TRANSFORMATION OF UV-FILTERS IN THE PRESENCE OF AQUEOUS CHLORINE: KINETICS AND TRANSFORMATION PRODUCTS

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TRANSFORMATION OF UV-FILTERS IN THE PRESENCE OF AQUEOUS CHLORINE: KINETICS AND TRANSFORMATION PRODUCTS

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Thesis

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ABSTRACT

The aqueous chlorination of two UV-filters (Oxybenzone and Dioxybenzone) was studied in the pH range 6-11 and at 25±1 °C. Under these conditions, both UV-filters were rapidly oxidized by aqueous chlorine. For a total UV-filter concentration of 1 µM, and chlorine concentrations ranging from 10-75 µM, 90% degradation of the parent UV-filter occurred over 20 seconds (pH 8-9) and up to one hour (pH 6). Observed first-order rate coefficients (k_{obs}) were determined at various pH. The k_{obs} were used to determine the apparent second-order rate coefficient (k_{app}) at each pH level studied. The results showed that chlorination exhibits an overall second-order reaction rate and first-order with respect to each reactant. Assuming elemental stoichiometry describes the reaction between aqueous chlorine and each UV-filter, a model was developed to determine intrinsic rate coefficients (k_{int}) from the k_{app} as a function of pH for both UV-filters. The rate coefficients for the reaction of HOCl with ionized oxybenzone and dioxybenzone were 4.4×10^{3} M^{-1} s^{-1} and 1.65×10^{3} M^{-1} s^{-1}, respectively. The rate coefficients for HOCl with neutral species of each UV-filters were found to be 5.7 M^{-1} s^{-1} (oxybenzone) and 6.9 M^{-1} s^{-1} (dioxybenzone). Monochlorinated and dichlorinated transformation products of both oxybenzone and dioxybenzone were identified, as major products prior to ring cleavage. Finally, the potential for oxybenzone and dioxybenzone to form chloroform in the presence of excess aqueous chlorine was assessed. Chloroform forms rapidly, appearing after only two minutes of reaction time. Final yields of chloroform were lower
than predicted with molar yields of 0.016 μM CHCl₃/μM OXY and 0.011 μM CHCl₃/μM DiOXY at pH 8.
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CHAPTER I
INTRODUCTION

1.1 Perspective

Recently, attention has been focused on the presence of pharmaceutical and personal care products (PPCP) in drinking water sources. Surface waters, used as drinking water sources, undergo conventional drinking water treatment (i.e., coagulation, flocculation, sedimentation, and disinfection). These waters are often disinfected with chlorinated oxidants, aqueous chlorine or monochloramine, in order to mitigate the risk of waterborne pathogens. In the presence of chlorinated oxidants, PPCP’s and other anthropogenic chemicals can react and be transformed into known and unknown (i.e., regulated and unregulated) disinfection byproducts (DBPs) (Rule et al, 2005; Duirk and Collette, 2006; Dodd and Huang, 2007). Formation of DBPs from the reaction between chlorinated oxidants and PPCPs is a cause for concern because DBPs can elicit toxic, carcinogenic, and mutagenic affects adversely impacting public health (Richardson et al, 2007; Liviac et al, 2010). Public immersion waters also use chlorinated oxidants to mitigate the outbreak of waterborne diseases. However, very few studies have addressed the issue of DBP formation in public immersion waters. Of the three major DBP exposure pathways: dermal absorption, inhalation, and oral ingestion, studies have found that oral ingestion and inhalation cause an immediate increase in blood trihalomethane (THM) levels, while dermal absorption due to prolonged immersion causes the largest
overall increase in blood THM levels. Therefore, dermal exposure to DBPs may be significant to individuals who frequent public or private immersion waters.

The presence of organic UV-filters, more commonly known as “sunscreen chemicals” in immersion and surface waters has raised concern about their possible human health and environmental effects. In surface water samples, concentrations of UV-filters have ranged from the low ng L\(^{-1}\) in environmental samples to the µg L\(^{-1}\) level in immersion waters (Poiger, et al, 2004; Balmer et al, 2005). Direct release from skin in immersion waters, industrial wastewater, and indirect releases (e.g. by showering, clothes washing and urinary excretion) through domestic wastewater, represent the main entry routes of anthropogenic compounds into water bodies (Richardson, 2007). The available information suggests that some UV-filters are persistent (i.e. refractory) pollutants in the aquatic environment.

Unfortunately, DBP formation from UV-filters in drinking water sources and immersion waters has not been thoroughly investigated. It is possible that chlorinated oxidants used to disinfect potable and immersion waters could react with UV-filters to form DBPs; therefore, it is necessary to elucidate the fate of UV-filters in the presence of chlorinated oxidants. Determining the fate of UV-filters in the presence of chlorinated oxidants would provide valuable exposure information, which could help in balancing the risk of pathogenic microbes with the possible adverse health effects of DBP exposure.

1.2 Research Objectives

The overall objective of this research is to elucidate the reaction pathways and identify major transformation products of UV-filters in the presence of excess aqueous chlorine. Specific objectives include:
Objective 1: Measure the degradation of UV-filters in the presence of aqueous chlorine as a function of pH. Experiments will be conducted in batched reactors dosed with a fixed concentration of UV-filter under pseudo first-order conditions in the presence of excess aqueous chlorine concentrations. Pseudo-first order conditions are when the concentration of one reactant is in large molar excess in relation to the other analyte. Varying the pH will allow evaluation of the effects of acid/base speciation of aqueous chlorine and the UV-filters on the reaction rate and degradation pathways of UV filters.

Objective 2: Develop and evaluate a model that describes UV-filter transformation in the presence of aqueous chlorine under batch reactor conditions at a fixed UV-filter concentration and excess aqueous chlorine concentrations as a function of pH.

Objective 3: Identify the major reaction products of UV filters and aqueous chlorine. Reaction products will be derivatized via the 2,3,4,5,6-pentafluorobenzyl bromide method from Rule et al. (2005). Results will be analyzed using GC/MS.

1.3 Research Approach

A thorough literature review on the occurrence of UV-filters in natural waters and the reactions of anthropogenic chemicals with aqueous chlorine was conducted. Batch experiments were performed to examine the effect of varying aqueous chlorine concentration on the transformation rate of UV-filters over the pH range 6-11. The UV-filters chosen for this study, oxybenzone (OXY) and dioxybenzone (DiOXY) are substituted phenols, which have been shown to react with aqueous chlorine in previous studies when in the phenolate form (Rebenne, Gonzalez, & Olson, 1996).
Using experimental data gathered from the batch reactor experiments, a model was developed that describes the reaction rate between UV-filters and aqueous chlorine was used to determine intrinsic rate coefficients independent of pH by accounting for acid-base speciation of all reacting species. The model developed by Rebenne, Gonzalez, and Olson to describe the degradation of dihydroxybenzenes in the presence of aqueous chlorine was used as the basis for the model developed in this work (1996). Major reaction products were identified by derivatization with pentafluorobenzyl bromide. The potential for chloroform formation was evaluated by allowing the reaction of UV-filters with aqueous chlorine to occur over an extended period of time, one to 4 hours.
CHAPTER II
LITERATURE REVIEW

The oxidation of organic chemicals by aqueous chlorine has been studied extensively over the past few decades. Researchers have developed detailed models describing the reaction pathways of anthropogenic chemicals with chlorine that predict the formation of disinfection byproducts (DBPs), which can broadly be defined as products formed due to the reaction with aqueous chlorine. This extends the definition of DBPs beyond the known and regulated classes of trihalomethanes (THMs) and haloacetic acids (HAAs). Limited research has been conducted on the reaction of ultraviolet filtering chemicals (UV-filter) with aqueous chlorine. The purpose of this review is to establish a foundation for the development of a model for the reaction of UV-filters with aqueous chlorine under drinking water conditions (<3.5 ppm as Cl₂) and in the increased chlorine conditions present in many recreational immersion waters (>3.5 ppm as Cl₂).

Existing reaction models that describe the reaction of aqueous chlorine with anthropogenic chemicals will be evaluated to develop the foundation for the model development within this work. Also, a review of UV-filters occurrence in drinking and immersion waters was performed to establish the need for this work. Finally, a review of DBPs health effects through different exposure pathways was conducted. This literature review was divided into three sections: occurrence of UV-filters, reactions of
pharmaceutical and personal care products (PPCPs) with aqueous chlorine resulting in DBP formation, and the health effects and exposure pathways of specific DBPs.

2.1 Occurrence in Natural and Immersion Waters

Ultraviolet (UV) filtering compounds, such as oxybenzone (OXY) are being added to personal care products (PCPs) (cosmetics and sunscreens) in order to protect individuals from the harmful effects from exposure to UV radiation (Diaz-Cruz, Llorca, & Barcelo, 2008) (Fent, Zenker, & Rapp, 2010). UV-filters can either absorb UV radiation (organic) or reflect UV radiation (inorganic). This review will concentrate on the organic UV-filters. Three to eight different organic UV-filtering compounds (e.g. OXY, DiOXY, sulisobenzone, avobenzone, Padimate O, octyl methoxycinnamate, octoctrylene, and cinoxate) are found in the majority of PCPs and can make up to 10% of the product’s mass (Schreurs, Lanser, Seinen, & Van der Burq, 2002). UV-filters are released into the environment by two main pathways, indirectly via insufficiently treated wastewater effluent and directly by washing off the skin during recreational activities in drinking water sources (Kasprzyk-Hordern, Dinsdale, & Guwy, 2008).

Fent et al. (2010) studied the presence of various UV-filters at ten sites before and after wastewater treatment plants along the River Glatt in Switzerland. Four UV-filters were detected: sulisobenzone (SUL) was detected at concentrations up to 24 µg/POCIS (Polar Organic Chemical Integrative Sampler). OXY, 3-(4-methyl) benzylidene camphor (4-MBC), and 2-ethyl-hexyl-4-trimethoxycinnamate (EHMC) were detected at concentrations up to 0.1 µg L\(^{-1}\), as well as these UV-filters were detected in fish samples (305 ng g\(^{-1}\) lipid tissue). Poiger et al. (2004) found similar results in Lake Huttnersee, where OXY was the most frequently detected over the concentration range 5 – 125 ng L\(^{-1}\)
Balmer et al. (2005) studied the presence of four UV-filters: OXY, 4-MBC, EHMC, and octoctrylene (OC): in fish tissue, surface waters, and wastewater effluent in Switzerland. WWTP effluent had the greatest concentration of UV-filters with OXY occurring at a maximum concentration of 700 ng L\(^{-1}\). Kasprzyk-Hordern et al. (2008) studied the presence of PCPs in surface waters of South Wales, UK, with comparatively lower concentrations of UV-filters detected and only SUL exceeding 100 ng L\(^{-1}\) in samples. Li et al. (2007) studied the presence of four UV-filters (OXY, 4-MBC, EHMC, OC) in the influent of a wastewater reclamation plant in Tianjin, China. All four UV-filters were detected with 4-MBC having the highest concentrations (299 – 2128 ng L\(^{-1}\)), followed by OXY (68 – 722 ng L\(^{-1}\)). Nakata et al. (2009) studied the concentration of UV-filters in aquatic organisms in the Ariake Sea, Japan; UV-filters were detected in the concentration range of 10-100 ng g\(^{-1}\) in oysters and other indiginenous tidal flat species. UV Filters were also detected in the sediments of the Ariake Sea, ranging in concentration from 2.3 – 320 ng g\(^{-1}\) sediment. OXY and Padimate O (Pad-O) have been detected in the influent water of three cities in North Eastern Ohio (Akron, Barberton, and Ravenna) with concentrations ranging from 16.5 to 8754 ng L\(^{-1}\) over the Summer months during 2010 (Figure 2.1).

2.2 Reaction of Anthropogenic Micropollutants with Aqueous Chlorine

Chlorine is the most commonly used chemical oxidant for drinking water disinfection in the world (Deborde and Von Gunten, 2008). Addition of chlorine occurs at one or two points in the treatment process, as a pretreatment and/or as a post-treatment. Used as disinfectant, aqueous chlorine is effective at reducing the populations of pathogenic microorganisms in finished drinking water. As an oxidant, aqueous chlorine
can react with many anthropogenic organic micropollutants found in water (phenols, pesticides, etc.) (Duirk and Collette, 2006; Gallard and von Gunten, 2002; Arnold, et al, 2008). Some of these transformation products are more toxic than the parent compound.

![Figure 2.1](image)

**Figure 2.1** Average monthly concentration of UV filter agent Padimate O detected in source water samples collected weekly from the city reservoirs of Akron, Barberton, and Ravenna, OH, June – September, 2010.

Aqueous Chlorine has disadvantages in spite of its high usage and efficacy as a disinfectant. Chlorine chemistry in aqueous solution is complicated due to the various species of chlorine which may be present, which is dependent on the pH of the aqueous system. The major forms of chlorine found under drinking water conditions (pH 6-9) are hypochlorous acid (HOCl) and hypochlorite ion (OCl\(^-\)). Hypochlorous acid is in equilibrium with the hypochlorite ion according to the following equilibrium reaction:

\[
\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+ \quad \text{pK}_a = 7.54 \quad (2.1)
\]
These two forms of aqueous chlorine (hypochlorous acid and hypochlorite ion) demonstrate significant differences in their reactivity towards organic micropollutants (Deborde and von Gunten, 2008). Variability is therefore observed in the oxidation efficiency of chlorine depending on the pH of the water. Organic micropollutants are not generally mineralized during chlorine disinfection; therefore, numerous different transformation products may be formed as a due to oxidation/substitution reactions of organic compounds with aqueous chlorine (Gallard and von Gunten, 2002; Dodd et al., 2005; Rule et al., 2005; Duirk and Collette, 2006). The most common elementary oxidation reaction that occurs under drinking water conditions is:

\[ \text{HOCl} + X \rightarrow \text{Products} \]  

(2.2)

where X is an organic compound (Deborde and von Gunten, 2008).

The reaction of phenols with chlorine is a well studied electrophilic substitution/oxidation reaction (Gallard and von Gunten, 2002; Acero et al, 2005). The hydroxyl group on the aromatic ring is ortho/para-directing resulting in chlorination of the aromatic ring by a stepwise substitution of the 2, 4, and 6 positions followed by ring cleavage ultimately leading to chloroform formation (Gallard and von Gunten, 2002). The substituent groups (OH, O\(^-\)) on the aromatic ring influenced the rate of chlorine substitution by changing the charge density of the aromatic ring, leading to a faster observed reaction rate of hypochlorous acid with the phenolate form. The initial reaction of phenolic compounds with aqueous chlorine is an overall second-order, with first-order kinetics observed with respect to both chlorine and phenolic compounds.

Rebenne et al. (1996) studied the reaction of substituted dihydroxybenzenes (resorcinol, 4-chlororesorcinol, 4,6-dichlororesorcinol, and orcinol) with chlorine and
observed similar results. The hydroxyl groups on the aromatic ring directed substitution in the *ortho/para* direction, resulting in a stepwise substitution of the 2, 4, and 6 positions on the aromatic ring. As chlorine substitution on the aromatic ring increased, the apparent reactivity of aqueous chlorine with respect to resorcinol substrates increased. Ring cleavage during chlorination reactions was not explored.

In the case of both phenols and dihydroxybenzenes, elementary oxidation/substitution reactions were proposed to explain the chlorination reaction at a given pH. In the first proposed reaction, HOCl reacts with the ionized and neutral species of each compound (Eqs. 2.3 and 2.4). In the second proposed reaction, HOCl reacts with the neutral form of the compound, via an acid-catalyzed reaction (Eq. 2.5). Subsequent to this work it has been demonstrated that at pH < 5 the more probable pathway was a reaction of Cl$_2$(aq) with the neutral form of the compound (Eq. 2.6) (Gallard and von Gunten, 2002; Cherney, et al., 2006).

\[
\text{HOCl} + \text{phenol} \rightarrow \text{product} \quad (2.3)
\]
\[
\text{HOCl} + \text{phenolate} \rightarrow \text{product} \quad (2.4)
\]
\[
\text{H}^+ + \text{HOCl} + \text{phenol} \rightarrow \text{products} \quad (2.5)
\]
\[
\text{Cl}_2\text{(aq)} + \text{phenol} \rightarrow \text{products} \quad (2.6)
\]

For both phenolic compounds and dihydroxybenzenes, it was demonstrated that the most important reactions pathway over drinking water pH was the reaction of HOCl with the phenolate form of the compounds studied (Gallard and von Gunten, 2002; Rebenne et al., 1996).

Duirk and Collette (2006) examined the reaction of chlorpyrifos, an organophosphorus pesticide, in the presence of excess aqueous chlorine under simulated...
drinking water conditions. Chlorpyrifos (CP) was found to oxidize quickly in the presence of aqueous chlorine resulting in the formation of chlorpyrifos oxon (CPO), which is three orders of magnitude more toxic than CP. The oxidation reaction occurred more rapidly at lower pH, indicating that the primary oxidation reaction occurred between CP, and HOCl. Additionally, OCl\(^-\) served as a super-nucleophile accelerating the alkaline hydrolysis of both CP and CPO to form 3,5,6-trichloro-2-pyridinol. It was hypothesized that this effect occurred due to the lone pairs of electrons on both oxygen and chlorine in the structure of OCl\(^-\), which served to increase the nucleophilic character of the molecule.

Dodd and Huang (2007) studied the reaction of the antibacterial agent Trimethoprim (TMP) with aqueous chlorine. The reaction of TMP with aqueous chlorine is first order with respect to each reactant, and overall second-order reaction, reacting readily with chlorine at pH values between 3 and 9. The proposed reaction pathway of TMP changes based on the pH of the solution. At pH <5 the main reaction occurs via chlorination of TMP’s 3,4,5-trimethoxybenzyl moiety, by Cl\(_2\)\(_{aq}\), producing mono- and dichloro- substituted products. At pH >5, it is proposed that HOCl reacts readily with the 2,4-diaminopyrimidinyl moiety, leading to a wide variety of (multi)halogenated and hydroxylated transformation products.

The reaction of triclosan, a commonly used antimicrobial agent, and aqueous chlorine was studied over the pH range of 4-11.5 (Rule et al., 2005). The reaction was second-order overall and first-order with respect to chlorine and first-order with respect to triclosan. Over the pH range studied the kinetics were pH sensitive, due to the speciation of both triclosan (pKa = 7.9) and HOCl (Rule et al., 2005). The proposed
reaction pathway for triclosan, a phenolic ether, was between the ionized phenolate of triclosan and HOCl, with initial chlorine attack occurring at the ortho/para position to the phenol moiety. 2,4-Dichlorophenol was detected under all reaction conditions, forming via ether cleavage of triclosan. A model was developed to describe the transformation pathways of triclosan resulting in chlorophenoxyphenol intermediates, followed by ether cleavage during subsequent electrophilic chlorine substitutions to form 2,4-dichlorophenol.

The antibacterial agent Sulfamethoxazole’s (SMX) reaction with aqueous chlorine (under excess and sub-stoichiometric conditions) was studied to evaluate the effect of chlorination on the fate of sulfanomides in drinking water systems (Dodd and Huang, 2004). The reaction of SMX with aqueous chlorine was observed to decrease rapidly as excess HOCl concentration was decreased, indicating that the primary oxidant in the reaction was HOCl. The chlorination reaction occurred via two different mechanisms depending on the amount of available aqueous chlorine in solution. When SMX was in excess, chlorine reacted directly with the nitrogen-aniline moiety, yielding an organic chloramine. Under excess chlorine conditions, while the initial chlorine substitution occurs at the nitrogen-aniline moiety further chlorine substitutions lead to aqueous chlorine reacting with SMX by cleaving? the sulfonamide moiety, yielding multiple chlorinated reaction products.

Deborde, et al. (2004) studied the chlorination kinetics of six endocrine disruptors (EDs: 4-nonylphenol, β-estradiol, estrone, estriol, 17α-ethinylestradiol, progesterone) in the presence of excess chlorine. Under the conditions studied (pH: 3.50-12) the five EDs with phenol moieties were rapidly oxidized by chlorine. However, progesterone did
not react with chlorine under these conditions. Similarly to the results obtained by Gallard and von Gunten (2002), the phenolate form of the EDs reacted $10^4$ times faster than the neutral forms of the EDs.

To date, there has been only a single study published in peer-reviewed literature regarding the reaction of UV-filters in chlorinated waters (Negreira, et al., 2008). The work studied the stability of three UV-filters: 2-ethylhexyl salicylate (ES), Padimate-O (ODPABA) and oxybenzone (OXY), in chlorinated waters. ES was found to exhibit minimal reactivity in the presence of chlorine, with less than a 40% reduction in concentration under excess chlorine conditions ([Cl$_2$]:[ES] > 10:1) after half an hour. ODPABA and OXY readily reacted with available chlorine, through two proposed degradation pathways. The proposed degradation pathway for ODPABA consists of electrophilic substitution of chlorine on the ortho- carbons to the amino moiety, resulting in monohalogenated products. For OXY the phenol moiety was ortho/para directing resulting in mono- and dihalogenated substitution by-products prior to ring cleavage and formation of halogenated forms of 3-methoxyphenol.

2.3 Health Effects of Disinfection Byproducts

Over 600 drinking water disinfection byproducts (DBPs) have been identified in drinking water (Richardson et al, 2007). DBPs are formed from the reaction of chlorinated oxidants with natural organic matter (NOM) and some anthropogenic chemicals not removed through conventional drinking water treatment (i.e. coagulation, flocculation, and filtration) (Duirk and Collette, 2006; Rule et al., 2005; Gallard and von Gunten, 2005). The two most prevalent classes of DBPs resulting from drinking water chlorination are the trihalomethanes (THMs) (chloroform, bromodichloromethane,
dibromochloromethane, bromoform) and the haloacetic acids (HAAs) (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA)). Combined they account for approximately 25% of the halogenated DBPs in chlorinated drinking water (Krasner et al., 2006). Public health concerns exist due to the prevalence of HAAs and THMs in chlorinated drinking and recreational waters (Richardson et al., 2007). Studies have shown that THMs and HAAs are carcinogenic and genotoxic (Richardson et al., 2007). Toxicological studies have shown that DBPs can cause developmental and reproductive effects in laboratory animals as well as humans (Dodds, et al., 2008; Graves, Matanoski, and Tardiff, 2000). Exposure studies have demonstrated that THMs can enter the bloodstream by ingestion, inhalation, or dermal contact (Leaven, et al., 2007; Wolf and Butterworth, 1997; Villanueva et al., 2006). The different exposure pathways can elicit various concentrations in the human body, in one study blood concentrations of bromodichloromethane, following oral and dermal exposure, were as much as 41x more concentrated following dermal exposure, and were detectable in the blood for 6x longer than for oral exposure to similar concentrations (Leavens, et al., 2007).

2.3.1 Genotoxicity of Disinfection By-Products

The genotoxicity of the four regulated THMs (chloroform, bromodichloromethane, dibromochloromethane, chloroform) has been well studied (Kargalioglu, et al., 2002; Landi et al., 2003; Kogevas, et al., 2010). Bromoform, dibromochloromethane, and bromodichloromethane, have not generally induced genotoxic responses except in the presence of glutathione S-transferase theta (GSTT1-1), a common enzyme in mammalian cells (Richardson, et al., 2007). In the presence of
GSTT1-1 all three have been observed to induce genotoxic effects in a study of human lung tissue, and in various strains of salmonella (Landi, et al., 2003; Kargalioglu, et al.; 2002). Chloroform, does not generally induce genotoxic effects, with the notable exception that it was weakly correlated to genotoxic effects in human lung tissue (Kargalioglu, 2002; Landi, et al., 2003).

Three of the five regulated HAAs (MBAA, DBAA, MCAA) were mutagenic in bacteria and Chinese hamster ovary cells (Kargalioglu et al., 2002; Plewa, et al., 2002). DCAA has been observed to be only weakly genotoxic, producing effects inconsistently and only at high dosages (<50% effect occurrence rate at dosages ≥0.5 g L⁻¹) (IARC, 2004a). Trichloroacetic acid has not been shown to be genotoxic in peer reviewed studies (IARC, 2004b).

2.3.2 Carcinogenicity of Disinfection By-Products

During two year rodent carcinogenicity studies, all four of the THMs were carcinogenic (NTP, 1989; NTP, 1985; NTP, 2006, NCI, 1976). Chloroform and bromodichloromethane are found to be carcinogenic in both mice and rats (NTP, 2006; NCI 1976). Of the remaining THMs, Bromoform was carcinogenic in rats, and dibromochloromethane was carcinogenic in mice (NTP, 1989; NTP 1985).

In humans, long-term exposure to THMs has been linked to an increased risk of cancer. Villanueva et al. (2006) found that long-term exposure to an average level of >49 µg/L THMs increased the lifetime risk of bladder cancer by 100% versus an average exposure of ≤ 8 µg/L. Additionally, Villanueva, et al. (2006) linked dermal exposure to THMs in recreational waters and from showering with an increase in the lifetime risk of cancer by 57%. Inhalation of THMs while showering corresponded to an increased
lifetime risk of cancer by 83%. By contrast, ingestion of THMs only increased the lifetime risk of cancer by 35% (Villanueva, 2006). Wang, Deng, and Lin (2007) obtained similar results to Villanueva, et al. (2006), using a Monte-Carlo simulation. The simulation showed that the exposure pathway with the highest associated risk was from inhalation while showering, while dermal exposure was not significant when compared with the inhalation and ingestion routes.

Three of the five regulated HAAs (dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), dibromoacetic acid (DBAA)) are known to elicit carcinogenic responses in rodents through oral exposure (Bull, et al., 1990; Melnick et al; 2007). Monochloroacetic acid (MCAA) did not elicit a carcinogenic response through oral exposure (NTP, 1992). No carcinogenicity studies concerning monobromoacetic acid (MBAA) have been published in peer reviewed literature to date (Richardson et al., 2007). To date, no studies have been published in peer reviewed journals linking exposure to HAAs with increased risk of cancer in human populations.
CHAPTER III

EXPERIMENTAL METHODS

This Chapter contains experimental methods, materials, analytical methods, and apparatus used to conduct the research presented in this thesis. All experiments were conducted at the University of Akron (Akron, OH) in the Auburn Science and Engineering Center Room 411.

3.1 Materials

The following UV-filters, oxybenzone(98%) (OXY), dioxybenzone(98%) (DiOXY), and Padimate O(98%) (ODPABA) were purchased from Sigma Aldrich (Milwaukee, WI). Commercial 10-13% sodium hypochlorite (NaOCl), also purchased from Sigma Aldrich, contained equimolar amounts of OCl⁻ and Cl⁻. Aqueous stock solutions and experiments used laboratory prepared deionized water (18 MΩ cm⁻¹) (DI water) from a Barnstead NANOpure system (Barnstead-Thermolyne Corporation, Dubuque, IA). Phosphate and carbonate salts used for buffer solutions were dissolved in DI Water and filtered through a 0.45µm cellulose nitrate filter (Whatman Corporation, Kent, United Kingdom). The pH for the solutions was adjusted using either 1N H₂SO₄ or NaOH. All pH measurements were taken with an Orion 5 star pH meter and ROSS ultra combination pH probe (ThermoFisher Scientific, Pittsburgh, PA). All other organic and inorganic chemicals were certified ACS reagent grade and used without further purification. The glassware used in this study was prepared by soaking it in a
concentrated free chlorine solution for 24 hours, rinsed with DI water, and dried prior to use.

![Atomic Structures of Oxybenzone and Dioxybenzone](image)

Figure 3.1 Atomic Structures of Oxybenzone and Dioxybenzone

3.2 UV-filter Oxidation Experiments

All UV-filter experiments were conducted at constant temperature (25±1°C). For UV-filter oxidation experiments, each UV-filter was spiked by adding 250 µL of a 4 mM stock solution in ethyl acetate into an empty 1 L borosilicate glass Erlenmeyer flask. A gentle flow of nitrogen gas was used to evaporate the ethyl acetate and then 980 mL of DI water was added to the flask. The solution was slowly stirred and allowed to dissolve for 12 hours resulting in an aqueous concentration of 1.02 µM. Prior to addition of aqueous chlorine, 20 mL of the appropriate buffer solution was added to the vessel, resulting in an aqueous concentration of 1 µM. UV-filter chlorination experiments were conducted under pseudo-first-order conditions: total chlorine to UV-filter molar ratios of 10:1, 25:1, and 50:1 were used. Chlorine was added under rapid mix conditions achieved with a magnetic stir plate and PTFE-coated stir bar.

Experimental pH was maintained utilizing two different buffers, from pH 6 to pH 8, 10 mM [PO₄] was utilized, above pH 8 10 mM [CO₃] was added to the reacting
vessel. Over the pH range studied the loss of both oxybenzone and dioxybenzone was very fast. Therefore, 8 100-mL aliquots of the 1 L solution containing 10 mM of buffer and 1 μM of UV-filter were placed in a 250-mL Erlenmeyer flask. The purchased aqueous chlorine solution was first diluted to 250 mM then added to the aqueous system in the 250-mL Erlenmeyer flasks. At each discrete sampling interval a reacting vessel was sacrificed in its entirety. In the vessel, free chlorine was quenched using sodium sulfite (Na₂SO₃). The pH of the sample was then adjusted to 3 using concentrated sulfuric acid, prior to extraction.

3.3 Quantification of UV-filters and Degradation Product Identification

The UV-filters and their degradation products were analyzed by the following liquid-liquid extraction method. Following quenching and pH adjustment, ~30g of anhydrous sodium sulfate (Na₂SO₄) was added to each vessel, and mixed thoroughly by hand for one minute. Then, the sample was spiked with 0.4 μM of Padimate O (internal standard), and shaken by hand for thirty seconds. Next, 3 mL of Ethyl Acetate was added to each vessel, which was then placed on a wrist action shaker (Burrell Scientific, Pittsburgh, PA) for thirty minutes prior to final extraction.

Quantification for each analyte was compared to eight extracted standards over the concentration range of 0.00-1.00 μM. All kinetic experiments used to estimate rate coefficients measured at least 85% loss in the parent compound. The method used was an adaptation of Cuderman and Heath (2007). A Hewlett-Packard 7890A GC, equipped with a 6973C MSD, was used to analyze Oxy, Dioxy, and Octi. GC conditions were as follows: 30-m Restek RTX-5ms, with a 0.25 μm ID, and 0.5 μm film thickness, operated in scanning mode (50-550 m/z), helium was used as the carrier gas with a flow rate of 1.5
20 mL min\(^{-1}\). The temperature profile was as follows: 150°C increased at 10°C min\(^{-1}\) to 180°C and held for 10 minutes, then increased at 2°C min\(^{-1}\) to 280°C and held for 5 minutes.

Daughter product analysis was carried out by derivitization with pentafluorobenzyl bromide (99%; PFBBBr) (Nakamura, S., et al., 2001). 100 µl of PFBBBr (5%, in ethyl acetate) and 100 µl of 10% aqueous potassium carbonate were added to the samples. The sample bottles were then set in a water bath at 80°C for 45 min. After cooling, the samples were dried under nitrogen until ~0.1 mL remained. Finally, 1.0 ml of ethyl acetate was injected into the sample vials along with 5 µl of internal standard (4.0 mM, Pad O). GC-MS analysis of daughter products was carried out under the conditions stated above.

3.4 Chloroform formation and quantification

Experiments were performed to monitor the formation of chloroform under headspace-free conditions in 128-mL amber reaction vessels stored in the dark at 25 ± 1°C. Chloroform was quantified using a liquid-liquid extraction (LLE) procedure, followed by GCMS injection for analysis.

At each discrete sampling interval a reacting vessel was sacrificed in its entirety. In each vessel 28 mL was removed and discarded to leave a final volume of 100-mL for extraction and quantification. The remaining free chlorine was quenched with 1 ml of Na\(_2\)SO\(_3\), then the pH of the aqueous solution was adjusted to <0.5 using concentrated H\(_2\)SO\(_4\). ~30g of anhydrous Na\(_2\)SO\(_4\) was added to each vessel, and mixed thoroughly by hand for one minute. Then, the sample was spiked with 10 µL of 1,2 dibromopropane (internal standard, 0.5 mg/mL in MeOH), shaken by hand for thirty seconds, and then 3
21 mL of methyl tert-butyl ether (MtBE) was added to each vessel, which was then placed on a wrist action shaker for thirty minutes prior to final extraction.

Quantification for chloroform was compared to eight extracted standards over the concentration range of 0 to 0.84 µmol/L. The GC conditions were as follows: 30-m Restek RTX-5ms, with a 0.5 µm film thickness and a 0.25 mm ID, operated in full scan mode (30 – 550 m/z). The temperature profile was as follows: 35 C for 5 minutes, and then 20 C min\(^{-1}\) to 250 C.
CHAPTER IV
RESULTS AND DISCUSSION

This chapter has been divided into three sections. The first section discusses the observed rate of loss, reaction order, and apparent rate coefficients of oxybenzone (OXY) and dioxybenzone (diOXY) in the presence of aqueous chlorine at pH 6-11. The second section discusses the development of a chemical kinetic model for OXY and diOXY degradation in the presence of aqueous chlorine and determination of the intrinsic rate coefficients. The final section discusses the major reaction products and chloroform formation due to the continued transformation of OXY and DiOXY in the presence of aqueous chlorine.

4.1 UV-Filter Observed Loss, Reaction Order, and Apparent Rate Coefficients

Very little is known about the kinetic rate of UV-filter degradation and products in the presence of aqueous chlorine. UV-filters have been shown to degrade in the presence of aqueous chlorine (Negreiera, et al; 2008); however transformation rates and products of the reaction of UV-filters with aqueous chlorine have not been previously elucidated in peer reviewed literature.

The observed loss of OXY and DiOXY in the presence of excess aqueous chlorine was assumed to be first order with respect to OXY and DiOXY concentration. This assumption is valid if linearity is observed when plotting ln([UV-Filter]/[UV-Filter]₀) versus time(t). Under these conditions, the slope of the regression line is the
observed first-order rate coefficient \( (k_{\text{obs}}) \) of the analyte as described by the following equation.

\[
\ln \left( \frac{[\text{UVF}]}{[\text{UVF}]_0} \right) = -k_{\text{obs}} t \tag{4.1}
\]

Both OXY and DiOXY exhibited first-order dependency with respect to itself in the presence of excess aqueous chlorine. Figures 4.1 and 4.2 show the first order observed loss of OXY and DiOXY at pH=9.5 and 8, respectively, and \([\text{Cl}_2]_T = 10, 25, 50,\) and 75 \( \mu \text{M}. \) The first-order rate coefficients for the various conditions were determined from the slopes of the regression lines displayed in the appendix figures A.1-A.12.

The reaction order with respect to aqueous chlorine was determined by plotting the log of the observed first-order rate coefficients versus the log of the initial aqueous chlorine concentration (Figures 4.3, 4.4, Appendix Figures A.13-A.24). As has been observed in previous work with anthropogenic chemicals in the presence of aqueous chlorine (Duirk & Collette, 2006), the slope of the regression line indicates the reaction order, and was approximately 1 at pH 8 and over the entire pH range studied for both OXY and DiOXY, figures 4.3 and 4.4 respectively. The apparent loss of OXY and DiOXY in the presence of aqueous chlorine at a specific pH can then be described by the following rate expression:

\[
\frac{d[\text{UVF}]}{dt} = -k_{\text{app}}[\text{UVF}]_T[\text{HOCl}]_T \tag{4.2}
\]

where \( k_{\text{app}} \) is the apparent second order rate coefficient at a given pH, and UVF refers to either OXY or DiOXY.
Figure 4.1 Observed first-order rate of OXY loss in the presence of aqueous chlorine at pH 7.0: $[\text{OXY}]_0 = 1.0 \ \mu\text{M}$, $[\text{CO}_3]^T = 10 \ \text{mM}$, and temperature $= 25\pm1 ^\circ\text{C}$. 

The graph shows the relationship between the natural logarithm of the concentration of OXY over time at different chlorine concentrations ($[\text{Cl}_2]^T = 10, 25, 50, 75 \ \mu\text{M}$). The data points and lines indicate a first-order reaction pattern.
Figure 4.2  Observed first-order rate of DiOXY loss in the presence of aqueous chlorine at pH 8.0: $[\text{DiOXY}]_0 = 1.0 \, \mu\text{M}$, $[\text{CO}_3]_T = 10 \, \text{mM}$, and temperature $= 25\pm1 \, ^\circ\text{C}$.
Figure 4.3 The reaction order of aqueous chlorine with OXY at pH 8.0. $[\text{OXY}]_0 = 1.0 \, \mu\text{M}$, $[\text{PO}_4]_T = 10 \, \text{mM}$, temperature $= 25 \pm 1 \, ^\circ\text{C}$, and $[\text{Cl}_2]_T = 10-75 \, \mu\text{M}$. 
Figure 4.4 The reaction order of aqueous chlorine with DiOXY at pH 8.0. \([\text{DiOXY}]_0 = 1.0 \ \mu\text{M}, [\text{PO}_4]_T = 10 \ \text{mM}, \text{temperature} = 25 \pm 1 ^\circ\text{C}, \text{and} [\text{Cl}_2]_T = 10-75 \ \mu\text{M}.\]

The \(k_{\text{app}}\) at each pH was determined by plotting \(k_{\text{obs}}\) versus the total aqueous chlorine (Figures 4.5, 4.6), which \(k_{\text{obs}}\) increased linearly with increasing chlorine concentration at pH 8.0 for both OXY and DiOXY. At each pH investigated, the observed rate of loss increased linearly with increasing aqueous chlorine concentration, Figures A.25-A.35 in the appendix. The \(k_{\text{app}}\) for OXY increase as pH increases from pH 6 to pH 9 and then decrease as pH increases above pH 9 (Figure 4.7). For DiOXY, the same overall trend is observed, however the apparent reaction rates begin to decrease at pH 8 (Figure 4.8).
Apparent second-order rate coefficients for OXY in the presence of aqueous chlorine at pH 8.0 and 10.0: \([\text{OXY}]_0 = 1.0 \mu\text{M}, \text{Buffer} = 10 \text{ mM}, \text{temperature} = 25 \pm 1 ^\circ\text{C}, \text{and } [\text{Cl}_2]_T = 0-75 \mu\text{M}.\) Error bars represent 95% confidence intervals.
Figure 4.6  Apparent second-order rate coefficient for DiOXY in the presence of aqueous chlorine at pH 9.0 and 9.5: $[\text{DiOXY}]_0 = 1.0 \, \mu\text{M}$, Buffer = 10 mM, temperature = 25 ± 1 °C, and $[\text{Cl}_2]_T = 0-75 \, \mu\text{M}$. Error bars represent 95% confidence intervals.
Figure 4.7  The pH dependence of $k_{\text{app}}$ for the loss of OXY in the presence of aqueous chlorine: $[\text{OXY}]_0 = 1.0 \, \mu\text{M}$, $[\text{Buffer}] = 10 \, \text{mM}$, temperature $= 25 \pm 1 ^\circ\text{C}$, and $[\text{Cl}_2] = 10$, 25, 50, and 75 $\mu\text{M}$. Error bars represent 95% confidence intervals.
The pH dependency of the reaction of UV-filters does not allow for simple regression techniques to determine intrinsic rate coefficients ($k_{\text{int}}$) describing the reactions of aqueous chlorine and either OXY or DiOXY. Therefore, a kinetic model was developed for the reaction of OXY and DiOXY with aqueous chlorine using Scientist (Micromath, St Louis, MO) and Sigmaplot (Systat Software, San Jose, CA). The apparent rate coefficient exhibits a minimum at pH 6 and pH 11, and a maximum at pH 8-9 for DiOXY and OXY respectively. The shape of the rate profile can partially be explained by the differing reactivities of the ionized and un-ionized forms of the UV-

4.2 Kinetic Model of the degradation of UV-Filters with aqueous chlorine

The pH dependence of $k_{\text{app}}$ for the loss of DiOXY in the presence of aqueous chlorine: [DiOXY]$_0$ = 1.0 µM, [Buffer]$_T$ = 10 mM, temperature = 25±1 °C, and [Cl$_2$]$_T$ = 10, 25, 50, and 75 µM. Error bars represent 95% confidence interval.

Figure 4.8 The pH dependence of $k_{\text{app}}$ for the loss of DiOXY in the presence of aqueous chlorine: [DiOXY]$_0$ = 1.0 µM, [Buffer]$_T$ = 10 mM, temperature = 25±1 °C, and [Cl$_2$]$_T$ = 10, 25, 50, and 75 µM. Error bars represent 95% confidence interval.

4.2 Kinetic Model of the degradation of UV-Filters with aqueous chlorine

The pH dependency of the reaction of UV-filters does not allow for simple regression techniques to determine intrinsic rate coefficients ($k_{\text{int}}$) describing the reactions of aqueous chlorine and either OXY or DiOXY. Therefore, a kinetic model was developed for the reaction of OXY and DiOXY with aqueous chlorine using Scientist (Micromath, St Louis, MO) and Sigmaplot (Systat Software, San Jose, CA). The apparent rate coefficient exhibits a minimum at pH 6 and pH 11, and a maximum at pH 8-9 for DiOXY and OXY respectively. The shape of the rate profile can partially be explained by the differing reactivities of the ionized and un-ionized forms of the UV-
filter substrates. Phenolate species are more susceptible to electrophilic substitution than the parent phenol species (Rebenne, et al., 1996). HOCl is the dominant reactive aqueous chlorine species for the majority of anthropogenic micropollutants due to its oxidizing potential and the polarity of the Cl-O bond (Cl$^\delta+$→OH$^\delta-$), allowing HOCl to react with organic molecules via an electrophilic substitution reaction (Deborde & von Gunten, 2008; Edwards & Pearson, 1961). The maximum in the $k_{app}$ profiles can then be explained if HOCl is the main reactive species in solution and the reactivity of OCl$^-$ is negligible.

The mechanism proposed by Rebenne for the aqueous chlorination of dihydroxybenzenes was adapted to develop a model for the degradation of UV-filters by aqueous chlorine (1996). The rate expression for the degradation of UV-filters in the presence of aqueous chlorine was developed from the following elemental stoichiometric equations that incorporate the speciation for both aqueous chlorine and UV-Filter (equations 4.3-4.11):

$$HOCl \rightleftharpoons OCl^- + H^+ \quad \text{pKa} = 7.5 \quad (4.3)$$

**Oxybenzone**

$$OXY(OH) \rightleftharpoons OXY(O^-) + H^+ \quad \text{pKa} = 10.2 \quad (4.4)$$

$$OXY(OH) + HOCl \rightarrow \text{products} \quad \text{(slow)} \quad (4.5)$$

$$OXY(O^-) + HOCl \rightarrow \text{products} \quad \text{(fast)} \quad (4.6)$$

**Dioxybenzone**

$$\text{DiOXY(OH)}_2 \rightleftharpoons \text{diOXY(OH)O^-} + H^+ \quad \text{pKa} = 9.5 \quad (4.7)$$

$$\text{DiOXY(OH)}O^- \rightleftharpoons \text{diOXY(O^-)}_2 + H^+ \quad \text{pKa} = 11.3 \quad (4.8)$$

$$\text{DiOXY(OH)}_2 + HOCl \rightarrow \text{products} \quad \text{(slow)} \quad (4.9)$$
DiOXY(OH)O’ + HOCl → products \( (fast) \) \( (4.10) \)

DiOXY(O’)\(_2\) + HOCl → products \( (fast) \) \( (4.11) \)

The resulting general rate expressions for OXY and DiOXY for the proposed reaction mechanism are:

\[
\begin{align*}
- \frac{d[\text{OXY(OH)}]}{dt} &= k_1[\text{OXY(OH)}][\text{HOCl}] + k_2[\text{OXY(O}^-)][\text{HOCl}] \quad (4.12) \\
- \frac{d[\text{DiOXY(OH)}_2]}{dt} &= k_1[\text{DiOXY(OH)}_2][\text{HOCl}] + k_2[\text{DiOXY(OH)}O^-][\text{HOCl}] + k_3[\text{DiOXY(OH)}_2][\text{HOCl}] + k_4[\text{DiOXY(OH)}][\text{HOCl}] \quad (4.13)
\end{align*}
\]

By introducing the following chemical species mass balance equations

\[
\begin{align*}
[\text{OXY(OH)}]_T &= [\text{OXY(OH)}] + [\text{OXY(O}^-)] \quad (4.14) \\
[\text{DiOXY(OH)}_2]_T &= [\text{DiOXY(OH)}_2] + [\text{DiOXY(OH)}O^-] + [\text{DiOXY(O}^-)]_2 \quad (4.15) \\
[\text{Cl}_2]_T &= [\text{HOCl}] + [\text{OCl}^-] \quad (4.16)
\end{align*}
\]

where \( \alpha_i^{\text{OXY}} \) is the speciation coefficient of OXY substrate species, with \( i = 0 \) or 1, for OXY(OH) and OXY(O’\(^-\)) respectively, \( \alpha_i^{\text{di}} \) is the ionization fraction of DiOXY substrate species with \( i = 0, 1, \) or 2, for DiOXY(OH)\(_2\), DiOXY(OH)O’\(^-\), and DiOXY(O’\(^-\))\(_2\), and \( \alpha_i^{\text{Cl}} \) is the ionization fraction for hypochlorous acid with \( i = 0 \) or 1, for HOCl and OCl’\(^-\), respectively, the rate expression can be rewritten as:

\[
\begin{align*}
\nu^{\text{OXY}} &= (k_1 \alpha_0^{\text{OXY}} + k_2 \alpha_1^{\text{OXY}}) \alpha_0^{\text{Cl}} \times [\text{OXY(OH)}]_T[\text{HOCl}]_T \quad (4.17) \\
\nu^{\text{diOXY}} &= (k_1 \alpha_0^{\text{di}} + k_2 \alpha_1^{\text{di}} + k_3 \alpha_2^{\text{di}}) \alpha_0^{\text{Cl}} \times [\text{DiOXY(OH)}_2]_T[\text{HOCl}]_T \quad (4.18)
\end{align*}
\]

Based on eq. 17, the \( k_{\text{app}} \) in eq. 2 can be rewritten for OXY as

\[
k_{\text{app}}^{\text{OXY}} = \frac{(k_1[H^+] + k_2K_a^{\text{OXY}})}{[H^+] + K_a^{\text{OXY}}} \times \frac{[H^+]}{[H^+] + K_a^{\text{Cl}}} \quad (4.19)
\]

and for DiOXY as
The intrinsic constants for OXY, $k_1$ and $k_2$ were fit to the data in figure 4.9 with a non-linear least squares regression and Marquardt-Levenberg solution method, which minimizes the sum squares of the residual error between model predictions and the apparent rate coefficients. The intrinsic constants for DiOXY, $k_1$, $k_2$, and $k_3$ were fit to the data in figure 4.10. Acid dissociation constants were held fixed at the values given in Table 3.1. Fitted rate values for all of the intrinsic rate constants are presented in Table 4.1.

The models developed above were experimentally validated under the following conditions: [UV-filter]$_0$ = 1 µM, [Cl$_2$]$_T$ = 100 µM, pH = 5.50, and temperature = 25±1 °C.

The data from the experimental validation was then compared to the model predictions for the reaction conditions. A reasonably close fit was obtained for OXY when comparing model predictions to the actual data, as shown by the solid line in Figure 4.11, hence the postulated mechanism is consistent with the data. The model results for DiOXY are significantly more rapid than the actual data. This can be explained due to the error in the fit at pH 6, where the model predicts a more rapid $k_{app}$ than the experimental data. At low pH hypochlorous acid transforms to elemental Cl$_2$, the reduced concentration of HOCl due to the formation of Cl$_2$ was not accounted for in this model. This error may continue to be significant at pH less than 6, leading to the error in the model fit, hence the postulated mechanism may be consistent with the data.
Table 4.1 Rate Constants for Proposed Reaction Mechanisms at 25 °C in M$^{-1}$ s$^{-1}$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxybenzone</td>
<td>5.7</td>
<td>4.4×10$^3$</td>
<td>N/A</td>
</tr>
<tr>
<td>DiOXYbenzone</td>
<td>6.9</td>
<td>1.65×10$^3$</td>
<td>10</td>
</tr>
</tbody>
</table>

Source: This study

Figure 4.9  Apparent rate coefficient-pH profile for the reaction of HOCl with OXY at 25 °C. The solid line is a non-linear regression analysis of the sum of the least squares between the observed and predicted results for the $k_1$ and $k_2$ rate coefficients.
Figure 4.10  Apparent rate coefficient-pH profile for the reaction of HOCl with OXY at 25 °C. The solid line is a non-linear regression analysis of the sum of the least squares between the observed and predicted results for the \( k_1 \), \( k_2 \), and \( k_3 \) rate coefficients.
Figure 4.11 OXY degradation model predictions versus experimental data for OXY degradation. Model lines were generated using equation 4.12: \([OXY]_0 = 1 \mu M, [Cl_2]_1 = 100 \mu M, [PO_4]_1 = 10 \text{ mM}, \ \text{pH} = 5.5\) and temperature = 25 ± 1 °C.
Figure 4.12  DiOXY degradation model predictions versus experimental data for DiOXY degradation. Model lines were generated using equation 4.12: $[\text{DiOXY}]_0 = 1 \, \mu\text{M}$, $[\text{Cl}_2]_T = 100 \, \mu\text{M}$, $[\text{PO}_4]_T = 10 \, \text{mM}$, pH = 5.5 and temperature = 25 ± 1 °C
Initial estimates for the pKa of both OXY and DiOXY were obtained from SPARC (University of Georgia, Athens, GA). The estimates were then correlated with data obtained from Gallard and von Gunten (2002), and Deborde, et al. (2004), for confirmation. Gallard and von Gunten studied the reaction of phenols substituted in the ortho- and para- positions with aqueous chlorine. The data obtained in the study showed that reactivity of the phenolate form of the compounds with aqueous chlorine increased with pKₐ. Figure 4.13 shows that in the case of OXY and DiOXY the plot of k_{int} versus pKₐ was in line with the results previously obtained by Gallard and von Gunten.

![Graph showing linear correlation between log(k₂) and pH](image)

**Figure 4.13**  Linear correlation between the log(k₂) and molecule pKa for compounds monitored: (○) in this study and (●) by Gallard and Von Gunten (2002). Dashed lines represent 95% Confidence intervals.
4.3 Transformation Product Identification and Chloroform Formation

4.3.1 Transformation Product Identification

Retention times of the major transformation products from the reaction of OXY and DiOXY with aqueous chlorine are shown in Table 4.2. The transformation products are the result of chlorine substitution reactions at the aromatic rings of both UV-filters. Positions where those replacements occurred was not confirmed experimentally; however considering the structures of parent species (Fig 3.1) and the activation of hydroxyl groups towards electrophilic/substitution reactions, the most probable reaction centers are the carbons in ortho- and para- to the hydroxyl groups of OXY and DiOXY. For both OXY and DiOXY mono- and di- chlorinated transformation products were identified. Benzene was identified as a transformation product of OXY, indicating that ring cleavage occurs following chlorination of the parent UV-filter. Chlorinated methoxyphenols have been identified as possible transformation products of the reaction of aqueous chlorine with OXY in a prior study (Negreiera et al, 2008); these products were not observed, due to the decreased length of time that reactions were monitored when compared to the prior study.

<table>
<thead>
<tr>
<th>UV-Filter</th>
<th>Daughter Product</th>
<th>Retention Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXY</td>
<td>Cl-OXY</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>Cl₂-OXY</td>
<td>32.9</td>
</tr>
<tr>
<td>DiOXY</td>
<td>Cl-DiOXY</td>
<td>34.4</td>
</tr>
<tr>
<td></td>
<td>Cl₂-DiOXY</td>
<td>38.5</td>
</tr>
</tbody>
</table>
4.3.2 Chloroform Formation

The potential for the reaction of OXY and DiOXY to form chloroform (CHCl$_3$) when reacted with excess aqueous chlorine was investigated. Prior studies have shown that chlorinated phenols can act as precursors to chloroform formation (Rule et al, 2005; Gallard & von Gunten, 2002). Experiments were conducted employing a 5× excess of aqueous chlorine and measured CHCl$_3$ production as a function of pH to assess the chloroform formation potential of OXY and DiOXY. Figures 4.14, and 4.15 show that CHCl$_3$ is readily produced when OXY and DiOXY react with aqueous chlorine at pH 6, 8, 9, and 10, after 1 hour. The formation of CHCl$_3$ over 4 hours at pH 6, 8, and 10 is detailed in Figures 4.16 and 4.17.

After 1 hour, 0.16 µM and 0.11 µM concentrations of chloroform had formed at pH 8 for initial OXY and DiOXY concentrations of 10 µM. After 4 hours, 1 µM and 0.19 µM concentrations of chloroform had formed at pH 8 for initial OXY and DiOXY concentrations of 10 µM. The molar yield of chloroform (.016 µm CHCl$_3$/µm OXY, .011 µm CHCl$_3$/µm DiOXY) after one hour is low when compared to the majority of phenolic compounds studied by Gallard and von Gunten (2002). The molar yield of CHCl$_3$ (.019 µm CHCl$_3$/µm DiOXY) with respect to DiOXY is also low when compared to the data from Gallard and von Gunten. With respect to OXY (.1 µm CHCl$_3$/µm OXY), CHCl$_3$ formation is in line with the results obtained by a previous study for phenols (Gallard and von Gunten, 2002).

The increase in CHCl$_3$ formation for OXY when compared to DiOXY after four hours, may be explained by the presence of an additional activated benzene ring on the
DiOXY parent structure. The presence of the second activated benzene ring increases DiOXY’s reactivity towards aqueous chlorine so that additional sites will be chlorinated prior to and post ring cleavage before formation of CHCl₃.

In a previous study, CHCl₃ formation was greatest at circumneutral pH and lower under basic conditions (pH > 8) (Rule et al, 2005). In this study CHCl₃ was formed rapidly at circumneutral pH; however, the molar yields of CHCl₃ were greatest at pH 10, with the exception of OXY over the four hour period. This can be explained by hypochlorite ion acting as a super-nucleophile in solution at pH >8 enhancing the hydrolysis of the ketone linkage in the cleaved compound structure towards successive aqueous chlorine substitutions (Edwards et al, 1961), leading to increased chloroform production via a modified haloform reaction mechanism, similar to the mechanism proposed by Dore, et al (1982).
Figure 4.14 Chloroform formation due to the reaction of aqueous chlorine with OXY at pH 6, 8, 9, and 10: $[\text{OXY}]_0 = 10.0 \ \mu\text{M}$, $[\text{Cl}_2]_T = 50 \ \mu\text{M}$, Buffer = 10 mM, and temperature = $25 \pm 1 ^\circ\text{C}$. 
Figure 4.15 Chloroform formation due to the reaction of aqueous chlorine with OXY at pH 6, 8, 9, and 10: \([\text{OXY}]_0 = 10.0 \text{ µM}, [\text{Cl}_2]_T = 50 \text{ µM}, \text{Buffer} = 10 \text{ mM}, \text{and temperature} = 25 \pm 1^\circ \text{C} \).
Figure 4.16 Chloroform formation due to the reaction of OXY with aqueous chlorine over 4 hours at pH 6, 8, and 10: $[OXY]_0 = 10.0 \, \mu M$, $[Cl_2]_T = 50 \, \mu M$, Buffer = 10 mM, and temperature = $25 \pm 1 \, ^oC$. 
Figure 4.17  Chloroform formation due to the reaction of OXY with aqueous chlorine over 4 hours at pH 6, 8, and 10: $[\text{OXY}]_0 = 10.0 \, \mu\text{M}$, $[\text{Cl}_2]_T = 50 \, \mu\text{M}$, Buffer = 10 mM, and temperature = 25 ±1 °C.
CHAPTER V
SUMMARY AND RECOMMENDATIONS

5.1 Summary

From Chapter 1, Section 2, three objectives were outlined in the introduction. The first objective was to measure the degradation of UV-filters in the presence of aqueous chlorine. The second objective was to develop and evaluate a model that describes UV-filter degradation in the presence of aqueous chlorine. The third objective was to identify the major reaction products due to the reaction of UV-filters and aqueous chlorine. All three of these objectives were met through this study.

UV-filter degradation followed overall first-order kinetics with respect to each reactant. As pH increased, the observed first-order rate of UV-filter degradation increased until pH 8 and pH 9 for DiOXY and OXY, respectively. The observed first-order degradation rate increased with pH due to increasing concentration of the phenolate form of the UV-filters in solution. As pH increased above 8, the observed first-order rate of UV-filter degradation decreased due to speciation of HOCl.

A kinetic model has been developed which incorporated speciation of UV-filters, aqueous chlorine, and pH to predict the $k_{app}$ as a function of pH and chlorine concentration. The model predicted the degradation of OXY in the presence of excess aqueous chlorine reasonably well, indicating that the proposed mechanism is consistent with the data. The model prediction for the degradation of DiOXY in the presence of
excess aqueous chlorine inadequately predicted the DiOXY degradation rate, due to the low accuracy of the model fit to the data at pH lower than 7.

The potential for OXY and DiOXY to form chloroform in the presence of excess aqueous chlorine was assessed. The results indicated that while chloroform formation occurs rapidly, the final yield of chloroform is lower than the class of substituted phenols as a whole with molar yields of chloroform less than .02 µM CHCl$_3$/µM UV-Filter in this study.

5.2 Recommendations

Recommendations for future work include:

1. Perform comprehensive kinetic studies with additional UV-filters and aqueous chlorine to determine reaction rate coefficients for the degradation of UV-filters in the presence of aqueous chlorine.

2. Comprehensively identify UV-filter transformation products to elucidate transformation pathways.

3. Study the chloroform formation potential of additional UV-filters in the presence of aqueous chlorine.

4. The reactivity of UV-filters with aqueous chlorine as a class should be determined. LFERs and QSARs should be constructed to correlate substituent effects and activities of the molecules with intrinsic reactivities.

5. The reactivity of UV-filters with chloramines should be investigated.

6. Perform simulated immersion water studies using multiple UV-filters at different concentrations to determine the effect of variable UV-filter load on degradation of UV-filters in “real-life” situations.
7. Perform kinetic studies with actual sunscreen formulations and aqueous chlorine.

8. Perform chloroform formation potential under conditions not rate-limiting by chlorine concentration.

9. Perform more DiOXY degradation experiments at pH 6 to improve the model fit to the data.
REFERENCES


APPENDICES
APPENDIX A

Observed Degradation Rates for OXY and DiOXY at Various pH

The following equations were used to model the degradation of OXY in the presence of aqueous chlorine from pH 6 – pH 11. The independent and dependent equations are shown as well as the initial conditions.

OXY Degradation in the presence of Aqueous Chlorine:

Independent Variables: pH

Dependent Variables: \( k_{\text{app}} \)

Parameters: \( k_1, k_2 \)

\[
\begin{align*}
aO_1 &= \frac{H}{(H+KO)} \quad \text{‘OXY(OH) Conc.} \\
aO_2 &= \frac{KO}{(H+KO)} \quad \text{‘OXY(O') Conc.} \\
aC &= \frac{H}{(H+KC)} \quad \text{‘HOCl Conc.} \\
KO &= 6.31\times10^{-11} \quad \text{‘OXY pKa=10.20} \\
KC &= 2.88\times10^{-8} \quad \text{‘HOCl pKa=7.54} \\
H &= 10^{-x} \quad \text{‘H^+ Conc.} \\
f &= a\exp(-0.5\times((aC\times(aO1\timesK1+aO2\timesK2)-c)/b)^2) \\
\text{fit } f \text{ to } y
\end{align*}
\]

Initial Conditions:

\( k_1 = 1 \quad \text{‘intrinsic coefficient for reaction of OXY(OH) and HOCl} \)
The following equations were used to model the degradation of DiOXY in the presence of aqueous chlorine from pH 6 - pH 11. The independent and dependent equations are shown as well as the initial conditions.

DiOXY Degradation in the presence of Aqueous Chlorine:

Independent Variables: pH
Dependent Variables: \( k_{app} \)
Parameters: \( k_1, k_2, k_3 \)

\( KD_1 = 3.16e-10 \) ‘DiOXY pKa\(_1\)=9.30
\( KD_2 = 5.01e-12 \) ‘DiOXY pKa\(_2\)=10.20
\( KC = 2.88e-08 \) ‘HOCl pKa=7.50

\( a_{D0} = H^2/(H^2+H*KD1+KD1*KD2) \) ‘Diox(OH)\(_2\) Conc.
\( a_{D1} = (H*KD1)/(H^2+H*KD1+KD1*KD2) \) ‘Diox(OH)O Conc.
\( a_{D2} = (KD1*KD2)/(H^2+H*KD1+KD1*KD2) \) ‘Diox(O)\(_2\) Conc.
\( a_{C} = H/(H+KC) \) ‘HOCl Conc.

\( H = 10^{-x} \) ‘\( \text{H}^+ \) Conc.

\( f = a*\exp(-.5*((a_C*(a_{D0}*K1+a_{D1}*K2+a_{D2}*K3)-c)/b)^2) \)

fit \( f \) to \( y \)

Initial Conditions:
\( k_1 = 1 \) ‘intrinsic coefficient for reaction of DiOXY(OH)\(_2\) and HOCl
\[ k_2 = 1 \quad \text{‘intrinsic coefficient for reaction of DiOXY(OH)O’ and HOCl} \]

\[ k_3 = 1 \quad \text{‘intrinsic coefficient for reaction of DiOXY(O’)}_2 \text{ and HOCl} \]
APPENDIX B

Observed Degradation Rates for OXY and DiOXY over the pH Range 6-11

Figure A.1  Observed first-order rate of OXY loss in the presence of aqueous chlorine at pH 6.0: $[\text{OXY}]_0 = 1.0 \, \mu\text{M}$, $[\text{PO}_4^2-]_T = 10 \, \text{mM}$, and temperature $= 25 \pm 1 \, ^\circ\text{C}$.
Figure A.2 Observed first-order rate of OXY loss in the presence of aqueous chlorine at pH 8.0: $[\text{OXY}]_0 = 1.0 \ \mu\text{M}$, $[\text{PO}_4]_T = 10 \ \text{mM}$, and temperature $= 25 \pm 1 \ ^\circ\text{C}$.
Figure A.3  Observed first-order rate of OXY loss in the presence of aqueous chlorine at pH 9.0: [OXY]₀ = 1.0 µM, [CO₃]_T = 10 mM, and temperature = 25±1 °C.
Figure A.4  Observed first-order rate of OXY loss in the presence of aqueous chlorine at pH 9.5: \([\text{OXY}]_0 = 1.0 \, \mu\text{M}, [\text{CO}_3]_T = 10 \, \text{mM}, \text{and temperature} = 25\pm1^\circ\text{C}.

Figure A.5  Observed first-order rate of OXY loss in the presence of aqueous chlorine at pH 10.0: \([\text{OXY}]_0 = 1.0 \text{ µM}, [\text{CO}_3]^T = 10 \text{ mM}, \text{ and temperature} = 25\pm1 \degree \text{C}.\)
Figure A.6 Observed first-order rate of OXY loss in the presence of aqueous chlorine at pH 11.0: \([\text{OXY}]_0 = 1.0 \mu\text{M}, [\text{CO}_3]^T = 10 \text{ mM}, \text{and temperature} = 25\pm1 \degree\text{C}.\)

\[
\ln\left(\frac{[\text{OXY}]}{[\text{OXY}]_0}\right) = -kT_t t
\]
Figure A.7 Observed first-order rate of DiOXY loss in the presence of aqueous chlorine at pH 6.0: [OXY]₀ = 1.0 µM, [PO₄]ₜ = 10 mM, and temperature = 25±1 °C.
Figure A.8 Observed first-order rate of DiOXY loss in the presence of aqueous chlorine at pH 7.0: $[OXY]_0 = 1.0 \mu M$, $[PO_4]_T = 10 \text{ mM}$, and temperature $= 25 \pm 1 ^\circ C$. 

\[ \ln \left( \frac{[\text{DiOXY}]}{[\text{DiOXY}]_0} \right) \]
Figure A.9  Observed first-order rate of DiOXY loss in the presence of aqueous chlorine at pH 9.0: $[\text{OXY}]_0 = 1.0 \, \mu\text{M}$, $[\text{CO}_3]_T = 10 \, \text{mM}$, and temperature $= 25\pm1 \, ^\circ\text{C}$.
Figure A.10  Observed first-order rate of DiOXY loss in the presence of aqueous chlorine at pH 9.5: \( [\text{OXY}]_0 = 1.0 \, \mu\text{M}, [\text{CO}_3]^\text{T} = 10 \, \text{mM}, \) and temperature \( = 25 \pm 1 \, ^\circ\text{C}. \)
Figure A.11  Observed first-order rate of DiOXY loss in the presence of aqueous chlorine at pH 10.0: [OXY]₀ = 1.0 µM, [CO₃]ₜ = 10 mM, and temperature = 25±1 °C.
Figure A.12  Observed first-order rate of DiOXY loss in the presence of aqueous chlorine at pH 11.0: $[\text{OXY}]_0 = 1.0$ µM, $[\text{CO}_3]^T = 10$ mM, and temperature $= 25\pm1$ °C.
APPENDIX C

Reaction Order of Aqueous Chlorine with OXY and DiOXY over the pH Range 6-11

Figure A.13  The reaction order of aqueous chlorine with OXY at pH 6.0. \([\text{OXY}]_0 = 1.0 \mu\text{M}, [\text{PO}_4]_T = 10 \text{ mM}, \text{temperature} = 25 \pm 1 \, ^\circ\text{C}, \text{and} \, [\text{Cl}_2]_T = 10-75 \, \mu\text{M}.\)
Figure A.14 The reaction order of aqueous chlorine with OXY at pH 7.0. \([\text{OXY}]_0 = 1.0 \, \mu\text{M}, [\text{PO}_4]_T = 10 \, \text{mM}, \text{temperature} = 25 \pm 1 \, ^\circ\text{C}, \text{and} \, [\text{Cl}_2]_T = 10-75 \, \mu\text{M}.\)

\[ y(x) = 0.956(x) + 2.8786 \]

y(x)=0.956(x)+2.8786
Figure A.15  The reaction order of aqueous chlorine with OXY at pH 9.0.  $[\text{OXY}]_0 = 1.0 \ \mu\text{M}$, $[\text{CO}_3]_T = 10 \ \text{mM}$, temperature $= 25 \pm 1 \ ^\circ\text{C}$, and $[\text{Cl}_2]_T = 10-75 \ \mu\text{M}$. 

$$y(x) = 1.0186(x) + 2.7277$$
Figure A.16 The reaction order of aqueous chlorine with OXY at pH 9.5. \([\text{OXY}]_0 = 1.0 \, \mu\text{M}, [\text{CO}_3^-]_T = 10 \, \text{mM}, \text{temperature} = 25 \pm 1 \, ^\circ\text{C}, \text{and} [\text{Cl}_2]_T = 10^{-75} \, \mu\text{M}.\)
Figure A.17  The reaction order of aqueous chlorine with OXY at pH 10.0.  

\[ [OXY]_0 = 1.0 \text{ µM}, [CO_3]_T = 10 \text{ mM}, \text{ temperature} = 25 \pm 1 \text{ °C}, \text{ and } [Cl_2]_T = 10^{-75} \text{ µM} \]
Figure A.18  The reaction order of aqueous chlorine with OXY at pH 11.0. \([\text{OXY}]_0 = 1.0 \, \mu\text{M}, [\text{CO}_3]_T = 10 \, \text{mM}, \text{temperature} = 25 \pm 1 \, ^\circ\text{C}, \text{and} \, [\text{Cl}_2]_T = 10-75 \, \mu\text{M}.\)

\[ y(x) = 1.0283(x) + 3.9027 \]
Figure A.19 The reaction order of aqueous chlorine with DiOXY at pH 6.0. \([\text{DiOXY}]_0 = 1.0 \ \mu\text{M}, \ [\text{PO}_4^{\text{T}}] = 10 \ \text{mM}, \) temperature = 25 ±1 °C, and \([\text{Cl}_2]_T = 10-75 \ \mu\text{M}.\)
Figure A.20 The reaction order of aqueous chlorine with DiOXY at pH 7.0. $[\text{DiOXY}]_0 = 1.0 \, \mu\text{M}$, $[\text{PO}_4]_T = 10 \, \text{mM}$, temperature $= 25 \pm 1 \, ^\circ\text{C}$, and $[\text{Cl}_2]_T = 10-75 \, \mu\text{M}$.

$y(x) = 1.1700(x) + 3.2627$
Figure A.21 The reaction order of aqueous chlorine with DiOXY at pH 9.0. $[\text{DiOXY}]_0 = 1.0 \mu\text{M}$, $[\text{CO}_3]_T = 10 \text{ mM}$, temperature $= 25 \pm 1 \degree\text{C}$, and $[\text{Cl}_2]_T = 10^{-75} \mu\text{M}$.

\[ y(x) = 1.1195(x) + 2.9193 \]
Figure A.22  The reaction order of aqueous chlorine with DiOXY at pH 9.5.  $[\text{DiOXY}]_0 = 1.0 \ \mu\text{M}$, $[\text{CO}_3]^T = 10 \ \text{mM}$, temperature $= 25 \pm 1 \ ^\circ\text{C}$, and $[\text{Cl}_2]^T = 10^{-75} \ \mu\text{M}$.
Figure A.23 The reaction order of aqueous chlorine with DiOXY at pH 10.0. 
[DiOXY]₀ = 1.0 µM, [CO₃]ᵣ = 10 mM, temperature = 25 ± 1 °C, and [Cl₂]ᵣ = 10-75 µM.

\[ y(x) = 1.1242(x) + 3.6378 \]
Figure A.24 The reaction order of aqueous chlorine with DiOXY at pH 11.0. 
[DiOXY]₀ = 1.0 μM, [CO₃]ᵢₜ = 10 mM, temperature = 25 ± 1 °C, and [Cl₂]ᵢₜ = 10⁻⁷⁵ μM.
APPENDIX D

Apparent Degradation Rates for OXY and DiOXY over the pH Range 6-11

Figure A.25 Apparent second-order rate coefficient for OXY in the presence of aqueous chlorine at pH 6.0: \([\text{OXY}]_0 = 1.0 \, \mu\text{M}, \text{Buffer} = 10 \, \text{mM}, \text{temperature} = 25 \pm 1 \, ^\circ\text{C}, \text{and} [\text{Cl}_2]_T = 0-75 \, \mu\text{M}. \) Error bars represent 95% confidence intervals.
Figure A.26  Apparent second-order rate coefficients for OXY in the presence of aqueous chlorine at pH 7.0: [OXY]₀ = 1.0 µM, Buffer = 10 mM, temperature = 25 ±1 °C, and [Cl₂]ₜ = 0-75 µM. Error bars represent 95% confidence intervals.
Figure A.27  Apparent second-order rate coefficients for OXY in the presence of aqueous chlorine at pH 9.0: [OXY]₀ = 1.0 µM, Buffer = 10 mM, temperature = 25 ± 1 °C, and [Cl₂]₀ = 0-75 µM. Error bars represent 95% confidence intervals.

\[ k_{\text{app}} = 0.0020 \, \mu\text{M}^{-1} \, \text{s}^{-1} \]
\[ y(x) = 0.0020(x) - 0.0007 \]
Figure A.28  Apparent second-order rate coefficients for OXY in the presence of aqueous chlorine at pH 9.5: [OXY]₀ = 1.0 µM, Buffer = 10 mM, temperature = 25 ± 1 °C, and [Cl₂]ₜ = 0-75 µM. Error bars represent 95% confidence intervals.
Figure A.29  Apparent second-order rate coefficients for OXY in the presence of aqueous chlorine at pH 11.0: [OXY]₀ = 1.0 µM, Buffer = 10 mM, temperature = 25 ±1 °C, and [Cl₂]₀ = 0-75 µM. Error bars represent 95% confidence intervals.
Figure A.30  Apparent second-order rate coefficients for DiOXY in the presence of aqueous chlorine at pH 6.0: \([\text{DiOXY}]_0 = 1.0 \, \mu\text{M}, \text{Buffer} = 10 \, \text{mM}, \text{temperature} = 25 \pm 1 \, ^\circ\text{C}, \text{and} \, [\text{Cl}_2]_T = 0-75 \, \mu\text{M}. \) Error bars represent 95% confidence intervals.
Figure A.31  Apparent second-order rate coefficients for DiOXY in the presence of aqueous chlorine at pH 7.0: [DiOXY]₀ = 1.0 µM, Buffer = 10 mM, temperature = 25 ± 1 °C, and [Cl₂]₀ = 0-75 µM. Error bars represent 95% confidence intervals.

\[ k_{\text{app}} = 0.0013 \text{ µM}^{-1} \text{ s}^{-1} \]
\[ y(x) = 0.0013(x) - 0.0048 \]
Figure A.32  Apparent second-order rate coefficients for DiOXY in the presence of aqueous chlorine at pH 8.0: [DiOXY]₀ = 1.0 µM, Buffer = 10 mM, temperature = 25 ±1 °C, and [Cl₂]₀ = 0-75 µM. Error bars represent 95% confidence intervals.
Figure A.33  Apparent second-order rate coefficients for DiOXY in the presence of aqueous chlorine at pH 9.5: \([\text{DiOXY}]_0 = 1.0 \, \mu\text{M}, \text{Buffer} = 10 \, \text{mM}, \text{temperature} = 25 \pm 1 \, ^\circ\text{C}, \text{and } [\text{Cl}_2]_T = 0-75 \, \mu\text{M}. \) Error bars represent 95% confidence intervals.

\[ k_{\text{app}} = 0.001 \, \mu\text{M}^{-1} \, \text{s}^{-1} \]

\[ y(x) = 0.001(x) - 0.0004 \]
Figure A.34  Apparent second-order rate coefficients for DiOXY in the presence of aqueous chlorine at pH 11.0: [DiOXY]₀ = 1.0 µM, Buffer = 10 mM, temperature = 25 ±1 °C, and [Cl₂]ₜ = 0-75 µM. Error bars represent 95% confidence intervals.

\[ k_{\text{app}} = 7.41 \times 10^{-5} \text{µM}^{-1} \text{s}^{-1} \]
\[ y(x) = 7.41 \times 10^{-5}(x) + 0.0002 \]
APPENDIX E

Mass Spectra of UV-Filter Agents

Figure A.35  Mass Spectra of Oxybenzone (CAS: 131-57-7).  Source: Chemstation, Agilent Technologies, Santa Clara, CA.
Figure A.36  Mass Spectra of Dioxybenzene (CAS: 131-53-3). Source: Chemstation, Agilent Technologies, Santa Clara, CA.