Recent Insights into Interfacial Transport and Chemical Reactions of Plasma-Generated Species in Liquid

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Abstract

The chemistry of plasma-liquid interactions involves a complex interplay of physical and chemical processes at the plasma-liquid interface. These interactions give rise to the generation, transport, and transformation of various reactive species. Since publication of the Lorenz Roadmap in 2016, significant progress has been made in understanding the interfacial transport and coupled reactions of plasma-generated species with inorganic and organic compounds. However, critical aspects of plasma-liquid chemistry and mass transfer still require further investigation. This review summarizes recent work on processes at the plasma-liquid interface and coupled reactions in the liquid. We highlight key findings related to the involvement of O atoms, H radicals, solvated electrons, photons, and nitrogen-derived species at the interface and within bulk liquid.

Key Words: non-thermal plasma, plasma treatment, radicals., ~~plasma treatment~~

1. Introduction

The Lorenz Roadmap (LR) published in 2016 [1] provided the status of research on gas-liquid phase physical and chemical processes at that time and made specific suggestions on future work necessary to develop this field. It was found that the study of plasma-liquid interactions would benefit from integrating results from other fields such as "aerosol science and atmospheric chemistry, colloidal and interfacial surface chemistry, evaporation and condensation, and phase equilibrium and gas/liquid solubility". Further, atomic and molecular scale simulations of the gas-liquid interface were suggested. The transport of gaseous plasma species into the liquid was divided into transport of neutral species, ions, and electrons. The fluid dynamics, heat and mass transport, plasma induced liquid phase convection, and mass transfer were found to be areas of additional need, although at that time, there were results and simulations on fluid flow induced by electrodes over surfaces in the pin to surface and plasma jet configurations. Considerations of reaction rates in the gas, plasma, and liquid as well as determination of where the key chemical species are formed were needed. While many other interesting and useful reviews have been published since the LR [2-13], our goal here is to provide an update on work related to the interfacial transport and coupled reactions that has been conducted since the LR was published.

Analysis of transport at the plasma-liquid interface is clearly a complex process and starts with the identification of the plasma-liquid interaction. These interactions are not solely defined by the myriads of chemically reductive and oxidative species generated by the plasma but are also influenced by factors such as the gas-liquid interfacial area, species fluxes to the plasma-liquid interface, solution pH, electrical conductivity, chemical composition, and the rate of fluid renewal under the plasma. Physical phenomena such as electrical double layer formation and plasma sheath significantly contribute to the complexity of the plasma-liquid interface dynamics. In the LR (Figure 2 - LR), six configurations of the plasma contacting the liquid were initially considered. We have now included five slightly modified configurations based upon research that includes chemical analysis and transport processes at the interface. These include a) plasma jets impinging directly onto the surface, b) pin electrodes oriented normal to the liquid surface, c) direct discharge underwater with needle or pin electrodes, d) discharges in bubbles in water, and e) mists or sprays of droplets into a plasma. Each of these configurations significantly affects the underlying hydrodynamics as well as other properties of the plasma and the interface (e.g., contact area, temperature profiles, thickness of the boundary layers) that affect interfacial transport. For example, high velocity jets of plasma gas impinging on the liquid can induce recirculation patterns in the liquid and the gas as well as distort the shape of the gas-liquid interface. The pin to surface configuration can have similar but less intense effects on the flow patterns. The magnitude of the plasma effect on the surface and flow is also affected by the nature of the plasma discharge, where large electric fields might induce alternations in the fluid flow through electrohydrodynamic forces. Discharges with bubbles (either inside bubbles or outside bubbles) and with mists or sprays are more complicated with respect to the analysis of the two-phase flow patterns and mass transfer,

and underwater discharges have been less well studied from this perspective. Further complications may arise due to the different types of plasma generation means (e.g., mainly dielectric barrier discharge and pulsed discharge, but others are possible).

Conversion of the energy introduced into the plasma into chemical reactivity via electron collisions with background gas molecules or atoms results in the formation of a range of ions, molecular species, and neutral atoms, in addition to (V)-(UV-) photons. Emission spectra in the UV-Vis range of plasma sources operating in humid air, as an example, reveal the signatures of a range of molecular and atomic species including $^{\bullet}OH$, molecular nitrogen (N_2), nitrogen molecular ions (N_2^+), nitric oxide ($^{\bullet}NO$) and atomic oxygen (O), among others. The presence of a noble gas additionally introduces excited atoms and ions. At the interface, the primary species such as $^{\bullet}OH$, $^{\bullet}H$, N, and O concurrently solvate and recombine with the background gas to produce a multitude stable species which subsequently diffuse into the bulk liquid. Both modeling and experimental efforts have been used to describe complex reaction mechanisms responsible for the formation and transfer of these species into the bulk liquid.[14] The LR identified the plasma gas phase chemistry, transport of chemical species into and through the interface, the evaporation of liquid water, and transport of liquid phase components into the plasma as the key processes that occur at the plasma-gas-liquid interface (Figure 1 - LR). The main factors that affect these reaction-transport processes are the chemical reaction rates, the length scales for diffusion or electric field driven transport, the underlying gas and liquid hydrodynamics that affect convective transport, and the temperature and thermal gradients.

Below, we summarize the progress made in understanding the interfacial transport of plasma-generated species and their reactions with various inorganic and organic compounds at the interface and within bulk liquid, focusing on reactions involving non-OH species.

2. Interfacial transport

2.1 Plasma Jets – The plasma jets (helium or argon jets of plasma gas impinging upon a liquid surface) are perhaps the most well-studied configuration in terms of model simulations and experiments. Published studies describe the hydrodynamics in both the gas and liquid phases, as well as the multiple chemical reactions that can occur in both phases, including interactions with air where nitrogen oxide chemistry becomes critical. The emphasis on this configuration is due to the more structured and distinct gas and liquid phases that facilitate determination of the fluid flow fields as well as the significant interest in this configuration for biomedical and agricultural applications. As discussed below, significant advances in understanding the plasma jet configuration have been made, including detailed studies of the hydrodynamics – such as turbulent flow and electrohydrodynamic models – in both the gas and liquid phases, using both experimental approaches and computational simulations.

The most stable and commonly measured chemical species in the liquid contacting the plasma is hydrogen peroxide (H_2O_2), which has been well known for many years. [15-17] Many computational and experimental studies of plasma jets include H_2O_2 as a major diagnostic and representative species since it is generally easy to measure, provided proper account is made when dealing with solutions with continuously reacting components such as H_2O_2 and various nitrogen oxides. [18] When air or any gas containing nitrogen is present, nitrogen oxides are well-known to form, with nitrite (NO_2^-) and nitrate (NO_3^-) being the major species in the liquid phase, as has also been established for many years. [19] In a 1-D drift-diffusion model considering 15 species (compounds containing only oxygen and hydrogen) and 39 chemical reactions in the liquid phase, Du et al. simulated mass transfer (based on Henry's law) from the plasma jet to water to show penetration depths of H_2O_2 to 1 mm of $^{\bullet}OH$, $HO^{\bullet}_2$, and O_3 to 0.020 mm, and $O^{\bullet}_2^-$ to 0.2 mm. This model included mass transfer processes with electric field-driven transport of ions (including solving Poisson's equation for the electric field) and a stationary gas-liquid interface but no convection in the fluids. [20] A 2-D model of a helium plasma jet using a flat stationary interface and the Navier-Stokes equation for the gas flow in the absence of plasma, with species balances including convective-diffusion transport, was developed by Lu et al. to determine the fluxes of reactive species (in the absence of liquid phase balances or reactions [21]). In this model, a 0.2 mm reactive boundary layer was utilized based on results from the gas flow fluid model. The chemistry aspect of the model was based upon humid air with 59 species and 624 reactions. The main stable chemical species in the boundary layer were H_2O_2, HNO_2, NO, and HNO_3, along with the radical and metastable species $^{\bullet}OH$ and $N(^2D)$. The flux to the liquid water phase was dominated by H_2O_2, $^{\bullet}OH$, $HO^{\bullet}_2$ and HNO_2 when water evaporation into the gas was considered. These findings are consistent with other models, though quantitative comparison with experimental data was not provided.

In another drift-diffusion model which included the gas phase flow, a helium with air plasma jet over liquid water was analyzed by Liu et al. with a fixed gas-liquid interface in 2-D cylindrically symmetric geometry. [22] The Navier-Stokes equation was used to model the gas phase flow, while the drift-diffusion approximation was used for species transport in the gas and liquid phases. An electron energy balance was solved in the gas phase, and Poisson's equation for the electric field was used in both phases. The model included 51 species and 223 reactions in the gas, and 47 species with 148 reactions in the liquid. Three different interfacial boundary conditions (thermodynamic, diffusive, kinetic) and the uncertainty of Henry's law constants were assessed. The simulations showed no effect of the different boundary conditions or the uncertainty of the Henry's law constants on the H_2O_2 and NO_3^- in the bulk liquid phase. Consistent with the previous model that did not include hydrodynamics, H_2O_2 penetrates farthest from the interface to the mm range, while $^{\bullet}OH$ exhibits a steep drop beyond about 10 to 20 nm from the boundary, subject to time variations. The maximum H_2O_2 concentration in the liquid was in the mM range after 10 seconds.

To consider in more detail the liquid phase and gas phase hydrodynamics, Kamidollayev and Trelles developed a model of interphase transport for an argon plasma jet impinging on water utilized a 3-D model with turbulent gas flow, flow induced in the liquid, gas-liquid interfacial dynamics, and chemical species transport and reaction. [23] This work builds upon other fluid models for this system [24-28], with the consideration of turbulent flow in the gas as a key contribution. Different diffusion models were utilized, including the mixture diffusion model by Marschall et al.[29], harmonic mean mixture diffusion model by Haroun et al.[30], and unified mixture diffusion model by Deising et al. [31], which accounts for surface curvature. Of these, the harmonic mean mixture model was found to be the best and subsequentially utilized. This work included six species for a gas containing some nitrogen (open to air) including OH, H_2O_2, NO, NO_2, N_2O_4, and HNO_2 and seven chemical reactions. These were used as representative species in the afterglow of a kINPen argon atmospheric plasma jet. The maximum induced liquid velocity was 45 mm/s for an impinging gas flow of 1.7 slm, and recirculation flow patterns were comparable to those observed in other experimental studies. Comparison of experimentally measured H_2O_2 concentration in the liquid with the model results showed reasonable agreement, with some larger discrepancies at higher concentration for short plasma contact times and lower concentrations at longer times.

For an argon jet impinging on a liquid surface, another computational model based upon the Navier-Stokes equation with turbulent flow was developed under isothermal conditions by Semenov et al. [28] The gas phase transport utilized mixture-averaged diffusion coefficients, and Henry's law with mass transfer was used for transport across the gas-liquid interface. H_2O_2 transport was modeled without any chemical reactions. A 0.010 mm diffusion film layer between the gas and liquid was assumed, and the H_2O_2 transport into the liquid phase was compared with data for different times, showing reasonable agreement and best results at longer times of 40 seconds.

Experimental studies by Brubaker et al. of the hydrodynamics in a helium plasma jet impinging onto water utilized particle image velocimetry (PIV) for velocity profiles in the liquid, infrared (IR) for temperature determination, pH measurements and dye decoloration for chemical activity, and Schlieren imaging for gas flow patterns. The fluid flow showed similar liquid recirculation and velocity patterns where the jet impinges on the surface, consistent with other fluid models discussed above. The formation of the cavity where the plasma impinges on the liquid surface, along with the volume and the size of the cavity and the effect of the plasma power on the impact force to the liquid surface, were determined. Of significance is the determination of heat transfer and the role of evaporative cooling due to the impact of the plasma jet at the surface. Liquid flow velocities were found to be on the order of mm/s in the circulation flow and less than 1 mm/s elsewhere. The pH spatial profile was used as indicator of chemical activity. [32]

Another 2D fluid model for an argon plasma jet (with nitrogen oxides) over water by Verlackt et al. considered the plasma afterglow region. This model included the Navier-Stokes k-e turbulence model, a thermal energy balance, and balances for 20 gas phase species and 22 liquid phase species with 57 gas phase reactions and 42 liquid phase reactions. [24] Consistent with experiments and other models, the major species generated include, in order, H_2O_2, NO_3^-, and NO_2^-.

Experimental measurements by Park et al. using shadowgraphs methods and computational fluid dynamics showed the effect of ionized gases in jets at interfaces on stabilizing hydrodynamic instabilities. [33] Surface waves were generated in the meniscus with a microwave argon plasma torch, and the plasma properties, including rotational temperature and electron energy, were determined by Marinova et al. [34] H_2O_2 concentration in the liquid solution increased with plasma exposure to about 0.1 mM.

Using a 2-D transport model (including fluid flow by Navier-Stokes, a thermal energy balance and species convective diffusive transport) with a 0-D reaction model (90 species with 1437 chemical reactions in the plasma) the argon-contacting air plasma Cost jet contacting the liquid phase (25 species and 52 chemical reactions) coupled with a microfluidic device was simulated and compared to experimental data by Bissonnette-Dulude et al. Henry's law equilibrium was used at the gas-liquid interface. H_2O_2 transferred into the liquid, where a microfluidic device is connected to the plasma effluent from the COST Jet. H_2O_2 concentrations in the range of 20 to 30 mM from the model compare well with those from experiments. [35]

From the above studies and additional reviews [36], it appears that the production and transport of the key reactive oxygen and nitrogen species (RONS) such as H_2O_2 and NO_2^-/NO_3^- into the liquid phase from plasma jets, where the plasma is not electrically connected to the liquid surface, are reasonably explained by the fluid/transport/reaction models. These key species are relatively stable and highly water soluble. The hydrodynamic flow fields in the plasma jets and contacted liquids are well explained by the proposed models, and the transport into the liquid phase of these key species at the interface is rapid and not sensitive to some details of the models (e.g, Henry's law constants and form of mass transfer). Further work on comparison of models with experiments on other chemically highly reactive species is needed. For example, in the case of nanosecond pulsed helium plasma jets on a water surface, experimental measurements using optical emission spectroscopy, OES, showed the effects of pulse width on $^{\bullet}OH$ production by Song et al. [37] Connecting the formation of such radicals with the destruction of organic compounds and modeling of reaction rates and products of organic contaminants are needed for water cleaning applications. For example, a DBD plasma jet, was used to decompose organophosphorus compounds (chlorpyrifos, dimethoate, parathion, dimethyl methylphosphonate) with consideration of various reaction degradation products and plasma properties by Yehia et al. [38]

Additional reviews of interest related to plasma jets include the following. A detailed review of modeling and experiments for plasma jets directed at solid surfaces (not liquids) shows the effects of surface properties on plasma electron density variation with distance from the nozzle across a wide range of literature [9]. Another review by Vanraes and Bogaerts provides a detailed consideration and perspective on the plasma-liquid interface (sheath) and how it controls electrical coupling, mass transfer and chemistry. It reviews the fundamentals and historical context of plasma sheaths and argues for more studies with significant emphasis on biological processes. [39]

2.2 Pin to surface – The second most studied configuration concerning fluid and transport models is the pin to water surface configuration. This system, which dates back to many experimental studies from 20 to 30 years ago (see review for early references and context to electrical breakdown of liquids and chemical studies [40]), is similar to the plasma jet, but without gas-jet flow impinging on the liquid surface. Instead, the plasma propagates from the gas phase electrode to the surface, and it can spread across the liquid surface. Recent work has considered both experimental and modeling approaches including hydrodynamics as well as additional studies of plasma propagation along the interface. Electrohydrodynamics may play a role in some cases, particularly if the underlying liquid is stationary.

A computational 2-D model by Silsby et al. of mass and thermal energy transport, including the plasma and electric field simulation in a pin over water discharge with air was compared with experiments regarding water vaporization. [41] The model agreed reasonably with average water temperature measurements and was used to predict the spatial variation of temperature and the evaporation of water. A 0.010 mm thick high-temperature liquid film was bounded by a cooler interfacial region of 1 mm extending to the bulk liquid. The gas phase showed a high temperature region where electrohydrodynamic flow occurred, and the vaporization of water generated a 0.1 mm region containing 20 to 35% water vapor. While different plasma conditions and reactors may have different temperatures, this work supports the importance of water vaporization into the gas phase and its subsequent reactions in the plasma as a key reactant in the formation of H_2O_2, $^{\cdot}OH$, and other species, as recognized in the early work on this subject. [16]

Electromechanical coupling at the plasma liquid interface for the pin to water surface configuration was analyzed using a 2-D computational model and compared with experimental data using PIV in both the air and water by Dickenson et al. [42]. The model includes the Navier-Stokes equation with electrohydrodynamic forces, as well as the electrical terms in the stress tensor (Maxwell's stress). The results showed that the solution conductivity (deionized water vs. tap water) determines the dominant flow where at low conductivity the electric surface stress dominates while at high conductivity the electrohydrodynamic flow generated in the gas controls the liquid phase flow.

In a needle discharge over water, Schlieren flow visualization by Shimizu et al. showed that the induced gas velocity was strongly affected by the solution conductivity. [43] Low conductivity (0.8 mS/cm) led to velocities of 28 m/s while higher conductivity of 5 mS/cm led to 8 m/s. Longer lasting higher electric fields at the low conductivity were found to explain the higher velocities. Another study by Furusato et al. of a needle electrode over the water surface with time-resolved shadowgraph imaging demonstrated the formation of shockwaves (1.7 km/s) that moved into the liquid. [44] These underwater shockwaves, combined with the plasma reactions at the air-water interface, are expected to enhance reactions in the liquid.

Experiments with model simulations by Akishev et al. (electrostatic model of the electric field and current distribution) were used to consider plasma propagating along the gas-liquid interface from a point electrode. This was done to determine the length of the plasma, the structure of the plasma (i.e., branching), the electric field, and the velocity of the plasma for different input voltages, water depts, and channel shapes. [45] Plasma length (positive streamers) increased with applied voltage, with distilled water having lengths 4 times larger than tap water. In long narrow channels, streamer lengths up to 120 mm were found. Velocities up to the order of 10^6 cm/s were observed. In another pin to surface configuration, but with nanosecond pulses in air over water, the effects of various operational parameters, including voltage polarity, amplitude, pulse width, and gap distance on plasma properties (rotational temperature) and chemical species (NO_2^-, NO_3^-, H_2O_2, pH and conductivity changes, and methylene blue degradation) were determined by Hamdan et al. [46] Trends in the data were consistent with previous work on such systems, but energy yields were not provided.

2.3 Underwater discharges – Most of the recent work on underwater plasma discharges focuses on plasma propagation [47-49], spectroscopy by Pongrac et al. [50], breakdown of conductive liquids Panov et al. [51] in the dependence of electrical characteristics in the range of sub-microsecond and nanosecond pulse duration by Rataj et al. [52], with little emphasis placed on modeling or analysis of mass transfer and hydrodynamics. Typically, underwater discharges exhibit very high electric fields and fast plasma propagation. [53] The effects on fluid flow are difficult to determine, and in some cases, mixing is externally supplied. These underwater systems tend to have lower energy efficiency [16, 54] although interesting results were reported for production efficiency of hydrogen peroxide (9.2 g/kWh) using underwater discharge with pulse duration of 100 ns by Rataj et al. [52] and are increasingly used in nanoparticle synthesis. [55]

2.4 Bubbles – Bubbles have been introduced into plasma reactors in a variety of ways. For example, in some early studies on underway discharges, gas flowed through hollow needle electrodes, and discharges were formed in the gas bubbles as they emerged into the solution from the electrode. [56, 57] In addition, discharges in large bubbles have been demonstrated [58], and the characterization of plasma propagation on and inside large bubbles [59] has fundamental implications for plasma generated in small channels. Since those early studies and focusing on

work since the LR, more attention has been devoted to microbubbles. For example, a DBD plasma chamber has been used to inject bubbles containing ozone into an adjacent liquid solution, and various operational parameters (power and flow) were assessed in the decolorization of the crystal violet dye. [60] Although the energy efficiency of this reactor (10^{-9} mol/J) was better than that of other DBD reactors, it still does not outperform plasma reactors with thin films and water sprays (ranging to 6.6 x10^{-7} mol/J for various dyes, as reviewed in [61]). Another DBD reactor with microbubbles was extensively analyzed through modeling and experiments to characterize species formation, showing high values of NO_3^-, but experimental results and efficiencies were not reported. [62] In a pulsed nanosecond discharge with Ar-O_2 gas flowing through the underwater electrode (akin to the configuration used in the early literature) to form bubbles, H_2O_2 formation and methylene blue decolorization were determined, along with OES measurements. [63] The dye decolorization was about 10^{-10} mol/J, in the range of other reported work in this field with pulsed discharges in various configurations, including bubbles. [61] Recent work conduced on a tubular reactor with microsecond pulses and a concentric rod-cylinder electrode configuration has shown that bubble column contactors significantly enhance the utilization of plasma-generated reactive species for contaminant degradation by distributing them over a large contact area. [64] This results in a better match between the plasma species interfacial flux and the interfacial contaminant concentration, leading to improved treatment energy efficiency. The same work reported energy efficiencies for the degradation of caffeine of 10 g/kWh (1.4x10^{-8} mol/J) for caffeine and for rhodamine B of 60 g/kWh (3.5x10^{-8} mol/J).

2.5 Other approaches to enhancing plasma contact and mass transfer – Various approaches have been made to improve mass transfer and interfacial contact between the plasma gas and the liquid, including using sprays of mists [65], droplets [66-69], narrow microchannels [70, 71], foam trickle bed [72], spinning disks [73], a hybrid bubble reactor [74], and a type of surface discharge with streamers as the water-air interface. [75] In the first case, an atomizer was used to generate micron sized water droplets, which subsequently flowed in an oxygen gas stream into a DBD plasma reactor to produce H_2O_2. The concentration and efficiency were determined with variation of the applied voltage and discharge frequency, yielding the highest energy efficiency of about 2 g/kWh [65], which is in the range of other gas-liquid plasma reactors. [16] In another approach, gases flowing through a DBD generated in a microchannel with subsequent bubbling into the liquid phase showed high efficiency for tetrabromobisphenol removal of about 1.3x10^{-8} mol/J [70, 71], comparable to some of the higher efficiency plasma reactors for phenol oxidation (bubbled oxygen and falling films; see [61] for a review of these other reactors). In this case, the oxygen plasma generates ozone before entering the liquid phase of the reactor. A ceramic foam trickle-bed DBD was developed to enhance mass transfer and plasma contact [72], with the best energy yield for tetracycline hydrochloride of 0.6 g/kWh (5x10^{-10} mol/J). This value is within the range reported for other complex organics [61], but no measurements of reactive species (H_2O_2 or OH) were reported to determine if the reactor improves mass transfer efficiency. In another version of a hybrid reactor (gas-liquid hybrid plasma reactors were first proposed in [76, 77]) two discharges

are generated with the same power supply, one in a tube with flowing gases and a second one over the liquid surface where the bubbling gases were injected. [74] This system was used to generate plasma activated water (PAW), including H_2O_2, NO_3^-, and NO_2^-. The energy yield for total RONS was approximately 10^{-8} mol/J. Another type of surface discharge with streamer discharge at the water-air interface was used for plasma activated water. [75] The concentrations and energy yields of NO_2^- (0.6 mM and 30 mmol/kWh – $8.3x10^{-9}$ mol/J) and H_2O_2 (0.3 mM and 20 mmol/kWh – $5.6x10^{-9}$ mol/J) were reported. An argon atmospheric plasma jet was used with a spinning disk reactor to provide a well-defined fluid flow patterns and the ability to control the liquid residence time. [73] This system was characterized by H_2O_2 generation and rhodamine B dye degradation. The dye degradation energy yield of 5.39 g/kWh ($3.1x10^{-9}$ mol/J) is comparable to that of other reactors, including DC discharge over thin films of water (4.86 g/kWh – $2.8x10^{-9}$ mol/J), but lower than the yield of water spray into a DBD with an oxygen carrier (45 g/kWh – $2.6x10^{-8}$ mol/J).[61]

3. Non-OH chemistry at the interface and within bulk liquid

Various techniques, ranging from Electron Paramagnetic Resonance (EPR), Laser-Induced Fluorescence (LIF) to chemical probe approach, have been applied extensively to detect and quantify Reactive Oxidative Species (ROS) in liquid water, including $^{\bullet}OH$, H_2O_2, and O_3 .[78] These species are responsible for the vast majority of plasma-induced aqueous reactivity and as such play a significant role in plasma medicine, water treatment, microbial inactivation and plasma agriculture. In contrast to oxidative processes, the reactions of non-OH plasma-generated species, including O atoms, H radicals, free (e^-) and solvated electrons (e^-_{aq}), ozone (O_3), singlet oxygen ($^1O_2$), hydroperoxyl radicals/superoxide radical anion ($HO_2^{\bullet}/O_2^{\bullet-}$), and nitrogen-derived species, are less understood. There are several reasons for this. First, generating many of these species directly in water or through water splitting is challenging. Second, if generated in the gas phase, their aqueous solubility is low. Additionally, these species react rapidly, making direct detection difficult. Furthermore, in the presence of $^{\bullet}OH$, which is often the case for humid plasmas, OH radical fluxes and oxidation potential often exceed those of other species, complicating the understanding of the role of non-OH species. Lastly, many plasma-generated species have identical reaction pathways with various molecules, preventing the use of byproducts to infer which species was responsible for the reaction. Consequently, there is strong theoretical but limited experimental evidence on the solvation and chemical reactivity of many of these non-OH species, and their formation mechanisms are not well understood. Apart from neutral species and electrons, independent modeling efforts suggest that (solvated) gas-phase ions which have liquid penetration depths of about < 3 nm as well as various metastable species are likely to participate in transformations of chemical compounds. [79] Plasmas in contact with water are also expected to deliver both UV and VUV fluxes to the liquid surface, which could induce photochemical reactions with molecules other than water, depending on the photon intensity and wavelength.

Below, we present selected literature evidence for the involvement of O atoms, H radicals, solvated electrons, photons and nitrogen-derived species in the chemical transformation of organic

compounds. The literature on other species, including metastables, ions, and singlet oxygen is limited and thus not included. While the reactions of ozone have been studied extensively, they provide very little information regarding the role of ozone in chemical transformations of aqueous molecules. This is because the solubility of ozone in water is low, and most studies have used dyes that are known to be susceptible to degradation by multiple agents, including $^{\bullet}OH$ ~~radicals~~, light, and chlorine-derived species.

The atomic oxygen is formed in discharges involving oxygen, air and their admixtures in the absence of humidity through the electron impact dissociation of O_2 molecules (reaction 1). [80, 81] Subsequent reactions generate significant amounts of metastable $O(^3P)$, superoxide ($O_2^{\bullet-}$), and ozone (reactions 2-4). When in contact with water (humidity or aqueous solutions), these oxygen-derived species can react with water molecules or dissolve in the solution, undergoing direct reactions in the liquid phase (reactions 5-8). Detailed reaction networks and mechanistic details for discharges in oxygen, air and noble gases are published elsewhere. [82]

(1) $O_2 + e \rightarrow O + O + e$
(2) $O + e \rightarrow O(^3P) + e$
(3) $O_2 + e \rightarrow O_2^{\bullet-}$
(4) $O_2 + O + M \rightarrow M + O_3$
(5) $O(^3P) + H_2O \rightarrow 2\,^{\bullet}OH^{\bullet}$
(6) $O_2^{\bullet-} \rightarrow {}^1O_2 + e$
(7) $O_2^{\bullet-} + H_2O_2 \rightarrow {}^1O_2 + OH^{\bullet} + OH^-$
(8) $O_2^{\bullet-} + {}^{\bullet}OH^{\bullet} \rightarrow {}^1O_2 + OH^-$

The solvation of gas-phase O atoms has been confirmed using techniques such as laser induced fluorescence (LIF), two-photon absorption laser induced fluorescence (TALIF), and electron paramagnetic resonance (EPR). [83-86] Both EPR and chemical probe approaches have been used to identify and quantify superoxide radical anions in aqueous solutions.[85, 87] However, studies reporting reliable measurements of the singlet oxygen are scarce.[86]

The work of Hefny et al.[88] and Benedikt et al.[89] has confirmed that O atoms generated in an RF-driven atmospheric-pressure He/O_2 plasma exist as stable species in water and react directly with organic compounds, such as phenol, resulting in hydroxylation reactions similar to those of $^{\bullet}OH$ (Figure 1). The hydrogen atom on the resulting OH group originates either from the aromatic ring or water. When the phenol solution was treated with a similar plasma source, but with the feed gas type extended to include He, He/H_2O, and $He/O_2/H_2O$, $^{\bullet}OH$ dominated the oxidative effects induced in water. [88]

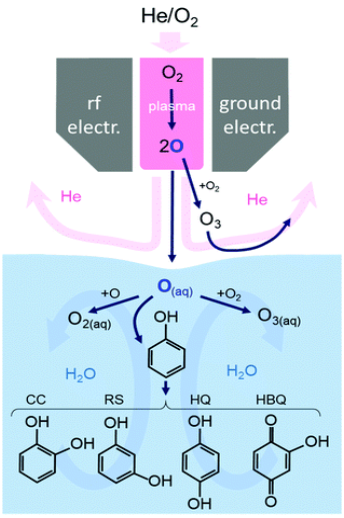

Figure 1. The reaction pathways of O atoms in the gas phase and the phenol solution. The solid arrows summarize the main reaction pathways, and the broad arrows in the background indicate the gas and liquid movement. Reproduced with permission from [90].

It is important to note that in these studies, the surfactant nature of phenol molecules enabled the detection of O atoms. The kinetics and inherent nature of interfacial processes depend not only on the composition of the background/feed gas and the production rates of various plasma-generated species, but also on the proximity of the chemical compound to the plasma-liquid interface (Gibbs surface excess). Nayak et al.[90] demonstrated this by measuring removal rates of formate ions contained within liquid microdroplets and treated by atmospheric pressure RF-driven diffuse glow discharge in helium with different gas admixtures (argon, oxygen and humidified helium). A combination of experiments and modeling revealed that in the presence of water vapor in the background gas, the formate decomposition was mainly driven by $^{\bullet}$OH ~~radical~~ attack. Although the $^{\bullet}$H ~~radical~~ density was an order of magnitude higher than the $^{\bullet}$OH density in He/H_2O plasma, the role of the $^{\bullet}$H ~~radical~~ in formate decomposition was considered negligible due to its Henry's law solubility constant being several orders of magnitude smaller than that of $^{\bullet}$OH ~~radicals~~. Furthermore, in water-containing plasmas, neither O atoms nor electrons were assumed to participate in formate decomposition due to their fluxes being lower than that of $^{\bullet}$OH ~~radicals~~. When no water vapor was added to the helium feed gas, the observed enhanced formate decomposition was explained by the increased electron/ion flux to the droplet, which was estimated to be like the expected $^{\bullet}$OH flux. According to the authors, the subsequent injection of ions or electrons into the liquid could induce various charge exchange or recombination reactions, leading to the formation of solvated electrons, $^{\bullet}$OH and $^{\bullet}$H ~~radicals~~, which might become the key

reactants in the decomposition process. The similarity in formate decomposition between He/O_2 and He/H_2O plasmas, despite a higher bulk density of $^{\bullet}O$ ~~radicals~~ in the He/O_2 plasma, was explained by the conversion of $^{\bullet}O$ to $^{\bullet}OH$ ~~radicals~~ due to droplet evaporation. Similarly, the authors further proposed that the electron-induced dissociation of water vapor around the droplet surface produces H radicals, which can recombine with incoming $^{\bullet}O$ ~~radicals~~ to produce $^{\bullet}OH$. Therefore, in the presence of even the smallest concentrations of water vapor, it may be impossible to distinguish between the reactions of $^{\bullet}O$ and $^{\bullet}OH$. The work of Henfy and Benedikt and co-authors presented earlier did not discuss the significance of evaporation in the degradation of phenol by He/O_2 plasmas.

This inability to distinguish between the oxidative pathways of $^{\bullet}O$ and $^{\bullet}OH$ was demonstrated during the oxidation of D-glucose by an argon-based dielectric barrier discharge plasma jet (kINPen). Ahmadi and co-authors [91] discovered that only when O_2 was added to argon did $O(^3P)$ emerge as the primary oxidant of glucose, resulting in a higher level of oxidation and yielding more oxidized products compared to pure argon. The authors proposed that the mean free path of $O(^3P)$ is larger than for $^{\bullet}OH$, allowing a reaction with the glucose to also take place in the boundary layer below the gas-liquid interface. Experiments further confirmed that neither superoxide generated in the discharge nor singlet oxygen, which is largely formed from superoxide (reactions 6-8), played a role in the oxidation of D-glucose. It is worth mentioning that in pure argon, singlet oxygen participated in the chemical transformation of L-histidine, used as a chemical scavenger, alongside atomic oxygen. To date, multiple additional studies have confirmed that $^{\bullet}O$ ~~O atoms~~ generated in the gas phase can dissolve, diffuse, and react with bulk liquid organic species, despite participating in various additional chain propagation and termination reactions.[88, 92-96]

The finding that He/O_2 plasmas produce copious amounts of $^{\bullet}O$ ~~O atoms~~ was used by Ogunyinka et al. [97] and Xu et al. [98] to drive the epoxidation of trans-stilbene in solution. Experiments using a microplasma jet operating in He/O_2 revealed that $^{\bullet}O$~~O atoms~~, but not $^1O_2$ or O_3 produce trans-stilbene epoxide, which was the intended product. Reactions of both O_3 and singlet oxygen yielded undesired byproducts such as benzaldehyde, as shown in Figure 2, and played no role in the formation or destruction of the epoxide.

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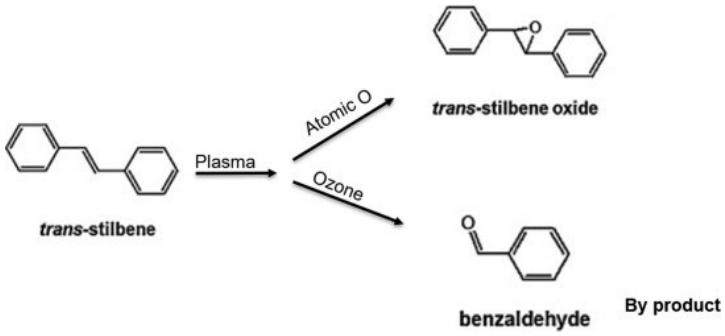

Figure 2. He/O_2 atmospheric-pressure plasma epoxidation and ozonolysis of trans-stilbene. Reproduced with permission from [99].

In addition to the reactivity of $^{\bullet}O$ ~~O atoms~~ with organic compounds, it has been experimentally and numerically demonstrated that $^{\bullet}O$ ~~O atoms~~ can promote chemical reactions at the gas/liquid interface and within a bulk liquid containing inorganic material. An example is the direct reaction of O atoms with chloride ions to produce hypochlorite [94, 100-103]. The kinetics of hypochlorite formation and the chemical processes derived from plasma chemically produced OCl^- in plasma-treated saline solutions were determined by Jirasek et al.[100]. The produced hypochlorite was shown to be directly proportional to the NaCl concentration, indicating a direct reaction of Cl^- with O atoms with the 2nd order rate constant of reaction $O+Cl^- = OCl^-$ being $k = 1.64 \times 10^5$ $(M\ s)^{-1}$. Three chlorine oxoacids or their conjugate bases were detected in the plasma-treated saline: hypochlorites $HOCl/OCl^-$, chlorites ClO_2^-, and chlorates ClO_3^-. Subsequent post-discharge chemical processes of oxychlorine species in the bulk plasma-treated saline solution were found to lead to the disproportionation of hypochlorite into different oxidation states of chlorine (Figure 3).

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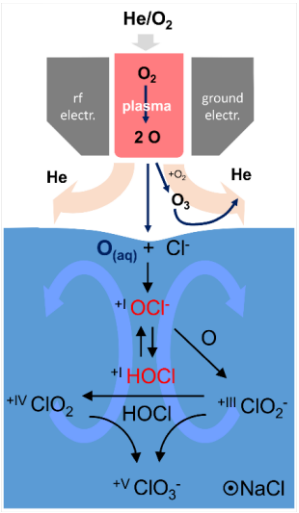

Figure 3. Oxychlorine chemistry induced by He/O_2 plasma in NaCl. [100]

A numerical model based on molecular dynamics simulations was developed to explore interfacial reactions and transfer mechanisms of O atoms at the gas-liquid interface. The simulation results revealed that charge-transfer, proton-transfer, and hydrogen transfer play important roles in pure water, with O atoms in the singlet state producing oxywater O-OH_2 and perhydroxyl anion as transient products, and H_2O_2 as the final product (reactions 9-12) [80, 104]. Simulation work focused on the interactions of O atoms with Cl ions in a water matrix determined that a singlet oxygen atom directly combines with Cl^- to produce ClO^- via an oxygen transfer reaction [103]:

(9) $O(^1D) + H_2O \rightarrow O{-}OH_2$

(10) $O{-}OH_2 + H_2O \rightarrow O{-}OH^- + H_3O^+$

(11) $H_3O^+ + H_2O \rightarrow \cdots \rightarrow H_2O{+}H_3O^+$

(12) $H_3O^+ + O{-}OH^- \rightarrow H_2O_2 + H_2O$

Oxychlorine chemistry has been shown to play an important role in chemical transformations of saline-containing mixtures of organic compounds treated by plasma [105-108]. Chemical changes and antibacterial properties of amino acids – leucine, phenylalanine, and tyrosine – treated in phosphate-buffered saline (PBS) by helium plasma jet were determined. Chlorination and the formation of mono- and dichloramines of amino acids by hypochlorite, produced through the

reaction of plasma-generated O atoms with Cl^- ions, were the major processes. These processes were accompanied by the oxidation of the amino acid aromatic ring by atomic oxygen (Figure 4). Plasma-modified solutions of amino acids, as well as cell culture media, have shown long-term post-discharge reactivity characterized by the decay of organic chloramines to secondary products and by strong bactericidal effects enhanced by acidification and longer plasma treatment times. These observations have significant implications for understanding the biochemical effects of plasma-activated media.

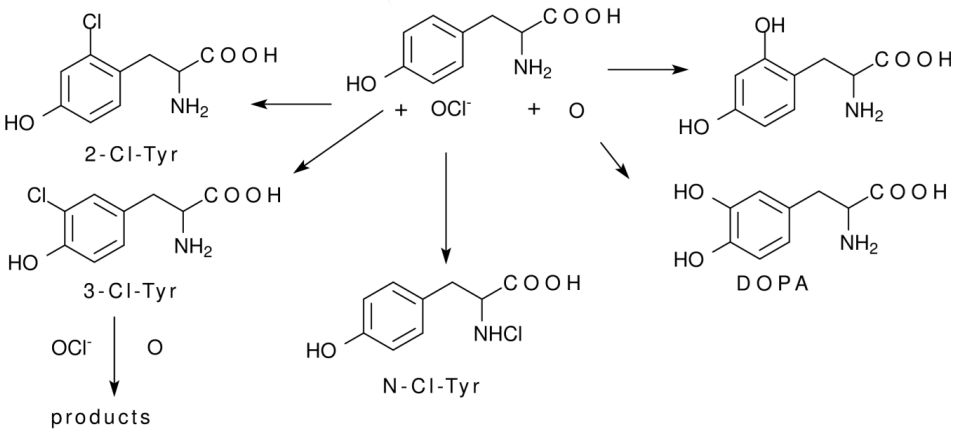

Figure 4. He/O_2 atmospheric-pressure plasma chlorination and oxidation of tyrosine. [106]

Gas plasmas can be tuned to create high levels of not only oxygen- but also nitrogen-containing species. Nitrogen-containing plasmas have been shown to produce nitric oxygen radicals ($^{\bullet}NO$), nitric dioxide radicals ($^{\bullet}NO_2$), dinitrogen trioxide (N_2O_3), peroxynitrite ($ONOO^-$), as well as NO_2^- and NO_3^-. Multiple spectroscopic and analytical techniques have been employed to identify and quantify these species, and their reaction mechanisms have been investigated in relation to the formation of PAW. [109] While Reactive Nitrogen Species (RNS) will be formed in any plasma system in the presence of even minuscule quantities of nitrogen in the feed gas, their reactions with organic materials have largely been limited to biological systems. Multiple studies have observed both nitration and nitrosylation of biomolecules, suggesting that RNS, most likely, $^{\bullet}NO_2$, N_2O_3, and $ONOO^-$ have the capability to chemically modify biological and other complex chemical structures.

The work conducted on the previously mentioned tyrosine treated with the kINPen source, revealed that nitration reactions are significant for dry Ar/O_2 plasma containing nitrogen. [96, 110, 111] In the presence of nitrogen, gaseous $^{\bullet}NO_2$ was found to be responsible for the direct nitration

of tyrosine at the gas–liquid interface and involved in the formation of peroxynitrite and nitric oxide radicals. Peroxynitrite, but not nitric oxide radicals, contribute significantly to the degradation of tyrosine in the bulk liquid. Without nitrogen, the impact of RNS is minimal and the degradation proceeds via direct oxidation by $^{\bullet}O$ ~~O atoms~~ (Figure 4).

Nitrogen plasmas have also been shown to enable chemical syntheses at gas-liquid interfaces with special interest in plasma-assisted nitrogen fixation into NH_3. This process is of interest because it provides a sustainable method for producing ammonium without relying on traditional energy-intensive Haber-Bosch processes. [112] Gorbanev et al. [113] used atmospheric pressure plasma jet operated with N_2 containing H_2O vapor in contact with liquid H_2O to produce ammonia in plasma-treated water. The highest selectivity toward NH_3 was observed with low amounts of added H_2O vapor, but the highest production rate was reached at high H_2O vapor contents. They showed the added H_2O vapor as the main source of H for NH_3 generation suggesting that most of the reactive chemistry in plasma-liquid systems occurs in the gas (vapor) phase. However, further research is needed to specify the transfer mechanisms of NH_x radicals through the gas-liquid interface and selectivity plasma chemical production of NH_3. The formation of inorganic chloramines NH_2Cl in saline solutions treated by the nitrogen plasma was also proposed by Maheux et al. [114] Two independent studies demonstrated the use of nitrogen-containing atmospheric pressure plasmas – one using pure nitrogen and the other using ammonia – to carry out the amination of liquid benzene. [115, 116] Both studies revealed high selectivity to produce aminated byproducts, although the yields and the formation of undesired products depended on the nitrogen source. In the presence of ammonia, in addition to aminated products, both hydrogenated and dimerized compounds were formed. Hydrogen and NH_2 radicals formed by the dissociation of ammonia were critical in generating these byproducts. In presence of nitrogen, Xu et al. [116] demonstrated the production of aryl amine at very high yields. The process was assumed to be accomplished mainly through the reactions of electronically excited molecular N_2^* rather than atomic N and the production of diazo-like structures, as shown in Figure 5.

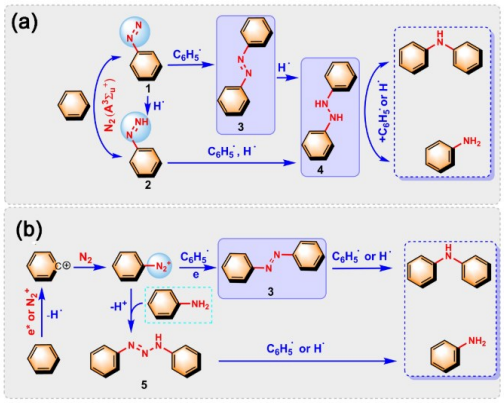

Figure 5. Proposed reactions channels for benzene amination. (a) The excited N_2 ($A^3\Sigma_u^+$) route. (b) The benzenediazonium route [116].

At the plasma–liquid interface, electrons from the gas phase can transfer to the liquid phase and become solvated, producing solvated electrons, which are the strongest reductive species generated by plasma.[117] When the plasma is positively biased, gaseous ions move towards the solution surface and produce solvated electrons mainly through the ionization of water. Conversely, when the plasma is negatively biased, relatively lower-energy free electrons are injected from the gaseous plasma into water, where they solvate without ionizing the solvent. Total Internal Reflection Absorption Spectroscopy (TIRAS) has been used to directly detect the presence of solvated electrons.[118] The reactions of solvated electrons with metal ions, particularly silver, to produce zero-valent metals, as well as the reduction of ferricyanide ($[Fe(CN)_6]_3^-$) to ferrocyanide ($[Fe(CN)_6]_4^-$), have been employed to indirectly demonstrate the presence of these species. [117, 119] More recently, the reactions of solvated electrons have been extended to synthesize nanoparticles of silver in glycerol as well as tungsten oxide.[120] Beyond these studies, which have mainly been carried out using DC and RF plasmas with ionic precursors, the evidence for the involvement of solvated electrons in chemical transformations of organic compounds is virtually non-existent. An exception is the nanosecond gas-liquid discharge in argon, which demonstrated the degradation of chloroacetate due to its reaction with solvated electrons.[119] Despite this, research has suggested that chemical reactions involving solvated electrons play a significant role in the degradation and removal of certain compounds for a range of different plasma sources and process gases. For example, the degradation of per- and polyfluoroalkyl substances (PFAS), particularly perfluorooctanoic acid (PFOA), a non-oxidizable compound, has been attributed to solvated electrons.[121, 122] Because PFOA can be degraded by a multitude of other non-OH pathways, including photodissociation and charge transfer reactions involving gaseous ions, finding direct evidence for the involvement of solvated electrons in the transformation of these

compounds is extremely challenging. Another challenge contributing to this uncertainty is the high reactivity of electrons solvated in water. Even a small amount of O_2 in the gas phase can significantly reduce the flux of plasma electrons reaching the liquid surface, thus limiting their ability to solvate. Additionally, dissolved O_2 and other long- and short-lived ROS can scavenge solvated electrons, further complicating the understanding and the assessment of their role in chemical degradations. Despite this, solvated electrons remain near the interface for more than 750 ps and penetrate up to 2.5 nm in depth, which makes them important reactants in any chemistry occurring within the interface.[117] In the absence of chemical scavengers, solvated electrons react with water to form hydroxide ions and molecular hydrogen.

Another powerful reducing agent generated by water splitting is the H radical which has been observed experimentally in the gas phase using optical emission spectroscopy. While plasma-derived hydrogen radicals can solvate in liquids and their concentrations have been measured using chemical probes, their low solubility and high reactivity limit their direct impact on chemical reaction pathways involving organic compounds in aqueous solutions.[83, 87, 123] Nevertheless, solvated hydrogen radicals have been identified as key agents in reducing metal ions like Ag^+ to form nanoparticles.[124] The chemistry of hydrogen radicals is usually distinguished from that of solvated electrons by lowering the solution pH, where hydronium ions effectively scavenge solvated electrons.

Plasma, particularly noble gas plasma, emits a considerable number of photons across a wide spectrum. The emission region from argon excimers, for example, ranges from the vacuum UV (105 nm) to the near-infrared (1000 nm) and includes ultraviolet radiation (100 – 400 nm). The ionizing nature of radiation in the 10-125 nm range means that even low levels emitted by argon metastables produced by atmospheric pressure plasmas can have enough energy to significantly impact organic molecular structures.[125-128] Indeed, in biological applications of plasmas, antimicrobial effects and the impacts on DNA are well documented.[69] However, less is known regarding the roles of photons, particularly UV radiation, in the chemical transformations of other molecules. These mechanisms likely proceed through the absorption of radiation, leading to the creation of excited forms that ultimately initiate photo-oxidation reactions.

Using the argon-driven kINPen plasma source and applying different optical filters, Bruno et al. [125] discovered that plasma-generated (V)UV radiation was effective in chemically transforming cysteine, both directly and indirectly. Direct treatment resulted in the dissociation of the C-S bond, while indirect treatment relied on the formation of $^{\bullet}OH$ ~~radicals~~ generated by the photolysis of water due to (V)UV radiation emitted by argon excimers. Notably, in the presence of oxygen, the (V)UV radiation was eliminated. Plasma-generated UV light was shown to be the primary factor responsible for rhodamine B degradation during a spark discharge between two point electrodes positioned above the liquid surface, without any physical contact with the liquid.[129] The most recent study demonstrating the involvement of photons in chemical transformations was conducted

by Bruggeman and coauthors who treated water microdroplets containing formate and PFOA with a radiofrequency glow discharge plasma using He, He/Ar, and He/H_2 gases.[123] A series of control experiments involving afterglow, UV, and (V)UV exposures suggested that (V)UV photons significantly contribute to the decomposition of these two aqueous compounds when using He and He + Ar plasmas. The amount of (V)UV photons required to explain the results was consistent with the measured (V)UV fluxes in similar RF-driven plasmas reported in the literature. The impact of plasma-produced gas-phase $^{\bullet}$H ~~radicals~~ on decomposition was shown to be insignificant due to their low solubility in the liquid.

4. Conclusions and outlook

Significant work has been conducted since the LR was published in 2016. We have highlighted some major aspects related to plasma liquid chemistry and the connections with the mass transfer from the plasma to the liquid. There remain several important areas that need further work.

a) **Connections with experiments**. Much of the modeling work focuses on comparison with easily measured species such as H_2O_2 and various nitrogen oxides, mainly NO_3^- and NO_2^-. While this is a very good start, more work should be performed to connect the modeling results with a wider range of measured chemical species. This requires additional experimental data on a wider range of chemical species such as for example, H_2, O_3, O_2, and various radicals as described above.
b) **Model predictions connected with experimental data**. To fully test the validity of a model simulation, the model should be used to compare with data developed independently of the model. More effort is needed to connect models with independently measured chemical species.
c) **Further understanding of non-OH chemistry**. Non-OH species play a significant role in the chemical transformation of organic compounds in plasma systems. Understanding the conditions under which these species dominate is crucial for optimizing plasma systems for selective degradation of organic pollutants and chemical syntheses.
d) **Chemical reactions of complex compounds – byproduct formation.** Many papers have explored various chemical mechanisms, including reaction products from, for example organic compound degradation. This work needs to continue for a wider range of compounds and carbon, fluorine and chlorine mass balances must be established and closed. There are many experimental challenges that need to be overcome in the analytical chemistry of detecting low concentrations of parent and degradation compounds within complex mixtures. In addition, modeling efforts need to be connected to experimental work to provide more accurate descriptions of reaction pathways of complex organic compounds and to identify the major pathways for degradation.

Acknowledgments
S. M. Thagard would like to thank the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences, General Plasma Science Program (Award Number DE-SC-0020232) and the National Science Foundation ECO-CBET Program (Award Number 2318494).

Table of Contents

This review summarizes recent advances in processes at the plasma-liquid interface and the reactions occurring within the liquid. We highlight key findings on the interfacial transport of plasma-generated species, with a particular focus on non-OH species. The discussion emphasizes their reactions with various inorganic and organic compounds, particularly the roles of O atoms, H radicals, solvated electrons, photons, and nitrogen-derived species.

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