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"Chlorine Reactions of Ozonation Byproducts: Model Compound Studies"

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Introduction: Ozone in Water Treatment

Ozone use in water treatment is increasing as utilities attempt to meet the requirements of the U. S. Environmental Protection Agency Surface Water Treatment Rule (SWTR) and the forthcoming Disinfectants and Disinfection By-Product (D-DBP) Rule. Benefits of ozone to conventional treatment processes such as filtration, coagulation, flocculation, disinfection and flotation are well known. Ozonation of natural organic matter (NOM), ubiquitous in surface supplies, results in the formation of many mono- and dialdehydes, such as formaldehyde, acetaldehyde, methyl glyoxal and glyoxal which are routinely detected at the μg/L level. Other oxo compounds, such as keto-acids, mono- and dicarboxylic acids, are likely to be ozonation by-products (OBPs) but trace-level quantification presents a significant analytical challenge. Of primary interest in the field of water treatment are: 1) the fate of OBPs through treatment processes, 2) reactions with chlorine and other disinfectants, and 3) the suitability of OBPs as biological substrates or assimilable organic carbon (AOC) in distribution systems. OBPs are likely to react with aqueous chlorine via either oxidation or substitution mechanisms during disinfection. Carbonyl compounds with alpha carbon sites should be more amenable to chlorine substitution. Since chloroorganics are generally considered to present a potential human health risk, their presence in drinking water is a primary concern of regulatory agencies and water treatment professionals. The amount of total organic halide (TOX) formed is therefore a useful surrogate for evaluating potential health risks posed by disinfection byproducts.

Objectives and Scope

The objective of this research is to investigate the kinetics and stoichiometry of chlorine demand and total organic halide (TOX) formation as a function of pH when specific OBPs are dosed with chlorine. The proposed model for OBP-chlorine reactions is

predicated on the second order rate law (1), where C is the substrate (specific OBP) concentration:

$$\frac{dC}{dt} = -k * [Cl_2] * C \qquad (1)$$

This model also applies to the consumption of chlorine over time. With C in excess (C: $[Cl_2] > 10:1$) this can be replaced by a pseudo first order model (2):

$$\frac{d[Cl_2]}{dt} = -k' * [Cl_2] \qquad (2)$$

where k' is the product k*C. Reaction stoichiometry can be determined from chlorine demand experiments where chlorine is in excess of a known substrate concentration, thus yielding the molar chlorine consumption per mole of substrate. This data may then be used to predict mechanisms and byproducts, therefore substantially adding to current knowledge regarding the use of ozone in water treatment. Low molecular weight (e.g., C_1-C_3) compounds are evaluated in this study; this range of compounds is most prominent among identified OBPs.

Results and Discussion

Marked differences in chlorine reactivity are observed between carbonyls bearing alpha carbons and other carbonyls. Experiments with methyl glyoxal, a species with an alpha carbon, and glyoxal illustrate the nature of this effect. Figure 1 shows log chlorine concentration versus time as a function of pH for chlorination of methyl glyoxal under pseudo first order conditions (e.g., large excess of aldehyde). These results indicate that: 1) chlorine versus time data agree well with a pseudo first order model, and 2) the rate of chlorine consumption increases with pH. Figure 2 shows that the pseudo first order rate constant k' (where k' is k*C) is highly pH dependent. The percentage of chlorine consumed in TOX formation for methyl glyoxal is significant, ranging from 22% at pH 6 to 36% at pH 10. While this is significant in terms of potential health risks, it is also likely that the majority of oxidation products are higher oxidized species, possibly including formic and acetic acids. Table 1 shows the predicted half lives for methyl glyoxal obtained using the kinetic model (1) at chlorine residuals of 1 and 4 mg/L. These results suggest that at pH > 7, reactions of methyl glyoxal in distribution systems could 1) produce TOX during a typical detention time and 2) result in a substantial loss of the aldehyde along with some fraction of the chlorine residual.

From work completed at this point, it appears that the presence of an alpha carbon strongly influences chlorine demand reaction rates and pathways as predicted from standard mechanistic theory. Observed rates are much slower for glyoxal and no TOX formation is observed upon chlorination. These results suggest that 1) chlorine substitution is fast relative to oxidation, and 2) compounds bearing alpha carbons are likely to undergo chlorine substitution in distribution systems. Current work is addressing the mechanisms of formation and possible identification of chlorinated by-products. Knowledge of chlorine-OBP reactions could be highly beneficial to water utilities in meeting the goals of the SWTR and D-DBP rules and evaluating their contribution to AOC in distribution systems.

The presentation will summarize the results obtained from model compound studies. Possible mechanisms of formation and byproduct identifications will be introduced.

Table 1. Predicted Half Lives for Methyl Glyoxal in the Presence of Chlorine.

pH	k ($M^{-1}s^{-1}$)	$t_{1/2}$ at $[Cl_2]$ = 1 mg/L	$t_{1/2}$ at $[Cl_2]$ = 4 mg/L
6	0.08	166 hrs	42 hrs
7	0.17	78 hrs	20 hrs
8	0.82	17 hrs	4 hrs
9	1.1	13 hrs	3 hrs
10	3.6	4 hrs	1 hr

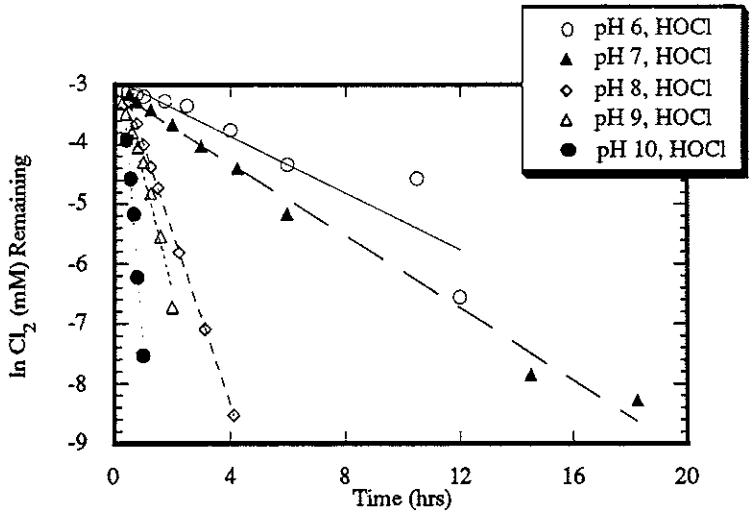

FIG. 1. Chlorine Residual as a Function of Time: Methyl Glyoxal.

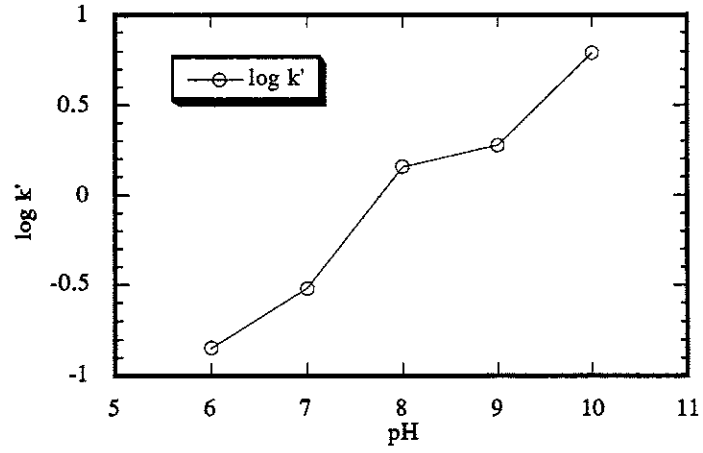

FIG. 2. Pseudo First Order Rate Constants as a Function of pH: Chlorine Demand of Methyl Glyoxal.