reported in the gas phase,⁴⁸⁻⁵² in aqueous solution, and in snow ices.⁵³⁻⁵⁸ The reported photolysis rate constants for H₂O₂ are $4.8 \times 10^{-6} \text{ s}^{-1}$ in the gas phase and $1.5 \times 10^{-5} \text{ s}^{-1}$ in aqueous solution.⁵⁹ For CH₃OOH, the rate constants are 1.3×10^{-6} and $1.1 \times 10^{-6} \text{ s}^{-1}$ in the gas phase⁵¹ and $4.5 \pm 1.0 \times 10^{-5} \text{ s}^{-1}$ in aqueous solution.⁵⁸

Hydrogen peroxide is much more soluble in water than methyl hydroperoxide (the Henry's law coefficients are 1.0×10^5 and $3.0 \times 10^2 \text{ mol}\cdot\text{dm}^{-3}\cdot\text{atm}^{-1}$, respectively⁵⁹). However, according to molecular dynamics (MD) and quantum mechanics/molecular mechanics (QM/MM) calculations,^{46,60-62} both species accumulate at the air–water interface, leading to an increase in concentration that can enhance the importance of interfacial photochemistry.^{46,62} However, few works have focused on the photochemistry of these species at the air–water interface,^{27,62,63} and the results are contrasting. On one hand, Nissenson and co-workers⁶³ studied the photochemistry of H₂O₂ in water with a focus on cage effects on the photolysis quantum yields upon the addition of 2-propanol as an OH scavenger. The authors estimated the photolysis rate constant at the surface to be $9.3 \times 10^{-8} \text{ s}^{-1}$, much smaller than the experimental values reported by other authors for the gas phase and in the bulk,⁵⁹ although no discussion on this issue was provided. On the other hand, Martins-Costa and co-workers⁶² conducted QM/MM MD calculations to study the photolysis of CH₃OOH at the air–water interface. The calculated UV-visible spectra reveal a significant blue shift of the main absorption band corresponding to the interface (0.42 eV). This blue shift is attributed to the hydrogen-bond interactions between methyl hydroperoxide and the water molecules. While one would expect this blue shift to significantly decrease the photolytic rate constant, the calculations also show a broadening of the absorption band corresponding to the air–water interface that results in comparable cross sections in the red part of the band compared to the gas phase [Fig. 3(a)]. As a result [see Fig. 3(b)], the photolysis rate constant at the interface ($J_{\text{CH}_3\text{OOH}} = 0.76 \times 10^{-6} \text{ s}^{-1}$) is only slightly smaller than that in the gas phase ($J_{\text{CH}_3\text{OOH}} = 1.05 \times 10^{-6} \text{ s}^{-1}$). All in all, the rate of OH production rate has been shown to be much higher at the interface than in the gas phase, primarily due to the higher concentration of methyl hydroperoxide in this environment and, to a minor extent, the contribution of Reaction 6.

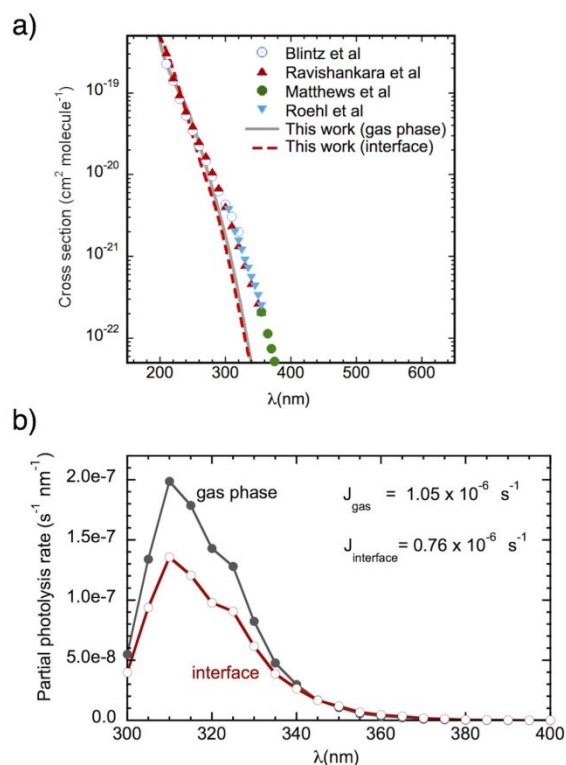
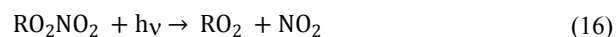
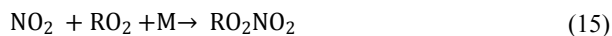
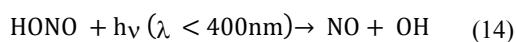
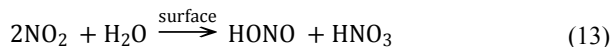
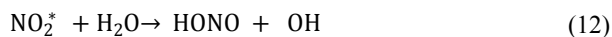
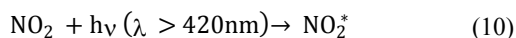
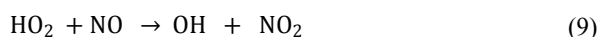
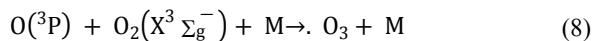
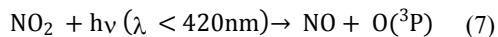


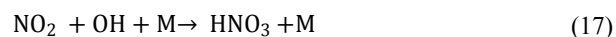
Figure 3. (a) Calculated absorption cross sections of CH₃OOH in the gas phase and at the air–water interface along with different experimental values reported for the gas phase. (b) Calculated partial photolysis rates for CH₃OOH. Integrated total rates are indicated. Reproduced from Ref. ⁶² with permission from the PCCP Owner Societies.

2.2 Reactive Nitrogen Species (RNS)

RNS are key compounds in atmospheric and biological chemistry. Like ozone, nitrogen dioxide is a target compound for measuring atmospheric pollution worldwide. Nitrogen dioxide may cause serious health problems by reducing immunity to lung infections. Reactions 7–17 and Fig. 1 summarize the most relevant redox processes involving oxygenated nitrogen species; these processes are strongly interwoven.^{22,25,43,64}



(RO₂ stand for HO₂ or for any peroxy radical)



Reaction 7 generates atomic oxygen, which reacts with molecular oxygen (reaction 8) producing atmospheric ozone in gas phase, while Reaction 9 regenerates NO₂. Reactions 10 and 11 are precursors of OH radicals in the gas phase, which is formed via Reaction 12.⁶⁵ The hydrolysis of NO₂ (Reaction 13) has been suggested to occur via heterogeneous processes⁶⁴ that produce HONO and HNO₃, and the photolysis of nitrous acid is a major source of hydroxyl radicals in the atmosphere (Reaction 14).²² The reaction of nitrogen dioxide with peroxy radicals (Reaction 15) produces RO₂NO₂, an atmospheric reservoir of NO₂ that can be transported and released by photolysis through Reaction 16.⁶⁶ Finally, nitrogen dioxide can react with hydroxyl radicals to produce nitric acid (Reaction 17).²⁵

The photochemistry of nitrogen dioxide adsorbed on different interfaces has been studied. QM/MM MD simulations at the air–water interface predict an excess concentration of approximately ten times relative to the gas phase^{67,68} along with a significant enhancement in the absorption cross section,⁶⁸ as plotted in Fig. 4(a). The calculated photolysis rate constants for Reaction 7 are J₇ = 10.8 × 10⁻³ s⁻¹ in the gas phase (the experimental value⁶⁹ is 8.8 × 10⁻³ s⁻¹) and J₇ = 15.3 × 10⁻³ s⁻¹ at the air–water interface. For Reaction 10, the calculated photolysis rate constants are similar for both environments (J₁₀ = 2.2 × 10⁻² s⁻¹ in the gas phase and 2.5 × 10⁻² s⁻¹ at the air–water interface), and the estimated OH production rate at the air–water interface as a function of the NO₂ concentration [Fig. 4(b)] is approximately two orders of magnitude larger than in the gas phase (for details, see Ref. ⁶⁸).

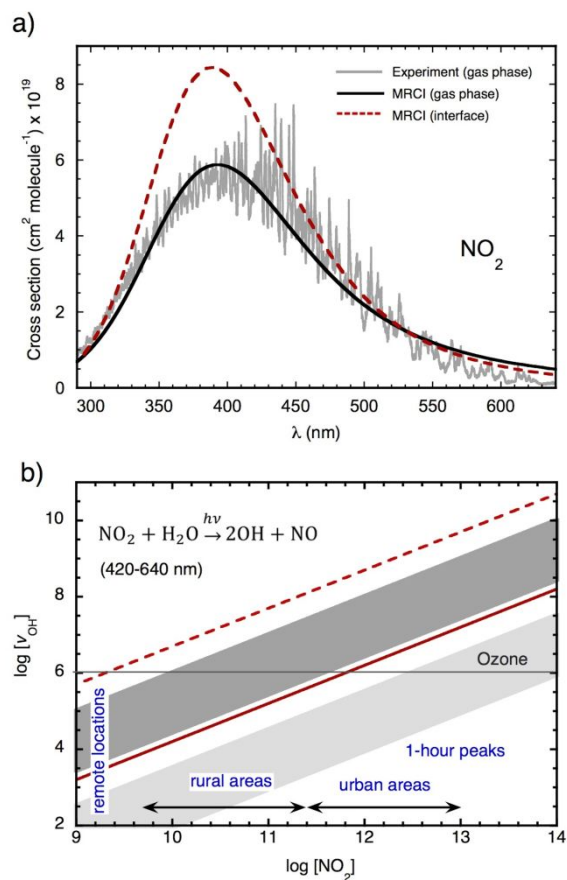
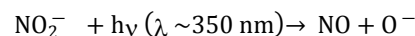
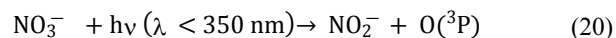
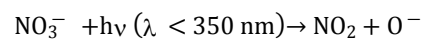
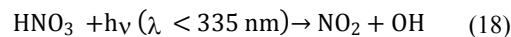


Figure 4. (a) Experimental UV spectrum of NO_2 in the gas phase and calculated spectra in the gas phase and at the air–water interface. (b) Estimated upper and lower limits of the OH production rate ($\text{molecule}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$) for different gas-phase concentrations of NO_2 ($\text{molecule}\cdot\text{cm}^{-3}$). Calculations in the gas phase (light gray) and at the air–water interface (dark gray) using k_{12} from reference.⁷⁰ The plain and dashed red lines respectively correspond to the gas-phase and interfacial values using k_{12} from reference⁷¹. The gas-phase values assume a relative humidity of 20%. The horizontal plain line represents a typical OH production rate from ozone photolysis. Reproduced with permission from Ref. 68

Further interesting results are available regarding the photochemistry of NO_2 adsorbed on other surfaces. Adsorbed NO_2 releases significant amounts of HONO. Thus, the irradiation of NO_2 in the range of 300–700 nm on organic surfaces containing phenols, aromatic ketones, humic acid, aromatic and polycyclic aromatic hydrocarbons, or even urban grime^{72–77} results in HONO formation in both the UV-A spectral region and in the visible region under atmospheric conditions.⁷³ The observed flux densities of HONO in these processes range between 3.2×10^9 and 5×10^{10} $\text{molecules}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$.^{73,77} In these processes, radiation is not directly absorbed by NO_2 . Instead, the radiation is absorbed by a photosensitizer (e.g., 4-benzoylbenzoic acid), which then reacts with an organic compound on the surface (e.g., phenols) to form a reductant (e.g., phenolate) capable of converting NO_2 to NO_2^- . Finally, the protonation of NO_2^- produces HONO.^{72,73}

The photochemistry of nitric acid at the air–water interface is also an interesting process that has raised many questions. In the troposphere, HNO_3 has long been considered as a sink of NO_x species; however, recent studies have stressed its role in chemical⁷⁸ and photochemical^{79–86} renoxification processes that generate HONO, NO, and NO_2 . Thus, nitric acid may be a reservoir of nitrogen oxides as well as a sink. Here, we focus on its photolysis, which directly produces hydroxyl radicals in the gas phase (Reaction 18). When nitric acid is dissolved in water, it mainly exists in the form of nitrate, and its photolysis produces O^- radicals, which react with water to form OH (Reactions 19–21).



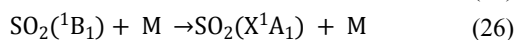
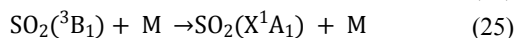
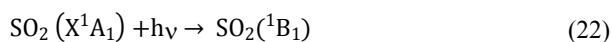
The rate constants for HNO_3 photolysis in the gas phase (Reaction 18) and nitrate photolysis in bulk water (Reactions 19 and 20) are very small ($J_{18} = 8.2 \times 10^{-7} \text{ s}^{-1}$,⁶⁹ $J_{19} = 8.5 \times 10^{-7} \text{ s}^{-1}$, $J_{20} = 4.5\text{--}8.5 \times 10^{-8} \text{ s}^{-1}$).^{53,54,69,83,87,88} Note that the NO_2^- formed in Reaction 20 can either be protonated, releasing HONO, or photolyzed ($J_{21} = 1 \times 10^{-4} \text{ s}^{-1}$).^{63,87,89,90} However, photolysis at different interfaces is far more important. On one hand, field observations have shown that the photolysis of HNO_3 adsorbed on the forest canopy surface is an important source of HONO.⁸² On the other hand, experiments in thin water films containing nitrate, chlorine, and bromine salts have shown that the photolysis of NO_3^- occurs much faster at interfaces than in the bulk,^{63,81,90–94} with J values ranging between $1.2 \times 10^{-3} \text{ s}^{-1}$ and $3 \times 10^{-6} \text{ s}^{-1}$ depending on the features of the interface.^{63,83,95,96} A potential explanation for this enhancement is associated with the solvation of nitrate anion. In bulk water, nitrate is surrounded by a solvent cage that facilitates both the recombination of the NO_2 and OH radicals produced by Reaction 19 and their deactivation by collision with solvent molecules, thus decreasing the photolysis quantum yield.^{63,87,89,90} MD simulations have shown that when halide anions (especially bromide) are present, nitrate ions are dragged closer to the interface so that the water solvent cage surrounding them is reduced,^{90,97} arguably making the escape of NO_2 to the gas phase easier.^{63,81,90–94} Nevertheless, despite the large amount of work done on nitrate photochemistry, open issues remain that are not yet completely understood. For instance, it was recently shown that an important part of nitric acid remains undissociated at the air–water interface,^{81,98–106} and the relevance of the corresponding photochemistry is still undetermined.

2.3 Sulfur dioxide (SO_2)

The ground-state chemistry of SO_2 has been broadly studied.^{107–110} Generally, SO_2 is oxidized in the atmosphere to higher sulfur oxides or sulfuric acid. SO_2 is emitted by the burning of fossil fuels, industrial processes, ships and other

vehicles, and volcanic eruptions. It is eliminated by dry and wet deposition, which contributes to particulate matter and aerosol formation along with acid rain. Exposure to SO₂ or particulate matter harms the human respiratory system and makes breathing difficult.^{69,111-113} The atmospheric concentrations of SO₂ are extremely variable, with mixing ratios ranging from 20 ppt to over 1 ppb in continental background air, 20–50 ppt in the unpolluted marine boundary layer, several hundreds of ppb in urban areas, and much higher in volcanic gases.¹¹¹

Recent studies have shown that SO₂ can act as an oxidizer via the photochemistry of its triplet excited state. Upon the UV irradiation of a mixture of SO₂ and water vapor without any other oxidants, Donaldson and co-workers¹¹⁴ observed the formation of new particles, which Kroll and co-workers¹¹⁵ ascribed to the formation of HOSO and OH radicals according to Reactions 22–26. UV light excites SO₂ into its first singlet electronic state that evolves to a triplet electronic state via ISC. This triplet electronic state is quite reactive and abstracts one hydrogen atom from water, producing HOSO and OH radicals. In this mechanism, SO₂ behaves as a photoinitiator.



The reaction between the excited triplet electronic states of SO₂ and H₂O (Reaction 24) may follow two different reaction paths,¹¹⁶ for which the potential energy surfaces are schematized in Fig. 5(a). These pathways correspond to either a conventional hydrogen atom transfer (*hat*) or a proton-coupled electron transfer (*pcet*), which requires lower activation energy.

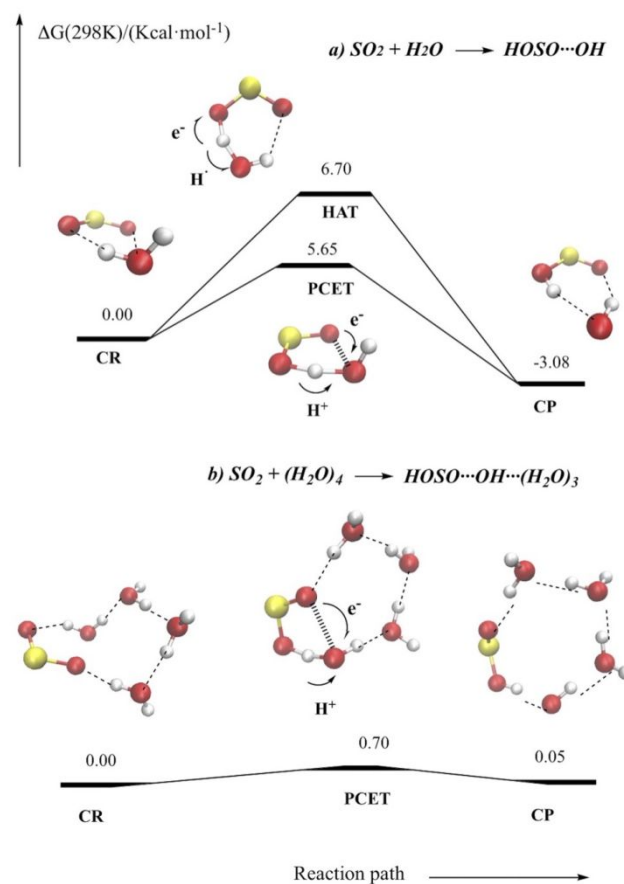


Figure 5. (a) Schematic of the free energy surface at 298 K for the reaction of SO₂ (*a*³B₁) with one water molecule. (b) Schematic free energy surface at 298 K for the reaction of SO₂ (*a*³B₁) with a cluster of four water molecules. Reproduced from Ref. ¹¹⁶ with permission from the PCCP Owner Societies.

The most relevant electronic features describing these processes are collected in Fig.6. The *pcet* mechanism is described by a two-center three-electron structure, where the single-occupied 8a₁ orbital of SO₂ interacts with the lone pair [lp(O)] of water in a way that the electron density in the doubly occupied orbital 20a is shared between the oxygen atom of the water moiety and the terminal oxygen atom of SO₂. In contrast, in the single-occupied orbital 22a, the antibonding combination is formed. This situation depicts an electron transfer from the oxygen atom of water to one oxygen atom of SO₂; at the same time, one proton jumps from water to the other oxygen atom of SO₂.

In the hydrogen atom transfer mechanism, the single-occupied 8a₁ orbital of SO₂ interacts with one of the σ(O–H) bonds of water to form the doubly occupied orbital 20a with bonding character and the single-occupied orbital 22a with antibonding character. This situation also corresponds to a three-center three-electron system; however, in this case, the electronic density lies over the O–H–O moiety, indicating the simultaneous breaking and forming of the covalent bonds (OS)O–H–O(H). Indeed, elementary reactions occurring through a *pcet* mechanism in the oxidation of organic and

inorganic species by radicals have been found to be more favorable than oxidation processes occurring through the *hat* mechanism.¹¹⁷⁻¹²⁷

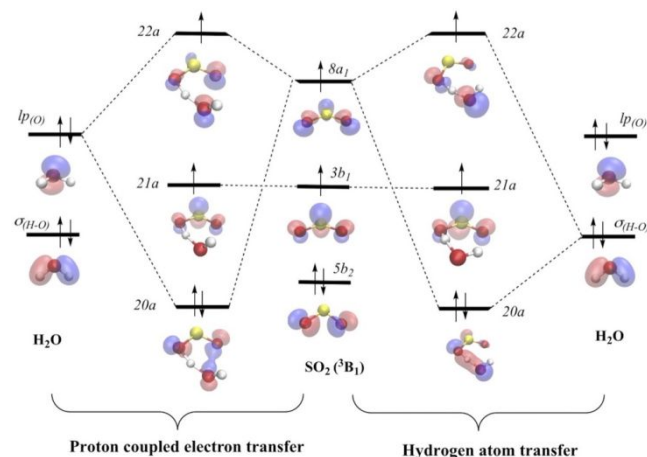


Figure 6. Orbital diagram for the *pcet* and *hat* mechanisms for the reaction SO_2 (a^3B_1) + H_2O . Reproduced from Ref. ¹¹⁶ with permission from the PCCP Owner Societies.

The reaction of SO_2 (a^3B_1) with up to four water molecules¹¹⁶ [Fig. 5(b)] sheds light on the microsolvation effect on this process and can be considered as a model for reactivity at the air–water interface, where, as for the other species discussed above, SO_2 accumulates.¹²⁸⁻¹³³ Indeed, the free energy barrier of the *pcet* mechanism is quite small ($0.70 \text{ Kcal}\cdot\text{mol}^{-1}$), suggesting that the reaction could be spontaneous at the interface, making this photochemical mechanism a significant source of OH radicals, as confirmed by further QM/MM simulations.¹³³ For instance, for a relative humidity of 100% and a gas-phase SO_2 concentration of $10^{12} \text{ molecules}\cdot\text{cm}^{-3}$, which is typical of urban areas, the rate of formation of OH radicals is estimated to be approximately $10^5 \text{ molecules}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$ in the gas phase. In comparison, the rate reaches $7 \times 10^8 \text{ molecules}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$ when the process occurs at the air–water interface for the same gas-phase concentration.¹³³

Beyond the formation of OH radicals, another outcome of the interfacial photochemistry of SO_2 is the acidification of the medium because HOSO is quite acidic ($\text{pK}_a = -1$) and undergoes fast ionic dissociation at the interface, as shown by QM/MM MD simulations (see Fig. 7).¹³⁴ Moreover, the formed SO_2^- ions can be further oxidized by H_2O_2 , O_3 , OH, or HO_2 to produce sulfuric acid.¹³⁴

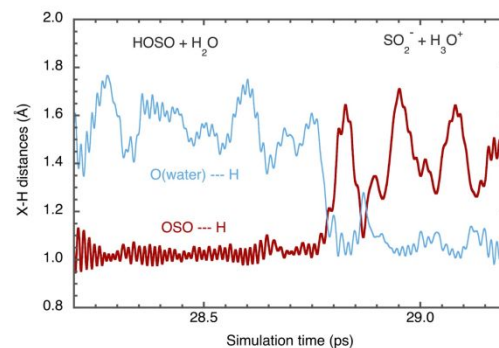
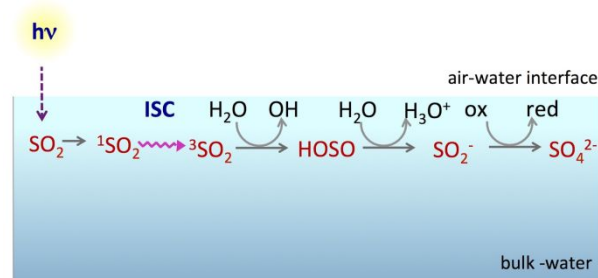


Figure 7. Different steps of the photo-oxidation of SO_2 leading to sulfate. QM/MM MD simulations at the air-water interface reveal that as HOSO radical is formed, it rapidly ionizes. This is shown in the bottom part of the Figure by the time evolution of OH distances in the $H_2O \cdots HOSO$ system (bottom, right). The structure of the transition structure for proton transfer is also displayed (bottom, left). Adapted with permission from Ref. ¹³⁴

3. Direct photooxidation of organic species

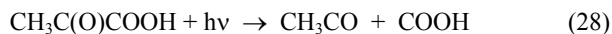
The photooxidation of organic species at the aqueous interface represents a vast field of research and turns out to be much more complex than the chemistry of OH precursors. To some extent, the role of organic radicals formed in the early stages of the photochemical process can be compared to the role played by the oxidizing OH radicals in overall atmospheric chemistry. As noted in the introduction, this photochemistry generally involves the presence of photoinitiators or photosensitizers. Such reactions are also enormously important in atmospheric and environmental chemistry because organic matter accumulates at the surfaces of cloud water droplets and aerosols as well as on surface waters, lakes, rivers, and, most importantly, oceanic surface microlayers, which are enriched with organic matter such as humic acid, fatty acids, amino acids, proteins, lipids, and other biogenic materials.¹³⁵⁻¹³⁹ To illustrate these processes, we have chosen two examples that have received considerable attention in recent publications.

3.1 Pyruvic acid (PYA), a versatile photoinitiator

An intriguing case study is PYA, which has major biological significance and is also relevant in atmospheric chemistry as a product of the atmospheric oxidation of isoprene.¹⁴⁰ PYA is detected in clouds and aerosols¹⁴¹ and is important in prebiotic chemistry.¹³⁹ The photochemistry of PYA has been investigated in different environments as a model of α -dicarbonyl compounds. A unique feature of PYA is that its photochemistry

is totally different in the gas phase than in aqueous environments.

In the gas phase, the main photolytic process starts with absorption to the first excited singlet electronic state ($n \rightarrow \pi^*$ transition, $\lambda_{\max} = 350$ nm), which induces PYA cleavage into carbon dioxide and methylhydroxycarbene (Reaction 27) via hydrogen transfer from the acidic group to the keto oxygen atom.^{142,143} Excitation at higher energies (up to $\lambda = 300$ nm) leads to the formation of acetyl and carboxyl radicals (Reaction 28).¹⁴⁴



In the aqueous phase, the photolysis is far more intricate than in the gas phase, and the mechanisms are totally different. A first challenge is the coexistence of different forms in aqueous solution, namely PYA and its conjugated base pyruvate (pK_a of 2.45), the corresponding hydrated *gem*-diols (PYT), and oligomeric species such as parapyruvic acid (PPA) and zymonic acid (ZYA; see Fig. 8). PYA may also undergo keto-enol equilibria.¹⁴⁵

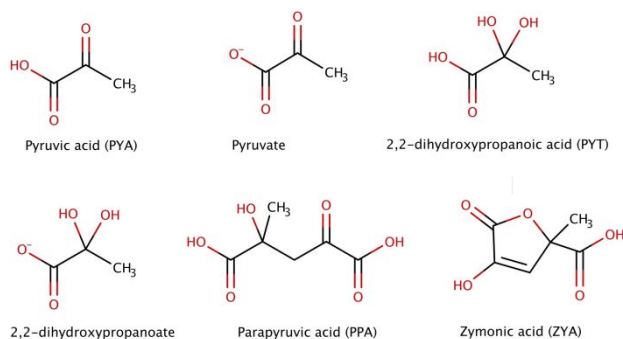


Figure 8. Chemical structures of pyruvic acid, pyruvate, the corresponding *gem*-diols, parapyruvic acid and zymonic acid

Several works have investigated PYA photochemistry in water under highly acidic conditions ($\text{pH} = 1\text{--}2.5$).^{139,146-156} Absorption to the single excited state [$^1\text{S}(n,\pi^*)$] is blue-shifted ($\lambda_{\max} = 320$ nm) with respect to gas phase.¹³⁹ The excited singlet then undergoes ISC with the lowest-lying triplet excited state [$^3\text{T}(n,\pi^*)$], which becomes the reactive species (see Fig. 2). This triplet state can react with another PYA or PYT molecule in its ground electronic state through a mechanism that involves either the abstraction of the acidic hydrogen atom via proton-coupled electron transfer¹⁴⁶ or a concerted hydrogen atom abstraction.¹⁴⁷ This initiates a chain of reactions that cause decarboxylation, the formation of oligomers, dimethyltartaric acid, acetoin, acetic and lactic acids, and oxo-C8 and C7 products.^{26,146,147,157} However, controversy exists regarding the entire mechanism and the formation of several products.¹⁴⁷⁻¹⁵² As the pH increases, the *gem*-diol form diminishes, and the pyruvate concentration grows, resulting in an increase in absorption intensity and a moderate blue shift ($\lambda_{\max} = 316$ nm).¹⁵⁸ Another mechanism then becomes competitive: the triplet excited state of PYA abstracts one of the hydrogen atoms of the methyl group (instead of the acidic group) from the ground electronic state of another PYA molecule. The main

oligomeric species formed in this mechanism are PPA and ZYA.¹⁵³ Some of the newly formed compounds (PPA in particular) can act as secondary photosensitizers that contribute to or initiate the formation of oligomers^{26,153,158} and participate in cross-reactions with glyoxylic acids, fatty acids, and fatty alcohols.^{153,154,159} Interestingly, PYA has been shown to behave as a photosensitizer, affecting the atmospheric multiphase reactions of ozone with oxalic acid.¹⁶⁰

The enormous versatility of this bulk photochemistry is also expected at the air–water interface. However, the interfacial mechanisms remain poorly understood. Using vibrational sum-frequency spectroscopy, Gordon and co-workers¹⁶¹ identified the oligomers PPA and ZYA at the air–water interfaces of PYA solutions, demonstrating that these compounds are surface active. Additionally, they performed MD simulations in the bulk and at the air–water interface; the corresponding density profiles are collected in Fig. 9. Interestingly, the results indicate the depletion of PYT and the accumulation of PYA, PPA, and ZYA at the air–water interface, which suggests that the enhanced photoreactivity of the interface might boost oligomerization reactions. Moreover, Eugen and co-workers¹⁶² demonstrated a reduction of 1.8 units in the effective pK_a of PYA at the air–water interface, which would increase the undissociated fraction of PYA and further enhance the photoreactivity at the air–water interface.

Very recently, Fu and co-workers¹⁶³ employed time-of-flight secondary ion mass spectrometry (SIMS) to investigate the products of PYA photolysis at the air–water interface and in bulk water. The SIMS analyses were carried out with dry samples, and inevitable drying effects may have influenced the results of the study. However, the authors established a reaction flow chart, which is displayed in Fig. 10. The radical, decarboxylation, esterification, and anhydride formation reactions have been identified. In addition, at the interface, oxygen from the air forms other oxidation products. As a rule, it is observed that radical reactions and the formation of high-molecular-weight compounds are enhanced at the air–water interface.

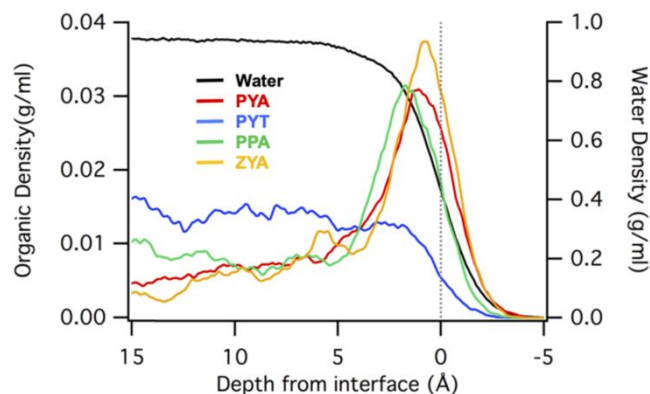


Figure 9. Density profiles from MD simulations of a mixed aqueous solution containing PYA (red), PYT (blue), PPA (green), and ZYA (yellow). The concentration of each species was ~ 0.25 M. The vertical dotted gray line indicates the approximate interface boundary. Reproduced with permission from Ref. ¹⁶¹.

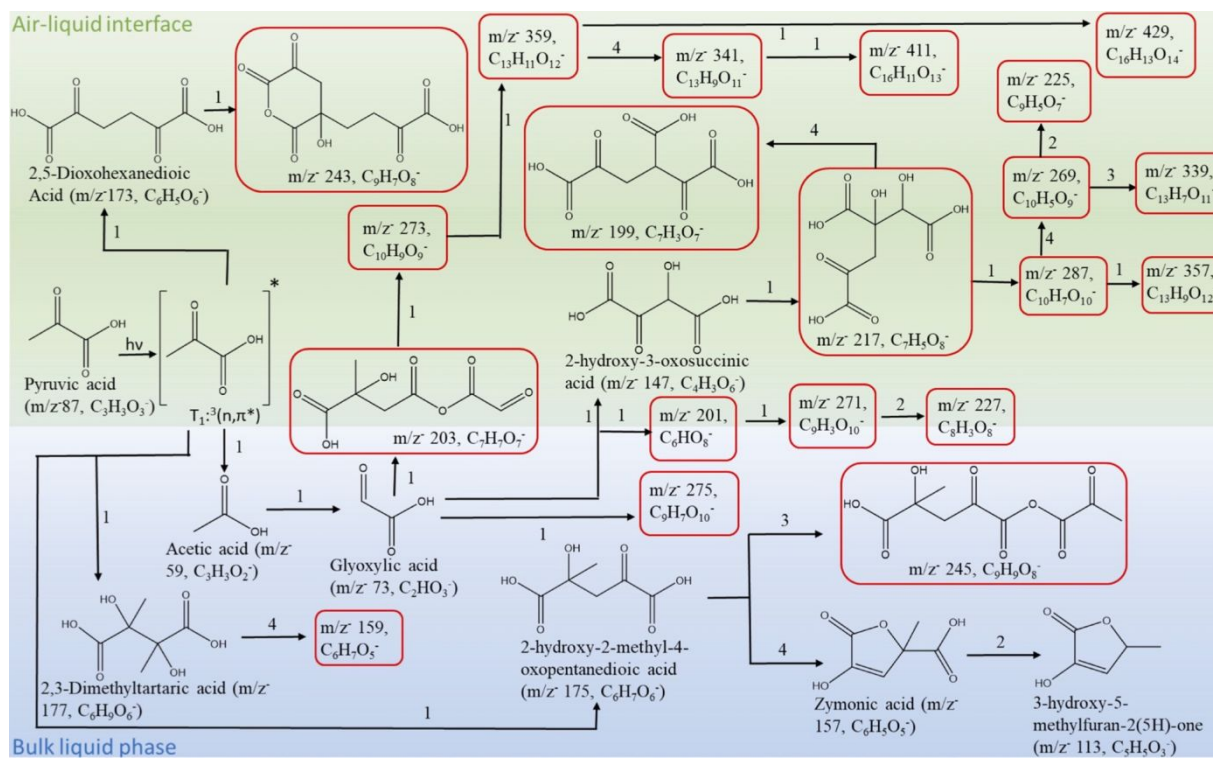


Figure 10. Reaction flow chart showing reactions in bulk water and at the air–water interface. Numbers on arrows indicate reaction types: 1) radical reactions, 2) decarboxylation reactions, 3) anhydride formation, and 4) esterification formation. Red squares indicate new products identified by the authors, and chemical formulae correspond to undetermined or to too-large structures. Reproduced with permission from Ref. ¹⁶³

3.2 Fatty acids

Another illustrative example is the photoinduced reactivity of fatty acids and fatty alcohols initiated by photosensitizers in chromophoric dissolved organic matter (CDOM).¹⁶⁴⁻¹⁶⁶ Imidazole 2-carboxaldehyde, 4-benzoylbenzoic acid, and humic acids have been widely studied as suitable proxies for CDOM photosensitizers. This represents an important environmental photooxidation chemistry, especially at the sea surface microlayer and interfacial bubbles at the sea surface, which are enriched by many amphiphilic organic compounds with biogenic origins. Fatty acids have been identified in these organic layers, and photosensitizers such as those cited above show a propensity for partitioning to them.¹⁶⁵

The starting mechanism involves the formation of a triplet electronic state via ISC from the excited singlet state reached by the absorption of sunlight by the photosensitizer. The triplet state then reacts with the organic species at the air–water interface, usually via the abstraction of one hydrogen atom or through electron transfer. In this way, two radicals are formed and initiate a chain of complex chemical reactions that has been thoroughly described for nonanoic acid as a fatty acid proxy.¹⁶⁵⁻¹⁶⁷ The proposed mechanism with humic acid as the photosensitizer is displayed in Fig. 11.¹⁶⁶

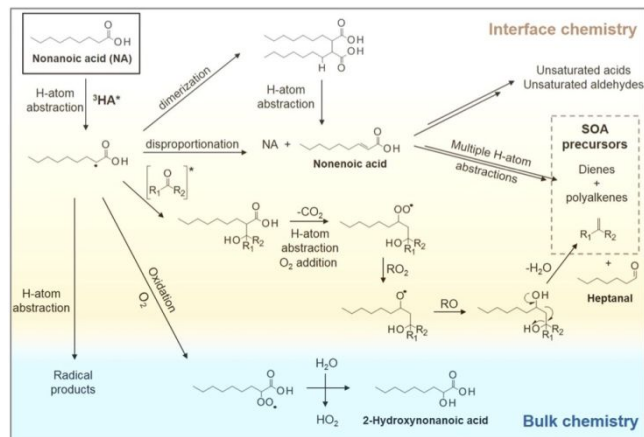


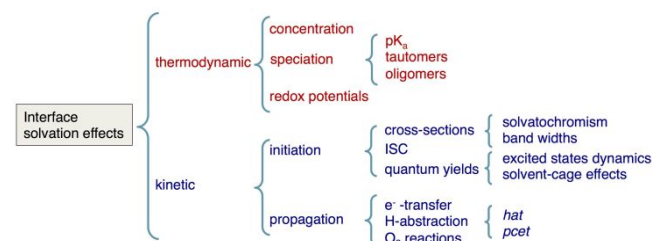
Figure 11. Proposed mechanism for the photochemical degradation of nonanoic acid at the air–water interface in the presence of humic acid as photosensitizer. Reproduced with permission from Ref. ¹⁶⁶. Further permissions related to the material excerpted should be directed to the ACS.

Figure 11 shows that the triplet excited state of humic acid (^3HA) abstracts one hydrogen atom of nonanoic acid via the photosensitizer, unleashing a chain of processes involving dimerization, disproportionation, cross-reactions, and decarboxylation. Moreover, the availability of O_2 from the gas phase and water molecules at the air–water interface promotes reactions such as the addition of O_2 to form peroxide radicals, allowing the formation of other oxidized products such as hydroxyacids.

Despite organic acids does not absorb light in the actinic range, recent experiments¹⁶⁷ have indicated the presence of radical reactions when a monolayer of nonanoic acid at the water surface is irradiated in the region of 280–330 nm in the absence of any additional photosensitizer. Although a low rate was observed, this study suggests that nonanoic acid itself acts as a photosensitizer at the air–water interface.¹⁶⁷ According to this study, the absorption of radiation by nonanoic acid leads to a triplet state that can dissociate into radicals or react with another fatty acid molecule to form a diol radical. However, other studies on this reaction with different experimental setups could not confirm this mechanism and concluded that if this mechanism exists, it is of minor relevance compared to processes triggered by photoinitiators.^{138,159,164-166}

4. DISCUSSION

In the preceding section, we briefly described a few representative examples of photooxidation reactions at the air–water interface. These and other studies^{17,18,27,168} on related systems reveal that the photochemical reactivity at the interface may differ considerably from those in both the gas phase and the bulk. Despite this large body of work, a full understanding of the solvation effects on interfacial photochemistry is not yet available. Hereafter, we briefly discuss some of the thermodynamic and kinetic factors (see Scheme 1) that can be advanced to explain the observed effects but that still require verification through further experiments and calculations.



Scheme 1. Factors affecting photo-induced reactions at the air–water interface

The prominent role played by aqueous interfaces in atmospheric and environmental photochemistry has several explanations. The most obvious one is the amphiphilic character of a large fraction of organic matter and chromophoric compounds. The biogenic surfactants mentioned earlier are an emblematic example as they are ubiquitous in environmental interfaces.^{137,168,169} Indeed, the photochemistry of microlayers at the ocean surface is a major source of volatile organic compounds, which compete with emissions from marine biology.¹⁷⁰ In addition, the accumulation of organic matter at the ocean's surface acts as a solar filter that changes the

intensity and spectral distribution of the radiation that penetrates into the inner water layers, thereby modifying the photochemistry there.¹⁶⁸ However, accumulation at aqueous interfaces is not reserved to surfactants, and both simulations and experiments have clearly demonstrated that many small polar molecules and even soft anions, including important oxidants from the ROS/RNS chemical families, display affinity for interfaces.^{45,46,171} The accumulation of organic matter, chromophores, and oxidants in the same location therefore represents an important driving force of photooxidation chemistry at environmental aqueous interfaces.

Nevertheless, the solvation power of the air–water interface is still incompletely understood. Attempts to establish scales of interfacial polarity¹⁷² have faced challenging problems¹⁷³ due to the asymmetry of the interfaces and preferential stabilization of some solute orientations, resulting in quite different solvent responses for compounds bearing similar groups but having different stereochemistries.¹⁷⁴ The enthalpic and entropic contributions to the interfacial free energy of solvation have been discussed for some organic molecules showing that the stability at the surface is mainly driven by the enthalpic component (Fig. 12)¹⁷⁵. Similar studies have been carried out for ions.¹⁷⁶ However, in this case, the interface affinity remains incompletely understood, as discussed in many previous reviews.¹⁷⁷⁻¹⁸⁶ Briefly, hard and multiply charged ions are repelled from the interface, while soft and large polarizable anions (e.g., I^- and Br^-) tend to accumulate at the air–water interface.^{177,178} In any case, the difference in solvation energy between the interface and the bulk has direct consequences for the equilibrium constants of conformational, tautomeric, and acid/base equilibria, which remains a subject of intense debate in the literature (see, for instance, Refs. ^{187,188}). Changes in equilibrium constants imply changes in speciation and thus changes in photochemical behavior. The photochemistries of nitric acid and PYA described above are good examples illustrating these issues. For similar reasons, one expects variations in the effective redox potentials at the interface with respect to bulk values, particularly for ROS/RNS couples.^{171,189} Estimations for the O_2/O_2^- couple indicate a decrease as large as 0.32 V due to the poor solvation of the anion at the interface.¹⁷¹

Interface solvation not only controls the concentration of the species, it also affects the electronic properties (i.e., the reactivity). This happens in the initiation steps (absorption, photolysis, and ISC) as well as in the subsequent propagation steps (electron transfer, hydrogen transfer, and reaction with oxygen). As for bulk solvation, interfacial solvation may be the origin of solvatochromism effects, producing blue shifts (hydroperoxides) or red shifts (ozone) in the gas-phase absorption bands. On the other hand, large fluctuations of the solvation shell influence the shapes of the bands, and both effects (band shifts and broadening) eventually modify the photochemical rate constants.⁴⁵ Moreover, solvation effects modulate ISC in photosensitizers, as shown by experiments^{190,191} and calculations,^{192,193} and in the more general case of conical intersections.¹⁹³⁻¹⁹⁷ In contrast, interfacial solvent effects on quantum yields have not yet been fully investigated. The case of PYA represents a limiting case in which the photochemistry at the aqueous interface differs from

that in the gas phase.^{146-148,153} The case of nitrate illustrates the change in quantum yield due to solvent cage effects.^{63,87,89,90}

After the photochemical formation of the initial radicals, reactions proceed via energy or electron transfer, *hat* or *pcet* mechanisms, reaction with oxygen, etc. The relaxation of the photosensitizer triplet state via phosphorescence is also conceivable and may compete with other processes. Electron transfer at interfaces has a long history that is justified by a broad applicability ranging from electrochemistry to biology and solar energy technologies (see Ref. ¹⁹⁸ for a recent review on these processes). Likewise, in bulk solution, Marcus theory¹⁹⁹⁻²⁰² can account for the observed solvent effects on electron transfer at interfaces.^{203,204} A study of photoinduced electron transfer at water/dimethylaniline interfaces^{205,206} concluded that the interfacial processes are faster than the bulk processes, possibly due to faster solvation dynamics at the interface.²⁰⁷ The stability of solvated electrons at aqueous interfaces has also been studied,²⁰⁸⁻²¹⁰ and simulations have predicted that the water surface electron affinity is ~ 0.6 eV higher than in the bulk, and that the conduction band edge is deeper in energy. Electron transfer is also relevant in *pcet* mechanisms and can be significantly affected by aqueous solvation, as shown for the $^3\text{SO}_2 + \text{H}_2\text{O}$ reaction¹¹⁶ and the $\text{H}_2\text{CO} + \text{HO}_2$ reaction.¹⁸⁹ One should note that the kinetics of such bimolecular reactions are often controlled by differences in intermolecular energy differences between the highest occupied and lowest unoccupied molecular orbitals. At the interface, these differences depend strongly on the electric field created by the polarized water surface, which in turn varies with the proton donor or acceptor character of the reactants.¹⁸⁹

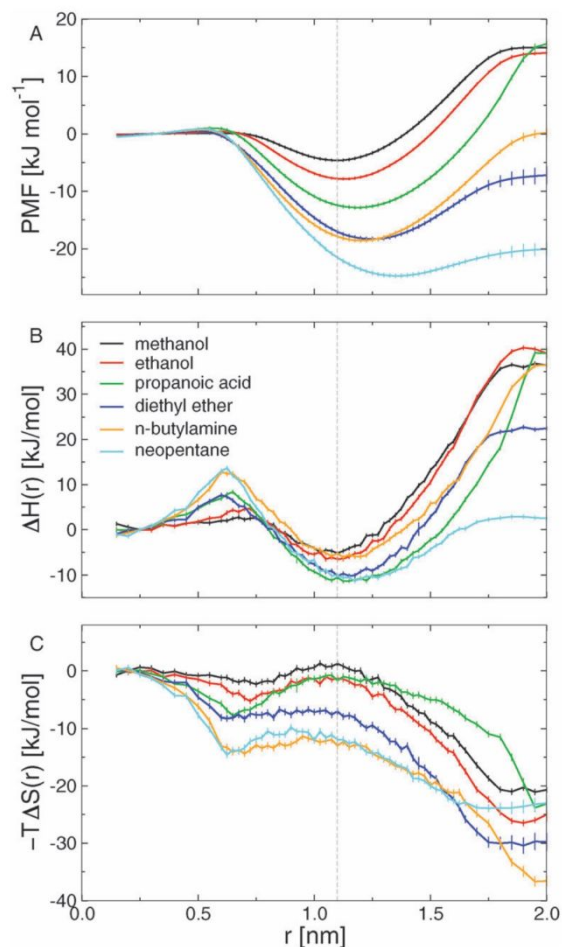


Figure 12. Free energy profiles for water accommodation of six polar and apolar organic compounds (A), and the corresponding enthalpic (B) and entropic components (C) as a function of position in a water droplet. The grey dashed line shows the Gibbs dividing surface. Reproduced with permission from Ref. ¹⁷⁵

5. Conclusions

Similarly to thermal reactions, many photoinduced oxidation reactions at the air-water interface are significantly enhanced in comparison with the corresponding gas-phase or bulk processes. However, despite a considerable amount of experimental and theoretical work, the precise mechanisms by which this effect is achieved remain incompletely understood. Enthalpic and entropic factors may result in the accumulation of photoactive species at the interface, where partial hydration modify the electronic absorption energies, as well as the reactivity of the radicals formed in the early stages of the photo-oxidation processes. Interfacial dynamic effects are important as well. They have been found to be responsible for band broadening and the increase of photolytic rate constants. Likewise, solvent cage effects reducing the quantum yields turn out to be less important at the interface than in the bulk and this

also contributes to enhance the photoreactivity. Various other effects have been briefly presented in the discussion above: changes in equilibrium constants (tautomeric, acid/base), effective redox potentials, rate constants for electron of hydrogen transfer, etc. All of them deserve further examination through a combination of new experiments and theoretical simulations in order to achieve a deeper understanding of these challenging phenomena, which have implications in many areas. For instance, incorporation of photo-oxidation mechanisms on cloud water surfaces would represent a considerable improvement in atmospheric models. Accounting for enhanced interfacial photochemistry is also relevant to design novel applications in water treatment and disinfection technologies, which already use the photolysis of O₃ and H₂O₂ to trigger the oxidation of organic matter. Finally, these processes also open avenues in synthetic organic chemistry. On-water reactions are now broadly studied in microdroplets, thin films and microfluidic systems thanks to the development of innovative setups, and in many cases processes have been found to be dramatically accelerated in comparison to bulk reactions. Photo-induced oxidation on-water is likely to experience similar success in the coming years.

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The manuscript was written through contributions of all authors

Notes

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