NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: Electrophilic aromatic iodination in chloraminated water: A kinetic investigation of a chemical mechanism relevant to iodinated disinfection byproduct formation

Graduate Fellow: Michael Rose

Advisor: A. Lynn Roberts

Institution: Johns Hopkins University, Baltimore, Maryland

Background and Introduction

The transfer of iodine from inorganic species to organic compounds, an *iodination* reaction, can be problematic during water treatment because it generates an iodinated disinfection byproduct (I-DBP), some of which are potent toxins.[1-2] Our laboratory investigation quantifies relationships between water characteristics, such as pH, and iodination reaction rates under experimental conditions that are relevant to conventional water disinfection. Chemists have studied iodination reactions in water for decades,[3] but most experiments used high iodide (I^-, oxidation state = -1) concentrations, which is unlikely to be used for disinfected water.

Iodide is quickly oxidized to hypoiodous acid (HOI, oxidation state = +1) by chemical disinfectants such as free chlorine, chloramine, and ozone.[4] HOI and other iodine(+1) species are known *iodinating agents*, the inorganic species that transfer iodine to organic compounds.[3] Iodide affects the iodine(+1) species distribution by bonding with HOI to form I_2, I_3^-, and HOI_2^-, and the iodinating agents in water with iodide may not be the same as in water without it.

We are the first to employ chloramine as an oxidant in iodination experiments to maintain negligibly low iodide concentrations. Our goal was to identify the active iodinating agent(s) of a model compound, dimethenamid, under experimental conditions that are relevant to disinfected water.

Hypothesis
Hypoiodous acidium ion (H_2OI^+) is an iodinating agent of dimethenamid under conditions relevant to drinking water treatment (low iodide concentration, pH 5 –9).

Research Objectives

- Quantify the rate of iodine transfer to a model compound, dimethenamid, in water with an oxidant residual.

- Identify the iodinating agent(s) of dimethenamid in chloraminated water.

Needs Served by This Research

This work contributes to the fundamental understanding of iodine reactivity in water, which lags behind that of chlorine and bromine. This understanding could help reduce I-DBP formation during water treatment.

Progress to Date

Experimental Design

We simulated water disinfection in the laboratory by adding reagent-grade chemicals to ultra-pure water, which allowed precise control of the experimental conditions, including pH, chloride concentration, and ionic strength. The reactors were glass bottles with pump dispensers, kept in a constant temperature bath at 25 °C. To prepare the reactor solutions, ammonia (NH_4^+/NH_3) and free chlorine ($HOCl/OCl^-$) were combined to form chloramine (NH_2Cl). Chloramine is critical to our approach because it oxidizes iodide but not iodine(+1), including iodinating agents.[4] Our work is the first iodination kinetic study to employ an oxidant residual in order to maintain very low iodide concentrations.

After allowing a moment for chloramine to form, sodium perchlorate was added to adjust the ionic strength. Sodium acetate, phosphate, or borate solutions were added to buffer pH. The pH buffer concentration was minimized because buffer species can catalyze iodination reactions[3] as well as a side-reaction called HOI disproportionation ($3\ HOI \rightarrow 2\ I^- + IO_3^- + 3\ H^+$).[5] HOI disproportionation consumes iodine(+1), which can interfere with iodination experiments.[6] In our reactors, iodine(+1) was then formed by adding potassium iodide solution to the reactor dropwise. After allowing a moment for chloramine to oxidize iodide to iodine(+1), the iodination reaction was initiated by adding dimethenamid quickly and shaking vigorously to mix.

The progress of the iodination reactions was monitored using gas chromatography (GC) with a micro-electron capture detection (μ-ECD). Water samples were collected in glass centrifuge tubes with *N,N*-dimethylaniline. The iodine and *N,N*-dimethylaniline reacted instantaneously to produce 4-iodo-*N,N*-dimethylaniline, which is amenable to GC analysis.[7] Then, sodium thiosulfate was added to quench the chloramine. The chemicals of interest were extracted from the water using a small volume of toluene, and were injected into the GC for analysis. We synthesized iodo-dimethenamid to quantify its concentration in our samples because a commercial standard is not available. This analytical scheme allowed us to monitor the iodine mass balance by measuring the concentrations of both iodine(+1), as 4-iodo-*N,N*-dimethylanline, and the iodinated reaction product, iodo-dimethenamid, at each observation. Monitoring iodine mass balance enabled detection of influence from side reactions, such as HOI disproportionation.

Data Analysis

In each experiment, the dimethenamid was present in excess relative to iodine, such that the dimethenamid concentration was approximately constant. This simplified the data analysis, allowing calculation of observed first-order rate constants by least-squares regression of the natural log of iodine concentration or the iodo-dimethenamid concentration versus time. The observed first-order rate constants were converted to apparent second-order rate constants (k_{app}) by dividing by the dimethenamid concentration. The k_{app} values were plotted against the variable solution condition, such as pH, chloride concentration, or iodide concentration. These plots were compared to trends in iodine species concentrations calculated for the experimental conditions using a thermodynamic speciation model, similar to that described in reference 8.

Results and Discussion

Our kinetic results are consistent with a bimolecular reaction, which is commonly reported for iodination.[3, 9] The variation in iodine mass balance was typically less than 10 percent, indicating that the iodination reaction of interest dominated in most of our experiments. The influence of pH (4.4 – 9.3) was assessed in the presence of minimal chloride concentration, minimal pH buffer concentration, and constant ionic strength. The dimethenamid iodination rate decreased as pH increased (Figure 1a), in other words the rate increased as hydrogen ion concentration ($[H^+]$) increased (pH = $-\log[H^+]$). HOI is commonly considered the only iodinating agent in disinfected water (pH > 3.5),[10] but it could not have produced these results because its concentration does not vary appreciably with pH under our experimental conditions (Figure 1b).
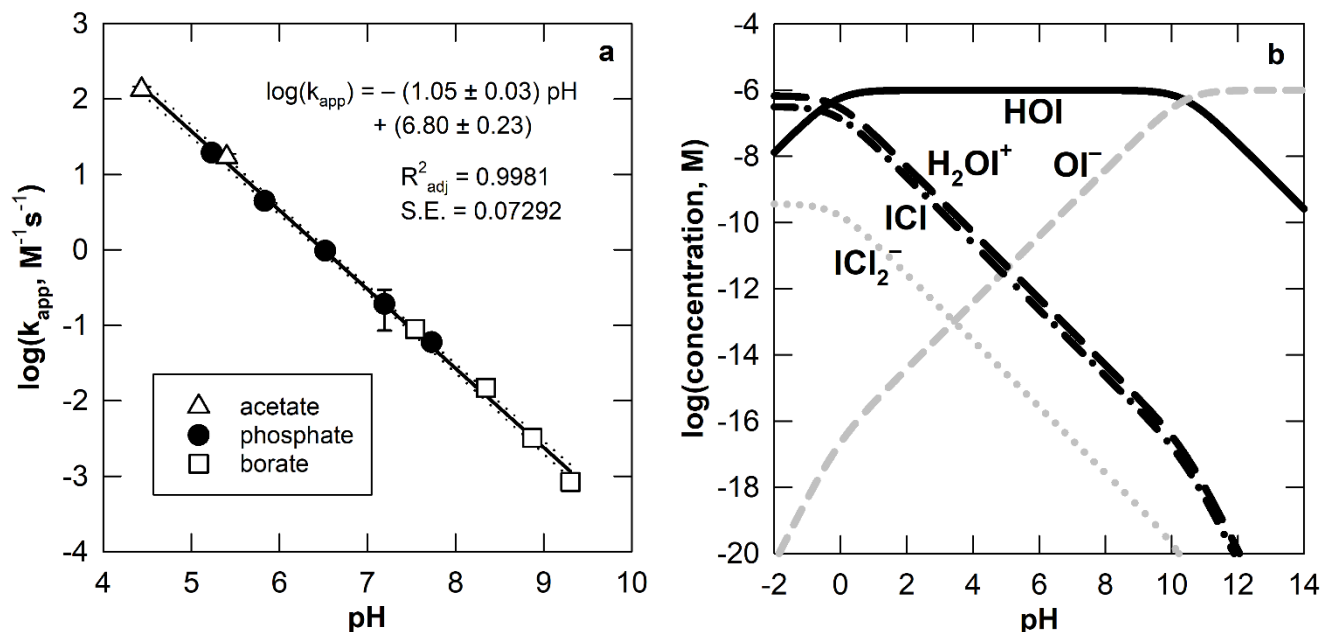
Figure 1. a) Dimethenamid (DM) iodination apparent second-order rate coefficient (k_{app}) as a function of pH. [DM] = 36 – 48 µM, [iodine(+1)]$_{T,0}$ = 1 µM, [NH$_2$Cl]$_0$ = 15 µM, Cl/N = 0.6 (M/M), total [acetate], [borate], or [phosphate] = 1.0 – 2.0 mM, ionic strength = 0.04 M (NaClO$_4$), T = 25.0 ± 0.1°C. Error bars and dotted lines show 95% confidence intervals, unless contained within data symbol or regression line, respectively. b) Iodine(+1) speciation as a function of pH in the absence of free I$^-$. Darker lines show potential iodinating agents under the experimental conditions.

Unlike HOI, the concentrations of both H$_2$OI$^+$ and ICl depend on pH under our experimental conditions (Figure 1b). To distinguish between the influence of H$_2$OI$^+$ and ICl, chloride concentration was varied at constant pH and ionic strength because only ICl concentration should be affected (HOI + H$^+$ + Cl$^-$ = ICl + H$_2$O).[11] The iodination rate did increase with chloride concentration (2 – 10 mM) but not to the extent expected if ICl were the dominant iodinating agent. To investigate further, we increased the chloride concentration to 100 mM (Figure 2). If H$_2$OI$^+$ and ICl were to compete as iodinating agents, the sensitivity of the iodination rate to chloride should increase at higher chloride concentrations because ICl would prevail as its concentration increases while H$_2$OI$^+$ concentration remains
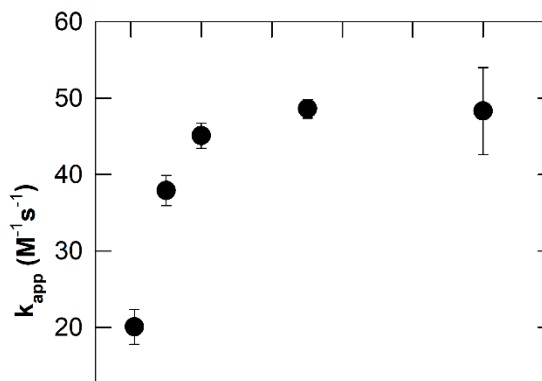
Figure 2. DM iodination apparent second-order rate coefficient as a function of total chloride concentration ([Cl$^-$]) up to 100 mM. Solution pH = 5.36 ± 0.01, [DM] = 37 µM, [iodine(+1)]$_{T,0}$ = 1 µM, [NH$_2$Cl]$_0$ = 15 µM, Cl/N = 0.6 (M/M), total [phosphate] = 1.0 mM, ionic strength = 0.1 M (NaCl + NaClO$_4$), and T = 25.0 ± 0.1°C. Error bars depict 95% confidence intervals.

constant at fixed pH and ionic strength. Instead, chloride catalysis exhibited a plateau above 20 mM chloride concentration (Figure 3). The influence of chloride is complex, and we are investigating it further using kinetic isotope effect analysis (see *Next Steps*). In the meantime, we were able to demonstrate that the influence of the background chloride concentration in our reactors (< 0.02 mM) did not influence the iodination rate significantly, revealing H_2OI^+ as the predominant iodinating agent of dimethenamid.

In select experiments, potassium iodide was added in excess of chloramine to introduce free iodide. Free iodide is not expected to persist in drinking water treated with conventional disinfectants,[4] although it could influence I-DBP formation by iodine-based disinfectants.[12] Increasing free iodide concentration suppressed the DM iodination rate (Figure 3a), a phenomenon that has been widely reported for iodination.[3, 9] Under our experimental conditions, the iodine(+1) species distribution shifts from HOI to I_3^- (Figure 3b), and H_2OI^+ concentration decreases directly with HOI concentration at constant pH ($H_2OI^+ = HOI + H^+$), accounting for the decrease in iodination rate. This suggests that I_2 and DM do not react appreciably under the conditions studied.
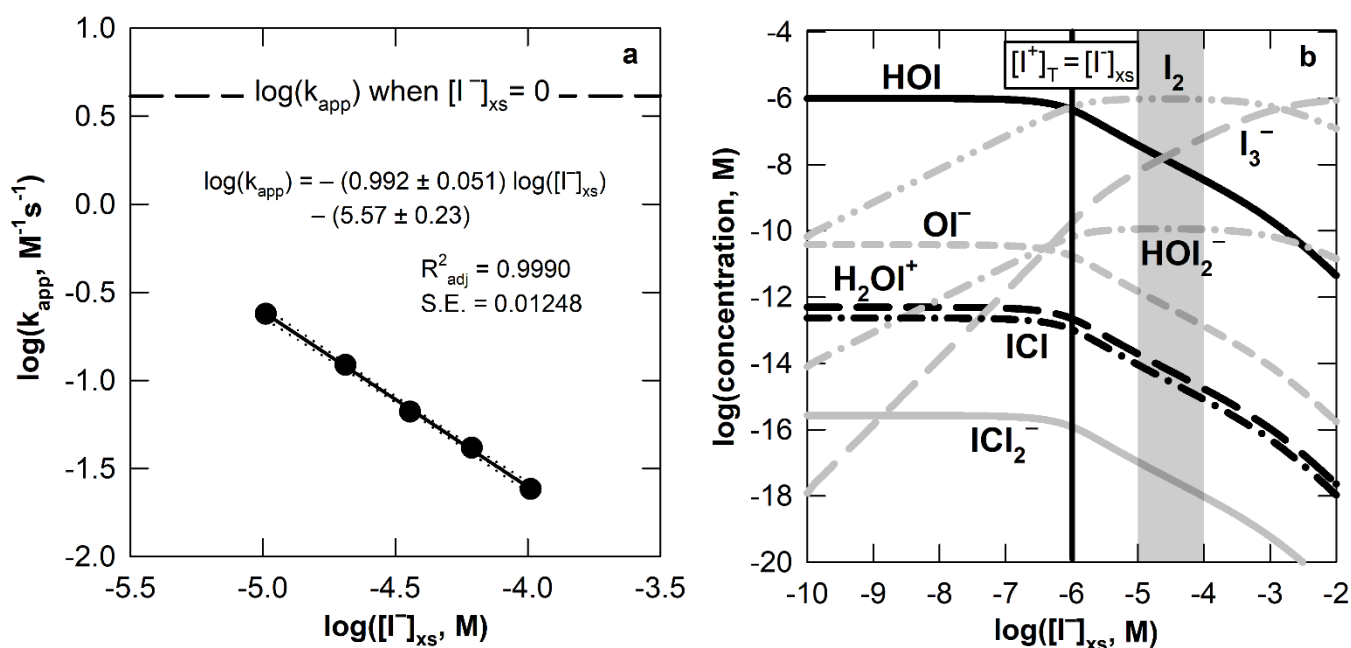
Figure 3. a) DM iodination apparent second-order rate coefficient (k_{app}) as a function of free iodide concentration ($[I^-]_{xs} = [KI]_{added} - [NH_2Cl]$). Solution pH = 5.9, [DM] = 37 ± 1 μM, $[NH_2Cl]_0$ = 15 μM, Cl/N = 0.6 (M/M), $[phosphate]_T$ = 1.0 mM, ionic strength = 0.04 M ($NaClO_4$), T = 25.0 ± 0.01 °C. Error bars and dotted lines show 95% confidence intervals, unless contained within data symbol or regression line, respectively. b) Iodine(+1) speciation as a function of $[I^-]_{xs}$ at pH 5.9. Assumes $[iodine(+1)]_T$ = 1 μM, [chloride] = 14 μM. The dark vertical line shows the x-coordinate (-6) at which $[iodine(+1)]_T = [I^-]_{xs}$. The shaded area corresponds to experimental conditions in the presence of excess iodide (part a).

Conclusions

The common assumption that HOI is the sole iodinating agent responsible for I-DBP formation in drinking water implies that the intrinsic reactivity of iodine does not depend on pH. In contrast, we demonstrate acid catalysis of DM iodination and attribute it primarily to H_2OI^+. H_2OI^+ has previously been identified as an iodinating agent at low iodide concentration but only below pH 3.5,[10] whereas we demonstrate its influence in a pH range (4 – 9) encountered in water treatment.

Iodo-trihalomethane (I-THM) production is a common surrogate for I-DBP formation potential,[2, 10, 12-13] although the chemical structure of most total organic iodine (TOI) measured in finished drinking water is unknown.[13] Such reliance on I-THM measurements could obfuscate the influence of pH on TOI production because the rate of the

final step in THM production is base promoted. Indeed, the conversion from TOI to I-THMs has been shown to increase with pH (5 – 10) in laboratory-chloraminated water.[13] Our demonstration of acid catalysis of iodination under water treatment conditions warrants further investigation of the influence of pH on TOI formation, especially in water treated with chloramine. Drinking water plants sometimes switch from chlorine to chloramine to reduce regulated Cl/Br-DBPs.[2] I-DBPs, however, may undermine this approach if iodine is present, especially considering toxicity assays correlate with TOI more so than with total organic chlorine.[14]

Next Steps

The research described herein will soon be submitted to a peer-reviewed journal.

Currently, we are conducting kinetic isotope effect experiments to clarify the complex role of chloride in dimethenamid iodination as well as to identify the rate determining step of this iodination mechanism. We have collaborated with Dr. Keith Reber, a synthetic chemist at Towson University in Towson, Maryland, to produce the deuterated dimethenamid needed for these experiments. We will also apply the kinetic isotope effect analysis to chlorination and bromination for comparison.

Moving forward, I plan to apply this experimental design to other model compounds. Ultimately, my goal is to conduct similar investigations under more realistic conditions using a non-targeted analytical approach, such as TOI analysis or high-resolution mass spectrometry.

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