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Photolysis Kinetics of Aromatic Pollutants in Liquid and Solid Environmental Condensed Phases

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Abstract

Condensed phases in the environment are often chemically complex. Reactivity can differ significantly depending on the physical state (i.e. solid or liquid) and composition. Many laboratory studies that investigate reaction kinetics in condensed phases are done under simplified conditions that do not accurately reflect the complexity found in the environment. I have measured photolysis rate constants of the aromatic pollutants toluene, ethylbenzene, xylenes (TEX) and anthracene under environmentally-relevant conditions in order to improve fate predictions. The photolysis kinetics of TEX in water, ice and at ice surfaces were investigated using environmentally-relevant wavelengths. Previously, photolysis has not been considered a viable degradation pathway for these compounds in the environment because their absorbance spectra in water does not overlap with wavelengths that reach the Earth's surface. However, I observed photolysis in ice granules, suggesting direct photolysis could be an important removal pathway for TEX in snow-covered environments.

Sodium chloride (NaCl) and organic matter (OM) are common constituents of condensed phases in the environment. However, the combined effects of salt and organic matter on anthracene photolysis rate constants have previously not been investigated. Therefore, I measured anthracene photolysis rate constants in water, octanol, and phase-separated aqueous-organic mixtures containing varying concentrations of sodium chloride. In aqueous-organic mixtures, anthracene photolysis rate constants were largely explained by a salting-out effect. However, these results are complicated by turbulence, as evidenced by different kinetics observed in stirred and stagnant mixtures. My results suggest that anthracene photolysis kinetics in the environment may not be well described by simple matrices.

Photolysis Kinetics of Aromatic Pollutants in Liquid and Solid Environmental Condensed Phases

by

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Dissertation
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Chapter One:

Introduction

1.1 Aromatic Pollutants in the Environment

1.1.1 Production and Emission

Aromatic pollutants are common atmospheric species. Some aromatic compounds are produced through biogenic processes, but many, such as benzene, toluene, ethylbenzene, xylenes (BTEX) and polycyclic aromatic hydrocarbons (PAHs), can be produced through anthropogenic processes. Such processes include fossil fuel extraction, combustion, production of consumer goods, landfills, and metal and steel processing.[1–5] According to the U.S Environmental Protection Agency (USEPA), approximately 22,000 metric tons of BTEX and 30,000 metric tons of PAHs were emitted by anthropogenic sources in 2015.[6–9] For BTEX, the most dominant sources are automobiles and industrial practices. Toluene, ethylbenzene and xylenes are common industrial solvents and cleaners. Industrial practices make up 5-10% of all BTEX emissions.[5] The rest primarily come from automobiles. In fact, 68% of the national benzene inventory comes from on-and-off road vehicles alone.[10] Conventional gasoline typically consists of 20-30% BTEX.[11,12] Automobiles are also a major source of PAHs, accounting for about 20% of total annual PAH emissions globally.[1,7] Consequently, BTEX and PAHs are ubiquitous in the environment and can even be found in extremely remote areas such as the Arctic.

1.1.2 Human and Environmental Health Effects of BTEX and PAHs

The Clean Water Act of 1977 defined 16 PAHs as priority pollutants due to their toxicity and genotoxicity.[13] Many PAHs are carcinogenic and their carcinogenicity tends to increase as their molecular weight increases.[2] Lower molecular weight PAHs tend to exist in significantly higher concentrations in the gas phase whereas higher molecular weight PAHs tend to be bound to particulate matter in the air.[4,14–16] Human exposure to PAHs primarily occurs through inhalation and ingestion.[17,18] Exposure through inhalation is of particular concern because when inhaled, PAHs are capable of entering the blood stream more easily.[19,20] Upon exposure, PAHs are metabolized into PAH-DNA adducts which can interfere with metabolic processes and cause mutations that ultimately lead to cancer.[2,18,21,22] PAH metabolites may also cause oxidative damage to macromolecules in the body by forming reactive oxygen species.[23] Due to their lipophilicity, PAHs are also easily absorbed by the gastrointestinal tract when ingested and are distributed to fat cells which can result in bioaccumulation in the body.[19] PAHs can undergo chemistry that results in products that are often more toxic than the parent compound.[2,24,25] For example, a recent study that evaluated the photomutagenicity of 16 PAHs determined at least 6 PAHs to be strongly photomutagenic, meaning they became significantly more mutagenic when exposed to UV light, and 5 PAHs to be weakly photomutagenic.[26] When exposed to PAHs, humans are not only likely exposed to a mixture of different PAHs but these potentially more toxic products as well.

Benzene, toluene, ethylbenzene and xylenes are also on the list of priority pollutants identified by the Clean Water Act.[13] Benzene is classified as a category A carcinogen by the USEPA and its carcinogenicity, and particularly its link to leukemia, has been well studied.[10,27,28] Toluene, ethylbenzene and xylenes are classified as potential carcinogens and acute exposure to these compounds has been linked to central nervous system, pulmonary and renal toxicity.[29] For example, prolonged exposure to toluene vapor has been shown to cause peripheral nerve damage.[19,29] Long term exposure to ethylbenzene has resulted in kidney and liver tumors in rats as well as irreversible hearing damage.[19,29,30] Xylenes have also been suggested to cause liver and kidney damage in humans exposed to high concentrations.[19,29] Recently, it has been suggested that BTEX may be associated with reproductive health issues such as sperm abnormalities and reduced fetal growth.[5,31] BTEX has also been suggested to have endocrine disrupting properties.[5] Other health effects of BTEX include nausea, dizziness, eye, ear and throat irritation, muscle weakness and loss of balance or coordination.[19,29] Due to their relatively high vapor pressures, humans are primarily exposed to BTEX through inhalation.[32] Once inhaled, BTEX is readily absorbed by the lungs and distributed to fat cells or metabolized to form oxidized products. Similar to PAHs, BTEX can also react in the environment to form products that are more toxic than the compounds themselves.[24]

PAHs and BTEX do not only pose human health risks but ecological health risks as well. PAHs and BTEX have been implicated in altering bacteria diversity which can negatively affect plant health and growth.[33] Some species of plants have exhibited adverse reactions when exposed to elevated concentrations of PAHs. For example, PAHs have been suggested to be associated with aging and chlorophyll degradation in spruce trees.[34] PAHs and BTEX have also been observed to impact aquatic life. Zooplackton abundance was reported to decrease upon exposure to PAHs and PAHs have also been suggested to cause coral bleaching.[35,36] Furthermore, BTEX has been shown to be toxic to certain algae species; it was reported to change morphology and decrease chlorophyll in *Euglena gracilis* algae.[37]

1.2 Fate of PAHs and BTEX in the Environment

1.2.1 Physical Fate/Partitioning/Transport

Both PAHs and BTEX are non-polar, hydrophobic molecules. Octanol-water partition coefficients (Log K_{ow}) for PAHs range from 3 to 7 while BTEX partition coefficients range from 2 to 3.[8] Consequently, both PAHs and BTEX prefer to associate with organic phases such as organic matter in surface waters or aerosols. Detectable amounts of both BTEX and PAHs have been observed in the aqueous phase as evidenced by several field studies which have detected PAHs and BTEX in various environmental waters.[38–41] Henry's law constants (Log K_{aw}) for

BTEX range from ~ -0.5 to -0.7 whereas constants for some PAHs span a much wider range of ~ -1 to -4.[8,42] These values indicate favorable partitioning to water over air for both BTEX and PAHs but predict greater potential for PAHs to partition to water from air than BTEX.

PAH and BTEX partitioning in the environment cannot be fully described from these values alone. This is because condensed phases in the environment often contain a variety of species which can affect partitioning. For many environmentally relevant matrices, experimental partition coefficients are not available.[8] Thus, these values are often estimated using thermodynamic calculations.[8,43] The singular effects inorganic salts have on the partitioning of organics has been well studied.[8,44–46] Generally, partition coefficients between the aqueous phase and non-aqueous phase increase with increasing amount of salt for large, non-polar organics.[8] This phenomenon is commonly referred to as salting out. The magnitude of this effect depends on the compound and types of ions present.[8,44] However, environmental condensed phases will usually contain a mixture of salts. Very few studies have investigated partition coefficients of organics in salt mixtures. Specifically, it is largely unknown whether the effects of multiple salts are additive.[47] The salting out of naphthalene and toluene were found to increase when in the presence of a mixture of salts.[47,48] But, the salting out of benzene was reported to decrease.[49] These findings illustrate the difficulties in predicting partition coefficients for organics in environmental condensed phases.

There are numerous routes PAHs and BTEX may take to enter natural waters. Some of those routes include sewage runoff, wet/dry deposition, and leeching from soils.[2,50–52] Both PAHs and BTEX are commonly adsorbed onto aerosols which can be washed out through precipitation and transferred to surface waters.[11,53,54] Detectable amounts of BTEX (1 to 30 µg/L) have been observed in surface waters.[55,56] Concentrations of low molecular weight PAHs (≤ 3 aromatic rings) in surface waters have been found up to hundreds of ng/L and higher molecular weight PAHs have been found up to ~ 30-50 ng/L.[2,57–59] However, even higher concentrations have been observed in areas with significant fossil fuel production. Extremely high gas-phase mixing ratios (> 40 ppbv) for BTEX have been observed in a region with significant hydraulic fracturing activity; average ambient mixing ratios range from 1-10 ppbv.[60,61] Total benzene and toluene emissions from this region were estimated to be 1-2 kg yr^{-1}.[61] Furthermore, elevated BTEX emissions/concentrations were observed in "produced water ponds" from the same region.[62] "Produced water" is water that is coextracted along with natural gas or oil and is often stored in open ponds so that it can be removed via evaporation.[62] These studies suggest hydraulic fracturing operations may be significant point sources for BTEX. Oil, gas, petroleum, solvent or fracking fluid spills are also very important transmission routes for PAHs and BTEX as a single event is capable of releasing extremely high concentrations of these compounds into the environment.[63,64]

PAHs and BTEX can also be adsorbed onto ice and snow particles.[65,66] This leads to the detection of both classes of compounds found in snowpacks or entrapped in ice.[65–68] Multiple studies have detected concentrations of BTEX on the order of hundreds of µg/L in both rural and semirural snow packs.[67,69,70] Concentrations of PAHs have been reported to range from 100 ng/L to several µg/L in urban snow packs.[71–73] In the arctic, PAH concentrations of up to 100 ng/L have been reported.[74,75] Thus, snow and ice melt are another route PAHs and BTEX can take to enter bodies of water. In fact, multiple studies have observed that organic contaminants in melting snowpacks will be transported to surrounding environments in short, concentrated pulses.[76–78] This transfer is even more rapid in urban areas mostly covered with impervious surfaces.[76]

PAHs and BTEX can be found in remote regions of the world due to long range atmospheric transport. Long range atmospheric transport is typically facilitated by aerosols or other particles. Gas phase transport is possible at high altitudes but, at lower altitudes gaseous phase PAHs and BTEX tend to react quickly with OH radicals, and condensed phase or sorbed lifetimes are typically much longer than gaseous lifetimes.[24,79,80] Consequently, both groups of compounds are regulated as part of the United Nations Economic Commission for Europe Convention on Long Range Transboundary Air Pollution.[81] When sorbed to particles, PAHs and BTEX may undergo chemical reactions that will affect their lifetimes. Thus, understanding their chemical fate in these systems is important to understanding their long-range transport potential and overall fate in the environment.

1.2.2 Photochemical Fate

1.2.2.1 Direct Photolysis

Direct photolysis refers to a compound undergoing a transformation after absorbing light.[8] Direct photolysis is an important sink for PAHs in the environment but is not considered a major sink for BTEX. This is because absorption spectra of BTEX do not overlap with the wavelengths of sunlight that reach the Earth's surface.[82] BTEX absorb strongly between 240-260 nm in condensed phases and < 200 nm in the gas phase.[8,24,82] However, solar wavelengths shorter than ~290 nm are typically filtered out by stratospheric ozone and therefore do not reach the Earth's surface.[24] Thus, BTEX was not believed to be able to undergo direct photolysis in the environment. However, recent research has suggested that benzene is able to undergo direct photolysis when on ice surfaces.[82] This is attributed to benzene exhibiting a red-shift in its absorbance spectrum when on the ice surface.[82] The direct photolysis of BTEX on ice surfaces will be discussed in greater detail in Chapter 3.

PAHs are able to undergo direct photolysis in both the gas phase and condensed phase. Typically, photolysis occurs more rapidly in condensed phases than the gas phase.[2,24] The proposed mechanisms for PAH photolysis in aqueous solution include direct ionization or reaction with molecular oxygen.[83–85] Direct ionization has been reported to not be an important pathway for PAHs at the Earth’s surface due to photons with wavelengths < 290 nm required for this pathway to occur.[83] Therefore, molecular oxygen likely plays an important role in the degradation of some PAHs, though its exact mechanist role is unknown. Currently the two proposed mechanisms involving molecular oxygen are reaction of triplet state PAH (Scheme 1) or electron transfer (Scheme 2).[83,85] It is important to note that not all PAHs will react via the same photolysis mechanism. For example, the PAHs pyrene and benzo[a]pyrene react via a singlet state whereas anthracene reacts primarily through the triplet state.[84] Furthermore, some PAH photolysis kinetics do not show a dependence on O_2, suggesting an alternative mechanism.[83]

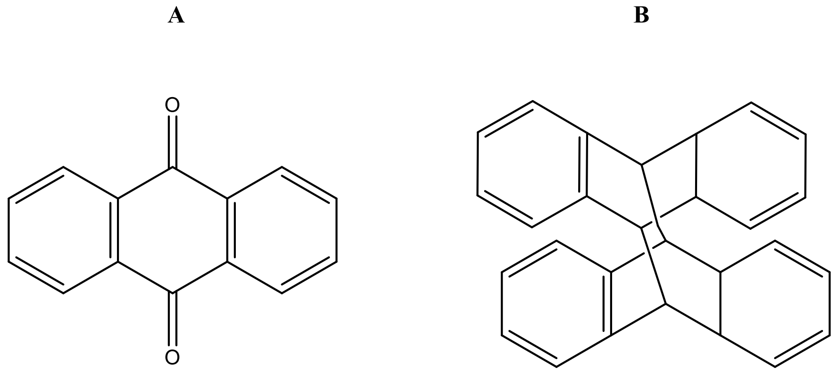
Scheme 1: Proposed reaction of triplet state PAH with oxygen (adapted from Reference 83).

$$\mathrm{PAH} \overset{h\upsilon}{\rightarrow} {}^{1}\mathrm{PAH}^{*} \rightarrow {}^{3}\mathrm{PAH}^{*} + {}^{3}\mathrm{O}_2 \rightarrow [\,{}^{3}\mathrm{PAH}^{*} - {}^{3}\mathrm{O}_2] \rightarrow \mathrm{Product}$$

Scheme 2: Proposed reaction of singlet state PAH with oxygen (adapted from Reference 83).

$$\mathrm{PAH} \overset{h\upsilon}{\rightarrow} {}^{1}\mathrm{PAH}^{*} + {}^{3}\mathrm{O}_2 \xrightarrow{-e^{-}} \mathrm{PAH}^{\cdot +} + \mathrm{O}_2^{-} + \mathrm{H}_2\mathrm{O} \xrightarrow{-\mathrm{H}^{+}} \mathrm{Product}$$

The local environment can greatly affect reaction kinetics. Solvent polarity has been shown to have a significant effect on PAH photolysis rate constants, with photolysis rate constants increasing as solvent polarity increases.[86–89] Different photolysis products in organic solvents than aqueous solvents have also been reported, suggesting that the reaction mechanisms may differ between condensed phases.[24,90,91] The products formed from the direct photolysis of PAHs include aldehydes, quinones and other oxygenated products.[2,8,25] For example, the products of anthracene photolysis are primarily oxidized derivatives of anthracene.[8,24,92] The main product of anthracene photolysis in both polar and apolar solvents is 9,10-anthraquinone (Figure 1.1).[24,92] However, photodimer products that have not been found in polar solvents have been found in apolar solvents.[92] If the apolar solvent is purged of oxygen then the 9,10-photodimer will become the major product formed (Figure 1.1).[92] It is currently not well understood why these differences in products are observed. It has been suggested that the solvent's hydrogen donor potential may play a role, but this has not been thoroughly investigated.[90,92]



9,10-anthraquinone

9,10-photodimer

Figure 1.1: Photolysis products for anthracene in aqueous solution (A) and purged, non-polar solution (B).

Different photolysis rates have also been reported for BTEX and PAHs on several atmospheric surfaces compared to in aqueous solution, suggesting a different reaction mechanism there.[82,85,87,93,94] The photolysis of PAHs on the surface of black carbon has been reported to almost negligible, with reported half-lives greater than 1,000 hours.[95] Conversely, some PAHs have been reported to photolyze more quickly on silica and alumina surfaces than in aqueous solution.[95–99] The photolysis of PAHs and BTEX on ice surfaces will be discussed in more detail in section 1.3 and Chapter 3. However, it is important to note that some PAHs and benzene have been reported to photolyze more quickly on ice surfaces as well.[93,94,100–104] Thus, it is evident that photolysis kinetics will depend on the physical and chemical properties of the substrate. Photolysis products will also depend on the properties of the substrate as evidence by studies which report different photolysis products for aromatic pollutants on surfaces than in solution.[87,95,105] Products not observed from pyrene photolysis in aqueous solution were observed on silica surfaces.[91,106] In another study, different photochemical products on ice than in aqueous solution were observed for chlorobenzenes and chlorophenols.[105] One reason proposed as to why different products are observed is that there is greater aggregation of these compounds at the surface than in aqueous solution.[95,105] However, competing mechanisms have been proposed for the same PAHs on silica surfaces and mechanisms on ice surfaces have not been extensively studied.[96,106,107]

1.2.2.2 Indirect Photolysis

Indirect photolysis can be defined as a compound undergoing a transformation as the result of light absorption by another chemical in the system.[8] With respect to the fate of organic contaminants, the most important indirect photolytic reactions are photosensitization and generation of highly reactive species. Photosensitization is an energy, electron or hydrogen transfer reaction that occurs as a result of light absorption by a chemical other than the analyte.[8] One of the most environmentally relevant photosensitized reactions is reaction with triplet state chromophoric dissolved organic matter (^{3}CDOM*).[108] In these reactions, CDOM is first excited to a short lived singlet state (^{1}CDOM*) and then is converted to a longer lived triplet state

($^3CDOM^*$).[8] This excited triplet state molecule can then go on to react with PAHs, BTEX or other organic pollutants directly, or can produce reactive species including hydroxyl radicals (OH), singlet oxygen ($^1O_2$), hydrogen peroxide, ozone, carbonate, sulfate and nitrite radicals, and halogen radicals (Figure 1.2).[8,109–112] All of these compounds can potentially react with PAHs or BTEX as well, often at faster rates than possible via direct photolysis.[8]

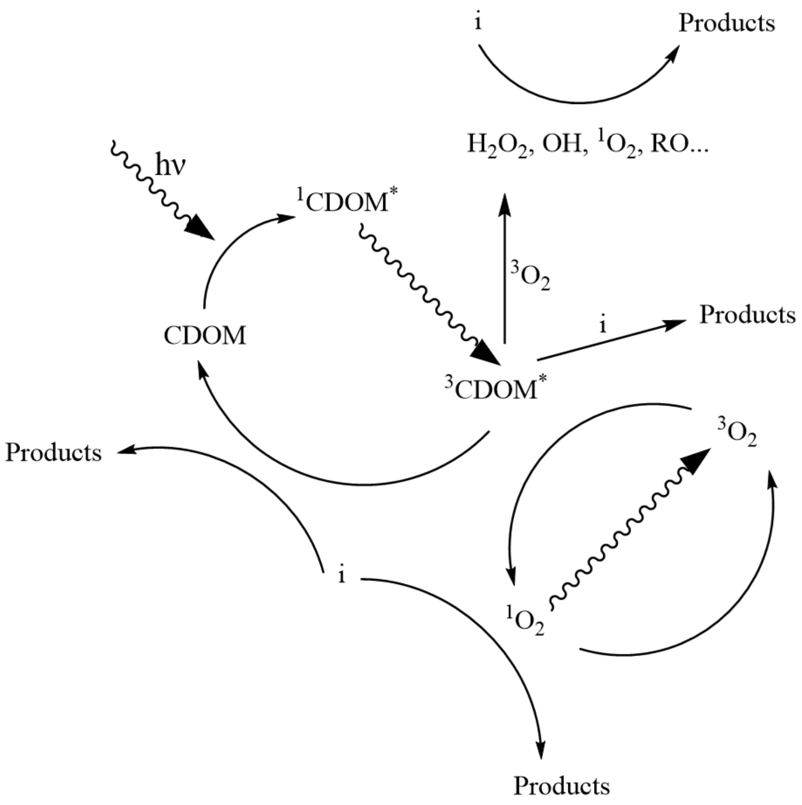


Figure 1.2: Possible pathways for indirect photolysis of organic pollutant *i* with CDOM (adapted from Reference 8).

1.3 Photolysis of PAHs and BTEX in Condensed Phases

1.3.1 Overview

Understanding chemical complexity and reactivity in condensed phases within the environment has been a major focus of environmental chemistry research. Condensed phases include surface waters, aerosols, snow and ice to name a few. They are important chemical reactors with distinct chemical and physical properties. Consequently, reaction kinetics can vary significantly between different environments such as surface waters and snow, for example.[82,85,102,105,113–123]

1.3.2 Water

1.3.2.1 Overview

Surface waters are important sinks for BTEX and PAHs. Comparatively, the aqueous chemistry of these compounds has been more studied than their snow and ice chemistry. However, much still remains to be known about the subject such as how different components of environmental waters will affect their kinetics. Natural waters contain many different components which can affect reaction kinetics and mechanisms. Some of these components include halides, organic matter, reactive oxygen species, bacteria and metals. Since photolysis is believed to be one of the most important reaction pathways, much of the discussion has been based on their photochemical fate. However, many studies on the subject have been carried out under simplified conditions that do not accurately reflect the complexity of the natural environment. Thus, much remains unknown about the photochemical fate of PAHs and BTEX in natural waters.

1.3.2.2 Effects of Halides

Halides such as chloride, bromide and iodide are common in surface waters. They are also commonly found in atmospheric particles such as cloud droplets and aerosols.[124,125] Chloride concentrations in seawaters average around 0.5 M. Bromide and iodide concentrations are generally much lower than chloride, with average bromide and iodide seawater concentrations on the order of micromolar and nanomolar, respectively.[126,127] In freshwater, lower concentrations are observed; typically freshwater chloride concentrations range from micromolar to millimolar.[128] However, significantly high (> 6 M) chloride concentrations can be present in atmospheric particles.[24,124]

Halides have been shown to have variable effects on the photolysis kinetics of some aromatic species. For some compounds, the rate constants have increased, some have decreased and some have exhibited no change.[115,116,129–134] For example, work from our group showed that pyrene photolysis was unaffected by the presence of halides but anthracene photolysis rates increased.[134] The mechanisms by which halides affect the photolysis of aromatic organics are not well understood. Proposed mechanisms include the production of hydroxyl radicals, enhanced intersystem crossing leading to enhanced singlet oxygen production, and the formation of halogen radicals.[8,133,135] We determined that anthracene photolysis rates increased in the presence of halides due to enhanced singlet oxygen production.[134]

1.3.2.3 Effects of Organic Matter

High organic matter concentrations can be present in natural waters. Organic matter is also often associated with aerosols, fog and rain droplets. The presence of OM can greatly affect PAH photolysis kinetics and mechanisms. However, the effect organic matter has on PAH photolysis kinetics will vary depending on the viscosity, polarity and type of organic matter. For example, McDow et. al. examined the photolysis rate of benz[a]anthracene in 10 different classes of organic solvents and observed significantly different rates.[136] A number of studies have investigated the effects of viscosity and polarity on PAH photolysis. The presence of OM in some cases can result in a highly viscous mixtures or phases. For example, OM in secondary organic aerosols can be so highly viscous that some researchers describe it as an amorphous solid rather than a liquid.[137,138] The photochemical reaction rates of some atmospheric species have been reported to decrease with increasing viscosity.[137–139] This decrease is largely attributed to the viscous solvent slowing or hindering molecular motion.[138] However, when in the presence of a photosensitizer or radical precursor, the photodegradation rates of some nitro-PAHs were reported to increase when in highly viscous organic solvents.[139] This effect was enhanced when the viscous solvent was polar as opposed to non-polar.[139,140] In aqueous solution, benz[a]anthracene quantum yields were observed to decrease with increasing acetonitrile fraction.[92] Several other studies have reported that some PAHs, including anthracene, photolyze more slowly in organic solvents than in aqueous solution.[86–89] Work from our group suggests that this is due to polarity effects.[86]

Organic matter is often classified as chromophoric (absorbs sunlight), or non-chromophoric (does not absorb sunlight). Each type has unique effects on photolysis kinetics. Non-chromophoric organic matter can potentially suppress photolysis rates by affecting partitioning and polarity as described above. Chromophoric organic matter (COM) can enhance photolysis kinetics by acting as a photosensitizer or producing reactive oxygen species.[94,141–143] Chromophoric organic matter can be further classified into chromophoric dissolved organic matter (CDOM) or humic like substances (HULIS).[144] Traditionally, HULIS refers to chromophoric organic matter that is found in aerosols or cloud droplets.[145] CDOM refers to chromophoric organic matter found in surface waters.[145] HULIS generally originates from terrestrial sources whereas CDOM originates from aquatic sources. HULIS can be further divided into three categories: fulvic acids, humic acids and humin.[144–146] Fulvic acids are soluble in water at all pH levels whereas humic acids are not soluble in water with $pH < 2$.[145] Humin is not soluble in water at any pH.[145] These compounds have high molecular weights and contain a variety of functional groups including (but not limited to): carboxylic acids, ketones, aldehydes, quinones, phenols and unsaturated hydrocarbons.[144,146] Their exact structures are not known but their effects on the photochemical fate of aromatic pollutants in natural waters has been studied.[147–150] These studies determined that fulvic acid and humic acid could have differing effects on photolysis kinetics. For example, phenol was reported to degrade more quickly in aqueous solutions containing humic acid than solutions containing fulvic acid.[147] Furthermore, the effects are not the same for all compounds. Anthracene's photolysis rate constant was observed to increase in the presence of fulvic acid.[149] But, in the same study, the photolysis rate constants for 11 other PAHs were observed to be largely unchanged.[149]

In some cases, organic matter can exist as a distinct phase such as sea surface microlayers or organic films coating the surface of inorganic or aqueous aerosols.[89,151–154] Even a monolayer of immiscible OM on the surface can affect reactivity and partitioning. The reaction of anthracene with ozone was observed to be faster at air-water interfaces covered with a monolayer of 1-octanol than at pure air-water interfaces.[155,156] Similarly, other studies have reported enhanced ozonation kinetics of aromatics at air-water interfaces containing organics such as chlorophyll.[89,157,158] It is suggested that these faster reaction kinetics are due to enhanced uptake of ozone to the air-water interface. Several studies have observed an increase in uptake of ozone to the air-water interface when coated with a thin film of organic matter.[155,157,158] Enhanced uptake of some PAHs to an air-water interface covered in a single monolayer of 1-octanol (compared to a pure water surface) has been observed as well.[159] Due to their hydrophobicity, aromatic organic pollutants such as PAHs and BTEX are expected to preferentially partition to the organic phase in phase-separated aqueous-organic mixtures. Previous work in our group reports slower anthracene photolysis kinetics in phase-separated aqueous-octanol mixtures than in aqueous solution.[86] Therefore, the presence of even small amounts of organic matter in natural waters can significantly alter pollutant fate.

1.3.2.4 Effects of Reactive Oxygen Species, Bacteria and Metals

Species other than halides and organic matter, such as reactive oxygen species, bacteria and metals can affect pollutant fate in surface waters as well. The effects these species have on PAH and BTEX fate in condensed phases will not be discussed in detail in later chapters. However, they are involved in many important processes that determine organic pollutant fate. Therefore, they are worth briefly mentioning. Reactive oxygen species include singlet oxygen, hydrogen peroxide, superoxide, and hydroxyl radicals (OH). Numerous studies have reported increased degradation rates for a variety of aromatic pollutants when these species are present.[8,24,141,160,161] Hydroxyl radicals are primarily formed through photolysis from precursors such as nitrate, nitrite, hydrogen peroxide, and CDOM.[8,24] They react very quickly with aromatic organics in aqueous phases. Therefore, reactions involving OH are of particular interest to environmental chemistry. Hydroxyl radicals are also formed through Fenton chemistry. The Fenton reaction is the reaction of Fe(II) with hydrogen peroxide to produce Fe(III) and OH (Scheme 3, Reaction 1).[8] This reaction is catalytic and will produce Fe(II) again through reduction of Fe(III) by hydrogen peroxide (Scheme 3, Reaction 2).[8] Fenton chemistry occurs even in the absence of sunlight and is one of the most important sources of OH in waters during the night.[162,163] However, the rate of the reaction is very slow without sunlight. Recent work from our group has shown that the rate of this reaction in the dark can be increased by up to a factor of 6 when in the presence of *Shewanella oneidensis*, a species of iron reducing bacterial found in natural waters.[163] In the same study, it was also demonstrated that this chemistry can result in rapid degradation of anthracene in the dark.[163] This is not the first study to report bacteria-assisted degradation of organic pollutants; other species of bacteria can directly degrade organics as well.[164,165] This illustrates the importance reactive oxygen species, metals and bacteria can have on aromatic pollutant fate in natural waters.

Scheme 3: Dark Fenton Reaction (adapted from Reference 163).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH^{-} \qquad (1)$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^{\bullet}/O_2^{\bullet-} + H^{+} \qquad (2)$$

1.3.3 Snow and Ice

1.3.3.1 History of Snow Photochemistry

Snow and ice chemistry remains poorly understood. For many years, snow and ice were believed to only act as physical sinks for atmospheric species and not play a significant role in chemistry. It was not until the 1980s, when it was discovered that the destruction of ozone in the atmospheric boundary-layer in the arctic could only be explained through photochemical reactions taking place in the snow pack and on the surfaces of aerosols, that ice and snow chemistry began to receive considerable attention.[166,167] Following this discovery, numerous field campaigns and laboratory studies were conducted which largely focused on snow and ice chemistry.[166,168–174] These studies yielded important observations about snow and ice chemistry's impact on the composition of the atmospheric boundary-layer. The atmospheric boundary-layer is the layer of atmosphere just above the Earth's surface. It is the layer most strongly influenced by the surface. The thickness of this layer will vary greatly depending on the temperature; it can range from several km during the warmer daytime to less than 1 km during the night (Figure 1.3).[175] A similar phenomenon is observed between hot climates and cold climates; more shallow boundary layers are observed in arctic regions than hot, arid regions.[175] Temperature is also one of the factors which determines the extent of mixing in this layer. In warmer climates, significant mixing can occur which aids in the dispersion and transportation of pollutants or other species emitted from the surface to other parts of the atmosphere.[175] However, in cold, snow covered regions, little vertical mixing occurs, and the boundary layer is often very stable.[166] Consequently, species emitted from the snowpack are confined to the atmospheric boundary-layer which can significantly affect the atmospheric chemistry observed there.[166]

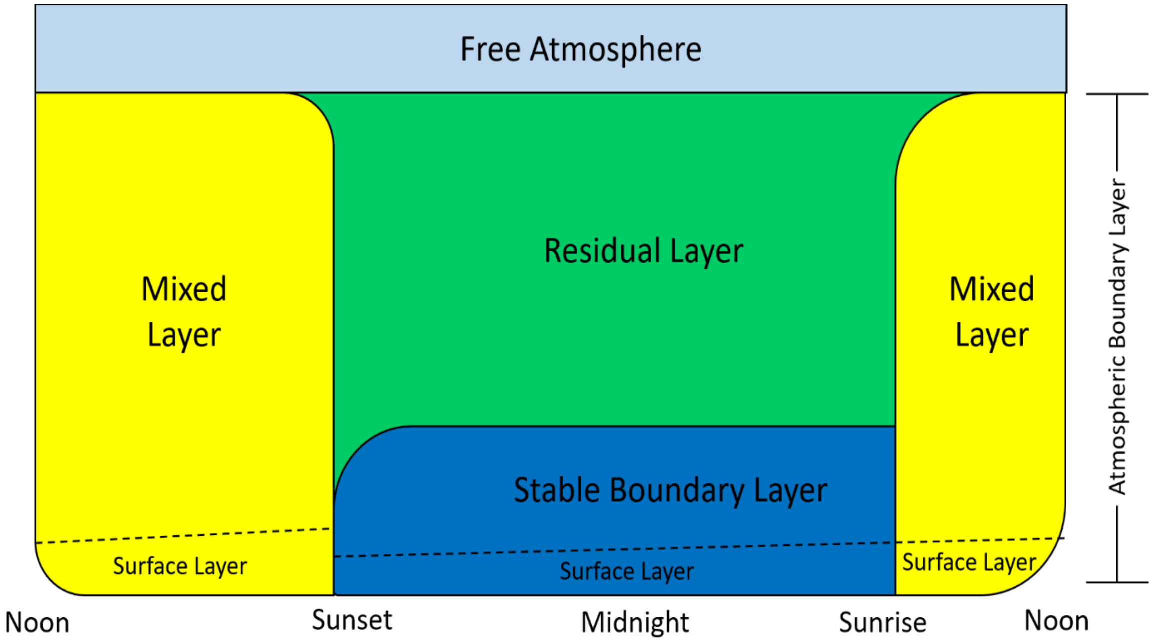


Figure 1.3: Illustration of the daily cycle of the atmospheric boundary-layer (adapted from Reference 175).

In 2000, flux measurements taken in Summit, Greenland provided evidence that sunlit snowpacks are able to emit NO_x, which explained the daily variation of NO_x observed in the polar springs and summers.[170] In another study, it was revealed that atmospheric OH concentrations in the south pole were 10 times higher than predicted by gas-phase models, suggesting that snowpack chemistry played a significant role in the production of OH.[173] Concentrations of many other atmospheric compounds including but not limited to formaldehyde, acetaldehyde, acetone, nitrous acid (HONO), and peroxy radicals ($HO_2^\cdot$) were much higher above the snowpack than predicted by models (Table 1.1).[113,169,174] All of these compounds have significant influence on the atmospheric lifetimes of pollutants and the oxidizing capacity of the boundary layer.

Table 1.1: Measured concentrations of gaseous species in April 2000 at Alert, Canada compared with values predicted by gas-phase chemistry models (adapted from Reference 166).

Species	Value measured over snow	Value predicted based on gas-phase chemistry
HCHO	200 pptv	70 pptv
CH_3CHO	80 pptv	40 pptv
NO_X	25 pptv	1 pptv
HONO	20 pptv	1 pptv
OH	0.03 pptv	0.003 pptv
HO_2	3.7 ppt	0.9 ppt
O_3	0.07 ppb	30-34 ppbv
Hg^0	0.02 pptv	0.17 pptv

The underlying chemistry and mechanisms associated with many of the observations described above are still not well understood to this day. However, since these observations were first made, there have been considerable advances in our understanding of snow and ice chemistry. Perhaps the most influential discovery was the role of snow and ice chemistry in the catalytic destruction of ozone. It is now recognized that the ozone depletion events observed during springtime in the arctic (which cause the large discrepancy between the predicted and measured ozone levels reported in Table 1.1) are due to halogen activation.[24,115,166,169,176–179] Halogen activation refers to when relatively inert halide salt ions are converted into reactive halogen species.[24] Concerning tropospheric ozone depletion events, bromide ions at ice surfaces are converted to Br_2 according to Scheme 4.[176,180] This is then released to the gas phase where it photolyzes to form reactive bromine atoms.[176] The reactive bromine atoms can then go on to react with ozone to produce BrO, which can then be used to regenerate HOBr (Scheme 4).[176,180] Thus, tropospheric ozone is catalytically destroyed through this series of reactions. This discovery helped explain the ozone hole observed in the Antarctic about a decade earlier.[24,176,181] It is now widely accepted that stratospheric ozone destruction occurs through chlorine activation taking place on the ice surfaces which make up polar stratospheric clouds.[24,107,144,166,181–183] Together, these studies helped establish the snowpack as a complex chemical reactor as well as the field of atmospheric ice chemistry.

Scheme 4: Bromine activation and destruction of ozone (adapted from Reference 180)

$$\mathrm{HOBr + Br^- + H^+ \rightarrow H_2O + Br_2} \quad (1)$$

$$\mathrm{Br_2 \xrightarrow{h\nu} 2Br} \quad (2)$$

$$\mathrm{Br + O_3 \rightarrow BrO + O_2} \quad (3)$$

$$\mathrm{BrO + HO_2 \rightarrow HOBr + O_2} \quad (4)$$

1.3.3.2 Properties of Ice and Ice Surfaces

Much of the lack of understanding of snow and ice chemistry stems from a lack of understanding of the chemical and physical properties of ice and ice surfaces. Reactions in ice can take place in pockets and veins of liquid water within the ice or on the ice surface.[184] In bulk ice, solutes are believed to primarily exist in the pockets and veins of water.[184–186] Therefore, reactivity in bulk ice has been reported to be similar to that in water.[93,187,117] During the formation of ice, solutes are excluded from the ice matrix during freezing, resulting in higher solute concentrations within these pockets and veins or at the surface.[186,188] In some cases, this phenomenon can result in unique reactivity. For example, the enhanced reactivity of bromide with ozone at the air-ice interface has been attributed to freeze exclusion.[189] Increased reactions rates were observed after freezing for some organics, such as p-nitroanisole (PNA) and pyridine, as well.[102] However, freeze exclusion does not completely explain the reactivity observed at ice surfaces. Many compounds that have been deposited onto ice from the gas phase, and therefore did not undergo freeze exclusion, have been observed to have different reactivity.[103] These findings suggest there are other factors which may influence reactivity at ice surfaces.

The ice surface consists of a disordered layer of water molecules referred to as the quasi-liquid layer (QLL).[184,185] The existence of this disordered layer is not unique to ice; other solids such as metals and colloids also contain a disordered layer at their surface as dictated by thermodynamics.[188] Many studies have attempted to elucidate the exact structure of the QLL but its structure and physical properties are still not completely clear. For example, the temperature dependence of the thickness is not well understood; different dependencies have been observed across multiple experiments.[188] Other experiments have investigated properties such as its density and temperature of formation, all of which have produced conflicting results; the QLL was observed to begin formation at temperatures ranging from 113 to 259 K.[190–192] These varying results illustrate that very little is known about the physical properties of the QLL.

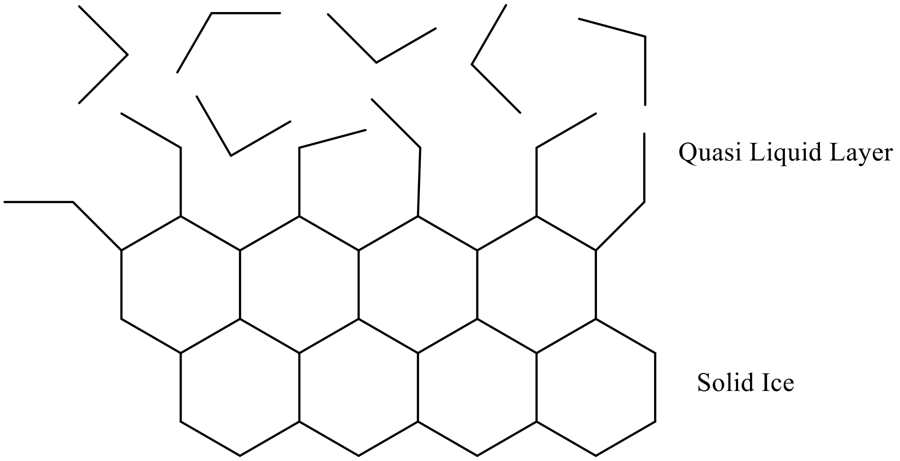


Figure 1.4: Sketch of a cross section of ice near the air-ice interface (hydrogen and oxygen atoms not shown for clarity).

Some researchers have treated the QLL to be like liquid water for the purpose of predicting reaction kinetics. Some atmospheric models treat ice as an inert solid covered by a layer of liquid water and treat all reactions as taking place in this layer. Thus, they assume that reactions which take place on ice surfaces are similar to those in water and some models utilize rate constants measured in aqueous solution to describe kinetics at ice surfaces.[193,194] There are a number of reasons why this assumption may not be accurate. First, the ice surface is likely not completely coated by liquid.[195] Work from our group has shown using Raman microscopy that even ice with high ionic strength (containing up to 0.6 M NaCl) is not completely wetted; the brine formed separate domains or channels on the surface.[196] This suggests that the assumptions described above may not even accurately describe ice containing high amounts of solutes. Secondly, the idea that impurities only exist in this liquid layer is not valid. Rather, impurities in ice can be embedded into the crystal lattice, adsorbed onto the surface or exist in pockets and veins of liquid within the ice.[184,186,195] As eluded to previously, the reactivity of impurities in ice will vary depending on their location within the ice.[184,186,195] Therefore, the assumption that all impurities reside in a liquid layer at the surface may not accurately describe the reactivity occurring. Thirdly, the assumption that light absorbing impurities are contained only in this liquid layer will likely result in inaccurate estimations of the actinic flux in snow.[195] This is because light absorbing impurities will likely behave differently depending on their location within the snow or ice.[195] Finally, there is now an emerging, large body of evidence that suggests the QLL is different than water. Some notable differences include: the electrical conductivity is 6 times greater than that of water,[197] its viscosity is significantly greater than supercooled water,[198] and the hydrogen bonding network present there is different from that of liquid and solid water.[100] Furthermore, unlike liquid water, it is expected that the QLL properties will change across its depth.[188] Consequently, reactivity at ice surfaces has been observed to differ significantly from that in liquid water.[66,82,85,93,94,104,113,115,186,188,199] Thus, the assumption that kinetics at the air-ice interface can be described using aqueous kinetics is not well supported by evidence.[195]

1.3.3.3 Photolysis of PAHs and BTEX in Snow and Ice

Recently, considerable attention has been given to understanding the fate of organic pollutants, such as PAHs and BTEX, in snow and ice. One reason for this is because, as described previously, PAHs and BTEX are capable of long-range atmospheric transport and can be found in even highly remote regions such as the arctic. Seasonal variations in the snowpack can cause these compounds to contaminate surrounding environments, often in highly concentrated pulses.[66,76–78]

Some aromatic organic pollutants, such as some PAHs and benzene, have been observed to photolyze more quickly at ice surfaces than in liquid water.[82,85,93,94,187,103,104,113] This rate enhancement is hypothesized to be due to unfavorable interactions at the ice surface resulting in self-association.[82,85,116,200] Molecular dynamic simulations suggest that aromatic compounds will self-associate when on ice surfaces.[200] In some instances, this self-association has resulted in a red shift in the absorption spectra. For example, as described above, benzene is unable to absorb sunlight in water but when on the ice surface, it exhibits a red shift in its absorption spectrum which allows it to photolyze.[82] For other compounds, shifts in their absorption spectra when on ice surfaces cannot fully explain the photolysis kinetics observed.[85]

Overall, much remains to be known about the photolysis of aromatic pollutants on ice surfaces. Photolysis rate constants for these compounds in ice and on ice surfaces are difficult to predict due to reactivity differing greatly depending on the location of the compounds within the ice.[66,85,104,186,195] For example, anthracene and benzene will react quickly with hydroxyl radicals when in aqueous solution and bulk ice, but when on the ice surface these compounds are unreactive towards hydroxyl radicals.[104] Photolysis rate constants at ice surfaces have not been experimentally determined for a number of aromatic compounds, likely in part due to difficulties in probing the ice surface.[100,195] Products formed from the photolysis of PAHs and benzene on ice surfaces are largely unknown but they are suggested to be more toxic than the parent compounds.[82,85,113] Only one study has attempted to identify photolysis products for benzene on ice.[82] The results of this study suggest the photolysis products of benzene on ice surfaces may have much higher molecular weights than benzene but their exact structures were not elucidated.[82] Furthermore, few experiments have investigated the effects of solutes such as halides and organic matter on PAH photolysis kinetics at ice surfaces. Harmine photolysis on ice surfaces was suppressed when in the presence of sodium chloride or sodium bromide.[116] Anthracene photolysis on ice surfaces was also suppressed in the presence of both non-chromophoric and chromophoric organic matter.[93,94] This illustrates how little is known about photochemistry of aromatic pollutants on ice surfaces in the presence of environmentally-relevant solutes.

1.4 Goals of Research

Most laboratory studies investigating the photochemical fate of PAHs and BTEX in the environment have been done under conditions that do not accurately reflect conditions found in the environment. Many studies utilize light sources with wavelengths that are not environmentally relevant. These studies utilize short wavelengths that are filtered out by ozone in the stratosphere and thus are not relevant to PAH photochemistry in the troposphere. Furthermore, most laboratory studies involving the fate of PAHs in waters have been done using deionized water. Water found in the environment is rarely pristine. Common constituents of natural waters are organic matter and halides. Very few studies have attempted to elucidate the effects organic matter and halides have on PAH photolysis kinetics, and fewer have investigated the effect multiple constituents have on PAH photolysis kinetics, even though halides and organic matter are commonly found together in the environment.

In order to accurately predict pollutant fate in condensed phases, an understanding of how different environments affect reactivity is needed. Chapter 2 of this work investigates the combined effects of organic matter and sodium chloride on the photolysis kinetics of the PAH anthracene in liquid water. Chapter 3 of this work describes the photolysis kinetics of toluene, ethylbenzene and xylenes in water, ice, and at ice surfaces. The rate constants measured in these studies can be used in chemical fate models in order to improve their accuracy. Furthermore, the results of this work can be used to better predict the fate of these pollutants in the environment and consequently their effects on human health and water quality.

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Chapter Two:

Effects of Sodium Chloride on Anthracene Photolysis Kinetics in Aqueous, Organic, and Mixed Aqueous-Organic Phases

2.1 Abstract

Water in the environment is rarely pristine and often contains significant fractions of organic matter (OM) and halide salts. Understanding how reactivity varies in these complex environments is necessary to accurately predict pollutant fate. We measured photolysis kinetics of the polycyclic aromatic hydrocarbon (PAH) anthracene in aqueous, organic, and aqueous-organic mixtures containing varying concentrations of sodium chloride (NaCl). In water, anthracene photolysis rate constants exhibited a non-linear dependence on NaCl concentration; as salt concentration increased, rate constants increased at low concentrations (up to 0.27 M), decreased at high concentrations (> 0.27 M and < 6.1 M) and then increased again at saturated concentrations (≥ 6.1 M). Conversely, a positive linear dependence was observed in octanol. In aqueous-organic mixtures, photolysis rate constants decreased with increasing salt concentration at low salt concentrations. At high NaCl concentrations, photolysis rate constants were independent of NaCl concentration in stagnant mixtures but depended positively on NaCl concentration in turbulent (stirred) mixtures. The effect of NaCl on photolysis kinetics in aqueous-organic mixtures appeared to be largely explained by salting out. Anthracene self-association at solid salt surfaces may account for the increase in rate constants observed at high salt concentrations in all media. Other factors such as singlet oxygen production were determined not to be significant except in water at NaCl concentrations below 0.27 M.

2.2 Introduction

Aromatic pollutants such as polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment.[1–4] They are pollutants of concern due to their toxicity and the fact that they often form more toxic products after degrading in condensed phases such as surface waters or aerosols.[5] Photolysis is one of the most important degradation pathways for PAHs in condensed phases. Therefore, accurate photolysis kinetics are needed in order to predict their environmental fate and health effects. Most laboratory studies have measured PAH photolysis kinetics in simple matrices such as deionized (DI) water or pure, organic solvents. However, these matrices do not reflect the complexity found in the environment. Kinetics can vary greatly depending on the phase and composition. Therefore, reaction kinetics measured under these simplified conditions may not be applicable to reactions which take place in the environment.

The presence of organic matter (OM) can have a large impact on pollutant fate.[6–9] Many condensed phases found in the atmosphere or environment contain a significant fraction of OM. OM has been shown to have a complex effect on PAH photolysis kinetics. For example, chromophoric OM, which can absorb light, can decrease photolysis rates by competitively absorbing photons or it can increase photolysis rates by acting as a photosensitizer or producing reactive species.[9–14] Non-chromophoric organic matter can decrease photolysis rates by reducing local polarity; some PAHs have been reported to photolyze less rapidly in organic solvents than in water.[8,15,16] To further complicate the matter, not all OM is miscible with water and its presence can result in phase-separated aqueous-organic mixtures, such as observed in some aerosols and at the surface of oceans.[1,16–18] Due to their hydrophobicity, PAHs preferentially partition to the organic phase. However, small amounts remain in the aqueous phase which means they can potentially react in both phases.[8,19] Previous work in our lab investigated PAH photolysis kinetics in immiscible aqueous-organic mixtures.[8] Anthracene photolysis rate constants increased with increasing aqueous fraction in miscible and immiscible aqueous-organic mixtures.[8] When the mixtures were stirred during photolysis (to mimic non-equilibrium conditions e.g. caused by mixing due to wave or wind action) the positive dependence on water fraction was much stronger. Photolysis in pure water in mixtures containing 25% water was as rapid as that in pure water; under stagnant conditions photolysis was much slower than in pure water at aqueous fractions as high as 80%.[8] Our results indicated that non-chromophoric OM, local polarity and perturbations in partitioning equilibria (e.g. caused by turbulence) can have a significant effect on PAH photolysis kinetics.

Halide salts are also ubiquitous in the environment. They are common components of natural waters and aerosols. Halides can have variable effects on PAH photolysis kinetics. Photolysis rate constants for some aromatic species have been reported to increase in the presence of halides whereas rate constants for other species have been reported to decrease or show no change.[20–25] Previous work in our lab measured photolysis rate constants of pyrene and anthracene in aqueous solutions containing chloride, bromide, and iodide.[26] Pyrene photolysis kinetics were insensitive to the presence of halides, while anthracene photolysis rates increased with increasing halide concentration at low concentrations and decreased at high concentrations. The maximum rate constant observed (in the presence of 0.27 M NaCl) was a factor of 5 greater than that measured in DI water. It was determined that this rate enhancement was due to production of singlet oxygen.

Many atmospheric aqueous phases, including sea surface microlayers and sea salt aerosols, contain both OM and halide salts. In fact, salt concentrations in aerosols can be much higher than those found in surface waters.[5] As discussed above, both solutes can affect PAH photolysis kinetics in complex ways. It is not known whether these effects are additive. In this work, we measured photolysis rate constants of anthracene in aqueous, organic, and phase-separated aqueous-organic solutions with varying concentrations of sodium chloride. The results presented in this study will provide greater insight into the fate of anthracene in the environment and may improve chemical fate models of PAHs.

2.3 Experimental

2.3.1 Sample Preparation

Solutions containing anthracene (Acros Organics, 99%) in 18 MΩ·cm deionized water or octanol (Acros Organics, 99%) were prepared weekly and allowed to stir overnight. For experiments in water and octanol, solid sodium chloride (NaCl, Fisher, ≥ 99.5%) was added directly to the solution. Aqueous-organic mixtures were prepared by combining octanol solutions containing anthracene with aqueous NaCl solutions. In some experiments, 3.5 µL furfuryl alcohol (FFA, Acros Organics, 98%) was added to the solution immediately prior to the experiment (for a final FFA concentration of 0.01 M). Final solutions had volumes of 4 mL and anthracene concentrations of 1×10^{-7} M.

For experiments performed under "turbulent" conditions, samples were stirred for at least two hours prior to photolysis as well as during photolysis. For "stagnant" experiments, samples were allowed to equilibrate for at least two hours prior to photolysis and were not stirred during photolysis. All samples were stored in the dark until the start of the experiment in order to prevent photolysis due to fluorescent lighting.

2.3.2 Photolysis

Photolysis was performed as described in previous publications.[8,26] To summarize, the output of a 150 W xenon arc was reflected off of a cold reflecting mirror and passed through a 295 nm long pass cutoff filter before illuminating the sample. Homogenous solutions were contained in a 1 cm path length quartz cuvette, and immiscible mixtures were contained in a 17 mm diameter 4 mL quartz bowl. In these experiments, the output of the lamp was reflected 90°

downwards on to the sample. The photon flux reaching the samples was previously determined to be (3.15 ± 0.08) × 10^{13} photons cm^{-2} s^{-1} using chemical actinometry.[10]

Photolysis rate constants were determined by measuring the change in anthracene fluorescence intensity as a function of irradiation time. Anthracene fluorescence spectra were acquired prior to irradiation and after every 4-10 minutes of irradiation up to 40 minutes. Fluorescence spectra were obtained with a Photon Technology International QuantaMaster 40 fluorimeter. Samples were stirred in the fluorimeter while obtaining the fluorescence spectra to distribute anthracene evenly throughout the volume of the cuvette. Anthracene was excited at 252 nm and emission was monitored at 380 nm. First order photolysis rate constants were calculated from the slope of the best fit line resulting from plotting the left side of equation 1 against time, where I is the fluorescence intensity after time t, I_0 is the fluorescence intensity at $t = 0$, and k is the first order rate constant (s^{-1}).

$$\ln\left(\frac{I}{I_0}\right) = -kt \tag{1}$$

In experiments involving immiscible mixtures, the sample was irradiated in a flat bottom quartz bowl. After a known time period the sample was transferred to a quartz cuvette, and a fluorescence spectrum was acquired as described above. The sample was then transferred back into the quartz bowl to undergo further irradiation. In turbulent experiments, the sample was stirred in the quartz bowl during both irradiation and analysis. In stagnant experiments, the sample was stirred while obtaining a fluorescence spectrum but was then allowed to equilibrate in the dark for at least 20 mins after being transferred to the quartz bowl and before irradiation resumed.

2.3.3 Singlet Oxygen

Furfuryl alcohol was used as a singlet oxygen trap to determine singlet oxygen production rates. Samples containing FFA, anthracene, and NaCl were irradiated in 2 min intervals for up to 10 mins. After each interval, a 0.5 mL aliquot was removed and analyzed by HPLC to measure the concentration of 6-hydroxy-2,3-dihydro-6H-pyrano-3-one (“pyranone”), which is the product of the reaction of FFA with singlet oxygen.[27] The yield of pyranone from this reaction is approximately 85%.[26,27] Therefore, singlet oxygen production rates can be calculated according to equation 2:[26]

$$\frac{d[^1O_2]}{dt} = \frac{d[pyranone]}{dt} \times 1.33 \qquad \textbf{(2)}$$

The HPLC used in these experiments was an isocratic Shimadzu Prominence-i LC-2030 equipped with a UV detector and a C18 reverse-phase column (Restek, 150 mm × 4.6 mm, 5 µm particle size); the column temperature was maintained at 40 °C. The mobile phase was 50/50 methanol/water with a 1 mL/min flow rate. A 1 µL injection volume was used. Pyranone was detected by monitoring absorbance at 219 nm.

2.4 Results and Discussion

2.4.1 Photolysis Kinetics in Aqueous Solution

Figure 2.1 shows anthracene photolysis rate constants in aqueous solution as a function of sodium chloride concentration. We have previously reported anthracene photolysis rate constants in aqueous solution containing up to 0.56 M NaCl.[26] In the current study, anthracene photolysis kinetics were measured in aqueous solution containing up to 10 M NaCl, which is much higher than sodium chloride’s saturation limit in water (6.1 M).

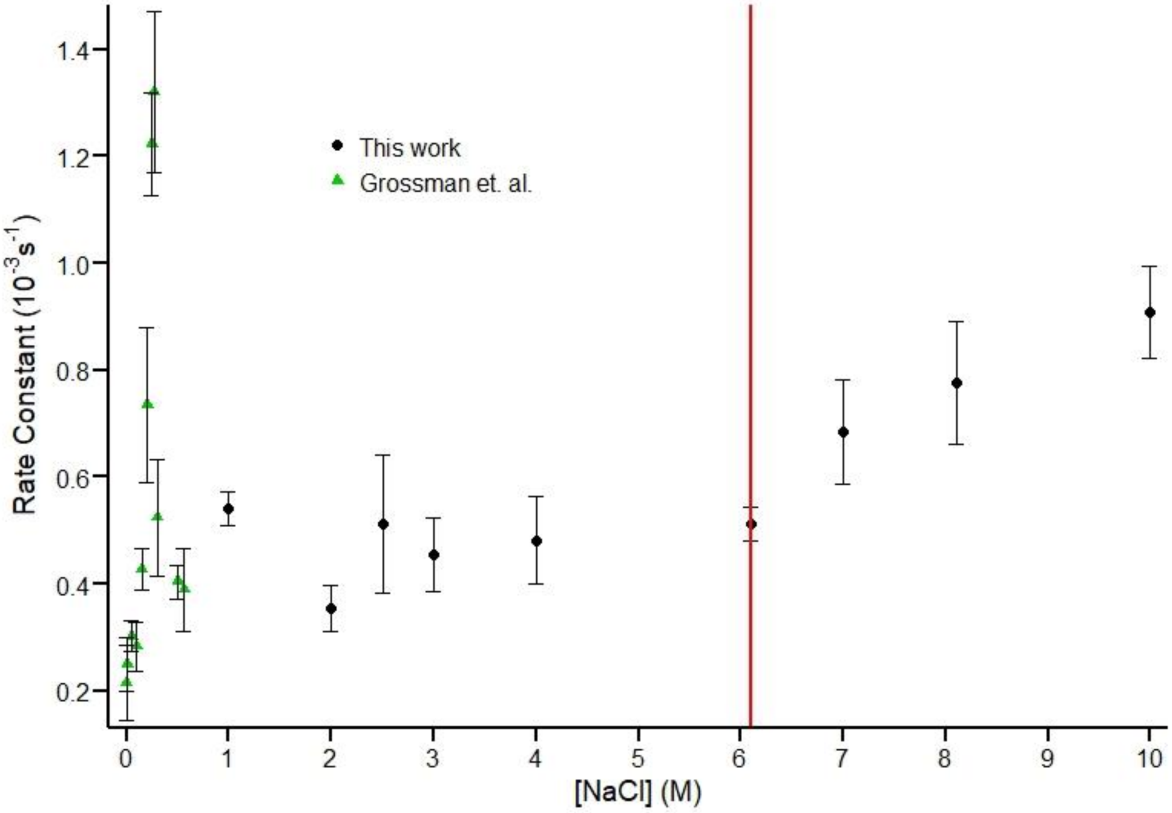

Figure 2.1: First order photolysis rate constants for anthracene in aqueous solution as a function of sodium chloride concentration. The solid vertical line denotes sodium chloride's saturation limit in water. Error bars represent the standard deviation of at least three trials. Data points at chloride concentrations lower than 1 M are from ref 27.

At relatively low NaCl concentrations (< 0.27 M), anthracene photolysis rates increased rapidly with increasing concentration; at higher NaCl concentrations (< 1 M), anthracene photolysis rates decreased. We have ascribed this to enhanced singlet oxygen production at low NaCl concentrations, and quenching of excited anthracene by NaCl at higher concentrations.[26] Extending the measurements to higher NaCl concentrations reveals two additional, distinct concentration regimes. First, the rate constant plateaus between 1 and 6 M NaCl at an average rate of 4.76×10^{-4} s^{-1} which is approximately a factor of 2 greater than the rate constant in the absence of NaCl. Then, at NaCl concentrations greater than the saturation limit (6.1 M), anthracene photolysis rate constants increase up to at least 10 M NaCl (although much less rapidly than at very low NaCl concentrations). This may be due to the formation of excimeric anthracene. Anthracene's photolysis rate constant in DI water has been reported to increase when excimers are present.[10] It is possible that at NaCl concentrations greater than saturation, the extent in which anthracene self-associates increases due to a salting out effect. Another possibility is anthracene partitioning to solid NaCl surfaces. Anthracene has been shown to photolyze more rapidly on some surfaces than in solution. For example, anthracene photolyzes more quickly on ice surfaces and silica surfaces than in liquid water.[7,10,28–30] This increase in rate when on surfaces is suggested to be due to anthracene self-association.[7,10,28] The fact that we observe this linear dependence only when solid salt is present in solution (i.e., above the saturation limit) suggests that surface effects may contribute to the observed increase.

To determine whether singlet oxygen also plays a role in the positive rate constant dependence on NaCl observed at very high concentrations, we irradiated anthracene solutions containing 8 M NaCl and 10 mM FFA to determine $^1O_2$ production rates. We measured a $^1O_2$ production rate of $(2.9 \pm 0.3) \times 10^{-8}$ M s^{-1}. In our previous study, $^1O_2$ production rates lower than 4×10^{-8} M s^{-1} resulted in anthracene photolysis rate constants smaller than 4×10^{-4} s^{-1}.[26] Despite the low $^1O_2$ production rate in solutions containing 8 M NaCl in the current study, anthracene's photolysis rate constant was 8×10^{-4} s^{-1}, which is much larger than can be explained by $^1O_2$ production. We therefore conclude that singlet oxygen production is not primarily responsible for enhanced anthracene photolysis in saturated aqueous NaCl solutions.

2.4.2 Photolysis Kinetics in Organic Solution

Figure 2.2 shows anthracene photolysis rate constants in octanol as a function of sodium chloride concentration. Photolysis rate constants increased linearly with increasing sodium chloride concentration. To determine the cause of this increase, we investigated the role of singlet oxygen and excimer formation. We did not observe any pyranone production in irradiated octanol solutions containing 1 M NaCl and 10 mM FFA, which suggests that there is negligible singlet oxygen production. We note that the slopes of the best fit lines of anthracene photolysis rate constants plotted as a function of NaCl concentration are similar in octanol and in saturated aqueous solution (6.49 × 10^{-5}[Cl^-] and 9.59 × 10^{-5}[Cl^-] respectively). Since NaCl is insoluble in octanol (and present primarily in solid form), the similar dependence of anthracene photolysis rate constants on NaCl concentration in octanol and in saturated aqueous solutions may suggest that the observed increase is due in part to reactions at salt surfaces.

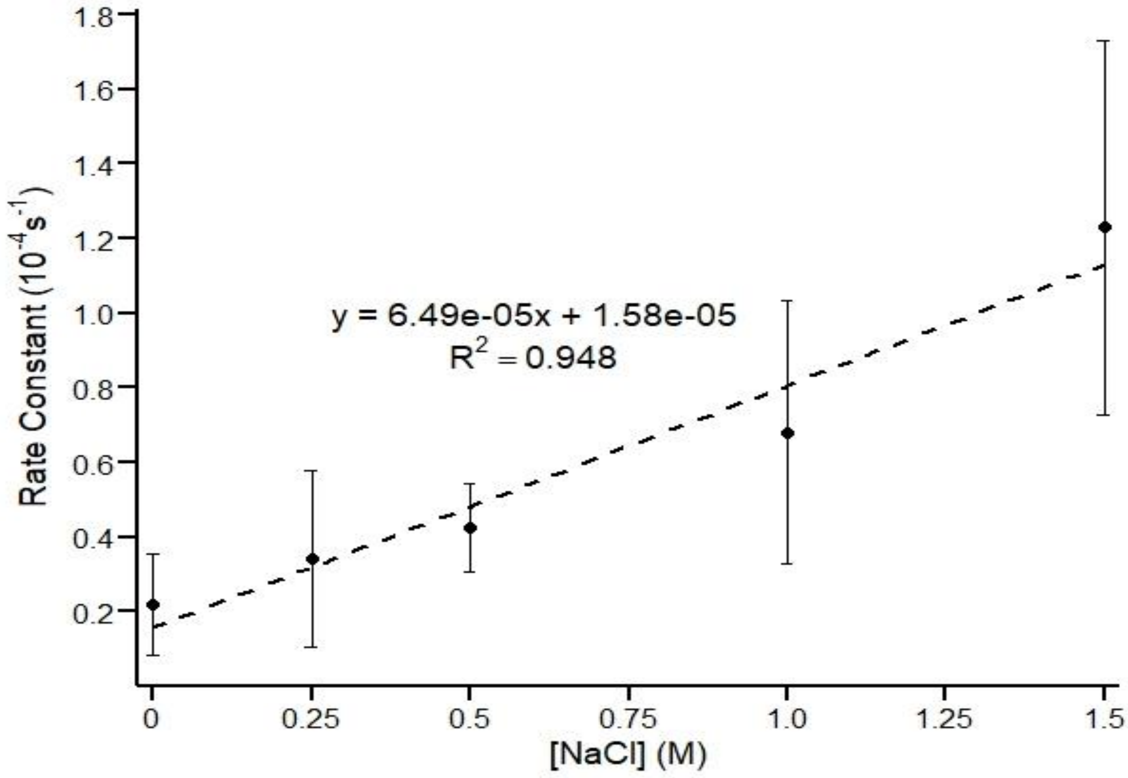

Figure 2.2: First order photolysis rate constants for anthracene in octanol as a function of sodium chloride concentration. The error bars represent the standard deviation for at least three trials. The dashed trace is the best fit line through the averaged data points.

2.4.3 Photolysis in Mixed Aqueous-Organic Solution

Table 2.1 shows anthracene photolysis rate constants in water, octanol, and water-octanol mixtures in the absence of salt. Anthracene's photolysis rate constant in aqueous solution is approximately 11 times larger than in octanol, in agreement with previous work.[8,31] Anthracene's photolysis rate constant was 2.5 times greater in stagnant mixtures than in 100% octanol, and 6.5 times greater in turbulent mixtures. We have previously shown that anthracene's rate constant depends much more strongly on the fractional water content in turbulent aqueous-octanol mixtures than in stagnant mixtures.[8] In stagnant mixtures containing 75% water, the rate constant was only 40% that measured in DI water. Conversely, in turbulent mixtures, photolysis rate constants reached those measured in DI water at aqueous fractions as low as 25% by volume. We have ascribed the faster photolysis in the turbulent mixtures to increased partitioning of anthracene to the aqueous phase.[8] We note that stirring 100% octanol or 100% aqueous solutions had no effect on observed anthracene rate constants.

Table 2.1: Anthracene photolysis rate constants in water, octanol, and aqueous-organic mixtures containing 80% v/v octanol

Medium	**Rate Constant (10^{-4} s^{-1})**
Water	2.2 ± 0.7
Octanol	0.2 ± 0.1
Stagnant Mixture	0.5 ± 0.2
Turbulent Mixture	1.3 ± 0.4

Figure 2.3 shows the effects of NaCl on anthracene photolysis kinetics in octanol and in 80% octanol mixtures under stagnant and turbulent conditions. As the sodium chloride concentration increased, photolysis rate constants initially decreased in both stagnant and

turbulent aqueous-octanol mixtures. This may be due to an increase in the fraction of anthracene in the organic phase caused by salting out, since anthracene photolysis is significantly slower in octanol than in water. At NaCl concentrations greater than 0.5 M, different concentration dependences were observed for the turbulent and stagnant mixtures. No concentration dependence was observed in stagnant mixtures. The average rate constant under stagnant conditions at NaCl concentrations between 0.25 and 1.5 was (3 ± 1) × 10^{-5} s^{-1}. This is larger than the rate constant measured in 100% octanol in the absence of NaCl ((2 ± 1) × 10^{-5} s^{-1}) but is within experimental uncertainty. The turbulent mixture shows a positive NaCl concentration dependence above 0.5 M, similar to that observed in 100% octanol and 100% water at NaCl concentrations greater than the saturation limit. We hypothesize that stirring enables a greater amount of salt to partition to the organic phase, resulting in similar salt-PAH interactions as in pure octanol. Unlike in octanol, this increase appears to plateau at NaCl concentrations greater than ~1 M. As discussed above, almost all of the NaCl is in the aqueous phase. As the aqueous phase concentration increases, the organic phase concentration increases proportionally. However, at a nominal concentration of 1.22 M, the actual NaCl concentration in the aqueous phase (which makes up 20% of the total sample volume) will be 6.1 M (i.e., the aqueous phase will be saturated). Saturation of the aqueous phase may be responsible for the observed plateau in anthracene's photolysis rate constant at nominal NaCl concentrations greater than 1.0 M.

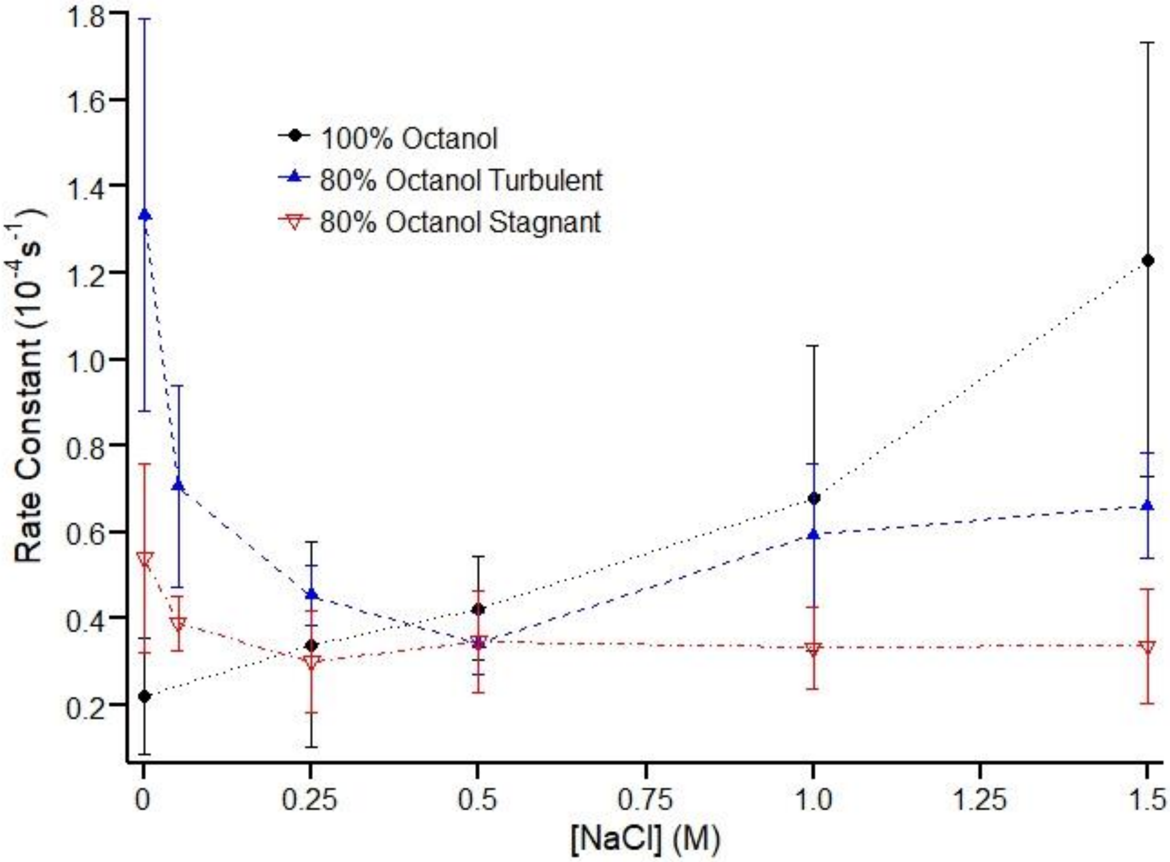

Figure 2.3: First order anthracene photolysis rate constant in octanol and in 80% octanol mixtures under stagnant and turbulent conditions as a function of sodium chloride concentration. Error bars represent the standard deviation for at least three trials. Dashed and dotted traces are included to guide the eye.

We measured pyranone production rates in stirred mixtures containing 80% octanol and 1 M NaCl to determine whether singlet oxygen contributed to the observed rate enhancement at high NaCl concentrations. We were unable to detect pyranone after 10 minutes of irradiation, which suggests that singlet oxygen does not account for the enhancement.

2.5 Atmospheric Implications

The results of this work can be used to determine: (1) under what conditions it is appropriate to use rate constants measured in DI water to predict reactivity in atmospheric condensed phases; and (2) how changing the composition of atmospheric condensed phases will affect pollutant reactivity. With respect to the first point, we have previously shown that anthracene photolysis rate constants measured in DI water will overpredict (sometimes by more than an order of magnitude) rate constants in organic phases (or in aqueous-organic mixtures containing large organic fractions), and that rate constants measured in DI water will underpredict rate constants in aqueous solutions containing between 0.05 and 0.56 M NaCl (by up to a factor of 6, but closer to a factor of 2 at most Cl^- concentrations).[8,26] In this work, we show that kinetics measured in DI water will underpredict anthracene photolysis rate constants at even higher Cl^- concentrations (up to at least 10 M). We note that photolysis kinetics of some other aromatic pollutants, such as pyrene, are not affected by Cl^- (at least at concentrations lower than 0.56 M). The specific effects of Cl^- on the photolysis kinetics of each pollutant of interest should therefore be considered.

To illustrate the second point, we consider an atmospheric aerosol containing an aqueous core surrounded by an organic shell (Figure 2.4). For a recently emitted sea spray aerosol, the aqueous core will contain ~0.5 M Cl^-. Anthracene in this aerosol will be partitioned primarily to the organic phase, and photolysis will be similar to that in an organic phase (that does not contain water or NaCl). If the NaCl concentration increases due to evaporation of water, anthracene's photolysis rate constant will either increase (under turbulent or otherwise non-equilibrium conditions) or remain relatively unchanged (under equilibrium conditions). If the water evaporates completely, leaving a chloride-containing organic aerosol, the rate constant will be larger than that in the aqueous-organic mixture but smaller than that in an aqueous aerosol in the absence of OM. The exact rate constant will depend on the chloride concentration. This simplified representation does not account for effects of other reactive processes such as indirect photolysis.

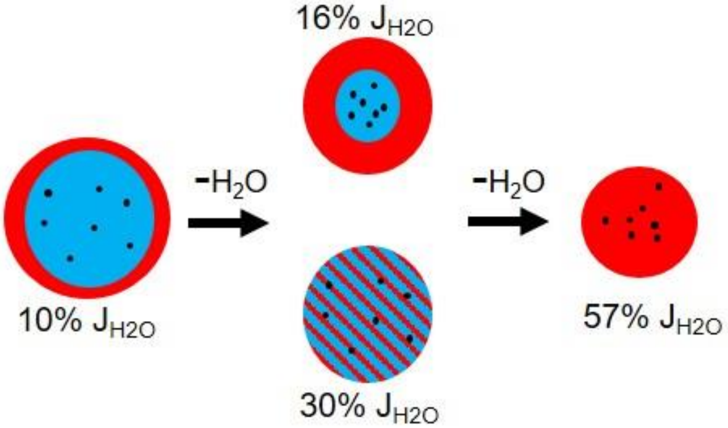

Figure 2.4: Cartoon showing the predicted effects of water evaporation on anthracene photolysis rate constants in a phase-separated aqueous-organic aerosol containing NaCl. Aqueous and organic phases are represented by red and blue, and the turbulent aqueous-organic mixture is represented by red and blue stripes. The black dots represent chloride ions. Photolysis rate constants based on the measurements in this work are given as percentages of the rate constant measured in DI water ("% J_{H2O}"). The arrows represent evaporation of water, notated as "-H_2O".

This work adds to our understanding of matrix effects in condensed-phase atmospheric photochemistry. It shows that solute effects can be non-linear, complex, and variable in different environments. Finally, it demonstrates the potential for fundamental, well-constrained experiments using well-defined multi-component systems to provide kinetic data that can improve predictions of pollutant fate in complex atmospheric condensed phases.

2.6 Acknowledgements

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Chapter Three:

Photolysis Kinetics of Toluene, Ethylbenzene and Xylenes at Ice Surfaces

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Stathis, A. A**.;** Hendrickson-Stives, A. K.; Kahan, T. F.; Photolysis Kinetics of Toluene, Ethylbenzene and Xylenes at Ice Surfaces. *Journal of Physical Chemistry A*. **2016** 120 (34), 6693-6697

3.1 Abstract

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are important organic pollutants. These compounds do not undergo direct photolysis in natural waters because their absorbance spectra do not overlap with solar radiation at the Earth's surface. Recent research has suggested that benzene is able to undergo direct photolysis when present at ice surfaces. However, the photolysis of toluene, ethylbenzene, and xylenes (TEX) at ice surfaces has not been investigated. Using fluorescence spectroscopy, photolysis rate constants were measured for TEX in water, in ice cubes, and in ice granules which reflect reactivity at ice surfaces. No photolysis was observed in water or ice cubes. Photolysis was observed in ice granules; rate constants were $(4.5 \pm 0.5) \times 10^{-4}$ s^{-1} (toluene), $(5.4 \pm 0.3) \times 10^{-4}$ s^{-1} (ethylbenzene), and $(3.8 \pm 1.2) \times 10^{-4}$ s^{-1} (xylenes). Photolysis of TEX molecules appears to be enabled by a red shift in the absorbance spectra at ice surfaces, although photosensitization may also occur. The results suggest that direct photolysis could be an important removal pathway for TEX in snow-covered environments.

3.2 Introduction

Organic contaminants such as benzene, toluene, ethylbenzene and xylenes (BTEX) are of importance due to their potential health effects. For example, acute exposure to this class of compounds has been linked to central nervous system, pulmonary and urinary toxicity in humans and other mammals.[1] Emission of BTEX into the environment is primarily through fossil fuel combustion. However, the concentrations of these compounds in the environment can significantly increase due to oil leaks, spills, and fracking fluid flowback or runoff.[2,3]

Snow packs have been investigated as a potential reservoir and reaction medium for organic pollutants. Multiple studies have detected VOCs such as BTEX in rural, semi-rural and arctic snow packs in concentrations on the order of hundreds of μg/L.[4–6] In some rural snow packs, toluene concentrations have been reported to be greater than 300 μg/L.[4] Upon melting, these pollutants can eventually enter rivers, streams, oceans and even public water sources. Thus, the fate of these organic pollutants in snow packs are of importance. Several studies have examined the photolysis of aromatic species such as pesticides, chlorinated benzenes, and polycyclic aromatic hydrocarbons (PAHs) in ice and at ice surfaces.[7–13] Such compounds are able to absorb in the actinic region (~290 – 400 nm) and therefore can undergo photolysis in aqueous solutions as well as snow and ice. Unlike these compounds, BTEX do not absorb strongly in this region. Figure 3.1 shows absorbance spectra for aqueous solutions of toluene, ethylbenzene, and xylenes (TEX) compared to the solar irradiance at the Earth's surface in Syracuse, NY at noon in the winter; it is evident that the two spectra do not overlap. Therefore, photolysis is generally not considered to be a viable environmental degradation pathway for these pollutants.

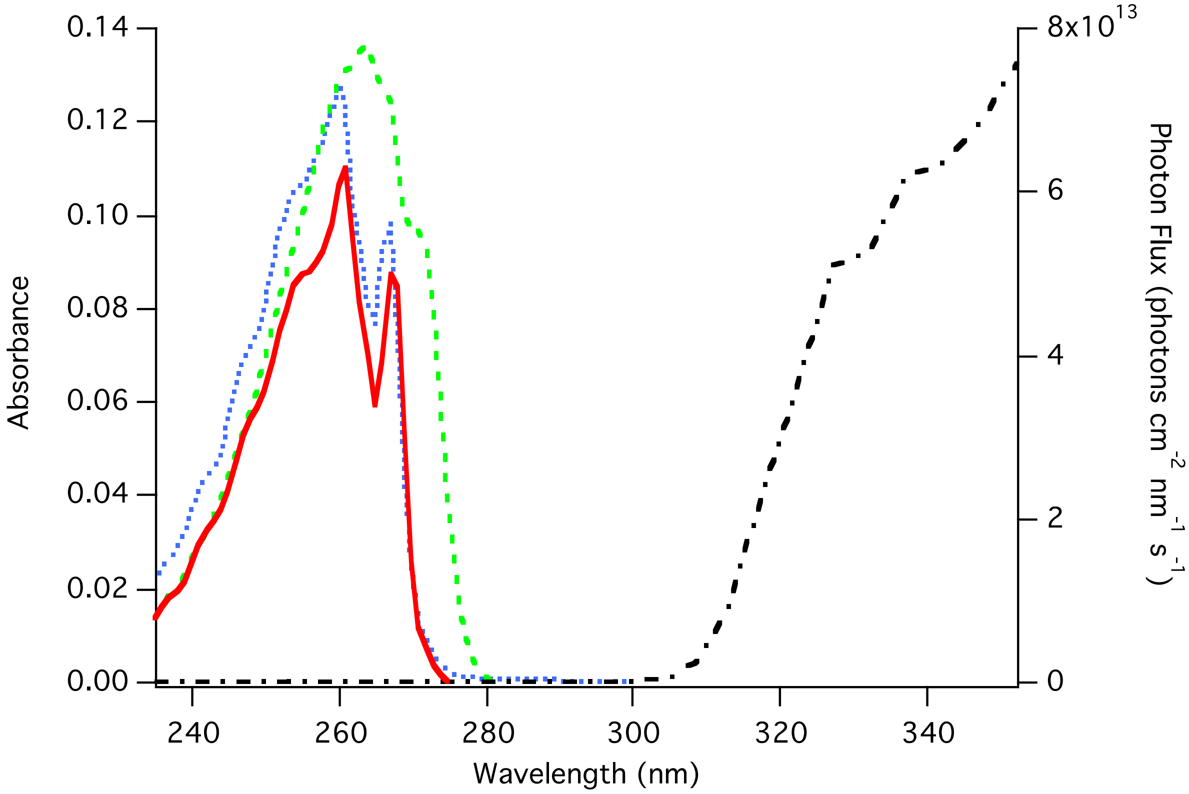

Figure 3.1: Left y-axis: Absorbance spectra of 2 ×10^{-3} M aqueous toluene (red solid line), ethylbenzene (blue dotted line), and xylenes (green dashed line). Right y-axis: Solar irradiance (black dash-dotted line) in Syracuse, NY at 12:00 p.m. EST during midwinter as predicted by the TUV model.[14]

As with TEX, dilute benzene solutions do not absorb wavelengths longer than ~280 nm. However, Kahan and Donaldson demonstrated that benzene undergoes photolysis at ice surfaces when irradiated with simulated sunlight.[15] They attributed this change in reactivity to a red shift in benzene's absorbance spectrum at the air-ice interface leading to overlap with solar irradiance at the Earth's surface. It is possible that TEX can also be photolyzed at ice surfaces; however, these reactions have yet to be investigated. In this work, we measure TEX photolysis kinetics at the air-ice interface in order to determine whether direct photolysis of TEX is possible. Understanding the photolysis kinetics of these compounds will provide greater insight into the fate of TEX in the environment.

3.3 Experimental

3.3.1 Sample Preparation

Solutions containing toluene (Aldrich, ≥ 99.5%), ethylbenzene (Acros, 99.8%) or mixed xylenes (Cole Palmer, 98.5%) in 18 MΩ·cm deionized water were prepared and allowed to stir overnight. Concentrations of the solutions were: 5.0×10^{-3} M (460 mg/L, toluene), 5.0×10^{-4} M (53 mg/L, ethylbenzene) and 5.0×10^{-4} M (53 mg/L, xylenes). Some experiments were also performed with 1×10^{-5} M (1 mg/L) ethylbenzene. Ice samples were prepared by freezing 5 mL aliquots in an ice cube tray ("ice cubes"). For some experiments, ice cubes were crushed into a powdery solid ("ice granules") prior to photolysis.

3.3.2 Photolysis

Samples were irradiated with a 150 W xenon arc lamp. The light passed through a 295 nm long-pass cut off filter and aluminum mesh that was used as a neutral density filter. The light was reflected downwards at a 90º angle, through a flat-bottom quartz dish filled with 25 mL of DI water which acted as an IR filter before reaching the sample. Aqueous samples were contained in a sealed 1 cm quartz cuvette, and frozen samples were contained in a stainless steel vessel connected to a recirculating chiller; the temperature within the vessel was maintained at -15 ºC. Unpublished results from our lab show photon fluxes (between 290 nm and 400 nm) within each sample type of $(2.8 \pm 0.5) \times 10^{13}$ photons cm^{-2} s^{-1} (water), $(4.1 \pm 0.4) \times 10^{13}$ photons cm^{-2} s^{-1} (ice cubes), and $(5.0 \pm 0.8) \times 10^{13}$ photons cm^{-2} s^{-1} (ice granules) using 2-nitrobenzaldehyde actinometry.[16,17] These fluxes are approximately three orders of magnitude lower than sunlight reaching the earth's surface at noon during the winter, which is on the order of 10^{16} photons cm^{-2} s^{-1}. Dark control experiments were conducted for each set of experimental conditions.

Photolysis kinetics were determined by measuring the change in TEX fluorescence intensity over irradiation time. Liquid samples were irradiated in 5 minute intervals for 40 – 50 minutes. Ice cubes and granules were removed from the stainless steel vessel after a known irradiation time and transferred to a sealed jar where the sample was allowed to melt in the dark. Samples were irradiated in 3 or 5 minute intervals for up to 30 minutes. The melted samples were transferred to a capped, 1 cm quartz cuvette before analysis. All fluorescence measurements were obtained using a commercial fluorimeter. Excitation wavelengths of 250 nm (toluene), 262 nm (ethylbenzene), and 268 nm (xylenes) were used. The fluorescence intensity was monitored at 281 nm (toluene), 280 nm (ethylbenzene), or 288 nm (xylenes). Photolysis rate constants were determined from the slope of the best fit line of the first order kinetics plot according to Equation 1, where I is the fluorescence intensity after time t, I_0 is the fluorescence intensity at $t = 0$, and k is the first order rate constant (s^{-1}).

$$\ln \frac{I}{I_0} = -kt \qquad \textbf{(1)}$$

3.3.3 Indirect photolysis

Toluene photolysis kinetics were measured in the presence of benzophenone, a photosensitizer, and different concentrations of rose bengal, a singlet oxygen source, in aqueous solution.[18,19] Photolysis was initiated by the output of a 150 W xenon arc lamp equipped with a cold reflecting mirror to act as an IR filter. The photon flux reaching the sample in these experiments (between 290 and 400 nm) was $(1.47 \pm 0.04) \times 10^{14}$ photons cm^{-2} s^{-1}.[20] For benzophenone experiments, the output of the lamp passed through a 295 nm long pass cut-off filter before reaching the sample contained in a 1 cm sealed quartz cuvette. For rose bengal experiments, a 480 nm long pass cut-off filter was used and the cold mirror was removed. Samples were irradiated in 5 minute intervals for 40 minutes. The toluene concentration in these experiments was 5.0×10^{-5} M (4.6 mg/L). Some samples also contained 1×10^{-6} M rose bengal, 2×10^{-5} M rose bengal, or 2.5×10^{-5} M benzophenone. For all experiments, the change in toluene fluorescence intensity over irradiation time was monitored using the same procedure described above. Three trials for each mixture were performed and then analyzed to determine the first order rate constants. The photolysis kinetics of toluene were also measured in ice granules containing 5.0×10^{-5} M toluene and 2.5×10^{-5} M benzophenone.

3.3.4 Absorbance Spectra

Absorbance spectra of solutions containing 2.0 × 10^{-3} M toluene, ethylbenzene, and xylenes in 18 MΩ·cm deionized water were acquired in quartz cuvettes using a commercial UV-Vis spectrometer.

3.4 Results and Discussion

Table 3.1 shows the average rate constants measured during irradiation of toluene, ethylbenzene, and xylenes in liquid water, ice cubes, and ice granules. Table 3.1 also includes the average rate constants measured during dark runs of ice granules and water where the xenon arc lamp was kept off throughout the experiment. As discussed previously, TEX molecules in aqueous solutions are not expected to photolyze due to their absorbance spectra not overlapping with sunlight at the Earth's surface (Figure 3.1). However, a measurable loss of TEX was observed in aqueous solution. We attribute this to evaporative loss as opposed to photolysis due to the fact that fluorescence intensity decreased at similar rates in the dark.

Table 3.1: Photolysis rate constants of TEX in water and in ice samples. The error represents the standard deviation about the mean for at least 3 trials.

	Rate Constant (10^{-5} s^{-1})		
Medium	**Toluene**	**Ethylbenzene**	**Xylenes**
Water	2.5 ± 1.0	3.7 ± 0.6	2.8 ± 1.4
Water (dark)	1.7 ± 0.1	2.9 ± 0.4	4 ± 3
Ice cubes	-	-	-
Ice granules	45 ± 5	54 ± 3	38 ± 12
Ice granules (dark)	-	-	-

No loss in fluorescence intensity was observed when ice cubes containing TEX were irradiated (Table 3.1). Within bulk ice there exists pockets and veins of liquid water; solutes in ice are thought to be distributed between the ice surface and these liquid regions due to exclusion during freezing.[21–24] Photolysis kinetics of other aromatic compounds in ice cubes have been reported to be more similar to kinetics in water than to those at ice surfaces.[7–9] Since decreases in fluorescence intensity in water were likely due to evaporation as opposed to photolysis and all ice experiments were performed at -15 ºC, we did not expect to observe loss of TEX during irradiation in ice cubes.

The fluorescence measurements made in this study are not selective to ice surfaces. However, by crushing ice samples into fine granules, and thus increasing the surface-area-to-volume ratio (SAV) of the samples, the fraction of solutes present at the surface increases.[7,9] Previous studies have shown that photolysis kinetics of aromatic compounds in ice samples with high SAV are comparable to those measured at ice surfaces.[7,9,25] Therefore, the kinetics measured in ice granules are expected to be representative of kinetics at the air-ice interface.

Loss of TEX fluorescence intensity was observed in ice granules (Table 3.1). Since no evaporative loss was observed in ice cubes, we ascribe all loss in ice granules to photochemical loss. This chemical loss was much more rapid than the evaporative loss observed in aqueous solution for all three compounds studied (by a factor of 15, on average). Figure 3.2 shows TEX emission intensity as a function of irradiation time in aqueous solution and in ice granules. A distinct decrease in fluorescence intensity in ice granules is observed over time. Dark controls did not produce any observable loss of fluorescence intensity for samples in ice granules (Table 3.1). Furthermore, the reaction chamber was maintained at a constant temperature of –15 ºC so the observed decay of TEX in ice granules is not likely due to sample heating or evaporation. These results suggest that TEX is able to undergo photolysis when exposed to solar radiation at ice surfaces.

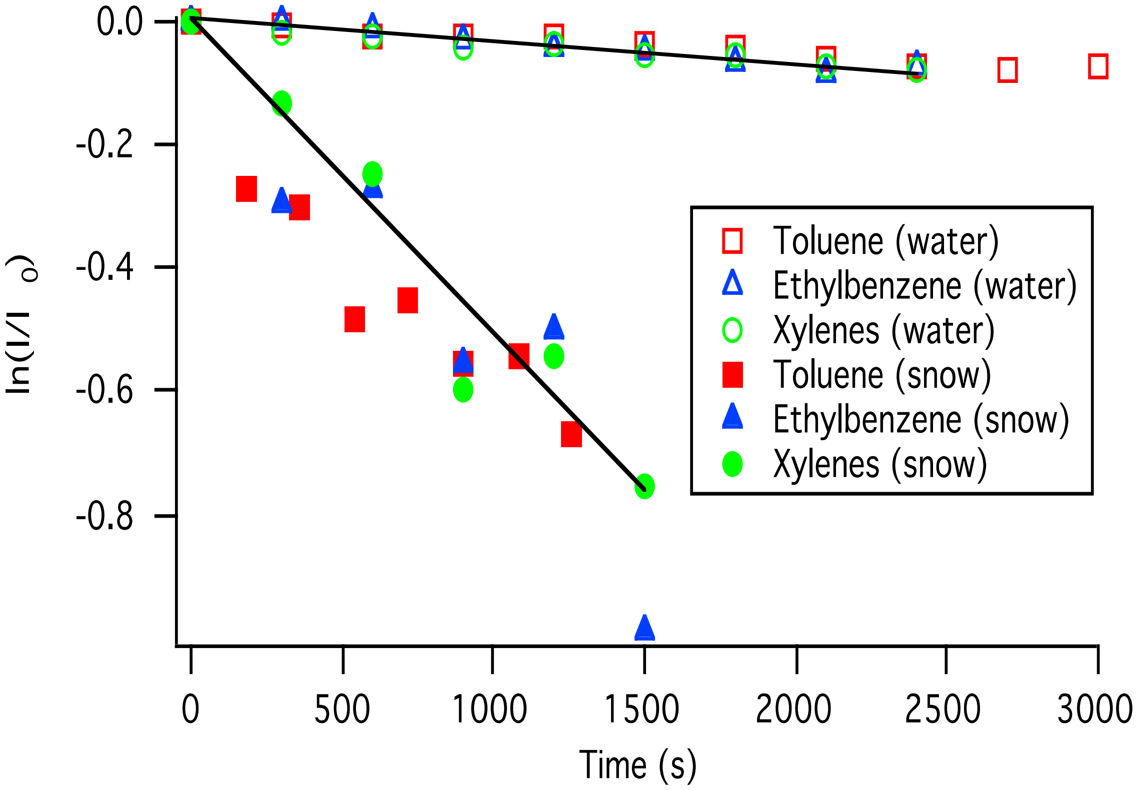

Figure 3.2: Plot of time-dependent decay of fluorescence intensity for toluene, ethylbenzene, and xylenes in aqueous solution and in ice granules. Solid traces are fits to the averaged data in the two media.

Photolysis mechanisms of poorly-absorbing aromatic pollutants in ice and ice granules remain largely unknown.[15,26] One possible explanation is that TEX undergo a red shift in their absorbance spectra at ice surfaces. Aromatic species are thought to self-associate at ice surfaces due to unfavorable interactions with water molecules.[9,15,27,28] In fact, emission from benzene and other aromatic molecules attributed to excimers (i.e. self-associated molecules) has previously been measured at ice surfaces using laser-induced fluorescence, and a red shift in benzene's absorption spectrum has been suggested to be responsible for its ability to undergo photolysis at ice surfaces.[15,25,28–30] We measured the photolysis kinetics of ethylbenzene in ice granules using different longpass cut-off UV filters to determine whether a red shift in its absorption spectrum could explain the observed photolysis. In the presence of a 305 nm filter, we measured a rate constant of $(5.3 \pm 1.7) \times 10^{-4}$ s^{-1}, which agrees with that measured with the 295 nm filter within our experimental uncertainty. In the presence of a 320 nm filter, however, no photolysis was observed. These results are consistent with a red shift in ethylbenzene's absorption spectrum enabling photolysis at ice surfaces under illumination by solar radiation at Earth's surface.

TEX photolysis in the environment will likely occur at different rates than in the laboratory. Three major factors that will affect photolysis kinetics are photon flux, TEX concentration, and the presence of other solutes. Photon fluxes from sunlight at the Earth's surface can be up to 3 orders of magnitude greater than those measured in our experiments. Photolysis rate constants may not scale linearly with photon flux, however. Nonlinear photon flux dependences have been reported for aromatic molecules, including benzene, in aqueous solution and at ice surfaces.[7] If similar nonlinearities exist for TEX, linear extrapolations from photon fluxes in the laboratory to solar fluxes might significantly overestimate photolysis rates in the environment. It should also be noted that photon fluxes measured within or at the surface of a snowpack may not accurately reflect the photon flux at the location of the TEX molecules. A recent study reported that photon fluxes within ice granules (prepared similarly to those in our experiments) were approximately 50% greater than those in larger discs of ice, and 80% greater than those in aqueous solution.[17] The photon fluxes we report were measured within each individual sample; we observe similar enhancements in ice cubes and ice granules.

The TEX concentrations used in this study ranged from 1 to 460 mg/L. These concentrations are greater than typical environmental concentrations, but are relevant to polluted regions. For example, TEX concentrations of 100 mg/L have been reported in contaminated groundwaters, and benzene and toluene mixing ratios greater than those in polluted megacities were recently measured in the air above snow near hydraulic fracturing operations.[3,31] It is possible that TEX molecules will only be photolabile in highly contaminated snow, as self-association at ice surfaces may not occur at low TEX concentrations. However, we measured identical ethylbenzene photolysis rate constants at concentrations of 1 mg/L and 53 mg/L, and red-shifted benzene spectra have been reported at ice surfaces at concentrations lower than 100 μg/L; these observations suggest that self-association (and red-shifted spectra) will occur even at low TEX concentrations.[15]

The effects of solutes on the photochemistry of aromatic pollutants in ice and at ice surfaces are not well known. Halide salts have been shown to suppress photolysis of the aromatic dye harmine at ice surfaces, likely by forming a liquid brine at the ice surface and causing photolysis to occur in aqueous solution.[32] This suggests that TEX photolysis may be significantly suppressed in snow and ice with high salt concentrations such as sea ice. We have reported that PAH photolysis is slower in ice and at ice surfaces in the presence of the immiscible organic species octanol and decanol.[9] The aromatics and the aliphatic organics are likely excluded to the same regions within the ice, resulting in a reaction environment that is more similar to octanol and decanol than to ice. In the presence of aliphatic species that do not actively participate in photochemistry (i.e. that do not absorb sunlight), we predict that TEX photolysis will be suppressed.

Many organic species commonly found in snow and ice do absorb sunlight, and can participate in photochemistry. We therefore investigated the possibility that indirect photochemical processes could contribute to the observed reactivity of TEX at ice surfaces. It has recently been shown that reactive oxygen species (ROS) and photosensitization may play important roles in the photodegradation of some organic pollutants in ice.[18,26,33,34] We measured toluene photolysis kinetics in aqueous solution in the presence of rose bengal, a singlet oxygen source, and benzophenone, a photosensitizer, to determine whether indirect photochemistry is likely important to toluene's chemical fate.[18,19] The presence of rose bengal did not affect toluene photolysis kinetics in aqueous solution ($k_{obs} = (3.3 \pm 0.6) \times 10^{-5}\ s^{-1}$), suggesting that toluene is not reactive toward singlet oxygen. However, the presence of benzophenone resulted in enhanced toluene loss in both aqueous solution and ice granules, with observed rate constants of $(6.7 \pm 1.5) \times 10^{-5}\ s^{-1}$ and $(6.1 \pm 0.7) \times 10^{-4}\ s^{-1}$. Assuming that toluene does not react directly with benzophenone, the observed rate constants are the sum of the rate constants for evaporation and photosensitization (in water), and direct photolysis and photosensitization (in ice granules). We calculate photosensitization rate constants for toluene of $(4.2 \pm 1.8) \times 10^{-5}\ s^{-1}$ and $(1.7 \pm 0.9) \times 10^{-4}\ s^{-1}$ in water and ice granules. The photosensitization rate constant in the ice granules is much greater than that in aqueous solution, likely due to higher local benzophenone concentrations resulting from freeze exclusion. However, photosensitization will be a more important chemical fate for toluene (and likely other BTEX molecules) in aqueous solution than at ice surfaces, since direct photolysis does not occur there. At ice surfaces, photosensitization may contribute to BTEX loss, but direct photolysis will likely be the dominant transformation process.

3.5 Environmental Implications

We have demonstrated that toluene, ethylbenzene, and xylenes undergo photolysis at ice surfaces when exposed to simulated sunlight. Photolysis appears to be enabled by a red shift in the absorbance spectra of TEX at ice surfaces compared to in aqueous solution. Photolysis rates at ice surfaces may increase in the presence of photosensitizers. To our knowledge, photolysis initiated by sunlight has not been considered as a potential reaction pathway for TEX. This work will improve predictions of BTEX fate in snow-covered environments. This may become increasingly important in the Arctic, where human activity is expected to increase as shipping lanes open up due to a warming climate. It may also affect regions used for oil and gas extraction, where very high benzene and toluene mixing ratios have been measured.

The effects of BTEX photolysis at ice surfaces on snow and air quality remain unknown; since this is largely a previously unconsidered mechanism, reaction products have not been investigated. Given that photolysis products of aromatic pollutants are often more toxic than the parent compounds, and that photolysis in ice can form products not observed in the aqueous phase, identification of BTEX photolysis products is an important endeavour.[13,35,36]

3.6 Acknowledgements

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Education

Syracuse University, Syracuse NY

PhD Candidate, Chemistry **Expected December 2018**

Dissertation Title: *Photolysis Kinetics of Aromatic Pollutants in Liquid and Solid Environmental Condensed Phases*

Stonehill College, Easton MA

Bachelor of Science Degree, Chemistry

2014

Research Experience

Syracuse University, Syracuse NY **2014-Present**

Advisor: Tara Kahan

- Investigated the fate and transport of pollutants in natural waters, ice and ice surfaces
- Measured the photolysis kinetics of toluene, ethylbenzene and xylenes in water, ice and on ice surfaces using fluorescence spectroscopy
- Measured the photolysis kinetics of polycyclic aromatic hydrocarbons (PAHs) and volatile, organic compounds (VOCs) in water, snow and ice
- Evaluated the effects of salts and organic matter on PAH photolysis in water and snow
- Developed methods to identify trace contaminants in environmental matrices using HPLC, GC/MS and fluorescence
- Examined the photolysis kinetics of nitrate and nitrite in water using Ion chromatography and Raman microscopy
- Managed collaboration projects with other labs at Syracuse University and Villanova University

Stonehill College, Easton MA **2013-2014**

Advisor: Deno DelSesto

- Prepared thiol and thioether solutions used to synthesize self-assembled monolayers on Au (111)
- Designed methods to create chemically etched Pt-Ir tips and mica supported Au (111) films
- Characterized thiol and thioether monolayers of varying length using STM, IR and Raman spectroscopy

Publications

Stathis, A. A.; Blaha, K.; Kahan, T. F.; Effects of Sodium Chloride on Anthracene Photolysis Kinetics in Aqueous, Organic, and Mixed Aqueous-Organic Phases. (*In Preparation)*

Stathis, A. A.; Hendrickson-Stives, A. K.; Kahan, T. F.; Photolysis Kinetics of Toluene, Ethylbenzene and Xylenes at Ice Surfaces. *Journal of Physical Chemistry A*. **2016** 120 (34), 6693-6697

Conference Presentations

"Effects of Sodium Chloride on Anthracene Photolysis Kinetics in Aqueous, Organic, and Mixed Aqueous-Organic Phases." **Stathis A. A.**, Kahan T. F. *American Geophysical Union Fall 2018 Meeting, Washington D.C.* December 2018

"Photolysis Kinetics of Toluene, Ethylbenzene and Xylenes at Ice Surfaces." **Stathis A. A.**, Kahan T. F. *American Geophysical Union Fall 2016 Meeting, San Francisco CA.* December 2016

"Investigation of Thiol and Thioether Self-Assembled Monolayers on Au(111) Using Scanning Tunneling Microscopy and Raman Spectroscopy" **Stathis A. A.**, DelSesto D.F. *247th American Chemical Society National Meeting, Dallas TX.* March 2014

Teaching Experience

General Chemistry II Laboratory Teaching Assistant, Syracuse University **Spring 2015, Spring 2016**

- Instructed sections of approximately 20-30 students on a range of basic laboratory techniques. Duties included lecturing, grading, and leading study sessions

Physical and Analytical Laboratory Teaching Assistant, Syracuse University **Fall 2015**

- Designed undergraduate experiments to demonstrate physical and analytical chemistry concepts. Instructed sections of approximately 10-15 students on advanced analytical laboratory techniques. Other duties included drafting lab readings and procedures, lecturing and grading.

General Chemistry for Engineer's Laboratory Teaching Assistant, Syracuse University **Fall 2014**

- Instructed sections of approximately 20-30 engineering students on a range of basic laboratory techniques used in engineering applications. Duties included lecturing, grading and leading study sessions.

Math and Chemistry Tutor, Stonehill College **Fall 2013, Spring 2014**

- Tutored undergraduate and high school students in general chemistry and calculus I.

Other Experience

Massachusetts Water Resources Authority Data Management Intern, Southborough MA **2018**

- Performed statistical analyses and created data visualizations in MATLAB using yearly water quality monitoring data collected from Wachusett reservoir.
- Developed algorithms to estimate reservoir thermocline depth.
- Conducted quality assurance on water quality data collected from reservoir and drinking water treatment system.
- Assisted laboratory technicians with field sampling and experiments.

Water Quality Testing Consultant, North Haven CT **2011-2013**

- Analyzed water samples using EDTA titrations and UV-Vis spectroscopy.
- Advised clients on methods to resolve their water quality issues.

Skills

Instruments & Techniques

Fluorescence spectroscopy**,** LC/HPLC, UV-Vis spectroscopy, GC/MS, Ion chromatography, FT-IR, Water Isotope Analyzer, CTD/SONDE measurements, EDTA titrations, water quality analysis, pollutant fate and transport, photolysis kinetic measurements, chemical actinometry, surface/groundwater sampling, streamflow measurements, greenhouse gas sampling, technical writing, project management, science communication, data analysis/visualization, data management

Computer

R (ggplot2), SQL, MATLAB, Python, Java, Excel, Power Point, Word, Access

Awards

- **EMPOWER NSF Research Traineeship Fellowship**
- **Syracuse University Water Initiative Fellowship**

Professional Activities

Education Model Program on Water-Energy Research **2016-Present**

Trainee in interdisciplinary graduate education program focused on research involving water and energy

Women in Science and Engineering (WiSE) **2015-Present**

Member of professional development organization for women in STEM fields