Reactions of Aldehydes and Ketones with Residual Disinfectants in the Drinking Water Distribution System

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Background:

Taking secondary wastewater through a series of advanced treatment steps that cleans water to a potable quality is potable water reuse. Direct potable reuse takes this advanced treated water and sends it to a drinking water treatment plant or directly into the distribution system of a community [1]. A standard treatment step in most of these advanced treatment trains is reverse osmosis (RO) [1]. However, it has been found that low-weight molecules, including oxidation byproducts aldehydes and ketones, are not completely stopped by RO [1]. These molecules that get through RO will enter the distribution and react with common residual disinfectants, such as chlorine (present as hypochlorous acid, HOCl). Chlorine can react with residual bromine (Br-) to form small amounts of hypobromous acid HOBr. The reactions between aldehyde and ketone with the disinfectants HOCl and HOBr are poorly understood and need to be studied along with the formation of potential unintended byproducts of treatment.

Research Objective:

Determine the reaction rates of aldehydes and ketones in an excess of chlorine (HOCl) or bromine (HOBr).

Theory:

The reaction between a given aldehyde [Ald] or ketone with chlorine or bromine is taken to be a pseudo-first-order as described by Equation 1 [2]:

$$\frac{d[Ald]}{dt} = -k_{obs} * [Ald] \tag{1}$$

Where the k_{obs} value is the reaction rate multiplied by the assumed constant concentration of chlorine or bromine, $\frac{d[Ald]}{dt}$ is instantaneous change in the concentration of aldehyde over time, and $[Ald]$ is the instant concentration of aldehyde. Equation 1 can be rearranged to form Equation 2 [2]:

$$\frac{[Ald]}{[Ald]_0} = e^{-k_{obs}*t} \tag{2}$$

Where $[Ald]_0$ is the original concentration at the start of the reaction, t is the time after the start of reaction, and the remaining variables are the same. To determine the reaction rate, these methods only need the concentration of a given compound and how that concentration changes in time (found by comparing concentrations over a known time interval) when reacting with a known concentration of chlorine.

Method:

Each compound was tested at a concentration of 0.05mM. Buffers of pH 5 to 10 were prepared at 50mM (acetate for pH 5, phosphate for pH 6-8, and borate for pH 9 and 10). All unique combinations of pH, disinfectant, and compound were tested in duplicate or triplicate.
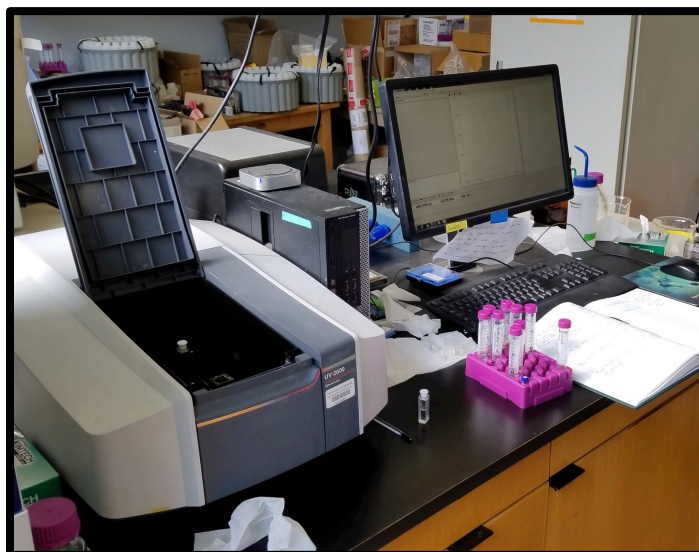

Figure 1. Picture of UV-vis Spectrophotometer Setup

UV-vis spectrophotometry was used to measure the light absorbance of the given sample over a wavelength range of 200-400 nanometers (nm). An initial absorbance measurement of just the compound alone in the sample was made with the respective buffer as reference. After this initial measurement, chlorine was added and the absorbance measured every 60 seconds for 30 minutes; slower reactions were tested for 60 minutes. The wavelength with the largest absorbance measurements was used to calculate the observed rate constant (k_{obs}).

Results:

The reaction rates of aldehydes and ketones with chlorine from acceptable tests were averaged for each unique combination and consolidated into two bar graphs. Figure 2 shows the bar graph of reaction rates for each unique combination in excess of chlorine.

Discussion:

A few general patterns found about the reaction rates based on the structural shapes of the compounds are noted here. The majority of compounds have an increase in reaction rate as pH increases. This suggests that OCl- is the reactive species, as it dominates at pH values over 7.5, the pK_a of the HOCl/OCl⁻ acid/conjugate base system. However the opposite occurs for 2,4-heptadienal and 2,4-heptadien-6-one. The difference between the two double bonds versus a single double bond suggests that the additional double bond is an important point of the reaction mechanism.

Shorter carbon chained compounds are found to be more reactive. The addition of methyl groups further decreases the rate of reaction. Ketones are less reactive than aldehydes. A possible explanation for these patterns is that longer carbon chains are electron donating and could cause a decrease in reactivity; furthermore, the additional methyl groups could be decreasing the reaction rate due to steric hindrance as the reactive site is more blocked.
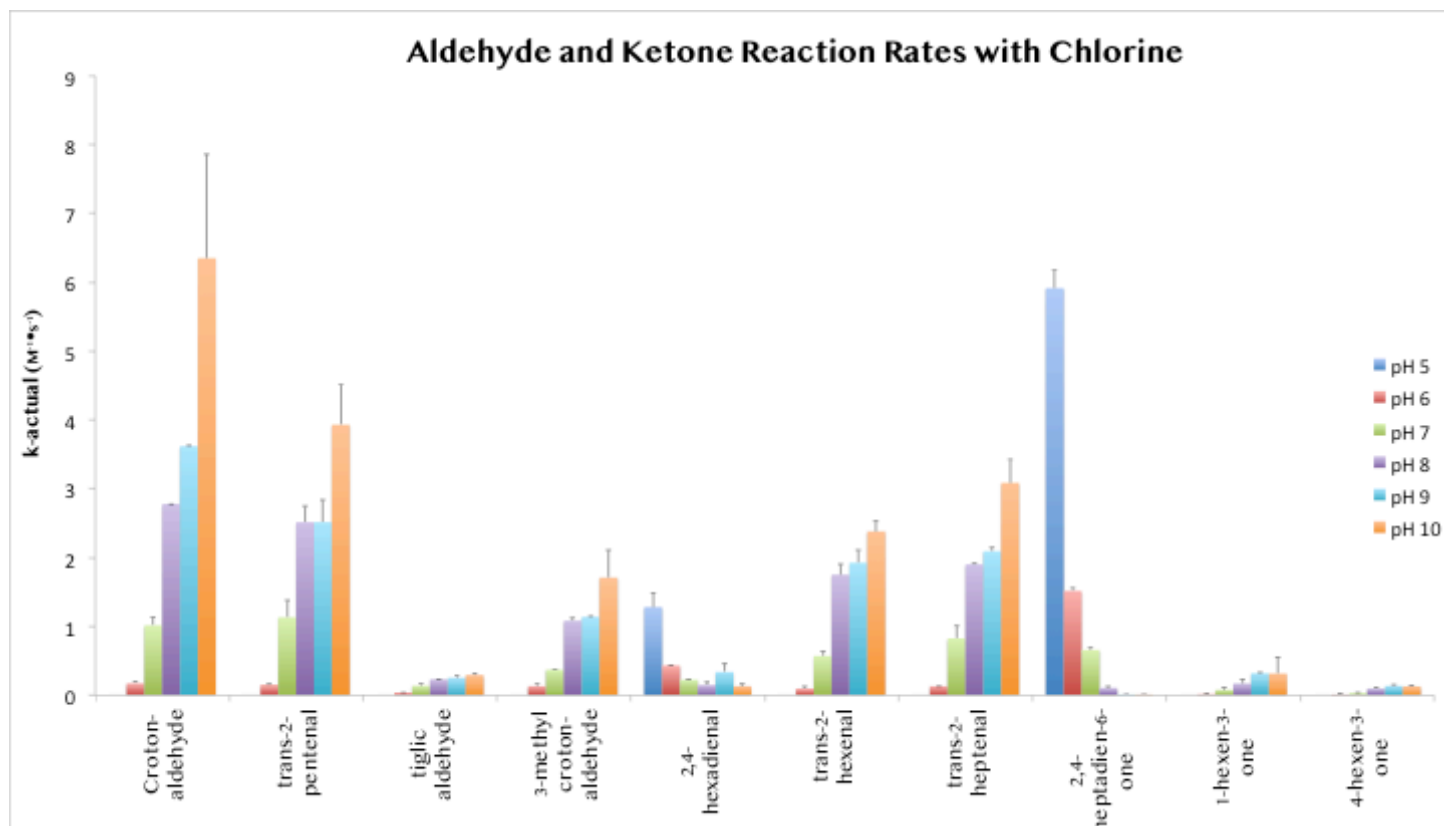
Figure 2. Graph of reaction rate constants of unsaturated aldehydes and ketones with HOCl

Reactions with aldehydes and ketones with bromine (HOBr) was tested, however not enough data was collected to provide reliable patterns, thus the data is not shown here.

One important consideration of the presence of these compounds reacting in a drinking water distribution system is how much of each compound will react away in the time the water spends going from the treatment plant to the tap? The residence time of the water in the pipes of a city distribution system is 23.3 hours [3]. With a dose of 1 mg/L chlorine in pH 7.5 water from the treatment plant, persistence of these compounds varies depending on their reactivity with HOCl. Faster reacting compounds, crotonaldehyde and acrolein, have over 80% of the original concentration reacting away in the time it takes water to flow from treatment to the tap. The slower reacting compounds, tiglic aldehyde and 4-hexen-3-one, have only 50% or even as little as 6% of concentration reacting away in the same time.

The pH relationship suggests a possible reaction where the nucleophile OCl- produced by the chlorine attacks the electrophilic compounds at a carbon in the double bond forming a chlorinated aldehyde or ketone [4]. However, the products are not yet identified, therefore the exact reaction mechanism is still unknown. Preliminary data from NMR indicates that the product of the reaction is stable in the presence of chlorine.

Conclusion:

Low molecular weight aldehyde and ketone molecules that can pass through RO membranes in advanced water treatment react with chlorine and bromine disinfectants forming unintended byproducts. The reaction rate of these various compounds in a chlorine rich environment were determined at six pH-values to better understand what happens to these compounds in the drinking water distribution system. The shorter chained compounds are found to be more reactive. Both reactants and products will be present within a distribution system and any further study into these unintended byproducts should focus on identifying exact structure of the compounds and how they may affect the environment or public health.

References:

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