REACTIONS OF OZONATION BYPRODUCTS WITH CHLORINE AND CHLORAMINES

Andrew McKnight
Graduate Research Assistant

David A. Reckhow, Ph.D.
Associate Professor

Environmental Engineering Program
Department of Civil Engineering
University of Massachusetts
Amherst MA 01003

INTRODUCTION

Ozone use in water treatment is increasing as water utilities attempt to meet the requirements of the U. S. Environmental Protection Agency Surface Water Treatment Rule and the forthcoming Disinfection and Disinfection By-Product Rule (D-DBP Rule). While finished water quality as defined by classical water quality parameters is often improved by the use of ozone, the presence of ozonation by-products (OBPs) may actually cause a degradation of water quality as measured by some non-classical parameters. Several compounds, such as formaldehyde, acetaldehyde, methyl glyoxal and glyoxal are routinely detected in ozonated waters at the μg/L range[1]. Recently, the presence of three keto-acids in ozonated water have been reported at higher concentrations than previously identified compounds[2]. Other compounds, such as epoxides, mono- and dicarboxylic acids, are likely to result from ozonation but quantification is a significant analytical challenge. The formation of OBPs has not precluded the use of ozone in practice; the benefits to conventional treatment processes such as filtration, coagulation, flocculation, disinfection and flotation are well known[3]. Ozone is being used increasingly as a pretreatment to reduce the formation of potentially harmful chloroorganics (i.e., trihalomethanes, haloacetic acids, etc.) during disinfection. Ozone is a vigorous oxidant and an excellent disinfectant; however, its rapid decomposition in water necessitates application of secondary disinfectants such as chlorine or chloramines to maintain a disinfectant residual in distribution systems. Of primary interest to water treatment professionals are 1) the fate of OBPs through treatment processes, 2) reactions with chlorine based disinfectants, and 3) the suitability of these compounds and their byproducts as assimilable organic carbon (AOC) for biological regrowth in distribution systems.

The objective of this study was to investigate the reactions of specific OBPs with chlorine and chloramines through evaluation of the kinetics and stoichiometry of chlorine demand and total organic halide (TOX) formation as a function of pH. Several OBPs routinely found in practice were selected for study due to their simplicity and minor variations in chemical structure. All of the compounds studied in this work have a carbonyl (C=O) functionality, and thus the types of chemical reactions may be similar. The nature of the chemical substituent (e.g., methyl group, hydrogen, etc.) adjacent or alpha to the carbonyl carbon has a strong bearing on the reactivity of the compound. Simple compounds were chosen from three classes of carbonyl compounds, aldehydes, keto-aldehydes, and keto-acids, in order to study the relationships between structural characteristics (e.g., functional groups and alpha substituents) and reactivity towards secondary disinfectants (kinetics, stoichiometry, chlorinated byproducts). These compounds include C_1-C_4 aldehydes (formaldehyde, acetaldehyde, propanal and butanal), two keto-aldehydes (glyoxal and methyl glyoxal), and three keto-acids (glyoxylic, pyruvic and keto-malonic acids). Three general classifications of alpha substituents can be made; compounds bearing 1) an alpha methyl group, 2) methylene group, or 3) other moieties (hydrogen, hydroxyl, carboxylic acid, etc.). Correlations between these characteristics and

chlorine consumption behavior may help to focus the understanding of OBP significance in distribution systems (i.e., persistence of OBPs, formation of chloroform or other DBPs, etc.).

THEORY

Chlorine (Cl_2) is consumed by reactions with natural organic matter, micropollutants, and byproducts of chemical processes[4]. The reaction of free (FC) or combined (CC) chlorine with specific compounds (Sub) can therefore be written as;

$$nCl_2 + Sub \text{ ------> } Products \qquad (1)$$

where n is the stoichiometric coefficient in units of moles of chlorine consumed per mole of substrate reacted. The proposed kinetic relationship for loss of each reactant is predicated on the second order rate law (2 and 3);

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

$$\frac{d[Sub]}{dt} = -\left(\frac{k}{n}\right) * [Cl_2] * [Sub] \qquad (3)$$

where [Sub] is the substrate (specific OBP) molar concentration, $[Cl_2]$ is the molar concentration of free or combined chlorine, n is the stoichiometric coefficient, and k is the reaction rate constant.

The determination of k and n can be made from simple chlorine demand experiments depending upon the molar ratio of chlorine to substrate at the beginning of the reaction. Introduction of a large excess of substrate relative to total chlorine species allows the use of a pseudo first-order analysis (4) for loss of residual chlorine;

$$\frac{d[Cl_2]}{dt} = -k' * [Cl_2] \qquad \text{where } k' = k * [Sub] \qquad (4)$$

A plot of log $[Cl_2]$ versus time has a slope equal to the pseudo first-order rate constant k'. A second experimental approach is to introduce the compounds in the same ratio as the stoichiometric coefficient. This allows the assumption that the concentrations of each reactant should be in the same ratio throughout the experiment, and thus the concentration of substrate can be assumed to be equal to the chlorine concentration (5);

$$\frac{d[Cl_2]}{dt} = -k * [Cl_2]^2 \qquad (5)$$

A plot of reciprocal chlorine concentration versus time has a slope equal to the second-order rate constant k.

The measurement of the TOX formed in the reaction can be used to determine the distribution between chlorine consumed in substitution and other pathways such as oxidation. When specific byproducts such as chloroform and trichloroacetic acid (TCAA) are measured, a mass balance on TOX species can be performed. Additionally, the fraction of consumed chlorine in the TOX can be used to calculate a predicted stoichiometric coefficient.

EXPERIMENTAL DESIGN

The experiments were designed to use measurement of residual chlorine versus time and the ultimate TOX formation to obtain the desired stoichiometric and kinetic

information. All glassware used for these procedures was rendered chlorine demand free by immersion in 10 to 200 mg/L hypochlorite solution for >1 hour. Buffered waters (10-25 mM phosphate) were prepared for a range of pH from 6 to 12. These solutions were then chlorinated at a chlorine dose of 4 to 20 mg/L. Solutions were stirred rapidly for five minutes and allowed to stand in darkness 30 to 60 minutes prior to addition of the specific OBP. Reactions were conducted in darkness at 20°C (unless otherwise specified) and allowed to react for 72 hours or until the chlorine residual was depleted. Samples were periodically taken for residual chlorine analysis. At the end of some procedures, samples were taken for TOX[5], aldehyde[6], chloroform[7], haloacid[8], and keto-acid[9] analyses.

RESULTS AND DISCUSSION

Chlorination of Acetaldehyde

The free chlorination of acetaldehyde was selected as a model system due to its simplicity and the relatively small number of possible products. These results could then be used to help make interpretations of the reactions of more complex molecules. Acetaldehyde was found to react substantially with free chlorine at a variety of pH (Figure 1). Two types of reactions would be expected from chemical principles. One pathway would be the oxidation of acetaldehyde to acetic acid, which would follow 1:1 stoichiometry. Since acetaldehyde has a methyl group alpha to the carbonyl carbon, a second possibility is a chlorine substitution pathway. If this reaction proceeds similarly to the chlorination of acetone, the substitution of the first chlorine atom would be rate limiting followed by the rapid addition of the second and third chlorine atoms[10]. The formation of trichloroacetaldehyde or chloral hydrate would thus consume three moles of chlorine per mole of acetaldehyde consumed. This compound may in turn undergo base-catalyzed hydrolysis to produce chloroform and formic acid. These reaction pathways and the intermediates are shown in Figure 2.

The chlorination of chloroacetaldehyde was studied to determine the distribution between oxidation (formation of monochloroacetic acid) and substitution (formation of chloral hydrate). This reaction resulted in essentially 100% yield of chloral hydrate (Table 1). This suggests that if acetaldehyde does undergo an initial chlorine substitution reaction, then the reaction should rapidly proceed to form the trichlorinated product, chloral hydrate. The stoichiometric coefficient for the chlorination of acetaldehyde was found to be between 2.6 and 3.0 at or above neutral pH, suggesting that chloral hydrate was the major byproduct (Table 2). The large fraction of identified TOX at pH 7 and the increased predominance of chloroform in the TOX with increasing pH indicates that chloral hydrate does undergo base-catalyzed hydrolysis to chloroform (Table 3). The rate of this reaction was investigated by both the pseudo first-order and second order analyses (Figures 3 and 4). The rate constants were found to increase with pH over the range studied (7 to 10), suggesting a dependence on hydroxide ion (Figure 5). These results were used to propose a modified rate law for the disappearance of acetaldehyde;

$$\frac{d[Ac]}{dt} = -\left(\frac{k^*}{n}\right) * [Cl_2] * [Ac] * [OH^-]^A \qquad (6)$$

where k* and A are the intercept and slope obtained from linear regression of log k versus pH. The values of n, k* and A are presented for acetaldehyde and other substrates in Table 4.

Chlorination of Other Compounds Bearing an Alpha Methyl Group

Methyl glyoxal and pyruvic acid were chlorinated in order to study the effects of the functional group on the stoichiometry, byproducts, and reaction kinetics. The chlorination of pyruvic acid was rapid and thus the rate constant could not be quantified using the techniques of this research. Similar trends to the chlorination of acetaldehyde were

observed with respect to byproduct formation. Unidentified TOX was large at pH 7, while at pH 12 the TOX consisted mostly of chloroform (Table 5). The stoichiometry of this reaction varied more with pH than was observed for acetaldehyde (Table 2). The results at pH 7 and 9 suggest that another reaction mechanism which consumed zero or one moles of free chlorine per mole of pyruvic acid consumed may be significant. The value of 2.5 observed at pH 12 is in good agreement with previously reported values[11].

The chlorination of methyl glyoxal also resulted in significant chlorine substitution; however, the percentage of chloroform in the TOX decreased from pH 9 to 12 (Table 5). The unidentified by-product(s) apparently does not undergo base-catalyzed hydrolysis in the manner of the products of chlorination of acetaldehyde and pyruvic acid. The reaction rates for chlorination of methyl glyoxal increased with pH and were one to two orders of magnitude higher than for the chlorination of acetaldehyde.

Chlorination of Propanal and Butanal

The higher aldehydes reacted more slowly and with less TOX formation than acetaldehyde. The observed stoichiometries for these reactions were close to one (Table 2). The increased length of the alpha substituent apparently decreases the reactivity of the alpha hydrogens, and thus the substitution pathway becomes less favorable. The rates of chlorination of these compounds appear to follow a similar rate law as acetaldehyde (Table 4), but react slowly enough so that they would be expected to persist in distribution systems under the conditions of drinking water treatment.

Chlorination of Other OBPs

The remaining keto-acids, glyoxylic and keto-malonic acids, reacted rapidly and thus the rate constants could not be obtained by the techniques of this research. Unlike the chlorination of pyruvic acid, only minor amounts of chlorinated byproducts were observed. The stoichiometries of these reactions were less than or equal to one (Table 2), which suggests reaction pathways which involve free chlorine-catalysis (thus consuming zero M/M) or oxidation (1 M/M). Although the byproducts could not be identified, these compounds could be sources of AOC or pose human health risks. The rates of reaction are much faster than the aldehydes and keto-aldehydes. The formation of byproducts would appear to be significant under the conditions studied (pH 7 and 9, 4 mg/L free chlorine dose).

Formaldehyde appeared to be generally unreactive towards free chlorine. The most logical pathway for consumption of free chlorine would be oxidation to formic acid. This research suggests that this reaction is slow at or near neutral pH. It is therefore likely that formaldehyde would persist in distribution systems.

Glyoxal reacted with free chlorine at a slower rate and with minor TOX formation relative to methyl glyoxal. The byproducts of this reaction might be expected to include glyoxylic acid due to oxidation; however, this compound was not observed in any of the chlorination experiments. The loss of glyoxal in the presence of free chlorine occurs more rapidly than the C_2-C_4 aldehydes. This reaction appears to include a significant zero M/M pathway, since the observed stoichiometry varied from approximately 0.2 to 0.4 (Table 2). This suggests that this compound is probably not a significant precursor of oxalic acid, which has recently been reported to be the major organic acid resulting from ozonation of natural organic matter[12].

Kinetic Simulation of Substrate Decomposition

The rate laws and kinetic constants at 20°C obtained in this research were used to generate decomposition curves. The fraction of each compound remaining at any time during the reaction is a function of the stoichiometric coefficient, the rate constant, and the chlorine dose. Since the rate of chlorination of several of these compounds exhibited a pH

dependence, this will also be a factor. Figure 6 is a conservative estimate of the decomposition of these compounds without any additional inputs. This is an unrealistic assumption for real systems, since these compounds can also be products of reactions of disinfectants with residual natural organic matter. These curves do provide a useful measure of the relative reactivity of the compounds towards free chlorine. The keto-acids could not be simulated due to the lack of rate constant data, but would decompose rapidly relative to the other two compound classes. The effects of temperature have not been quantified.

Chloramination of Model OBPs

Chloramines are generally assumed to be less reactive than free chlorine under conditions of drinking water treatment, and are used in practice as an alternative disinfectant to reduce chlorinated byproduct formation. Little or no TOX was produced upon chloramination of all the model compounds studied in this work. The reaction rates at pH 7 were comparable to free chlorination for the C_1-C_4 aldehydes, which was a significant and surprising finding. The reactions of the two keto-aldehydes was approximately a half an order of magnitude less than for free chlorination at neutral pH. The reaction rates for both compound classes were only weakly dependent upon pH in the range studied. As with free chlorination, the keto-acids reacted too rapidly with chloramines at pH 7 and 9 to be measured using the techniques of this research. The stoichiometries for the reactions studied were all less than or equal to one. Most of the plausible mechanisms for chloramine reactions (e.g., formation of imines, nitriles, etc.) follow 1:1 stoichiometry, which correlates well with the results of this research. The formation of nitriles (such as acetonitrile from chloramination of acetaldehyde) may be a significant mechanism[13]. The results obtained in this work do not contradict this finding.

CONCLUSIONS

These results suggest that acetaldehyde, methyl glyoxal and pyruvic acid could be important chloroform precursors in chlorinated systems under certain conditions. The higher aldehydes studied react slowly with free chlorine and produce minor amounts of TOX. The keto-acids reacted rapidly with both free and combined chlorine. The reaction rates for chlorination and chloramination of the three compound classes studied here follow (from fastest to slowest);

Keto-acids >> Keto-aldehydes > Aldehydes

Chloramination of the model OBPs studied resulted in little measurable TOX formation. The rates for chlorination and chloramination at pH 7 were comparable for all three compound classes, but the rates of chlorination increased dramatically with pH. Chloramination rates appear to be only weakly dependent upon pH.

SIGNIFICANCE TO ENGINEERING PRACTICE

These results suggest that aldehydes may persist in distribution systems at low (< 2 mg/L) chlorine doses and neutral pH, but can undergo significant decomposition at higher chlorine doses and pH. The keto-acids are likely to react rapidly at low chlorine doses and pH 7 or greater. The reactions of the OBPs studied in this work may be dwarfed by the sum of overall OBP reactions. These compounds may also be generated in distribution systems by the reactions of disinfectants with natural organic matter. These compounds and their byproducts may be sources of AOC, and thus their presence in a distribution system may be of concern.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the expert help of Dr. Yuefeng Xie for his keto-acid analyses and assistance with chemical interpretations. The contributions of Xuejun Zhou (aldehyde analyses), Qing-Wen Zhu (haloacid analyses), and Andrew MacNeill (chloroform analyses) are also gratefully noted. This work was carried out under funding provided by Dr. Reckhow's National Science Foundation Young Presidential Investigator award.

REFERENCES

1. Glaze, W.H., et al., "Trends in Aldehyde Formation and Removal Through Plants Using Ozonation and Biological Active Filters", Proceedings of the 1991 American Water Works Association Annual Conference, Philadelphia PA, June 20-24.

2. Xie, Y., and Reckhow, D.A., "A New Class of Ozonation By-products: The Keto-acids", to be presented at the 1992 AWWA Annual Conference, Vancouver BC, June 18-22, 1992.

3. Langlais, B., Reckhow, D.A., and Brink, D., editors, Ozone in Water Treatment: Application and Engineering, AWWA Research Foundation and Compagnie Generale des Eaux, Lewis Publishers, Chelsea, MI 1991.

4. Fleishacker, S.J., and Randtke, S.J., "Formation of Organic Chlorine in Public Water Supplies", *Jour. Am. Water Works Assoc.*, 75:3:132, 1983.

5. APHA, AWWA and WPCF, Standard Methods for the Examination of Water and Wastewater, 17th Ed., APHA, Washington DC, 1989.

6. Sclimenti, M.J., et al., "Ozone Disinfection By-Products: Optimization of the PFBHA Method for the Analysis of Aldehydes", Proceedings of 1990 AWWA WQTC, San Diego CA.

7. Koch, et al., "Analysis of Halogenated Disinfection By-Products by Capillary Chromatography", Proceedings of 1988 AWWA WQTC.

8. APHA, AWWA and WPCF, Standard Methods for the Examination of Water and Wastewater, 18th Ed., APHA, Washington DC, 1992.

9. Xie, Y., and Reckhow, D.A., "Identification and Quantification of Ozonation Byproducts: Keto-acids in Drinking Water", Proceedings of Ozonation for Drinking Water Conference, International Ozone Association, Pasadena CA, 1992.

10. Bartlett, P.D., and Vincent, J.R., "The Rate of the Alkaline Chlorination of Ketones", *J. Am. Chem. Soc.*, 56:967, 1935.

11. Reckhow, D.A., and Singer, P.C., "Mechanisms of Organic Halide Formation During Fulvic Acid Chlorination and Implications with Respect to Pre-Ozonation", in Water Chlorination: Environmental Impact and Health Effects, Vol. 5, Lewis Publishers, Chelsea MI, 1985.

12. Edwards, M., and Benjamin, M.M., "Transformation of NOM by Ozone and its Effect on Iron and Aluminum Solubility", *Jour. Am. Water Works Assoc.*, 84:6:56-66, 1992.

13. Le Cloirec, C., and Martin, G., "Evolution of Amino Acids in Water Treatment Plants and the Effect of Chlorination on Amino Acids", in Water Chlorination: Environmental Impact and Health Effects, Vol. 5, Lewis Publishers, Chelsea MI, 1985.

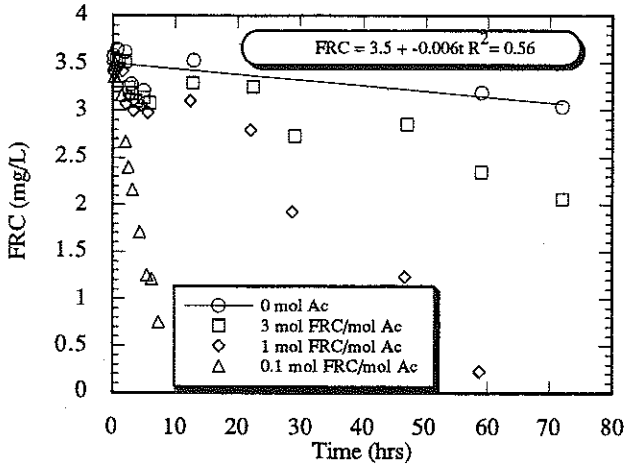

FIGURE 1. Free Chlorine Concentration Versus Time for Chlorination of Acetaldehyde at pH 9 and Three Initial FC/Sub Ratios (20°C).

$CH_3CHO \Rightarrow CH_2ClCHO \Rightarrow CHCl_2CHO \Rightarrow CCl_3CHO \Rightarrow CHCl_3 + HCOOH$

Acetaldehyde Chloroacetaldehyde DCA TCA Chloroform + Formic Acid

$\Downarrow$ $\Downarrow$ $\Downarrow$ $\Downarrow$

CH_3COOH $CH_2Cl\text{-}COOH$ $CHCl_2\text{-}COOH$ $CCl_3\text{-}COOH$

Acetic Acid MCAA DCAA TCAA

FIGURE 2. Possible Reaction Pathways for Chlorination of Acetaldehyde

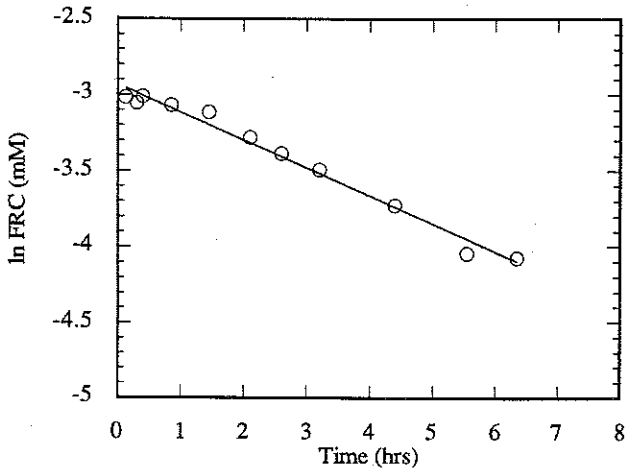

FIGURE 3. Pseudo First-Order Kinetic Analysis of Data from Free Chlorination of Acetaldehyde at pH 9 and 20°C.

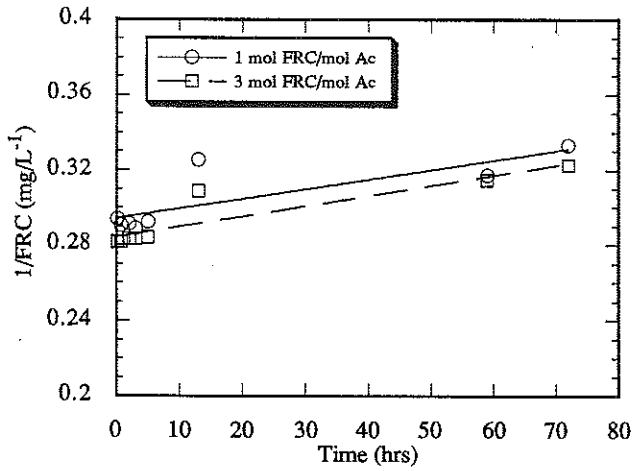

FIGURE 4. Second-Order Kinetic Analysis on Data from Chlorination of Acetaldehyde at pH 9 and Two FC/Sub Ratios (20°C).

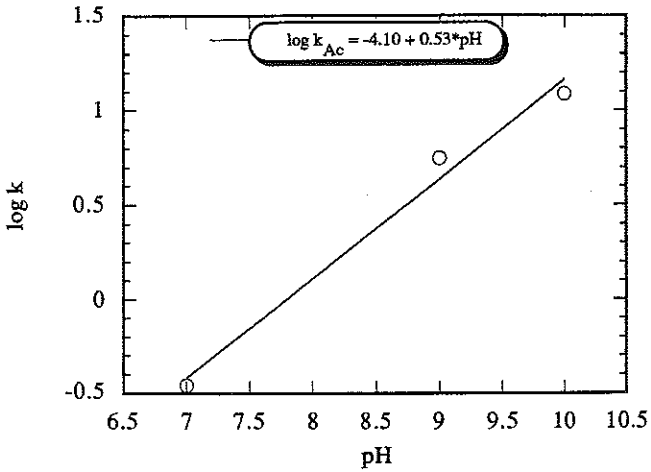

FIGURE 5. Variation in Rate Constant with pH for Free Chlorination of Acetaldehyde (20°C).

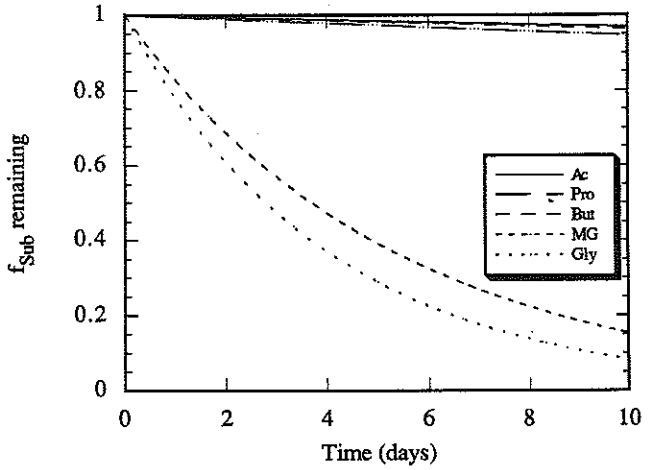

FIGURE 6. Kinetic Simulation of Substrate Decomposition at FC Dose of 1 mg/L and pH 7 (20°C).

TABLE 1. Byproducts of Free Chlorination of Chloroacetaldehyde*.

pH	FC Dose (mg/L)	Cl-Ac_0 (mg/L)	% of FC in MCAA	% of FC in Chloral Hydrate
9	4	2	<1%	99%

* Reaction time 72 hours, ionic strength 25 mM, FC dose 4 mg/L, FC/Sub 2.5 M/M.
FC Free Chlorine.
Cl-Ac_0 Initial chloroacetaldehyde concentration.
MCAA Monochloroacetic acid.

TABLE 2. Estimated Stoichiometric Coefficients for Consumption of Free Chlorine.

Alpha Substituent	Substrate	n_p		
		pH 7	pH 9	pH 12
Methyl	Acetaldehyde	2.6	3.0*	2.6
	Methyl Glyoxal	1.4	1.6	2.0
	Pyruvic Acid	1.3	1.3	2.5
Methylene	Propanal	§	1.2	§
	Butanal	§	1.2	§
Hydrogen	Formaldehyde	1.0**	1.0**	1.0**
CHO	Glyoxal	</= 1.0**	</= 1.0**	</= 1.0**
COOH	Glyoxylic Acid	</= 1.0**	</= 1.0**	</= 1.0**
COOH	Keto-malonic Acid	</= 1.0**	</= 1.0**	</= 1.0**

§ Not analyzed.
* Assumed based on 100% incorporation.
** Assuming maximum consumption of 1 M/M.

TABLE 3. Mass Balance on 72 Hour TOX Formation During Free Chlorination of Acetaldehyde*.

pH	% of TOX in Specific DBPs				TOX (μM)	% Cl Inc.
	$CHCl_3$	DCAA	TCAA	Total		
7	< 0.1	1	0.3	1.4	7.6	79
9	15	0.2	0.3	15.5	22.7	124
12	137	0.1	0.1	137	19.7	78

* Ionic strength 25 mM, FC dose 4 mg/L, FC/Sub 2.5 M/M.

TABLE 4. Parameters Used for Estimation of Loss of Substrates

Substrate	log k* ($M^{-1}min^{-1}$)	A	n $(\frac{\Delta FC}{\Delta Sub})$	pH Range
Acetaldehyde	-4.1	0.5	2.6	7-10
Propanal	-2.9	0.3	1.1	7-9
Butanal	-3.6	0.4	1.2	7-9
Methyl Glyoxal	-1.7	0.4	1.6	6-10

TABLE 5. Percentage of Chloroform and Unidentified Compounds in TOX.

	pH 7		pH 9		pH 12	
	$CHCl_3$	Unident. TOX	$CHCl_3$	Unident. TOX	$CHCl_3$	Unident. TOX
Acetaldehyde	< 0.1	99	15	85	137	< 0.1
Methyl Glyoxal	2.4	75	99	< 0.1	34	63
Pyruvic Acid	7.7	86	42	70	94	0.7