ORGANIC NITROGEN REACTIVITY WITH FREE CHLORINE: EFFECTS ON DISINFECTION BY-PRODUCT FORMATION AND POLYAMIDE MEMBRANE STABILITY

by

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Dedicated to My Family

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

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Title: Organic Nitrogen Reactivity with Free Chlorine: Effects on Disinfection By-product Formation and Polyamide Membrane Stability
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Organic nitrogen compounds are important in environmental systems because they are prevalent in natural waters but are also components of polymers within membrane filters that are used for water treatment. In both of these cases, these compounds can be exposed to free chlorine during disinfection, which can trigger a set of reactions that can form a host of different halogenated by-products. When such by-products form during water treatment disinfection, these by-products, known as nitrogen-based disinfection by-products (N-DBPs), can be highly toxic and affect human and ecosystem health. Alternatively, when such reactions occur during membrane filtration, the organic nitrogen compounds, which are embedded within the upper layer polymer structure of the membrane filter, can degrade when free chlorine is applied. Therefore, this research was aimed at exploring the chemistry behind how specific types of organic nitrogen compounds which are found in these applications, such as tertiary amines and amides, react with free chlorine. It particularly focused on assessing the kinetics and by-product formation of these reactions under variable water quality conditions (e.g., pH, halide concentrations, and precursor doses).

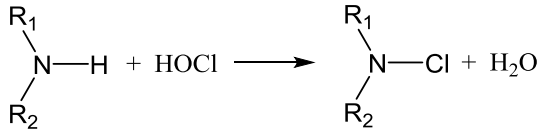
More specifically, in the first phase of this work, the roles of tertiary amines in enhancing disinfection by-product (DBP) formation, such as trihalomethanes (THMs) and haloacetic acids (HAAs), during chlorination of aromatic compounds were studied. The results indicated that in synthetic solutions, chloroform ($CHCl_3$) and trichloroacetic acid (TCAA) were enhanced by up to 20× with tertiary amines at low dose ($[\text{tertiary amine}]_0 = 0.5\times[\text{aromatic compound}]_0$). The enhancement effect was also dependent on the aromatic compound type, tertiary amine type and dose, and water conditions such as pH and bromide concentrations. Thus, THMs and HAAs were predicted to be enhanced when the aromatic compound reacted with $R_3N\text{-}X^+$ (X=Br or Cl) and was not outcompeted by aromatic compound or tertiary amine reaction with free chlorine or bromine alone. In the second phase of this work, the reaction kinetics, by-product formation, and overall

mechanisms of a polyamide-based monomer with chlorine were evaluated under varying water conditions. The current known mechanism, Orton Rearrangement, was reevaluated, and new mechanisms were proposed, where it was found that N-halogenation and ring halogenation were two independent pathways. The ability to choose either pathway was highly dependent on the water quality condition of the aqueous solution. The roles of different chlorinating/brominating agents were also investigated where certain species-specific rate constants were obtained. For the N-halogenation pathway, only chlorination and no bromination occurred in which the reactivity of the chlorinating agents likely decreased such that ClO^->HOCl. However, for the ring halogenation pathway, both chlorination and bromination occurred in which the reactivity of the chlorinating and brominating agents decreased such that Cl_2 >HOCl, and BrCl > BrOCl > Br_2 > Br_2O > HOBr, respectively. Overall, this study suggests that a number of unique reactions can occur for various types of organic nitrogen compounds which: (i) allow them to affect water quality by enhancing DBP formation, (ii) but, when integrated into a polymer matrix used for water treatment, can induce reactions that lead to permanent structural damage of the polymer. In all cases, the extent of these reactions is strongly governed by the surrounding water matrix.

CHAPTER 1. INTRODUCTION

Organic nitrogen compounds are important in environmental applications because they are highly prevalent in both natural and engineered systems. However, in the aqueous phase, their occurrence is closely related to water type and the sources. For example, surface waters typically have higher levels of dissolved organic nitrogen (DON) as compared to other waters (e.g. groundwaters), with a median of 0.37 mg N/L.[1] Their presence in surface waters is primarily due to the soluble microbial products originating from wastewater discharges, bacteria, algae, and the DON that is leached from soil.[1, 2] In addition, wastewater and agricultural impacted waters are also likely to have the highest DON levels due to the proteinaceous materials in the sewage and because of the use of organic or inorganic nitrogen fertilizers.[1] Notably, organic nitrogen can also come from engineered systems, where they can be components of: (i) polyamide thin-film composite membranes, which are the most widely used membrane materials for reverse osmosis (RO) and nanofiltration (NF)[3, 4], and (ii) the popular polymer-based pipe linings (e.g. polyurethane and polyurea)[5], which contain amines and amide functionalities, can undergo degradation in the presence of hydroxyl and hydronium ions, leading to the depolymerization and release of monomers into water supplies.[6]

Therefore, one major focus of this thesis is aimed at exploring the chemistry of how various organic nitrogen compounds behave in the aqueous phase. In addition, one particular area of interest is when these compounds are exposed to chlorine-based disinfectants (e.g. free chlorine or chloramines). Previously, amine functionalities have been known to form nitrogenous disinfection by-products (N-DBPs) during chlorination or chloramination. N-DBPs are important because they affect human and ecosystem health and are often more genotoxic, cytotoxic, or carcinogenic than carbonaceous DBPs.[7-9] Studies have also evaluated the reactivity of amines with free chlorine, where aliphatic amines (primary, secondary and tertiary) exhibited high reactivity and resulted in rapid formation of chloramines.[10] The second-order rate constants were in the range of 10^7-10^8 $M^{-1}s^{-1}$ for primary and secondary amines[11-15], and 10^3-10^4 $M^{-1}s^{-1}$ for tertiary amines[11]. Primary and secondary amines reacted rapidly with HOCl because the reactions were water-assisted, where water molecules were first hydrogen bonded to both nitrogen and HOCl, followed by proton and chlorine transfer and then the formation of N-Cl.[11]



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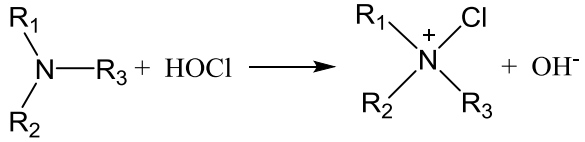
However, the focus of this thesis is centered on tertiary amines because the chlorination chemistry is quite different when compared to primary and secondary amines. This effect resulted from the fact that their reaction with HOCl was not water-assisted due to the absence of hydrogen bonds to the nitrogen. Instead, the chlorine transferred from HOCl to the amine N and formed a positively charged intermediate (eq. 2)[11] which was suggested to have higher chlorination potential than Cl_2.[16, 17] Previous research has also found that this intermediate was responsible for enhancing the degradation of various aromatic compounds (e.g. salicylic acid) [17-19] while in certain cases increasing chlorinated by-product formation.[19] Apart from this though, one aspect of its role that has not yet been evaluated is the potential effect that tertiary amines could have on enhancing DBPs that are formed further downstream. This includes DPBs such as trihalomethanes (THM) and haloacetic acids (HAA). Therefore, one major goal of this work is to explore this further.



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Moreover, the reaction between polyamide membrane surfaces and free chlorine is also of research interest since such membranes are known to react and degrade in the presence of free chlorine, which is applied to control biofouling.[20,21] Previous studies have been conducted to investigate the chlorine uptake of such polyamide surfaces and suggest that its amide functionality played an important role.[22-28] Mechanisms for how this occurs have also been proposed which include (i) N-chlorination at the amide N, where reactivity between the amide group and HOCl to generate N-Cl product was considerably lower than with amines due to the electron-withdrawing effect of the adjacent carbonyl group[10], and (ii) aromatic ring chlorination through direct electrophilic substitution by Cl_2 or indirect ring chlorination through Orton Rearrangement. In Orton Rearrangement, ring chlorination was suggested to proceed through N-chlorination, where the generated N-Cl product was first dechlorinated by hydrochloric acid (HCl) to form the unchlorinated amide and Cl_2, which then reacted to form ring chlorination products.[29, 30] Following this, the membrane failure was then thought to occur through amide link scission.[21, 23, 31]

Interestingly, while this proposed mechanism has persisted in the literature for decades, it is clear that certain aspects of it do not make sense from a water chemistry perspective. In addition, discrepancies also exist when re-visiting the original papers published by Orton and colleagues.[30, 32, 33] Therefore, another major goal of this thesis is to revisit this chemistry and also expand how other water quality conditions (e.g. halides and pH) can affect the degradation process. Halides, such as chloride and bromide, are of particular interest since the waters that are treated by RO and NF contain high concentrations of halides at up to g/L (e.g. seawater and brackish water). [34-36]

Overall, this research is intended to focus on two major efforts related to the chlorination of organic nitrogen compounds, which will evaluate: (i) how tertiary amines enhance regulated DBPs formation (e.g. THM and HAA) during chlorination of aromatic compounds under varying water quality conditions (e.g. pH and bromide concentrations), and (ii) the kinetics and reaction mechanisms involved when select monomers that are representative of the polyamide-based membrane are exposed to free chlorine and the effect that halides have on these processes. In the end, the obtained results will be used to derive a more comprehensive understanding how certain organic nitrogen compounds behave during chlorination in complex water matrices. More specifically with regards to the tertiary amine chemistry, this work is also intended to have important consequences to how regulatory agencies view their presence when assessing the formation of regulated DBPs. Alternatively, better isolating the kinetics and mechanisms of polyamide monomer degradation during chlorination is intended to help identify the key reactive sites that trigger membrane degradation and failure. Such results are then intended to provide guidance on how these polymer surfaces can then be chemically modified by membrane manufacturers to minimize this degradation effect.

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CHAPTER 2. EFFECT OF TERTIARY AMINES ON ENHANCING THM AND HAA FORMATION OVER TIME

2.1 Abstract

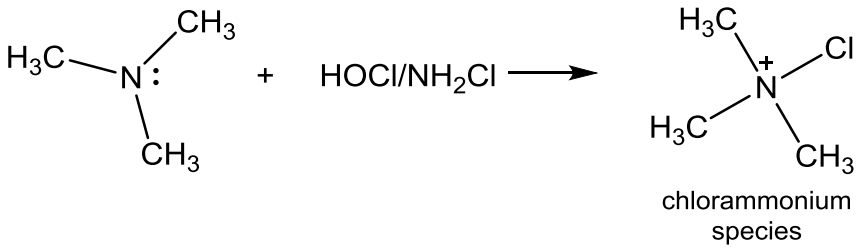
Tertiary amines are prevalent in waters due to anthropogenic inputs and are known to enhance organic compound degradation while increasing disinfection by-product (DBP) formation, via the strong chlorinating agent, $R_3N\text{-}Cl^+$. This study explored how tertiary amines can enhance trihalomethane (THM) and haloacetic acid (HAA) formation when various aromatic compounds (salicylic acid (SA), phenol (PHE) and resorcinol (RES)) are chlorinated over time. Two tertiary amines (2-(N-Morpholino)ethanesulfonic acid (MES) and tributylamine (TBA) were tested. In synthetic solutions, chloroform ($CHCl_3$) and trichloroacetic acid (TCAA) were enhanced by up 20× with tertiary amines, which also occurred at low amine doses ($[\text{tertiary amine}]_0$ = 0.5× $[\text{aromatic compound}]_0$). Enhancement decreased with aromatic compound type where SA > PHE > or ≈ RES for $CHCl_3$ and SA > PHE for TCAA. However, TBA generated up to 2.0 and 7.9% molar yields of TCAA and $CHCl_3$, respectively, with free chlorine alone. Thus, THMs and HAAs were predicted to be enhanced via aromatic compound reaction with $R_3N\text{-}Cl^+$ when not outcompeted by aromatic compound or tertiary amine reaction with free chlorine alone. Overall, low tertiary amine doses can potentially enhance THM and HAA formation when aromatic functional groups with low free chlorine reactivity are chlorinated.

2.2 Introduction

In recent years, tertiary amines have become more prevalent in surface and treated waters because of anthropogenic inputs from pharmaceuticals, personal care products and water treatment additives. They have been detected in such waters at concentrations ranging from ng/L to mg/L[1-3] and include or are constituents of compounds such as trimethylamine (TMA; a constituent of human urine)[4], ranitidine (RAN; an H2-antihistamine drug)[5] and caffeine (a stimulant)[3]. Tertiary amines are also constituents of amine-based polymers (e.g. polyamines) added as coagulant or flocculant aids during water treatment[6] or are present as impurities from anion-exchange resins.[7, 8] Their concentrations have also been recently measured in wastewaters using a newly developed bulk amine assay, although the study was unable to differentiate between tertiary and quaternary

amines.[9] Bulk amine concentrations were detected in the range of 8-150 µg/L when such wastewaters were exposed to primary, secondary and post-ozonation treatment.[9]

Tertiary amines have gained attention since they can form various disinfection by-products (DBPs) (e.g. trichloronitromethane (TCNM) and nitrosodimethylamine (NDMA)) when exposed to free chlorine or chloramines. These DBPs have formed over a wide range of molar yields, and different mechanisms have been proposed to describe their formation based on tertiary amine structure. For tertiary amines such as TMA, molar yields of TCNM and NDMA following chlorination and chloramination were observed at up to 0.012%[10] and 1.2%[11], respectively. Their formation was proposed to occur by initial chlorine transfer from $HOCl/NH_2Cl$ to the tertiary amine N to form the chlorammonium intermediate ($(CH_3)_3N\text{-}Cl^+$; eq. 1).[10, 12] Alternatively, for other tertiary amines such as RAN and 5-dimethylaminomethyl-furfuryl alcohol, where the dimethylamine group is adjacent to a furan ring (a benzyl-like functional group), molar yields of NDMA were reported at up to 89.9% following chloramination.[13, 14] Here, the first step of the proposed reaction mechanism included nucleophilic substitution by NH_2Cl with subsequent loss of chloride (eq. 2).[15, 16]



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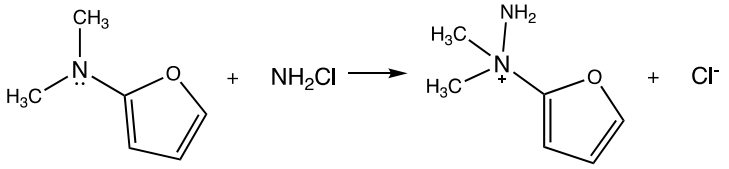

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These proposed reaction mechanisms are important to mention since the chlorammonium species, $R_3N\text{-}Cl^+$ (eq. 1), has also been identified as a catalyst towards enhancing the chlorination of organic compounds.[17-19] This is hypothesized to occur since $R_3N\text{-}Cl^+$ (eq. 1) is predicted to have a larger chlorination potential than molecular chlorine.[19, 20] While previous studies have not directly addressed why this occurs, it is hypothesized to be true given that $R_3N\text{-}Cl^+$ likely chlorinates organic compounds via electrophilic aromatic substitution, a pathway that similarly

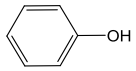
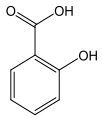
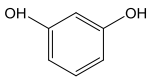
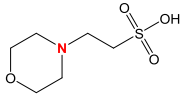
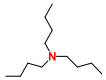
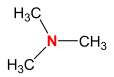
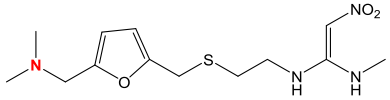
occurs with Cl_2 and HOCl. Previous studies have indicated that the chlorinating potentials of such reactants (e.g. Cl_2 and HOCl) are controlled by the strength of their leaving groups.[21] Similarly, $(CH_3)_3N^+$ which is the expected leaving group for $(CH_3)_3NCl^+$, has been shown to be a stronger leaving group than Cl^- and OH^-, the leaving groups for Cl_2 and HOCl, respectively.[22] Therefore, these effects lead $R_3N\text{-}Cl^+$ to serve as a stronger chlorinating agent than Cl_2 and HOCl. Overall though, only a limited number of studies have evaluated this phenomenon[17-19], but nevertheless, several tertiary amines with a wide range of structural properties (i.e. containing different R groups) have been tested.[17-19] These tertiary amines have significantly enhanced organic compound degradation while in parallel, increasing DBP formation during chlorination. These organic compounds include salicylic acid (SA), where substoichiometric concentrations of tertiary amines including 2-(N-Morpholino)ethanesulfonic acid (MES), quinine, quinuclidine, and TMA, increased SA loss by up to five orders of magnitude while also increasing chlorinated by-product (e.g. 3-chloro- (3-Cl) and 5-chloro- (5-Cl) salicylic acid (SA)) formation.[17, 18] In addition, similar findings were observed for organic compounds such as sorbate and several heterocyclic compounds (e.g., enrofloxacin, flumequine and trimethoprim).[18, 19] These organic compounds were found to degrade at enhanced rates following tertiary amine addition,[17-19] and in certain cases, increase chlorinated by-products formation.[18]

However, it is evident from this body of work that no known studies to date have explored how tertiary amines can enhance DBPs generated from aromatic precursors further downstream. This includes DPBs such as trihalomethanes (THM) and haloacetic acids (HAA) since they are formed from aromatic precursors during chlorination but where their molar yields vary widely depending on aromatic precursor type.[23-28] Some examples include SA, phenol (PHE), and resorcinol (RES) which form chloroform ($CHCl_3$) at 2.1[25], 3-11[23, 27, 29] and 67-95%[23, 26-28] molar yields during chlorination after 20-72 h ($[\text{free chlorine}]_0$ = 5-39 × $[\text{aromatic compound}]_0$ and pH 7-8), respectively. Their molar yields are believed to differ because these compounds bear varying de-activating and activating substituents (structures in Table 2-1).[23, 25-29] Similar observations were also made for HAAs including dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). PHE formed 1.8-4.6 and 35.3-37.1% molar yields for DCAA and TCAA, respectively, whereas RES formed < 10% molar yields of both DCAA and TCAA during chlorination after 24-72 h ($[\text{free chlorine}]_0$ = 10-38 × $[\text{aromatic compound}]_0$ at pH 7-8).[24, 27-29] Given this, it is desired to evaluate

if tertiary amines can further enhance THMs and HAAs from such aromatic compounds given their varied molar yields during chlorination alone.

Therefore, the goal of this work was to evaluate the potential for various tertiary amines to enhance THM ($CHCl_3$) and HAA (MCAA, DCAA, and TCAA) formation following chlorination of various aromatic compounds (SA, PHE, and RES). Two different tertiary amines were evaluated including MES and tributylamine (TBA) due to their various physical and chemical properties (i.e. varied R_1-R_3 functional groups and pK_a values; Table 2-1). Bench-scale experiments were then initiated by exposing both the select aromatic compound and tertiary amine to free chlorine where THM and HAA formation was monitored over time. Overall, these tests were designed to derive a comprehensive understanding of how tertiary amines present in chlorinated waters can enhance THM and HAA formation during water treatment.

Table 2-1. Properties of the aromatic compounds and tertiary amines assessed in this study.

		Structure	pK_a	k_{app} ($M^{-1}s^{-1}$) for the reaction with free chorine at pH 7	$CHCl_3$ molar yields (%) (mole/mole compound)	TCAA molar yields (%) (mole/mole compound)
Model Compounds	PHE		9.99[40]	18±1[23]	3-11[23, 27, 29, a], 6.7[c]	35.3-37.1[24, 29, b], 19[c]
	SA		3.0, 13.4[41]	7.8×10^{-2} [18]	2.1[25, a], 1.7[c]	1.1[c]
	RES		9.4[40]	≈ 4000[42]	67-95[23, 26-28, a], 76-100[c]	<2.0[c], 7.7-8.3[24, 29]
Tertiary Amines	MES		6.1[43]	11.3[18]	0.17-1.1[d]	
	TBA		10.89[44]	5.5[f]	3.1-7.9[d]	0.54-2.0[d]
	TMA[f]		9.8[45]	69[46]	0.12-1.7[d]	
	RAN[f]		8.2[2]	3×10^{3} [47, e]	0.3-13[d]	

[a] $[\text{free chlorine}]_0 = 5\text{-}39 \times [\text{aromatic compound}]_0$ and pH 7-8; [b] $[\text{free chlorine}]_0 = 10\text{-}38 \times [\text{aromatic compound}]_0$ at pH 7-8; [c] This study, $[\text{free chlorine}]_0 = 28 \times [\text{aromatic compound}]_0$ at pH 7.2; [d] This study, $[\text{free chlorine}]_0 = 5.6\text{-}56 \times [\text{tertiary amine}]_0$ at pH 7.2; [e] This reaction rate is the reactivity of free chlorine with the tertiary amine functional group of RAN. The second order rate constant of free chlorine with RAN is 1.4×10^9 at pH 7, and this high reaction rate is attributed to the combined reactivities of the thioether (7×10^8 $M^{-1}s^{-1}$) and acetamidine (5.3×10^8 $M^{-1}s^{-1}$) functional groups of RAN; [f] These two compounds were tested in Chapter 3.

2.3 Materials and Methods

2.3.1 Standards and Reagents

The standards and reagents used for these experiments included: PHE, SA, TBA, and NaOCl (13%$_{w/w}$) which were purchased from Acros Organics, and RES and MES which were purchased from Sigma-Aldrich. A neat solution (>99.8%) of $CHCl_3$ was purchased from Mallinckrodt Chemicals. The EPA 552.2 HAA analytical standard mix was purchased from Supelco and contained bromoacetic acid (MBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chloroacetic acid (MCAA), dibromochloroacetic acid (DBCAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), tribromoacetic acid (TBAA), and trichloroacetic acid (TCAA). Additional individual standards of these HAAs were purchased from either Sigma-Aldrich or AccuStandard and used to optimize the mass spectrometer (MS) detection parameters. These and other chemicals, such as NaOH, $Na_2HPO_4{\cdot}2H_2O$, $NaH_2PO_4{\cdot}H_2O$, MeOH, and acetonitrile (CH_3CN) were of reagent grade or higher and used without further purification. Reagent water (18.2 MΩ-cm) was generated from a Thermo Scientific Barnstead NANOpure water purification system.

2.3.2 Preparation of Chemical and Oxidant Stock Solutions

Various primary stock solutions were prepared at: (i) 30-60 mM PHE, SA and RES in MeOH, (ii) 50 mM TBA or MES in MeOH or water, respectively. Free chlorine stock solutions were measured spectrophotometrically by quantifying OCl^- at 292 nm (ε = 362 $M^{-1}cm^{-1}$).[30]

2.3.3 Experimental Setup

Kinetic experiments were conducted to assess THM and HAA formation over 24 h and at 24 ± 1 °C using batch reactors (capped 22 mL glass vials with septa) under headspace-free conditions. These batch reactors contained synthetic solutions that were buffered at pH 7.2 (10 mM phosphate buffer). The synthetic solutions also contained one aromatic compound which included either SA ($[SA]_0$ = 10 µM), PHE ($[PHE]_0$ = 10 µM), or RES ($[RES]_0$ = 1 µM), in which either no tertiary amine or a tertiary amine, MES or TBA ($[amine]_0$ = 10 or 50 µM), was added. For RES, an 1 µM initial concentration was used since 10 µM yielded up to 10 µM $CHCl_3$ after 10 min of chlorination, which far exceeded the instrument calibration range. Experiments were then initiated by exposing

these solutions to excess free chlorine at 280 µM (19.9 mg-Cl_2/L) for solutions containing SA and PHE, or 28 µM (2.0 mg-Cl_2/L) for solutions containing RES. Control experiments were similar but did not include the aromatic compounds. Samples were then periodically taken to measure the residual free chlorine or were quenched with ascorbic acid (2× [free chlorine]$_0$). The quenched samples were transferred to: (i) 10 mL capped headspace vials for THM analyses (ii) 10 mL capped plastic vials for HAA and MES analyses and (iii) 10 mL plastic capped vials for TBA analysis which also contained H_2SO_4 to drop the pH to 2.0 to prevent amine volatilization. A kinetic experiment to assess the apparent rate constant (k_{app}) for TBA with free chlorine was also performed by exposing a synthetic solution containing 10 µM TBA at pH 7 to 100 µM free chlorine in a capped headspace-free vial. Samples were taken periodically over 6 h and placed in 10 mL plastic capped vials for TBA analysis.

2.3.4 Analytical Methods

THMs were measured by GC-ECD (Agilent 7890B) using headspace injection. Samples (1 mL) were heated/shaken in an agitator for 15 min at 80 °C. A portion of the gas phase (0.5-1 mL) was then injected at 180 °C using a 1:10 to 1:50 split ratio onto a DB-624 (30 m × 0.32 mm × 1.8 µm) column. The oven program was held at 40 °C for 5 min, ramped to 240 °C at 20 °C/min, and then held at 240 °C for 5 min. The method detection limit (MDL) for $CHCl_3$ was 0.061 µM. HAAs were measured by IC/MS/MS in anion mode (Metrohm 940 Professional IC Vario with an Agilent 6420 Triple Quad MS). The HAA analytic method followed a modified approach from the EPA 557 method.[31] The IC was run using an A Supp 7-250/4.0 column at 45 °C and a flow rate of 0.7 mL/min in isocratic mode. The eluent contained 3.2 mM Na_2CO_3/1 mM $NaHCO_3$ with 15%$_{vol}$ acetonitrile (ACN) and was run for 35 min. Tandem MS analysis was conducted using electrospray ionization (ESI) in negative mode. The retention time, parent and product masses, source parameters, fragmentation voltage, collision energy (CE), and cell accelerator voltage (CAV) for each compound are summarized in Table S1 in Appendix. The MDLs for MCAA, DCAA and TCAA were 0.056, 0.020 and 0.013 µM, respectively.

MES was measured by IC/MS in anion mode (Metrohm 940 Professional IC Vario with Agilent 6420 Triple Quad MS). The IC was run in isocratic mode for 38 min using an A Supp 7-250/4.0 column at 45˚C and at a flow rate of 0.7 mL/min. The eluent contained 1.0 mM Na_2CO_3

and 4.0 mM $NaHCO_3$ with 15%$_{vol}$ ACN. The MS analysis was conducted using ESI in negative mode. The single quadrupole was run in scan mode (m/z 50 – 200) in which the parent mass (M-1) of m/z 194.1 was quantified. The retention time, source parameters, fragmentation voltage, and CAV were summarized in Table S1. The MDL for MES was 1.4 µM. TBA was analyzed by IC (Metrohm 940 Professional IC Vario) in cation mode equipped with a C4-150/4.0 column at 30°C. Separation was achieved in isocratic mode over 14 min with a flow rate of 0.9 mL/min. The eluent contained 3.2 mM oxalic acid with 20%$_{vol}$ acetone. The MDL TBA was 0.31 µM.

The residual free chlorine concentration was measured by the DPD spectrophotometric method.[32] However, it was unclear if the measured values also included the $R_3N\text{-}Cl^+$ concentration. This was further verified by reacting MES (50 µM) with a sub-stoichiometric amount of free chlorine ($[\text{free chlorine}]_0 = 0.5 \times [\text{MES}]_0$) for 44 and 30 min, respectively, in which samples were processed by the DPD method. Similarly, it is unclear if the measured residual tertiary amine concentrations were influenced by $R_3N\text{-}Cl^+$ as well. Several experiments were conducted to assess this, as outlined in Appendix Text S1.

2.4 Results and Discussions

Kinetic experiments were used to assess the potential for MES and TBA to enhance THM and HAA formation during the chlorination of SA, PHE, and RES. For these experiments, either no tertiary amine (henceforth referred to as the "no amine control"), MES or TBA was added at an 10 or 50 µM initial concentration. An additional control experiment excluded the aromatic compound (henceforth referred to as the "amine only control"). Overall, the results indicated that $CHCl_3$ and TCAA were the only THMs and HAAs formed above detection limits (d.l.) which was expected given the excess free chlorine applied without bromide. These findings also matched previous results where PHE and RES generated MCAA and DCAA at either very low (< 0.1%) or low (< 10%) molar yields, respectively, under excess free chlorine conditions.[24, 27-29]

Moreover, the term of enhancement will be used when discussing the results. It will be used to relate three types of experiments with each other that include (i) the no amine control, (ii) the amine only control, and (iii) the experiment containing the aromatic compound (AC) and tertiary amine (TA) when exposed to free chlorine (FC) (henceforth referred to as the "AC/TA/FC"

experiment, where different compounds will be substituted in when appropriate). THM or HAA enhancement will then occur when formation from the AC/TA/FC experiment (iii) is larger than the sum of the (i) and (ii) controls. An enhancement factor will also be assessed by dividing the THM or HAA formation from the AC/TA/FC experiment by the no amine control experiment. However, this will only be done when THM or HAA formation from the amine only control is negligible when compared to the AC/TA/FC experiment.

2.4.1 Role of MES

The results with MES indicated that it enhanced $CHCl_3$ and TCAA formation over time under specific experimental conditions (Fig. 2-1). This effect was not a result of MES forming $CHCl_3$ and TCAA directly since neither the 10 nor 50 µM MES only controls formed $CHCl_3$ and TCAA above 10 µg/L or above d.l., respectively (Fig. 2-1). Rather, the observed effects were a result of the combined interaction between the aromatic compound, tertiary amine, and free chlorine where the extent of the enhancement was controlled by the type of aromatic compound added and the amine dose applied. The results with SA first exemplified this effect. Initially, the no MES control (SA alone) generated low $CHCl_3$ and TCAA at 0.17 (1.7% molar yield) and 0.11 (1.1%) µM after 24 h, respectively (Fig. 2-1), which for $CHCl_3$ matched previously observed values (Table 2-1). With MES, $CHCl_3$ increased in formation with increasing MES dose such that 0.79-0.86 µM and 1.6-1.8 µM $CHCl_3$ were generated with 10 and 50 µM MES after 24 h, respectively (Fig. 2-1a). $CHCl_3$ was thus enhanced by a factor of 4.6-5.1× and 9.4-11× with 10 and 50 µM MES, respectively (Fig. 2-1a). This trend was slightly different for TCAA in that 2.0 and 0.98 µM TCAA formed with 10 and 50 µM MES after 24 h and was enhanced by a factor of 18 and 9.0×, respectively (Fig. 2-1c). Thus, TCAA was enhanced with MES but this enhancement decreased when MES increased from 10 to 50 µM (Fig. 2-1c). Their concentrations were also summed together for 10 and 50 µM MES to assess their total potential to be enhanced (Fig. 2-1e). Interestingly, the total $CHCl_3$ and TCAA concentrations began to merge as a total of 2.9 and 2.6 µM were generated with 10 and 50 µM MES with an overall enhancement of a factor of 10 and 9.3× after 24 h, respectively (Fig. 2-1e). Such results demonstrated that increasing MES from 10 to 50 µM led to a partial shift in the $CHCl_3$ and TCAA distribution where $CHCl_3$ was favored to form over TCAA (Fig. 2-1).

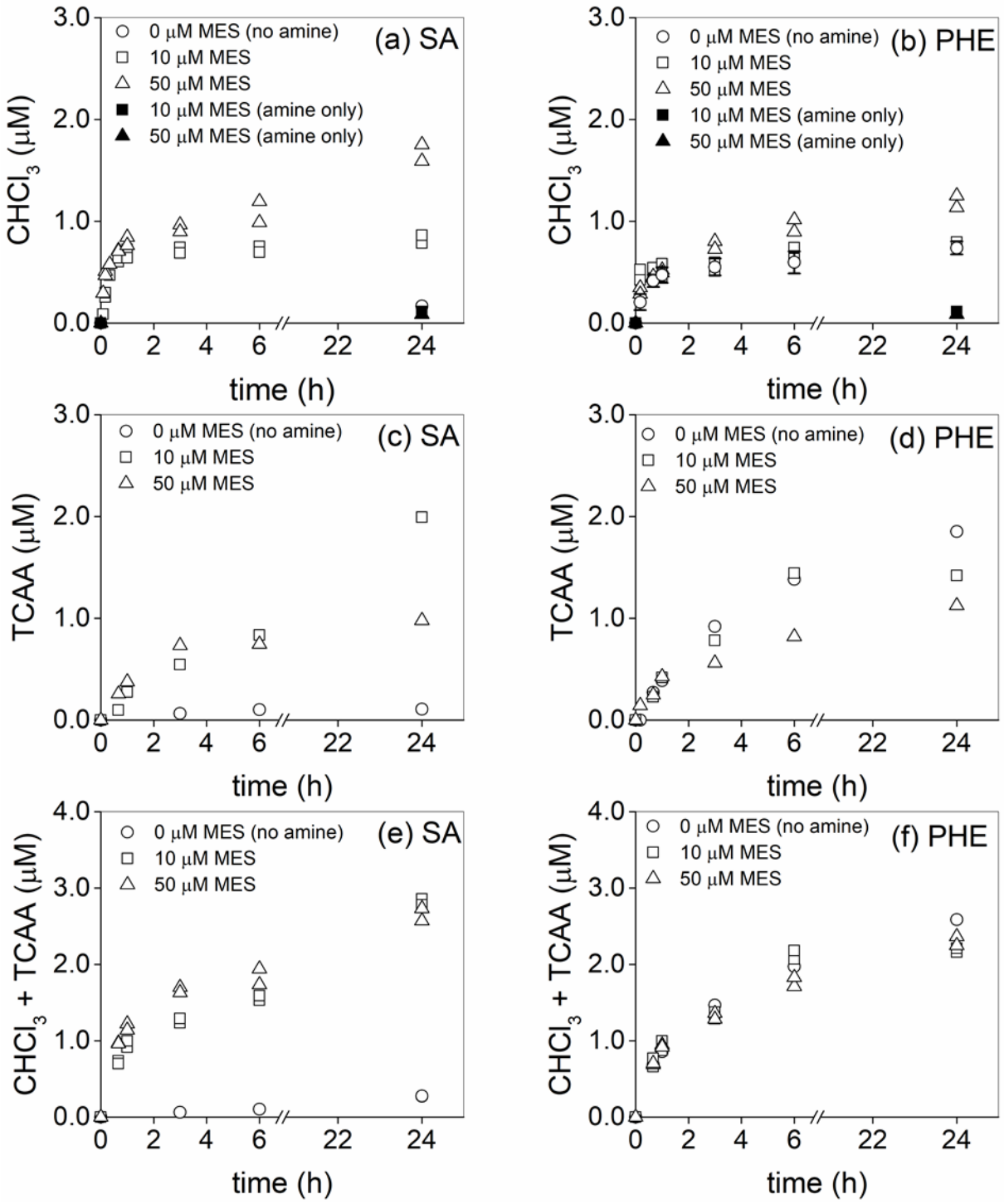
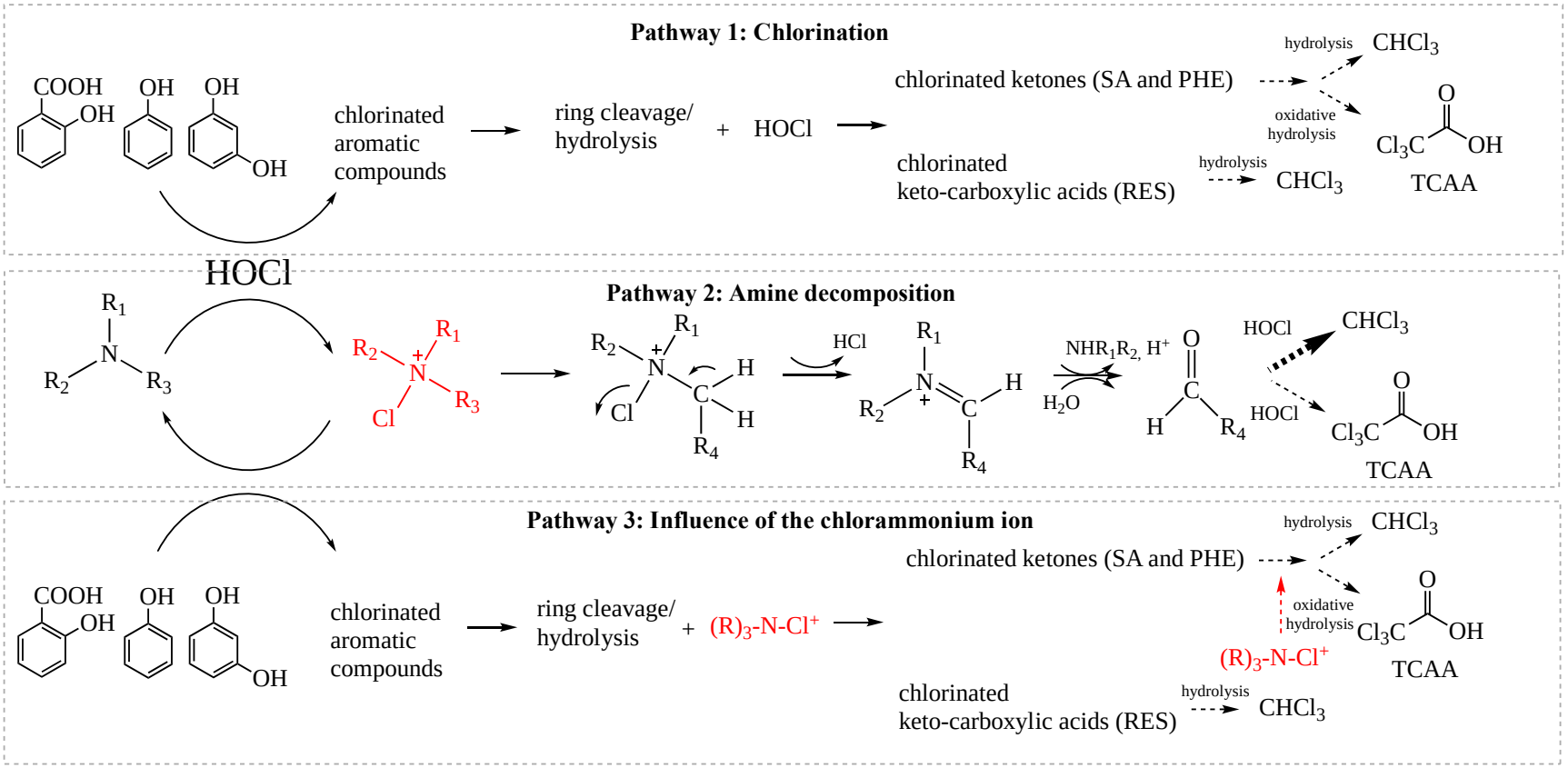


Figure 2-1. Effect of MES on formation of (a, b) $CHCl_3$ (c, d) TCAA and (e, f) the summed formation of $CHCl_3$ and TCAA over 24 h during chlorination of SA and PHE ($[SA \text{ and } PHE]_0$ = 10 μM; $[MES]_0$ = 0, 10 and 50 μM; $[\text{free chlorine}]_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2). Error bars represent the standard deviation of ≥ 3 replicates.

Scheme 2-1. The proposed reaction mechanisms involved in enhancing $CHCl_3$ and TCAA formation from aromatic compounds in the presence of tertiary amines.



Overall, these results can be further explained by a set of proposed reactions (Scheme 2-1). In this scheme, MES enhances $CHCl_3$ and TCAA with SA by first forming the chlorammonium ion ($R_3N\text{-}Cl^+$, MES-Cl^+ for MES) via reaction of the deprotonated MES (Table 2-1 for pK_a) with HOCl (Scheme 2-1). The potential for MES to form MES-Cl^+ under these reaction conditions was initially determined by modeling MES loss with free chlorine alone over 24 h using Kintecus[33] (see Table S2 for model equations). Both 10 and 50 µM MES (plotted as % MES remaining ($[MES]/[MES]_0 \times 100$) were completely consumed in < 1 h (Fig. S2g). These predicted values were also partially validated by the experimental MES values (Fig. S2g). However, these values also represented some percentage of the $R_3N\text{-}Cl^+$ concentration since ascorbic acid increased the residual MES concentration by a factor of 3.5× over 3 h as compared to an unquenched sample (see more details in Text S1). It is hypothesized that ascorbic acid converted MES-Cl^+ back to MES, as similarly observed for other N-chlorinated compounds.[34, 35] These experimental values were then considered more qualitatively as the upper limit of the actual MES concentrations. Given this, MES decreased by at least 50% after 1 h and at least 90% after 6 h for both the MES only controls and the SA/MES/FC experiments (Fig. S2g). These predicted and experimental MES values then indicated that MES-Cl^+ formed fairly rapidly and could assist in enhancing $CHCl_3$ and TCAA formation over 24 h.

Following this, MES-Cl^+ is then hypothesized to serve as a rapid chlorinating agent at multiple points in the reaction pathway to form $CHCl_3$ and TCAA from SA in pathway 3 (Scheme 2-1). Pathway 3 is similar to the reaction pathway proposed when SA reacts with free chlorine alone (pathway 1) which includes several steps: (1) chlorination of the ring to form 3-Cl, 5-Cl and 3,5-diCl SA, as observed previously,[18, 25] (2) subsequent hydrolysis and ring cleavage to form chlorinated ketone moieties that are then further chlorinated. These are a sequence of reaction steps similarly proposed for monohydroxybenzenes (e.g. PHE)[23] and meta-dihydroxybenzenes (e.g. RES)[25, 26] and (3) lastly, a common ketone intermediate is then expected to further undergo hydrolysis to form $CHCl_3$ or undergo oxidative hydrolysis to form TCAA, matching a similar pathway proposed to form $CHCl_3$ and TCAA from chlorinated freshwater.[36]

MES-Cl^+ is then predicted to influence pathway 1 along several points within the reaction mechanism to lead to pathway 3. First, MES-Cl^+ is predicted to enhance chlorination of the

aromatic precursor, which for SA means that 3-Cl, 5-Cl and 3,5-diCl SA are enhanced. A prior study directly observed this effect in the presence of MES and TMA and also found the molar distribution of these products to be unchanged.[18] MES-Cl^+ is also hypothesized to enhance chlorination of the ketone intermediate formed further downstream in pathway 3. This reaction step is important given that this step rather than the initial ring chlorination has been hypothesized to be the rate-limiting step in forming $CHCl_3$ during the chlorination of phenol.[23] Several aspects of the SA/MES/FC results support this possibility. In particular, residual free chlorine was found to be completely consumed within 3 h with 50 µM MES (Fig. S2g) while $CHCl_3$ and TCAA continued to increase in formation after 3 h by 0.76 and 0.24 µM, respectively (Fig. 2-1). These results demonstrated that if ketone chlorination was similarly the rate-limiting step for SA to form $CHCl_3$ and TCAA, MES-Cl^+ would be the only chlorinating agent available. Moreover, MES-Cl^+ must also play a role in the final reaction step in pathway 3 given that when higher MES was added from 10 to 50 µM, TCAA formation shifted to form $CHCl_3$ instead (Fig. 2-1). However, the exact role of MES-Cl^+ in driving this shift still remains unclear, and further research is needed to evaluate the exact mechanisms behind it.

With PHE, the no MES controls (PHE alone) led to 0.74 and 1.9 µM with 7.4% and 19% molar yields for $CHCl_3$ and TCAA after 24 h, respectively (Fig. 2-1), consistent with previous results for $CHCl_3$ but slightly lower for TCAA (Table 2-1). Thus, PHE formed more $CHCl_3$ and TCAA than SA, as also observed previously (Table 2-1). With MES, $CHCl_3$ formation did not increase when 10 µM MES was added and only slightly increased to 1.3 µM when 50 µM MES was added after 24 h (Fig. 2-1b). $CHCl_3$ was then either not enhanced or only slightly enhanced by a factor of 1.8× with 10 and 50 µM MES, respectively (Fig. 2-1b). Alternatively, TCAA decreased in formation to 1.42 and 1.13 µM and thus decreased by a factor of 0.77 and 0.70× when 10 and 50 µM MES were added after 24 h, respectively (Fig. 2-1d). These results were followed by summing the $CHCl_3$ and TCAA concentrations with PHE together. In this case, the values for both MES doses were found to be equivalent to each other at 2.2-2.4 µM which were also equivalent to the no MES control which generated 2.6 µM after 24 h (Fig. 2-1f). Such findings indicated that both MES doses did not enhance the total $CHCl_3$ and TCAA formed but rather shifted the distribution of these products from TCAA to $CHCl_3$, as also done with SA.

The reaction mechanisms in Scheme 2-1 further support the PHE results. This is evident by first noting that $CHCl_3$ and TCAA were either not or only slightly enhanced by MES with PHE This is due to the fact that PHE itself has a stronger potential than SA to form $CHCl_3$ and TCAA via pathway 1 alone. For PHE, pathway 1 is hypothesized to involve these sequential reaction steps: (1) chlorination of the ring to form a wide range of mono-, di-, or tri-chlorinated phenols at the 2,4, and 6- ring positions,[23] (2) ring cleavage and hydrolysis of these chlorophenols to form the ketone intermediate,[23] and (3) further chlorination and either hydrolysis or oxidative hydrolysis to form $CHCl_3$ or TCAA, respectively[23, 27] (Scheme 2-1). Although, while MES-Cl^+ is then expected to form since MES was depleted by 75% in < 2 h in the PHE/MES/FC experiments (Fig. S2h), its role in enhancing $CHCl_3$ and TCAA formation via pathway 3 is minimized given that it is unable to compete with pathway 1. However, the extent by which it is minimized is difficult to ascertain given that the $CHCl_3$ and TCAA formed via pathway 1 may also be reduced due to the increased chlorine demand (Fig. S2) incurred by pathway 3. Nevertheless, MES-Cl^+ is still predicted to influence the last reaction step in pathway 3 given that TCAA was shifted to form $CHCl_3$ instead for the PHE/MES/FC experiments, and did so in the 50 µM MES case in the absence of free chlorine after 6 h (Fig. S2h).

Alternatively, experiments with RES exhibited no enhancement effects (Fig. S3a). The no MES control (RES alone) led to 0.89 µM and < d.l. $CHCl_3$ and TCAA with molar yields of 89% and <1.3% after 24 h, respectively, which were similar to previously reported values (Table 2-1). RES is predicted to form such high $CHCl_3$ molar yields due to the meta- positioning of the two hydroxyl groups (Scheme 2-1).[25, 26] This structure then forms a keto-carboxylic acid intermediate which allows for the enol to be highly stabilized and be highly reactive to free chlorine.[25, 26] Given this mechanism, the results with MES were not surprising as no difference in $CHCl_3$ (Fig. S3) or TCAA formation was observed. These results though also supported Scheme 2-1. First, RES had an even stronger potential than SA and PHE to react with free chlorine alone (k_{app} = 4000 $M^{-1}s^{-1}$ at pH 7; Table 2-1) and generate $CHCl_3$ (Fig. S3) which allowed pathway 1 to play an even more dominant role over pathway 3. Notably, this data did not necessarily indicate that pathway 3 did not occur. MES-Cl^+ did form since at least 40% of MES was consumed within 3 h for the RES/MES/FC experiments (Fig. S2i). However, the MES/HOCl reaction is ~354× slower than the RES/HOCl reaction (Table 2-1) which could not be compensated by the 50× higher initial dose of

MES than RES. While this comparison indicates that MES-Cl^+ could then play a role downstream rather than upstream in pathway 3, it would still only serve to replace a fast reaction pathway (pathway 1) with another one (pathway 3). Moreover, the RES results also validated that the role of MES in enhancing $CHCl_3$ and TCAA did not occur through other pathways outside of Scheme 2-1, such as having the reactive intermediates formed during pathway 1, react with MES to form $CHCl_3$ and TCAA instead. Since the $CHCl_3$ and TCAA concentrations were not enhanced following the RES/MES/FC experiments, it can be concluded that such an alternative pathway was not involved.

2.4.2 Role of TBA

The results with TBA conveyed several parallels to MES, especially with regards to the influence of different aromatic compounds and amine doses. In addition, the TBA results with RES did not generate TCAA at > d.l. concentrations for the RES/TBA/FC experiments. However, the TBA results differed from MES especially due to the fact that the TBA only controls formed significant concentrations of $CHCl_3$ (up to 1.6 µM) and lower concentrations of TCAA (up to 0.27 µM) over 24 h (Fig. 2-2; % molar yields in Table 2-1). This contribution affected how to interpret the role of TBA in particularly enhancing $CHCl_3$ via pathway 3, as described in further detail below.

Thus, the role of TBA led to the following results with regards to forming $CHCl_3$. First, the 10 and 50 µM TBA only controls yielded up to 0.42 and 1.6 µM $CHCl_3$ with 280 µM free chlorine (Fig. 2-2) but yielded only up to 0.07 µM and < d.l. of $CHCl_3$ with 28 µM free chlorine (Fig. S3b) after 24 h, respectively. These observations were not particularly surprising given that other tertiary amines of similar structure (e.g. TMA, triethylamine, and diethylmethylamine) have previously been observed to react with free chlorine.[10, 20] These tertiary amines were found to produce secondary amines and aldehydes at yields that closed the carbon and nitrogen mass balances, and TMA in particular also generated low yields (up to 0.012%) of chloropicrin.[10] The fact that TBA formed up to 4.2% molar yields of $CHCl_3$ (Fig. 2-2) was unique though in that no known previous studies either measured or reported its formation from this or similar tertiary amines.

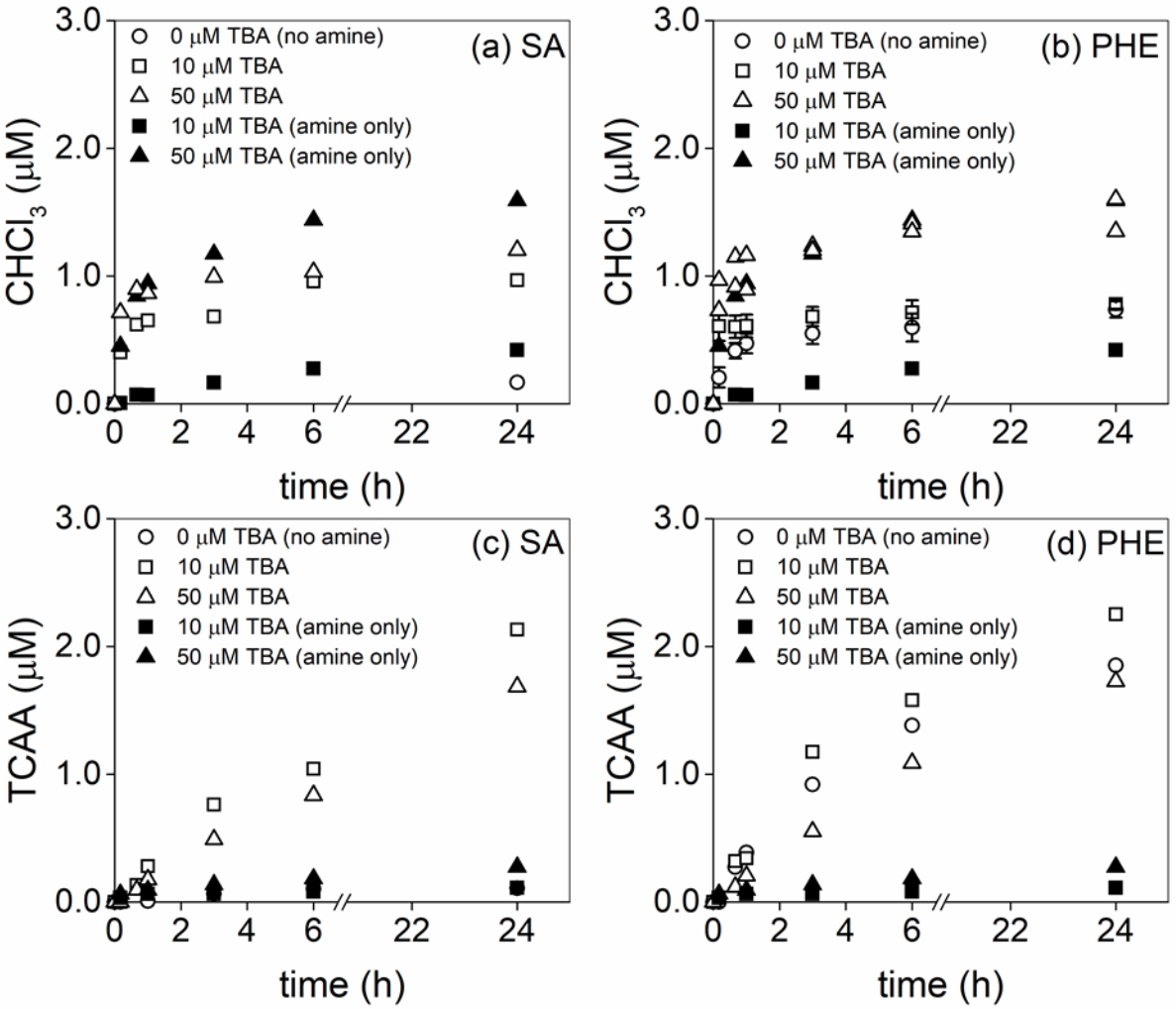


Figure 2-2. Effect of TBA on formation of (a, b) $CHCl_3$ and (c, d) TCAA over 24 h during chlorination of SA and PHE ($[SA \text{ and } PHE]_0$ = 10 μM; $[TBA]_0$ = 0, 10 and 50 μM; $[\text{free chlorine}]_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2). Error bars represent the standard deviation of ≥ 3 replicates.

TBA is hypothesized to form $CHCl_3$ through a proposed mechanism that initially leads to aldehyde formation but where the aldehyde is possibly chlorinated to generate $CHCl_3$ (pathway 2; Scheme 2-1). This pathway is proposed given that it is similar to other proposed pathways where phenolic-based moieties form $CHCl_3$ (e.g. pathway 1). Within this latter pathway, a ketone or di-ketone intermediate is formed which can subsequently become chlorinated at the α-carbon via deprotonation and enol formation and then be further hydrolyzed to form $CHCl_3$.[37] For tertiary amines, it is proposed that the aldehyde formed can undergo a similar sequence of reactions if the aldehyde also contains an α-carbon that can undergo deprotonation and enolization (pathway 2).

Simple aldehydes (e.g. acetaldehyde) can be present in the enol form and in fact bear carbonyl ↔ enol equilibrium constants (e.g. $k_{eq} \sim 5\times10^{-6}$ for acetaldehyde) that fall in between the same values for simple ketones (e.g. $k_{eq} \sim 6\times10^{-8}$ for acetone) and di-ketones (e.g. $k_{eq} = 3.2$ for acetylacetone).[38]

This proposed pathway is also considered plausible given two important findings from this work. First, the residual TBA results confirmed that it is > 90% consumed within 6 h for both the 10 and 50 μM TBA only controls (Fig. S4) which is then followed by $CHCl_3$ formation which increased in concentration over 24 h for both experiments (Fig. 2-2). For this case, the residual TBA concentration was either predicted (via Kintecus; see Table S2) or measured experimentally which represented the upper limit of its concentration (see previous discussions; Fig. S4). Second, $CHCl_3$ formed at up to 13% molar yields when either TBA or ranitidine (RAN) were chlorinated whereas MES and trimethylamine (TMA) only formed up to 1.7% molar yields of $CHCl_3$ over 24 h (Table 2-1; RAN and TMA results will be discussed further Chapter 3). This fact indicated that the structure of the tertiary amines and its alkyl chain substituents (R_1, R_2, and R_3) were critical factors in controlling $CHCl_3$ formation through pathway 2. For TBA and RAN, $CHCl_3$ formation was likely elevated given that the α-carbon moiety on the aldehyde was present. Although, it is clear that the α- and β- carbon bond on the aldehyde formed would also need to be cleaved in order to form acetaldehyde, but the exact nature of how this cleavage occurs remains unclear. For MES, $CHCl_3$ formation was likely inhibited given that aldehyde formation was constrained by the ring to form the imine intermediate. For TMA, this pathway could only form formaldehyde, which lacks the α -carbon needed to further generate $CHCl_3$. Further research is still needed though to derive a more comprehensive understanding of this mechanistic pathway.

Subsequently, for the AC/TBA/FC experiments, the $CHCl_3$ formed was directly compared to the $CHCl_3$ formed when summing the TBA only and no TBA controls (AC alone) experiments together. This procedure was adopted in for two reasons, first to assess how all three pathways (1, 2, and 3) compared to the sum of pathways 1 and 2, but also to see how pathway 3 could compensate for the chlorine loss incurred by pathways 1 and 2. The overall results then indicated that the ability for $CHCl_3$ to be enhanced could be directly linked to the ability for pathway 3 to compete with pathways 1 and 2. One example included a set of "weak" conditions where pathways 1 and 2 were limited by a slow-reacting aromatic compound (i.e. SA) and a low TBA dose (i.e. 10

μM). For these cases, the free chlorine was also only consumed by 10 and 51% for the no TBA and 10 μM TBA alone control, respectively (Fig. S4). Pathway 3 was then able to compete and exhibited enhanced $CHCl_3$ formation. The second example included a set of "strong" conditions where pathways 1 and 2 were dominant given a fast-reacting aromatic compound (i.e. PHE and RES) and a high TBA dose (i.e. 50 μM). For these cases, the free chlorine was consumed by up to 95% after 24 h (Fig. S4). Pathway 3 was then unable to compete and enhance $CHCl_3$ formation. The experiments with SA first demonstrated this effect where $CHCl_3$ formed up to 0.97 μM with 10 μM TBA after 24 h which was a factor of 1.6× greater than the sum of the controls (0.59 μM), indicating that $CHCl_3$ had been slightly enhanced (Fig. 2-2a). Alternatively, $CHCl_3$ formed up to 1.2 μM with 50 μM TBA which was a factor of 0.67× lower than the sum of the controls (1.8 μM) indicating that $CHCl_3$ had not been enhanced but was in fact lowered (Fig. 2-2a). Thus, the 10 μM TBA case minimized pathways 1 and 2 while allowing pathway 3 to play a larger role whereas the 50 μM TBA case led pathway 2 to dominate and lessen the potential for pathway 3 to play a role.

A similar competition between these pathways emerged with PHE. In this case though, pathway 1 had a stronger effect since PHE reacted faster with free chlorine alone (Table 2-1) and yielded higher $CHCl_3$ than SA (Fig. 2-2). Thus, for the PHE/TBA/FC experiments, $CHCl_3$ formed up to 0.78 and 1.6 μM with 10 and 50 μM TBA after 24 h which were a factor 0.65 and 0.70× lower than the sum of their controls (1.2 and 2.3 μM), respectively (Fig. 2-2b). $CHCl_3$ was not enhanced, likely due to the dominance of pathways 1 and 2 over pathway 3. A similar pattern emerged with RES, especially given that it reacted even faster than PHE (Table 2-1) and yielded higher levels of $CHCl_3$ (Fig. S3), allowing pathway 1 to further dominate. The RES/TBA/FC results indicated that $CHCl_3$ slightly decreased in formation by a factor of 0.78 and 0.67× when 10 and 50 μM TBA was added after 24 h, respectively (Fig. S3). This decrease can be attributed to TBA which appeared to incur an additional chlorine demand (Fig. S4) on pathway 1.

The results for TCAA were different given that the 10 and 50 μM TBA only controls formed < 0.27 μM TCAA over 24 h (Fig. 2-2). TCAA is predicted to form from TBA, albeit at lower molar yields, through a similar mechanistic pathway as $CHCl_3$ via pathway 2. In this case, the aldehyde formed following the reaction of TBA with free chlorine is predicted to be further chlorinated and oxidized to form TCAA (Scheme 2-1). This oxidation step is hypothesized to occur

given that aldehydes are known to react with various oxidizing agents (e.g. bromine or O_2) to form carboxylic acids.[39] Although, it remains unclear what specific oxidizing agent is responsible for forming TCAA in this system. For the SA/TBA/FC experiments, TCAA formed at up to 2.1 and 1.7 µM which was a factor 9.5 and 4.5× higher than the sum of the controls at 0.22 and 0.38 µM with 10 and 50 µM TBA, respectively (Fig. 2-2c). These results indicated that pathway 3 had a large effect on enhancing TCAA formation and thus could outcompete pathway 1 (the no TBA control led to < 0.12 µM after 24 h; Fig. 2-2) and 2 given their weak conditions. The increase in TBA from 10 to 50 µM did not further enhance TCAA formation (Fig. 2-2c). One reason this may have occurred is because TCAA formation shifted to form $CHCl_3$ instead when higher TBA concentration was added (10 to 50 µM) (Fig. 2-2c), as similarly observed with MES. Otherwise, this effect could also be related to the higher chlorine demand incurred by 50 µM TBA (Fig. S4) which would then limit the downstream reactions within pathway 3 to occur.

The results differed with PHE largely because pathway 1 played a larger role in forming TCAA since the no TBA control (PHE alone) formed up to 1.9 µM TCAA after 24 h (Fig. 2-2d). Therefore, the TCAA formed from the sum of the controls equaled 2.0 and 2.1 µM with 10 and 50 µM TBA, respectively (Fig. 2-2d). Following this, the PHE/TBA/FC experiment with 10 µM TBA generated up to 2.3 µM TBA after 24 h which was slightly higher than the summed value of 2.0 µM TCAA (Fig. 2-2d). This indicated that TCAA was only slightly enhanced with PHE, likely due to the strength of pathway 1 to outcompete pathway 3. This effect was further exaggerated with 50 µM TBA where the PHE/TBA/FC experiment generated 1.7 µM TCAA whereas the sum of the controls was 2.1 µM TCAA (Fig. 2-2d). This lowered concentration (by a factor of 0.81×) was predicted to occur either because TCAA shifted to form $CHCl_3$ within pathway 3 or because the higher 50 µM TBA dose allowed pathway 2 to dominate, consume more free chlorine, and limit pathway 3 from occurring.

2.5 Conclusions

As tertiary amines become more prevalent in natural waters, the aim of this study was to evaluate how these compounds could serve as catalysts towards enhancing THM and HAA formation during the chlorination of various aromatic compounds (SA, PHE, and RES). The results indicated that $CHCl_3$ and TCAA (the only two THMs and HAAs formed) were enhanced over time

but where the extent of this enhancement was strongly governed by several factors including the type of aromatic compound and tertiary amine added and the tertiary amine dose. $CHCl_3$ and TCAA decreased in enhancement depending on aromatic compound type, following the order where SA > PHE > or ≈ RES and SA > PHE, respectively. In addition, these two tertiary amines enhanced $CHCl_3$ and TCAA formation to varying degrees, but enhancement of up to a factor of 21× also occurred at low doses (< 10 µM; < 0.30 to 1.6 mg/L). Such results indicated that tertiary amine concentrations typically found in natural and treated waters of up to low mg/L (µM) concentrations[1, 2] could potentially enhance THM and HAA formation as well. TBA at up to 50 µM also formed $CHCl_3$ and TCAA at up to 7.9% and 2.0% molar yields, respectively, when chlorinated alone, which served as an alternate pathway to form these compounds than through the proposed catalytic cycle.

Overall, from these results, three major reaction mechanisms were predicted to control THM and HAA formation in the presence of tertiary amines. One of the pathways was hypothesized to involve $R_3N\text{-}Cl^+$, but this pathway could be minimized if the other two pathways, involving the aromatic compound reaction with free chlorine and tertiary amine degradation, were more favorable.

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CHAPTER 3. EFFECT OF TERTIARY AMINE TYPE, DOSE AND WATER QUALITY CONDITIONS ON THM AND HAA ENHANCEMENT

3.1 Abstract

Tertiary amines including MES and TBA have been shown to enhance THM and HAA formation to varied extents during chlorination of PHE, SA and RES, where the enhancement depended on the type of tertiary amine and aromatic compound, and tertiary amine dose. In this study, the types and doses of tertiary amines were further investigated under varied water conditions (e.g. pH and bromide concentration), where in addition to MES and TBA, trimethylamine (TMA) and ranitidine (RAN)) were also tested at varying doses. Moreover, one NOM extract, Suwannee River fulvic acid (SRFA), was exposed to free chlorine with tertiary amine, where THM and HAA formation were analyzed. When exposed to free chlorine, MES and TMA formed little or no THM and HAA, and exhibited similar levels of enhancement effect dependent on aromatic compound type, where SA > PHE ≈ RES for $CHCl_3$ and SA > PHE for TCAA. The enhancement effects were significant for both MES and TMA at low amine dose ($[\text{tertiary amine}]_0 = 0.5\times [\text{aromatic compound}]_0$). However, TBA and RAN generated up to 2.0 and 7.9% molar yields of TCAA and $CHCl_3$, respectively, with free chlorine alone. Both TBA and RAN exhibited enhancement effect at low amine dose, while at high amine dose, enhancement was lost since TBA or RAN either served as a strong $CHCl_3$ source or incurred a high chlorine demand, respectively. With MES, enhancement was maximized at pH 7 while brominated THMs and HAAs were not enhanced upon bromide addition. SRFA exhibited no or limited $CHCl_3$ and TCAA enhancement with MES, respectively, likely due to the presence of aromatic functional groups that strongly reacted with free chlorine alone. Overall, these results could be well explained by the scheme proposed and indicated that waters with low tertiary amine and bromide concentrations can potentially enhance THM and HAA formation when aromatic functional groups with low free chlorine reactivity are chlorinated.

3.2 Introduction

As noted in Chapter 2, tertiary amines can enhance the formation of $CHCl_3$ and TCAA when added to solutions where aromatic compounds are exposed to free chlorine. However, this effect is influenced by several factors including aromatic compound type, tertiary amine type and dose.[7] First, $CHCl_3$ and TCAA formation from aromatic compounds with lower reactivity towards free chlorine were enhanced to a greater extent, where the overall enhancement effect decreased as SA>PHE>RES. Second, the enhancement effect also highly depended on the structures of the tertiary amines. Previous literature observed that when tertiary amines are weak Lewis bases (i.e. a strong Lewis base is able to easily donate the amine nitrogen's electron pair to form R_3N^+-H), no enhancement effect is observed.[5] One example is creatinine (no relevant pK_a for the tertiary amine[9]), which exhibited no enhancement effect under pH 7.0-7.3 during chlorination of SA.[5] Certain tertiary amines that could serve as strong precursors of DBPs when directly exposed to free chlorine also exhibited little enhancement effect, such as TBA, which formed $CHCl_3$ at up to 4.2% molar yields when exposed to free chlorine at pH 7.0.[7] Last, the enhancement effect was also controlled by the tertiary amine dose. For example, when SA was chlorinated, and increasing MES dose lead to different patterns for $CHCl_3$ and TAA formation. For $CHCl_3$, formation increased with increasing MES dose whereas TCAA formation increased substantially at a low amine dose but then decreased as the amine dose increased further.[7]

Therefore, as an extension to the work conducted in Chapter 2, other tertiary amines except MES and TBA were evaluated, including trimethylamine (TMA) and ranitidine (RAN) over a varied amine dose range. TMA and RAN were selected since they have been detected in surface waters and primary effluents of wastewater treatment plant, and shown to be important precursors of NDMA during chloramination.[10, 11] In addition, aside from the aromatic compounds, Suwannee River fulvic acid (SRFA) was also tested since it contains phenolic moieties that can react with free chlorine to form THMs and HAAs.[12, 13] The effect of specific water conditions, including pH and bromide concentrations, on the enhancement effect was also a focus of this work. First, pH affected the species distribution of tertiary amines depending on their pK_a values, which was found to affect the enhancement effect of tertiary amines.[5] Second, Br^- can react with HOCl rapidly to form HOBr, which was hypothesized to react with tertiary amines to form R_3N-Br^+ and enhanced the formation of brominated THM and HAA.

Therefore, the goal of this work was to evaluate the potential for various tertiary amines to enhance THM ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$) and HAA (MCAA, DCAA, TCAA, MBAA, DBAA, TBAA, BCAA, BDCAA, and DBCAA) formation following chlorination of various aromatic compounds (SA, PHE, and RES) and a natural organic matter extract (SRFA). Four different tertiary amines were evaluated including MES, TBA, TMA, and RAN due to their various physical and chemical properties (i.e. varied R_1-R_3 functional groups and pK_a values; Table 2-1) and/or presence in natural or treated waters. Bench-scale experiments were conducted by exposing the select aromatic compound or SRFA and tertiary amine to free chlorine where THM and HAA formation was monitored: (i) under varying tertiary amine doses, (ii) with varying bromide concentrations, or (iii) under different pH conditions. In addition, kinetic experiments were also conducted to expose SRFA to free chlorine in the presence of MES or TBA, as similarly done with the aromatic compounds that were tested in both Chapters 2 and 3. Overall, these experiments were designed to derive a more comprehensive understanding of the enhancement effect of tertiary amines on THMs and HAAs formation during chlorination under various water conditions.

3.3 Materials and Methods

3.3.1 Standards and Reagents

In addition to the standards and reagents used in Chapter 2, other reagents used in these experiments included: TMA (as TMA-HCl), which was purchased from Acros Organics, and RAN which was purchased from Alfa Aesar. The THMs analytical standard mix containing chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) was purchased from AccuStandard. SRFA (Standard II) was purchased from the International Humic Substances Society (IHSS). These and other chemicals, such as NaBr and $Na_2B_4O_7{\cdot}10H_2O$ were of reagent grade or higher and used without further purification.

3.3.2 Preparation of Chemical and Oxidant Stock Solutions

The stock solutions of PHE, SA, RES, MES and TBA were prepared in the same way as described in Chapter 2. In addition, TMA and RAN were prepared at 50 mM in MeOH or 10/90% (v/v) MeOH/water, respectively. SRFA stock solutions were prepared by adding the extract to water and filtering it through an ashed 0.7 μm glass microfiber filter (GF/F; Whatman). The

dissolved organic carbon (DOC) concentrations in these stocks were determined as non-purgeable organic carbon (NPOC) using a total organic carbon analyzer (Shimazu TOC-L). HOBr stock solutions were prepared by reacting 30 mM HOCl/OCl^- with 50 mM bromide at pH 11.0 for 12−24 h resulting in 88-92% molar conversion. The HOBr concentration was determined spectrophotometrically by measuring OBr^- at 329 nm (ε = 332 $M^{-1}cm^{-1}$).[14]

3.3.3 Experimental Setup

Experiments containing a select aromatic compound or SRFA and a tertiary amine were exposed to excess free chlorine for 24 h in order to assess THM and HAA formation as a function of tertiary amine dose, pH, and bromide concentration. The experimental procedure and conditions used were identical to the kinetic experiments, except for the following changes. For the tertiary amine dose experiments, reactions containing SA, PHE, RES, or SRFA were exposed to free chlorine at pH 7.2 but with varying initial doses of MES, TBA, TMA, or RAN ($[amine]_0$= 0 to 50 µM). TMA was measured in the same way as TBA, and samples were also transferred to HPLC vials for RAN analysis. For the varying pH and bromide experiments, only SA and MES were tested, since they previously exhibited the greatest THM and HAA enhancement as compared to the other aromatic compounds and tertiary amines (see later discussions). Three types of experiments were conducted in which synthetic waters contained (i) only SA ($[SA]_0$ = 10 µM) (ii) only MES ($[amine]_0$ = 10 µM) or (iii) both SA ($[SA]_0$ = 10 µM) and MES ($[MES]_0$ = 10 µM). For the pH experiments, these three experiment types were then varied from pH 6 to 9 using 10-50 mM phosphate or borate buffer. For the bromide experiments, these three experiments were held at pH 7.1-7.2 (10 mM phosphate buffer) and either dosed with bromide ($[Br^-]_0$ = 0-100 µM) and then chlorinated or dosed with pre-formed HOBr ($[HOBr]_0$ = 0-100 µM).

3.3.4 Analytical Methods

THMs including $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ were measured using the same analytical method as $CHCl_3$ provided in Chapter 2. The method detection limits (MDLs) for $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ were 0.026, 0.025 and 0.028 µM, respectively. For measuring nine HAAs, the IC was run using an A Supp 7-250/4.0 column at 45 °C and a flow rate of 0.7 mL/min in gradient mode for 30 min with two eluents (eluent A and B). Eluent A contained 3.2 mM Na_2CO_3/1 mM $NaHCO_3$, and eluent B contained 50 mM KOH/7 mM Na_2CO_3. Both eluents

also contained 15%$_{vol}$ ACN. The gradient program was 100% A for 2 min, 35% A/65% B at 4 min, and 5% A/95% B from 7 to 25 min. Tandem MS analysis was conducted using electrospray ionization (ESI) in negative mode. The retention time, parent and product masses, source parameters, fragmentation voltage, collision energy (CE), and cell accelerator voltage (CAV) for each compound are summarized in Table S1 in Appendix (SI). The MDLs for MCAA, MBAA, DCAA, BCAA, DBAA, TCAA, BDCAA, DBCAA and TBAA, were 0.056, 0.059, 0.020, 0.017, 0.010, 0.013, 8.5×10^{-3}, 0.014 and 0.032 µM, respectively.

TMA was measured using the same method as TBA described in Chapter 2, and the MDL for TMA was 0.86 µM. RAN was measured by HPLC with a UV/vis diode-array detector (DAD) (Agilent 1260 Infinity). Separation was achieved using a Supelco C18 (25 cm × 4.6 mm, 5µm) column at 30 °C and at a flow rate of 0.4 mL/min in gradient mode. The mobile phases included 0.1% (v/v) formic acid (solvent A) and ACN (solvent B). The gradient program for RAN was 95% A/5% B for 5 min, ramped to 10% A/90% B at 15 to 17 min, and ramped to and then held at 95% A/5% B from 19 to 20 min. RAN was monitored by UV detection at 315 nm. The MDL for RAN was 0.13 µM.

3.4 Results and Discussions

3.4.1 Effect of Tertiary Amine Dose

MES, TBA, TMA and RAN, were used to assess how amine dose (0 – 50 µM) affected THMs and HAAs enhancement following chlorination after 24 h. Again, $CHCl_3$ and TCAA were the only DBPs that formed at > d.l. Their results were presented by either comparing different aromatic compounds with each other for one tertiary amine (first approach) (Fig. 3-1 and 3-2) or by comparing different tertiary amines with each other for one aromatic compound (second approach) (Fig. S5 and S6). From the first approach, several conclusions can be drawn. First, the role of different aromatic compounds for both MES and TBA at a wider amine dose range similarly matched and further supported the kinetic results discussed previously. For MES, this included the fact that: (i) the MES only controls formed low (< 0.17 µM) $CHCl_3$ (Fig. 3-1a) and < d.l. TCAA concentrations (Fig. 3-2a), (ii) enhancement decreased for the AC/MES/FC experiments according to aromatic compound type where SA > PHE > RES for $CHCl_3$ (Fig. 3-1a) and SA > PHE for

TCAA (Fig. 3-2a), and (iii) for TCAA, its enhancement either dropped by a factor of 0.43× for SA or its concentration was lower than the no MES control for PHE when MES was increased from 5 to 50 μM, respectively (Fig. 3-2a). This decrease was partially (for SA) or fully (for PHE) compensated for by shifting to form $CHCl_3$, as observed when summing the $CHCl_3$ and TCAA formation together as function of MES dose (Fig. S7a). The MES dose profile was notable though in that for SA, $CHCl_3$ and TCAA increased to 0.83 and 2.3 μM with an enhancement factor of 4.6× and 21× with only 5 μM MES, respectively (Fig. 3-1a and 3-2a), indicating that low MES doses can have high enhancement effects.

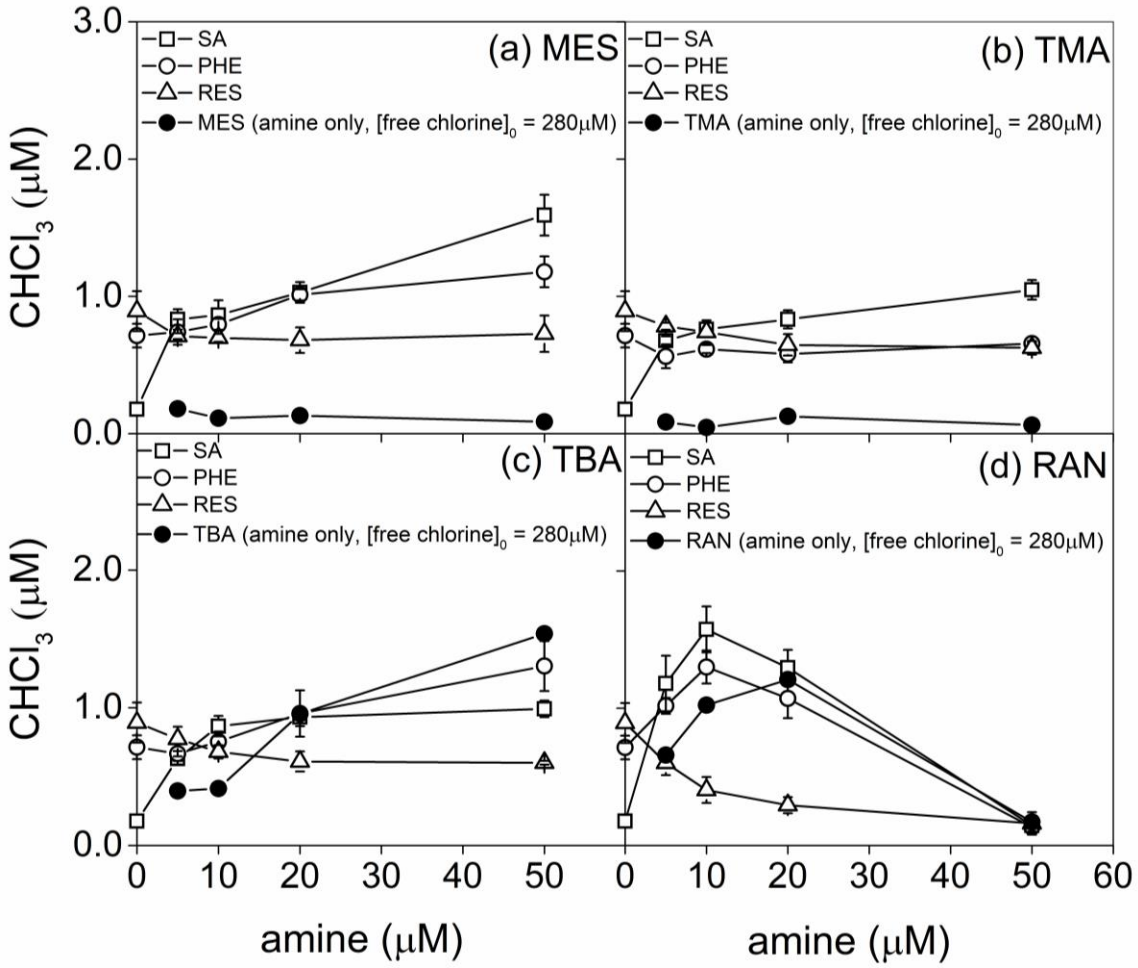

Figure 3-1. Effect of amine dose (0-50 μM) on $CHCl_3$ formation from different aromatic precursors (SA, PHE or RES) when exposed to (a) MES (b) TMA (c) TBA (d) RAN after 24 h of chlorination ($[SA \text{ and } PHE]_0$ = 10 μM; $[RES]_0$ = 1 μM; $[\text{free chlorine}]_0$ = 280 μM (19.9 mg/L-Cl_2) for SA and PHE, or 28 μM (2.0 mg/L- Cl_2) for RES; pH 7.1-7.2). Error bars represent the standard deviation of ≥ 3 replicates.

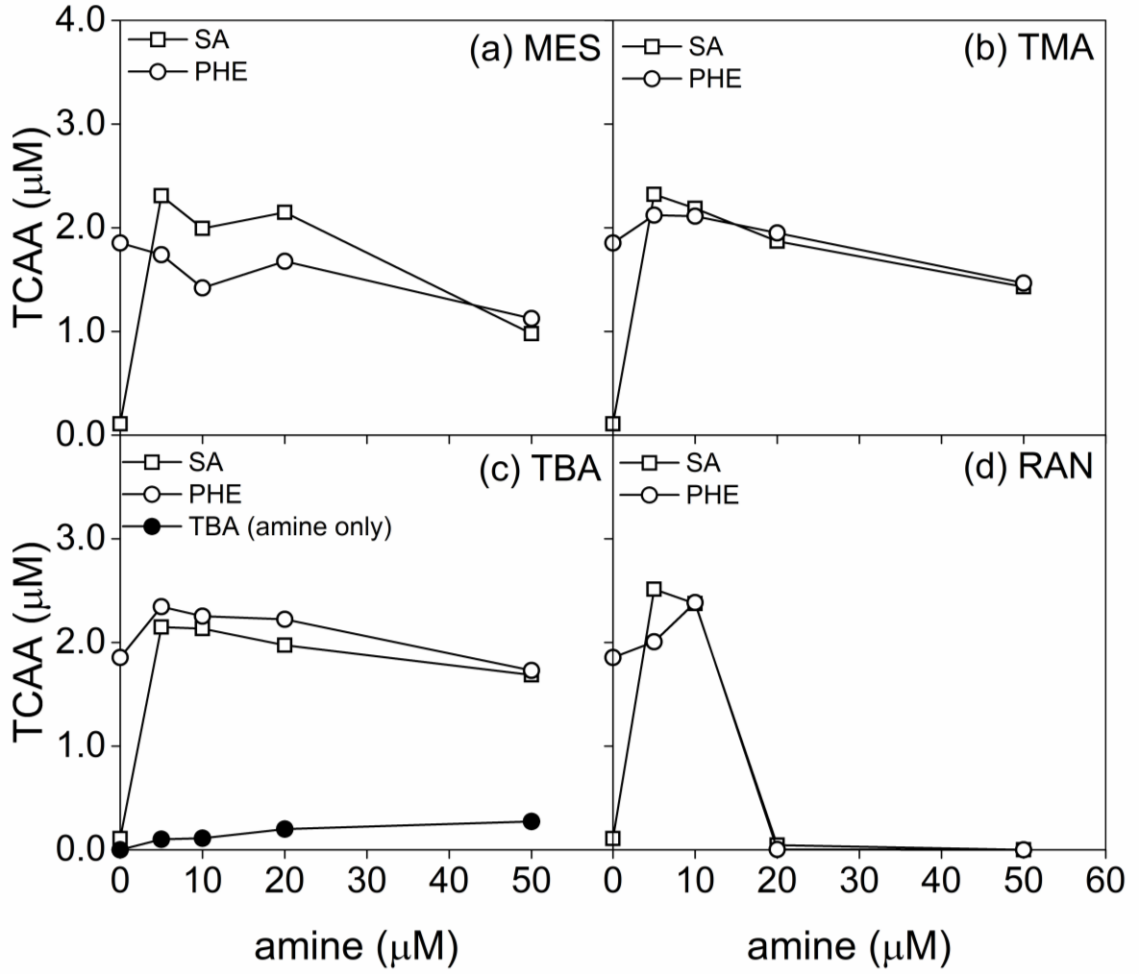

Figure 3-2. Effect of amine doses (0-50 μM) on TCAA formation from different aromatic precursors (SA or PHE) when exposed to (a) MES (b) TMA (c) TBA (d) RAN after 24 h of chlorination ([SA and PHE]$_0$ = 10 μM; [free chlorine]$_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2).

With TBA, previous kinetic data were also matched by the fact that: (i) the TBA only controls formed up to 1.5 μM $CHCl_3$ (Fig. 3-1c) and 0.27 μM TCAA (Fig. 3-2c) at up to 50 μM TBA, (ii) $CHCl_3$ was not enhanced with PHE and RES over 5 to 50 μM TBA but (iii) TCAA was slightly enhanced by a factor of 1.3× for PHE with 5-10 μM TBA but was not enhanced when 50 μM TBA was added (Fig. 3-2c). Interesting, the dose profile with SA found that $CHCl_3$ was enhanced at low amine doses (< 10 μM) by a factor of 4.8× but was not further enhanced once > 20 μM TBA was added (Fig. 3-1c). This pattern differed for TCAA since it was strongly enhanced by a factor of 20× with 5 μM TBA but then dropped so that TCAA was only enhanced by 16× with 50 μM TBA (Fig. 3-2c). Overall, such results again reflected two key points. First, the aromatic compound type where enhancement decreased according to SA > PHE > RES, continued to control $CHCl_3$ and

TCAA enhancement over the 5 to 50 µM TBA dose range, due to the competing importance of pathway 1 over 3. Second, TBA dose continued to control $CHCl_3$ and TCAA enhancement for reasons similarly outlined in the kinetic section. Here, $CHCl_3$ decreased in enhancement when TBA was > 10 µM with SA while TCAA also decreased in enhancement when TBA was > 5 µM with SA and PHE. Finally, these results demonstrated that low TBA doses (e.g. 5 µM) can trigger substantial $CHCl_3$ and TCAA enhancement.

Following this, TMA enhanced $CHCl_3$ and TCAA formation following a pattern that was similar to MES. First, the TMA only controls generated low $CHCl_3$ (< 0.13 µM, Fig. 3-1b) and TCAA (< d.l., Fig. 3-2b) concentrations with 5 to 50 µM TMA, for reasons described previously. Second, $CHCl_3$ and TCAA were both enhanced for the AC/TMA/FC experiments but this was also strongly dependent on aromatic compound type and TMA dose. $CHCl_3$ was found to: (i) increase to 0.68 and 1.0 µM with 5 and 50 µM TMA, respectively for SA, (ii) decrease slightly to 0.56 µM with 5 µM TMA and remain constant at this value up to 50 µM TMA for PHE, and (iii) decrease to 0.62 µM with up to 50 µM TMA for RES (Fig. 3-1b). Alternatively, TCAA was found to (i) increase considerably to 2.3 µM with 5 µM TMA and then steadily decrease to 1.4 µM with 50 µM TMA for SA, (ii) slightly increase to 2.1 µM with 5 µM TMA and subsequently decrease to 1.5 µM at 50 µM TMA for PHE, but (iii) not form TCAA at > d.l. from 5 to 50 µM TMA for RES (Fig. 3-2b).

Overall, varied TMA doses enhanced $CHCl_3$ and TCAA formation depending on aromatic compound type where SA > PHE ≈ RES for $CHCl_3$ and SA > PHE for TCAA which is again related to the competition of pathway 1 with 3. In fact, pathway 1 (scheme 2-1) appeared to dominate $CHCl_3$ formation with PHE and RES strongly enough such that an increasing TMA dose only contributed by incurring a chlorine demand (Fig. S8b). In addition, $CHCl_3$ and TCAA were also enhanced strongly at low TMA doses (e.g. 5 µM) but as the TMA dose was increased, mixed increasing versus decreasing trends between $CHCl_3$ and TCAA were observed with SA and PHE. Such results demonstrated that shifting between the two compounds occurred which was further verified by summing the $CHCl_3$ and TCAA concentrations together (Fig. S7b). In both cases, the summed concentrations still decreased slightly from 3.0 to 2.5 µM with SA and from 2.7 to 2.1 µM with PHE in the presence of 5 to 50 µM TMA, respectively (Fig. S7b). Thus, the $CHCl_3$

formed could only partially compensate for the decrease in TCAA but some TCAA did appear to shift to form $CHCl_3$ (Fig. S7b).

Lastly, RAN exhibited comparable results with TBA since the RAN only controls formed considerable levels of $CHCl_3$ but < d.l. levels of TCAA over 5 to 50 µM RAN. $CHCl_3$ formed at 0.66 and 1.2 µM with 5 and 20 µM RAN, respectively, but then decreased drastically to 0.17 µM with 50 µM RAN (Fig. 3-1d). RAN formed $CHCl_3$ at these lower RAN doses for reasons discussed previously, but at higher RAN doses, $CHCl_3$ formation decreased, likely due to the increased chlorine demand imparted by RAN's thioether and acetamidine functional groups (Table 2-1). These groups are known to react with free chlorine at a rapid combined rate (e.g. $k_{app} = 1.4 \times 10^9$; Table 2-1), that is ~ six orders of magnitude faster than the chlorination rate of its tertiary amine (Table 2-1). This effect is also believed to have led RAN to impart the greatest level of chlorine demand as compared to the other three amines over the full amine dose range (Fig. S8). This increased chlorine demand with increased RAN dose also appeared to carry over for the AC/RAN/FC experiments. For these cases, $CHCl_3$ was found to: (i) increase to 1.6 µM with 10 µM RAN and then decrease to 0.14 µM with 50 µM RAN for SA, (ii) increase to 1.3 µM with 10 µM RAN and then decrease to 0.13 µM with 50 µM RAN for PHE, and (iii) continuously decrease to 0.16 µM with 50 µM RAN for RES (Fig. 3-1d). At lower (5-10 µM) RAN doses, $CHCl_3$ was thus enhanced by a factor of 1.3-1.4× with SA, respectively, but was not enhanced with either PHE or RES (Fig. 3-1d). This pattern differed at higher RAN doses ($\geq$ 20 µM RAN) where $CHCl_3$ did not exhibit enhanced effects with either SA, PHE or RES (Fig. 3-1d).

In addition, TCAA was found to: (i) increase sharply to 2.4-2.5 µM with 5-10 µM RAN and then decrease sharply to < d.l. with 50 µM RAN for SA, (ii) increase to 2.4 µM with 10 µM RAN and then decrease sharply to < d.l. with 50 µM RAN for PHE, and (iii) form at < d.l. between 5 to 50 µM RAN for RES (Fig. 3-2d). Thus, TCAA was enhanced up to a factor of 23 and 1.3× at low (5-10 µM) RAN doses but was not enhanced at higher ($\geq$ 20 µM) RAN doses for SA and PHE, respectively (Fig. 3-2d). Overall, these trends were similar to those observed with TBA and suggested that RAN also took part in pathways 2 and 3, which then competed with pathway 1 to alter $CHCl_3$ and TCAA enhancement. Similar to TBA, $CHCl_3$ and TCAA were enhanced at low RAN doses and with SA since pathway 3 could compete pathways 1 and 2 whereas in all other

situations, pathway 3 was no longer able to compete (scheme 2-1). This issue was further strengthened by the fact that RAN has additional functional groups that also competed to consume free chlorine which significantly minimized $CHCl_3$ and TCAA formation at high RAN doses (> 20 μM).

Using approach 2, the $CHCl_3$ formed with RES for all four tertiary amines were plotted together given that their respective tertiary amine only controls formed $CHCl_3$ < d.l. (Fig. S5e). These results indicated that tertiary amine type only affected the level by which $CHCl_3$ decreased with increasing tertiary amine dose due to the chlorine demand that they incurred (Fig. S5e). In fact, the chlorine demand exhibited by the tertiary amines followed a decreasing order of RAN > TBA > TMA > MES (Fig. S10) which was similar to the level of decrease observed for $CHCl_3$ which followed the order of RAN > TBA ≈ TMA > MES (Fig. S5e). With SA and PHE, the data were subdivided to compare the MES and TMA data together (Fig. S5) and the TBA and RAN data together (Fig. S6) due to their differences in forming $CHCl_3$ and TCAA for their tertiary amine only controls. When comparing MES and TMA, $CHCl_3$ and TCAA were found to match well when assessing their formation trends but differ when comparing their overall level of formation as a function of amine dose (Fig. S5). For example, with SA, MES formed up to 0.6 μM higher $CHCl_3$ (3.4× higher enhancement factor) than TMA over the 5 to 50 μM amine dose range (Fig. S5a). With PHE, MES formed up to 0.52 μM higher $CHCl_3$ than TMA over the 5 to 50 μM amine dose range (Fig. S5c). This pattern differed with TCAA though in that similar levels of TCAA were formed with MES and TMA for SA whereas TMA formed up to 0.69 μM higher TCAA than MES for PHE over the 5 to 50 μM amine dose range (Fig. S6). It remains unclear why MES formed $CHCl_3$ to a greater extent than TMA but formed TCAA to either the same (for SA) or lower (for PHE) extent than TMA. In fact, their summed $CHCl_3$ and TCAA results (Fig. S9) for both SA and PHE overlapped for the majority of MES and TMA doses indicating that MES and TMA held similar capacities to enhance their total formation without regard to their distribution (Fig. S9). This data is in contrast to a previous finding which found that TMA was less effective than MES towards enhancing SA degradation when chlorinated over 6 h.[5] However, a lower excess level of free chlorine was applied in this previous case which could have then limited SA from reacting to completion with TMA.[5]

For the TBA and RAN results, the $CHCl_3$ and TCAA formed were not similar for either the tertiary amine only controls or the AC/(TBA/RAN)/FC experiments over the majority of the amine doses (Fig. S5). However, these values more closely matched when rather considering them in terms of enhancement. For $CHCl_3$, this effect was apparent at low TBA and RAN doses (5-10 μM) which were similarly enhanced between a factor of 1.1 and 1.5× for SA or exhibited no enhancement for PHE (Fig. S5). At high TBA/RAN doses (20-50 μM), enhancement was similarly lost since TBA or RAN either served as a strong $CHCl_3$ source or incurred a high chlorine demand, respectively (Fig. S10). This pattern was then replicated for TCAA at both low TBA and RAN doses (5-10 μM) where it was strongly enhanced between a factor of 20 and 23× with SA but only slightly enhanced between a factor of 1.1 and 1.3× with PHE (Fig. S6). This pattern diverged at higher TBA and RAN doses (20-50 μM) in that: (i) TCAA was not enhanced for either tertiary amine for PHE (Fig S6d), (ii) continued to be enhanced with TBA for SA (Fig. S6b), or (iii) was not enhanced with RAN due to the chlorine demand it exhibited for SA (Fig. S6b). Overall, all four tertiary amines do have the capacity to enhance $CHCl_3$ and TCAA formation to a similar degree through pathway 3. One example is for TCAA which was enhanced by a factor of 18 to 23× for all four amines at low doses for SA (Fig. S6). Subsequent differences in the enhancement were then due to the influence of competing pathways (e.g. pathways 1, 2, and chlorination of RAN's other functional groups) that then controlled $CHCl_3$ and TCAA formation.

3.4.2 Effect of Bromide

The effect of bromide (Br^-) was explored since it is often present in natural waters and can be rapidly oxidized by HOCl to form HOBr (eq. 2). HOBr is a strong brominating agent[15] and can react with natural organic matter (NOM) to form brominated THMs and HAAs.[16]

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad k_{app} = (1.2\text{-}5.3)\times10^3\ M^{-1}s^{-1} \text{ at pH 7 } ^{17\text{-}19} \qquad (2)$$

In this study, HOBr was predicted to react with tertiary amines to form $R_3N\text{-}Br^+$ which could then enhance brominated THMs and HAAs formation with various aromatic compounds through similar mechanistic pathways found in Scheme 2-1. To test this, SA was chlorinated with 10 μM MES which contained 0-100 μM bromide. All four THMs including $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ were observed (Fig. 3-3a), whereas only five HAAs including TCAA, BDCAA, DBCAA, DBAA and TBAA were found at > d.l. (Fig. 3-3b).

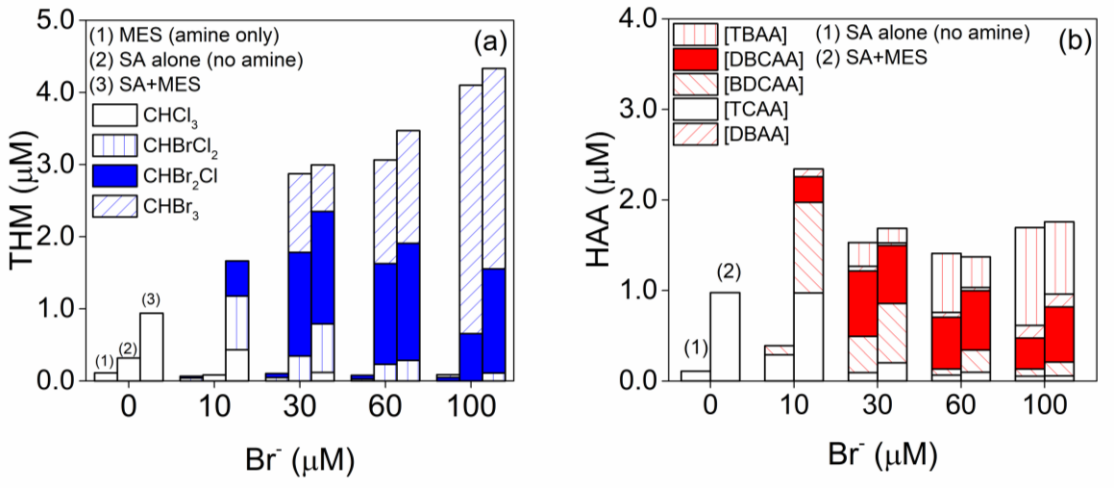

Figure 3-3. Effect of bromide (0-100 μM) on (a) THMs and (b) HAAs formation following chlorination of SA after 24 h in the absence or presence of MES ($[MES]_0$ = 10 μM; $[SA]_0$ = 10 μM; $[free\ chlorine]_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2). Each bromide dose includes two to three different columns representing the (1) no MES control (< d.l. for HAAs), (2) the MES only control, and (3) the SA/MES/FC experiment. Each column is also stacked to include the individual compound concentration and the total THMs and HAAs formed.

For the THM results, the MES only control did not form any THMs above 0.11 μM with 0 – 100 μM bromide (Fig. 3-3a). Alternatively, the no MES control (SA alone) formed increasing levels of brominated THMs ($CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$) that totaled from 2.9 to 4.1 μM as bromide increased from 30 to 100 μM, respectively (Fig. 3-3a). This shift from chlorinated to brominated species was expected given similar patterns observed previously when bromide was added to NOM-containing solutions during chlorination.[16] MES addition then increased total THM formation by a factor of 20× with low bromide (10 μM), but either did not or only slightly increased total THMs by a factor of 1.1× with high bromide (30-100 μM) (Fig. 3-3a). This increase was directly attributed to enhanced $CHCl_3$, $CHBrCl_2$ and $CHBr_2Cl$ formation but which dissipated by the fact that $CHBr_3$ was not enhanced by MES over the entire bromide dose range (Fig. 3-3a). The HAA results were similar in that: (i) for the MES alone control, no HAAs formed at > d.l., (ii) for the no MES control, a shift in HAA distribution from chlorinated (TCAA) to brominated HAAs (TBAA, DBAA, DBCAA and BDCAA) was observed with increasing bromide dose (30-100 μM), (iii) significant enhancement of total HAAs was observed with 10 μM bromide by a factor of 6×, (iv) no enhancement of total HAAs was observed at higher bromide levels (30-100 μM), and (v)

the loss of enhancement with 30 – 100 µM bromide is due decreased DBAA and TBAA formation upon MES addition (Fig. 3-3b).

Therefore, MES can have mixed enhancement effects when bromide is lower than the initial free chlorine applied in which solutions contained both HOCl and HOBr as well as NR_3-Cl^+ and NR_3-Br^+ upon MES addition. Chlorinated (e.g. $CHCl_3$ and TCAA) and mixed chlorinated/brominated THMs and HAAs (e.g. $CHBrCl_2$ and BDCAA) were thus produced at lower bromide concentrations (0-60 µM) and were enhanced upon MES addition (Fig. 3-3). However, brominated THMs and HAAs (e.g. $CHBr_3$ and TBAA) were preferentially formed at higher bromide concentrations (30-100 µM) but were not enhanced with MES (Fig. 3-3). This pattern then affected total THM and HAA formation which was similarly enhanced at lower bromide concentrations (10 µM) but not enhanced at higher concentrations (30-100 µM) (Fig. 3-3). To then better understand why bromide eliminated these enhancement effects, it was first hypothesized that HOBr was somehow not generated from HOCl. Although, this factor seemed unlikely given that eq. 2 was two orders of magnitude higher than the competing MES/HOCl reaction (Table 2-1). To test this, additional experiments with 10-100 µM pre-formed HOBr indicated that $CHBr_3$ (the only THM to form) was not enhanced following MES addition (Fig. S11). Other factors have then been considered to lead to these observed effects, which are predicted to inhibit specific steps within the proposed reaction pathway (Scheme 2-1). Other hypotheses suggest that: (i) HOBr is less reactive towards MES than HOCl in forming MES-Br^+. This seems unlikely though given that HOBr has a greater electrophilicity as compared to HOCl,[15] leading to its one order greater reactivity towards ammonia[15, 20] and primary/secondary amines[15, 21-23], (ii) MES-Br^+ forms but then does not react with SA or the ketone intermediate (Scheme 2-1). This possibility also seems unlikely given that SA and the ketone are brominated through electrophilic substitution reactions that similarly occur with HOBr[24-26] and are faster than with HOCl[15]. (iii) MES-Br^+ forms but does not react with SA because it decomposes faster than MES-Cl^+ via pathway 2. This possibility also seems unlikely since MES-Cl^+ and MES-Br^+ must first undergo elimination when they decay and form the secondary amine (pathway 2 in Scheme 2-1). The potential for elimination to occur is related by the Hammett ρ value where a higher ρ value of a group indicates that a more stable negative charge is developed by the halogen (Cl or Br) which subsequently speeds up the elimination reaction.[28] The ρ values for Cl and Br are 2.61 and 2.14,

respectively.[27, 28] Therefore, the elimination of HCl from MES-Cl^+ is expected to be faster than the elimination of HBr from MES-Br^+ thus leading MES-Cl^+ to be less stable than MES-Br^+. (iv) This effect could be related to the fact that reactions with HOBr within pathway 1 better outcompete those initiated by MES-Br^+ within pathway 3, a hypothesis that would be in line with the conclusions drawn from the previous sections. However, additional research is required to isolate which of these options serve as the controlling factor.

3.4.3 Effect of pH

Chlorinated experiments with SA and MES were varied in pH from 6 to 9 and resulted in $CHCl_3$ and TCAA formation where the experimental data were overlaid on MES and HOCl/OCl^- speciation curves (Fig. 3-4). First, the MES only controls yielded low $CHCl_3$ (< 0.25 µM) and TCAA (< d.l.) formation between pH 6 to 9 (Fig. 3-4). Second, the no MES controls and SA/MES/FC experiments led to similar trends for $CHCl_3$ and TCAA formation as a function of pH (Fig. 3-4). The no MES control generated increasing $CHCl_3$ from 0.074 to 0.79 µM from pH 6 to 8, respectively, but then dropped significantly to 0.46 µM at pH 9 (Fig. 3-4a). At pH < 8, the increased $CHCl_3$ with increased pH was expected given that $CHCl_3$ formation requires OH^- to initiate enol formation and subsequent chlorination of the ketone intermediate within pathway 1. At pH 9, $CHCl_3$ formation dropped, which was unexpected given that previous experiments with RES observed high but steady $CHCl_3$ formation from pH 6 to 9.[29] This drop is predicted to be directly due to the lower HOCl concentration present at pH 9 which more directly influences the slow kinetics of $CHCl_3$ formation from SA (Fig. 2-1a). This trend was maintained for the SA/MES/FC experiments where $CHCl_3$ increased from 0.27 to 1.3 µM from pH 6 to 8, respectively, and then decreased to 0.43 µM at pH 9 (Fig. 3-4a). In this case, the maximum $CHCl_3$ concentration formed at pH 8 at 1.3 µM whereas its maximum enhancement occurred at pH 7 by a factor of 5.9× (Fig. 3-4a).

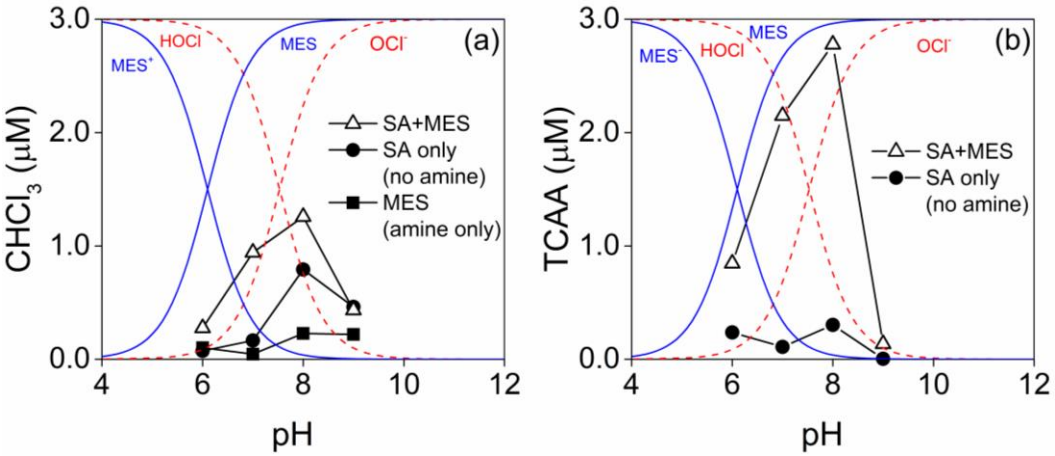

Figure 3-4. Effect of pH on (a) $CHCl_3$ and (b) TCAA formation when SA is exposed to MES after 24 h of chlorination ($[MES]_0$ = 10 µM; $[SA]_0$ = 10 µM; [free chlorine]$_0$ =280 µM (19.9 mg/L-Cl_2); pH 6.1-8 (phosphate buffer) and 9 (borate buffer)). The acid/base speciation curves for free chlorine ($HOCl/OCl^-$) and MES (MES^+/MES) are also included as colored lines.

The TCAA results as a function of pH were similar with MES. First, the no MES controls generated up to 0.30 µM TCAA between pH 6 to 9 but did so without exhibiting a consistent trend (Fig. 3-4b). A larger pH effect was observed for the SA/MES/FC experiment where TCAA increased from 0.85 to 2.8 µM from pH 6 to 8, respectively, and then decreased to 0.14 µM at pH 9 (Fig. 3-4b). In this case, the maximum TCAA concentration formed at pH 8 at 2.8 µM whereas its maximum enhancement occurred at pH 7 by a factor of 20× (Fig. 3-4b). Overall, these results indicated that the effect of pH incurred similar trends on $CHCl_3$ and TCAA formation in the presence or absence of MES. This was especially true for $CHCl_3$ but less so for TCAA, given that TCAA formed low concentrations overall for the no MES control. These similarities suggest that the pH-dependent factors driving $CHCl_3$ and TCAA formation without MES via pathway 1 remain the same in the presence of MES via pathway 3. The only difference is related to the presence of MES-Cl^+. Enhancement is predicted to be maximized at pH 7 since this is close to pH 6.8 which is where the kinetics of MES-Cl^+ are maximized as this value is equivalent to the average of the MES^+/MES and $HOCl/OCl^-$ pK_as. At pH 9, the role of MES-Cl^+ is then expected to be reduced given that the pH has moved away from this maximum value.

3.4.4 Effect of SRFA

Three types of kinetic and dose experiments were conducted with SRFA to assess THM and HAA formation with tertiary amines. These experiments included (i) kinetic experiments over 24 h with MES (Fig. S12), (ii) kinetic experiments over 24 h with TBA (Fig. S13), and (iii) dose experiments with 5 – 50 µM MES, TBA, TMA and RAN after 24 h (Fig. S14). $CHCl_3$ and TCAA were the only DBPs formed at > d.l. Overall, $CHCl_3$ was not enhanced with any of the tertiary amines for all of the kinetic (Fig. S12 and S13) and dose experiments (Fig. S14). Alternatively, TCAA exhibited mixed effects. TCAA was not enhanced with MES for either the kinetic or dose experiments but was enhanced for the majority of 5 to 50 µM TMA, TBA, and RAN doses (Fig. S14c). In this case, the no amine control (SRFA only) generated TCAA at < d.l. whereas the amine only controls were < d.l. for TMA and RAN but increased up to 0.27 µM with up to 50 µM TBA (Fig. S14c). TCAA then formed up to 0.097 and 2.2×10^{-3} µM with 5 µM TMA and RAN, respectively (Fig. S14c), further indicating that low amine doses can trigger an enhancement effect. TCAA was not further enhanced when the TMA, TBA, or RAN doses increased up to 50 µM and in fact was lowered with 50 µM RAN due to the higher chlorine demand incurred by RAN, since no residual free chlorine remained at this dose (Fig. S14e). Overall, the presence of SRFA led to no or slight enhancement of $CHCl_3$ and TCAA, respectively, for the majority of tertiary amines tested. This finding is consistent with earlier results since SRFA is comprised of a wide-range of phenolic-based functional groups that vary in their overall reactivity with HOCl.[30, 31] Given this, SRFA is thus hypothesized to contain functional groups similar to RES or PHE which exhibited no or limited enhancement of $CHCl_3$ and TCAA, respectively. These compounds are then predicted to control how free chlorine is consumed and also limit the potential for other functional groups that are less reactive to free chlorine (e.g. similar to SA) to further react with $R_3N\text{-}Cl^+$ via pathway 3 (scheme 2-1).

3.5 Conclusions

The aim of this study was to evaluate how different types of tertiary amines and specific water quality conditions (e.g. bromide concentration and pH) affected the enhancement effect of THM and HAA formation. This effect was evaluated during both the chlorination of various aromatic compounds as well as one NOM extract, SRFA. The results indicated that all four tertiary amines

enhanced $CHCl_3$ and TCAA formation to varying degrees, but enhancement of up to a factor of 21× also occurred at low doses (< 10 µM; < 0.30 to 1.6 mg/L). Such results indicated that tertiary amine concentrations typically found in natural and treated waters of up to low mg/L (µM) concentrations[1, 2] could potentially enhance THM and HAA formation as well. TBA and RAN at up to 50 µM also formed $CHCl_3$ and TCAA at up to 13% and 2.0% molar yields, respectively, when chlorinated alone, which served as an alternate pathway to form these compounds than through the proposed catalytic cycle. With MES, $CHCl_3$ and TCAA were also found to form at their maximum concentration at pH 8 whereas exhibit maximum enhancement at pH 7. Moreover, the results with bromide indicated that MES was unable to enhance brominated THM or HAA (e.g. $CHBr_3$ and TBAA) formation, although their mixed counterparts (e.g. $CHBrCl_2$, BDCAA, and DBCAA) were enhanced.

In addition, the SRFA results showed no or slight enhancement of $CHCl_3$ and TCAA, respectively, for the majority of tertiary amines tested. This suggested that waters containing aromatic compounds with low reactivity with free chlorine (e.g. SA) may be more likely to be influenced by tertiary amines, as compared to waters with aromatic compounds with a wide-range of free chlorine reactivities, such as SRFA. Overall, these findings indicate that tertiary amines can potentially have a strong impact on elevating the total THM and HAA concentrations formed in chlorinated waters under typical (low bromide and pH 7) water quality conditions.

3.6 References

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CHAPTER 4. DEGRADATION MECHANISMS OF THE POLYAMIDE MEMBRANE MONOMER DURING CHLORINATION

4.1 Abstract

Polyamide-based thin film composite membranes are the most widely used RO and NF membranes due to their excellent selectivity. One drawback of using these membranes is they undergo biofouling over time and can degrade and eventually fail when treated with free chlorine. The current known mechanisms of polyamide degradation during chlorination included chlorination of the amide N (N-chlorination), direct ring chlorination by Cl_2 or indirect ring chlorination through Orton Rearrangement, where the ring chlorination proceeded through N-chlorination. However, the Orton Rearrangement has flaws from a chemistry perspective. Therefore, this study is intended to (i) re-evaluate the mechanisms governing the chlorination of the polyamide-based membrane using select monomers, (ii) assess the role of water quality conditions including pH and effects of Cl^-, and (iii) in certain cases, derive species-specific rate constants in order to isolate which specific chlorinating agents are involved in driving the observed reactions. In order to achieve these goals, a polyamide-based monomer (benzanilide (BA)) and various modified monomers containing altered substituents were tested. These compounds were exposed to free chlorine at different pH conditions ranging from 4.0 to 9.2, with varying doses of Cl^- ranging from 2.3×10^{-4} to 0.540 M. Both the loss of the monomers and the formation of various chlorinated by-products were monitored. Thus, for BA, the results indicated that Orton Rearrangement did not occur under such water quality conditions, which are highly representative of the typical conditions used during membrane filtration. An alternative mechanism was proposed, where the chlorination occurred at two reactive sites including the amide N moiety and the anilide ring (i.e. the ring adjacent to amide group). It is hypothesized that chlorination occurs at these two reactive sites through independent pathways that are not linked together, as suggested by the Orton Rearrangement. Overall, the ability for one site to be chosen over the other was dependent on: (i) pH, (ii) Cl^- concentration, and (iii) the resulting chlorinating agents (e.g. Cl_2, HOCl, OCl^-, and Cl_2O) that were generated. As a result, the amide N became chlorinated to form the N-Cl moiety primarily at neutral and high pH, where OCl^- was likely the primary reactant. However, this reaction was susceptible to being reversed via base-catalyzed hydrolysis. Alternatively, the direct chlorination of the anilide ring at the ortho- and para-positions occurred at primarily at low pH

conditions where the addition of Cl^- significantly increased the kinetic loss of BA. At this low pH condition, species-specific reaction rate constants for different chlorinating agents were obtained and equaled $(7.6\pm0.19)\times10^1$ $M^{-1}s^{-1}$ for Cl_2, $(1.7\pm1.5)\times10^1$ for OCl^-, and $(2.1\pm0.71)\times10^{-2}$ for HOCl. The reaction rate for Cl_2O was not determined due to large uncertainties in the obtained value. In addition, the kinetic loss of modified monomers differed from BA and were explained based on the new proposed mechanism. Overall, this work derived a more comprehensive understanding of the how these polyamide-based monomers degrade during chlorination, and the kinetic and by-product results helped evaluate which types of chlorinating agents played a role chlorinating the monomer under different water conditions

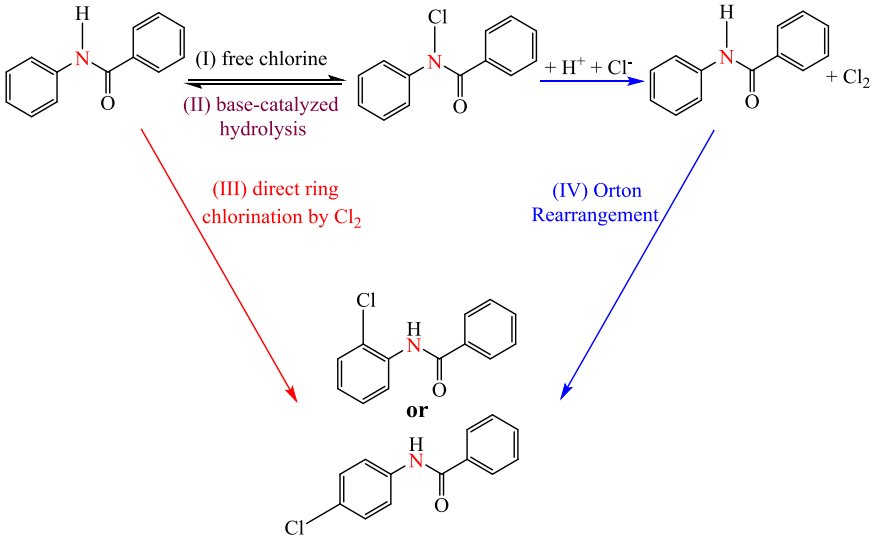
4.2 Introduction

Aromatic polyamide-based thin film composite membranes are the most widely used membrane types for RO and NF treatment because they exhibit several advantages over other types of membrane (e.g. cellulose acetate membranes).[1, 2] Compared to cellulose acetate membranes, which dominated the market from 1960-1980s[3, 4], polyamide-based thin film can remain more stable over a wide pH range with higher water permeability and better selectivity[1, 2]. However, the use of polyamide thin film composite also has drawbacks. First, they are prone to biofouling.[5] This problem can be reduced if free chlorine is added to the feed water, but the polyamide composite membrane is susceptible to attack by free chlorine which can lead to membrane performance failure.[6]

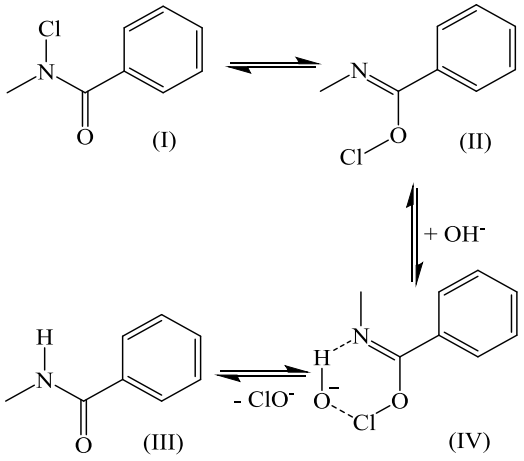
Many studies have been conducted to investigate how these polyamide-based membranes degrade when exposed to free chlorine and have attempted to propose various mechanisms.[7-13] In these studies, the polyamide-based membrane, a polyamide-based powder or individual model compounds that represent the monomer functional groups were exposed to excess free chlorine (0.14-28 μM (10-2000 mg/L as Cl_2)) at neutral pH (pH 6-7) for 1-24 h.[7-9, 13] Different instruments including ATR-FTIR, XPS, NMR and GC/MS were used to analyze the structural changes that were incurred by these substrates in order to identify the chlorination products. This information was used to hypothesize various mechanisms by which the substrates reacted with free chlorine.[7-9, 13] The mechanisms that were proposed included two key pathways, direct ring-chlorination and N-chlorination which can then later undergo ring-chlorination (Scheme 4-1).[6-8, 12, 13] This latter

pathway is widely known as the “Orton Rearrangement” and has been widely referred to as the mechanism to explain the membrane degradation during contact with chlorine.[9, 12, 13]

Scheme 4-1. Proposed mechanims for chlorination of polyamide based monomer



Within this overarching mechanism, there are several important reactions that are hypothesized to occur. First, N-chlorination can occur through the reaction between the amide N and free chlorine ((I), scheme 4-1). This reaction is also considered to be reversible due to the based-catalyzed hydrolysis of the formed N-Cl compound ((II), scheme 4-1).[12, 13] A detailed pathway was proposed for the hydrolysis of N-Cl amides, which occurs through the isomerization of the N-Cl compound ((I in eq. 1) to the iso-amide form (II in eq. 1)).[14, 15] Alternatively, ring chlorination can either occur directly when chlorinated by Cl_2 ((III), scheme 4-1)[6, 12, 13] or indirectly via the Orton Rearrangement (scheme 4-1).[12, 13] The Orton Rearrangement proceeds through two steps. First, the N-Cl compound is dechlorinated by hydrochloric acid (HCl) to form the unchlorinated amide and Cl_2 which is considered to be the rate-limiting step (scheme 4-1).[16, 17] Second, the ring adjacent to the amide N is then chlorinated by the Cl_2 that is generated to form the ring chlorination products (scheme 4-1). These ring chlorination products are widely known to reside at the ortho- and para- positions on the ring (scheme 4-1).[18, 19]



(1)

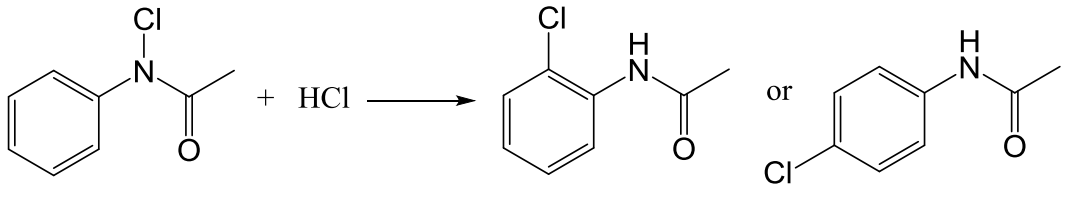
However, from a chemistry perspective, the Orton Rearrangement has several flaws. First, when Cl^- is present, Cl^- should be more reactive with HOCl (eq. 2) rather than with the N-Cl compound to form Cl_2 (first step of (IV), scheme 4-1) when H^+ is not limiting the reaction. This is because eq. 2 should be considerably faster ($k_f = 4.3 \times 10^4\ M^{-2}s^{-1}$)[20] than the reaction between, N-Cl, Cl^- and H^+ to form Cl_2, which was known to be the rate-limiting step in the Orton Rearrangement.[16, 17] Also, the N-Cl moiety needs to be first generated in the solutions (I in scheme 4-1) for Orton Rearrangement (IV in scheme 4-1) to occur, but amides were known to react with chlorine slowly ($k_{app} = 10^{-3}$-$10^{-1}\ M^{-1}s^{-1}$ at pH 7.2-7.4) due to the electron-withdrawing effect of the carbonyl group[21, 22].

$HOCl + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O$ logk = 3.36 (25 ˚C, 0 M)[23] (2)

Second, studies were also performed where anilides which are acyl derivatives of aniline (R_1-NHC(O)-R_2, R_1=aromatic ring), were exposed to HOCl, Cl_2 or Br_2.[9, 13, 24, 25] The structures of these anilides varied slightly in that the amide H was in certain cases substituted by methyl or ethyl group, or polymers with the repeating units of N-methyl-benzanilide and N-phenyl-benzanilide. The results for these compounds or polymers indicated that the ring was the only location that was chlorinated or brominated.[13, 24, 25] The results obtained with N-methyl or ethyl-compounds observed that direct ring chlorination/bromination could still occur without the involvement of the amide group (N-H)[13, 24, 25], further suggesting that the Orton Rearrangement pathway may not be necessary or involved. However, one study conducted with the polymers with the repeating units of N-methyl-benzanilide and N-phenyl-benzanilide observed no chlorination.[9] The different conclusions obtained were probably due to different experimental conditions (e.g. chlorine dose,

reaction time and pH), and the dominant substituting agents that were present such as Cl_2 or Br_2 which are known to be more reactive than HOCl.[23, 26, 27] Given these differences, it remained unclear if the Orton Rearrangement did or did not occur.[9, 13]

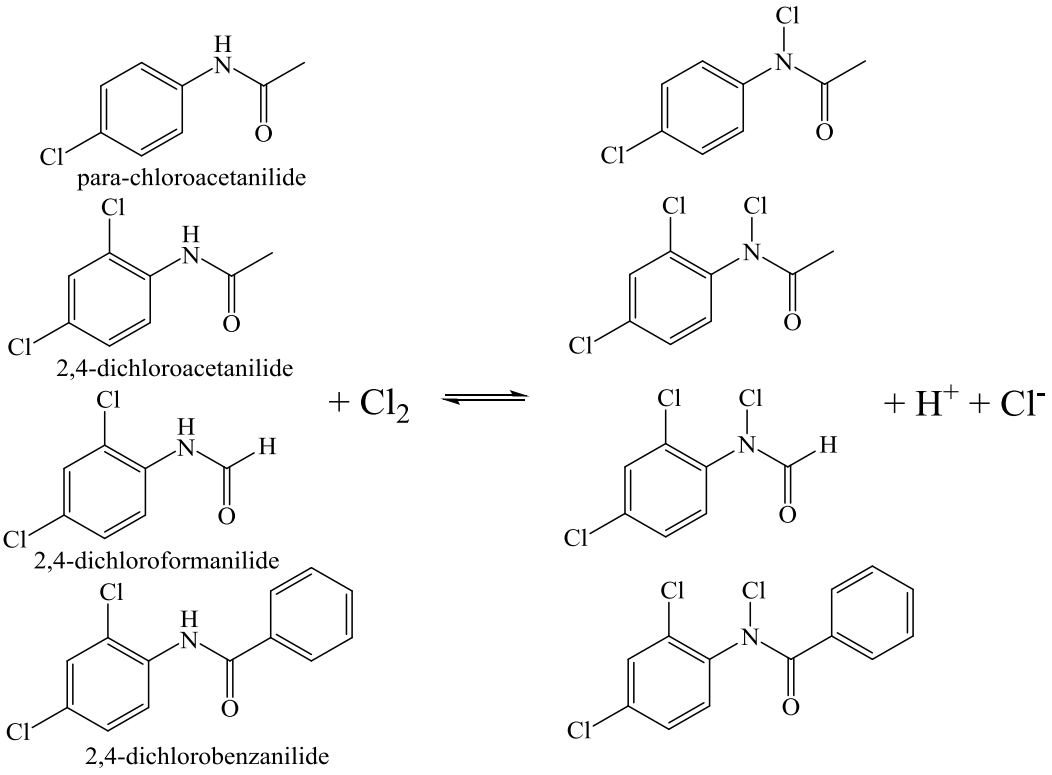
Interestingly, the mechanism of Orton Rearrangement also became more unclear when re-visiting the original literature published by Orton and colleagues.[18, 19, 28-33] A considerable number of papers were published on this subject during early 1900s, and there are several key findings that further raise doubt on what is *currently known* as the Orton Rearrangement. The general mechanism was initially explored in a study where hydrochloric acid (HCl) was added to glacial acetic acid (>99.5%) containing N-Cl-acetanilide (eq. 3). The formation of ring-Cl-acetanilide was then observed.[29]



(3)

Therefore, Orton and colleagues believed that N-Cl-anilides can undergo rearrangement to ring-Cl with Cl_2 formed as an intermediate, but this was not done in aqueous phase, where the hydrolysis of Cl_2 may occur.[29, 31] It should be also noted that in glacial acetic acid, the ionization of HCl did not occur either, which seemed to suggest that the Cl_2 generated by N-Cl-acetanilide reacting with unionized HCl, instead of Cl^- and H^+, which was mentioned in later studies[12, 13]. Later, a similar reaction was investigated in detail by exposing ring substituted anilides (e.g. para-chloroacetanilide, 2,4-dichloroacetanilide; eq. 4) where the ring sites were blocked by Cl, to Cl_2 in glacial or diluted acetic acid (eq. 4).[31] In this study, they observed that an equilibrium existed (eq. 4), but this equilibrium was highly dependent on the type of solvent that was used.[31] In a more aqueous solution (e.g. 50% acetic acid), where HCl was completely ionized, this equilibrium was entirely shifted to the right where N-Cl, H^+, and Cl^- coexisted.[31] However, in a more concentrated acetic acid (e.g. glacial acetic acid) solution or in organic solvents (e.g. chloroform), where acetic acid and HCl were not ionized, the equilibrium shifted to form Cl_2 and anilide.[31, 33] It should be noted that in acetic acid >50%, the hydrolysis of Cl_2 was not detected (back reaction of eq. 2).[31] This seemed to again suggest that in aqueous reactions, where polyamide membrane failure usually

occurs, the N-Cl-anilide form is more stable and its ability to react with H^+ and Cl^-, a component of the *current* Orton Rearrangement pathway, to occur is quite slow.



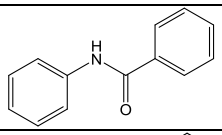
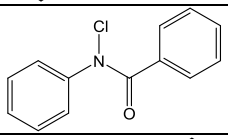
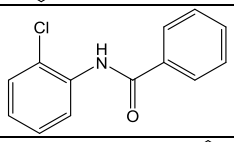
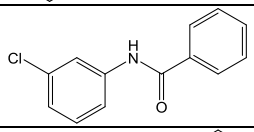
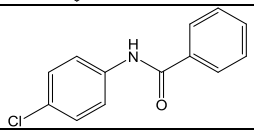
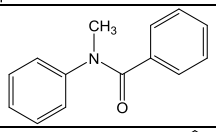
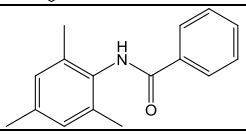
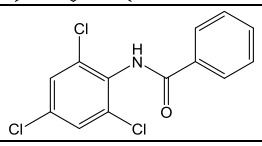
(4)

Notably, when investigating this equilibrium (eq. 4), unsubstituted acetanilide was not used.[31] This was because when unsubstituted acetanilide was used in this same study, the compound underwent ring chlorination rapidly when exposed to Cl_2 in 50-99.5% acetic acid (eq. 4), instead of establishing the equilibrium and forming the N-Cl compound (eq. 4).[31] As the percent of water increased up to 98 and 99.75% in the solvent, the formation of N-Cl-acetanilide increased to 10 and 64%, respectively, of the formed products.[19] At this point, it was not clear if this increased formation of N-Cl products happened because: (i) when lowering the percent of acetic acid to 0.25-2%, the pH significantly increased and led the equilibrium (eq. 4) to shift to the right and form more N-Cl-anilide, or (ii) in an more aqueous solution (<50% acetic acid), Cl_2 hydrolyzed to form HOCl (back reaction of eq. 2)[19], which could chlorinate the amide N to form N-Cl-acetanilide[29]. The second hypothesis (ii) was more plausible since when preparing N-Cl-anilide (e.g. N-Cl-acetanilide), HOCl was used rather than Cl_2.[29] These results suggest that acetanilide preferred to undergo direct ring chlorination when Cl_2 present[31], and N-Cl product likely formed by the reaction

of anilides with other chlorinating species (e.g. HOCl/OCl^-)[29, 34]. Therefore, if Cl^- was present in a solution containing acetanilide and HOCl, the reaction should not start with HOCl reacting with acetanilide to form N-Cl-acetanilide, followed by Orton Rearrangement to form ring chlorination products ((IV), scheme 4-1). Instead, Cl^- should react with HOCl to form Cl_2 when H^+ is not limiting the reaction, and Cl_2 directly chlorinated the ring to form ring chlorination products. Polyamide membrane was expected to behave similarly as when reacting with free chlorine, since acetanilide was also proven to be a good model compound when investigating polyamide degradation.[13]

Given the lack of clarity in the mechanisms involved, this study intended to address these gaps by providing a more comprehensive study which evaluated how the polyamide-based monomer reacted with various chlorinating agents. The polyamide-based monomer was evaluated, which was purchased commercially as benzanilide (BA) (structure provided in Table 4-1), and from this point forward will be referred to as BA. BA has been proven to be a good model compound for studies related to the chlorination of polyamide-based membrane where the benzoyl aromatic ring (i.e. the ring not adjacent to the amide) is considered inert since its chlorination has never been previously observed.[6, 13] In addition, other modified monomers were evaluated where various reactive sites were substituted. They include N-Methyl-N-phenylbenzamide (N-CH_3-BA)**,** N-Mesitylbenzamide (2,4,6-trimethyl-BA)**,** and N-(2,4,6-trichlorophenyl)benzamide (2,4,6-trichloro-BA) (Table 4-1).

Table 4-1. Compound names, structures and acronyms used in this study.

Compound Names	Structures	Acronyms
benzanilide		BA
N-Chloro-N-phenylbenzamide		N-Cl-BA
N-(2-Chlorophenyl)benzamide		ortho-Cl-BA
N-(3-Chlorophenyl)benzamide		meta-Cl-BA
N-(4-Chlorophenyl)benzamide		para-Cl-BA
N-Methyl-N-phenylbenzamide		N-CH_3-BA
N-Mesitylbenzamide		2,4,6-trimethyl-BA
N-(2,4,6-Trichlorophenyl)benzamide		2,4,6-trichloro-BA

All of these compounds were then exposed to free chlorine with or without the presence of chloride under pH 4-9 in which the kinetics of the parent compound loss and, in certain cases, the by-products formed were evaluated. The structures of various by-products that were predicted to form, including N-chlorinated and ring chlorinated by-products, are also listed in Table 4-1. The role of chloride (Cl^-) was a particular focus of this work given its presence in saline waters (Table 4-2) and because it may play a significant role in either directly or indirectly (via the Orton Rearrangement) chlorinating the ring functional group through the formation of Cl_2. In addition, this experimental regime was further evaluated since other chlorinating agents such as Cl_2O (eq. 5), can potentially form but which have been overlooked in previous studies. In fact, Cl_2O has been found to be more reactive than HOCl when undergoing halogenation.[23, 26]

$2HOCl \rightleftharpoons Cl_2O + H_2O$ $\log k_4 = -2.06$ (25 ˚C, 0 M)[35] (5)

Table 4-2. Halide concentrations in various water types commonly treated by RO and NF.

Water Type	Chloride (g/L (M))	Bromide (mg/L (mM))	Iodide (µg/L (µM))
Seawater	19.2 (0.540)[36]	67 (0.84)[36]	60 (0.5)[36]
Brackish Groundwater	≤ 13 (0.37)[37]	≤ 0.5 (0.007)[38]	not determined
Industrial Wastewater (coal-fired power plants-flue gas desulfurization)	≤ 5.3 (0.15)[39]	≤ 96 (1.2)[40]	not determined
Industrial Wastewater (chemical/gas and oil industry)	≤ 27 (0.76)[41]	not determined	not determined
Industrial Wastewater (leather industry)	≤ 80 (2.3)[42]	not determined	not determined

As a result of this work, we were then able to (i) re-evaluate the Orton rearrangement pathway, (ii) propose a new mechanism, (iii) derive a more complete understanding of what specific reactants were involved under varying water quality conditions, and (iv) in certain cases, derive rate constants for these species-specific reactions. Overall, these results will also help to better understand the mechanisms of membrane failure when such membranes are used in NF and RO treatment. In addition, efforts have been taken to modify the polymer structure of these membranes to improve chlorine resistance, such as blocking the amide N site using epoxide[43], or coating the membrane surface with silane compounds[44]. This work can thus help inform how such these polyamide-based polymers are re-designed to avoid or alleviate membrane failure upon contact with free chlorine in various water quality matrices.

4.3 Materials and Methods

4.3.1 Standards and Reagents

The standards and reagents used for these experiments included: (i) phenol, sodium hypochlorite (13%$_{w/w}$), ascorbic acid, sodium sulfite, acetic acid, and sodium acetate which were purchased from Acros Organics, (ii) BA and naphthalene-d8 which were purchased from Sigma-Aldrich, (iii) 2,4,6-trichloro-BA (≥ 90% purity) which was purchased from Mcule, Inc. (Palo Alto, CA), and (iv) 2,4,6-trimethyl-BA (≥ 90% purity) was from ChemBridge Corporation (San Diego, CA). These and other chemicals, such as NaCl, $Na_2HPO_4 \cdot 2H_2O$, $NaH_2PO_4 \cdot H_2O$, $Na_2B_4O_7 \cdot 10\ H_2O$,

MeOH, dichloromethane (DCM) and acetonitrile (CH_3CN, ACN) were purchased at reagent grade or higher and used without further purification. Reagent water (18.2 MΩ-cm) was generated from a Thermo Scientific Barnstead NANOpure water purification system.

Several compounds were synthesized by Dr. Keith Reber at Towson University, including N-Cl-BA, para-, meta-, and ortho-Cl-BA, and N-CH_3-BA (structures see Table 4-1). All of these compounds exhibited a purity of > 90% when initially synthesized. The majority of these compounds (meta-, para-, and ortho-Cl-BA and N-CH_3-BA) also remained stable at this purity when shipped overnight to Purdue and left at -18 ˚C for up to 9 months. However, the N-Cl-BA standard was found to be unstable over this length of time when stored as a solid at either -20 or -80 ˚C. This instability was determined by initially measuring its purity within two weeks of arrival which was determined to be 74 and 80% when analyzed by HPLC and GC/MS, respectively. These values were measured by first noting that the other compounds present in this standard also included peaks for compounds that were known, including BA, ortho-, meta-, and para-Cl-BA. Since standards existed for each of these compounds, their concentrations could be quantified, and the purity of the N-Cl-BA standard could then be calculated. After this, this compound underwent decomposition as the solid was found to change color, and thus no purity was determined later. Due to these issues, this mixture was not used to quantify the formation of N-Cl-BA for any of the experiments tested but was used only for qualitative purposes (see later discussions for details). This mixture will also be accordingly defined as the "N-Cl mix" when mentioned in later discussions.

4.3.2 Preparation of Stock Solutions

Stock solutions of all model compounds were prepared at 3.6-25 mM in ACN, stored at -18 °C and used within one month. Free chlorine stock solutions were prepared daily in water and measured spectrophotometrically by quantifying the hypochlorite (OCl^-) concentration at 292 nm (ε = 362 $M^{-1}cm^{-1}$).[63] However, the free chlorine stock solution also contained a significant Cl^- concentration ([Cl^-]/[free chlorine] = 1.2-1.4:1) which was measured by ion chromatography (IC).

4.3.3 Setup of Kinetic Experiments

Kinetic experiments were conducted using synthetic solutions that were placed in 20-100 mL capped glass vials or bottles and run for up to 48 h at room temperature (24±1˚C). These synthetic solutions contained 7-12 µM of an individual model compound (BA, N-CH_3-BA, 2,4,6-trichloro-BA or 2,4,6-trimethyl-BA) and were buffered at various pH conditions from pH 4-9 with either 10 mM acetate (pH 3.9-4.1), 10 mM phosphate (pH 6.0-8.1) or 10 mM borate buffer (pH 8.6-9.3). Reactions were initiated by adding excess free chlorine and in certain cases, with various amounts of Cl^-. The details of each reaction condition, which are sub-categorized within different experimental types, are listed in Table 4-3 provided below. Table 4-3 also includes the concentrations of Cl^- that were not purposefully amended to the solutions but rather came from the HOCl. These concentrations are denoted as originating from the background. Samples were then periodically taken to measure: (i) the residual free chlorine concentration or (ii) were quenched using different quenching techniques (see next section for further details) to measure the remaining model compound concentration and the by-products formed. Other kinetic experiments with BA or N-methyl-BA were further amended to reach to the final Cl^- concentrations of 60-540 mM (type 2 in Table 4-3). For certain cases, parallel experiments with varied concentrations of $NaClO_4$ were also tested to serve as ionic strength controls. Overall, this set of experiments was conducted in order to generate other chlorinating agents, as noted by eqs. 2 and 5.

In addition, one experiment with the N-Cl mix was conducted to specifically evaluate if what is currently considered to be the “Orton Rearrangement” (Scheme 4-1) was valid. This experiment was performed by adding Cl^- (540 mM) to a solution containing 8.8 mg/L of the N-Cl mix at pH 4.0. In this solution, the N-Cl-BA concentration was determined to be approximately 7.0 mg/L (30 µM), given an approximate purity of 80% measured by GC/MS in the same week as this experiment.

Table 4-3. Kinetic experiments in which the model compounds reacted with free chlorine.

Type	pH	Model compound	Model compound concentration (μM)[b]	HOCl (mM) [b]	Cl^- (mM)		
					Amended	From the background[a]	Total
1	4.0-9.0	BA	10	0.2-0.5	0	0.23-0.58	0.23-0.58
	7.0	N-CH_3-BA	10	0.2	0	0.27	0.27
	7.0	2,4,6-trimethyl-BA	10	0.2	0	0.27	0.27
	7.0	2,4,6-trichloro-BA	10	0.2	0	0.27	0.27
2	4.0-7.0	BA	10	0.2	60-540	0.23-0.27	60-540
	3.9	N-methyl-BA	10	0.2	540	0.23	540

[a] Including Cl^- concentrations from the free chlorine stock and buffer solutions

[b] These values are the targeted initial concentrations. The actual concentrations of the model compounds ranged from 8.3-12 μM, and free chlorine concentrations ranged from 0.19-0.23 mM.

4.3.4 Quenching Technique and Analytical Methods

In order to perform each kinetic experiment, a quenching agent was needed to stop the reaction and remove the excess chlorinating agents from solution at various time points. Initially, it was difficult to find an appropriate quenching agent since the polyamide-based monomer was hypothesized to undergo chlorination at the amide N (i.e. form the N-Cl moiety)[7-9] and plausibly reverse back to its parent compound by typically used quenching agents. This problem was considered likely to occur since other compounds containing the N-Cl functional group (e.g. chlorinated primary and secondary amines) also reverted back to their parent compounds when the solution was quenched with thiosulfate ($S_2O_3^{2-}$) or bisulfate (HSO_4^-).[45, 46] In fact, both $S_2O_3^{2-}$ an HSO_4^- are commonly used to quench HOCl and HOBr by serving as nucleophiles but are strong enough to react with N-Cl moieties as well.[45, 46] To assess this possibility, various quenching techniques were tested which either initiated the back reaction (i.e. unsuccessful techniques), or did not initiate the back reaction (i.e. successful techniques). In the end, both techniques were used to assess the reaction kinetics when N-Cl-BA either was or was not the dominant by-product formed or for other reasons (see later discussions). These different quenching techniques subsequently required that two different analytical approaches be used. The first approach included using a quenching technique coupled with LC-UV/vis or LC/MS analysis (approach 1) whereas the second approach included quenching the samples with liquid/liquid extraction coupled with GC/MS analysis (approach 2). The discussions below document how both approaches were designed as well as the challenges and limitations that were incurred by each approach.

Approach 1: Sample Quenching Coupled with LC-UV/vis or LC/MS analysis. In this approach, samples were analyzed by either the HPLC with UV/vis diode-array detection (DAD) (Agilent 1260 Infinity) or by the LC/MS (Agilent 6420 Triple Quadrupole MS). Separation was achieved using an Eclipse Plus C18 column (2.5 mm × 150 mm, 3.5 µm) in which the eluent flow rate was held at 0.3 mL/min. The mobile phase consisted of water (eluent A) and HPLC grade ACN with 0.1% formic acid (eluent B) in isocratic mode at 75% A/25% B for 11 min. For the LC/MS method, the mobile phase consisted of water (eluent A) and MeOH with 0.1% formic acid (eluent B). All of the other LC parameters including the column, flow rate, and run conditions were similar to the HPLC/DAD method. The MS was run using electrospray ionization (ESI) in

positive mode. The single quad was run in scan mode (m/z 50 – 400) in which the parent masses (M+1) of m/z 198 and 232 were quantified for BA and its chlorinated (para-, meta- and ortho-Cl-BA, structures see Table 4-1) by-products. This method was also used to identify and/or quantify several model compounds including N-CH_3-BA, 2,4,5-trimethyl-BA and 2,4,6-trichloro-BA. Their identities were confirmed by cross-comparing their peaks with known standards as well as by confirming their compound molecular weights by LC/MS. The HPLC-DAD method detection limits (MDLs) for BA, ortho-Cl-BA, para-Cl-BA, meta-Cl-BA, and N-CH_3-BA were 22, 42, 40, 15 and 51 nM, respectively. Along with these techniques, the formation of N-Cl-BA was also identified and indirectly quantified by adding SO_3^{2-}, a strong nucleophile, which was determined to fully revert N-Cl-BA back to BA (Fig. 4-1b; see later discussions for further details). Thus, the amount of N-Cl-BA formed could be obtained by calculating the increase in the BA concentration after SO_3^{2-} quenching.

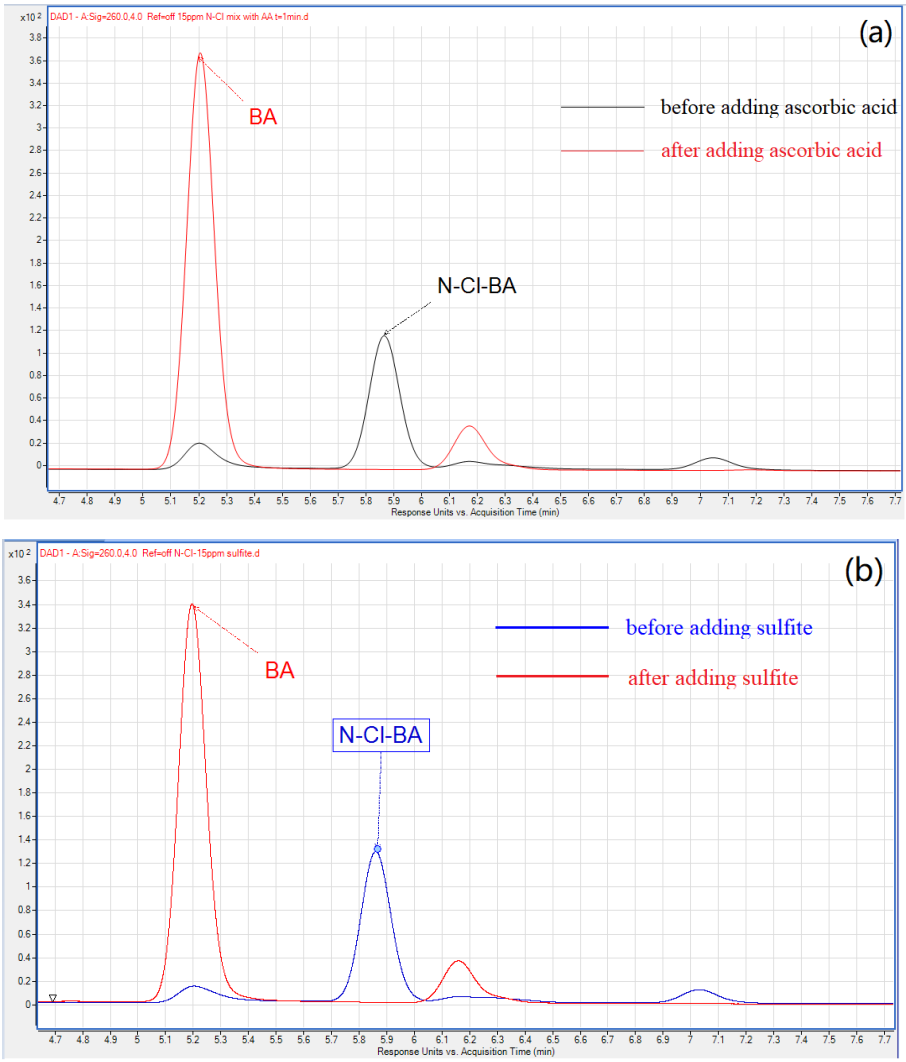


Figure 4-1. The overlaid chromatograms before and after the N-Cl mix was exposed to (a) ascorbic acid and (b) SO_3^{2-}. ([N-Cl mix] = 15 mg/L; [ascorbic acid or SO_3^{2-}]$_0$ = 0.4 mM; [ascorbic acid]$_0$/[N-Cl-BA]$_0$ ≈ 9.3; pH 7.0 with 10 mM phosphate buffer).

Furthermore, it should be noted that for both of these chromatographic methods, eluent B contained formic acid in order to lower the pH to 2.7. The lowered pH was important since it appeared to stabilize the chromatographic signal of the N-Cl-BA peak when the N-Cl mix, dissolved in ACN, was repeatedly injected. For example, the N-Cl-BA and BA peak areas were not consistent without formic acid (Fig. 4-2a) but were quite consistent when adding formic acid (Fig. 4-2b). These results indicated that N-Cl-BA likely incurred some type of reaction during the separation process at neutral pH conditions (Fig. 4-2a) while the lower pH condition minimized this effect (Fig. 4-2b).

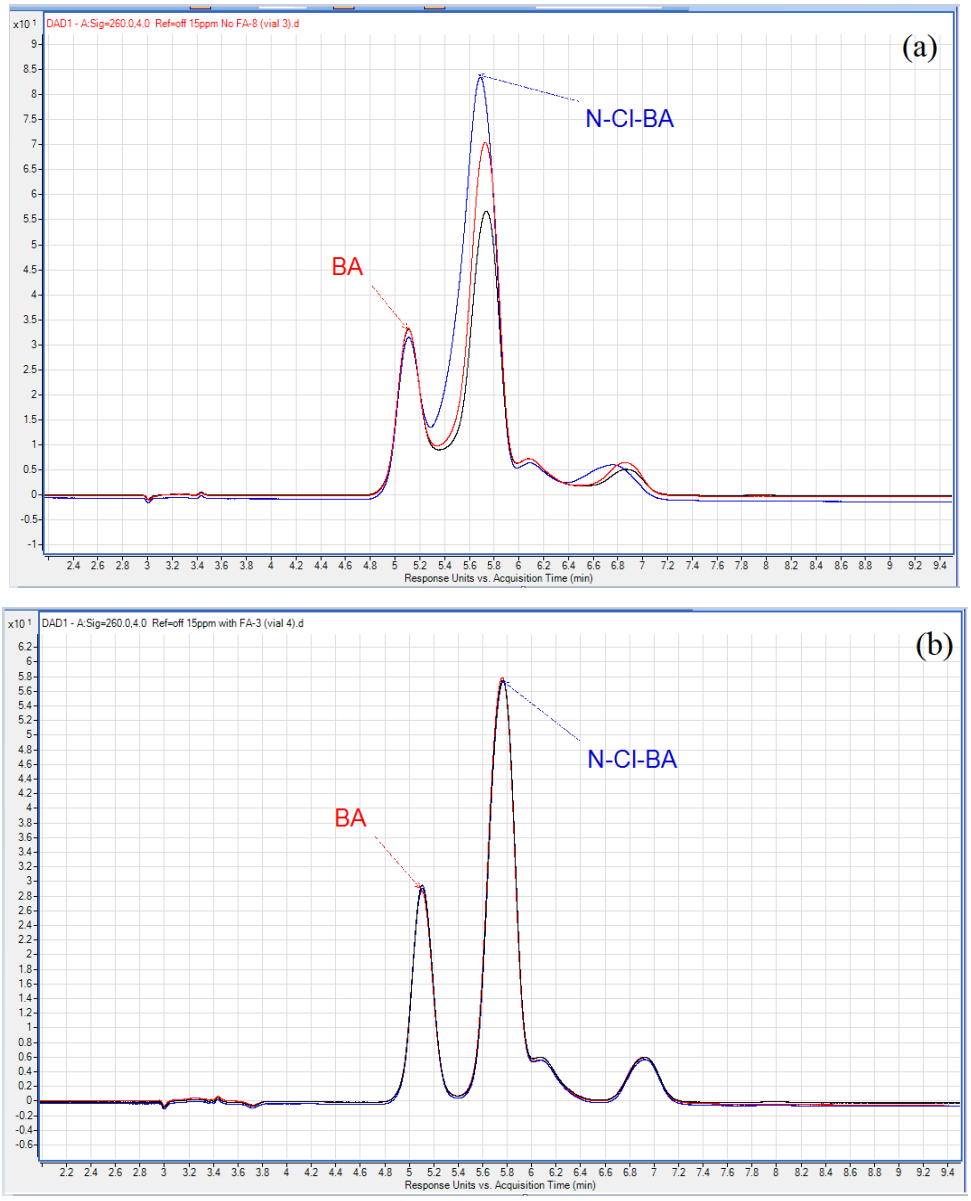


Figure 4-2. An overlay of three HPLC/DAD chromatograms from three different injections of the N-Cl mix (15 mg/L) which either (a) did not contain formic acid in the eluent or (b) did contain formic acid in the eluent.

Several strategies were then tested to see how samples from the kinetic experiments could be quenched. The first option included running samples directly onto the LC system where no specific quenching agent was added but the reaction was quenched or terminated by simply separating the compounds by way of the column. This option was not possible though because it required that chlorine be injected as well and under the lowered pH condition of the eluent, BA loss appeared to be accelerated (Fig. 4-3). The data provided in Fig. 4-3 demonstrated this effect well. In this

figure, the responses of the unquenched samples with formic acid were lower over time than the samples extracted by liquid/liquid extraction and analyzed by the GC/MS, a method later demonstrated to provide accurate BA loss values (see later discussions for more details). Alternatively, the responses of BA initially decreased slightly but then increased again when running unquenched samples without formic acid (Fig. 4-3). This effect was likely due to the instability of the N-Cl-BA compound under the neutral pH conditions, as described above, were potentially hydrolyzed back to form BA (Fig. 4-3). These results subsequently indicated that a quenching agent must be added to the samples to fully remove the residual chlorine or bromine prior to HPLC injection.

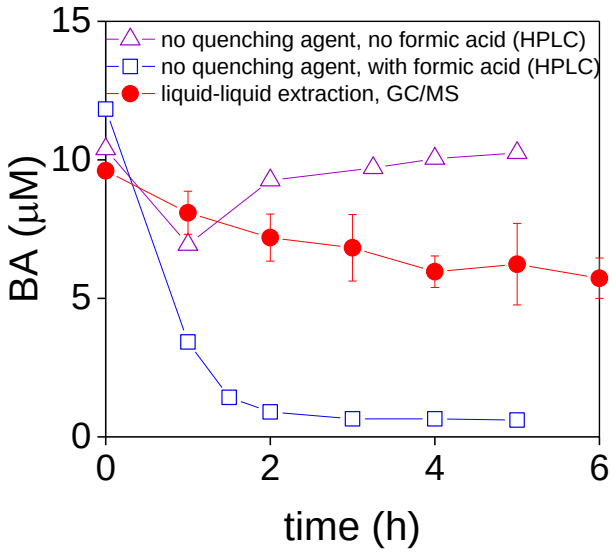


Figure 4-3. A comparison between the kinetic data obtained when not adding a quenching agent to the reaction (with and without formic acid in the HPLC eluent) with that obtained when quenched by liquid/liquid extraction and measured by the GC/MS. ($[BA]_0$ = 9.5-12 μM, [free chlorine]$_0$ = 200 μM, pH 7.0, 10 mM phosphate buffer).

Following this, the effect of various quenching agents including SO_3^{2-}, ascorbic acid and phenol, were all tested and found to reverse BA-N-Cl back to BA to varying degrees. The use of NH_4Cl as a "soft" quenching agent was also considered here since it was previously known to prevent the reversal of several N-Cl containing compounds.[45] However, this approach was inappropriate for these experiments because it involved increasing the pH to ~8.3 to initially form NH_2Cl. This pH increase could potentially have enhanced the hydrolysis of N-Cl-BA to reform

BA (eq. 1), which was an artefact that was not desired. Therefore, the role of SO_3^{2-}, ascorbic acid and phenol was instead evaluated by injecting a 15-20 mg/L standard of the N-Cl mix onto the HPLC. Prior to injection, the sample was either exposed or not exposed to a particular quenching agent. The responses from either condition were then compared to each other in terms of their resulting N-Cl-BA and BA peak areas (Fig. 4-1 and 4-4). First, SO_3^{2-} and ascorbic acid ([ascorbic acid or $SO_3^{2-}]_0$ = 0.4 mM; [ascorbic acid]$_0$/[N-Cl-BA]$_0$ ≈ 9.3) were found to immediately (< 30s) convert N-Cl-BA back to BA (Fig. 4-1).

Lastly, phenol was tested as a quenching agent. In this procedure, phenol was added in considerable excess to free chlorine ([phenol]$_0$/[HOCl]$_0$ = 50) in order for the reaction between phenol and free chlorine (k_{app} = 28 $M^{-1}s^{-1}$ at pH 7, 25 ˚C[47]) to out-compete the reaction of BA with free chlorine (k_{app} ~ 10^{-3}-10^{-1} $M^{-1}s^{-1}$ for amides at pH 7.2-7.4[48]) without causing the decomposition of N-Cl compound to anilide[34]. However, this approach was also found to be unsuccessful since phenol also converted the N-Cl-BA back to BA over time. This result was clearly observed in Fig. 4-4 when phenol was initially added to a sample of the N-Cl mix, representing t = 0 min, and then was injected repeatedly onto the HPLC after different reaction times. In this case, the BA concentration, calculated based on its known calibration curve, steadily increased while the N-Cl-BA peak area steadily decreased for up to 50 min (Fig. 4-4). Alternatively, the responses from the control experiment, where the N-Cl mix (15 mg/L) was dissolved into the buffer at pH = 7.0 alone, were more stable over 50 min in which the BA and N-Cl-BA peak area only increased or decreased slightly (Fig. 4-4). These slight changes in responses of the control experiment were probably due the fact that the sample was residing in water at a pH of 7.0 and likely experienced a small amount of hydrolysis to reform BA over 50 min (eq. 1). Subsequently, these data indicated that phenol could also reverse the N-Cl-BA back to BA, and thus was not appropriate to serve as a quenching agent for samples containing the N-Cl-BA compound.

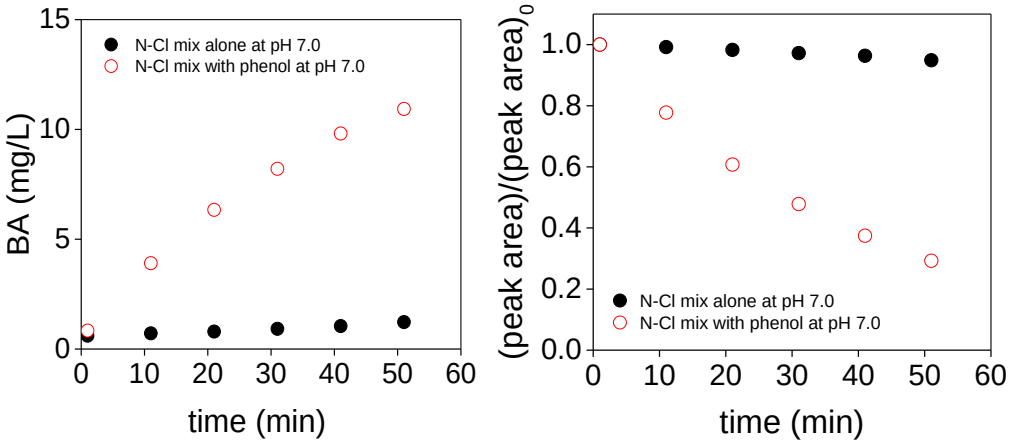


Figure 4-4. Effect of phenol in converting N-Cl-BA back into BA as noted by the changing (a) BA concentration and (b) N-Cl-BA peak area over time. ($[\text{N-Cl mix}]_0$ = 20 mg/L, $[\text{phenol}]_0$ = 10 mM, pH = 7.0, 10 mM phosphate buffer).

Thus, due to these results, the LC-based methods incurred several limitations in this study for assessing the compounds of interest. First, these methods required that the solutions to be quenched prior to injection onto the LC system. However, since all of the quenching agents that were tested including SO_3^{2-}, ascorbic acid or phenol also reacted with the N-Cl moiety, none of these agents could be used to assess the loss of BA when N-Cl-BA served as the dominant by-product. Instead, this method was used for two purposes: (i) measure the model compound and by-products when < 10% of the N-Cl by-product was generated (e.g. experiments involving N-CH_3-BA as the model compound) and (ii) indirectly measure the N-Cl by-product concentration (e.g. N-Cl-BA) by subtracting the BA concentration (determined using a successful quenching approach via the GC/MS; see next section) from the LC-derived BA concentration when using SO_3^{2-} as quenching agent (= [BA] + [N-Cl-BA]).

Approach 2: Sample Quenching Coupled with GC/MS analysis: Since none of the quenching agents tested with the LC were appropriate to use when N-Cl compounds were formed, another quenching technique was attempted using liquid-liquid extraction. This procedure was aimed to physically transfer all of the model compounds and their by-products from the aqueous phase to the organic phase at each reaction time point. Thus, any reaction that these compounds incurred were considered to be terminated during this process because of two effects. First, certain charged chlorinating agents, such as OCl^-, were considered to remain in the aqueous phase and not be

transferred.[49] Second, certain chlorinating agents that are more non-polar (e.g. Cl_2) could plausibly get extracted but were experimentally determined to not undergo any further chemical reactions within the organic solvent phase. This was determined through control experiments where the extracted organic solvent phase was immediately (< 10 min) injected onto the GC/MS but where the same sample was then repeatedly injected over 24 h. The BA concentration was stable over this time frame.

Thus, the extraction procedure consisted of the following steps. Initially, samples (9 mL) at each time point were taken and extracted for 1 min by 1.5 mL DCM which led the sample to be concentrated by a factor of 6. The DCM solvent also contained 3.0 mg/L naphthalene-d8 served as an internal standard. The recovery of BA during the extraction was calculated by comparing two different calibration curves, which were obtained by either (i) dissolving 2.5-15 μM BA into aqueous phase and extracting it by DCM, and (ii) directly dissolving 15-90 μM BA (accounting for the 6-fold concentration factor) into DCM. The obtained calibration curves were similar (Fig. 4-5), and thus the extraction efficiency was determined to be 100%. The recovery of all other model compounds by this same extraction technique were considered to be similar given that their chemical structures were similar to that of BA. In addition, the extraction time of 1 min was considered to be minimal when compared to the overall time frame of the reactions tested which fell over 0.3 to 48 h. A small volume (1 mL) of the DCM layer was then transferred to an autosampler vial and injected onto the GC/MS.

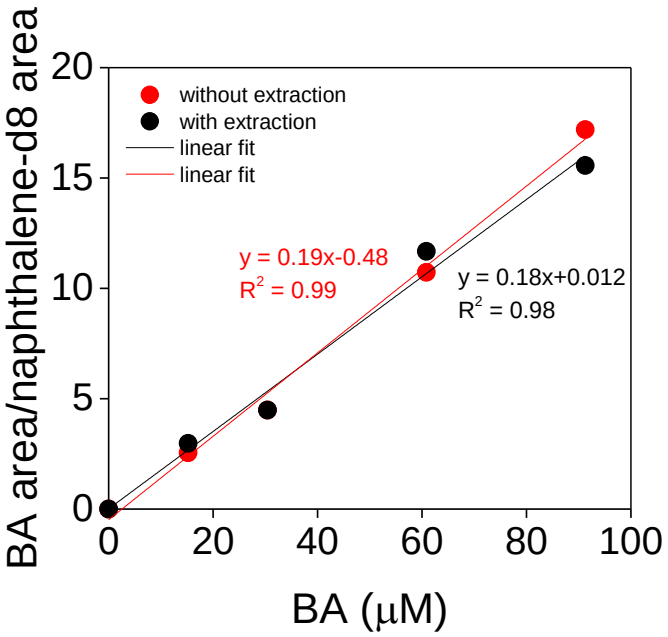


Figure 4-5. Comparison of the BA calibration curves obtained with and without extraction in order to assess its recovery. The y-axis represented the ratio of BA area to naphthalene-d8 (internal standard) area.

The compounds were then analyzed by GC/MS (Finnigan PolarisQ) using liquid injection. Samples (1 µL) were injected at 180 °C using a 1:10 split ratio onto a HP-5MS (30 m × 0.25 mm × 0.25 µm) column. The oven program was held at 80 °C for 1 min, ramped to 240 °C at 25 °C/min, and then held at 240 °C for 4 min. The MS analysis was conducted using electron ionization (70 eV) in positive mode. The MS was run in selected ion monitoring (SIM) mode, and the parameters for each analyte including molecular weight (MS), base peaks (m/z) and ions used for quantifications were summarized in Table 4-4. The MDLs for BA, para-Cl-BA, ortho-Cl-BA, meta-Cl-BA, 2,4,6-trimethyl-BA, and 2,4,6-trichloro-BA were 42, 97, 17, 95, 60 and 360 nM, respectively.

Table 4-4. Details regarding the physical properties, column retention, and ions extracted for the compound analyzed by GC/MS.

Analyte	MW (g/mole)	Retention Time (min)	Ions Used for Quantitative or Qualitative Analysis
naphthalene-d8	136.2	5.36	**136**[a]
BA	197.2	9.20	**105**, 197
N-Cl-BA[b]	231.7	8.93	**105**, 197
ortho-Cl-BA	231.7	9.46	105, **196**, 231
para-Cl-BA	231.7	10.28	**105**, 231
meta-Cl-BA	231.7	10.31	**105**, 231
2,4,6-trichloro-BA	300.6	11.38	**105**, 264, 266
2,4,6-trimethyl-BA	239.3	10.16	**239**

[a] bold values represented the base peaks
[b] only a qualitative assessment was made for this compound

Additional testing was also conducted in order to validate that the liquid-liquid extraction technique quenched the samples in an accurate manner. Two types of experiments were conducted here in which: (i) BA was exposed to excess HOBr at pH 7.0 (Fig. 4-6a and 4-6b) and (ii) N-CH_3-BA was exposed to excess HOBr in the presence of Br^- at pH 6.2 (Fig. 4-6c and 4-6d). For both of these experiments, < 10 % of the N-halogenated (e.g. N-Cl-BA and N-Br-BA) by-products formed (see details in Chapter 5). This fact enabled samples from these experiments to be quenched using two different techniques, liquid-liquid extraction and analysis via GC/MS and SO_3^{2-} quenching and analysis via HPLC, which could then be cross-compared with each other. For both experiments, the data were either plotted as a function of BA concentration (Fig.4-6a and 4-6c) or as a pseudo-first order loss (Fig. 4-6b and 4-6d). The results indicated that when BA reacted with excess HOBr, both quenching techniques exhibited identical kinetic trends where their observed rate constants (k_{obs}) similarly equaled 9.0×10^{-5} s^{-1} (Fig. 4-6b). Similar results also were obtained with N-CH_3-BA where close k_{obs} values of 1.0×10^{-4} s^{-1} were obtained for both quenching techniques (Fig. 4-6d). In the end, these results confirmed that liquid extraction was a valid quenching technique and could be further used to measure the kinetic loss of the model compounds evaluated in this study.

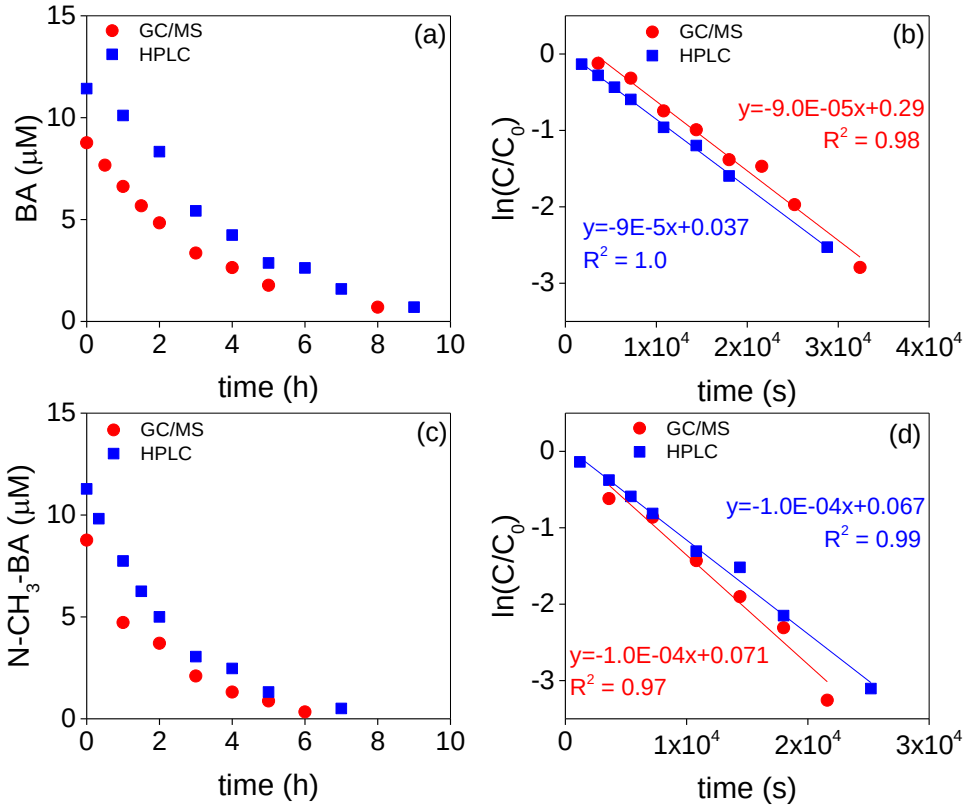
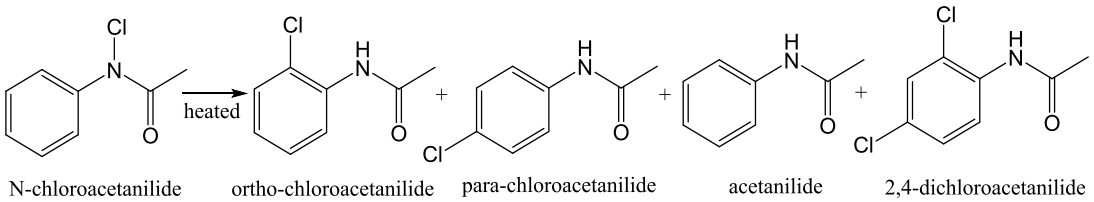


Figure 4-6. Comparison of SO_3^{2-} quenching coupled with HPLC (approach 1) with liquid extraction coupled with GC/MS (approach 2) for reactions of (a, b) BA with HOBr at pH 7.0 ($[BA]_0$ = 9.0-11 μM, $[HOBr]_0$ = 200 μM, 10 mM phosphate buffer), and (c, d) N-CH_3-BA with HOBr in the presence of Br^- at pH 6.2. ($[N\text{-}CH_3\text{-}BA]_0$ = 9.0-11 μM, $[HOBr]_0$ = 200 μM, $[Br^-]_0$ = 0.84 mM, 10 mM phosphate buffer).

Moreover, one last concern for this extraction method was related to the fact that the N-halogenated by-products (e.g. N-Cl-BA) could potentially decompose to reform the parent compound (e.g. BA) within the injection port, given its high temperature of 180 °C. This concern arose because of previous literature, which indicated that N-Cl compounds were not thermally stable and could undergo decomposition when heated.[29, 50] For example, N-chloroacetanilide was observed to decompose to ortho- (17-18%) and para- (41-51%) chloroacetanilide, acetanilide (6.3%) and 2,4-dichloroacetanilide (4.0-7.0%) at 100°C (eq. 6).[50] Also, N-Cl-BA was observed to decomposed to para-Cl-BA and benzoyl chloride at 120-130 °C (eq. 7).[29] This information suggested that if the N-Cl compound (e.g. N-Cl-BA) was generated and did decompose to the parent compound (e.g. BA), this would alter the true kinetic loss of BA over time that was measured by this instrument. Therefore, to evaluate if this was the case, the injection port

temperature was varied from 160 to 260 ˚C to assess how the peak area of BA was subsequently affected. This procedure was used since it was hypothesized that if N-Cl-BA did decompose to BA in the injection port, the extent of decomposition (e.g. [decomposed N-Cl-BA]/[injected N-Cl-BA]) would increase as the injection port temperature increased. In addition, various concentrations of N-Cl-BA concentrations were injected, since it was also suspected that the higher concentration of N-Cl-BA might have larger effect.



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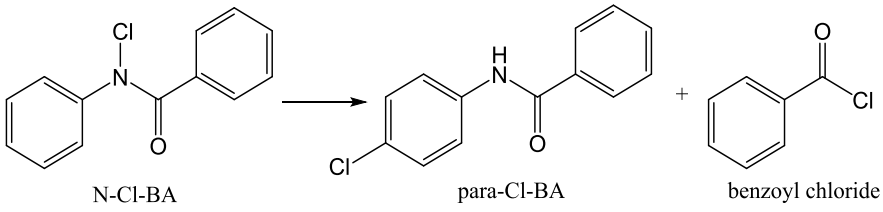


(7)

In order to test this, two types of samples were evaluated including pure BA standards (5.0 and 10 μM), and samples taken at certain time points (3 to 29 h) during the reaction of BA with free chlorine. These samples were determined to contain both BA, which were directly measured based on calibration curve, and ~0.5 to 2.8 μM N-Cl-BA, which were indirectly quantified using the sulfite (SO_3^{2-}) quenching approach. The BA standards were run so that they could serve as control experiments to account for any response differences driven solely by changing injection port temperature. The results indicated that as the injection port temperature increased, the peak areas of BA from both pure BA standard (control) and the samples containing both BA and N-Cl BA decreased slightly (Fig. 4-7).

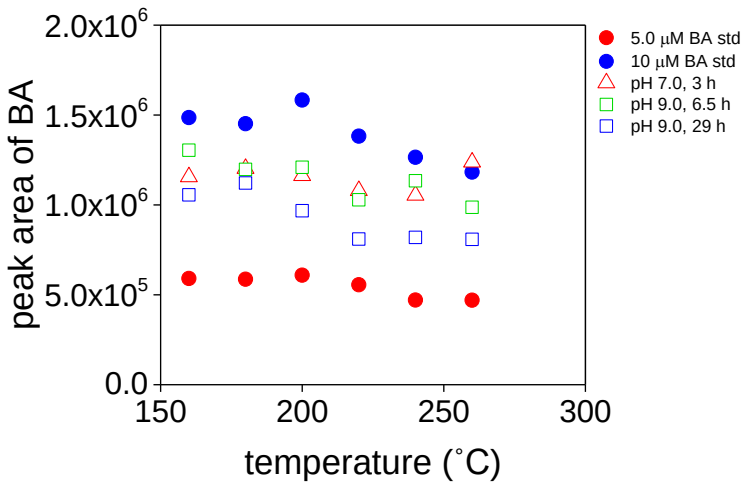


Figure 4-7. The BA peak areas as a function of injection port temperature when either injecting two BA standards ($[BA]_0$ = 5.0 and 10 μM) or three samples in which BA reacted with HOCl at pH 7.0 and 9.0. ($[BA]_0$ = 10 μM, $[HOCl]_0$ = 200 μM, 10 mM phosphate (7.0) or borate (9.0) buffer).

In the end, such results suggested that either: (i) the decomposition of N-Cl-BA to BA was not significant over this temperature range, or (ii) the N-Cl-BA present in solution had already fully converted to BA at the starting injection port temperature of 160˚C, such that any further increase in temperature was not needed to initiate greater decomposition. However, additional evidence from previous literature supports the fact that option (i) rather than option (ii) occurred. In one study, only 6.3% of N-Cl-acetanilide decomposed back to its parent compound, acetanilide, when heated.[50] Moreover, another study suggested that the thermal decomposition of N-Cl compounds (e.g. N-chloroacetanilide) to form the amide was highly solvent dependent.[51] Their results found that, the chlorine could be transferred from the N-Cl compound to the solvent in readily substituted solvents (e.g. acetoacetic ester) to form anilide.[51] This further supported that the decomposition of N-Cl-BA to BA did not happen in this study, since the samples were extracted by DCM, of which the substitution reaction with chlorine required much higher temperatures (400-650 °C).[52]

4.3.5 Measurement of residual chlorine and chloride (Cl^-)

The residual concentrations of the total chlorinating agents were measured by the DPD spectrophotometric method at 515 nm.[53] This method was conducted for experiments that lasted longer than 6 h in order to ensure that the chlorinating agents (e.g. HOCl/OCl^-) were still in excess when compared to the model compound concentration. In addition, the Cl^- concentration in various buffers and the free chlorine stock was measured by IC (Metrohm 940 Professional IC Vario).

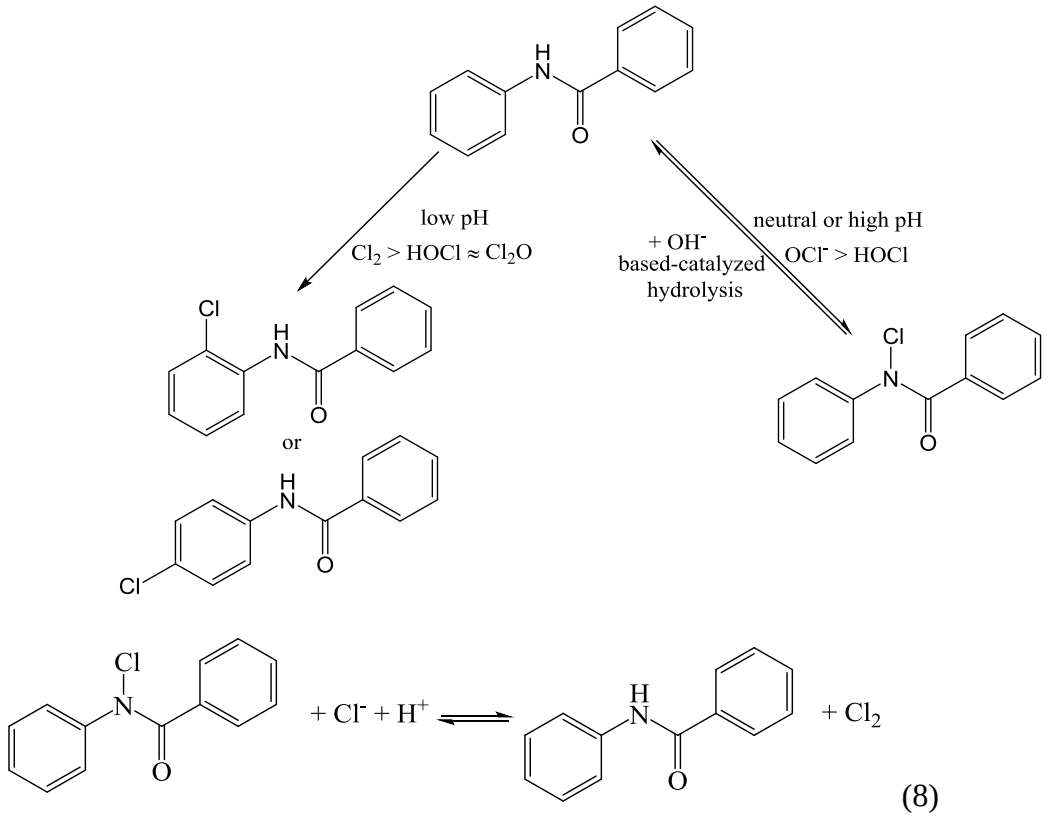
Separation occurred using an A Supp 7-250/4.0 column at 30 ˚C. The eluent contained 1.0 mM Na_2CO_3 and 4.0 mM $NaHCO_3$ and was run at a flow rate of 0.7 mL/min. The MDL for Cl^- was 1.2 µM.

4.4 Results and Discussions

4.4.1 Overview of the Reaction Mechanisms Involved

Overall, a new reaction mechanism for the chlorination of the polyamide-based monomer is proposed (scheme 4-2), given the experimental data collected in this study and by revisiting previous literature. The proposed reaction mechanism differs significantly from what is currently known as the "Orton Rearrangement" (scheme 4-1), which was initially questioned for several reasons. First, it was unclear why the chlorinated amide (N-Cl) reacted with H^+ and Cl^- in solution to generate Cl_2 (forward reaction in eq. 8) since H^+ and Cl^- can directly react with HOCl to form Cl_2 (eq. 2), as discussed in the introduction.

Scheme 4-2. New Proposed mechanims for chlorination of polyamide based monomer



Apart from these kinetic differences, experiments were also conducted to determine if the Orton Rearrangement (scheme 4-1) would in fact take place under the experimental conditions defined in this pathway. Thus, two experiments were conducted to evaluate this, where (i) N-Cl-BA was exposed to Cl^- at a relatively low pH (pH 4.0) so that the H^+ concentration was increased and not a limiting factor, and (ii) BA was exposed to excess free chlorine under the same conditions (Cl^- concentration and pH). It was expected that if N-Cl-BA reacted with Cl^- and H^+ to form Cl_2 (forward reaction in eq. 8), the ring would then be directly chlorinated and the concentrations of the ortho- and para- ring products would increase. Thus, if the Orton Rearrangement pathway was taking place, the fact that N-Cl-BA was the starting reactant in the first experiment (i), rather than initially being generated in experiment (ii), suggested that ring-Cl by-product formation should be faster for experiment (i) than (ii). However, the results indicated that for experiment (i), both BA and the chlorinated ring products (an initial concentration of the ring products were present due to the impurity of the N-Cl-BA standard), did not change over 48 h (Fig. 4-8a). Alternatively, for experiment (ii), 79% of BA reacted within 15 min and generated para- and ortho-Cl-BA products which represented 85% of the total products formed (Fig. 4-8b), and meta-Cl-BA was not observed above d.l.. These findings suggested either that N-Cl-BA did not readily react with Cl^- and H^+ to form Cl_2 (forward reaction in eq. 8) or that the formed Cl_2 did not directly chlorinate the ring ((III) in scheme 4-1). The latter possibility did not seem likely though due to other results obtained in this study (see later discussions) and also because it was well known that ring of acetanilide can react with Cl_2 directly to form ring by-products.[6, 12, 33] Therefore, the ring-Cl products formed in experiment (ii) in the presence of Cl^- at pH 4.0 should be due to an alternative pathway, likely direct chlorination, rather than via Orton Rearrangement.

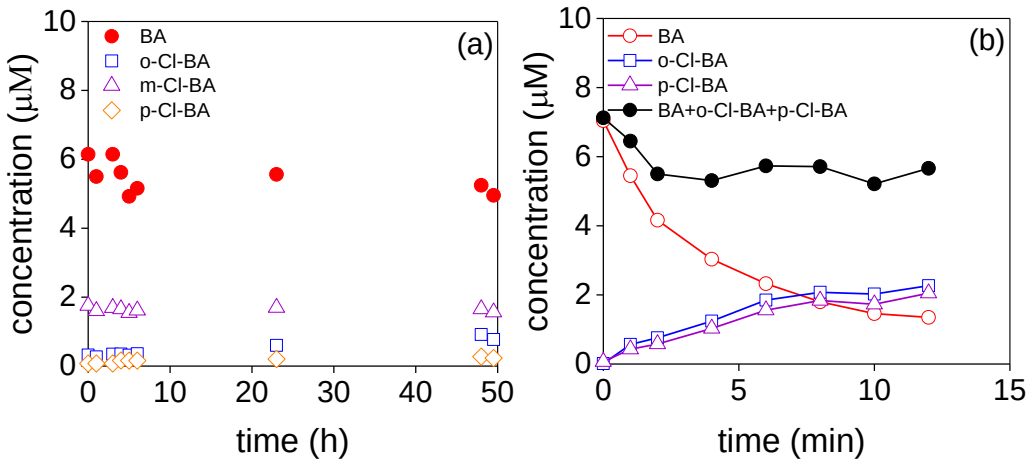


Figure 4-8. The changes in concentrations of BA and ring chlorinated products including ortho-, para- and meta-Cl-BA versus time when (a) exposing N-Cl-BA to Cl^- at pH 4.0, and (b) exposing BA to free chlorine in the presence of Cl^- at pH 4.0. ($[N\text{-}Cl\text{-}mix]_0$ = 4 mg/L, $[BA]_0$ = 7 μM, [free chlorine]$_0$ = 200 μM, and $[Cl^-]_0$ = 540 mM; 10 mM acetate buffer)

Moreover, N-CH_3-BA was also used to investigate if the ring moiety could be directly chlorinated rather than cycling through the amide N, since the amide N moiety was no longer available due to the presence of the methyl group. In this case, N-CH_3-BA was exposed to free chlorine alone at pH 7.0 as well as at pH 4.0 but with 540 mM Cl^- added to the solution in order to trigger greater formation of Cl_2 (eq. 2). Interestingly, N-CH_3-BA did react under these conditions in which 29% loss was observed after 50 h with free chlorine alone at pH 7.0, whereas 45% loss was observed after 24 h with free chlorine and Cl^- at pH 4.0 (Fig. 4-9). These results indicated that ring chlorination could still occur even without the N-H functional group present, especially when higher amounts of Cl_2 existed (eq. 2; $[Cl_2]_{\text{with Cl-/pH 4.0}}$: $[Cl_2]_{pH7.0}$ = 3.1×10^{-5} M: 1.0×10^{-11} M (Table 4-5)). Further details on how the kinetics of the N-CH_3-BA reactions compare to BA and the role of various chlorinating agents will be provided in later discussions.

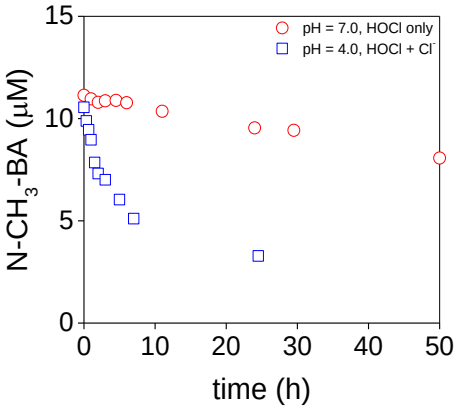


Figure 4-9. Degradation of N-CH_3-BA versus time when reacting with free chlorine at pH 7.0, and in the presence of Cl^- at pH 4.0. ([N-CH_3-BA]$_0$ = 10 µM; [free chlorine]$_0$ =200 µM; [Cl^-] = 540 mM; 10 mM phosphate (7.0) or acetate buffer (4.0)).

Table 4-5. Equilibrium concentrations of chlorinating agents under different conditions**

pH	$[HOCl]_0$ (µM)	$[Cl^-]_0$ (mM)	$[HOCl]_{eq}$ (M)	$[Cl_2]_{eq}$ (M)	$[Cl_2O]_{eq}$ (M)	$[OCl^-]_{eq}$ (M)
4.0	200	0.23	2.0×10^{-4}	1.2×10^{-8}	3.5×10^{-10}	5.5×10^{-8}
6.2	200	0.27	1.9×10^{-4}	8.2×10^{-11}	3.2×10^{-10}	8.8×10^{-6}
6.5	200	0.27	1.8×10^{-4}	3.7×10^{-11}	2.9×10^{-10}	1.8×10^{-5}
7.0	200	0.27	1.5×10^{-4}	1.0×10^{-11}	2.1×10^{-10}	4.7×10^{-5}
9.3	200	0.24	3.6×10^{-6}	1.2×10^{-15}	1.1×10^{-13}	2.0×10^{-4}
7.0	200	60	1.7×10^{-4}	3.7×10^{-9}	2.4×10^{-10}	3.3×10^{-5}
4.0	200	540	1.7×10^{-4}	3.1×10^{-5}	2.5×10^{-10}	3.6×10^{-8}
6.5	200	540	1.9×10^{-4}	9.9×10^{-8}	3.0×10^{-10}	1.4×10^{-5}

**The approaches to calculate the equilibrium concentrations were described in section 3.4.2.2.

4.4.2 Chlorination of Polyamide-based Monomers

Based on the discussion above, BA is hypothesized to not follow the Orton Rearrangement pathway but to instead have two separate reactive sites which are independent of each other (Scheme 4-2). These reactive sites include the amide N and the ortho- and para- positions of the anilide ring. The ability for one reactive site to be chosen over the other is dependent on which pathway is kinetically preferred, which is a function of: (i) pH, (ii) Cl^- concentration, and (iii) the resulting chlorinating agents (e.g. Cl_2, HOCl, OCl^-, and Cl_2O) that are generated. The following sections provide additional results that detail how these factors differ for various water quality conditions and affect the kinetics of the reactions, while also further supporting this new proposed pathway.

4.4.2.1 Chlorination of the amide N

Kinetic experiments indicated that BA reacted with free chlorine to primarily chlorinate the amide N moiety and form N-Cl-BA over the full pH range tested (pH 4 to 9) but especially under neutral and high pH conditions. These results were initially observed at neutral pH conditions (pH 6 to 7) in which BA decayed fast at the beginning, where 45-60% loss (1-$[BA]_t/[BA]_0$) was observed within 12 h, and then reached more of a plateau over 48 h where < 15% loss was observed (Fig. 4-10a). The residual free chlorine concentration was also measured since the reaction times were relatively long, and free chlorine was found to decrease by 22%, 44%, and 21% for pH 6.2, 6.5 and 7.0, after 48 h, respectively (Fig. 4-10b). At first, a second-order rate expression was used to characterize these kinetics (eq. 9) so that an apparent second-order rate constant (k_{app}, $M^{-1}s^{-1}$) could be obtained. To do this, the change in the total free chlorine concentration was accounted for by integrating its concentration over time to create a free chlorine exposure term (eq. 10), which then generated eq. 11:

$$\frac{d[BA]_t}{dt} = -k_{app}[BA]_T[free\ chlorine]_T \qquad (9)$$

$$ln\frac{[BA]_t}{[BA]_0} = -k_{app} \cdot \int_0^t [free\ chlorine]_T dt \qquad (10)$$

$$ln\frac{[BA]_t}{[BA]_0} = -k_{app} \cdot free\ chlorine\ exposure \qquad (11)$$

The kinetic data were then fitted to eq. 11 to obtain k_{app}, which was equivalent to the slope of the line, but a non-linear response was observed (Fig. 4-10c). This non-linear fit could be explained by the reformation of BA, which occurred through the base-catalyzed hydrolysis of N-Cl-BA (eq. 1).[14, 15, 34]

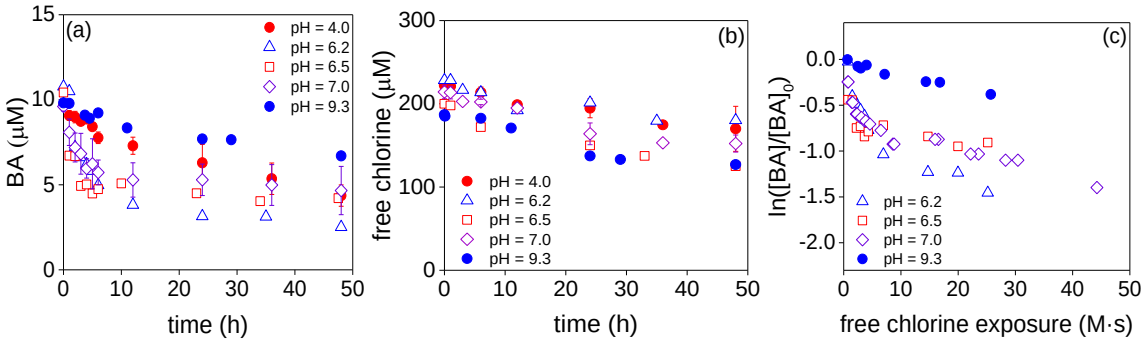


Figure 4-10. Degradation of (a) BA and (b) free chlorine versus time, and (c) loss of BA versus free chlorine exposure during reaction of BA with free chlorine at pH 4.0-9.3. ($[BA]_0$ = 10 μM; $[free\ chlorine]_0$ =200 μM; 10 mM acetate (pH 4.0), phosphate (pH 6.0-7.0) or borate (pH 9.2) buffer). Error bars represent the standard deviation of ≥ 3 replicates.

This conclusion was reached since N-Cl-BA was also further identified to be the main by-product formed at pH 7.0, where 3.6 µM was generated after 48 h which represented > 90% of the total by-products generated (Fig. 4-11a). This concentration was indirectly determined by the SO_3^{2-} quenching approach via HPLC where [N-Cl-BA] = $[BA]_{quenched/HPLC}$ - $[BA]_{GC/MS}$ (see section 3.3.4 for further details). Alternatively, other by-products including para- and ortho-Cl-BA were also formed but their summed concentrations only made up < 10% of the initial BA concentration (Fig. 4-11a). The concentrations from all three by-products and the residual BA were then summed together which represented >95% of the initial BA concentration, which suggested that the total mass balance was nearly closed (Fig. 4-11a). Similar results were also obtained for pH 6.2 and 6.5, where the formation of ring chlorinated products including para- and ortho-Cl-BA from BA was <10%, and N-Cl-BA likely filled the gap in terms of the overall mass balance (Fig. 4-11b and 4-11c).

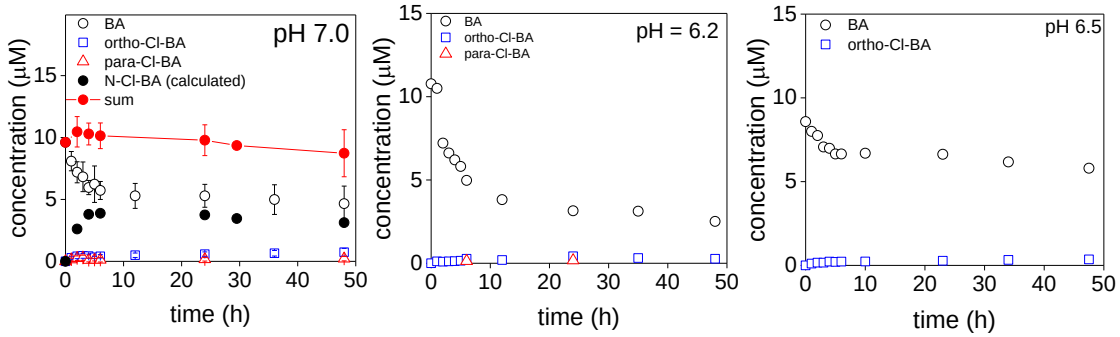
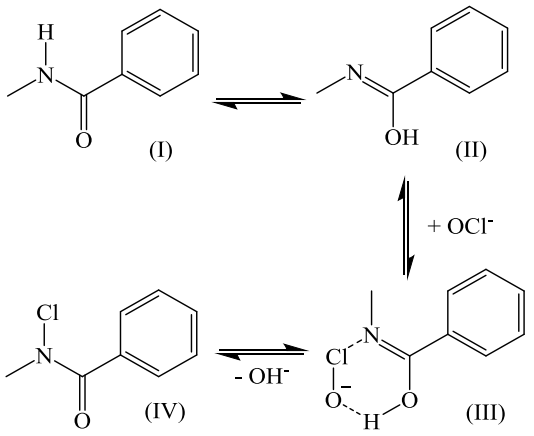


Figure 4-11. Products formation versus time during reaction of BA with free chlorine alone at (a) pH 7.0, (b) pH 6.2 and (c) pH 6.5. ($[BA]_0$ = 10 µM; $[\text{free chlorine}]_0$ =200 µM; 10 mM phosphate buffer)

Since the specific hydrolysis rates were not known, it was difficult to model this kinetic pattern and further ascertain what specific chlorinating agents were responsible for initiating the reaction. However, previous studies did indicate that when various anilides were exposed to free chlorine, the amide N was chlorinated to form the N-Cl moiety (eq. 3). These studies found that hypochlorite, OCl^-, the conjugate base of free chlorine, rather than the conjugate acid, HOCl, was the dominant chlorinating agent involved.[14, 15, 22, 29, 34, 54, 55] In this case, the amide N (eq. 12) can always tautomerize between the I and II forms (eq. 12). Once in form II, it can then form multiple hydrogen bonds with OCl^-, (II, eq. 12) to generate a highly stable six membered ring (III, eq. 12).[14, 15, 34] At this point, hydroxide (OH^-) can then be lost to generate the N-Cl compound (IV, eq. 12). [14, 15, 34]

Due to this reaction, HOCl is perceived to have a lower reactivity with the amide N to form N-Cl since the hydrogen bond between the O^- and Cl (III, eq. 13) would be considerably weakened.[55] In addition, rate constants determined for other amides supported that OCl^- was a stronger reactant than HOCl (Table 4-6).



(12)

Table 4-6. Rate constants for N-chlorination of secondary amides (R_1-C(O)NH-R_2)[54]

R_1	R_2	k_{HOCl} ($M^{-1}s^{-1}$)	k_{OCl^-} ($M^{-1}s^{-1}$)
CH_3	CH_3	1.7×10^{-3}	1.82×10^{-2}
H	CH_2CH_3	1.7×10^{-3}	1.15×10^{-1}
H	CH_3	1.7×10^{-3}	2.1×10^{-1}

To then investigate this chemistry further, a wider pH range (pH 4.0 and 9.3) for this reaction was tested. At pH 4.0, the loss of BA was relatively slow at the initial phase (< 5h) of the reaction but steadily decreased such that a slightly greater loss of 45% over 48 h was observed as compared to the pH 6-7 condition (Fig. 4-10a). Thus, a more linear response ($R^2 = 0.99$) was obtained when plotting the exponential loss of BA versus time (Fig. 4-12). This trend of BA loss was then coupled with the by-products formed in which up to 2.1, 1.7, and 1.7 µM of ortho-Cl-BA, para-Cl-BA, and N-Cl-BA were generated after 50 h, which represented up to 38, 31, and 31% of the total by-product distribution, respectively (Fig. 4-13a). The sum of these by-products along with the residual BA concentration also led the mass balance to be completely closed (Fig. 4-13a). As a result, this data has led to several key findings. First, the fact that this data resulted in a more linear first order loss suggested that: (i) all of the chlorinating species were either in excess or at steady-state concentrations throughout the reaction and (ii) the re-formation of BA via base-catalyzed was likely not significant (eq. 1), which was expected given the lower pH condition of 4.0. Moreover,

the slower degradation of BA at the initial phase of the reaction (< 5 h) at pH 4.0 as compared to pH 6-7 conditions was also an important difference given that the effect of hydrolysis in both cases was considered to be minimal at this initial phase. This difference indicated that the chlorinating agents formed at pH 7.0 reacted faster with BA than the sum of the chlorinating agents involved at pH 4.0. One hypothesis to account for this finding proposes that this effect is driven by the greater reactivity of the amide N with OCl^- as compared to HOCl, since the OCl^- concentration increases by three orders of magnitude when moving from pH 4.0 to 6.0-7.0 (Table 4-5). This hypothesis would then match the results obtained from previous literature as discussed above.[22, 54, 55] It is also hypothesized the greater OCl^- concentration at pH 7.0 also seemed to outcompete the reactions involved with other chlorinating agents at pH 4.0 (e.g. Cl_2), which likely led to the formation of the ring by-products at pH 7.0 (see later discussions for further details).

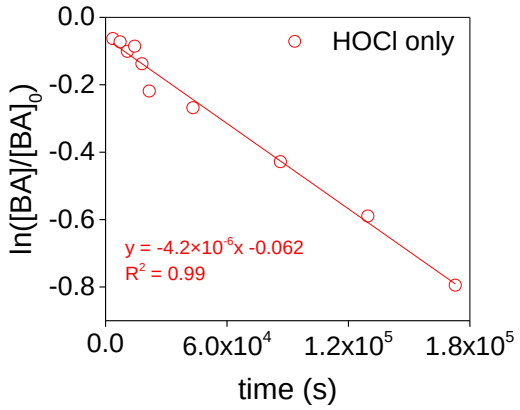


Figure 4-12. Exponential loss of BA versus time during reaction of BA with free chlorine alone at pH 4.0. ($[BA]_0$ = 10 µM; $[\text{free chlorine}]_0$ =200 µM; 10 mM acetate buffer)

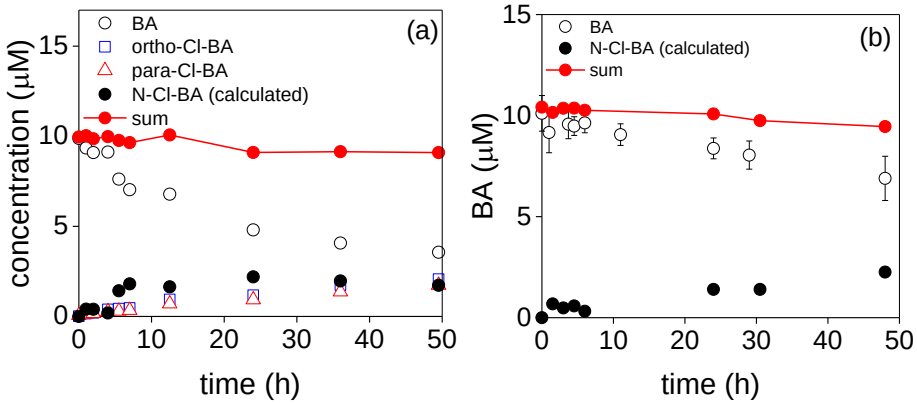


Figure 4-13. Products formation versus time during reaction of BA with free chlorine alone at (a) pH 4.0 and (b) pH 9.0. ($[BA]_0$ = 10 µM; $[\text{free chlorine}]_0$ =200 µM; 10 mM acetate (4.0) or borate (9.0) buffer).

Moreover, results at pH 9.3 indicated that the overall degradation of BA was considerably slower than at pH 6-7 but only slightly slower than at pH 4.0 (Fig. 4-10a). At this pH, N-Cl-BA was also determined to be the only by-product that formed after 48 h, again indicating that the amide N was the main reactive site during chlorination (Fig. 4-13b). Its concentration along with the residual BA concentration also led the overall mass balance to be completely closed (Fig. 4-13b). Such results were interesting since they suggested that while the reaction overall appeared to be quite slow, this slow rate was possibly due to both the forward chlorination reaction (eq. 12) and backwards base-catalyzed hydrolysis reaction (eq. 1) being quite fast. These dual reactions then counteracted each other, which led the overall loss of BA to be lower than the other pH conditions. This effect was especially triggered at this high pH because the forward reaction (eq. 12) was likely accelerated by the greater OCl^- concentration (2.0×10^{-4} M, Table 4-5) while the backwards reaction (eq. 1) was similarly accelerated by the greater OH^- concentration. Overall though, it should be noted that to derive a more definitive assessment of how different chlorinating agents present in this system affected the degradation of BA, a kinetic model would need to be fitted to this data. It was not possible to build this model within the framework of this study since the hydrolysis rate constants were not known and could not be experimentally determined given several experimental limitations (see section 3.3.4 for further details). As a result, the kinetic equation was left with too many unknowns. A closer attempt to derive a model and determine reaction rate values for different chlorinating agents was made in the next section by operating under conditions where the role of hydrolysis was minimized (see details in next section). However, aside from such efforts, it is clear that future research is needed to build a more robust kinetic model over this tested pH range and subsequently isolate the specific reaction rate constants associated with specific chlorinating agents.

4.4.2.2 Chlorination of the anilide ring

For the experiments where only free chlorine was added at pH 4.0-7.0, varying amounts of ring chlorination products were also formed, with the highest levels formed at pH 4.0. Given that, as discussed above, the Orton Rearrangement likely did not occur, as similarly noted by previous literature,[31] it is hypothesized that the ring by-products were generated when BA directly reacted with Cl_2, or HOCl to a much lesser degree. Cl_2 is predicted to serve as the more dominant reactant since it is well known to be a stronger chlorinating agent than HOCl.[23, 26, 56, 57] In these reactions,

Cl_2 was generated due to the fact that the free chlorine stock contained 0.23-0.27 mM Cl^-, which lead to 10^{-11}-10^{-8} M of Cl_2 to be formed between pH 4-7 (Table 4-5). The role of Cl^- was also observed before where it was concluded that the presence of a slight concentration of Cl^- in the solutions containing HOCl under pH 5.3-7.0 was sufficient to form Cl_2 (eq. 2), which chlorinated the aniline ring of acetanilide rapidly.[34]

Therefore, in order to further test the role of Cl^- given its presence in saline waters (Table 4-2) and ability to form Cl_2, additional experiments were conducted with varying chloride doses. Different concentrations of Cl^- or ClO_4^-, which served as an ionic strength control, were first added to the reaction solutions at pH 6-7 (Fig. 4-14 and 4-15). Cl^- was added to solutions at pH 6.5 and 7.0 at 540 and 60 mM, respectively, and the results indicated that Cl^- had minimal influences on altering the kinetics (Fig. 4-14) or by-product formation (Fig. 4-15) of BA. The degradation trend remained the same as when no extra Cl^- was added (HOCl only), probably because similar amounts of OCl^- were present and dominated the reaction in the system (Table 4-5) while a similar extent of based-catalyzed hydrolysis also existed given the same pH conditions. In addition, the product distribution at pH 6.5 with 540 mM Cl^- was also analyzed, where N-Cl-BA, determined by SO_3^{2-} quenching technique, still dominated, consisted of >80% of the formed products (Fig. 4-15). Moreover, when compared to the no reaction where no Cl^- was added (HOCl only), the presence of 540 mM Cl^- at pH 6.5 slightly enhanced the formation of ring chlorination products (Fig. 4-16), where the summed conversion of ortho- and para-Cl-BA from BA increased from 5.2% (HOCl only) to 12% (Fig. 4-16). This increase in ring chlorinated products formation was likely due to the slightly higher formation of Cl_2 that was initially formed (Table 4-5).

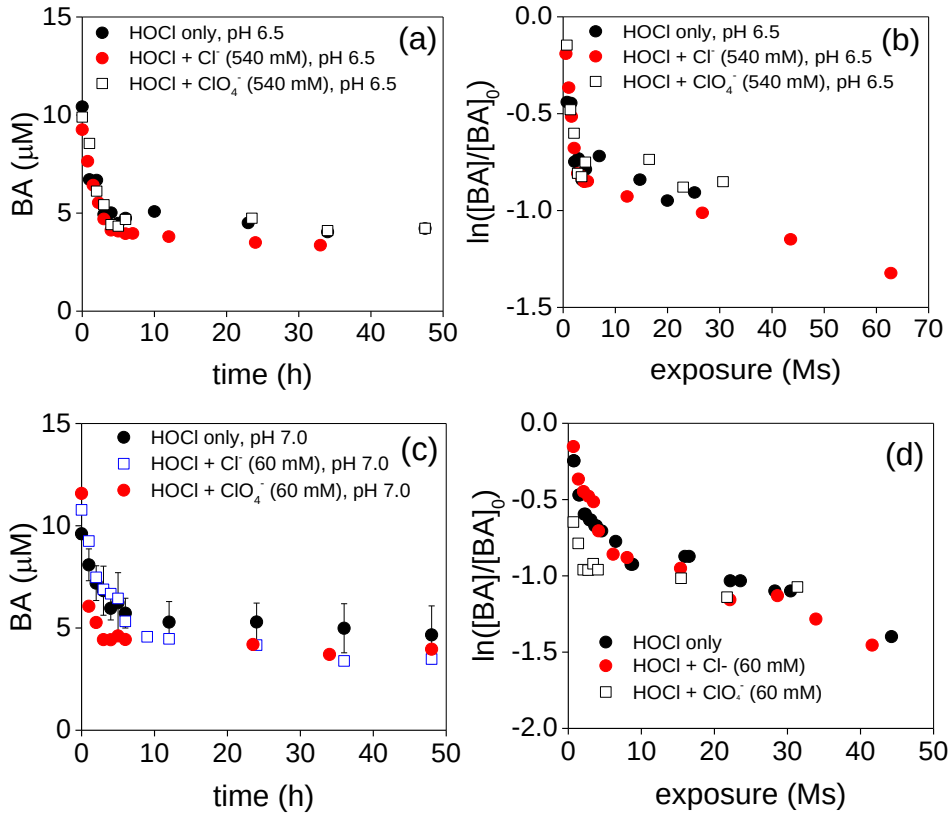


Figure 4-14. Degradation of (a, b) BA versus time and (c, d) loss of BA versus free chlorine exposure during reaction of BA with free chlorine alone, in the presence of Cl^- or ClO_4^-. ($[BA]_0$ = 10 μM; [free chlorine]$_0$ =200 μM; [Cl^- or ClO_4^-]$_0$ = 60 or 540 mM; pH 6.0-7.0; 10 mM phosphate buffer)

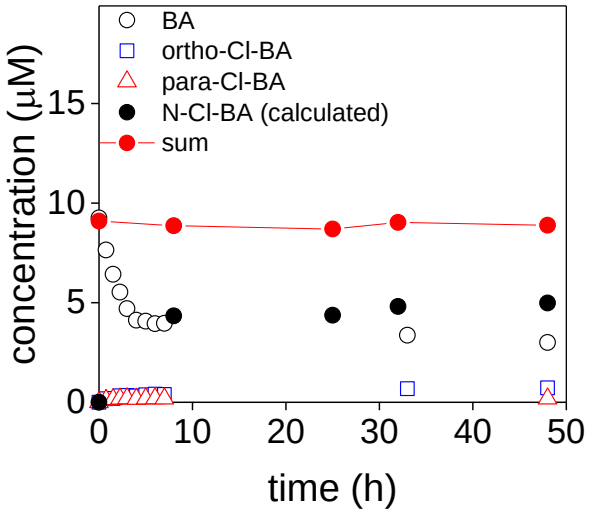


Figure 4-15. Products formation versus time during reaction of BA with free chlorine in the presence of Cl^- at pH 6.5. The N-Cl-BA formation was indirectly quantified by SO_3^{2-} quenching approach. ($[BA]_0$ = 10 μM; [free chlorine]$_0$ =200 μM; [Cl^-]$_0$ = 540 mM; 10 mM phosphate buffer)

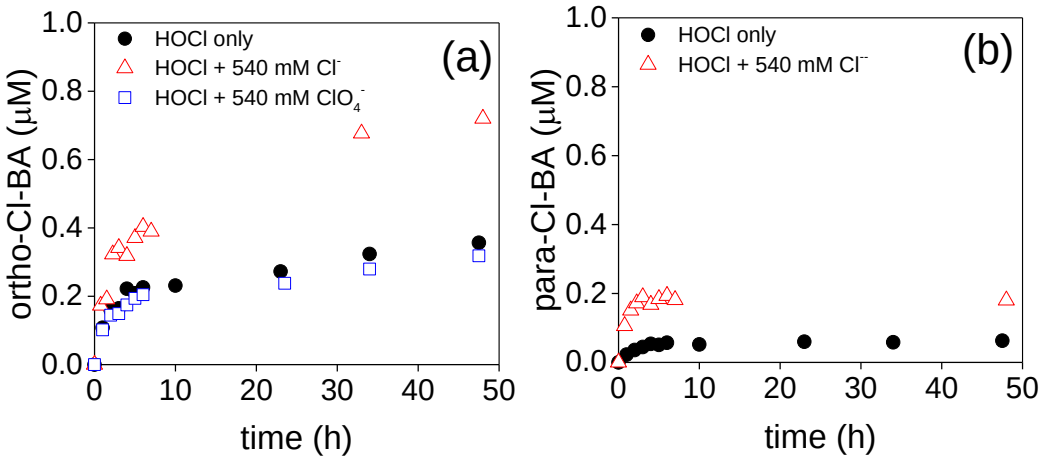


Figure 4-16. Formation of (a) ortho-Cl-BA and (b) para-Cl-BA during reaction of BA with free chlorine, in the presence of Cl^- or ClO_4^-. The para-Cl-BA formation for HOCl + ClO_4^- was below d.l. ($[BA]_0$ = 10 μM; [free chlorine]$_0$ =200 μM; [Cl^- or ClO_4^-]$_0$ = 540)

Therefore, any signs of enhancing the kinetics via Cl_2 formation (eq. 2) by reacting with the amide or ring sites seemed to be quite minimal at this pH range. This effect may be potentially due to the low formation of Cl_2 since eq. 2 was limited by H^+, or the stronger reactivity of OCl^- toward the amide N than Cl_2 with the ring. In addition, these results suggest that at pH 6-7, chlorination of the polyamide membrane surface is dominated by N-chlorination which can be reversed by hydrolysis, even as Cl^- concentrations reach seawater levels ([Cl^-] = 540 mM in open ocean water). These results further implied that under these conditions, the membrane should incur permanent damage slowly since most of the incorporated Cl can be removed by increasing the rate of hydrolysis by raising the pH. This result implied that if permanent membrane damage at this neutral pH range was observed in other cases, this effect was likely not due to the reaction with free chlorine only, or even in the presence of Cl^-, but triggered by other water quality conditions, such as the presence of other halides that can react with HOCl to form much more reactive agents.[58, 59]

In order to increase the formation of Cl_2, kinetic experiments were also conducted where 540 mM Cl^- was added at a lower pH of 4.0 (Fig. 4-17). At this pH condition, Cl^- addition significantly increased BA degradation, where more than 80% of BA reacted within 0.25 h (Fig. 4-17a). This increase was not caused by the increase in ionic strength because the addition of 540 mM ClO_4^- did not exhibit the same rapid loss of BA, and similarly matched the level of BA degradation observed with HOCl alone (Fig. 4-17a). In addition, when the data was plotted as exponential loss

of BA versus time, all three experiments was found to observe linear responses (Fig. 4-17b). The reasons behind why these linear responses occurred were similar to those outlined in the previous section. However, in the case where 540 mM Cl^- was added, it is hypothesized that the loss of BA is completely controlled by the reaction with Cl_2 via eq. 4, which directly chlorinates the anilide ring. This hypothesis was further supported by the results of product distribution, where no N-Cl-BA formed as determined by SO_3^{2-} quenching approach, and thus ring chlorination products were the only products formed under this condition (Fig. 4-8b).

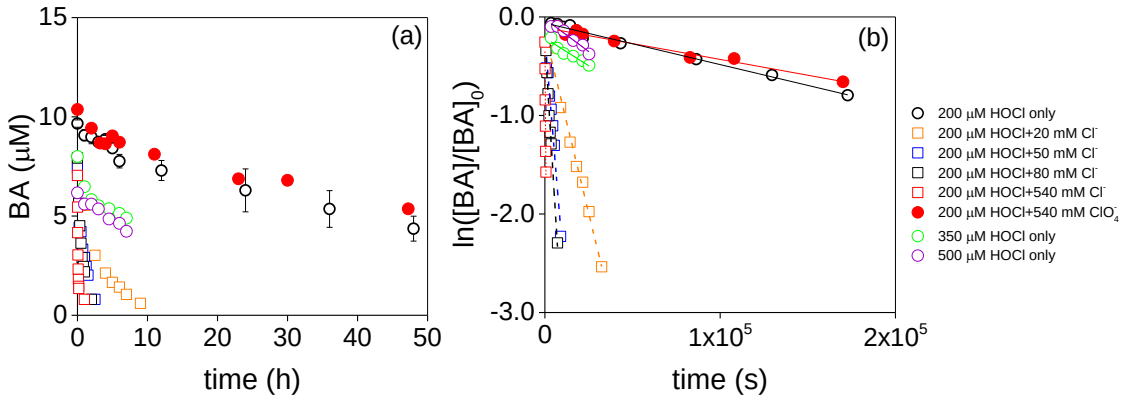


Figure 4-17. (a) Degradation and (b) exponential loss of BA versus time during reaction with free chlorine alone, in the presence of Cl^- or ClO_4^- at pH 4.0. ($[BA]_0$ = 10 μM; [free chlorine]$_0$ =200-500 μM; [Cl^- or ClO_4^-]$_0$ = 0.24-540 mM; 10 mM acetate buffer)

In addition, given the kinetics at this low pH condition, the k_{obs} value obtained from each of the experiments by plotting each data set in terms of ln([BA]/[BA]$_0$) versus time, where the slope was then equal to k_{obs} (eq. 15). This could be done because the reformation of BA via base-catalyzed hydrolysis was minimal, and linear trends were observed for experiments done under pseudo-first-order conditions at pH 4.0 (Fig. 4-17b). In this case, the k_{obs} value is in fact predicted to be a product of the apparent rate constant (k_{app}) and the total of all of the chlorinating agents (eq.14). These chlorinating agents include HOCl, OCl^-, Cl_2O, and Cl_2, all of which are either considered to be in excess (e.g. HOCl and OCl^-) or present at steady-state concentrations (Cl_2O and Cl_2). The experiments were conducted with varying initial concentrations of HOCl or Cl^- to generate different amounts of HOCl, Cl_2O and Cl_2 at equilibrium (eq. 2 and 5).

$$ln\frac{[BA]_t}{[BA]_0} = -k_{obs}t \qquad (13)$$

$$\frac{d[BA]}{dt} = -k_{app}[BA][chlorinating\ agent]_{total},$$

where

$$k_{obs} = k_{app} \cdot [chlorinating\ agent]_{total} = k_{HOCl}[HOCl] + k_{Cl_2O}[Cl_2O] + k_{Cl_2}[Cl_2] + k_{OCl^-}[OCl^-] \quad (14)$$

In order to determine the species-specific rate constants each of these chlorinating agents, the *first step* was to simultaneously solve for the equilibrium concentrations for Cl_2 and Cl_2O by using eqs. 2, 5 and 15 and their known equilibrium constants using Solver in Excel. Each equilibrium constant was adjusted for ionic strength according to each experimental condition using the Davies equation[60], where [Cl^-] varied from 0.23 to 540 mM at pH 4.0. In the *second step*, the rate constants were then determined for individual chlorinating agents by assuming: (i) these concentrations for Cl_2 and Cl_2O were at steady-state since they were assumed to undergo very fast reaction rates so that equilibrium were achieved instantaneously (eq. 2 and 5). Similar assumptions regarding their ability to be present at steady-state concentration has been made previously[23, 26], and (ii) the concentrations for HOCl, and OCl^- were also held constant since their concentrations were present at excess and did not undergo significant losses given the shorter time frame (< 6 h) for these reactions. Therefore, in the end, the equilibrium concentrations for Cl_2 and Cl_2O and the excess HOCl and OCl^- for all of the experiments placed into this model (eq. 14).

$HOCl \rightleftharpoons OCl^- + H^+$ $\log k_4 = -7.5$ (25 ˚C, 0 M) (Morris, 1966) (15)

The values of measured k_{obs} and calculated equilibrium concentrations were then fitted through a least-squares regression into eq. 14 to achieve the species-specific rate constants of k_{HOCl}, k_{OCl^-}, k_{Cl2} and k_{Cl2O} which were obtained sequentially. This least-squares regression was performed in OriginLab. A similar approach to determine each of these rate constants in this order was used in other previous research.[23, 26] For this study, the approach consisted of the following steps. Initially, the model only applied data where Cl^- was amended to the solutions. This limitation was incurred so that the contribution of k_{Cl2}*[Cl_2] to the reaction could be considered to be much greater than the sum of the k_{OCl^-}*[OCl^-], k_{Cl2O}* [Cl_2O] and k_{HOCl}* [HOCl] contributions due to the known higher reactivity of Cl_2. The resulting value of $k_{Cl2} = (7.6\pm0.19)\times10^1$ $M^{-1}s^{-1}$ was obtained, and the contribution of HOCl, OCl^-, and Cl_2O (k_{Cl2O}[Cl_2O]+k_{HOCl}[HOCl]+k_{OCl^-}[OCl^-]) were later determined to be <10% of k_{obs} which validated that the original assumption that was made was indeed correct. After this, all the other data except for the Cl^- amended experiments were used to

solve for k_{HOCl}, k_{OCl^-} and k_{Cl2O} using the fixed k_{Cl2} value (= 76 $M^{-1}s^{-1}$), and k_{HOCl} and k_{OCl^-} were determined to be $(2.1\pm0.71)\times10^{-2}$ and $(1.7\pm1.5)\times10^{1}$ $M^{-1}s^{-1}$. However, a large uncertainty was observed when simulating the data for k_{Cl2O}, which was determined to be $(0.021\pm1.9)\times10^{3}$ $M^{-1}s^{-1}$. The model was not able to be further optimized to enhance the accuracy of k_{Cl2O}. This problem arose because under the tested conditions, the Cl_2O concentrations were very low (~10^{-10} M), and the roles of other chlorinating agents were too significant, and thus creating a condition where Cl_2O played a larger role (e.g. > 30% of k_{obs}) was not possible. Notably, even though a large uncertainty existed for k_{Cl2O}, the accuracy of the whole model was not significantly affected. This occurred because the contribution of Cl_2O to the overall kinetic rate (k_{obs}) was < 15%, even when the upper 95% confidence limits (1.9×10^{3} $M^{-1}s^{-1}$) was used. Overall, the k_{Cl2} and k_{OCl^-} values were 3.7×10^{3} and 8.3×10^{2} times higher than the k_{HOCl} value. These results were expected given that Cl_2 is known to a stronger chlorinating agent as compared to HOCl for when chlorinating the anilide ring, while OCl^- has larger ability to chlorinate the amide N. In addition, the k_{Cl2} and k_{HOCl} value were at the same magnitude as previously determined for anilides (e.g. acetanilide).[24] The obtained species-specific rate constants are provided in Table 4-7.

Table 4-7. The species-specific k values for reaction between BA and various chlorinating agents (estimated at pH 4.0 conditions)

Species	**Second-order rate constants ($M^{-1}s^{-1}$)**
HOCl	$(2.1\pm0.71)\times10^{-2}$
Cl_2	$(7.6\pm0.19)\times10^{1}$
Cl_2O	$(0.021\pm1.9)\times10^{3}$
OCl^-	$(1.7\pm1.5)\times10^{1}$

4.4.2.3 Validity of Proposed Mechanism using Other Model Compounds

To further confirm which reaction pathways were involved, other compounds where the amide H or ring sites were substituted by -CH_3 or -Cl group were also tested, including N-CH_3-BA, 2,4,6-trimethyl-BA and 2,4,6-trichloro-BA (structures see Table 4-1). Overall, the results support the proposed mechanisms in that the reactions at amide N and the ring are independent pathways and likely compete with each other. The kinetic data will be shown here, along with product identification for certain experiments, including direct measurement of ring chlorinated products and indirect determination of N-Cl products by SO_3^{2-} quenching.

First, the N-CH_3-BA was tested since it helped understand the important role of the amide H in the ring chlorination, and also because the previous literature did not observe consistent results about whether this compound could be chlorinated or not.[9, 13, 24, 25] The experiments were conducted by exposing N-CH_3-BA to free chlorine alone at pH 7.0 or free chlorine with Cl^- at pH 4.0. The results indicated that the degradation of N-CH_3-BA was much slower than BA under the same reaction conditions. First, for the results at pH 7.0 with HOCl alone, 50% of BA reacted after 12 h and reached to a plateau, while only 28% of N-CH_3-BA reacted after 51 h (Fig. 4-18a). In addition, at pH 4.0 with Cl^-, more than 90% of BA reacted after 0.5 h, while less than 10% of N-CH_3-BA reacted (Fig. 4-18b). While in general, the results for N-CH_3-BA indicated that direct ring chlorination could occur, its reduced reactivity as compared to BA provided several interesting points regarding how this added CH_3 group affected the overall chlorination potential of BA.

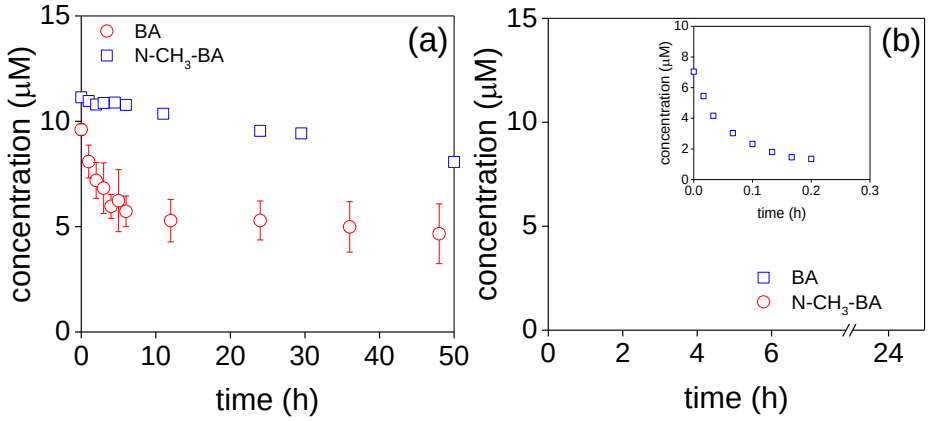
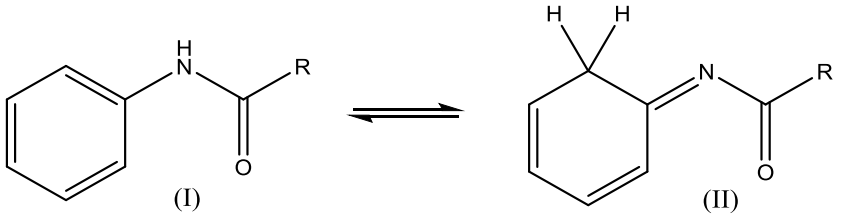


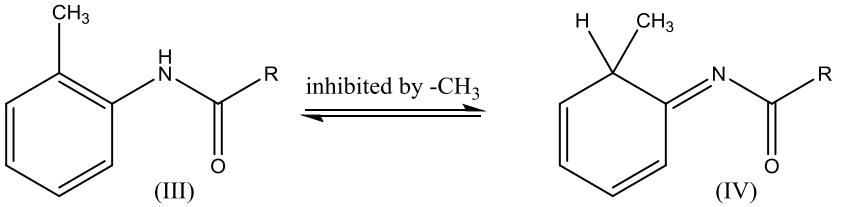
Figure 4-18. Degradation of BA and N-CH_3-BA versus time (a) at pH 7.0 with free chlorine alone, and (b) at pH 4.0 with 0.540 M Cl^- addition. ([BA or N-CH_3-BA]$_0$ = 10 μM; [free chlorine]$_0$ =200 μM; [Cl^-]$_0$ = 0.23-540 mM; 10 mM acetate or phosphate buffer)

However, rather than Orton Rearrangement, where it was believed the ring chlorination proceeded through N-chlorination, alternative explanations were provided.[24, 25] It was first suggested that this reduced reactivity was due to the steric inhibition by CH_3 on the tautomerization of anilide to form a more reactive intermediate (eq. 17). This was first observed with 2-methylacetanide (III, 17), of which the reactivity decreased by 20× when exposed to Br_2 or Cl_2 compared to unsubstituted acetanilide.[24, 25] Acetanilide (I, eq. 16) can undergo tautomerization to form an intermediate (II, eq. 16), which underwent substitution by Cl or Br more easily, while when the ortho-position was substituted by -CH_3 (III, eq.17), this tautomerization was inhibited by

the steric hindrance of CH_3.[25] This was also the case for N-CH_3-acetanilide, where the H and CH_3 were similarly placed as 2-methyacetanilide, and thus was affected by the same impedance.[25]

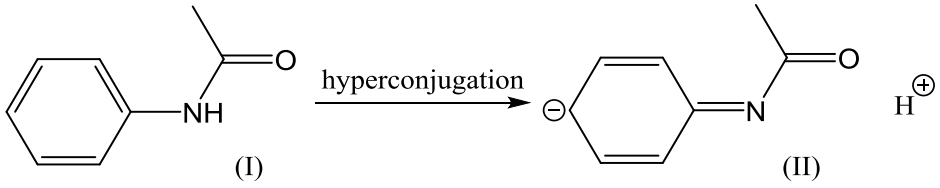


(16)



(17)

Therefore, this inhibition was predicted to decrease reactivity of N-CH_3-acetanilide by a similar factor (20×) compared to acetanilide, while the experimental data indicated that the N-CH_3-acetanilide was less reactive than acetanilide by a factor of 1200×.[24, 25] Since this first hypothesis did not explain the results fully, it was further hypothesized that the additional decrease in reactivity was probably due to the role of hyperconjugation. [24, 25] For BA, hyperconjugation of amide N-H group could then occur where the proton could be released which led the amide N to bear a negative charge (eq. 18). This negative charge could be transferred to the ortho and para positions of the anilide ring via resonance (eq. 19).



(18)

This resonance structure would then undergo halogen substitution more easily. [24, 25] Therefore, this effect is predicted to be one of the main reasons why the loss of N-CH_3-BA is significantly slower than BA. This is especially true when comparing both of these model compounds at pH 4.0 where it is clear that BA (Fig. 4-13a) along with N-CH_3-BA primarily undergo ring chlorination alone. This effect becomes a little less clear though when understanding the results at pH 7.0 because BA primarily undergoes chlorination at the amide N moiety rather than directly on the anilide ring. In this case, the loss of N-CH_3-BA is potentially slower than BA because it either: (i)

can no longer undergo chlorination of the amide N due to the absence of a reactive site or (ii) the pathways to form the low levels of ortho- and para- ring by-products by its reaction with Cl_2 are further lessened due to the steric inhibition and lack of the hyperconjugation effect.

In addition, two compounds with the ortho- and para- ring positions substituted by -CH_3 (2,4,6-trimethyl-BA) or -Cl (2,4,6-trichloro-BA) were tested. These experiments were used to evaluate how the chlorination chemistry would change given the presence of these substituents and how the new proposed mechanism would help to better understand the results that were observed. The experiments were first conducted with 2,4,6-trimethyl-BA, which was exposed to excess free chlorine at pH 7.0. It was initially expected that for this compound, amide H was the only moiety for chlorine to react with since all of the ortho- and para-positions on the anilide ring were fully occupied. Interestingly though, at the outset, the loss of 2,4,6-trimethyl-BA was observed to be considerably faster than BA, where less than 10% of 2,4,6-trimethyl-BA remained after 24 h (Fig. 4-19a).

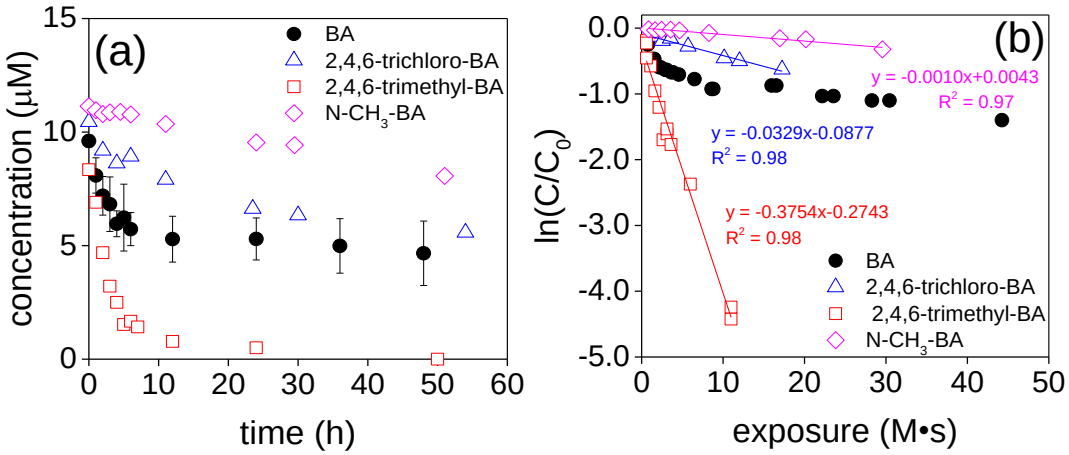


Figure 4-19. Comparisons in (a) the degradation of BA, 2,4,6-trichloro-BA, 2,4,6-trimethyl-BA and N-CH_3-BA versus time and (b) exponential loss versus free chlorine exposure during reaction with free chlorine at pH 7.0. No regression line was plotted for BA data because bad linearity was achieved. ([model compound]$_0$ = 10 μM; [free chlorine]$_0$ = 200 μM; 10 mM phosphate buffer)

To better understand which reactive site within this compound was playing a role, the reaction sample after 21 h was either not quenched or quenched by SO_3^{2-} to see if the N-Cl by-product was the dominant product formed. The chromatogram of the results is provided in Fig. 4-20 and demonstrates that a major by-product did form which is represented by the peak at 5.05 min on the

chromatogram (Fig. 4-20). However, its peak area did not change when the sample was quenched by SO_3^{2-} (Fig. 4-20). Such results indicated that one of the major by-products formed was not the N-Cl by-product and more likely a ring-chlorinated by-product.

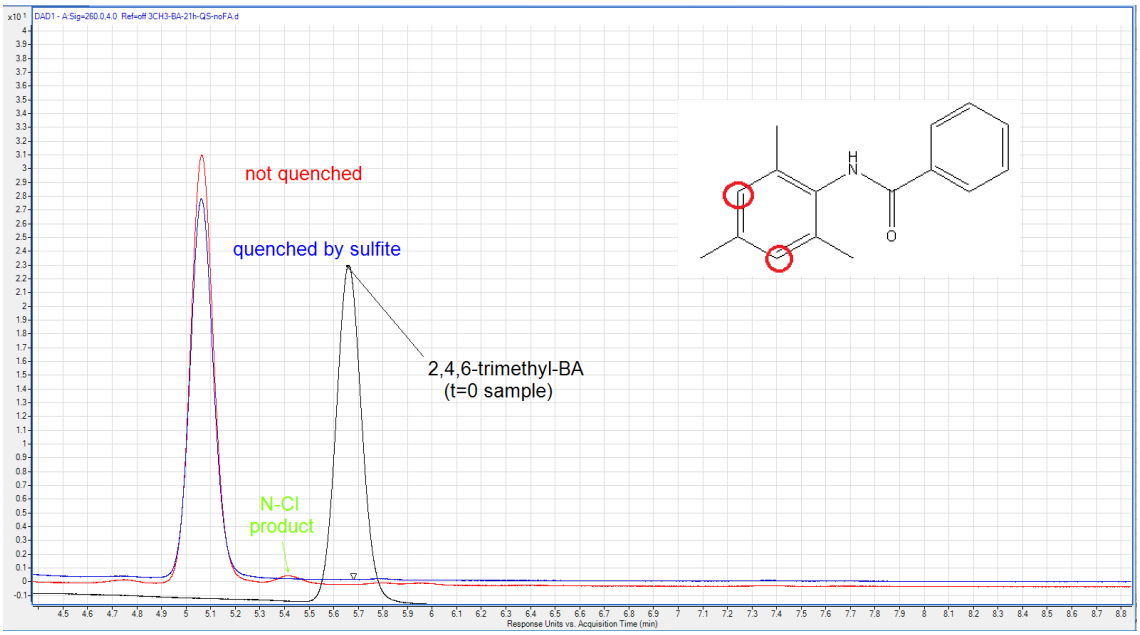


Figure 4-20. The overlaid chromatograms of the unreacted 2,4,6-trimethyl-BA (t=0 h sample), unquenched sample and sample quenched by SO_3^{2-} during reaction of 2,4,6-trimethyl-BA with excess free chlorine ($[2,4,6\text{-trimethyl-BA}]_0$ = 10 µM, $[\text{free chlorine}]_0$ = 200 µM, pH = 7.0).

The presence of a ring chlorinated by-product subsequently implied that 2,4,6-trimethyl-BA could undergo electrophilic substitution by Cl more easily than BA. In fact, this is not a surprising result, given the fact that these methyl substituents are electron-donating. Their electron-donating capacity is thus predicted to make the sites that at the ortho- and para- to each methyl group more susceptible to electrophilic substitution. Thus, it is predicted that the major by-product that is formed contains one or two Cl at the meta- positions of the anilide ring but that are ortho- and para- to the methyl substituents (exact positions circled in red in the structure provided in Fig. 4-20). The exact numbers of the Cl could not be validated further though since standards for these specific by-products were not obtained. Moreover, the ability for 2,4,6-trimethyl-BA to undergo direct chlorination on the ring further explains when a linear response was obtained when plotting its decay curve as a function of its exponential loss (y-axis) versus its free chlorine exposure (x-axis) (eq. 3-19b). This linear response was opposite to BA whose exponential loss was non-linear

(Fig. 4-19b). This result is expected though since the anilide ring was directly chlorinated and the chlorination and subsequent hydrolysis pathways involving the amide N were not involved, suggesting that the ring became the dominant reaction site when it was activated by electron-donating groups at neutral pH without Cl^- amended.

Alternatively, for 2,4,6-trichloro-BA, the experiment was conducted at pH 7.0 with free chlorine alone, and it was expected the amide N was the reactive site that reacted with OCl^- /HOCl/Cl_2 to form N-Cl compound. The results indicated that 2,4,6-trichloro-BA reacted slower with free chlorine than BA under the same condition (Fig. 4-19). When analyzing the products to help better understand the mechanism, the HPLC chromatogram were not clear and thus no valid conclusions could be drawn. Given this challenge, it was not clear what was leading the reaction to be slower. One hypothesis is that the electron-withdrawing effect of the Cl groups on the ring likely causes greater deprotonation of the N-H moiety when compared to BA where no Cl groups are present. This hypothesis supported the fact that the pK_a values of the N-H moiety decrease from 13.0 and 10.78 when moving from BA to 2,4,7-trichloro-BA, respectively.[61, 62] It is believed that this desire for the N-H moiety of 2,4,6-trichloroBA to become more acidic subsequently lowers the ability to form the N-Cl product, which requires formation of the ring through hydrogen bonding with N-H (eq. 12). This effect then lowers the overall reactivity of 2,4,6-trichloroBA to free chlorine.

Overall, the results with these modified compounds indicate that blocking the amide N with CH_3 group can significantly lower the reactivity with free chlorine, which was probably not due to the Orton Rearrangement. Instead, this reduced reactivity was proposed to be caused by the steric inhibition on tautomerization and lack of hyperconjugation to form more reactive intermediate. Alternatively, when the active ring sites were substituted by more electron-donating groups, the degradation of the compounds were significantly enhanced and the formation of ring chlorination products were more rapidly. In addition, substituting the ring sites with Cl reduced the reactivity, and N-Cl product likely dominated the product distribution, but further studies are needed to confirm this. Therefore, when modifying the polyamide membrane, efforts should be taken to (i) make the amide N to be the dominant or sole position of chlorination, such as blocking the ring with more electron-withdrawing groups (e.g. Cl or Br). In this case, the chlorination can

be reversed by raising the pH or adding strong reducing agent (e.g. SO_3^{2-}), or (ii) block the amide N (e.g. with -CH_3) where the reactivity can be significantly lowered.

4.5 Conclusions

Overall, the results obtained in this study suggest that the well-known Orton Rearrangement was not applicable when explaining the mechanisms behind how polyamide-based membrane are degraded when exposed to free chlorine. The ring chlorination occurred through direct ring chlorination by Cl_2, rather than via N-chlorination with Cl_2 formed as an intermediate (Orton Rearrangement). This finding was also supported by previous literature including the original publications of Orton and colleagues.[19, 29, 31] The new proposed mechanisms suggest that ring chlorination and N-chlorination were two independent pathways that likely competed with each other. The dominance of these two pathways strongly depended on the water conditions, such as Cl^- concentrations and pH, which affected the distribution of chlorinating agents that formed. N-chlorination dominated at neutral and high pH conditions, even with high amount of Cl^- (0.54 M), and this was because OCl^- was likely the primary reactant. In addition, N-chlorination was also reversible through the base-catalyzed hydrolysis, further indicating that polyamide-based membrane should incur permanent loss slowly under neutral and high pH. Alternatively, ring chlorination occurred through directly reacting with Cl_2 and dominated at low pH with the presence of Cl^-. The second-order rate constants obtained helped better understand what species were driving the reactions under different conditions. The results indicated that the reactivity with BA decreased as Cl_2 > OCl^- >HOCl, which supported the dominant roles of OCl^- at neutral and high pH and Cl_2 at low pH with Cl^- present.

Moreover, the results obtained from the modified monomers supported the proposed mechanisms and could also provide some suggestions for the future modification work. The results indicated that the reactivity of the anilide ring was significantly affected by the substituting groups, where electron-donating groups (e.g. -CH_3) enhanced the degradation while electron-withdrawing groups (e.g. -Cl) reduced the reactivity. In addition, N-CH_3-BA has larger chlorine resistance, but not due to Orton Rearrangement, but which resulted from steric inhibition and lack of hyperconjugation in forming intermediates that could undergo substation more easily. Therefore, chlorine-resistance can be enhanced by blocking the amide N with -CH_3, or blocking the active

ring sites including ortho- and para-positions with electron-withdrawing groups. Thus, this work overall derived a more comprehensive understanding of the how these polyamide-based monomers degrade during chlorination and evaluated which types of chlorinating agents played a role chlorinating the monomer under different water conditions.

4.6 References

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CHAPTER 5. EFFECT OF BROMIDE AND PH ON POLYAMIDE-BASED MEMBRANE DEGRADATION KINETICS AND BY-PRODUCTS FORMATION DURING CHLORINATION

5.1 Abstract

As mentioned in the previous chapter, polyamide-based thin film composite membranes are the most widely used membrane types for RO and NF treatment, but they are also known to undergo degradation when chlorine is applied as a biofouling control. Studies have been conducted to investigate the reaction mechanisms of the polyamide with chlorine, however, few studies evaluate the role of halides, and especially bromide, on this process. Therefore, the goal of this research was to further expand our understanding of the chemistry involved in halogenating benzanilide (BA), as initially evaluated in the previous chapter, by: (i) assessing how BA reacts with pre-formed HOBr when varying amounts of bromide and chloride were added, or amended with different concentrations HOCl, (ii) further understanding how the degradation kinetics of BA when reacting with chlorine are affected by varying bromide concentrations and pH, and (iii) deriving species-specific rate constants for different brominating agents (e.g. HOBr, Br_2, Br_2O, BrCl and BrOCl) when reacting with BA. In order to assess this, experiments were conducted by exposing BA, and a modified version of BA, N-CH_3-BA, to excess pre-formed HOBr. For BA, its loss as a function of time for all of the conditions tested followed a pseudo-first order decay. In addition, all of the by-products that formed were brominated ring products which included ortho- and para-Br-BA. These results suggested that this monomer reacted with HOBr to directly brominate the anilide ring functional group and likely no bromination of the amide N occurred. To then assess how different brominating agents were involved, additional experiments were conducted where synthetic solutions also contained varying concentrations of Cl^-, Br^- or HOCl at different pH conditions. This matrix allowed for different brominating agents to be formed which could dominate the reactions under select conditions. The results indicated that for most of these expanded experimental scenarios, bromination still only occurred on the anilide ring. However, this did not include the case where the formation of BrOCl was targeted to serve as the halogenating agent where chlorinated ring products were also observed. Individual species-species rate constant between the reaction of BA with HOBr, Br_2O, Br_2, BrOCl and BrCl were determined to be $(5.3\pm1.2)\times10^{-2}$, $(1.2\pm0.4)\times10^{1}$, $(3.7\pm0.2)\times10^{2}$, $(2.2\pm0.6)\times10^{4}$ and $(6.6\pm0.9)\times10^{4}$ $M^{-1}s^{-1}$,

respectively. This indicated that the ability for the brominating agents to undergo substitution decreased as BrCl>BrOCl>Br_2>Br_2O>HOBr. The results obtained with N-CH_3-BA indicated that the reactivity of this compound with brominating agents were lower than BA, but direct bromination still occurred. Overall, this work helps to understand the effect of halides, and particularly bromide, on polyamide membrane degradation during chlorination. The presence of bromide significantly accelerated the degradation of BA and also led to a considerably different by-product distribution as when no bromide and only chlorine is present. Such findings suggest that the presence of bromide can more easily incur permanent membrane damage at even low concentrations and over wider pH range.

5.2 Introduction

In recent years, numerous studies have been conducted to investigate the degradation mechanism of polyamide when treated with free chlorine.[1-7] However, one factor that has received little attention is the effect of halides on the membrane stability when free chlorine is applied. The role of halides was the focus of this work since many of the waters that are treated by RO and NF contain significantly high concentrations of halides at up to g/L concentrations (Table 4-2 in Chapter 4). The presence of halides, specifically Cl^- and Br^-, is especially important during water chlorination since they are known to form secondary chlorinating and brominating agents, including Cl_2, Cl_2O, Br_2, Br_2O, BrCl and BrOCl (eq. 2 and 5 in Chapter 4 and eq. 2-5 below). These chlorinating and brominating agents have often been overlooked in previous studies since their concentration are typically 4-7 orders of magnitude lower than HOBr and HOCl under typical water treatment conditions.[8-12] However, studies also suggest that they are up to 3-8 orders of magnitude more reactive than HOCl and HOBr when reacting with compounds such as dimethenamid and aromatic ethers.[9-12] The chlorinating species including HOCl, Cl_2, and Cl_2O have been investigated in Chapter 4, and thus the focus of this work will be the role of these various brominating agents, including HOBr, Br_2, Br_2O, BrCl and BrOCl.

$HOCl + Br^- \rightleftharpoons HOBr + Cl^-$ $\log k_1 = 5.18$ (25 ˚C, 0 M)[13] (1)

$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$ $\log k_2 = 7.95$ (25 ˚C, 0 M)[14] (2)

$HOBr + Cl^- + H^+ \rightleftharpoons BrCl + H_2O$ $\log k_3 = 3.68$ (25 ˚C, 0 M)[15] (3)

$2HOBr \rightleftharpoons Br_2O + H_2O$ $\log k_4 = 0.80$ (25 ˚C, 0 M)[9] (4)

$HOCl + HOBr \rightleftharpoons BrOCl + H_2O$ $\log k_5 = -0.46$ (25 ˚C, 0 M)[9] (5)

Limited studies have also been conducted to expose anilides or N-substituted anilides (e.g. N-CH_3-BA) to Br_2. The results suggest that direct ring bromination occurred.[16, 17] In addition, the transformation of N-Br to ring-Br compounds was also studied, where it was found that this mechanism occurred more easily than its corresponding chlorinated analog (N-Cl-anilide). The ability for the N-Br by-product to directly transfer to a ring-Br product was hypothesized to be general acid-catalyzed, such as with the presence of carboxylic acid.[18] It was also found that a slight amount of moisture could also trigger the change of solid N-Br-acetanilide to para-Br-acetanilide rapidly.[18] More generally though, it was not clear whether Orton Rearrangement (scheme 4-1 in Chapter 4) occurred when anilides react with Br_2, since no known studies observed the formation of N-Br products during the full length of their reaction.

Therefore, the goal of this research was to (i) explore the effect of bromination on the kinetics and mechanisms of the polyamide-based monomer when additional halide (Br^- and Cl^-) concentrations are added, (ii) derive a more complete understanding of what specific reactants were involved under varying water quality conditions, and (iii) derive rate constants for these species-specific reactions. Overall, these results will also help to better evaluate the mechanisms behind membrane failure when used in NF and RO treatment of waters of varied salinity. In order to achieve these, experiments were conducted with the polyamide-based monomer (i.e. BA) as similarly done in Chapter 4, where various water conditions (e.g. pH and Br^- and Cl^- concentrations) were varied. BA was exposed to free chlorine and/or pre-formed HOBr under pH 6-9 in the absence or presence of varying amounts of halides (e.g. Cl^- and Br^-). The by-products that were generated during certain reaction conditions were also identified and quantified to help understand the mechanistic pathways involved.

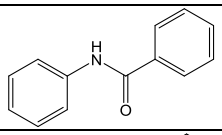
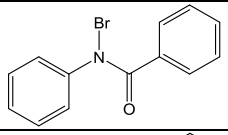
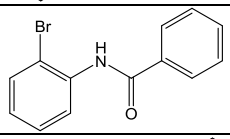
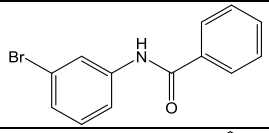
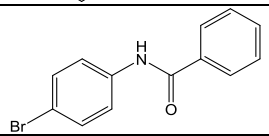
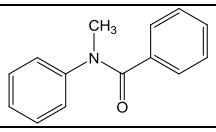
5.3 Materials and Methods

5.3.1 Standards and Reagents

In addition to the standards and reagents used in Chapter 4, other chemicals included NaBr, and NaOH, which were purchased at reagent grade or higher and were used without further purification. Several compounds were synthesized including N-Br-BA, para-, meta-, and ortho-Br-BA (structures see Table 5-1). All of these compounds exhibited a purity of > 90% when

initially synthesized by Dr. Keith Reber at Towson University. The majority of these compounds (meta-, para- and ortho-Br-BA) also remained stable at this purity when shipped overnight to Purdue and left at -18 ˚C for up to 9 months.

Table 5-1. Compound names, structures and acronyms used in this study

Compound Names	Structures	Acronyms
benzanilide		BA
N-bromo-N-phenylbenzamide		N-Br-BA
N-(2-Bromophenyl)benzamide		ortho-Br-BA
N-(3-Bromophenyl)benzamide		meta-Br-BA
N-(4-Bromophenyl)benzamide		para-Br-BA
N-Methyl-N-phenylbenzamide		N-CH_3-BA

5.3.2 Preparation of Stock Solutions

The stock solutions of model compounds and free chlorine were prepared in the same ways as in Chapter 4. In addition, hypobromous acid (HOBr) stock solutions were prepared by the reaction of 300 mM HOCl with 330-360 mM Br^- at pH 11.0, resulting in 88-96% yields of HOBr (eq. 1) after 12-24 h. The HOBr concentration was determined spectrophotometrically by measuring the hypobromite (OBr^-) concentration at 329 nm ($\varepsilon = 332\ M^{-1}cm^{-1}$).[19] Given the yields of this reaction (eq. 1), the HOBr stock also contained trace amounts of unconverted HOCl ([HOCl]/[HOBr] = 0.06-0.12:1), Br^- ([Br^-]/[HOBr] = 0.08-0.23:1) and higher amount of Cl^- ([Cl^-]/[HOBr] = 2.2-2.4:1).

5.3.3 Setup of Kinetic Experiments

Kinetic experiments were conducted using synthetic solutions that were placed in 20-100 mL capped glass vials or bottles and run for up to 48 h at room temperature (24±1˚C). These synthetic solutions contained 7-12 µM of an individual model compound (BA or N-CH_3-BA) and were buffered at various pH conditions from pH 6-9 with either 10 mM phosphate (pH 6.0-8.5) or 10 mM borate buffer (pH 8.6-9.3). Reactions were initiated by amending these solutions with either HOBr and, in certain cases, various halides (Cl^- or Br^-) or free chlorine. The details of each reaction condition, which are sub-categorized within different experimental types, are listed in Table 5-2. This table also includes the concentrations of Br^-, Cl^- and HOCl that were not purposefully amended to the solutions but rather came from the HOCl or pre-formed HOBr stocks or the buffer. These concentrations are denoted as originating from the background. Samples were then periodically taken to measure: (i) the residual concentrations of brominating agents or (ii) were quenched using phenol or ascorbic acid to measure the remaining model compound concentration and the by-products formed.

The experiments were then conducted with BA or N-methyl-BA, and the synthetic solutions contained either: (i) a pre-formed total concentration of HOBr of 0.20-1.2 mM (type 1 in Table 5-2), (ii) pre-formed HOBr concentration with a total HOCl concentration of 0.21-0.62 mM (type 2 in Table 5-2), (iii) pre-formed HOBr with a total Br^- of 0.11-0.93 mM (type 3 in Table 5-2) or (v) pre-formed HOBr with a total Cl^- of 10-80 mM (type 4 in Table 5-2). Overall, this set of experiments was conducted in order to generate a host of other chlorinating and brominating agents, as noted by eqs. 1-5.

Table 5-2. Kinetic experiments of model compounds reacting with bromine.

Type	pH	Model compound	Model compound concentration (μM)	HOBr (mM)	Br^- (mM)			Cl^- (mM)			HOCl (mM)		
					From the back-ground[a]	Amended	Total	From the back-ground[b]	Amended	Total	From the back-ground[a]	Amended	Total
1	8.6-9.3	BA	10	**0.20-1.2**[c]	0.049-0.25	0	0.049-0.25	0.47-2.8	0	0.47-2.8	0.022-0.081	0	0.022-0.080
2	8.8-9.3	BA	10	0.10-0.20	0.016-0.043	0	0.016-0.043	0.23-0.46	0.24-0.72[d]	0.47-1.2	0.014-0.015	0.20-0.60	**0.21-0.62**
3	6.1-9.0	BA	10	0.20	0.046-0.074	0.033-0.84	**0.11-0.93**	0.46	0	0.46	0.024-0.044	0	0.024-0.044
4	7.1-7.2	BA	10	0.20	0.065	0	0.065	0.46	10-80	**10-80**	0.041	0	0.041
other	7.0	N-CH_3-BA	10	0.20	0.033	0	0.033	0.46	0	0.46	0.012	0	0.012
	6.2	N-CH_3-BA	10	0.20	0.033	0.84	0.87	0.46	0	0.46	0.012	0	0.012

[a] Included concentrations from the HOBr stock.
[b] Included Cl^- concentrations from the HOBr stock and buffer solutions.
[c] Bold values indicate the varying parameters for each experimental type.
[d] Cl^- was not intentionally amended for type (iii) but it instead came from the amended HOCl.

5.3.4 Analytical Methods

All of the compounds in this part were analyzed using approach 1, sample quenching coupled with LC-UV/vis or LC/MS, as described in Chapter 4. These compounds included BA and its chlorinated and brominated ring products, including para-, meta- and ortho-Cl-BA, and para-, meta- and ortho-Br-BA, and N-CH_3-BA. This approach was chosen since no N-halogenated products (such as N-Cl-BA and N-Br-BA) were observed in any experiments (see later discussion). Certain experiments were also analyzed using approach 2 to cross-compare the results. The LC-DAD method detection limits (MDLs) for BA, ortho-Br-BA, para-Br-BA, meta-Br-BA and N-methyl-BA were 22, 30, 27, 10 and 51 nM, respectively.

5.3.5 Measurement of residual chlorine and chloride (Cl^-)

The residual concentrations of the total chlorinating or brominating agents were measured by the DPD spectrophotometric method at 515 nm (APHA/AWWA/WEF, 2012). This method was conducted for experiments that lasted longer than 6 h in order to ensure that the chlorinating or brominating agents (e.g. HOCl/OCl^- and HOBr/OBr^-) were still in excess when compared to the model compound concentration. In addition, the Cl^- concentration in various buffers and the free chlorine stock was measured by IC (Metrohm 940 Professional IC Vario) as described in Chapter 4.

5.3.6 Results and Discussions

The experiments were first conducted where BA was exposed to excess HOBr under different pH conditions (6-9), where the loss of BA and formation of by-products were monitored. The results indicated that the BA observed consistent loss over time for the pH conditions tested (6-9) (Fig. 5-1a), and linear responses were obtained when plotting the exponential loss versus time (Fig. 5-1b), in accordance to eq. 13 in Chapter 4.

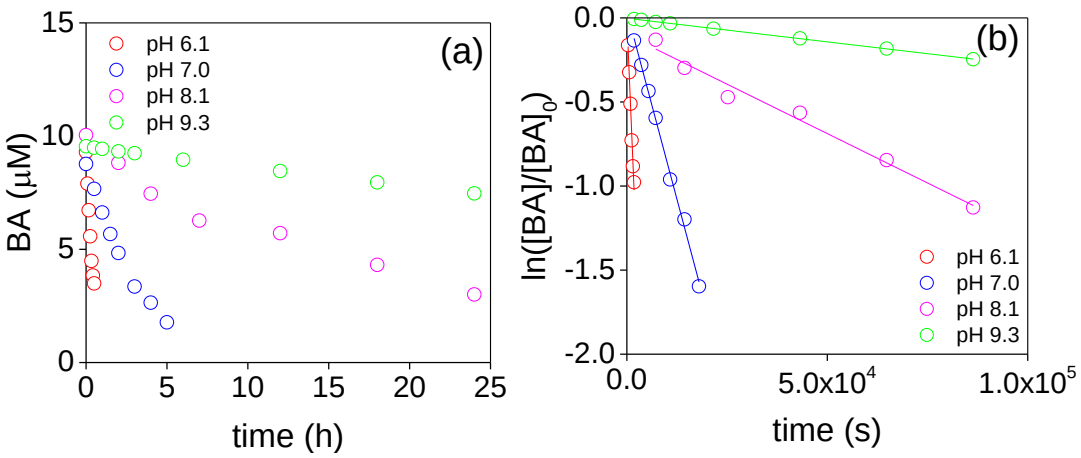


Figure 5-1. (a) Degradation and (b) exponential loss of BA versus time during reaction with HOBr at pH 6.2-9.3. ($[BA]_0$ = 10 μM; $[HOBr]_0$ = 200 μM; 10 mM phosphate (6.0-8.5) or borate (8.6-9.3) buffer)

This conclusion was different from the HOCl only experiments, where at neutral pH (6-7), BA decayed rapidly at the initial phase then reached to a plateau due to the reformation through based-catalyzed hydrolysis of N-Cl-BA (see details in Chapter 4). Therefore, it seemed that the hydrolysis of N-Br-BA was not significant since (i) N-Br-BA formed but did not undergo hydrolysis, (ii) the transformation from N-Br-BA to ring-Br-BA through Orton Rearrangement was instant, or (iii) N-Br-BA did not form, and BA loss was due to direct bromination of the ring. To better understand the mechanism, the by-products were also analyzed. The results indicated that ring-Br products including ortho- and para- were the only by-products observed above detection limits, and the mass balance could be fully closed when including the residual BA and these two by-products (Fig. 5-2 (a-d)).

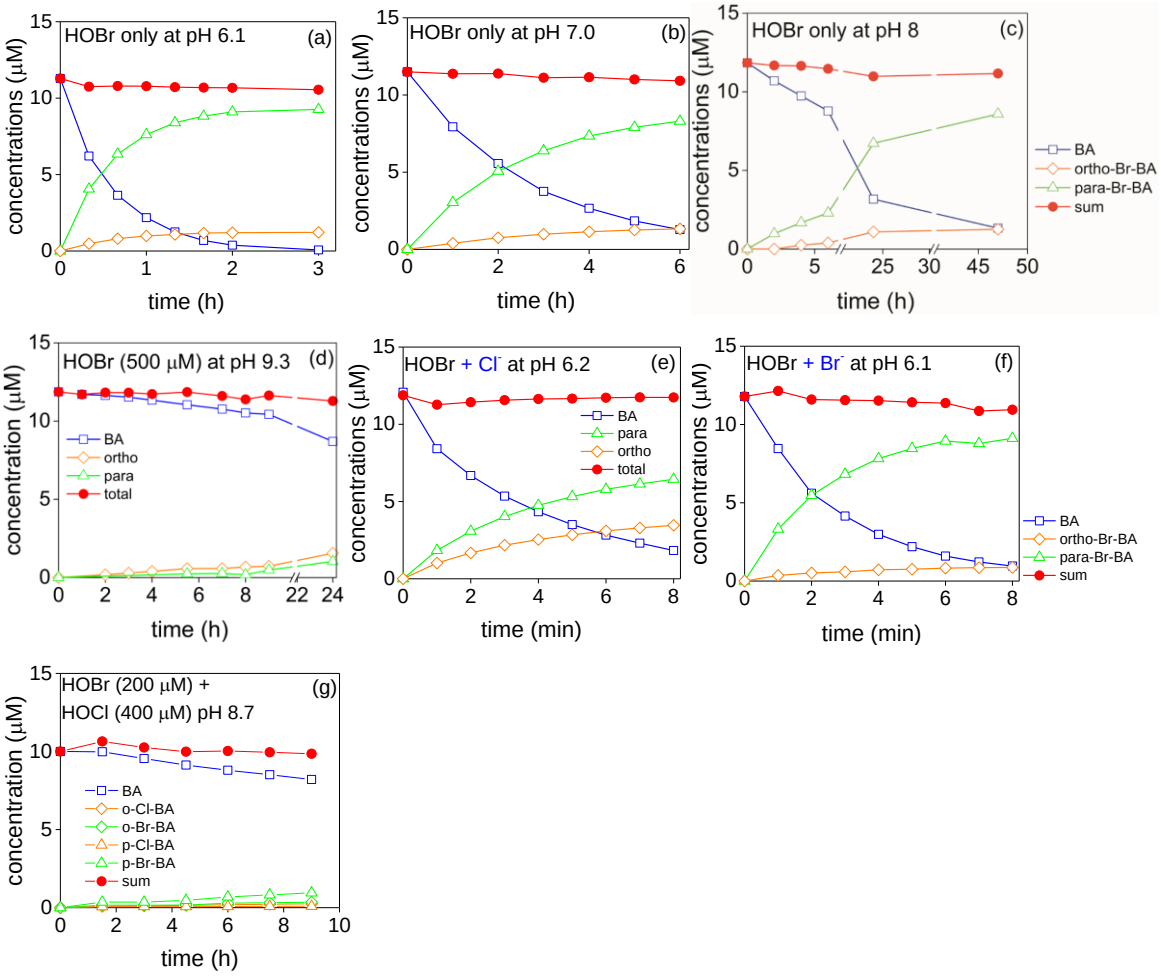


Figure 5-2. The loss of BA and the by-products formed over time when BA was exposed to (a-d) HOBr only (200-500 μM) at pH 6.1-9.3, (e) HOBr (200 μM) in the presence of Cl^- (60 mM) at pH 6.2, (f) HOBr (200 μM) in the presence of Br^- (840 μM) at pH 6.1, and (g) HOBr (200 μM) + HOCl (400 μM) at pH 8.7. ($[BA]_0$ = 10 μM; 10 mM phosphate (6.0-8.5) or borate (8.6-9.3) buffer)

In addition, the data obtained when analyzing BA using various analytical approaches (see section 3.3.4 for further details) also confirmed that N-Br-BA did not exist in the samples. This conclusion was reached by first observing the LC analysis of quenched (by SO_3^{2-}) and unquenched samples exhibited no difference in the loss of BA (Fig. 5-3). Thus, N-Br-BA did not appear to have formed, as it was not reduced back to BA by SO_3^{2-} during quenching.

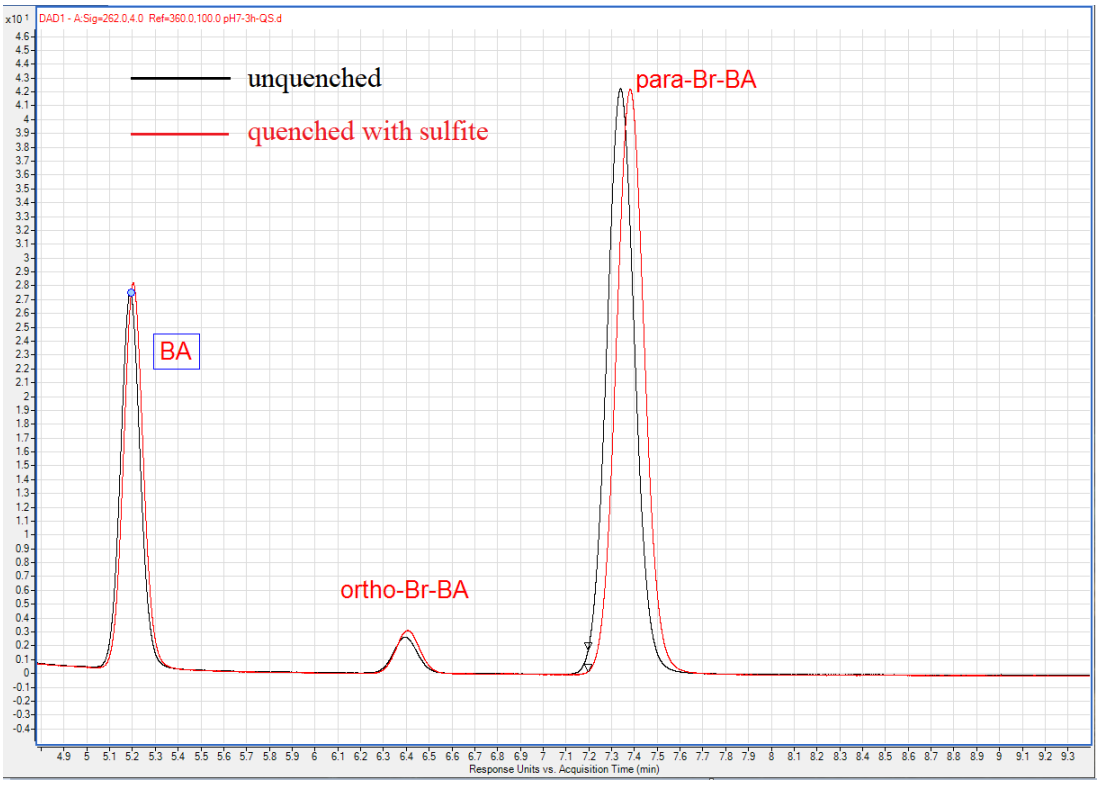
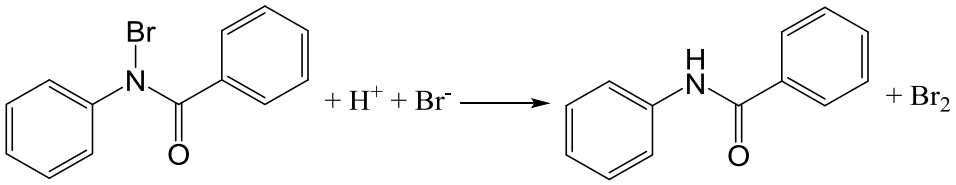


Figure 5-3. The overlaid chromatograms for quenched and unquenched samples during reaction of BA with HOBr at pH 7.0 ($[BA]_0$ = 10 µM; $[HOBr]_0$ = 200 µM; $[SO_3^{2-}]_0/[HOBr]_0$ = 2; reaction time = 3 h; 10 mM phosphate buffer)

Second, the results of BA degradation at pH 7.0 with HOBr alone were also compared when cross-comparing samples either processed through approach 1 (SO_3^{2-} quenching followed by LC analysis) or approach 2 (DCM extraction followed by GC analysis). The data were either plotted as a function of BA concentration (Fig. 4-6a) or as a pseudo-first order loss (Fig. 4-6b), and identical kinetic trends where their observed rate constants (k_{obs}) similarly equaled 9.0×10^{-5} s^{-1} (Fig. 4-6b). Given this, it was not believed N-Br-BA existed in these samples, otherwise approach 2 (extraction coupled with GC), where N-Br-BA was not reduced to BA by extraction, should observe a more rapid decay of BA.

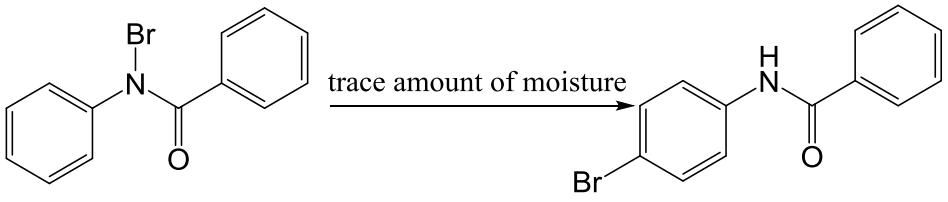
Based on these by-product results, hypothesis (ii) seemed unlikely since at high pH (pH 8-9) where the H^+ concentration was limited, N-Br-BA was still not observed (Fig. 5-2c and 5-2d). Alternatively, if it was assumed that N-Br-BA formed but then rapidly underwent Orton Rearrangement (scheme 4-1) via hypothesis (ii), it would first require that N-Br-BA react with Br^-

and H^+ to form BA and Br_2 (eq. 6; identical to the reaction in scheme 4-1 but with Br- as the specific halogen). This hypothesis is also not considered to be true if assumed this bromide-based reaction (eq. 6) was kinetically similar to the experiments conducted with N-Cl-BA and Cl^- (see details in 3.4.1). Therefore, it hypothesized that eq. 6 was unlikely to occur, especially at high pH (8-9).



(eq. 6)

However, previous literature also noted that N-Br-BA could rapidly transform into para-Br-BA when trace amounts of moisture were present, indicating that N-Br-BA was not stable in the presence of H_2O (eq. 7).[18] While the author did not provide the reason of this transformation, it probably occurred firstly through the hydrolysis of N-Br-BA to BA and HOBr, followed by reaction between HOBr and BA to form para-Br-BA. Thus, the hydrolysis of N-Br-BA should be fast enough to complete this rapid transformation, which suggested that hypothesis (i) was not possible either. Therefore, it is believed that the third hypothesis (iii) is the pathway likely involved where BA reacts with HOBr directly to form the brominated ring products. It should be noted that these results also suggested OBr^- did not react strongly with BA as OCl^- did. This was likely because the hydrogen bonds were hard to form between OBr^- and the amide N, leading to an N-Br product, and OBr^- also could not react with the ring by aromatic substitution, which was also supported by previous study[9, 10].



(eq. 7)

In addition, the experiments were also conducted by exposing N-CH_3-BA to (i) HOBr only at pH 7.0, and (ii) HOBr in the presence of Br^- at pH 6.1. The results indicated that in experiment (i), 12% of N-CH_3-BA reacted after 24 h, and for (ii) degradation of N-CH_3-BA was significantly enhanced under this condition, where more than 95% of N-methyl-BA reacted after 7 h (Fig. 5-4). Though the degradation of N-CH_3-BA was slower than BA under the same conditions (Fig. 5-4),

the results suggest that direct ring bromination could still occur. Also, when increasing the Br_2 formed in the solution, the degradation was significantly enhanced, which supported the previous study, where BA was exposed to Br_2, and only ring bromination by-products at ortho- and para-positions were observed.[16] In this prior study, it was believed that the ring bromination by-products resulted from direct bromination of the ring, since the IR and NMR spectra did not observe any weakening in the N-H stretch frequency.[16] The reduced reactivity of N-CH_3-BA compared to BA is hypothesized to be due to the same reasons that led it to also be reduced during chlorination (see prior discussions in Chapter 4).[17, 20]

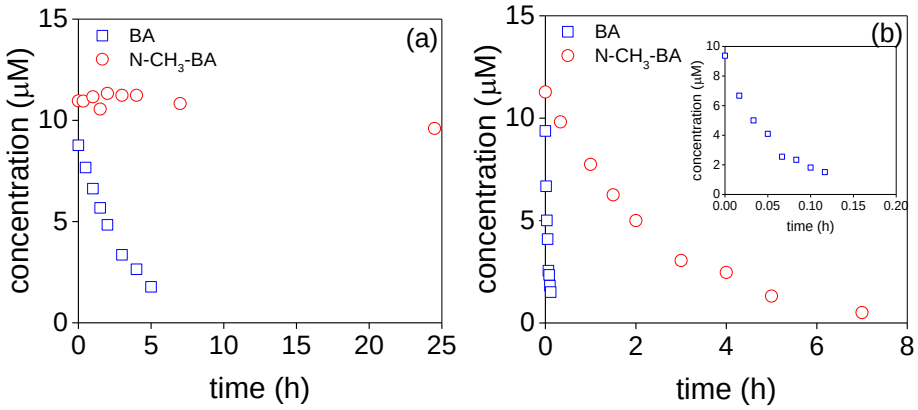


Figure 5-4. Degradation of BA and N-CH_3-BA versus time during reaction of BA or N-CH_3-BA (a) with HOBr at pH 7.0 and (b) with HOBr and extra Br^- at pH 6.2. ([BA or N-CH_3-BA]$_0$ = 10 μM; [HOBr]$_0$ =200 μM; [Br^-]$_0$ = 0.043-0.84 mM; 10 mM phosphate buffer)

Thus, given that linear pseudo-first order responses were observed for all of the kinetics observed with BA when excess HOBr was added, additional investigations were conducted to evaluate the specific brominating species that were involved. Initially, the HOBr stock was observed to contain specific amounts of unconverted HOCl and Br^- as well as Cl^- from the background (see Table 5-2 for details). These additional reagents could potentially form other brominating agents (eq. 1-5). Therefore, given the complexity of the brominating agents involved (eq. 8), the experimental conditions were expanded to isolate the importance of each brominating agent. Four types of experiments (1 to 4) were conducted to evaluate the roles of different brominating agents, including HOBr, Br_2O, Br_2, BrOCl and BrCl (Table 5-2; eq. 1-5). These reactions were conducted in order to magnify or decrease the importance of certain brominating

agents. For example, experimental type (1) was conducted at high pH conditions where HOBr and Br_2O dominated the reaction. Under this condition, the formation of Br_2 and BrCl were low at this high pH (eq. 2-3), and low formation of BrOCl was also expected due to the low initial HOCl concentration and high pH (eq. 5). The amounts of HOBr and Br_2O were the gerated because different HOBr was initially added to the solutions. Similarly, experimental type (2), (3) and (4) were designed to magnify the dominance of BrOCl, Br_2 and BrCl by amending the solutions with varying initial concentrations of HOCl, Br^- and Cl^-, respectively. In the end, all of these experiments led to linear pseudo-first order responses when plotting the experimental loss versus time (see eq. 13 in Chapter 4) (data not shown). In addition, the results of the by-product formed and their distribution indicated that only ortho- and para-Br-BA were observed for experiments in types 1, 3 and 4, where the reactants were dominated by HOBr and Br_2O (type 1), Br_2 (type 3) and BrCl (type 4) (Fig. 5-2). In all cases, no N-Br BA formation was observed. In addition, all of the mass balances could be fully closed when incorporating the residual BA concentration and these two ring by-products (Fig. 5-2). This was not surprising since HOBr was believed to directly brominate the ring, where OH^- behaved as the leaving group and left Br to substitute the ring. Also, previous study suggested that Br_2O, Br_2 and BrCl can undergo electrophilic aromatic substitution similarly as HOBr.[9, 10] For experiments in type 2, where varying amounts of HOCl were added to generate BrOCl, ortho- and para-Cl-BA were also generated, where the mass balance could be closed with these four ring chlorinated and brominated products (Fig. 5-2g). These results indicated that OBr^- and OCl^- within BrOCl can both behave as leaving groups and leave Cl and Br, respectively, to substitute the ring, which was never observed in previous study.[9, 10]

In this part, a model similar to what was built for chlorinating agents was also developed to obtain the species-specific rate constants for brominating agents, where k_{obs} value incorporated all of the brominating species (eq. 8).

$$k_{obs} = k_{app}[HOBr]_{total}$$
$$= k_{HOBr}[HOBr] + k_{Br_2O}[Br_2O] + k_{BrCl}[BrCl] + k_{BrOCl}[BrOCl] + k_{Br_2}[Br_2] \qquad (8)$$

Similarly, two assumptions were made, where first, the equilibrium of the brominating agents were established instantly, and second, the concentrations were constantly kept at this equilibrium concentrations. The equilibrium constants were adjusted for ionic strength according to each

experimental condition using the Davies equation.[21] The k_{obs} values and equilibrium concentrations, which were calculated by simultaneously solving eqs. 1-5 and 9-10 in Excel using Solver, which were then fitted to the kinetic model following a 5-step approach as follows. *Step 1*: only data from experimental type (i) were considered. Under these pH conditions, the contribution of BrCl and Br_2 were not significant because of the lack of H^+, excess Cl^- or Br^- (later determined to be <2.6% and 3.6% of k_{obs}, respectively). Also, the BrOCl contribution was negligible here (<2.6% of the k_{obs} value) because of the low initial HOCl concentration (derived from the unconverted HOCl present in the HOBr stock) and high pH condition, where OCl^- was the dominant form ($pk_{a,\ HOCl}$ = 7.47[15]). The following rate constants were obtained, where k_{HOBr} = $(5.3\pm1.2)\times10^{-2}$ and k_{Br2O} = $(1.2\pm0.4)\times10^{1}$. *Step 2*: in order to solve for k_{BrOCl}, data from experimental type (ii) were used. Similarly, the contributions of BrCl and Br_2 were minor (later determined to be <0.4% and 0.1% of the k_{obs} value, respectively). By assuming fixed values of $k_{HOBr} = 5.3\times10^{-2}$ and $k_{Br2O} = 1.2\times10^{1}$, the value of k_{BrOCl} was then determined to be $(2.2\pm0.6)\times10^{4}$ $M^{-1}s^{-1}$. *Step 3*: the data from experimental type (iii) were used to determine k_{Br2}. The contribution of BrCl was minor (later determined to be <6.9% of the k_{obs} value). By assuming fixed values of $k_{HOBr} = 5.3\times10^{-2}$ $M^{-1}s^{-1}$, $k_{Br2O} = 1.2\times10^{1}$ $M^{-1}s^{-1}$ and $k_{BrOCl} = 2.2\times10^{4}$ $M^{-1}s^{-1}$, the resulting k_{Br2} was $(3.7\pm0.2)\times10^{2}$ $M^{-1}s^{-1}$. *Step 4*: In order to solve for k_{BrCl}, data obtained from experimental type (iv) were considered, and fixed values of $k_{HOBr}=5.3\times10^{-2}$ $M^{-1}s^{-1}$, $k_{Br2O} = 1.2\times10^{1}$ $M^{-1}s^{-1}$, $k_{BrOCl} = 2.2\times10^{4}$ $M^{-1}s^{-1}$, and $k_{Br2} = 3.7\times10^{2}$ $M^{-1}s^{-1}$ were assumed. The resulting k_{BrCl} was $(6.6\pm0.9)\times10^{4}$ $M^{-1}s^{-1}$. Here, it should be noted that the order of step 3 and 4 did not matter, because similar values of BrCl and Br_2 were obtained if determining k_{BrCl} first and fixing it to solve for k_{Br2} or vice versa. In the end, switching the approach between the two did not improve the fittings. It should also be noted when simulating the data, OBr^- were not considered because kinetic and by-products data indicated that OBr^- was not an active brominating agent when reacting with BA. Also, including OBr^- into the model did not enhance the model fitting. The results indicated that the order of reactivity decreased as BrCl > BrOCl > Br_2 > Br_2O > HOBr (Table 5-3). This sequence of reactivity is not surprising and is backed up by literature, where it was suggested that Br_2O, Br_2 and BrCl underwent electrophilic aromatic substitution more easily than HOBr, since OBr^-, Br^- and Cl^- were better leaving groups than OH^-.[9, 10]

$$HOBr \rightleftharpoons OBr^- + H^+ \qquad \log k_6 = 8.7\ (20\ ^\circ C,\ 0\ M)^{19} \qquad (9)$$

$$HOCl \rightleftharpoons OCl^- + H^+ \qquad \log k_7 = 7.47\ (20\ ^\circ C,\ 1\ M)^{15} \qquad (10)$$

Table 5-3. Rate Constants for reactions of BA with different brominating agents

Step	Species ($M^{-1}s^{-1}$)	2nd-order rate constant
1	Br_2O	$(1.2\pm0.4)\times10^{1}$
1	HOBr	$(5.3\pm1.2)\times10^{-2}$
2	BrOCl	$(2.2\pm0.6)\times10^{4}$
3	Br_2	$(3.7\pm0.2)\times10^{2}$
4	BrCl	$(6.6\pm0.9)\times10^{4}$

5.3.7 Conclusions

The results obtained here indicated that if Br^- is present during the chlorination of BA, a host of brominating (e.g. HOBr, Br_2O, Br_2, BrOCl and BrCl) and chlorinating agents (e.g. BrOCl) would form that could directly halogenate the anilide ring. Overall, the formation of N-Br-BA was not observed probably because OBr^- was not as reactive as OCl^- with the amide group, and the Orton Rearrangement was likely not involved in any of the brominating mechanisms of BA. These results suggested that the presence of Br^- during chlorination could result in permanent membrane damage by directly reacting with the ring moieties, a process which cannot be reversed. These results also support the new scheme proposed in Chapter 4, where N-halogenation and ring halogenation are independent pathways. Since these brominating agents are known to be stronger electrophilic substituting agents, it was not surprising that ring bromination over-competed N-bromination. In addition, five species-specific rate constants were obtained, and the ability for the brominating agents to react with BA decreased as BrCl > BrOCl > Br_2 > Br_2O > HOBr. Therefore, the brominating species were much more reactive with BA than the chlorinating agents, especially when they were involved in chlorinating the anilide ring. Moreover, these obtained rate constants can help predict the degradation kinetics of BA during chlorination in a complex water matrix, which can then provide guidance on how the polyamide-based membrane degrades when used to treat halide-impaired waters. In addition, the kinetic results obtained with N-CH_3-BA indicated it was less reactive than BA when reacting with different brominating species. This finding was consistent with the chlorination results and thus further suggested that the polyamide-based membrane could be modified in this way to increase chlorine/bromine resistance.

Overall, these results indicated the presence of Br^-, even at low concentrations, can significantly enhance the degradation of BA and lead to ring bromination by-products over a wide pH range. This finding implies that the polyamide-based membrane would incur permanent

damage more quickly when used to treat bromide-containing waters where chlorine was applied to control bio-fouling.

5.4 References

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CHAPTER 6. RESEARCH CONTRIBUTION

Overall, the types of organic nitrogen compounds that were investigated in this thesis, particularly tertiary amines and amides, displayed highly unique chemical properties when they were exposed to free chlorine. These chemical properties are believed to be important to water treatment and water quality. This conclusion was reached because of two important findings from this work. First, tertiary amines appeared to serve as precursors or catalysts in forming regulated DBPs (THM and HAA) during chlorination. This enhancement occurred at low amine and bromide doses under neutral pH conditions, which are typical water quality conditions found during water treatment. More interestingly, this effect was largely controlled by the type of aromatic precursor that was involved, such that as aromatic compounds decreased in reactivity with free chlorine alone, the catalytic effect of tertiary amines on THM and HAA formation increased. This suggested that waters with *low chlorine reactivity are more susceptible* to the effect of this catalyst. Such results also appeared to have direct consequences to the tested DOM isolate, SFRA which contains a wide range of phenolic-based functional groups, where THM and HAA formation was not enhanced when tertiary various amines were added with HOCl. However, tertiary amines may indeed have an effect on enhancing THM and HAA formation for other waters with different types of DOM.

Therefore, such results provide a strong foundation for the fact that the presence of tertiary amines in various water types needs to be considered. Future efforts are first aimed at assessing this effect in enhancing other types of DBPs, including N-DBPs which are known to be more toxic than carbon-based DBPs[1]. In this case, it is expected that chlorination by the chlorammonium ion will similarly enhance N-DBPs when their formation mechanisms similarly involve substitution by chlorine (e.g. dichloroacetonitrile[1]). In addition, future efforts will also be extended to examine all of these effects with real waters, e.g. wastewater treatment plant effluents. Here, the enhancement effect of tertiary amines will be assessed by firstly quantifying the concentrations of both tertiary and quaternary amines using a novel bulk amine assay[2] and then assessing DBP formation. It should be noted that this bulk amine assay is unable to differentiate between tertiary and quaternary amines, and further research will examine if this method can be further modified to measure tertiary amine concentrations alone. This assay will also be used to remove both the

tertiary and quaternary amines from the same treated water, so that the baseline DBP concentrations can also be measured.

The second important finding of this work centered on the chemistry of amide functional groups and specifically those which are components of RO and NF polyamide-based membranes. The results of this study found that the polyamide-based monomer, BA, underwent a highly unique set of mechanisms that likely controlled its degradation pathways when exposed to free chlorine and in the absence or presence of halides. There were several key outcomes of this work. First, *the widely known Orton Rearrangement did not occur under the conditions where membrane filtrations usually work.* This conclusion was supported by both experimental work in this work and original publications by Orton and colleagues. Second, new mechanisms were thus proposed for the reactions between the polyamide monomer and free chlorine. The new proposed mechanisms indicated that N-chlorination and ring chlorination were independent pathways, and the dominance of one pathway over another was dependent on water quality conditions (such as halide concentrations and pH). In this part, the effects of halides on the reaction kinetics and mechanisms were also evaluated and rate constants of different brominating and chlorinating agents were obtained. These results can help better understand the degradation of polyamide membrane during treatment of halide-impaired waters when chlorine is applied as biofouling control. Moreover, the obtained second-order rate constants can help predict the decay of polyamide monomer in a given complex water matrix.

In the end, these observations are believed to dramatically alter our perception of how NF and RO polyamide surfaces likely degrade. From this work, it is also intended the type of substrate to be scaled up so that the kinetic and mechanistic pathways of monomers can be translated to larger oligomers and then to a solid surface. Evaluating the chemistry of monomers and oligomers are critical because currently there is *a large scientific gap* between the monomer chemistry, which, based on this thesis, differs significantly from the Orton Rearrangement, and studies that have only looked at commercial membranes. For example, many of the studies have focused on the halogen incorporation or flux decline of these membranes when exposed to free chlorine. However, it is difficult to understand from this information how the halogens are incorporated into the polymer matrix and how this leads to further breakdown of the membrane material.

Overall, this thesis focused on the reactivity of two types of organic nitrogen compounds, tertiary amines and amides, with chlorine under different water quality conditions. The results presented in this study are unique since this is the first study that: (i) evaluated the catalytic effects of tertiary amines on the formation of regulated DBPs, (ii) re-assessed the occurrence of the Orton rearrangement under typical water treatment conditions, and observed that the Orton Rearrangement likely does not occur in such waters, and (iii) proposed new mechanisms which makes sense from the chemistry perspective, and are also consistent with the experimental work in this study and the results obtained with commercial membranes from previous literature. These findings are critical for understanding the behavior of certain types of organic nitrogen compounds when chlorine is applied as a disinfectant or onto membrane surfaces for biofouling control. In addition, these findings can also be extended to other applications such as polymer-based pipe linings, where the materials contain tertiary amines and/or amides functionalities and are used under similar water conditions.

6.1 References

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APPENDIX

SUPPORTING INFORMATION

Text S1. Tertiary Amine Measurements

Additional experiments were performed to evaluate if the quenching agent, ascorbic acid, added prior to tertiary amine analysis potentially affected the measured tertiary amine values. This was of concern since ascorbic acid was added to reduce the residual free chlorine in the experimental samples, but it was unclear if the chlorammonium intermediate ($R_3N\text{-}Cl^+$) formed during these reactions could also be reduced back to its parent tertiary amine. This would then alter how the amine measurements were defined such that these values could potentially represent the concentration for only the residual amine or also include $R_3N\text{-}Cl^+$ as well. In order to evaluate this effect, MES was chosen as a representative tertiary amine to be first exposed to free chlorine over time, and then either not quenched or periodically quenched with excess (i) ascorbic acid, (ii) RES, or (iii) both RES and SA. The MES concentration in these samples were then immediately measured and were plotted in Fig. S1. In addition, the predicted MES concentration was also plotted in Fig. S1 by simulating its kinetic degradation during chlorination using Kintecus[1] (equations used in this model simulation provided in Table S2).

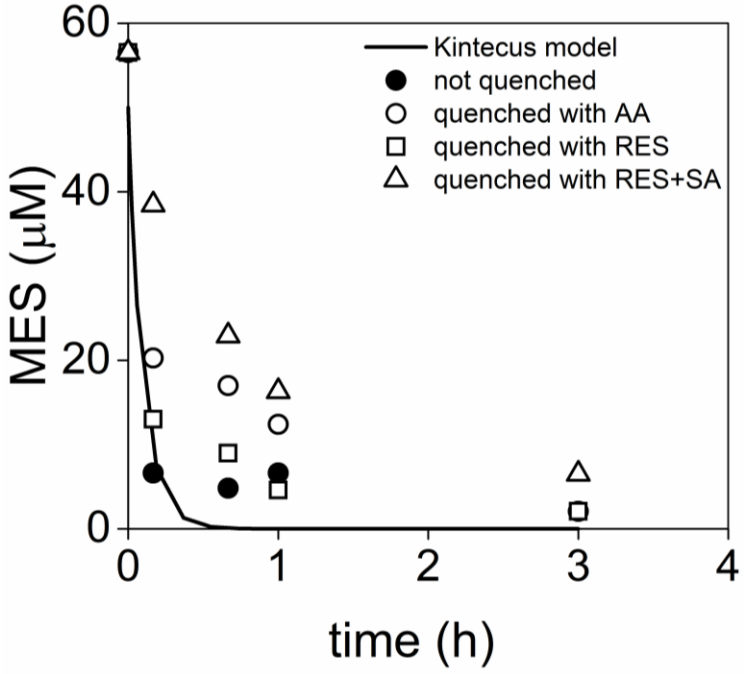

Figure S 1. The measured residual MES concentration following exposure to free chlorine after not quenching or quenching with either ascorbic acid (AA) (2 × [free chlorine]$_0$), RES (3mM), or both RES (3mM) and SA (3mM). The model curve represents the predicted MES degradation in the presence of free chlorine ([MES]$_0$ = 50 μM; [free chlorine]$_0$ = 280 μM; pH 7.1-7.2;)

The results first indicated a fairly close overlap between the unquenched samples and the model curve, which implied that the analytical technique used to quantify MES in these sample matrices was sound and no artifactual formation occurred. Second, it appeared that all three quenching techniques exhibited an increase in the MES concentration as compared to the unquenched values/model curve. For example, at 10 min, the MES concentrations for ascorbic acid, RES, and RES + SA were 2.8, 1.8, and 5.3 times higher than the model curve values (Fig. S1). This trend was followed through over 3 h, and it indicated that the greatest increase in MES for the three quenching techniques followed in the order of RES+SA > ascorbic acid > RES (Fig. S1). Such a pattern demonstrated that these quenching techniques, and especially ascorbic acid, did appear to have some effect on reducing the formed intermediate, MES-Cl^+, back to MES. The extent of how much was reformed though remained unclear since these R_3N-Cl^+ intermediates can potentially undergo elimination and degrade to other by-products as well (see later discussions and Scheme 2-1 in main text).

Text S2. Residual Free Chlorine Measurements.

Additional experiments were conducted to determine if the residual free chlorine measurements taken for samples that also contained tertiary amines reflected only the total free chlorine ([HOCl] + [OCl^-]) or also included other chlorinating agents (e.g., $R_3N\text{-}Cl^+$). These experiments were performed by exposing 25 μM free chlorine to MES or TMA ([TMA or MES]$_0$/[free chlorine]$_0$ = 2) for 44 or 30 min, respectively. These exposure times were selected since they were predicted to yield 95% conversion from the reactants to the respective chlorammonium species, which was determined by performing model simulations with Kintecus®,[1] (see Table 2-1 for rate constants used and Table S2 for the model reactions and conditions used). Samples were then quenched with DPD and measured for their absorbance at 515 nm. The results indicated that at these times, the absorbance readings were less than 0.01, which proved that the $R_3N\text{-}Cl^+$ generated did not react with DPD. These results were expected because $R_3N\text{-}Cl^+$ is only expected to participate in electrophilic substitution reactions rather than be involved in oxidation reactions. However, DPD must be oxidized through a one electron transfer reaction in order to form the Würster dye (pink dye which elicits a colorimetric response).[2] Therefore, the DPD method was found to only quantify the residual free chlorine concentration without interference from the $R_3N\text{-}Cl^+$ generated during these reactions.

Table S 1. The compound names, formula, molecular weights (MW), retention times (RT), parent and product masses, fragmentor voltages (FV), collision energies (CE), cell accelerator voltages (CAV), and source parameters (DGT, DGF, capillary and nebulizer) for LC/MS/MS analyses of HAAs and LC/MS analysis of MES.

Compound	Formula	MW (g/mole)	RT	Parent	Product	FV	CE	CAV	DGT	DGF	Capillary	Nebulizer
MCAA	$CH_2ClCOOH$	94.49	9.16	92.97	35.2	40	5	6	350	13	2500	40
MBAA	$CH_2BrCOOH$	138.95	9.39	136.92	78.9	55	13	2	350	10	4000	35
DCAA	$CHCl_2COOH$	128.94	11.59	126.93	82.9	60	5	6	350	13	2500	40
BCAA	CHBrClCOOH	173.39	11.96	170.88	126.8	60	5	4	300	10	4000	40
DBAA	$CHBr_2COOH$	217.84	12.32	214.83	170.7	55	9	2	350	10	4500	35
TCAA	CCl_3COOH	163.39	16.6	160.89	116.9	50	5	2	260	10	2500	40
BDCAA	$CHBrCl_2COOH$	207.84	18	160.85	78.9	55	9	2	290	10	5000	25
CDBAA	$CHBr_2ClCOOH$	252.29	20.7	204.8	78.9	55	9	2	260	10	4500	35
TBAA	CBr_3COOH	296.74	23.3	248.75	118.9	90	17	4	320	10	4500	30
MES	$C_6H_{13}NO_4S$	195.20	10.7	194.1		110		2	350	13	4000	40

Table S 2. A description of the reactions and conditions used to model the kinetics of the MES reaction with free chlorine. A similar method was used assess the model kinetics for other tertiary amines including TMA and TBA.

k ($M^{-1}s^{-1}$)	Reaction	Comments
3.34E+08	HOCl ==> OCl^- [a]	hypochlorite acid dissociation, pK_a = 7.45 [3]
6.66E+08	OCl^- ==> HOCl [a]	hypochlorite acid dissociation
9.26E+08	$MESH^+$ ==> MES [a]	MES dissociation, pK_a = 6.1[4]
7.36E+07	MES ==> $MESH^+$ [a]	MES dissociation
1.83E+01	MES + HOCl ==> MES-Cl^+ + OH^-	MES reaction with HOCl [5]

[a] These reaction rates were estimated by assuming k_f/k_b is equal to $[OCl^-]/[HOCl]$ which is $0.33\times10^9/0.67\times10^9$. This value represents the ratio between the two acid-base species at pH 7.2. These values were also multiplied by 10^9 in order to represent the fast equilibrium reached by these acid-base reactions.

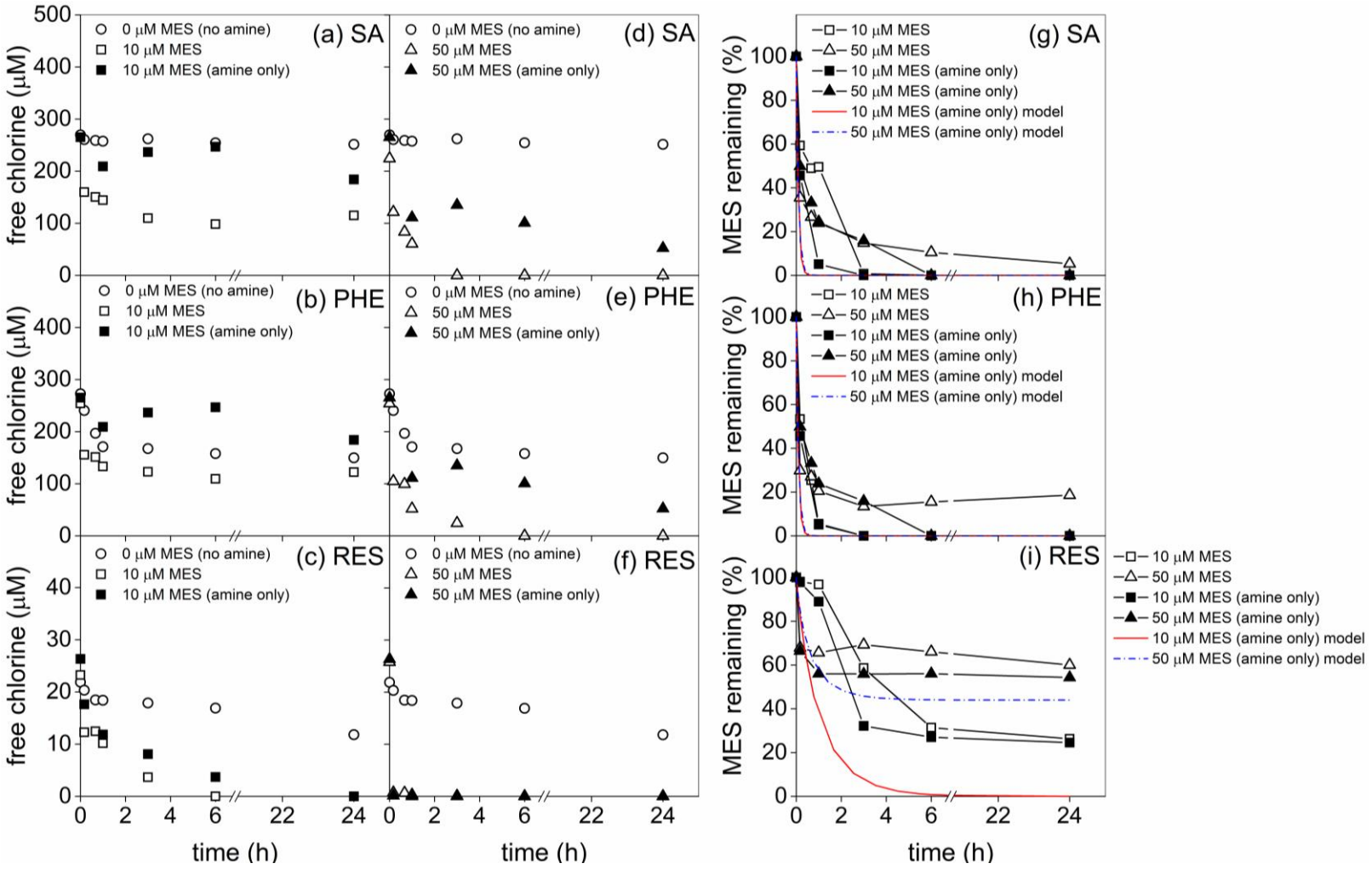

Figure S 2. Effect of MES on (a – f) the residual free chlorine and (g – i) MES % remaining over 24 h during chlorination of SA, PHE and RES in the presence of 10 or 50 μM MES ([SA and PHE]$_0$ = 10 μM; [RES]$_0$ = 1 μM; [MES]$_0$ = 0, 10 and 50 μM; [free chlorine]$_0$ = 280 μM (19.9 mg/L-Cl_2) for SA and PHE, or 28 μM (2.0 mg/L- Cl_2) for RES; pH 7.1-7.2).

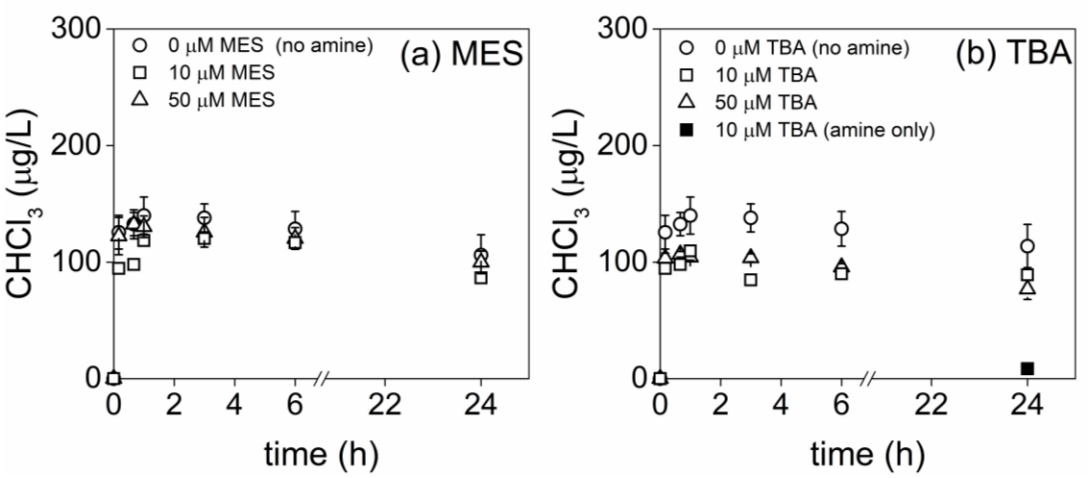

Figure S 3. Effect of (a) MES and (b) TBA on $CHCl_3$ formation over 24 h during chlorination of RES $(RES]_0$ = 1 µM; [MES or TBA]$_0$ = 0, 10 and 50 µM; [free chlorine]$_0$ = 28 µM (2.0 mg/L-Cl_2); pH 7.1-7.2). Error bars represent the standard deviation of ≥ 3 replicates.

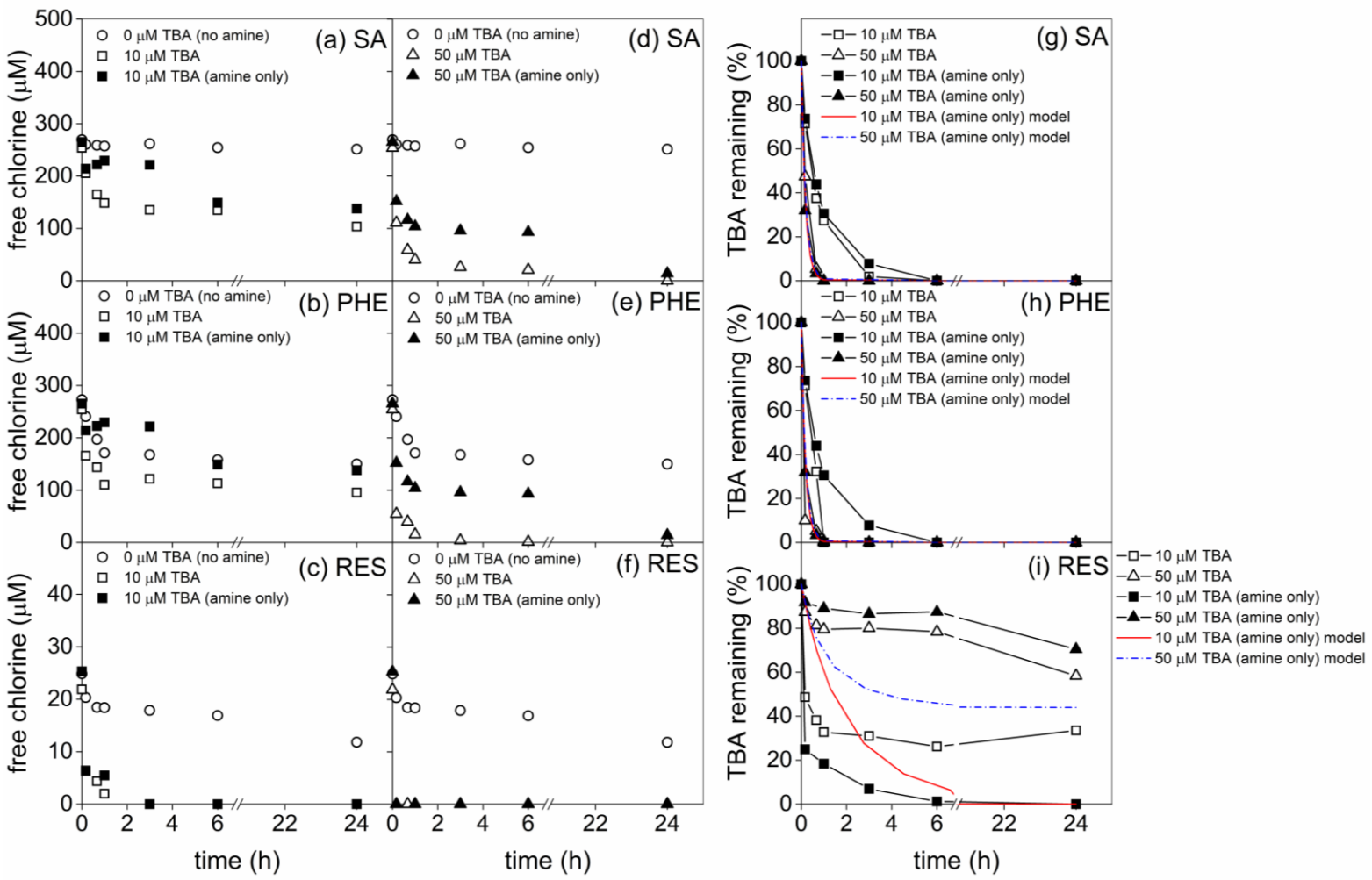

Figure S 4. Effect of TBA on (a – f) the residual free chlorine and (g – i) TBA % remaining over 24 h during chlorination of SA, PHE and RES in the presence of TBA ([SA and PHE]$_0$ = 10 μM; [RES]$_0$ = 1 μM; [TBA]$_0$ = 0, 10 and 50 μM; [free chlorine]$_0$ = 280 μM (19.9 mg/L-Cl_2) for SA and PHE, or 28 μM (2.0 mg/L- Cl_2) for RES; pH 7.1-7.2)

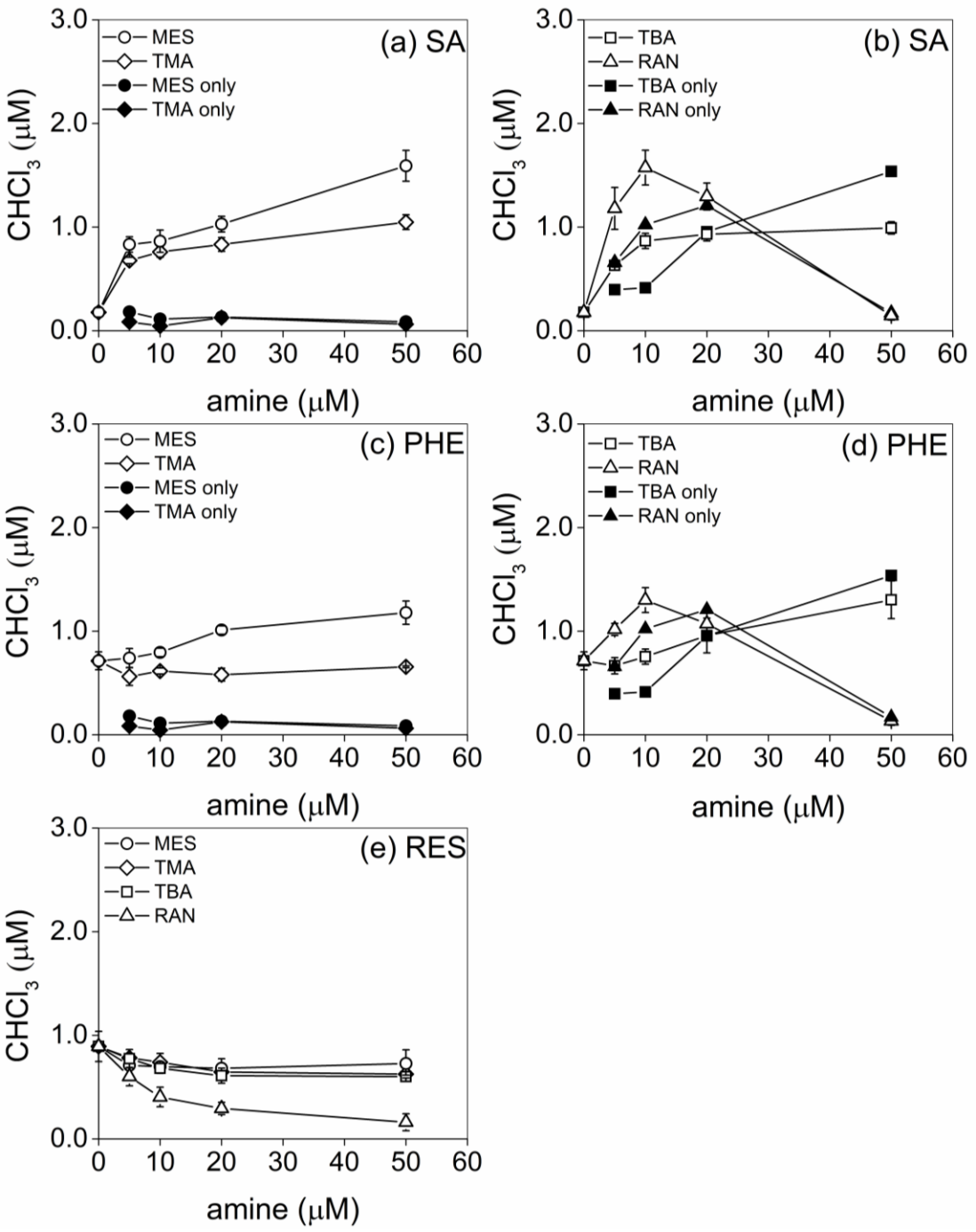

Figure S 5. Effect of amine dose (0 - 50 μM) on $CHCl_3$ formation from (a, b) SA (c, d) PHE and (e) RES when exposed to MES, TMA, TBA or RAN after 24 h of chlorination ($[SA \text{ and } PHE]_0$ = 10 μM; $[RES]_0$ = 1 μM; $[\text{free chlorine}]_0$ = 280 μM (19.9 mg/L-Cl_2) for SA and PHE, or 28 μM (2.0 mg/L- Cl_2) for RES; pH 7.1-7.2), Error bars represent the standard deviation of ≥ 3 replicates.

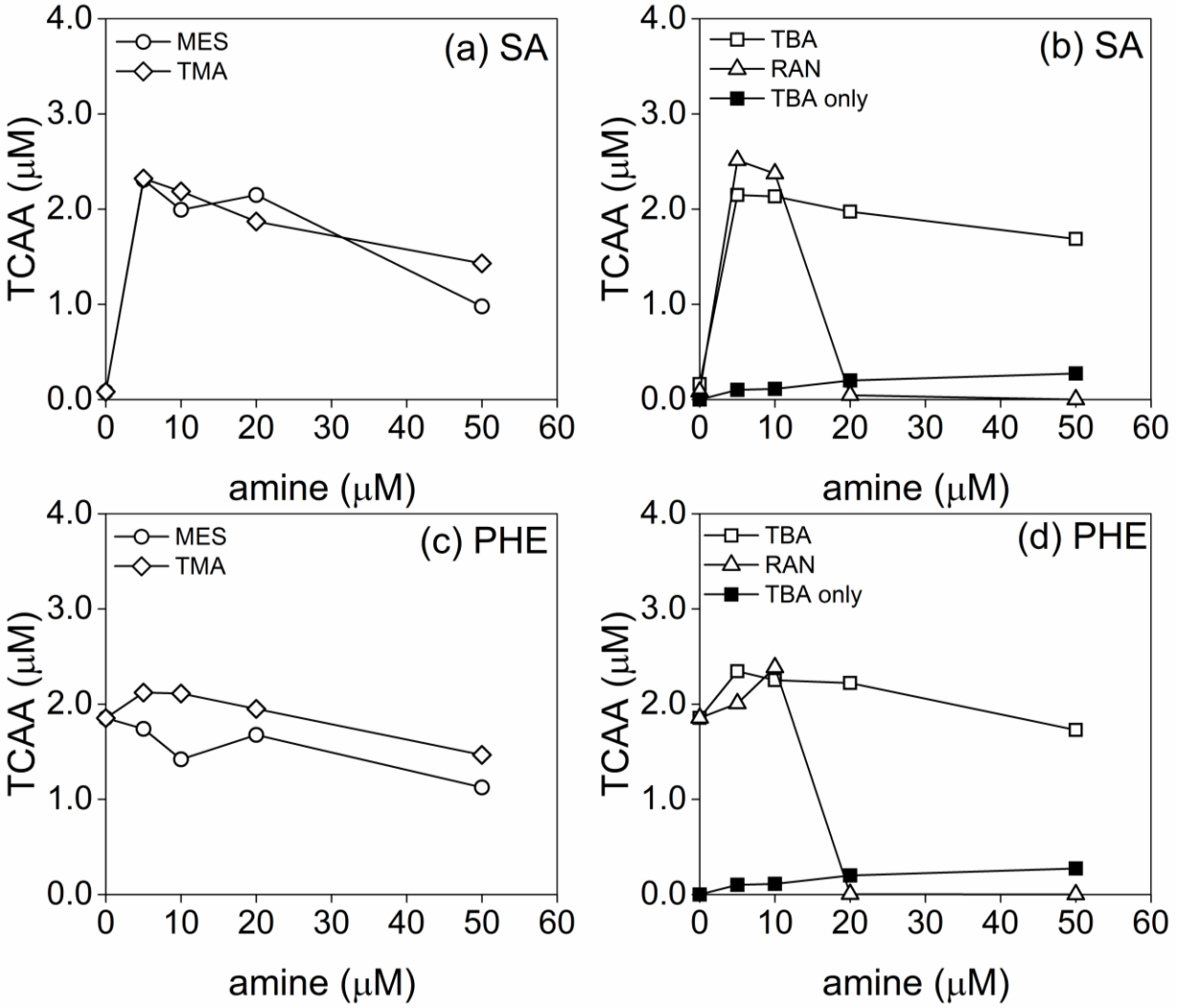

Figure S 6. Effect of amine dose (0 - 50 μM) on TCAA formation from (a, b) SA (c, d) PHE when exposed to MES, TMA, TBA or RAN after 24 h of chlorination ([SA and PHE]$_0$ = 10 μM; [RES]$_0$ = 1 μM; [free chlorine]$_0$ = 280 μM (19.9 mg/L-Cl_2) for SA and PHE, or 28 μM (2.0 mg/L- Cl_2) for RES; pH 7.1-7.2).

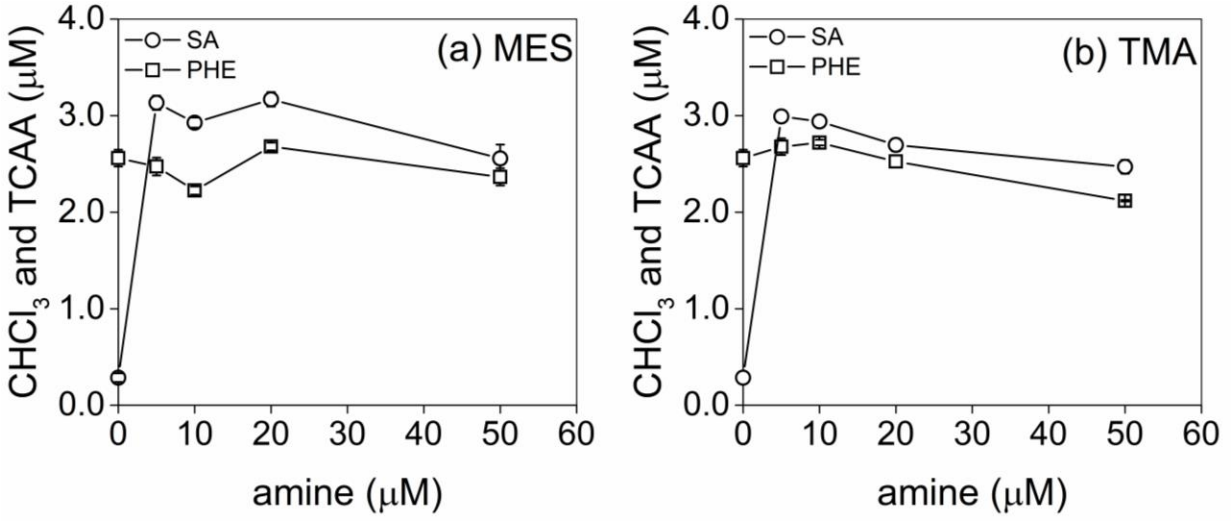

Figure S 7. Effect of amine dose (0 - 50 μM) on summed formation of $CHCl_3$ and TCAA from SA and PHE when exposed to (a) MES or (b) TMA after 24 h of chlorination ($[SA \text{ and } PHE]_0$ = 10 μM; $[\text{free chlorine}]_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2), Error bars represent the standard deviation of ≥ 3 replicates.

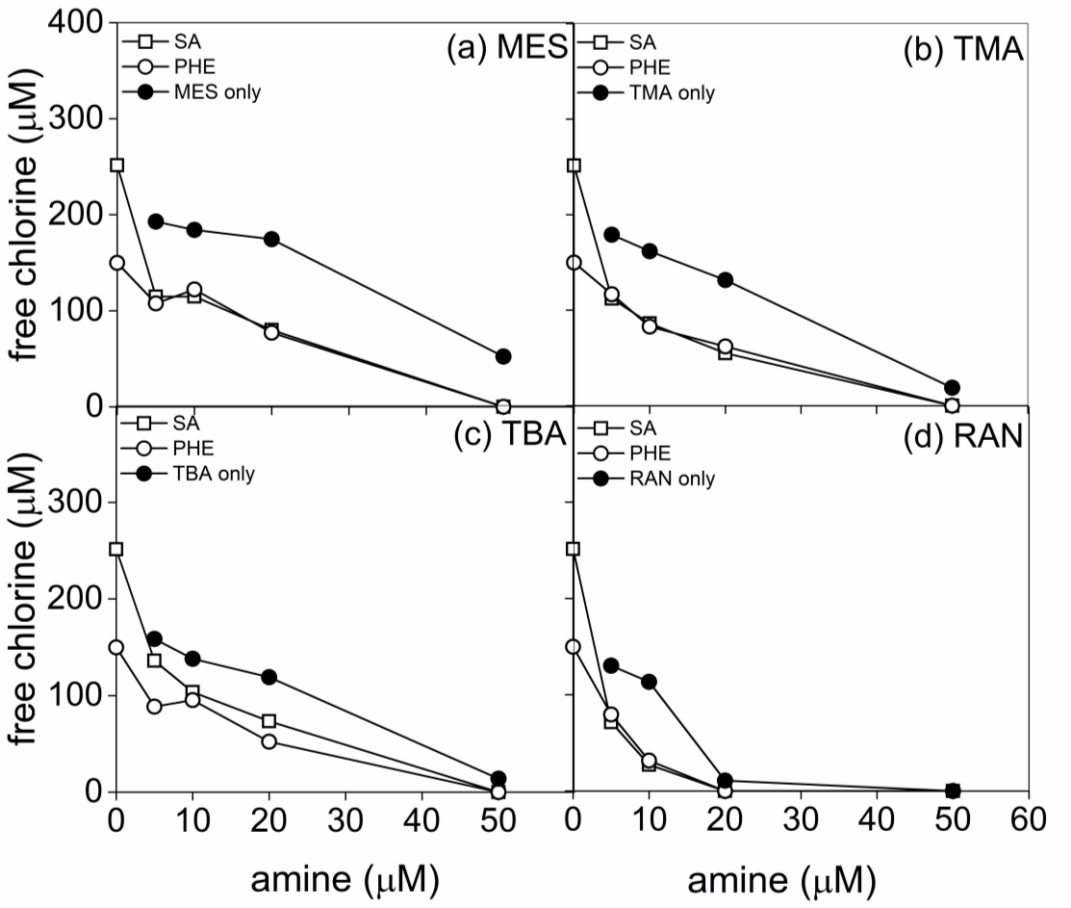

Figure S 8. Differences in residual free chlorine when SA or PHE was exposed to 5 – 50 μM of (a) MES (b) TMA (c) TBA (d) RAN after 24 h of chlorination ([SA and PHE]$_0$ = 10 μM; [free chlorine]$_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2).

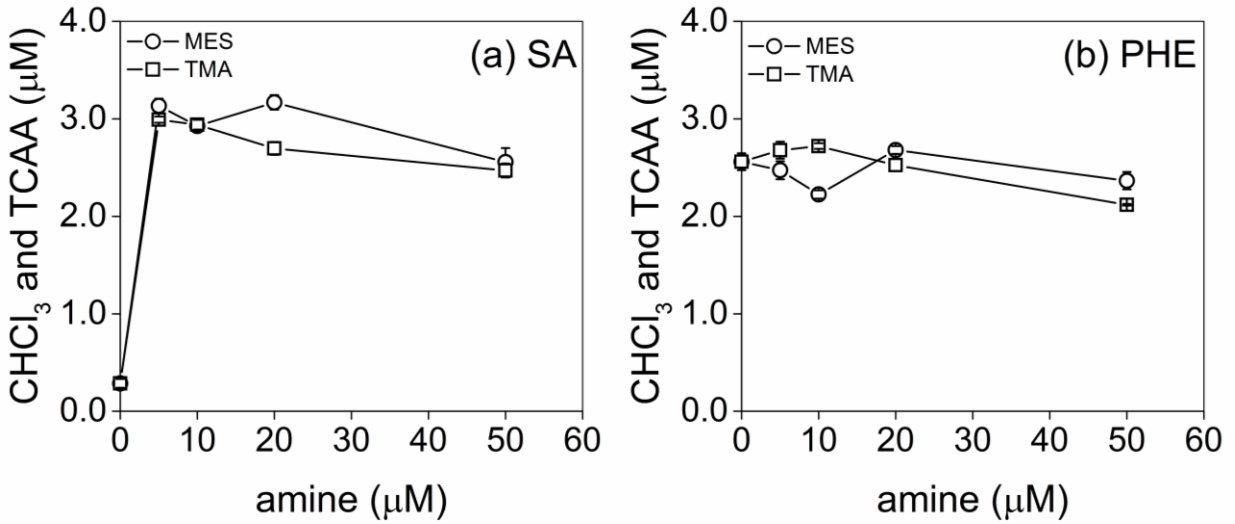

Figure S 9. Effect of amine dose (0 - 50 µM) on summed formation of $CHCl_3$ and TCAA from (a) SA and (b) PHE when exposed to MES or TMA after 24 h of chlorination ([SA and PHE]$_0$ = 10 µM; [free chlorine]$_0$ = 280 µM (19.9 mg/L-Cl_2); pH 7.1-7.2), Error bars represent the standard deviation of ≥ 3 replicates.

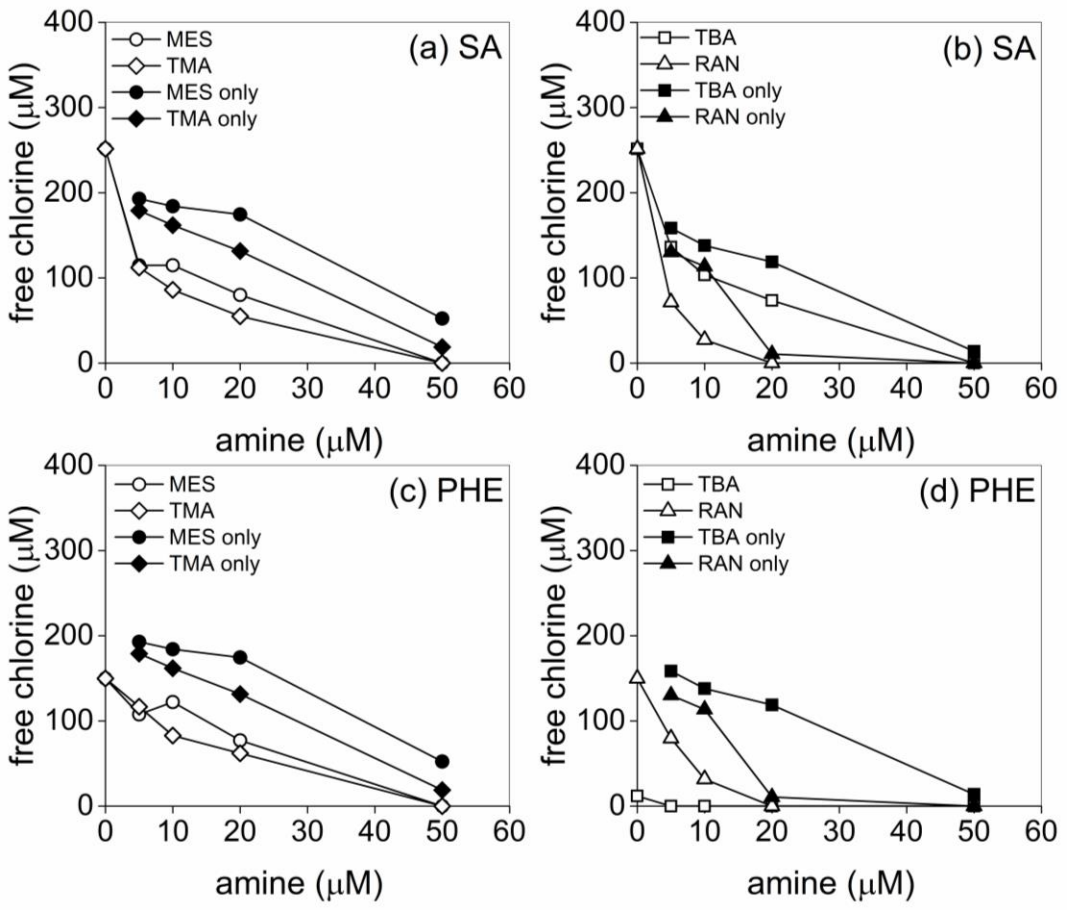

Figure S 10. Differences in residual free chlorine when (a, b) SA or (c, d) PHE was exposed to 5 – 50 μM of MES, TMA, TBA or RAN after 24 h of chlorination ([SA and PHE]$_0$ = 10 μM; [free chlorine]$_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2). RES-related data not plotted because residual free chlorine was < d.l. for all RES/TA/FC experiments.

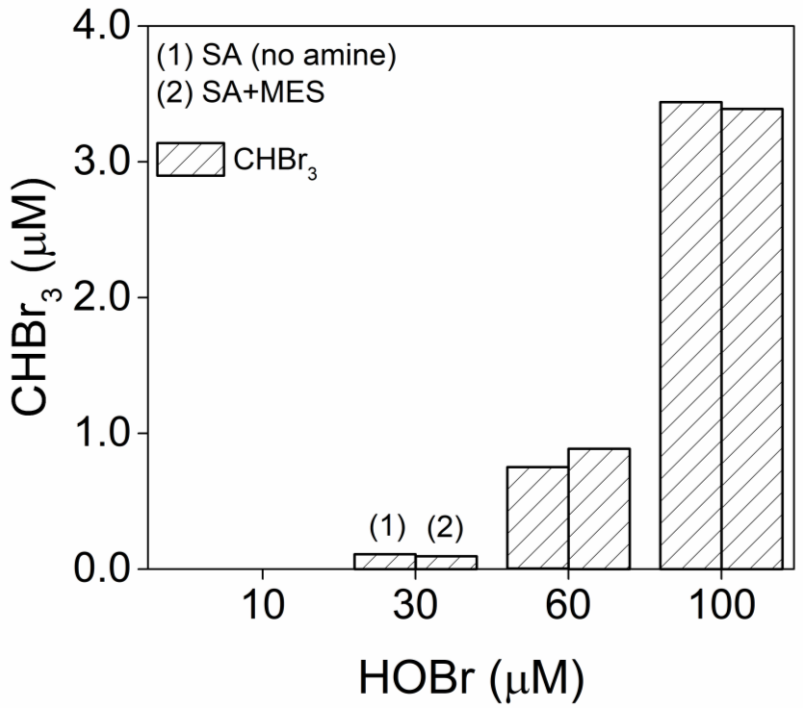

Figure S 11. Effect of MES on $CHBr_3$ formation when SA is exposed to varying HOBr doses (10 – 100 µM) after 24 h ($[MES]_0$ = 10 µM; $[SA]_0$ = 10 µM; pH 7.1-7.2).

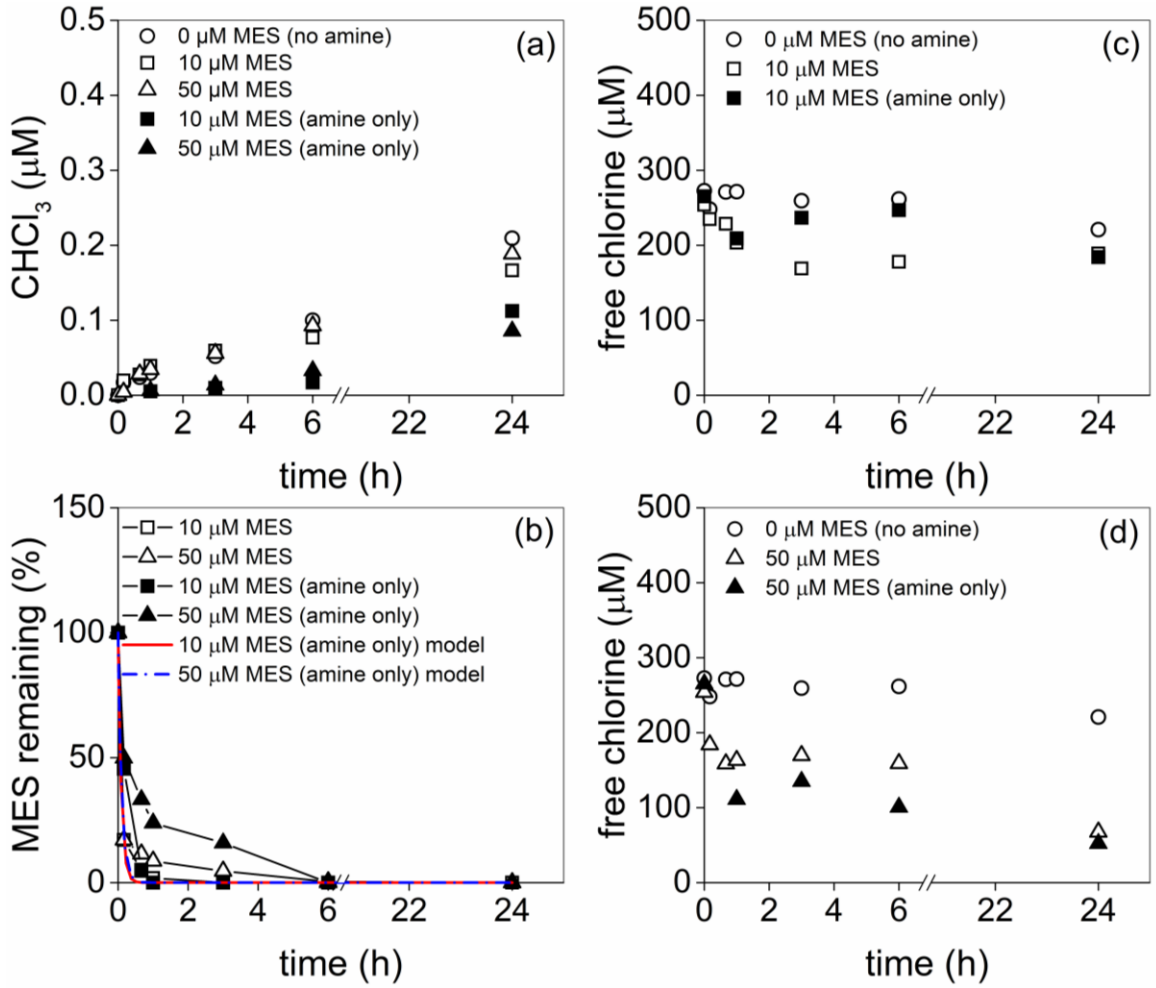

Figure S 12. Effect of MES on (a) $CHCl_3$ formation (b) MES % remaining and (c, d) residual free chlorine when SRFA is chlorinated over 24 h ($[SRFA]_0$ = 10 μM (0.12 mg/L as C); $[MES]_0$ = 0, 10 and 50 μM; $[\text{free chlorine}]_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2).

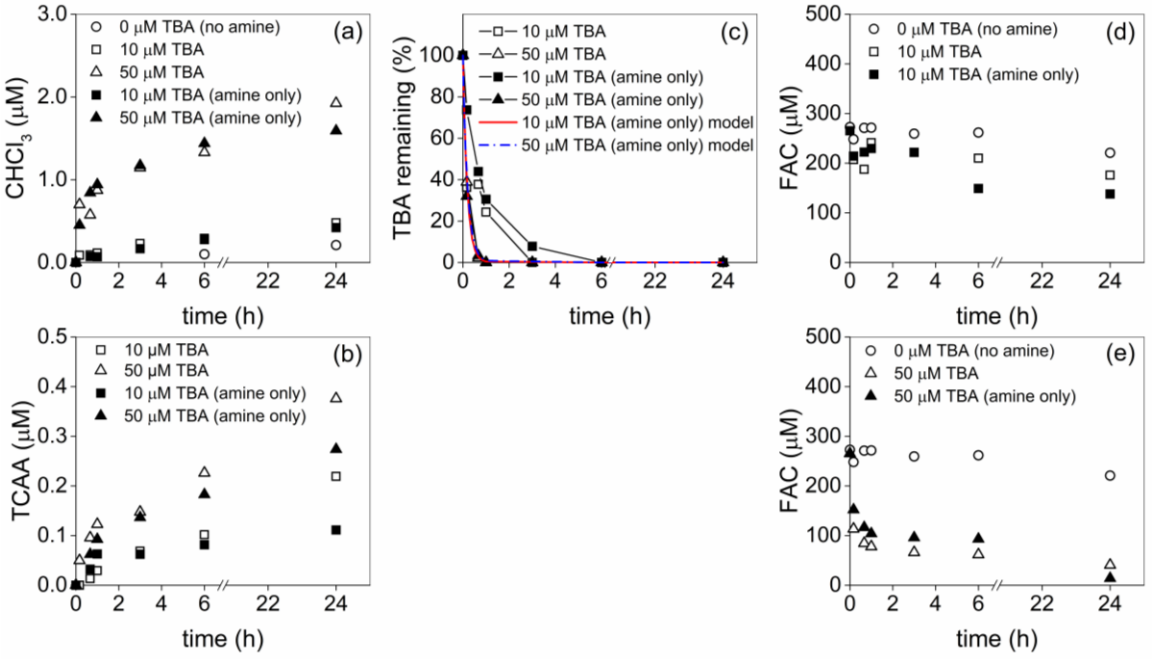

Figure S 13. Effect of TBA on (a) $CHCl_3$ formation (b) TCAA formation (c) TBA % remaining and (d, e) residual free chlorine when SRFA is chlorinated over 24 h ($[SRFA]_0$ = 10 μM (0.12 mg/L as C); $[TBA]_0$ = 0, 10 and 50 μM; $[free\ chlorine]_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2).

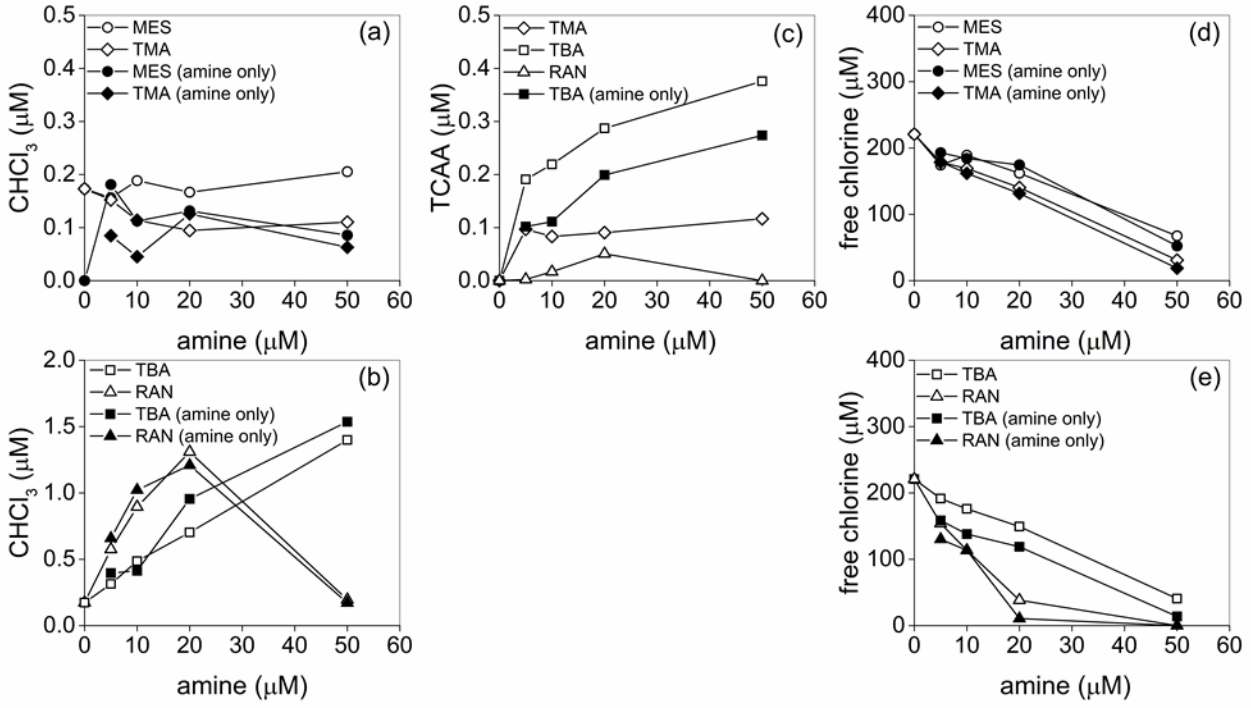

Figure S 14. Effect of varying MES, TMA, TBA and RAN doses (0 - 50 μM) on (a, b) $CHCl_3$ (c) TCAA formation and (d, e) residual free chlorine when SRFA is chlorinated for 24 h ($[SRFA]_0$ = 10 μM; $[\text{free chlorine}]_0$ = 280 μM (19.9 mg/L-Cl_2); pH 7.1-7.2).

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4. Good, N.; Winget, G.; Winter, W.; Connolly, T.; Izawa, S.; Singh, R., Hydrogen Ion Buffers for Biological Research. *Biochemistry* **1966,** *5*, (2), 467-&.
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