Chapter 1

Introduction and Summary

Introduction to Interfacial Chemistry

The general subject of this thesis is to investigate environmentally relevant reaction mechanisms and kinetics at aqueous interfaces and to demonstrate that in many cases heterogeneous chemistry may be just as, or more, important than homogeneous chemistry. Chemical reaction models tend to focus on homogeneous chemistry, as the fraction of total molecules associated with an interface is generally very small. However, there are cases when interfacial processes should be taken into consideration, such as when mass transfer between phases is rate-limiting and/or when reactions undergo surface catalysis. Recent observations have shown that interfacial chemical reaction mechanisms and kinetics are at variance with results from homogeneous systems.

Mass-transfer limitations can lead to interfacially dominated processes. The most obvious case is that of reactions at gas-solid and liquid-solid interfaces, since diffusion into amorphous and crystalline solids is negligible at standard temperatures and pressures. Biphasic reactions are therefore limited to the interface between the gas or liquid and solid. Similar mass-transfer limitations are active for gas-liquid interfaces. In particular, the air-water interface has been the focus of many recent experimental and computational studies. The distinct differences between gas-phase and aqueous-phase bulk properties lead to strong chemical partitioning between phases. Thus, most chemical species will be found predominantly either in the gas phase, such as nonpolar and large molecules, or in the aqueous phase, such as ions and hydrogen-bond donors and/or acceptors. Thermodynamically, the partitioning is mediated by a balance between the hydrogen bonds lost when forming a water cavity for the solute and the added intermolecular interactions between water and the solute. Some specific examples, with a focus on aqueous aerosols, of gas-interface-water partitioning and their implications for interfacial chemistry are given below.

Low molecular weight, nonpolar molecules will preferentially partition into the gaseous phase. For example, the atmospherically relevant gaseous oxidant ozone is found at surface concentrations in the range of 10 to 100 ppt and has



an air-water partitioning or Henry's constant, $K_{a-w/H}^{Ozone} = 0.0094 \text{ mol/kg/bar}$, yielding $O_{3(g)}/O_{3(aq)} = 5$ for equal volumes of air and water. The maximal sea spray aerosol-volume-to-air volume ratio in the marine boundary layer is in the range of 100 µL/m³ or 10^{-7} v/v , which is similar to maximal aerosol-to-gas volume ratios in clouds. Although the majority of the ozone molecules will be in the gas phase, it does not preclude heterogeneous reactions. Gaseous ozone molecules will frequently collide with aerosol interfaces, at 10^{-7} v/v : aerosol/water once per second, with an aerosol surface, and spend a short amount of time at the air-water interface before preferentially diffusing back into the gas phase. (See Scheme 1.1.) Gaseous ozone will undergo 100 to 1000 collisions with 'pure' water droplets before dissolution, thus there are many opportunities for the gaseous ozone molecule to react at the air-water interface.

Mass-transfer effects are not only observed in transferring from air to water, but also in transferring from water to air. Non-polar molecules that are either very high in molecular weight or that also contain an ionic functional group will preferentially accumulate at the air-water interface as the evaporation rate is limited by mass or hydration energy, respectively. Assuming the interfacial layers are limited to monolayers, the surface partitioning can be modeled with a Langmuir isotherm, eq. 1.1.

$$\Gamma^{\mathrm{X}}(\mathrm{mol/m}^{2}) = \Gamma^{\mathrm{X}}_{\mathrm{MAX}} \frac{\mathrm{K}^{\mathrm{X}}_{\mathrm{eq}}[\mathrm{X}]}{1 + \mathrm{K}^{\mathrm{X}}_{\mathrm{eq}}[\mathrm{X}]}$$
(1.1)

 Γ^{x} is the surface concentration of x in moles/m², Γ_{MAX}^{x} is the maximum possible surface concentration of x in moles/m², [X] is the bulk concentration of x, and K_{eq}^{x} is the bulkwater to air-water interfacial partitioning coefficient in M⁻¹. The air-water interface partitioning effects will be relevant for bubbles and aerosols, both of which have been examined in this thesis, where the surface-area-to-volume ratio is relatively large. Using the aerosol example again, in Table 1.1, the aqueous aerosol radius required for more

	$\Gamma_{\rm max} ({\rm mol/m}^2)$	K (M ⁻¹)	r (µm)
Acetate	8.5 x 10 ⁻⁶	0.17	0.004
Hexanoate	6.3 x 10 ⁻⁶	67	1.2
Decanoate	8.5 x 10 ⁻⁶	2,000	43
Fulvic Acids	3.2 x 10 ⁻⁶	1,200	11
Na-SDS	10 x 10 ⁻⁶	110	3.3
Na-SDS	2.7×10^{-6}	190.000	710
(0.5 M NaCl)	5.7 X 10	180,000	/10
PFOS	5.0 x 10 ⁻⁶	1870	28
PFHS	5.7 x 10 ⁻⁶	160	2.7
PFBS	4.4 x 10 ⁻⁶	40	0.53
PFOA	4.4 x 10 ⁻⁶	360	4.7
PFHA	4.8 x 10 ⁻⁶	76	1.0
PFBA	2.9 x 10 ⁻⁶	32	0.42

Table 1.1. Langmuir isotherm parameters for a number of hydrocarbons and fluorocarbons

than 99% of various organics at under surface saturation concentrations can be found at the air-water interface vs. bulk water.

In the first half of Table 1.1, the droplet radius values for number of hydrocarbons are listed. In all cases except acetate, at an aqueous droplet radius greater than 1 micron, the organic will be predominantly found at the interface. As the average radius of marine boundary layer droplets is 2 micron, most environmentally relevant marine organics (see fulvics) will be associated with droplet interfaces. The results for sodium dodecyl sulfate (SDS) are shown for both 'pure' water and typical marine ionic strengths (0.5 M). It is of note that in the high ionic strength system, the 'salting out' effect increases the SDS airwater interfacial partitioning coefficient by over three orders of magnitude. In the second half of Table 1.1 is listed the Langmuir isotherm parameters for a series of perfluorinated surfactants, which are the subject of a number of chapters of this thesis. It is of note that perfluoroctanesulfonate (PFOS⁻, $CF_3(CF_2)_7SO_3^-$) and perfluoroctanoate (PFOA, $CF_3(CF_2)_6CO_2^-$) have 8 and 7 hydrophobic tail carbons, respectively, yet both have

greater air-water-interface partition coefficients as compared to the hydrocarbon SDS, which has 12 tail carbons. PFOS has a similar partitioning coefficient to decanoate, which has 9 tail carbons.

Scheme 1.2. Representation of perpendicular and parallel orientations of naphthalene at the air-water interface

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Organics adsorbed at an air-water interface will have a specific molecular orientation. For example, in Scheme 1.2 the perpendicular (1) and parallel planar (2) orientations of naphthalene at the air-water interface are depicted. Due to hydrogen bonding with the conjugated p-orbitals and lower energy of bulk water cavity formation, the parallel planar configuration is preferred. Another example of molecular orientation of chemicals at the air-water interface is that of surfactants such as sodium dodecyl sulfate (CH₃(CH₂)₁₁OSO₃-Na⁺, SDS), which are composed of a hydrophobic alkyl tail and a hydrophilic anionic headgroup. SDS preferentially partitions to the air-water interface

since the hydrophobic tail is pushed out of the bulk aqueous phase, yet the hydrophilic sulfate group is anchored to the bulk aqueous phase. At low surface concentrations, the hydrophobic tail lays down flat against the air-water interface to maximize its intermolecular



interactions through van-der-waals-dipole forces with the interfacial water molecules. At high surface concentrations, the hydrophobic tails pack closely and align themselves nearly perpendicular to the air-water interface (Scheme 1.3). The alkyl tail hydrophobicity and tail-tail interactions are great enough such that the tails act like 'buoys' that pull the hydrophilic headgroups closer to the air-water interface and each other than would be predicted by only Coulombic repulsion. It is expected that both interfacial partitioning (mass transfer) and molecular orientation at the interface will to some extent affect chemical mechanisms and kinetics, as compared to previously determined bulk chemistry.

Mass transfer limitations act to limit homogeneous chemical kinetics, necessitating chemistry at the interface between two phases. The partitioning of a particular chemical is usually easy to experimentally measure or even calculate through simple thermodynamic estimations. Thus, it is easy to answer the question of 'where' a reaction is most likely to occur in terms of homogenously or heterogeneously. If the answer to this question is an interface between two distinct phases, then questions follow, such as; How do we predict the chemical mechanism and kinetics? How do we experimentally investigate the interface of low site density as compared to the bulk phases? And so on. Many of these questions have been answered for solid interfaces, where low instrumental penetration depths can allow for surface specific analyses and diffusion in the bulk is negligible. However, when dealing with the more fluid air-water interface, surface-specific analyses become more difficult.

In this thesis, the kinetic and mechanistic relevance of interfacial aqueous chemistry to the overall observed chemistry is evaluated for a number of environmentally relevant systems. Reaction mechanisms and kinetics are investigated using time-dependent reactant and product analyses of batch chemical reactions. The chemical reaction timedependencies are fit to kinetic models, which give insight into the plausible chemical mechanisms. This procedure is applied to various initial reactor conditions such as applied power, reactant speciation, reactant concentrations, etc., to make more in-depth conclusions about the observed chemistry. In most cases, it is determined that the aqueous interface chemistry dominates the overall reaction chemistry, primarily due to mass transfer effects. In some cases, the interfacial mechanisms and kinetics are determined to be unique as compared to previously determined homogeneous chemistry. The detailed results of the thesis are briefly overviewed in the following section.

Thesis Overview

Chemical reactions at air-water and at water-solid interfaces were examined for three environmentally relevant systems and are presented in the chapters in this order: 1) sonochemical remediation of aqueous fluorochemicals, 2) gaseous ozone oxidation of marine aerosol anions, and 3) electrochemical water-splitting for simultaneous hydrogen production and organic oxidation. Sonochemical remediation of fluorochemicals (1) involves the partitioning of fluorochemicals to the air-water interface of acoustically cavitating bubbles where they are pyrolytically destroyed. The thesis examines how this air-water interface partitioning mediates sonochemical transformation kinetics and how the adsorption kinetics is affected by high-velocity bubble oscillations. Gaseous ozone oxidation of marine aerosol species (2) is observed to primarily occur at the air-water The short-lived products and intermediates suggest that interfacial ozone interface. oxidation kinetics and mechanisms may be at variance with bulk aqueous chemistry. Electrochemical water splitting for hydrogen production using organic waste as a sacrificial electron donor (3) involves reactions at water-metal and water-semiconductor interfaces. Sections of most of the subsequent chapters have been published as scientific papers in journals such as the Journal of Physical Chemistry and Chemical Physics Letters.

Remediation of aqueous fluorochemicals and in particular PFOS and PFOA is the subject of Chapters 2 to 5. The chapters are results from a project that was funded by 3M, who used fluorochemicals in their formulations of stain-resistant coatings. My role in this project, was as scientific lead in determining the direction and objectives of the project and primary contact with 3M. I was the editor of all scientific papers (Chapter 2 will be submitted to ES&T, Chapters 3 to 5 are in press, a paper first-authored by graduate student Jie Cheng is in press, and at least eight more papers will be submitted for peer review in the near future). I also developed and maintained the primary analytical technique, HPLC-MS, used to analyze all fluorochemicals in question. Iwill now briefly review the subject of each chapter.

Chapter 2 is a review of the methods reported for the remediation of aqueous PFOS and PFOA. It is divided into removal, reductive, oxidative, and thermal methods, with the most promising degradation methods evaluated in terms of products, reaction kinetics, competition effects, and energy consumption. The most efficient destruction methods (persulfate photolysis, iodide photolysis, direct photolysis, sonolysis) still require at least 10,000,000 kJ/mol to transform PFOS and PFOA into their inorganic constituents, which is 3 to 4 orders of magnitude greater than the energy required to synthesize PFOS and PFOA electrochemically.

Chapter 3 investigates the sonochemical transformation of PFOS and PFOA into their mineralization products or inorganic constituents through time-dependent product analyses and kinetic estimations. The initial rate-determining step is determined to involve pyrolytic cleavage of the ionic headgroup at the acoustically cavitating bubble-water interface. The neutral, fluorochemical product partitions to the transiently

cavitating bubble vapor where temperatures can near 4000 K. The neutral, fluorochemical intermediate is quickly transformed into CO, CO₂, and HF through a series of pyrolytic, oxidative, and reductive pathways. HF will hydrolyze to a proton and fluoride. PFOS and PFOA mineralization kinetics were determined to be similar to initial PFOS and PFOA sonochemical decomposition kinetics, thus precluding the formation of any toxic intermediates.

Chapter 4 examines the adsorption of PFOS and PFOA to acoustically cavitating bubbles. The absolute sonochemical rate dependence on the initial PFOS/PFOA concentration was fit to the Langmuir-Hinshelwood model using empirically determined rate maximums. The air-water interfacial partitioning coefficient determined from the observed sonochemical kinetics was at variance with the equilibrium partitioning coefficient determined from surface tension measurements. This lead to the conclusion that when the bubble interface is lightly populated with PFOS and PFOA, the adsorption is sonochemically mediated due to high velocity radial bubble oscillations being much faster than bulk diffusion.

Chapter 5 investigates the decomposition kinetics and products of PFOS, PFOA, and shorter-chain fluorochemicals (C_6 and C_4) by aqueous electrons. Aqueous electrons are generated by UV photolysis of iodide and are observed to react with PFOS faster than PFOA in batch reactions. The perfluoroalkylsulfonates (PFAS) are observed to have prominent chain-length effects, whereas the perfluoroalkylcarboxylates (PFAC) had no such effects. The PFAS chain length affected the extent of defluorination (e.g., the number of fluorides produced was approximately the number of tail carbons), in contrast, all of the PFACs proceeded through 1 to 2 defluorinations. As PFAS chain-length decreased, so did the initial PFAS reduction kinetics. In contrast, PFAC chain length had no effect on reduction kinetics. Gaseous PFAS and PFAC reduction products were consistent with extent of defluorination.

The chemistry of aqueous, aerosol anions is the subject of Chapters 6 to 9. This was the first project I worked on in the Hoffmann Lab and the initial objective was quite different than the now published scientific papers. Experimental kinetic isotope effects and kinetic simulations of peroxone (ozone + hydrogen peroxide) chemistry suggested that the primary branching pathway of O_3 -H₂ O_2 reaction yielded H₂ O_3 . I developed an electrospray-mass-spectrometry-based (ES-MS) technique to monitor the products of this reaction on relatively short timescales, 1 to 10 ms. The ozone-ES-MS reactor can be thought of as a gas-aerosol stopped-flow reactor. The electrospray chamber was modified such that a Teflon ozone tube was brought into the chamber and held in place by a Teflon piece attached to the nebulizer needle, which only minimally affected the MS sensitivity. Although I have stated this work in a single sentence, the modification and optimization of the ozone-ES-MS system took nearly a year and a half. At $[H_2O_2] > 100$ mM, H_2O_2 could be detected mass spectrometrically as a positive cluster on the form $(H_2O)_m(H_2O_2)_nNa^+$. Initially, we believed we had detected H_2O_3 as a reaction product; however, it was an artifact of the ozone generator. Although the initial project did not come to fruition, the developed ozone-ES-MS system has now been utilized for examination of a number of gaseous oxidant-aqueous aerosol reactions.

After a seminar in Atmospheric Chemistry II where I suggested the developed system could be utilized for research into reactions specific to the air-water interface, graduate student Jie Cheng and I completed the initial ozone-ES-MS experiments on the gaseous ozone oxidation of aqueous iodide, which yielded some very interesting results. Since then the ozone-ES-MS system has been used to study reactions of gaseous ozone with sulfite, thiosulfate, iodide, ascorbic acid, tocopherol, and various combinations of these aqueous species, as well as to study reactions of gaseous NO_2 with various anions. Results have given insight into the importance of the air-water interface to aerosol reactions with low solubility gaseous oxidants and how the air-water interface affects chemical mechanisms and kinetics as compared to bulk aqueous or gaseous chemistry. There are some questions about the applicability of the results to real situations, as the reactions take place under a large electric field (> kV/cm).

As a result of developing the ozone-ES-MS system, researching the pertinent experiments (particularly those involving ozone and iodide), and teaching others how to operate and maintain the system, I was co-author on four scientific papers, three of which are included in this thesis. The first examined anion fractionation during the electrospray of aqueous anions (Cheng J.; Vecitis, C. D.; Colussi, A. J.; Hoffmann, M. R. *J. Phys. Chem. B*, **2006**, *110*, 25598.) and is not included in this thesis. It was observed that when equimolar anions were electrosprayed, the relative fractionation, as determined by relative mass spectrometric signal intensity, was correlated to anion radius or hydration energy and followed the Hofmeister series.

The second published scientific paper, Chapter 9, investigated the iodide-mediated gaseous ozone oxidation of bromide and chloride in aqueous aerosols. Aerosolic iodide reacts at diffusion-controlled rates with gaseous ozone to yield triiodide, I_3^- , and iodate, IO_3^- . Bromide and chloride are kinetically unreactive towards ozone alone; however, in the presence of iodide, dibromoiodide (IBr₂⁻), and dichloroiodide, (ICl₂⁻), are detected as

reaction products, respectively. This suggests that iodide can mediate the gaseous ozone oxidation of aerosolic bromide and chloride, likely through the production of the promiscuous hypoiodous acid, HOI, which oxidizes most species at diffusion-controlled rates. These reactions could possibly yield gaseous species such as ICl, IBr, Br₂, and Cl₂. These species would be quickly photolyzed ($\tau_{1/2} \sim 1$ to 2 min) in the atmosphere, yielding halogen radicals that could contribute to catalytic ozone destruction cycles, which are of importance to arctic ozone depletion events during polar sunrise, and general tropospheric ozone levels.

Chapters 7 and 8 encompass reactions of aqueous aerosolic thiosulfate $(S_2O_3^{2-})$ and sulfite (SO_3^{2-}) with gaseous ozone with and without iodide. The results of both are similar in many respects. Kinetic modeling of gaseous ozone oxidation of both $S_2O_3^{2-}$ and SO_3^{2-} suggests that the reaction predominantly (> 90%) occurs at the air-water interface. In both cases, intermediates containing I-S bonds are directly detected for the first time, indicating that an iodine-containing intermediate, likely HOI, can quickly oxidize both $S_2O_3^{2-}$ and SO_3^{2-} . This result is similar to that of Br⁻ and Cl⁻, suggesting a 'universal' iodide-mediated oxidation pathway via the hypoiodous acid (HOI) intermediate. In both cases, results from competition experiments suggest that either the interfacial ozone reaction with $S_2O_3^{2-}$ and SO_3^{2-} is enhanced vs. the bulk reaction or that interfacial ozone reaction with I is reduced, with the former being more likely than the latter since the bulk aqueous kinetics underestimate the measured product intensity from $O_{3(g)} + I_{(aer)}$ experiments. Overall these experiments display the importance of the airwater interface as a reaction 'zone' for chemistry between marine aerosols and gaseous oxidants such as ozone.

The final three chapters, 9 to 11, of this thesis focus on the hybridized electrochemical system for the production of hydrogen (H₂) and simultaneous degradation of organic pollutants. I worked on this project during my last few years at Caltech in collaboration with Dr. Hyunwoong Park. My role in the project was to develop analytical techniques and procedures (realtime EI-MS for monitoring gas products and HPLC-UV for analysis of phenol and phenol derivatives), manuscript editing, and discussion of results. The water-solid (metal-cathode, metal-oxide-anode) interface is vital, since all of the observed electrochemistry will initiate at these interfaces. Electron transfer activation barriers across the water-solid interface will mediate the energy required to drive observed chemistry. Energetic losses will occur if the oxidants produced at the metal oxide surface subsequently yield lower potential homogeneous oxidants (e.g., \equiv Ti-OH· (E⁰ = 2.7 V) \rightarrow Cl₂· (E⁰ = 2.0 V)) or homogenous oxidants are quenched at the cathodic surface (e.g., Cl₂· + e \rightarrow 2 Cl⁻).

Chapter 9 serves as a brief introduction to the idea of hybridizing alternative energy production with wastewater treatment. Electrolytic hydrogen (H₂) production is less economically viable than battery storage due to energetic losses during electrolytic H₂ production and its transformation back to electrical energy. By hybridizing electrolytic H₂ production with wastewater treatment, some of these losses will be negated by cleansing the water. An electrochemical system composed of a stainless steel cathode for H₂ production and a Bi-doped TiO₂ anode for oxidant production is presented. Results show that the hybrid system has H₂ production energy efficiencies (30% to 70%) that compete with commercial electrolyzers (50% to 75%), which operate under more extreme conditions (50 mM NaCl, 6 < pH < 11, 1 atm vs. 1 M NaOH, pH > 13, 20 atm).

It is shown that the system can degrade a number of common organic pollutants such as phenols and small acids. The electrochemical system can also be driven by a photovoltaic cell. Chapter 10 elaborates on the results of Chapter 9. The effects of variations in electrochemical cell current, voltage, and power, and initial phenol concentration on the H₂ and O₂ production rates, and current and energy efficiencies was investigated. Time-dependent electrolysis measurements of phenol, phenol oxidation intermediates, pH, total organic carbon (TOC), and mineralization products (CO₂) were also made. Maximum cathodic H₂ production current efficiencies were near 60% without phenol, near 70% with phenol with NaCl as background electrolyte, and reached 95% using Na₂SO₄ as background electrolyte. Anodic current efficiencies ranged from 3% to 17% depending on specific conditions. The hybrid system was shown to be applicable for the degradation of a range of organics, and it was also observed that upon addition of organic with NaCl as an electrolyte, the cathodic current efficiency increased.

Chapter 11 further investigates the primary oxidant in the electrochemical system and how this oxidant is involved in the observed enhancement in cathodic (H₂) current efficiencies upon addition of organics. The phenol electrolytic oxidation intermediates all contain chlorine, with the extent of chlorine increasing with time, indicating a chlorine-based oxidant. The degradation kinetics of a number of phenol derivatives was determined through time-dependent measurements and were plotted against known rate constants for a number of possible oxidants, such as \cdot OH, Cl₂ \cdot , Cl \cdot , and HOCI. Only known Cl₂ \cdot second-order rate constants correlated with the observed rate constants, indicating it was the primary oxidant. When no organics are present, it is postulated that Cl₂ \cdot can act as an electron shuttle and accept electrons at the cathode, thus reducing the H_2 production current efficiency. Thus, when organics are present and consume Cl_2 , its effect as an electron shuttle is reduced and the H_2 current efficiency subsequently increases.

Through the various areas of study in this thesis, aqueous interfaces are shown to be highly relevant to the chemistry observed. In many cases, the overall rate-limiting step of a chemical reaction series involves an interfacial chemical transformation, which subsequently leads to relatively fast homogeneous chemical kinetics in the liquid or gas phase. Phase transfer limitations of reactive species or mass transfer of species to the most reactive phase is the simplest explanation for interfacial rate determining steps. However, the more difficult question to answer is how these interfacial processes differ mechanistically and kinetically from their homogeneous analogs. Therefore, the cumulative research compiled in this thesis indicates that chemical reactions at aqueous interfaces are an important aspect of many environmentally relevant processes occurring at aqueous interfaces.