

Organic Nitrogen Reactivity with Free Chlorine: Effects on Disinfection By-product Formation and Polyamide Membrane Stability

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, 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, reacted 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 role 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 $20\times$ 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 $\text{R}_3\text{N-X}^+$ ($\text{X}=\text{Br}$ 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 $\text{ClO} > \text{HOCl}$. However, for the ring halogenation pathway, both chlorination and bromination occurred in which the reactivity of the chlorinating and brominating agents decreased such that $\text{Cl}_2 > \text{HOCl}$, and $\text{BrCl} > \text{BrOCl} > \text{Br}_2 > \text{Br}_2\text{O} > \text{HOBr}$, 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.