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THE EFFECTS OF OZONATION PATHWAYS ON THE FORMATION OF KETOACIDS AND ASSIMILABLE ORGANIC CARBON (AOC) IN DRINKING WATER

By

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ABSTRACT

THE EFFECTS OF OZONATION PATHWAYS ON THE FORMATION OF KETOACIDS AND ASSIMILABLE ORGANIC CARBON (AOC) IN DRINKING WATER

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In the United States most drinking water plants use chlorine for disinfection (98%). However, concern relating to the formation of disinfection byproducts has resulted in 332 (OzoneNews, 2000) facilities having replaced chlorination with ozonation. Although ozonation is effective at removing pathogens and organic pollutants, ozonation can result in an increase in the amount of biodegradable organic matter in the treated water, which can enhance the regrowth of bacteria in the distribution system. Moreover, the reaction of ozonation by-products with chlorine during post-disinfection leads to the formation of potentially toxic disinfection by-products (DBPs). The reaction of ozone with NOM (Natural Organic Matter) can occur by two different pathways: reaction of molecular ozone and the reaction of OH radicals, which are produced from the decomposition of molecular ozone. The molecular ozone reaction with NOM would preferentially form AOC and decrease precursors of DBPs rather than that of OH radical reaction.As such, the pathways for the reaction of ozone with NOM were controlled by the factors that affect the pathways of ozone decomposition to control the formation of AOC and DBPs.

The ratios of [OH·]/[O_3] under the various ozonation conditions were determined to investigate the pathways forming AOC and DBPs. The effect of operational parameters such as temperature, pH, HRT (Hydraulic Retention Time) and initial ozone concentration on the formation of AOC (Assimilable Organic Carbon), ketoacids, which is a portion of AOC as well as ozonation by-product, during ozonation and DBPs during post-chlorination were investigated. In addition, inorganic additives such as hydrogen peroxide, bicarbonate ion and phosphate ion, which affect the pathways of ozone decomposition, were used to control the formation of AOC, ketoacids and DBPs during ozonation. The conditions where the molecular ozone reaction predominated resulted in an increase in the formation of AOC and resulted in the formation of DBPs precursors.

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ABBREVIATION

NOM	Natural Organic Matter
AOC	Assimilable Organic Carbon
DBPs	Disinfection by-products
HRT	Hydraulic Retention Time
EPA	Environmental Protection Agency
ICR	Information Collection Rule
SDWA	Safety Drinking Water Act
THMS	Trihalomethanes
THMFP	Trihalomethane Formation Potential
HAAs	Haloacetic Acids
MCL	Maximum Contaminant Levels
BDOC	Biodegradable Organic Carbon
TOC	Total Organic Carbon
GAC	Granular Activated Carbon
UV254	UV 254nm absorbance
FBR	Fluidized Bed Reactor
FBT	Fluidized Bed Treatment
AWWA	American Water Works Association

1. OBJECTIVE

The major objective of this project is to investigate the effect of the reactions of molecular ozone and the OH radical on the biodegradability of NOM (Natural Organic Matter) upon ozonation.

The particular objectives are,

1) To determine the effect of molecular and radical reaction pathways on the formation of AOC (Assimilable Organic Carbon).
2) To investigate the effect of operational parameters (e.g. temperature, pH, HRT (Hydraulic Retention Time), dissolved ozone concentration) on the reaction pathways of ozone, in terms of the formation of AOC.
3) To evaluate the use of inorganic additives to control the pathways of the reaction of ozone with NOM and the formation of AOC.
4) To evaluate the formation of DBPs (Disinfection By-products) in waters in which the formation of AOC (and subsequent removal during biological treatment is optimized).

2. SIGNIFICANCE

In United States most drinking water systems (98%) use chlorination for disinfection (Irvine Ranch Water District, 1999). While the use of chlorine has successfully prevented outbreaks of many water-borne diseases, chlorine does have severe drawbacks. The chlorination of natural organic matter results in the formation of trihalomethanes (THMs) and other disinfection by-products (DBPs). The presence of these DBPs in treated water causes much concern because of their long-term health effects. For example, chloroform, the most prevalent THM, is a human carcinogen (Jolley et al., 1985). There is also concern that DBPs result in a high incidence of spontaneous abortions (Waller et al., 1998).

Concerns related to the health risks associated with DBPs have brought about stringent regulation for those DBPs. In 1994, the EPA (Environmental Protection Agency) proposed a Stage 1 D/DBP (Disinfectants/Disinfection by-products) Rule and Stage 2 D/DBP Rule in accordance with a specified schedule. According to the Information Collection Rule (ICR), modification can be made when new available information regarding toxicology is present. With the promulgation of the Stage 1 D/DBP rule, the MCL (Maximum Contaminant Levels) for total THMs were lowered from 100 μg/L to 80 μl/L and that for haloacetic acids (HAA) was set the MCL at 60 μg/L. The Stage 2 D/DBP Rule must be promulgated by May 2002 based on the U.S. SDWA (Safety Drinking Water Act). Although MCLs designated in the Stage 2 D/DBP Rule are tentative (40 μg/L of total THMs, 30 μg/L of HAA), it is likely that the MCL will continue to be reduced in accordance with the Information Collection Rule (ICR).

Therefore, the water treatment plants face technical problems to meet these regulations. Clearly new technologies must be developed to better and more cost-effectively solve these problems.

As a result of the concern over DBPs and in order to comply with increasingly the more stringent regulations concerning DBPs, many plants in the United States have ceased using prechlorination and are now using ozone. Although the use of ozone results in low concentrations of THMs in the treated water (Lykins et al., 1994; Speitel et al., 1993; Shukairy and Summers, 1992), ozonation can results in other problems, such as an increase in the formation of easily Biodegradable Organic Carbon (BDOC) which can enhance the regrowth of bacteria in the distribution system. Moreover, ozonation results in the formation of haloacetic acids and haloketo acids upon the post chlorination of ozonated water (Kuivinen and Johnsson, 1999; Najm et al., 1994; Speitel et al., 1993).

One method to control regrowth problems and to avoid the formation of precursors of chlorinated oxygenated species (such as chloroacetic acid) is to use biological treatment after ozonation and before chlorination. The advantage of using biological treatment is that any BDOC produced can be consumed by the microorganisms prior to chlorination and distribution. The goal of this biological treatment is then to convert all BDOC and AOC to CO_2, H_2O and minerals.

Although BDOC formation increases with increasing ozone dose (Paode et al., 1997; Volk et al., 1993), ozonation is rather expensive compared to the other conventional processes such as coagulation, sand filtration, and biological process (Yavich, 1998; Qasim et al., 1992). As such, reducing the applied ozone dosage as much as possible provides cost benefits.

For the last decade, There has been a research on the development of a combined ozonation/biological fluidized bed treatment process for the control of DBP precursors in drinking water. For example, the removal of THM precursors by combined ozonation and fluidized bed treatment (FBT), with no pretreatment, was comparable to that achieved at the Ann Arbor Water Treatment Plant (Ann Arbor, MI), which includes lime softening, coagulation, and GAC adsorption (Masten, 2000; Ann Arbor Sanitary Survey, 1999; Yavich et al., 1997). Moreover, the ozonation/FBT pilot system operated using source water (Huron River water) that had a higher organic loading than the one entering the Ann Arbor Plant, which consist of 80% Huron River water and 20% ground water. The cost analysis indicated that the ozonation/FBT process was more cost effective than the conventional processes similar to those employed at the Ann Arbor Water Treatment Plant (Masten, 2000). Because this novel system has a small footprint and generates virtually no sludge, the ozonation/FBT system can be very attractive for small water utilities and larger facilities, where space for retrofitting or expansion is limited.

In order to operate ozonation/biological process effectively in terms of BDOC and AOC minimization, ozonation must produce as much BDOC/AOC as possible so that the BDOC/AOC produced from ozonation can be completely removed in the subsequent biological process. Thus, if the ozone reaction pathways with NOM are controlled for the formation of BDOC, the applied ozone dosage can be reduced and a biologically stable water can still be produced. However, unlike in European countries, in the U.S. the combination of ozonation and biological treatment is unpopular due to fears associated with microorganisms present in the biological system. Nevertheless, in order to resolve the BDOC problem, some U.S. water treatment plants have modified their conventional process by trying to enhance biological growth in the sand or GAC (Granular Activated Carbon) filtration systems. Unfortunately, sand filtration does not effectively remove BDOC because of the frequently required back washing of the filters using chlorinated water. This problem is exacerbated by presence of microorganisms in the filter since they result in more rapidly increasing head loss, resulting in more frequent backwashing. As a result, it is difficult to maintain sufficient quantities of microorganisms to obtain efficient degradation of BDOC in the filters. Thus, for the water treatment plants that can not accomplish their biological treatment effectively after ozonation, they need to minimize the formation of BDOC during ozonation. The way to minimize BDOC formation is to control the ozonation process toward minimizing the formation of BDOC by ozone. The control of ozone decomposition pathways in water treatment, whether biological processes are used or not, can not only prevent microbial regrowth in the distribution system which eventually deteriorate the water quality but also save costs.

3. BACKGROUND

3.1. Chlorination

A. Usual practices in U.S.

Disinfection is the most important step in the drinking water treatment process to protect human from pathogens. For the past eight decades in United States, chlorine, well established as a disinfectant, has successfully reduced the number of incidences of water-borne diseases. For this reason, chlorination in United States drinking water has been used widely (98 %).

Chlorine can be dosed at one or both of two different steps during the drinking water treatment processes. Prechlorination is applied for the removal, inactivation or both of pathogenic microorganisms from water source. Postchlorine is used to maintain residual chlorine to prevent microbial regrowth in the distribution system. According to the Stage 1 D/DBP rule, the MRDL (Maximum Disinfection Residual Level) of chlorine is 4 mg/L. However, a minimum residual chlorine must also be maintained to hinder the growth of microorganisms.

In order to maintain required residual chlorine concentrations as well as disinfect pathogens during the water treatment process, chlorine dosages are controlled in the prechlorination and postchlorination steps. Chlorine decomposes or is consumed after prechlorination. Chlorine is also consumed through other unit processes such as sand filtration and GAC (Granular Activated Carbon). The chlorine dosage at post-chlorination is determined based upon the dose necessary to maintain the concentration of residual chlorine in the distribution system as required by the Safe Drinking Water Act. According to the questionnaire developed by the AWWA (American Water Works Association) Disinfection Committee, 96 % of 350 water utilities in U.S. dose the chlorine with 15 mg/L as the maximum (White, 1999). However, such high chlorine dosages have considerable side effects in terms of the water quality pertaining to DBPs. Even at much lower chlorine dosages the effects can be significant.

B. NOM

Natural organic matter (NOM) is a complex matrix of organic matter present in natural water. Humic substances, which comprise 40-60% of the dissolved NOM having a high molecular weight, and polyelectrolytic macromolecules, can be divided operationally into hydrophilic and hydrophobic substances (Manahan, 1991). Hydrophobic substances, called a humic fraction, consist of humic acids and fulvic acids. Hydrophilic substances, called a non-humic fraction, consist of hydrophilic acids, proteins, amino acids, and carbohydrates.

Humic substances are biologically recalcitrant materials formed during the decomposition of vegetation occurring as deposits in soil, marsh sediments, peat, coal, lignite, or in almost any location where large quantities of vegetation have decayed (Manahan, 1993). Humic acids usually have a molecular weight of 2000-5000 daltons or greater and aquatic fulvic acid usually has a molecular weight of less than 2000 daltons (Thurman, 1985). The phenolic content of humic acid is greater than that of fulvic acid, and there are more color centers on the humic acid molecule (Collins et al., 1986).

Non-humic substances are defined as compounds belonging to known classes of biochemistry, such as amino acids, carbohydrates, fats, waxes, resins, organic acids. (Stevenson, 1994). Non-humic substances have greater portions of biodegradable organic carbon (BDOC) than humic substances (Yavich, 1998, Paode, 1994).

The major problem in water treatment caused by chlorination is that humic substances can react during chlorination to produce trihalomethanes (THMs) and other undesirable halogenated organics such as haloacetic acids, haloacetronitriles, haloalcohols, and haloketones (e.g., see Richardson et al., 1999; Ichihashi et al., 1999; Stevenson, 1994; Singer, 1994; Boyce and Hornlg 1983; Christman et al., 1983).

Chloroform, dichlorobromomethane, dibromochloromethane, and bromoform are well established as the predominant THMs formed during chlorination (McGuire and Meadow, 1988). Some factors that affect the formation of THMs are the nature of humic substances, chlorine dose, chlorine incubation time, bromide ion concentration, temperature, and pH (Trussell and Umphres, 1978).

The other DBPs that have been reported to form upon chlorination of drinking waters are haloacetic acids (HAAs), carbon tetrachloride, and dichloromethane (Kuivinen and Johnson, 1999; Najm et al. 1994; Speitel et al. 1993). HAAs (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid) are often formed when chlorination follows ozonation of waters containing NOM (Reckhow and Singer, 1990; Uden and Miller, 1983).

3.2. Ozonation

In the United States the first ozone plant used for the disinfection was located at Philadelphia (PA) and installed in 1900-1905 (Rice, 1999). By 1979, a few water treatment plants had installed primary ozonation for taste and odor control as well as for color removal. Since the SWDA amendment of 1986, ozonation of drinking waters has become more popular in the U.S. As of 1997, more than 200 ozone plants are being operated for drinking water treatment in United States.

However, ozonation also produces by-products in the presence of NOM causing biological instability. Therefore, postchlorination is used to suppress biological regrowth. However, this results in additional production of DBPs as well as suppression of biological activity. As a result, the stringent D/DBP rule can be different to meet.

Unlike those in the United States, European water supplies commonly apply biological processes in the drinking water process. As an example, Zürich water supply in Switzerland and Mühleim process in Germany use slow filtration and GAC as a means of biological stabilization after ozonation. The use of biological process results not only in biological stabilization but also reducing the chlorine requirement, thereby, minimizing production of chlorination DBPs. Based on these successes, in the U.S. during the last decade biological water treatment has risen as a candidate process to meet both DBP rule and biological instability. Unlike in Europe, in the U.S. rapid sand filters are used widely and have been retrofitted biological degradation. However, rapid sand filtration often fails to exert biological treatability due to frequent clogging and to backwashing with chlorinated water.

3.3. Ozone by-products

While ozonation can replace prechlorination and reduce postchlorination disinfectant dosages, ozone still produces by-products upon reaction with NOM. Richardson et al. (1999) and Gracia et al. (1996) identified 110 different organic compounds, mainly carboxylic acids, aromatics, hydrocarbons, aldehydes, ketones, and furan-carboxylic acids, which formed from the reaction of ozone with humic substances. The by-products of the reaction of ozonation with fulvic acid were also identified by Benoit et al. (1993). The aliphatic compounds rich in oxygen were found at high ozone dosages whereas benzene polycarboxylic acids and polyhydroxy benzene polycarboxylic acids were identified in low ozone concentration.

Glaze et al. (1989) have developed a method to measure carbonyl compounds including aldehydes in drinking water. The most predominant aldehyde formed upon the ozonation of drinking water was formaldehyde (Schmidt et al., 1999; Carlson and Amy, 1998; Miltner et al., 1992; and Zhou et al., 1992). The formation of aldehydes is affected by alkalinity, ozone dosage, and DOC (Paode et al., 1997). Aldehydes are proportionally produced with DOC concentration and ozone dosage (Siddiqui et al., 1997). The reaction mechanism for aldehyde formation during ozonation was first proposed by Glaze et al. (1989). Molecular ozone attacks unsaturated carbon-carbon bonds forming epoxide intermediates, which subsequently decompose to form aldehydes. Waters having a high alkalinity (high bicarbonate concentration) yield low concentrations of aldehydes due to OH radical consumption by bicarbonate and carbonate (Paode et al., 1997). The scavenging of OH radicals results in a greater fraction of aldehydes. This may be explained that the ozone molecule reacts with NOM since the presence carbonate/bicarbonate favors reactions with molecular ozone. Schecheter and Singer (1995) also observed that ozonation at higher pH values produces lower concentration of aldehydes, most likely due to greater scavenging of OH radicals.

Three ketoacids, glyoxylic acid, pyruvic acid and ketomalonic acids also were identified in the ozonated drinking water as ozonation by-products. The concentrations of those ketoacids were observed to be much higher than that of aldehydes (Griffini et al., 1999; Carlson and Amy, 1998; Xie and Reckhow, 1992). The concentrations of the ketoacids increased with increasing ozone dose (Griffini et al., 1999; Xie and Reckhow, 1992). The ketoacids are also easily biodegradable organic compounds. The formation of aldehydes and ketoacids has been correlated with the formation of BDOC (Griffini et al., 1999). This result suggests that the aldehydes and ketoacids would be appropriate indicators of biologically stability.

A. BDOC formation

Ozone oxidizes NOM to more polar and biodegradable compounds (De Laat et al., 1991; Rice,1985). Volk et al. (1997) found that ozonation of NOM resulted in an average composition of BDOC of 75 % humic substance, 13 % carbohydrate, and 2 % amino acids. Cipparone et al. (1997) showed that BDOC formation was maximized at an ozone dose of 1 mg O_3/mg TOC. This result is consistent with other research results (Siddiqui et al., 1997; Volk et al., 1993). Although the BDOC formation was increased at higher ozone concentration (>1 mg), the effect of ozone concentration is less pronounced (Paode et al., 1997; Volk et al., 1993). BDOC formation is more affected by the ozone dose than contact time. Most BDOC formation occurred in the first two minutes of ozonation (Volk et al., 1993). Therefore, a short contact time associated with a high ozone dose is more effective at converting NOM to BDOC than is treatment at a long contact time with low ozone dose. BDOC formation also was maximized where the UV absorbance achieved maximum removal efficiency of ozonated water. Based on these studies involving the formation of ozonation by-products such as aldehydes and ketoacids, the ozone molecule yields more ozonation by-products which are biodegradable organic carbon than do radical reactions.

B. BDOC problems

BDOC formation can result in problems for water utilities since as BDOC provides a good carbon source for bacteria, their number can increase with distance away from the point of disinfection, as the disinfectant residual is reduced. This increase has been termed regrowth (Edge and Finch, 1987). Not only may regrowth result in the proliferation of potentially pathogenic bacteria (Burke et al., 1984; Wadowsky et al., 1982) but their presence may cause tastes, odor, color, and pipe corrosion problems (Levy et al., 1986).

C. AOC as a parameter to measure regrowth

Biodegradable or assimilable organic carbon is defined as either (1) the fraction of dissolved organic carbon (DOC) that can be used by the bacteria for growth and cell maintenance or (2) the degree to which microbial growth is stimulated by DOC (Langlais et al., 1991). Two different methods to determine biodegradability in drinking water have been developed. Van der Kooji et al. (1982) proposed the AOC (Assimilable Organic

Carbon) method, which measures assimilable organic carbon by measuring the growth of a pure bacterial culture using the standard method plate count. Bacteria used for AOC method are *Pseudomonas fluorescens* P17 and *Spirillum* NOX. The plate count is converted into units of sodium acetate by referring to a calibration curve measured. The AOC accounted for by the P17 organism utilized includes many of the easily biodegradable compounds: amino acids, carboxylic acids, hydrocarboxylic acids, alcohols, and carbohydrates (Van der Kooij, 1985). However, this P17 organism can not utilize certain major ozonation by-products such as oxalate, formate, and glyoxalate. In order to compensate this lack of capability, *Spirillum* NOX can be used for utilizing those compounds which can not be utilized by P17 organism.

Van der Kooij (1992) investigated the relationship between heterotrophic bacteria regrowh and AOC in 20 water supplies. The results showed that there exists a significant relationship between AOC and heterotrophic bacteria. However, DOC removal during controlled inoculation was shown to be unrelated to heterotrophic bacteria regrowth. Recent research showed that there appear to be a poor correlation between bacterial numbers and AOC concentrations (Miettinen et al., 1997; Gibbs et al., 1993,). This might be due to the low sensitivity of AOC measurement method. Also, another reason is that the bacterial growth is also affected by the physical conditions: temperature, dissolved oxygen, and turbidity (Power and Nagy, 1999).

The other method used to assess BDOC has been developed by Servais et al. (1987) with the objective of measuring DOC concentration at the beginning and end of a specific incubation period. In order to minimize the incubation time, the modified method was developed by Joret et al. (1988). Using this method, the sample is recycled through a sand column inoculated with biomass, and DOC is measured daily until the concentration of DOC no longer changes with time.

The methods of BDOC and AOC (P17) were compared by Frías et al. (1995) and Kaplan et al. (1994). These results show that the AOC method gives substantially lower values than that obtained using BDOC and a linear relationship between BDOC and AOC. This is not surprising since BDOC is a portion of DOC that can be mineralized by heterotrophic microorganisms, whereas AOC is the more restrictive portion that can be converted to cell biomass. The conceptual differences might explain the difference of BDOC and AOC values. However, Siddiqui et al. (1997) also shows as ozone dose was increased, BDOC and AOC followed a similar trend.

Zoungrana and Prévost (1998) reported that the determination of BOC is affected by bicarbonate concentration. The addition of bicarbonate into samples before ozonation or after ozonation resulted in lower BDOC than that determined without additional bicarbonate. The higher the concentration of bicarbonate added (25-100 mg/L as $CaCO_3$), the lower the BDOC obtained. This is thought to be due either to suppression of the ability of the bacterial biomass to degrade the BDOC or a modification of BDOC biodegradability. Thus, it might be worthy to take into account the bicarbonate effect when the bicarbonate is added into the water to be tested.

Miettinen et al. (1999) modified the AOC method by adding inorganic nutrients to the samples. This was done because inorganic nutrients, especially phosphorus, are often the limiting factor for microbial growth in treated drinking water. The modified AOC method, named $AOC_{potential}$, was compared to the AOC_{native} method developed by Van der Kooij et al. (1982). The $AOC_{potential}$ has a positive correlation with DOC whereas

AOC_{native} has poor correlation. As such, the $AOC_{potential}$ method would be more reliable method than AOC_{native} in demonstrating potential biological activity in treated drinking water.

Consequently, the parameter that has the best capability to measure bacterial regrowth or growth of coliforms is the AOC measurement. On the other hand, the parameter that best suited to measuring DBP formation potential or chlorine demand through a biological treatment process is DOC measurement with biomass inoculation (BDOC) (Huck, 1990).

3.4. BDOC control

A. BDOC/AOC formation by molecular ozone.

The formation of BDOC and AOC was affected by some conditions during ozonation. The total AOC was negatively correlated with alkalinity concentration during ozonation whereas BDOC was independent of alkalinity (Paode et al., 1997). Also, there exists only a limited amount of data discussing the effect of pH on BDOC or AOC formation during ozonation. In waters having pHs raging from 6 to 9, pH was shown to have no significant effect of BDOC formation during ozonation (Siddiqui et al, 1997). The effect of ozone contact time on the formation of BDOC has been observed (Volk et al., 1993). At ozone dose of 1.5 mg O_3/mg C, most of BDOC was formed in the first 5 minutes, then no significant increase of BDOC was observed upon longer contact times. The results indicate the different ozonation conditions may influence the formation of BDOC/AOC.

B. BDOC/AOC formation by ozone/hydrogen peroxide

The use of hydrogen peroxide combined with ozone (Peroxone) has been investigated as a means of ozone decomposition and increasing the concentration of OH radical (Glaze et al., 1987; Duguet et al., 1985; Brunet et al., 1984). The optimal stoichiometric ratio of hydrogen peroxide to ozone in pure water has been found to be 0.3-0.5 (w/w). However, natural water sources have different characteristics and concentrations of NOM. As such, the optimum $[O_3]/[H_2O_2]$ ratio varies with water characteristics. As the $[O_3]/[H_2O_2]$ ratio is increased, the yield of OH radicals also increases. However, the OH radical rapidly reacts with hydrogen peroxide and hydroperoxide (HO_2^-) so that the overall OH radical concentration decreases due to OH radical consumption by H_2O_2. As result, overdosing hydrogen peroxide may not only decrease the reaction efficiency but also increase chemical costs. As such, it is important to determine the optimum $[O_3]/[H_2O_2]$ ratio for the each water sources in terms of BDOC formation.

Ozone combined with hydrogen peroxide (ozone dosage: 3 and 6 mg O_3/L; $[H_2O_2]/[O_3]$: 0 – 1.0) has been observed to increase BDOC and AOC formation. However, at relatively high doses of hydrogen peroxide, AOC and BDOC formation decreased. The formation of BDOC and AOC by ozone/peroxide process has been compared with that formed during the reaction with ozone alone. (Speitel and Wanielista 1999; Miettinen, 1998; Siddiqui et al., 1997; Volk et al., 1997; Hacker et al., 1994; Volk et al., 1993). Using ozone alone, applied ozone dosages up to 4 mg/L (TOC: 2.3-3.7 mg/L) increased the AOC concentration. The use of the ozone/peroxide, which would result in OH radical reactions predomination, resulted in lower AOC concentrations than did ozone alone. At low peroxide dosages (H_2O_2/O_3: 0.05), the concentration of AOC increased (Hacker, 1994). Several researchers (Siddiqui et al. (1997). Volk et al. (1997), and Volk et al. (1993)) observed that the ozone/hydrogen peroxide process yields lower BDOC values than does ozone alone. On the contrary, Miettinen et al. (1998) found the opposite to be true. However, the overall TOC that could not be removed by ozone alone was removed during ozone/hydrogen peroxide treatment.

Speitel and Wanielista (1999) compared ozone, ozone/peroxide and peroxide/UV system for BDOC formation in Lake Austin water and Lake Houston water. Ozonation and Peroxide/UV treatment enhanced BDOC formation, whereas ozone/peroxide decreased BDOC in both water sources. The ozone doses and peroxide doses applied for Lake Austin water were 1 – 2 mg O_3/mg TOC and 0.2 – 1.3 mg H_2O_2/mg O_3, respectively. The lower dosages were applied for Lake Houston water (ozone dosages: 0.5-1 mg O_3/mgTOC and peroxide dosages: 0.4 -1.3mg H_2O_2/mg O_3) to see if the higher ozone dosages were masking the hydroxyl radical effects. However, after O_3/H_2O_2 treatment, the BDOC formation decreased only slightly with increased oxidant dosage and did not differ significantly from ozone alone. At larger ozone doses the BDOC concentration was observed to have decreased. In order to investigate the effect of OH radicals, it is thought that the reaction mechanisms and reaction rate of the oxidants (O_3, H_2O_2, $OH\cdot$) have to be determined for the each tested NOM. Moreover, at low concentrations of either ozone or hydrogen peroxide compared with the NOM concentration, the radicals might be consumed by the ozone decomposition, even though the concentration of OH radicals is enhanced. This is especially true if the rate of reaction of OH radical with NOM is slower than that of OH radicals with ozone or ozone decomposition intermediates.

C. BDOC/AOC formation by hydrogen peroxide/UV

The hydrogen peroxide/UV process is another method of generating OH radical. The main pathway of this process involving UV radiation energy is to cleave a peroxide molecule into two hydroxyl radicals (Legrini et al. 1993).

Speitel and Wanielista (1999) also have investigated the Peroxide/UV process to determine its effect on BDOC formation. At irradiation time of less than 16 minutes (UV dosage: 3 W-min/μmol TOC), the formation of BDOC increased with increasing UV irradiation time. However, at longer irradiation times both the BDOC and TOC concentration decreased consistently. Apparently, long irradiation times have a negative effect for the BDOC formation.

Although the hydrogen peroxide/UV process formed BDOC, the pathways of the formation include not only OH radical reactions but also photosensitized reactions as a result of UV irradiation. As such, the direct effect of UV on the humic substance structure makes it more difficult to distinguish reactions involving ozone molecule alone from radical species reactions involving OH radicals. The photosensitized reaction[1] may result in the production of OH radicals and other radical species from sensitized humic substance as well as resulting in change of the humic substance structures (Gao and Zepp, 1998).

D. Gamma ray/electron beam irradiation

Processes using gamma ray or electron beams also generate OH radicals. These reactions do not use ozone. Recently several researchers have developed such processes (Siddiqui et al., 1996; Cooper et al., 1992; and Gehringer et al., 1985). Usually, ^{60}Co radioisotope or an electron beam accelerator is used for an irradiation source. Irradiation of the solution produces some electronically excited state and free radicals. The products that have been formed in aqueous solution are:

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[1] The humic substance is a well known chromophore. In other words, the humic substance structure absorbs light in the UV and visible range. This absorption of light can result in the extinction of the humic substance molecules, allowing it to transfer its[1] excess energy to another molecule in the water (Schwarzenbach, R.P. 1992). This reaction is called photosensitization.

$$H_2O \rightsquigarrow [2.7]\ OH\bullet + [2.6]\ e^-_{aq} + [0.6]\ H\bullet + [0.7]\ H_2O_2 + [2.6]\ H_3O^+ + [0.45]\ H_2$$

(Bielski and Gebicke, 1970) Eq. 3.1.

The values in parenthesis stand for the G value (Eq. 3.1), which is the number of radicals, excited states, ions formed or lost in a system absorbing 100 eV energy. Those species formed by irradiation can react to remove contaminants. The irradiation process generates additional radical species reaction beyond the OH radical. The presence of the radicals makes it more difficult to investigate the OH radical reaction.

The effect of γ-irradiation/ozone on NOM was investigated (Arai et al. 1986). γ-irradiation with ozone cab be used to enhance OH radical concentration. However, there is insufficient information concerning the reactions between hydrated electrons, hydroxyl radicals, hydrogen atom and NOM. Karpel et al. (1997) conducted γ-irradiation/ozone experiments using NOM to investigate BDOC formation (γ-ray dose: 390 Gy, TOC: 2.5 mg/L, $NaHCO_3$: 4.5 mM, $Ca(NO_3)_2$: 0.4 mM). The results show that γ-irradiation with ozone and ozone/peroxide could enhance BDOC formation compared with ozone alone. The NOM tested surprisingly did not increase BDOC concentration at ozone dose 1 mg/mg C, and 23 % of BDOC was increased at ozone dose 2.5 mg/mg C. This may indicate that the NOM tested probably has low proportion of reactive sites with the ozone molecule. Thus, increasing the OH radical concentration relative to ozone/peroxide/UV processes can further oxidize NOM to BDOC. Although Karpel et al.(1997) found that ozone/peroxide and γ-irradiation/ozone which resulted in similar BDOC formation efficiencies, it is difficult to compare those two processes. γ-irradiation uses relatively more energy than other processes such as ozone, peroxide, and the mechanism of γ-irradiation involves not only OH radicals but also the hydrated electron. Thus, both reduction reaction and oxidation reactions occur in this process. Experiments with γ-irradiation alone support this hypothesis since γ-irradiation alone also could enhance the BDOC formation which could not be enhanced by ozone alone.

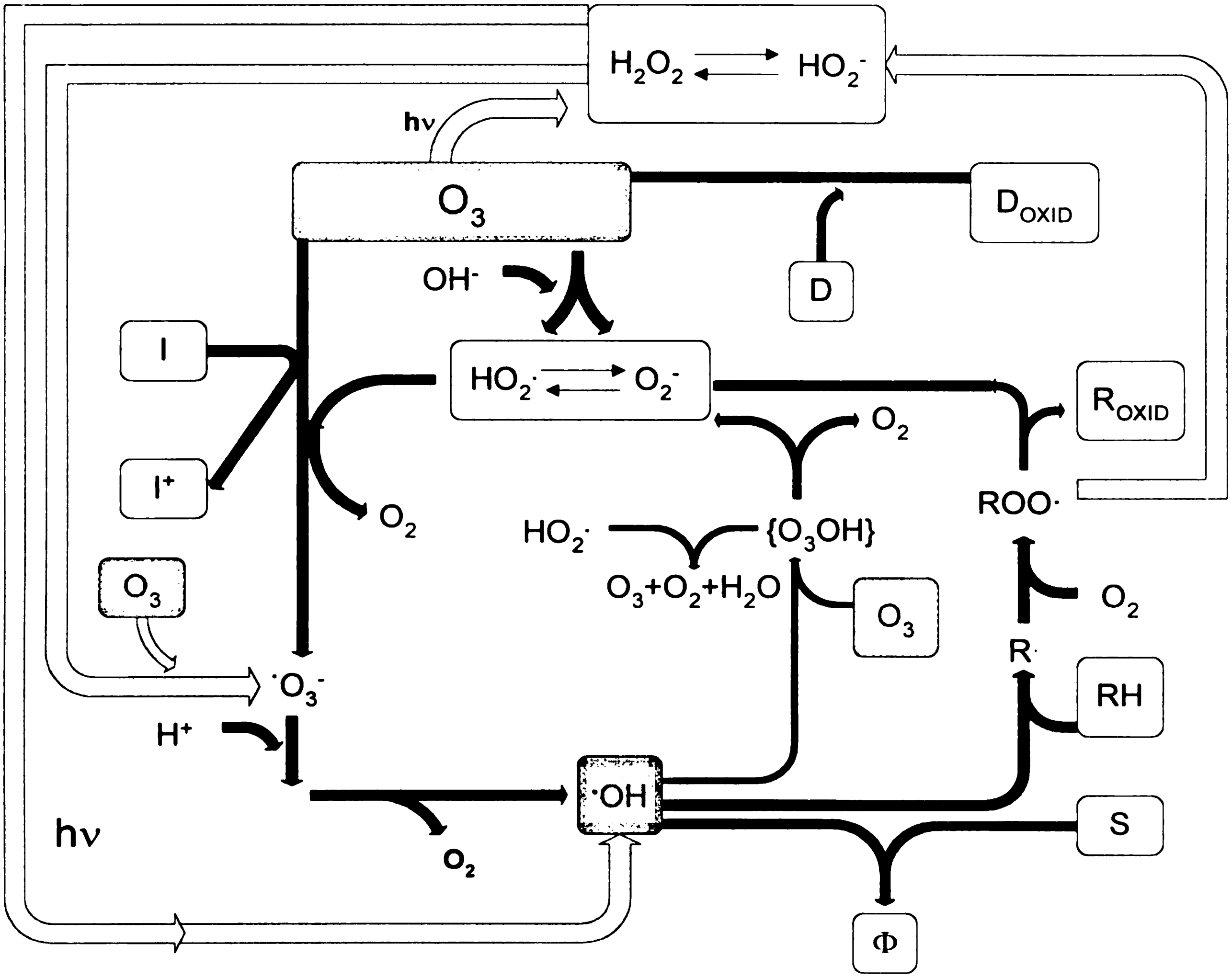
3.5. Ozone pathway

As mentioned in previous discussions the various processes used in water treatment to oxidize NOM result in significantly different pathways involving NOM to form BDOC. As such, it may be important to understand and control the pathway(s) of ozone decomposition to control BDOC formation.

A. Ozone decomposition reaction

The pathways of the ozone decomposition can be classified in three steps: initiation, promotion, and inhibition (Staehelin and Hoigné, 1985). As shown in Fig. 1., some compounds, such as hydroxide ion, hydroperoxide ion (HO_2^-), and primary alcohols, can initiate the decomposition of molecular ozone to superoxide ion (O_2^-) (Staehelin and Hoigné 1985). Hydroxide ions play a fundamental role in initiating the ozone decomposition. These ions initiate ozone decomposition by reacting with ozone, producing superoxide anions (O_2^-). Ozone then reacts with the superoxide anion to form ozonide radical ions and oxygen. The protonated ozonide ion rapidly decomposes to produce oxygen and hydroxyl radicals. The hydroxyl radicals decompose ozone further, producing more superoxide ions, which participate in the cycle reaction. (Masten and Davis, 1994; Bailey, 1978).

As mentioned previously, there are three steps involved in OH radical formation during the ozone decomposition: Initiation, promotion, and scavenging reaction. The commencement of free radical reactions during ozone decomposition to form a superoxide ion from the ozone molecule is called the initiation step. The promotion reaction serves to regenerate the superoxide ion (O_2^-) from hydroxyl radical. Typical promoters include organic compounds with aryl groups and primary alcohols. The scavenging reaction consumes OH radicals without producing superoxide ions. Carbonates, bicarbonates and phosphate ions may serve as promoters. Thus, if these steps could be controlled properly, OH radical formation from the ozone molecule could also be controlled and BDOC/AOC formation could be optimized.



The dark reaction that occur in "pure" water are shown in blue. The additional dark reactions that may occur when reactive solutes are present are shown in red. D is a compound that can react directly with ozone; I is a compound that, when it reacts with ozone via an electron transfer reaction, produces the ozonide radical ion (i.e., it is an initiator of ozone decomposition); RH is a promotor of ozone decomposition; and S is an ·OH scavenger. Propagation of the chain reaction may occur by the reaction of RH with ·OH to form an organoperoxide radical, ROO ·. Termination of the chain reaction may occur via reaction of S with ·OH to form a secondary radical, Φ, which dose not participate in the chain reaction. Additional reaction that occur in O_3/H_2O_2 and/or O_3/UV systems are shown in yellow.

Figure 3.1. Decomposition of ozone in waters. (Masten and Davies, 1994)

B. Factors affecting ozone decomposition

Ozone decomposition may be controlled by regulating inhibition, promotion, and inhibition reactions. Yuteri and Gurol (1988) found that the ozone decomposition kinetics were significantly influenced by such factors such as pH, TOC, and alkalinity as well as background NOM characteristics. The retardation of ozone decomposition by altering these factors will permit an increase in concentration of molecular ozone compared to that of the radical species. In contrast, the acceleration of the ozone decomposition would lead to the opposite situation.

B.1. pH

The hydroxide ion is a well known initiator of ozone decomposition. As an initiator, the high concentration of hydroxide ions at high pH accelerates ozone decomposition. The initiation of ozone decomposition in distilled water is first order in ozone and hydroxide ion concentration. The reaction rate of ozone with hydroxide was observed to be 70±7 $M^{-1}s^{-1}$ (Stahelin and Hoigné, 1982). The log values for the ozone decomposition rate were shown to be linear with pH (Stahelin and Hoigné, 1982; Sullivan and Roth, 1979).

B.2. Alkalinity

Staehelin and Hoigné (1982) found that carbonate and bicarbonate ions have the ability to stabilize molecular ozone. This has been confirmed by many other researchers (Yuteri and Gurol, 1988; Reckhow et al., 1986; Forni et al., 1982). However, as bicarbonate and carbonate are scavengers of OH radicals their presence, which is ubiquitous in most natural waters having a pH>7, will result in relatively low OH radical concentrations in these waters. This is especially true at higher pH values where the bicarbonate ion dissociates into carbonate ion to a greater extent (pKa = 10.3) (Snoeyink and Jenkins, 1980). Moreover, the reaction rate of bicarbonate with OH radical is greater than that of carbonate. As such, bicarbonate and carbonate ions may serve to counter some of the effects of OH radicals, thereby stabilizing molecular ozone.

Bicarbonate/Carbonate ions have also been found to result in more effective scavenging than do phosphate ions (See Table 3.1). The bicarbonate ion inhibits the radical chain reaction, hence increasing the concentration of molecular ozone. As such, the presence of radical scavengers could result in the predominance of reactions involving the ozone molecule and preferential reaction of the ozone molecule with the aromaticity of fulvic acid, a component of humic substance. Although bicarbonate and carbonate ions are effective at OH radical scavenging in the ozonation, they produce secondary oxidants, the bicarbonate radical and carbonate radical, which can oxidize some inorganic and organic compounds. Therefore, more careful attention of the carbonate/bicarbonate radical reactions that occur during ozonation needs to be made.

B.3. NOM

NOM also acts as a promoter and initiator of ozone decomposition (Elovitz et al. 1999; Staehelin and Hoigné, 1985). Westerhoff et al. (1996) attempted to simulate ozone decomposition mathematically. Without considering the promotion and initiation role of NOM on the ozone, the simulation results differ significantly difference from experimental data. The simulation results show a first order reaction rate during entire reaction period and slower decomposition rate than that of experimental results. However, when the promotion and initiation role of NOM was considered, the ozone decomposition rate results in two stages, with rapid rate decomposition at the early stage and followed by slower decomposition rate.

Ozone decomposition in the presence of NOM and t-butylalcohol, also an OH radical scavenger, has been investigated (Xiong and Legube, 1991). The results indicate that NOM plays both initiation and promotion roles in ozone decomposition. Fulvic acid did not participate in the radical reaction involved in ozone decomposition under very acidic conditions (pH = 2); whereas it becomes a promoter of the ozone decomposition with increasing pH due to increasing degree of dissociation of the acidic groups. The fraction of fulvic acid reacting via the radical reaction increases proportionally with increased initial $[O_3]/[FA]$ ratio. Consequently, the effect of NOM, as both a promoter and inhibitor, on ozone decomposition reactions should be considered when investigating the ozone – OH radical reaction.

Recently, Elovitz et al. (1999) investigated the rate of promotion and inhibition of ozone by NOM using γ-irradiation. This experiment also was conducted to determine the rate of hydroxyl radical scavenging by eleven NOM isolates. γ-irradiation results show that hydroxyl radical scavenging rates were relatively equal for all NOM isolates ($1.3 \pm 0.1 \times 10^4$ L/mg/s). The OH radical scavenging rate could be divided by the rate of promotion (superoxide production) and inhibition (non-superoxide production). The rate of promotion and inhibition were also relatively equal for all NOM isolates ($3.7 \pm 0.3 \times 10^4$ L/mg/s and $9.3 \pm 0.7 \times 10^4$ L/mg/s, respectively). This result indicates that the NOM predominantly behaves as direct consumer of ozone and promoter of ozone decomposition.

B.4. Temperature

Temperature also can affect the kinetics of ozone decomposition. Sotelo et al. (1987) showed that the ozone decomposition rate increased with increasing pH and temperature. The ozone initiation rate was negligible at pH below 3 at various temperatures (10 - 40 °C).

The elementary reaction rate increases as temperature is increased. Based on the elementary reaction of ozone decomposition, the OH radical concentration at steady state condition can be expressed as following equation.

$$[OH]_{ss} = \frac{2(k_{O_3,OH^-}[O_3])_T[OH^-]_{ss}}{(k_{HCO_3,OH})_T[HCO_3]} \qquad \text{Eq. 3.2.}$$

$$(k_o)_T = (k_{NOM,O_3})_T([O_3]_{ss})_T + (k_{NOM,OH})_T([OH]_{ss})_T \qquad \text{Eq. 3.3.}$$

The reaction rate that initiates the ozone decomposition and produces OH radicals (numerator in this equation) will increase as temperature increases. The OH radical scavenger reaction (denominator of the equation) will also increase with increasing temperature. Moreover, the rate of reaction of ozone molecule reaction with NOM also changes. Unfortunately, the activation energy for each reaction is not established.

Thereby, it is difficult to establish the extent to which the OH radical concentration will increase or decrease with changing temperature.

B.5. Hydrogen peroxide

As previously described, hydrogen peroxide can act as an initiator of molecular ozone decomposition. The addition of hydrogen peroxide in ozonation treatment can enhance OH radical concentrations because the ozone molecule is rapidly decomposed, producing OH radicals (Glaze et al., 1987; Duguet et al. 1985; Brunet et al., 1984).

The efficiency of OH radical production from hydrogen peroxide depends on pH. Hydrogen peroxide partially dissociates into hydroperoxide ion (HO_2^-) (pKa = 11.6). While the hydroperoxide ion is highly reactive with ozone, thus initiating ozone decomposition ($k = 10^6\ M^{-1}s^{-1}$), the reaction of hydrogen peroxide with ozone is very slow. As such, the ozone decomposition by hydrogen peroxide increases with increasing pH since hydroperoxide ion is predominant over pH 11.6. However, competition reactions occur at high pH since hydroxide ions are more effective at initiating molecular ozone than are hydroperoxide ions, and OH radicals are also consumed by bicarbonate and carbonate ions.

The effect of hydrogen peroxide on the oxidation of NOM by ozone was investigated by Tuhkanen et al. (1994) and Duget et al. (1986). The influence of different hydrogen peroxide concentrations on the ozonation of NOM were investigated by Duget et al. (1986). The use of hydrogen peroxide (1 mg/L) with ozone (3 mg/L) increased the extent of oxidation of NOM, especially, increasing the removal efficiency of UV absorbance (254 nm) in the early reaction times. However, at higher ozone concentrations

(> 1 mg/L), the removal rate of UV absorption did not increase. The results indicate that there exists, for each natural water, an optimum hydrogen peroxide concentration where by efficiency is maximized. In other words, the OH radicals produced from ozone/peroxide have to be used for NOM reaction as much as possible, thereby avoiding the consumption of reactive radicals reacting with hydrogen peroxide. Since the optimum dosage of hydrogen peroxide would also depend on the background organic matrix in the water, it is necessary to determine optimum ozone and peroxide doses in each water source.

B.6. Organics

Many compounds are able to initiate, promote, or inhibit the chain-reaction processes involving ozone (Staehelin and Hoigné 1985). Some organic chemicals have ability to initiate the decomposition of molecular ozone. The initiators include glyoxylic acid, formic acid and humic substances (Langlais et al., 1991). Several organic chemicals, including aryl groups, formic acid, glyoxalic acid, and primary alcohols, have been found to act as promoters (Staehelin and Hoigne 1985).

The common scavengers of OH radicals include bicarbonate and carbonate ions, alkyl groups, tertiary butyl alcohols (Staehelin and Hoigné 1985). Guittonneau et al. (1992) investigated the kinetics of the reaction of ozone with NOM in the presence of formic acid and t-butylalcohol. Formic acid acts as a promoter and t-butyl alcohol inhibits ozone decomposition (See Table 3.1). The ozonation of fulvic acid in the presence of bicarbonate was shown to be more effective for the removal of aromaticity. Fulvic acid consists of two parts: a nulceophilic aromatic moiety and a saturated aliphatic moiety. It can be expected that molecular ozone mostly reacts with the nucleophilic centers of fulvic acid, while the OH radical attacks aliphatic portion since OH radical is non-selective. This is consistent with the findings of Xing and Legube (1991). They found that when the radical scavengers, bicarbonate and tert-butyl alcohol, were added to ozone reaction on the fulvic acid, the aromaticity from fulvic acid was effectively removed (Xiong and Legube, 1991).

The dissociation of organic acids is a function of their pKa value. For example, the pKa value of acetic acid is 4.7. Although acetic acid predominates at pH values less than 4.7, acetate, the dissociated form of acetic acid, is predominant at pH values above 4.7. As shown in Table 1, the degree of ionization of the acid significantly affects the reaction rate constants of the acid with OH· and ozone. For bicarbonate (pka = 10.3) (Snoeyink and Jenkins, 1980) and phenol (pka = 9.9) (Hoigné and Bader, 1983b), the reaction rate of OH radical with these compounds and their dissociated form also show significant difference. Staehelin and Hoigné (1983b) also found that the formate ion reacts rapidly with ozone while the formic acid is practically inert.

Table 3.1. Rate Constants of Ozone and OH radical.

Solute	k_{O3} ($M^{-1}s^{-1}$)	k_{OH} ($M^{-1}s^{-1}$)	Solute	k_{O3} ($M^{-1}s^{-1}$)	k_{OH} ($M^{-1}s^{-1}$)
Acetic Acid	3×10^{-5}[*]	1.6×10^{7}[‡]	t-butyl alcohol	0.003[†]	3.1×10^{9}[‡]
Acetate ion	3×10^{-5}[*]	8.5×10^{7}[‡]	Bicarbonate	-	8.5×10^{8}[‡]
Formic acid	5[*]	1.3×10^{8}[‡]	Carbonate	-	3.9×10^{8}[‡]
Formate ion	100[*]	8.5×10^{7}[‡]	1-Propanol	0.37[†]	2.8×10^{9}[‡]
Methanol	~0.024[†]	9.7×10^{8}[‡]	Phenol	1.3×10^{3}[*]	6.6×10^{9}[‡]
Ethanol	0.37[†]	1.9×10^{9}[‡]	Phosphate ion	$<2.4\times10^{4}$[*]	$<1.0\times10^{9}$[‡]

[†] Hoigné and Bader (1983a)

[*] Hoigné and Bader (1983b)

[‡] Bouxton(1988)

3.6. Biodegradation of additives for ozonation

The biodegradability of the additives, which play a role in controlling ozone decomposition, has to be taken into account. Although the additives exert their role during the ozonation, there may be residual additives and/or their by-products after ozonation.

As shown in Table 2., the redox potentials (ΔG^0) of the candidates for ozonation additives appear to be fairly high. This is one of the indicators that the organic chemicals can be relatively easily biodegraded.

The ozonation of organic additives produce reaction by-products during the ozonation. Dalouche (1981) determined the by-products of alcohols to be aldehydes, ketones, acids, and esters, all of which are easily biodegraded. Thus, it is expected that the residual additives and their ozonation by-products also can assist to increase the biodegradability of ozonated water.

Table 3.2. Free Energy of Ozonation Additives.

Organics	ΔG^0 (kJ/elec. Mole)
Acetate	-27.40
Formate	-39.19
Ethanol	-31.18
Methanol	-36.84

Ref) McCarty, P.L. 1969.

4. RESEARCH APPROACH

The aim of the study is to investigate the ozonation pathways which optimize the formation of easily biodegradable organic compounds. The pathways by which ozone reacts with NOM are significantly affected by the following parameters: NOM characteristics, initial $[O_3]/[NOM]$ concentration ratio, pH, reaction temperature, reaction time, additives concentration.

The effect of operational parameters and the presence and concentration of additives on the concentrations of molecular ozone and the OH radical were determined in Phase I experiments. The influence of various operational parameters on biodegradability formation were determined in Phase II experiments. The effect of additives on biodegradability formation was investigated in Phase III experiments.

Phase I :

Determination of $[O_3]/[OH\cdot]$ concentration ratios in various conditions.

The experiments were conducted as following conditions. The effect of the initial ratio of $[O_3]/[NOM]$ on the concentration ratios of $[O_3]/[OH\cdot]$ also was investigated. At low initial ratios of $[O_3]/[NOM]$ reactions involving molecular ozone should predominate. In contrast, high initial ratios of $[O_3]/[NOM]$ should lead to radical reactions unless NOM were a scavenger of OH radical. This hypothesis was tested by monitoring $[O_3]/[OH\cdot]$ ratios at different initial ozone concentrations. Each NOM tested will have significantly different characteristics for ozonation since all NOM originated from different waters by different mechanism. Although similar experiments have been conducted by other researchers, it is necessary for us to conduct the experiment to compare our results with those already published.

The effect of pH (2-10) on the concentrations of [O_3] and [OH·] was investigated. At low pH, the ozone molecule predominates due to low concentrations of the hydroxide ion. On the other hand, at high pH the ozone molecule is rapidly decomposed by hydroxide ion so that the radical reaction is predominant. Although the range of the pH in water treatment plants varies only from 6 to 8, the extremely low or high pH values are necessary to observe the reaction pathways. Based upon the literature results, the experiments have been conducted over a narrow range of pH (6-9). These results can not explain which reaction is predominantly involved in NOM oxidation since both the molecular ozone and OH radical reactions compete at these pH ranges.

As pH changes, the concentration of OH radical scavengers, bicarbonate and carbonate, both also change. To compare the effect of pH, the scavenging capacity of the solution was maintained constant.

The effect of temperature on the ratio of [O_3] and [OH·] was studied. The water temperature in water treatment plants varies significantly with their locations and seasons. To cover this range, the temperature used in our experiments was varied from 5 to 35 °C. The temperature may influence the rates of both ozone decomposition and radical consumption by scavengers. From this study, we expected to be elucidate which of these reactions (molecular ozone vs. radical) is more significantly influenced by temperatures. If the ozone decomposition rate is influenced greater than radical consumption by scavenger on the temperatures, the concentration of OH radical would increase with increasing temperature.

Several additives were used to investigate their capability to control the reaction pathway (either ozone molecule reaction or OH radical reaction). In the presence of the additive that play either initiator or promoter roles, the OH radical concentration is expected to predominate. On the other hand, in the presence of the additive that plays an inhibitor role, the molecular ozone concentration will be predominant. The concentration of the additives also was varied (μmol to mmol), respectively, to compare the efficiency of the additives since the stoichiometry ratio of ozone to additive is important parameter in terms of OH radical production.

Phase II :

Effect of reaction pathways on the formation of biodegradability.

Using Phase I results, the ozonation step can be controlled toward reactions involving either the ozone molecule or OH radical by changing operational parameters including temperature, pH, HRT, and applied ozone concentration.

Ozonation was accomplished under conditions that allow us to compare AOC formation by reactions involving the ozone molecule and the OH radical. Based upon literature results, it is expected that the AOC may be increased with increased ozone molecule reaction rather than OH radical reaction. For the AOC analysis, the pH was adjusted to 7 after the sample was taken since a significantly low or high pH may inhibit the bacterial growth during AOC analysis.

The pH range tested was same as done in Phase I. Since at low pH, reactions with molecular ozone will predominate, AOC formation should be enhanced in waters having a low pH.

Except in experiments specifically conducted to study temperature effects, the temperature of the water was maintained at 25 °C. In those cases, the temperature was varied from 5 to 35 °C. In order to utilize same ozone dosage at different temperatures, the ozone mass transfer coefficient also was determined at each of the temperatures used.

It was expected that the concentration of AOC would increase with decreased hydraulic retention time (HRT) since it was expected that the molecular ozone reaction would predominate at short HRTs. Changes in the HRT, over the range from 5 min to 30 min, were investigated. The ozone dosage was held constant as HRT was varied.

The effect of applied ozone dose was investigated at a single HRT. The results conducted in Phase I were useful to explain these experiment results. It was expected that high $[O_3]/[NOM]$ ratios would decrease AOC formation due to OH radical prevalent condition.

A analyses included the following parameters: TOC, residual ozone concentration, UV254, AOC, ketoacids (glyoxylic acid, pyruvic acid and ketomalonic acids), SDS THMs, and SDS HAAs.

Phase III :

Evaluation of additives on the ozone reaction for the formation of biodegradability.

The results obtained from the Phase I gave information regarding the effectiveness of the additives in terms of controlling the ozone pathways. The effectiveness of additives in controlling biodegradability formation during the ozonation was compared. The initiators (hydroxide ion) and promoters (hydrogen peroxide, phosphate ion) were expected to decrease AOC formation due to the prevalent OH radical reaction. On the other hand, the OH radical inhibitors (bicarbonate) were expected to increase AOC formation due to prevalent molecular ozone reaction. Although there are various additives that could have been used, the inorganic additives were used for this study to avoid problems associated with the influence of organic compounds on AOC and TOC analysis. The residual organic additives affect TOC measurement so that TOC value increased due to carbon in residual additives. The organic additives and their ozonation by-products may influence the AOC values. Thus, use of inorganic additives is necessary to avoid analytical errors.

In addition, some experiments were conducted prior to beginning Phase III experiments. The inorganic additives in DI water were ozonated and then AOC concentrations were determined, respectively. An additive such as peroxide, bicarbonate, and phosphate may inhibit AOC concentration even though it does not produce such organic ozonation by-products. In order to determine the inhibition of inorganic additives on the formation of AOC, the AOC for the raw water containing various concentrations of additives was measured, respectively.

4.1. Experimental methods

Phase I .

Elovitz and Guten (1997) have developed a method to determine the ratios of $[O_3]/[OH\cdot]$ concentrations during ozonation using PCBA (*p*-chlorobenzoic acid) as an OH radical probe compound. Since PCBA has a negligibly low reactivity with molecular ozone but reacts rapidly with OH· ($k_{O3,\,PCBA} \leq 0.15\ M^{-1}\ s^{-1}$, $k_{OH\cdot,\,PCBA} = 5\times10^{9}\ M^{-1}s^{-1}$), the PCBA decomposition in the ozonation can be expressed by Eq. 4.1.

$$\frac{d[PCBA]}{dt} = -k_{OH\cdot,PCBA}[PCBA][OH\cdot] \qquad \text{Eq. 4.1.}$$

The equation can be rearranged and integrated to equation 4.2.

$$\ln\{\frac{[PCBA]_t}{[PCBA]_0}\} = -k_{OH\cdot,PCBA}\int[OH\cdot]dt \qquad \text{Eq. 4.2.}$$

Elovitz and Guten (1997) defined a term, R_{CT}, which describes for the ratio of $[OH\cdot]$ and $[O_3]$. (Eq. 4.3)

$$R_{CT} = \frac{\int[OH\cdot]dt}{\int[O_3]dt} \qquad \text{Eq. 4.3.}$$

Substitution of Eq. 4.3 to Eq. 4.2 yields Eq. 4.4.

$$\ln\{\frac{[PCBA]_t}{[PCBA]_0}\} = -k_{OH\cdot,PCBA} Rct \int [O_3] dt \qquad \text{Eq. 4.4.}$$

When the PCBA concentrations are plotted with respect to ozonation time, the slope represents $k_{OH\bullet,\ PCBA} \cdot R_{CT}$ value. Since the $k_{OH\bullet,\ PCBA}$ is well known to be 5×10^9 $M^{-1}s^{-1}$ (Elovitz and Guten, 1999), the R_{CT} value can be obtained from the slope.

Elovitz and Guten (1999) showed that R_{CT} value also equals to the ratio of [OH·] and [O_3] at steady state conditions where R_{CT} is constant. (Eq. 4.5.)

$$R_{CT} = \frac{\int [OH\cdot] dt}{\int [O_3] dt} = \frac{[OH\cdot]}{[O_3]} \qquad \text{Eq. 4.5.}$$

Thus, the ratio of [O_3] and [OH·] concentrations during the ozone reaction can be obtained from R_{CT} values. This result also gives the change of [O_3] and [OH·] with respect to reaction times since the concentrations of ozone and PCBA were simultaneously monitored during the ozone reaction time.

Using R_{CT} values obtained from experimental results, it not only was the ratio of [O_3]/[OH·] for the various operational conditions during ozonation, but also was the role of additives and operational parameters in controlling ozone pathways. In addition, the effect of additive concentrations in controlling ozone decomposition pathways could be observed.

The results obtained in the Phase I can also be used to calculate the rate constants for the reaction of OH radical with NOM ($k_{OH,NOM}$) based upon the methodology developed by Haag and Yao (1993).

The rate constant for the reaction of the OH radical with NOM was determined by using the Ω concept developed by Haag and Hoigné (1985). The Ω value is defined as the amount of ozone that is consumed in removing one log unit (37 %) of an OH radical probe compound. The Ω value can be determined from the slope of a plot of ln {[PCBA]/[PCBA]$_o$} vs. dosed initial ozone concentrations (Eq. 4.6), such that:

$$\Omega_{PCBA} = \frac{-\ln\dfrac{[PCBA]}{[PCBA]_0}}{[O_3]_{added}} \qquad \text{Eq. 4.6.}$$

If PCBA is present at a low concentration relative to that of NOM in water and the OH radical is consumed only by NOM, the assumption can be made as in Eq.4.7.:

$$k_{OH,PCBA}[PCBA] <<<< k_{OH,NOM}[NOM] \qquad \text{Eq. 4.7.}$$

Then, the concentration of very short lived OH radicals at steady-state can be determined by equation 4.8:

$$[OH\cdot]_{SS} = -\eta \frac{\Delta[O_3]}{\Delta t} \times \frac{1}{\Sigma k_{OH,NOM}[NOM]} \qquad \text{Eq. 4.8.}$$

where η is the stoichiometric yield of OH radicals from ozone decomposition. The value of 0.67 for η value is usually selected based on the based-catalyzed OH radical yield without promotion (Westerhoff et al. 1999).

The OH radical concentration can be applied to the PCBA degradation in Eq. 4.9.

$$-\frac{d[PCBA]}{dt} = k_{OH,PCBA}[PCBA][OH\cdot]_{SS} = k_{\exp eriment}[PCBA] \quad \text{Eq. 4.9.}$$

Thus, the OH radical concentration at steady-state can be described as Eq. 4.10.

$$[OH]_{SS} = \frac{k_{\exp eriment}}{k_{OH,PCBA}} \quad \text{Eq. 4.10.}$$

Integration of Eq. 4.9 and then substitution of Eq. 4.8 to Eq. 4.9 yields Eq. 4.11.

$$-\ln\frac{[PCBA]}{[PCBA]_0} = \eta\cdot\frac{k_{OH,PCBA}}{\Sigma k_{OH,NOM}[NOM]}\cdot\int_0^t d[O_3] = k_{\exp eriment}\times t \quad \text{Eq. 4.11.}$$

The ozone concentration consumed at the time when ln[PCBA]/[PCBA]$_o$ equals to 1 (PCBA is degraded 37 %) represents the Ω value. Thus, the Eq. 4.11 can be rewritten as Eq. 4.12.:

$$\eta \cdot \Omega_{PCBA} = \frac{k_{OH,NOM}}{k_{OH,PCBA}} \qquad \text{Eq. 4.12.}$$

The determination of Ω, and η values for the raw waters tested can be used to determine the OH radical rate constant with NOM. This could be used to understand the pathways for the ozonation of NOM in various water sources. When the concentration of either ozone or promotor is much lower than that of NOM and the rate of reaction of OH radical with NOM is slower than that of OH radicals with ozone or ozone decomposition intermediates, the radicals may be consumed by molecular ozone, even though the concentration of OH radicals is enhanced. The $k_{OH, NOM}$ values were used to elucidate the extent to which the OH radicals were involved in the reaction of NOM during ozonation. Consequently, the rate constant of OH radical with NOM is a good indicator of the extent to which molecular ozone and OH radicals are involved in the reactions with NOM.

The schematic of the bench scale system is shown in Figure 4.1. The saturated ozone solution was prepared in phosphate buffered D.I. water (1 L glass bottle) providing gaseous ozone into the solution. A syringe type (headspace-free) batch reactor (250 mℓ) was used for ozonation to prevent volatile loss of ozone from the solution. Prior to ozonation, the water samples were pre-filtered through a 0.45 μm membrane filter to remove any particulate matter. The stock solution of PCBA (20 ppm) was prepared in D.I. water The solutions tested were prepared by adding stock solution of PCBA (ppb level), additives and adjusting the pH and buffer capacity with phosphate, as required. When the desired concentration of ozone was achieved, an aliquot of the ozone stock solution was transferred immediately into the reactor. A magnetic stirrer at the bottom of the reactor was used to completely mix the solution. Samples to determine the PCBA concentration were taken at appropriate time intervals and ozone concentration was monitored continuously by the indigo method (Standard Method, 1995). In order to minimize detention time of the sample in the tubing from the reactor to the point where indigo solution is mixed with sample, 0.03 inch I.D. Teflon® tubing was employed and the length of the tubing was reduced as much as possible (approximately 10 cm). In order to study ozonation at different temperatures (5-35 °C), the reactor was maintained at a constant temperature during the reaction by providing cooling-heating water to the outside of the reactor. The temperature of the solution was monitored by a thermometer. After the ozone is completely decomposed, the sample also was taken to measure the residual additives and/or PCBA concentration.

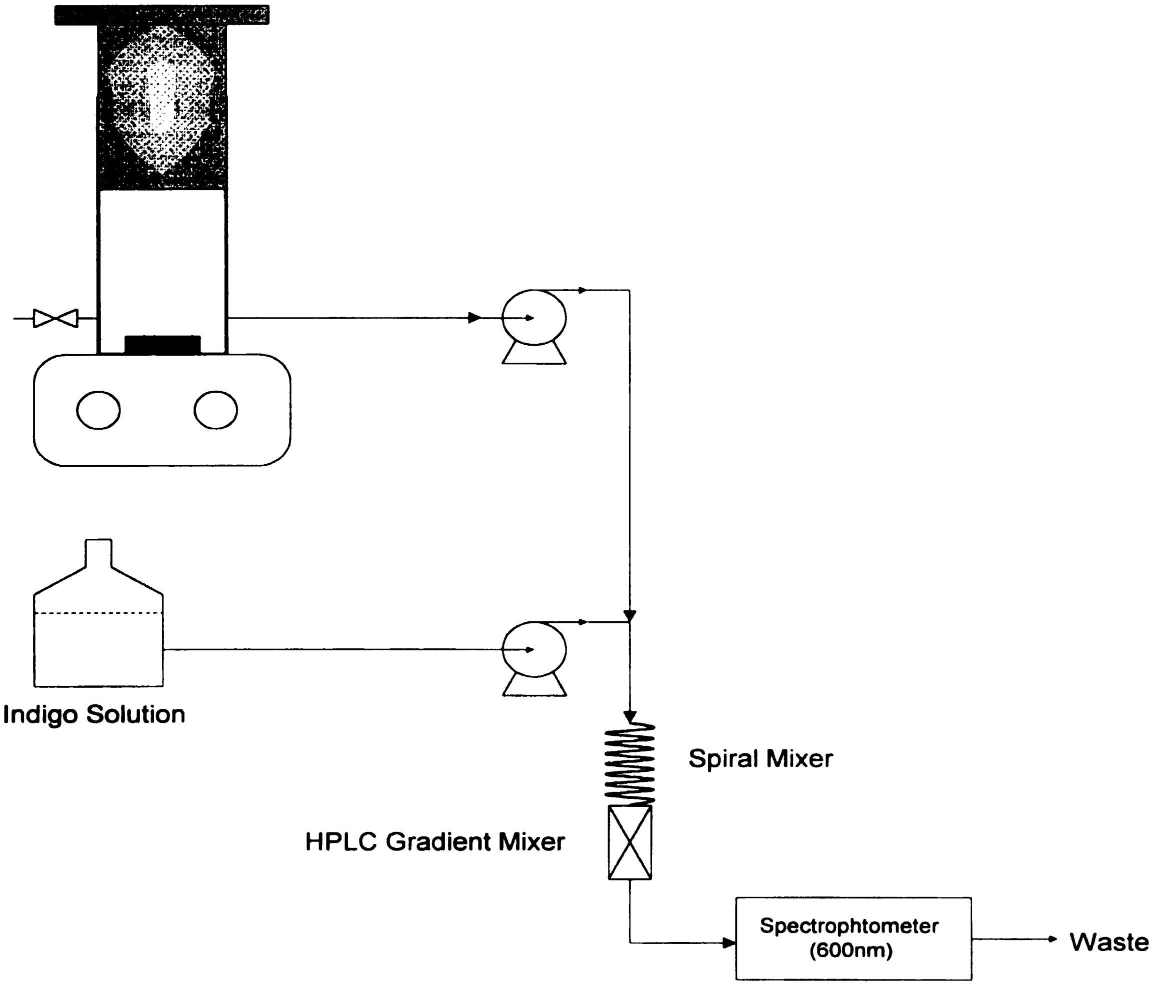


Figure 4.1. Schematic diagram of batch type ozone reactor.

Phase II .

A continuous semi-batch reactor (water-jacked glass reactor, 250mL) was used for ozonation experiments in which the formation of AOC, ozonation by-products (ketoacids), and DBPs under various conditions were conducted (See Figure 4.2). pH was adjusted as required. The water was continuously fed into the bottom of the reactor with a peristaltic pump. Another peristaltic pump also was provided at the top of the reactor to withdraw the ozone reactor effluent to maintain a constant liquid level in the reactor. Gaseous ozone made from pure oxygen was immediately introduced into the reactor. The ozone was dispersed in the reactor using a fritted glass diffuser. For improved gas transfer efficiency and solution mixing, a magnetic bar was used to stir the solution at the bottom of reactor. Once the conditions in the reactor reached steady-state, the concentrations of ozone in the influent and effluent of gas streams were monitored spectrophotometrically to calculate transferred ozone concentration. Thereafter, the samples for the analysis of AOC, ozonation by-products (glyoxylic acid, pyruvic acid and ketomalonic acids) and SDS THMs, and SDS HAAs were taken. The residual ozone was quenched by sparging the solution with a high purity helium gas (99.999 %). In addition, samples also were analyzed for residual aqueous ozone concentration using indigo method before quenching the residual ozone by purging Helium gas. pH and UV254 nm absorbance were also monitored in the effluents of ozonation.

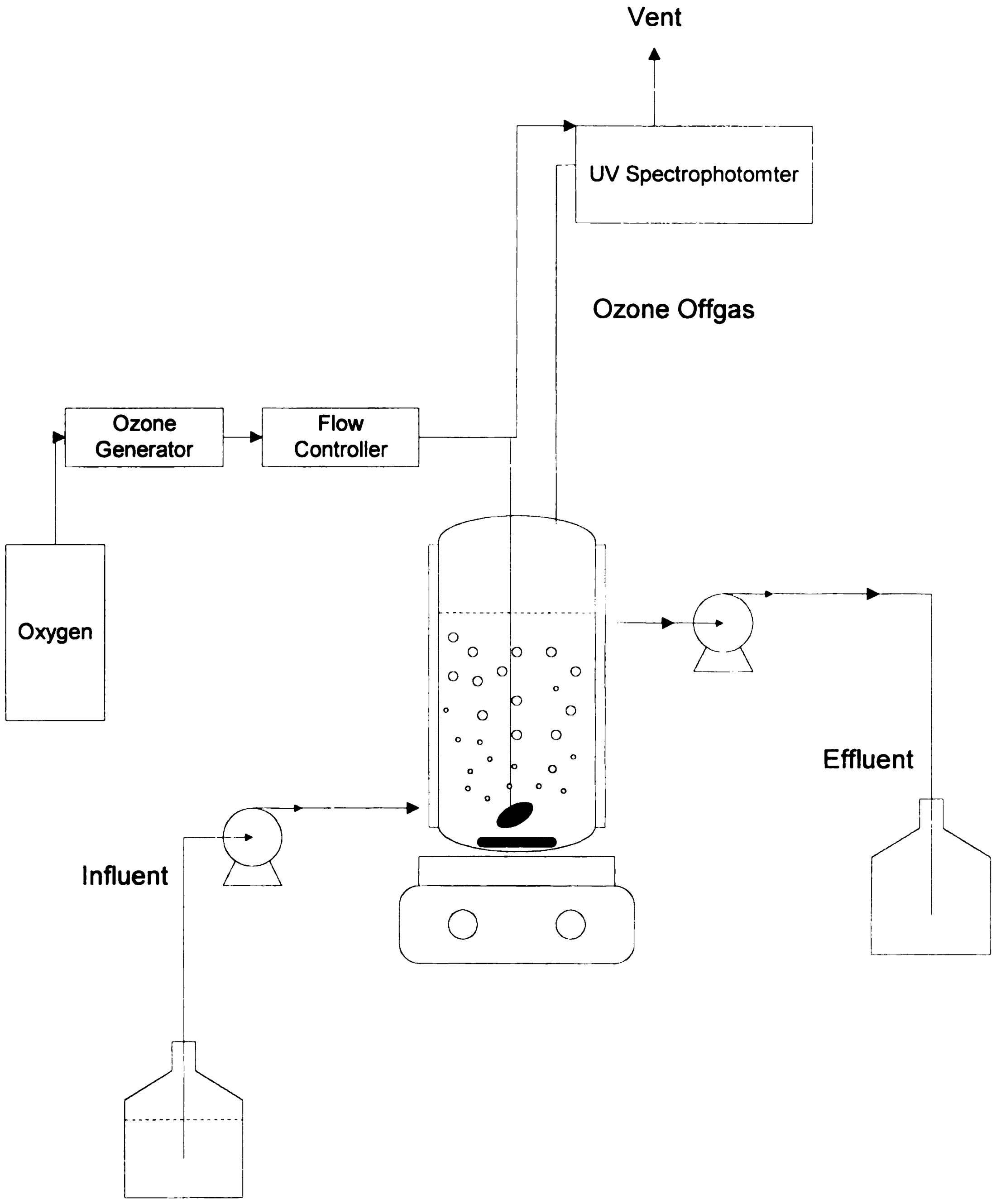


Figure 4.2. Schematic diagram of continuous semi-batch ozone reactor.

Phase III .

The same reactor as that used in Phase II experiments was used. Appropriate concentrations of additive, such as hydrogen peroxide and bicarbonate, were continuously be added with influent water. The parameters for analysis include residual additive concentration, TOC, residual ozone concentration, UV254, AOC, ketoacids (glyoxylic acid, pyruvic acid and ketomalonic acids), SDS THMs, and SDS HAAs.

4.2. Water sources and materials

The water sources tested in this study are followings:

Lake Erie (Monroe, MI) and Lake Lansing (Haslett, MI) water. Lake Erie water samples were taken from Monroe Water Treatment Plant intake.

The TOC values of the Lake Erie and Lake Lansing water are around 2.0 and 9.5 ppm, respectively. Thus, the experimental results could obviously show the effect of biodegradability on ozonation over the wide range of TOC. The compounds, used as OH radical scavengers, were bicarbonate and carbonate ion. The compounds, added as initiators/promoters were phosphate ion, and hydrogen peroxide.

The characteristics of water quality on the Lake Erie and Lake Lansing are presented in Table 4.1.

Table 4.1. Characteristics of Lake Erie and Lake Lansing water.

	Lake Erie	Lake Lansing
TOC	2.0	9.5
pH	7.8	8.0
Alkalinity (mg/L as $CaCO_3$)	90	140

4.3. Analytical method

Gas-Phase ozone analysis: The concentration of generated gaseous ozone was measured at UV 254 nm with a UV/Vis spectrophotometer (Milton roy Genesis-5). An extinction coefficient of 3000 $M^{-1}cm^{-1}$ at 254nm (Hoigné et. al, 1988) was used for calculating ozone concentrations.

Dissolved ozone analysis: Dissolved ozone was measured with the indigo method (Standard Method, 1995) or an amperimetric ozone analyzer (Orbisphere Laboratories, Geneva, Switzerland).

Residual additives:

- Hydrogen Peroxide: Low concentration of hydrogen peroxide was measured using DPD method (Hoingé, 1988), using peroxidase catalyzed oxidation of N,N-diethyl-p-phenylendiamine (DPD).

- Bicarbonate/Carbonate : Bicarbonate and carbonate ion concentration were determined by acid titration according to Standard Method (1995)

Natural Organic Matter (NOM): Due to the complexity of natural organic matter, the carbon concentration of the NOM commonly represents its concentration. In order to measure the organic carbon concentration, the samples were filtered by 0.45 μm glass-fiber filter, and then acidified with phosphoric acid (85 %) to lower pH to less than 4. The solution was purged with high purity helium gas (99.999%) for 5 minutes to avoid the presence of inorganic carbon in the sample. The samples were injected into TOC analyzer (OI Analytical Model 1010).

UV absorbance: UV absorbance was measured at a wavelength of 254 nm with a Milton Roy Genesis-5 spectrophotometer using an 1 cm quartz cell.

PCBA (*p*-chlorobenzoic acid): PCBA was analyzed by HPLC (Perkin Elmer series 200) with a UV-vis detector (Waters 2487) at 234 nm. Acetonitrile and D.I. Water mixture (60:40 wt %) were used for the HPLC eluent with flow rate of 1.0 ml/min.

Assimilable Organic Carbon (AOC): The procedure for the AOC method is described elsewhere (Background section and van der Kooji et al., 1982). A sample was heated at 60 °C for 30 min to inactivate bacteria originally present in the water. The pure cultures, *Pseudomonas fluorescens* P17 and *Spirilium* NOX, were then inoculated into sample. The plate count was determined after 7 days of incubation (20 °C). The yield coefficient of *Pseudomonas fluorescens* P17 and *Spirilium* NOX was established as 4.1×10^6 CFU P-17/μg acetate-C, and 1.2×10^7 CFU-NOX/μg acetate-C (Standard Method, 1992). For quality control, the yields were determined in the study to be 4.4×10^6 CFU P-17/μg acetate-C, and 1.6×10^7 CFU-NOX/μg acetate-C. Even though the yields were different

than literature values, the literature values were used in this study since the difference was insignificant.

Ketoacids: Glyoxylic acid, pyruvic acid and ketomalonic acids were monitored as ozonation by-products. Those compounds were determined by the PFBHA-diazomethane double derivatization procedure followed by GC/ECD equipped with DB-5 column (J&W Scientific, Folsom, CA) (Xie and Reckhow, 1992). The diazomethane was generated in the laboratory for every analysis. The generation method for diazomethane and a detailed procedure for ketoacids analysis are presented in Figure 4.3 and Figure 4.4.

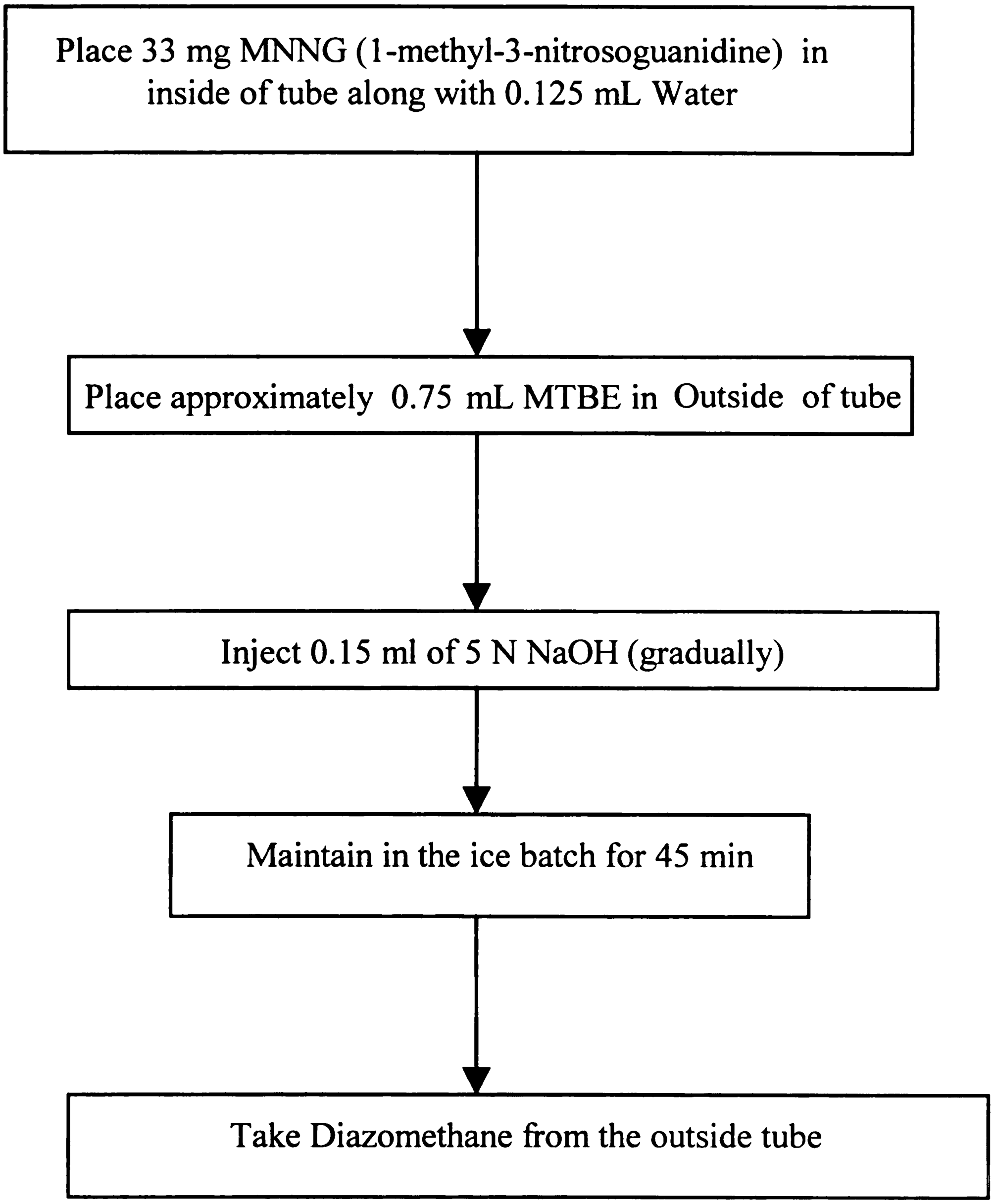


Figure 4.3..Procedure for generating diazomethane.

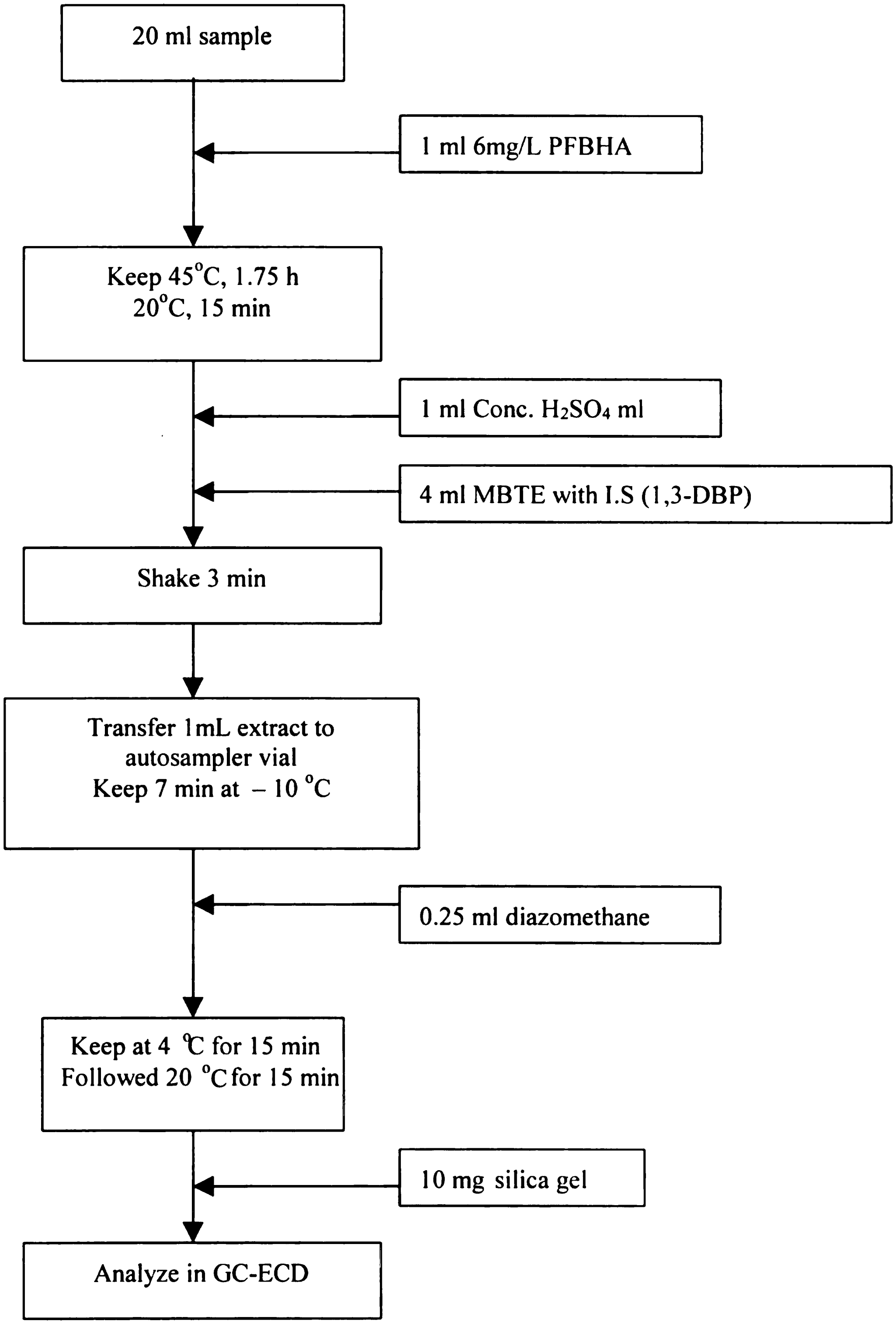


Figure 4.4. Procedure for ketoacids analysis

SDS THMs : The procedures for Simulated Distribution System THMs were employed. The samples were dosed a chlorine concentration which would allow residual concentration in the range of 0.5 to 2 mg/L after 48 hours incubation at room temperature (Standard Method 2350). The sample was prepared according to THMFP method in Standard Methods (1995). Extracted samples were analyzed by gas chromatography (DB-624 column, J&W Scientific, Folsom, CA) equipped with ECD. The oven temperature was programmed from 50 °C increasing to 150 °C with a rate of 10 °C/min. the carrier flow was 12.0 mL/min. The injector temperature and detector temperature were 275 and 350 °C, respectively

SDS HAAs : Samples were prepared according to the HAA method (Standard Methods ,1995). A Perkin Elmer Autosystem gas chromatograph (DB-1 column, J&W Scientific, Folsom, CA) equipped with an electron capture detector was used in these analyses. The oven temperature was programmed to hold 20 minute at 35 °C increasing to 250 °C with a rate of 10 °C/min. the carrier flow was 1.0 mL/min. The injector temperature and detector temperature were 160 and 350 °C, respectively. Detail procedure for HAAs is shown in Figure 4.5.

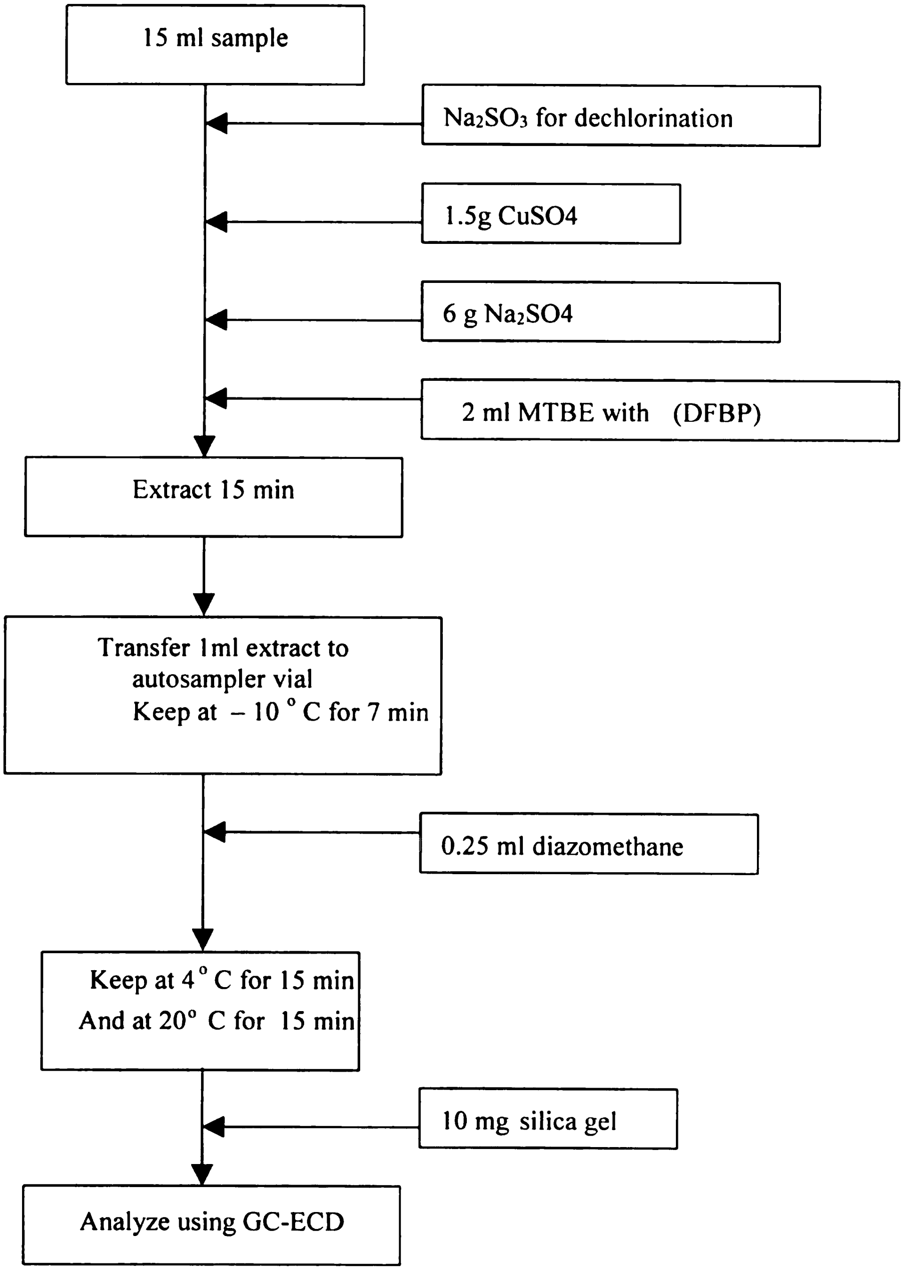


Figure 4.5. Procedure for HAAs analysis.

Other analyses: pH was measured by pH meter. The temperature of solution was measured by thermometer.

5. EFFECT OF OZONE DOSAGE

5.1 R_{CT} values for ozone dosages.

In order to investigate the effect of ozonation pathways on the formation of both DBPs and biodegradable compounds, it is necessary to determine the ratio of ozone/OH radical concentrations, which can be used to confirm the importance of the two mechanisms. The experiments were conducted by using the method developed by Elovitz and von Guten (1997) to determine $[O_3]/[OH\cdot]$ concentration ratio using PCBA (*p*-chlorobenzoic acid) as OH radical probe. They developed a term, R_{CT} value, i.e., the ratio of $[OH\cdot]/[O_3]$.

The RCT values were determined in two different water sources: those from Lake Lansing and Lake Erie (at the Monroe Water Treatment Plant intake). Each water source was tested to evaluate the R_{CT} value. As shown in Figure 5.1, the R_{CT} value increases as ozone dosage increased. In other word, the production of OH radical increases with increasing ozone dosage. This is due to the high concentration of ozone which auto-decomposes to produce the OH radical. Another reason for increasing OH radicals as increasing ozone concentration is due to the differences of NOM characteristics and/or background water characteristics of the water sources. Since NOM plays a promotion and inhibition role for ozone decomposition and inorganics present in water can scavenge OH radicals, these roles affect for the production of OH radical during ozonation.

In order to compare the effect of NOM on the OH radical and ozone reactions, the R_{CT} values were also determined at the same alkalinity (140 mg/L as $CaCO_3$) to exclude the effect of background OH radical scavenger (Figure 5.1). To accomplish this, the alkalinity of Lake Erie water was increased to that of Lake Lansing water. First, comparing the R_{CT} values of Lake Erie water at different alkalinities indicates that the increases in the R_{CT} values with ozone dosage in low alkalinity (90 mg/L as $CaCO_3$) was greater than that in waters of high alkalinity (140 mg/L as $CaCO_3$) (See Figure 5.1). Thus, it can be concluded that the reaction of NOM with OH radical is rather slow compared to the rate of reaction with bicarbonate ion and, at the high ozone dosage, the OH radical produced from ozone decomposition reacts predominantly with bicarbonate ions.

The alkalinity of Lake Erie water was increased so that R_{CT} values could be compared for Lake Erie and Lake Lansing waters at the same alkalinity (140 mg/L as CaCO3). A higher OH radical ratio was found in the Lake Erie water than in Lake Lansing water and no statistically significant differences (at a 95 % confidence interval) in RCT values of Lake Lansing water are observed as the concentration of ozone increased. The result indicates that the NOM present in Lake Erie water is a more effective promoter of OH radicals than is that in Lake Lansing water. Thus, not only low alkalinity but also this phenomenon results in the high Rct values measured in Lake Erie water. Consequently, it appears that the NOM of Lake Erie reacts with OH radicals more slowly than does the NOM present in Lake Lansing water. This suggests that the extent to which OH radicals react with OH radical scavengers increases as ozone dosage increases and that the NOM of Lake Erie water has the capability to promote a greater extent of OH radical formation than does that of Lake Lansing.

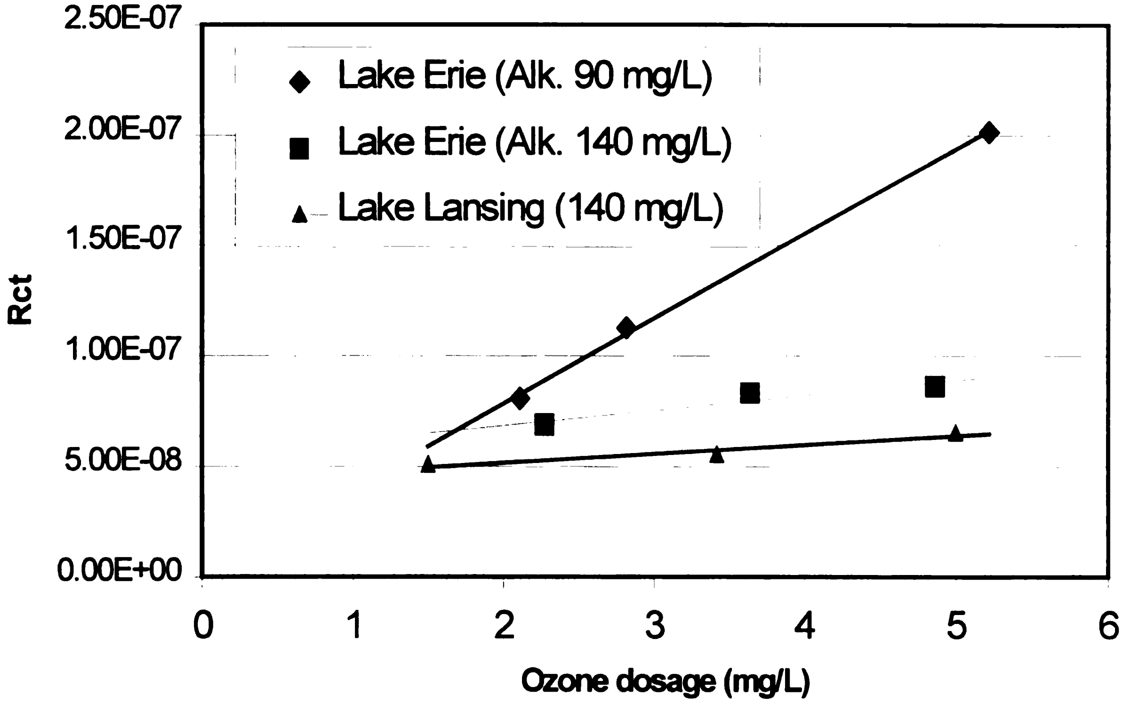


Figure 5.1. Effect of ozone dose on R_{CT} values (TOC: 2.0 mg/L for Lake Erie and 9.5 mg/L for Lake Lansing).

5.2. Formation of ketoacids with ozone dosage

Low molecular compounds form during the reaction with ozone and NOM. Richardson et al. (1999) and Gracia et al. (1996) identified 110 different organic compounds, mainly carboxylic acids, aromatics, hydrocarbons, aldehydes, ketones, and furan-carboxylic acids, that formed from the reaction of ozone with humic substances. The concentrations of ketoacids, as a portion of the ozonation by-products, were observed to be much higher than that of aldehydes (Griffini et al., 1999; Carlson and Amy, 1998; Xie and Reckhow, 1992). The concentrations of the ketoacids (gloxalic acid, pyruvic acid and ketomaloinc acid) increased with increasing ozone dose (Griffini et al., 1999; Xie and Reckhow, 1992). The formation of aldehydes and ketoacids, easily biodegradable compounds, has been correlated with the formation of BDOC (Griffini et al., 1999). This result implies that the aldehydes and ketoacids would be appropriate indicators of biologically stability. It is believed that the formation of ketoacids is favorable when the direct ozone reaction predominates (Griffini et al., 1999).

Based on the experimental results (Figure 5.2), the formation of ketoacids significantly increased during the ozonation of both water sources. The increase in the concentration of ketoacids with increasing ozone concentration was greater in Lake Lansing water which has a higher NOM concentration than Lake Eire water. Thus, it appears that the formation of ketoacids is also influenced by NOM concentration. Another factor affecting the formation of ketoacids was that the molecular ozone reaction in Lake Lansing was more important than that observed in Lake Erie water. According to the results from R_{CT} experiments (Figure 5.1), the NOM of Lake Lansing water promoted

OH radical less effectively than did the NOM in Lake Erie water. Moreover, the reaction of the OH radical with NOM in Lake Lansing water was restricted due to high alkalinity. The formation of ketoacids in Lake Lansing water leveled off at high ozone dosages while the formation of ketoacids in Lake Erie water continued to increase gradually even at high concentrations of ozone. This is thought to be the result of the NOM from Lake Lansing reacting more quickly at the early stages of ozonation (than does the NOM from Lake Erie water). After the initial reactivity of NOM, that which remains is essentially non-reactive with molecular ozone. On the other hand, the NOM from Lake Erie water, as it appears from the R_{CT} experiments, appears to react slowly and more continuously with ozone. These characteristics of NOMs favor the formation of ketoacids.

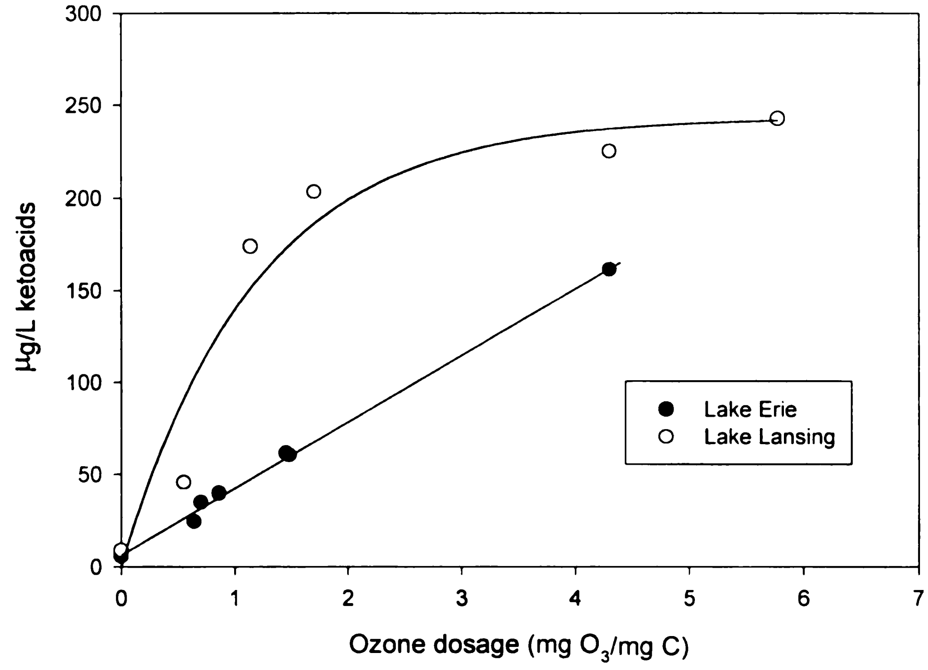


Figure 5.2. Formation of ketoacids for ozone dosages (TOC: 2.0 mg/L in Lake Erie, 9.5 mg/L in Lake Lansing, HRT: 12.5 min, Temperature: 25 °C).

5.3. Formation of AOC for ozone dosages.

AOC (Assimilable Organic Carbon) was measured by a method developed by Van der Kooji et al. (1982) and modified by adding inorganic nutrients, i.e., nitrate, phosphate, to the samples. These inorganic nutrients were added since they, especially phosphorus, are often the limiting factor for microbial growth in treated drinking water (Miettinen et al., 1999).

As described in the previous section, it is expected that AOC will increase with increasing prevalence of the molecular ozone reaction over the OH radical reaction. The formation of AOC during ozonation might be explained that molecular ozone produces hydrophilic compounds by the reaction with aromatic ring structures. Masten et al. (2000) found that the reaction of molecular ozone reaction with DEET(N,N-diethy-m-toluamide), which has an aromatic ring, produced several hydrophilic as by-products. Yao et al. (1998) found that the reaction mechanism of pyrene with molecular ozone attacks the double bond, causing ring cleavage of pyrene at the 4,5 (or 9,10) position. This results in formation of various carboxylic acids and aldehydes.

The AOC determination is based on culturing bacteria that utilize groups of specific compounds such as carboxylic acids or carbohydrates (van der Kooji, 1985). NOX, one of bacteria used for determination of AOC is capable of oxidizing methyl pyruvate, acetic acid, formic acid, DL-lactic acid, α-hydroxybutyric acid, α-ketobutyric acid, propionic acid, bromosuccinic acid and D-alanine. Of these compounds, formic acid, α-hydroxybutyric acid and α-ketobutyric acid are not utilized by P17. It was concluded that NOX is especially adept in the utilization of carboxylic acids (Charnock and KjØnnØ, 2000).

As shown in Figure 5.3, the formation of AOC increased as ozone dosage increased. The formation of AOC in Lake Lansing water leveled off at high ozone dosages (approximately 1 mg ozone/mg C) whereas the formation of AOC in Lake Erie water gradually increased even at high concentrations of ozone. The formation of AOC follows the same trends as that observed with ketoacids. Thus, it also can be concluded that the AOC formation predominates when the molecular ozone reaction is preferred over OH radical reactions.

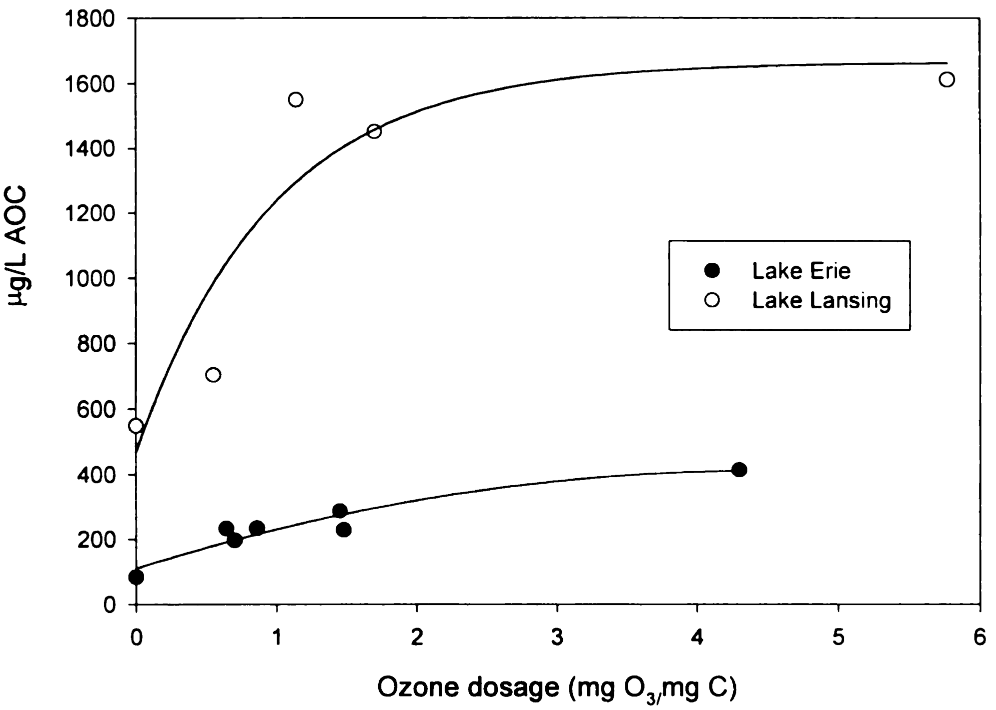


Figure 5.3. Formation of AOC for ozone dosages (TOC: 2.0 mg/L in Lake Erie, 9.5 mg/L in Lake Lansing, HRT: 12.5 min, Temperature: 25 °C).

5.4. Formation of THM and HAA for ozone dosages.

THMs (chloroform, dichlorobromoform, dibromochlroform, bromoform) and HAAs (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid) were measured as representative disinfection by-products.

The effect of ozone dosage on THM formation is shown in Figure 5.4. The formation of THMs decreased slightly as ozone dosage increased. Although the concentration of THM decreased with increasing $[OH\cdot]/[O_3]$ ratio, due to the reactivity of molecular ozone with NOM, especially with aromatic rings, (Yao et al., 1998), the reaction rate of NOM with molecular ozone increased as the ozone dosage increased. After the initial reactivity of NOM, that which remains is essential non-reactive with molecular ozone. NOM would, then, react with the OH radical. It is thought by Reckow et al. (1986) that the reaction of chlorine with NOM is less reactive than molecular ozone reaction with NOM. Thus, based on these and the R_{CT} experiments, THM formation appears to prevail when the molecular ozone reaction predominates (over the reaction of NOM with OH radicals).

Reckow et al. (1986) explains the formation pathway of DBP precursors on ozonation. Since both ozone and aqueous chlorine can act as strong electrophiles in such systems (Decoret et al., 1984; Morris, 1975), molecular ozone would destroy nucleophilic centers otherwise attacked by chlorine (e.g. highly activated aromatics such as dihydroxy benzenes). In contrast, OH radicals are more non-selective than molecular ozone and chlorine. Hence, it presumed that molecular ozone alters the moieties in the humic molecule which react with chlorine to produce THMs to a far greater extent than does the OH radical (Reckow et al 1986).

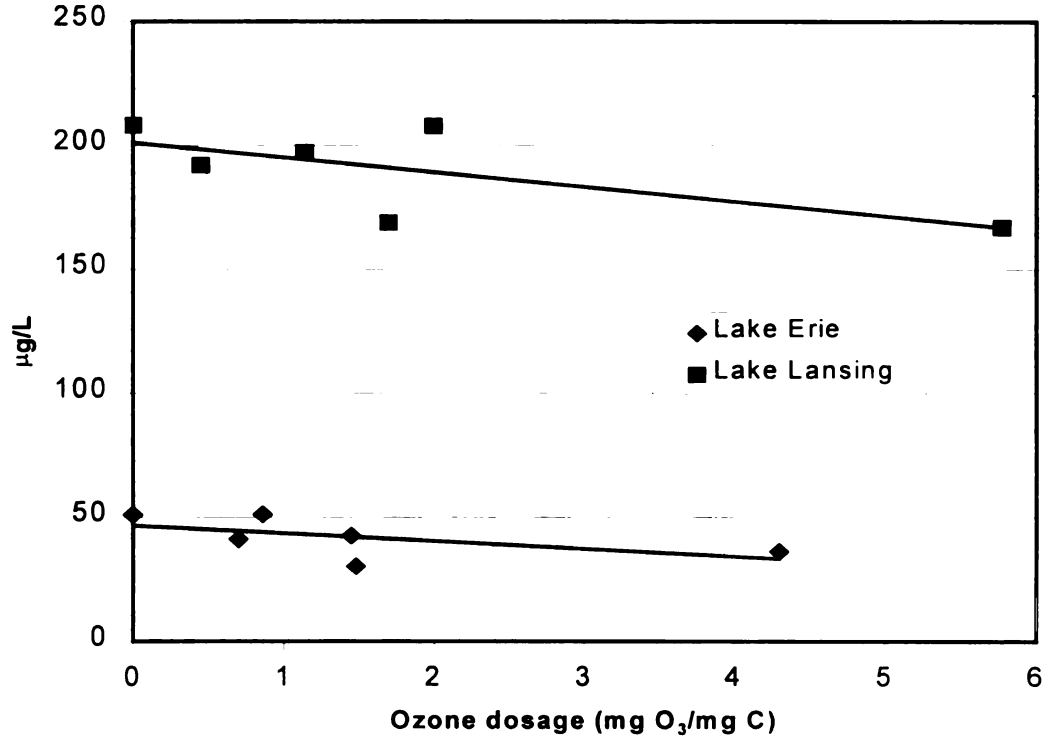


Figure 5.4. Formation of THMs on ozone dosages (HRT: 12.5 min, Temperature: 25 °C).

The formation of HAAs also follows similar trends compared with THM formation. (See Figure 5.5) This result indicates that THM and HAA formation follows similar reaction mechanisms involving chlorine and NOM.

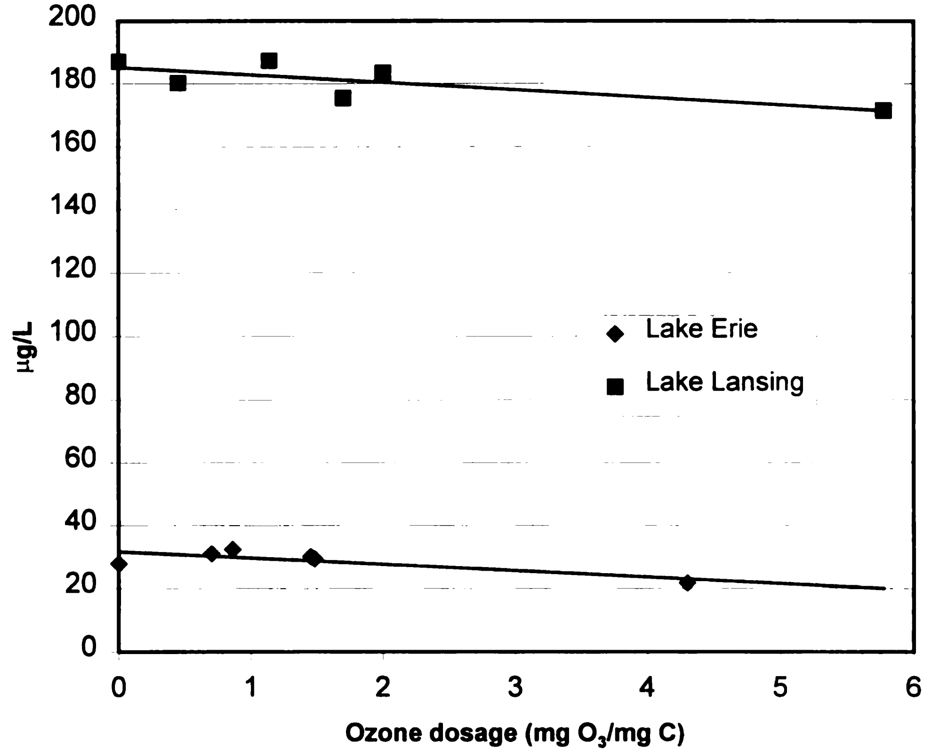


Figure 5.5. Formation of HAAs for ozone dosages (HRT: 12.5 min, Temperature: 25 °C).

6. Effect of Hydraulic Retention Time (HRT)

6.1. Effect of HRT on R_{CT} values.

In order to investigate the effect of the ratio of $[O_3]/[OH\cdot]$ on the formation of ketoacids, AOC, and DBPs formation potential, the concentrations of OH radicals in each water sources were investigated in a CSTR (since the experiments for the formation of ketoacids, AOC, and DBPs was conducted in CSTR) based on the R_{CT} values obtained in batch reactor. The effect of HRTs using an ozone dosage 1mg O_3/mg C was studied. Based on the R_{CT} values obtained in the batch studies (Figure 5.1), the OH radical concentrations during the ozone decomposition were determined (See Table 6.1). The calculated concentration of OH radical and the measured concentration of ozone was used for determine R_{CT} value with respect to time. The values of R_{CT} were $8.06 \times 10^{-8} \pm 7.73 \times 10^{-11}$ and $4.8 \times 10^{-8} \pm 3.61 \times 10^{-14}$ in Lake Erie water and Lake Lansing Water, respectively (See Table 6.1.). Comparing to the values presented in Table 6.1, it is apparent that the concentrations of OH radical were greater in Lake Erie water than that in Lake Lansing water. This supports previous results obtained when considering the effect of ozone dosage; that is, the NOM of in Lake Erie water has a greater capability to promote OH radical formation than does that of Lake Lansing water.

As shown in Figure 6.1 and 6.2, although the concentration of OH radicals and molecular ozone decrease with ozonation time, the ratio of $[OH\cdot]/[O_3]$ was almost constant during the ozonation process due to the significantly high concentrations of ozone compared to that of OH radical (a factor of 6 to 7).

Although the changes in the R_{CT} values with varying experimental conditions were small, the half-life of the OH radical is increased by a factor of approximately three between the maximum and minimum values during ozonation (See Table 6.1). Thus, it appears that, such small changes in the concentration and half-life of the OH radical are critical for the ozonation reaction. However, as expressed in Eq. 6.1, if the value of $k_{O3}[O_3][NOM]$ is greater than $k_{OH}[OH][NOM]$. The increased concentration of OH radical at high HRTs insignificantly affects the ozonation reaction involving NOM.

$$k_{O_3}[O_3]\bullet[NOM] \geq k_{OH}[OH]\bullet[NOM] \qquad \text{Eq. 6.1.}$$

Table 6.1. Comparison of R_{CT} values and half-life of OH radical in Lake Erie water and Lake Lansing water.

	Lake Erie				Lake Lansing			
Time (Sec)	Ozone [M]	[OH] x 10^{12} [M]	R_{CT} x10^{-8}	Half-life of OH radical (Sec)	Ozone [M]	[OH] x 10^{12} [M]	R_{CT} x10^{-8}	Half-life of OH radical (Sec)
0	4.2E-05	0	0		1.028E-04	0	0	0
60	2.49E-05	2.00	8.06	3.45E-07	8.91E-05	4.28	4.80	4.28E-05
120	2.08E-05	1.67	8.06	4.14E-07	7.39E-05	3.55	4.80	3.55E-05
180	1.74E-05	1.40	8.06	4.94E-07	6.15E-05	2.95	4.80	2.95E-05
240	1.49E-05	1.20	8.06	5.77E-07	5.47E-05	2.62	4.80	2.62E-05
300	1.3E-05	1.04	8.08	6.64E-07	4.73E-05	2.27	4.80	2.27E-05
360	1.12E-05	0.90	8.06	7.69E-07	4.08E-05	1.96	4.80	1.96E-05
420	9.51E-06	0.76	8.06	9.04E-07	3.53E-05	1.69	4.80	1.69E-05
480	8.17E-06	0.65	8.06	1.05E-06	3.04E-05	1.46	4.80	1.46E-05
540	7.14E-06	0.57	8.06	1.20E-06				
600	5.36E-06	0.43	8.06	1.60E-06				

According to previous research (Westerhoff et al. 1999), the reaction rate of OH radical with NOM was determined as 3.6 x 10^8 L (mol C)$^{-1}$ s^{-1} (assuming a mass of 12 g C per mole C) which corresponds to 6.0x10^4 s^{-1}, and 3.0x10^5 s^{-1} for Lake Erie water and Lake Lansing water, respectively. The concentration of OH radicals was approximately

10^{-12} M in both Lake Erie water and Lake Lansing water. In contrast, the concentration of ozone was 10^{-3} M. Thus, since the reaction rate of ozone with NOM is greater than 10^{-3} s^{-1}, such a small changes in R_{CT} values during ozonation time does not affect the reaction rate of ozonation with NOM.

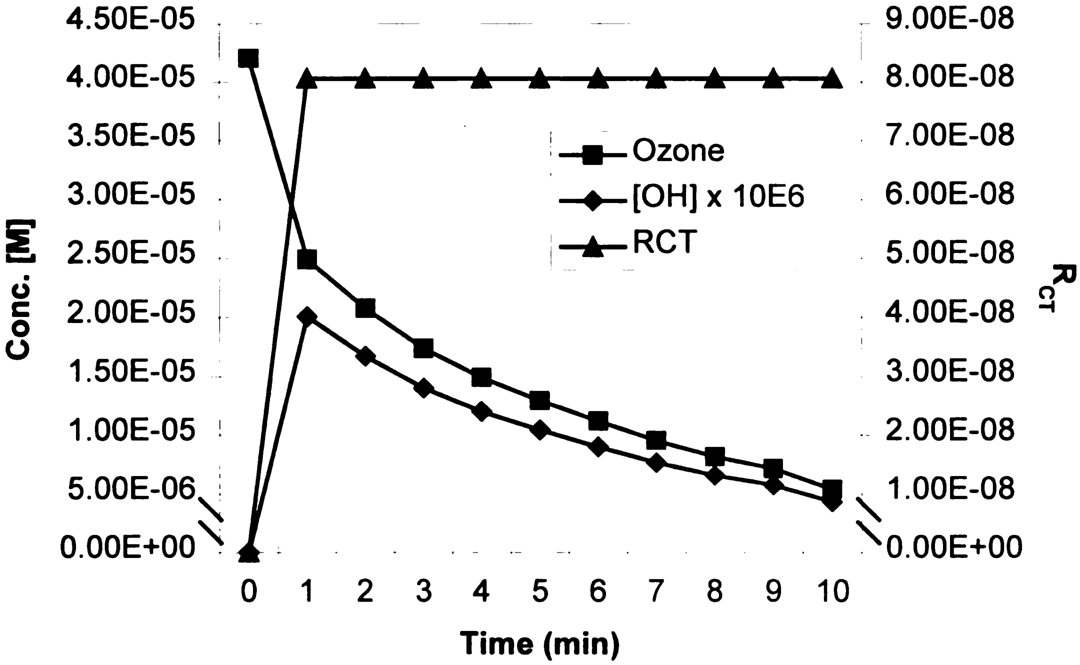


Figure 6.1. The effect of HRTs on Ozone, OH radical concentration and R_{CT} values in Lake Erie water (Ozone dosage: 1mg O_3/mg C, Temperature: 12.5).

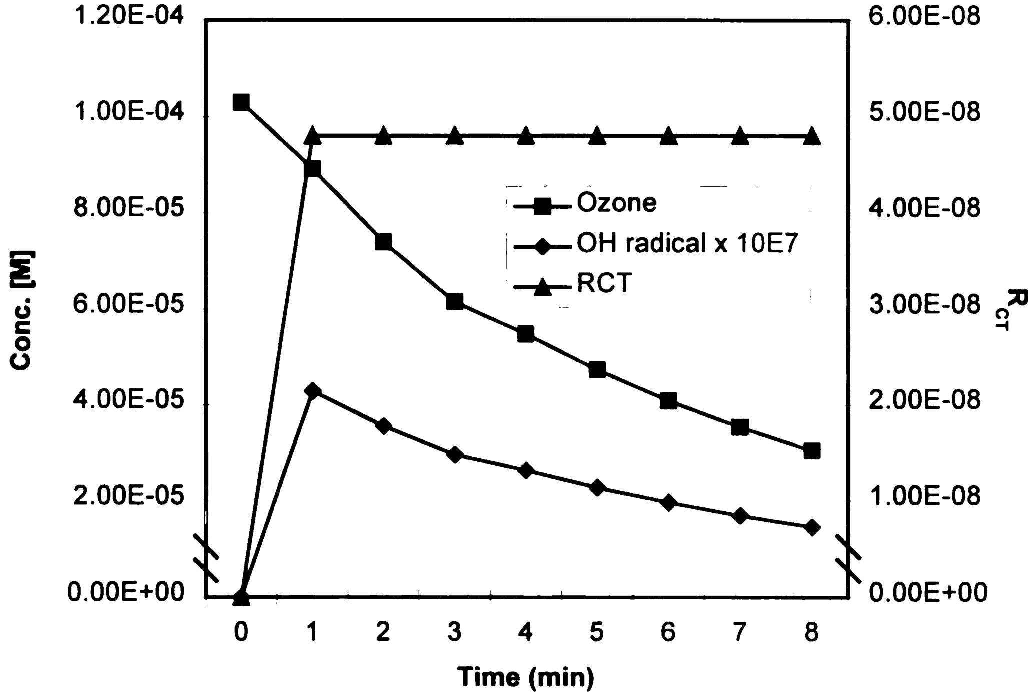


Figure 6.2. The effect of HRTs on Ozone, OH radical concentration and R_{CT} values in Lake Lansing water (Ozone dosage: 1 mg O_3/mg C, Temperature 25 °C).

6.2. Formation of ketoacids for HRTs

As shown in Figure 6.1 and 6.2, the ratios of OH radical concentration to molecular ozone concentration (R_{CT}) were constant for the HRTs studied. However, as shown in Figure 6.3, the formation of ketoacids in both water sources increased unexpectedly as the HRT in CSTR increased. It is thought that the formation of ketoacids depends on reaction time as well as R_{CT} value because the reaction of NOM with ozone to form ketoacids would be influenced by not only the concentration of ozone but also reaction time.

Although the R_{CT} values are constant with HRTs, the concentration of OH radical follows the trends for ozone concentration. The rate of formation of ketoacids in Lake Erie water was suppressed at short retention times due to high concentration of OH radical or the destruction of ketoacids by the OH radical. On the contrary, in Lake Lansing water, the concentration of ketoacids increased linearly with HRT increased. Thus, the high concentration of the OH radical present at short HRTs may play a role in suppressing the formation of ketoacids.

Consequently, high concentrations of OH radical at short HRTs results in a suppression of the formation of ketoacids in Lake Erie water. The reason that the concentration of ketocids in Lake Erie presents comparative low level even at low concentration of OH (at long retention time) is the low concentration of NOM in Lake Erie.

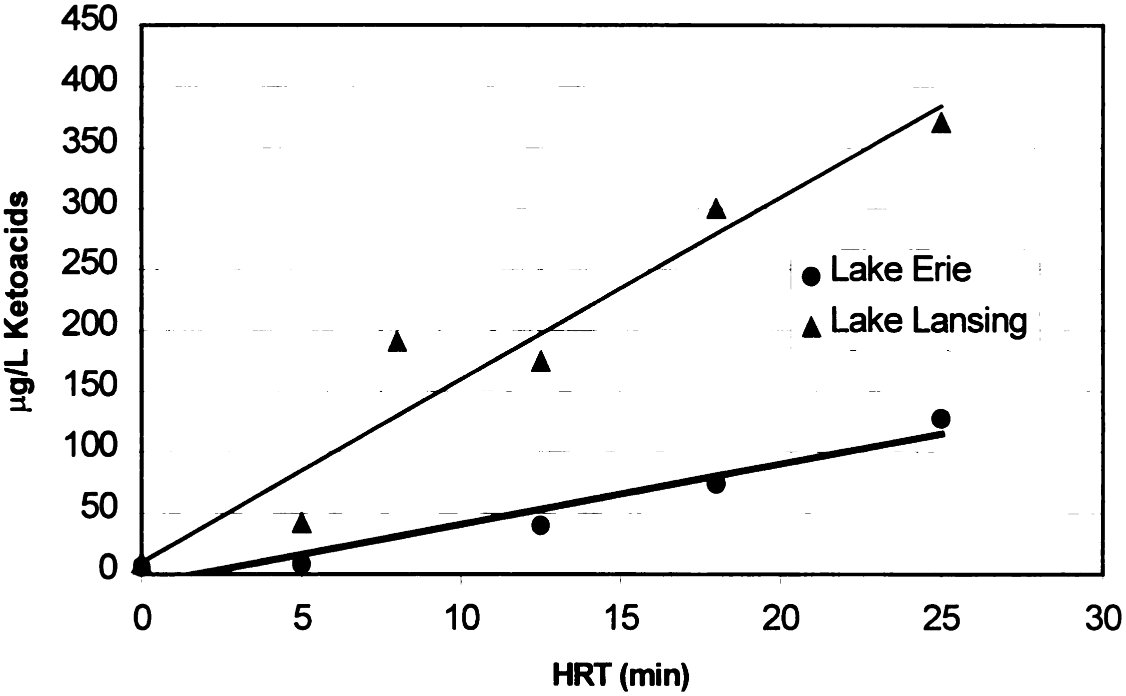


Figure 6.3. Formation of ketoacids for HRTs (Ozone dosage: 1 mg O_3/mg C,

Temperature: 25 °C).

6.3 Formation of AOC for HRTs.

Based upon consistency of the R_{CT} values with HRT, the concentration of AOC was expected to be constant with HRTs. As shown in Figure 6.4, the changes in AOC concentration with HRTs inversely followed trend in OH radical concentration, suggesting that the formation of AOC dependent on the R_{CT} values rather than the HRTs. The steady state AOC concentrations can be compared obtained in studying the effect of AOC with that obtained when investigating the effect of ozone dosage. In Lake Erie water, AOC concentrations of 400 µg/L could be achieved at HRT of 5 minute. However, at ozone dosage, less than 1 mg O_3/mg C, concentrations of approximately 200 µg/L were produced. In Lake Lansing water, AOC concentrations of 1600 µg/L could be achieved at HRT of 8 minute. However, at ozone dosage, less than 2 mg O_3/mg C, concentrations of approximately 1600 µg/L were produced.

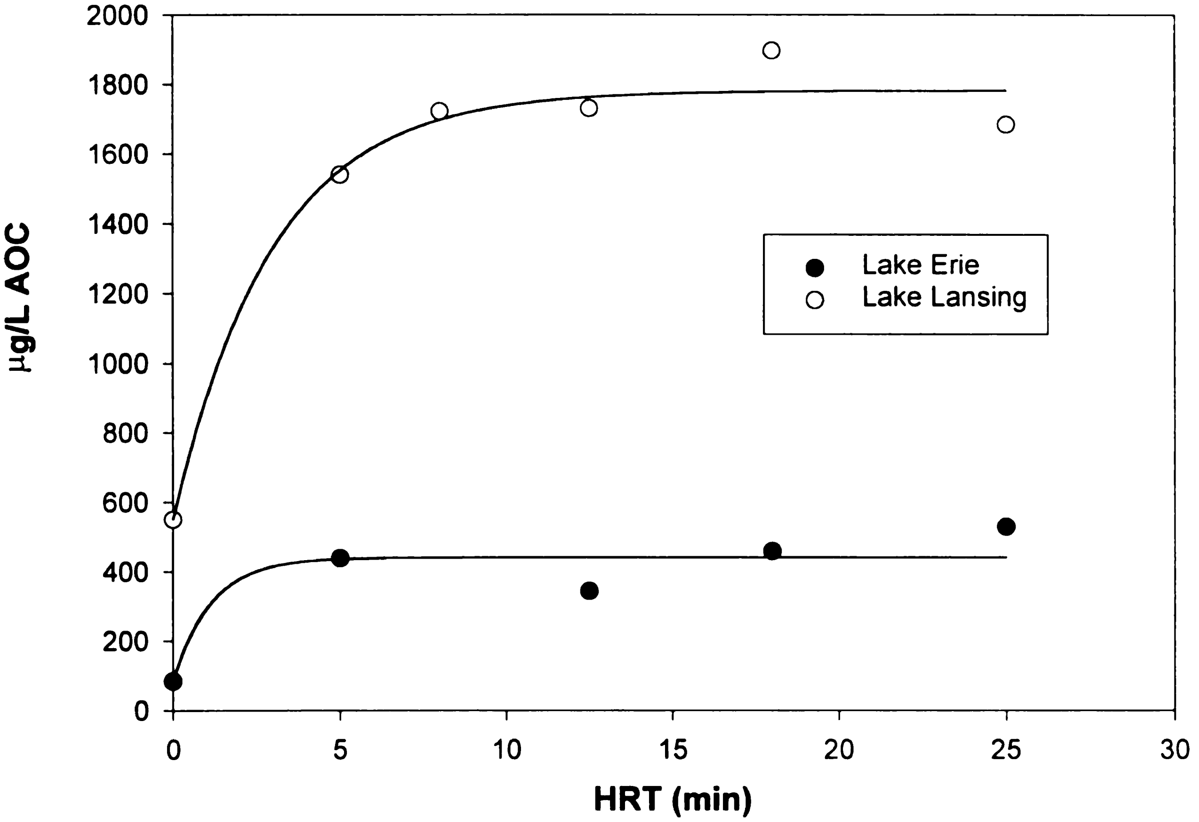


Figure 6.4. Formation of AOC for HRTs (Ozone dosage: 1 mg O_3/mg C, Temperature: 25 °C).

6.4 Formation of THMs and HAAs for HRTs.

The formation of THMs and HAAs was investigated for HRTs (See Figure 6.5 and 6.6). As HRT was increased, the concentrations of THMs decreased in Lake Lansing water while the concentration of THM in Lake Erie water remained essentially constant with increasing HRT. The changes in concentration of HAAs with HRT were statistically insignificant at a 95 % confidence interval. It appears that the formation of THM was independent of HRTs only in Lake Erie water. This indicates that the formation of THM precursors is influenced by the ratio of the concentration of OH radical and molecular ozone rather than reaction time. However, the formation of THM (except in Lake Lansing) and HAA was significantly influenced by R_{CT} ratios ($[OH\cdot]/[O_3]$) which were constant during the retention times.

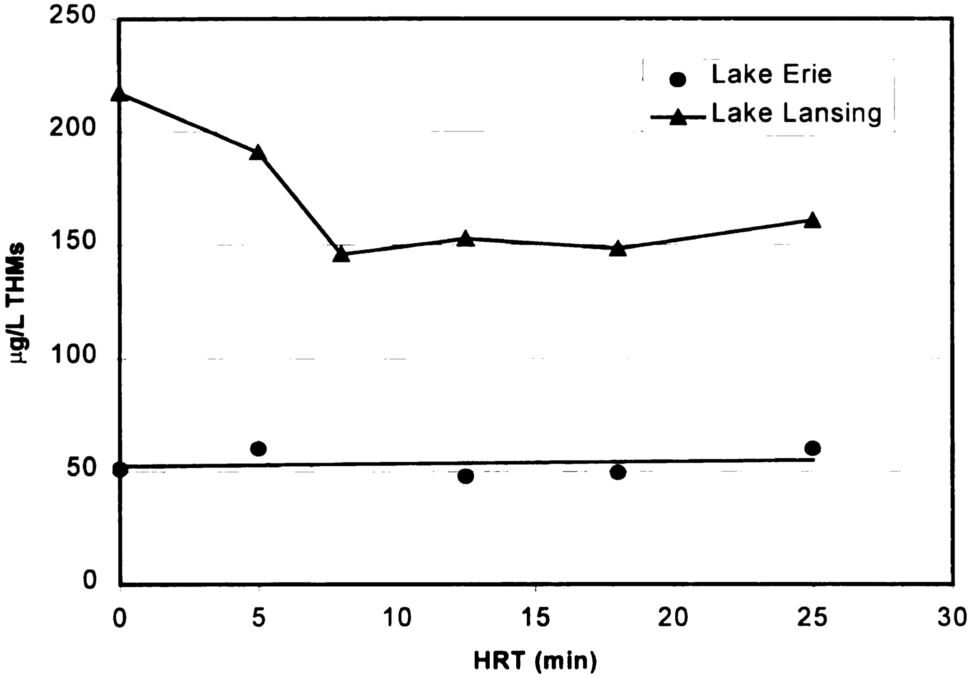


Figure 6.5. Formation of THMs for HRTs (Ozone dosage: 1 mg O_3/mg C, Temperature: 25 °C).

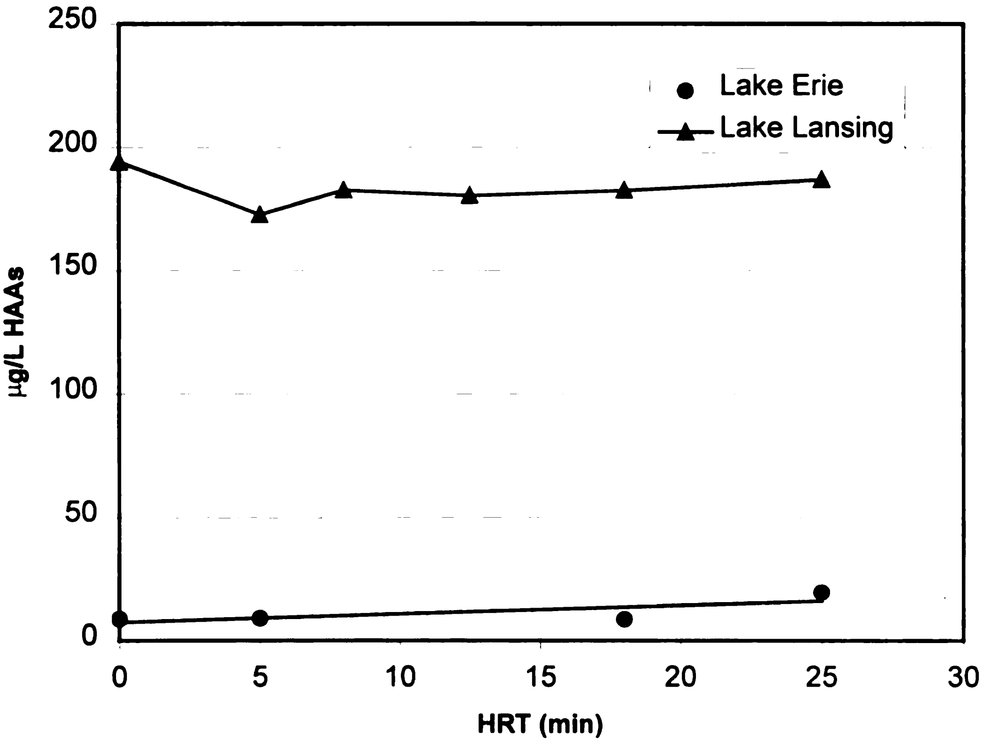


Figure 6.6. Formation of HAAs for HRTs (Ozone dosage: 1 mg O_3/mg C, Temperature: 25 °C).

7. EFFECT OF TEMPERATURE

7.1. R_{CT} values for temperatures

According to the Arrhenius law, elementary reaction rate increased with increasing temperature. Sotelo et al. (1987) showed that the ozone decomposition rate increased with increasing pH and temperature. The ozone initiation rate was negligible at pH below 3 at temperatures ranging from 10 - 40 °C.

Based on the elementary reaction of ozone decomposition, the OH radical concentration at steady state condition can be expressed by following equation (Eq. 7.1).

$$[OH]_{ss} = \frac{2(k_{O_3,OH^-}[O_3])_T[OH^-]_{ss} + (k_{O_3,NOM}[O_3])_T[NOM]}{(k_{HCO_3,OH})_T[HCO_3] + (k_{NOM,OH})_T[NOM]} \qquad \text{Eq. 7.1.}$$

The reaction rates that describe the initiation of ozone decomposition and the production of OH radicals are found in numerator in this equation will increase as temperature increases. The OH radical scavenger reaction rate (denominator of the equation) will also increase. Moreover, the rate of reaction of molecular ozone reaction with NOM also increases with increasing temperature.

When the Eq. 7.1 is divided by $[O_3]$, it can be expressed as R_{CT} term as Eq. 7.2.

$$\frac{[OH]_{SS}}{[O_3]} = \frac{2(k_{O_3,OH^-})_T[OH^-]_{SS} + (k_{O_3,NOM})_T[NOM]}{(k_{HCO_3,OH})_T[HCO_3] + (k_{NOM,OH})_T[NOM]} \qquad \text{Eq. 7.2.}$$

The activation energy and frequency factor of the reaction of bicarbonate with the OH radical was determined by Buxton et al (1988). Although the activation energy for the reaction of ozone with OH^- was determined by Hewes and Davison (1971), the frequency factor was not determined. However, since the rate constant of ozone with OH^- at 20 °C was determined (Stahelin and Hoigné, 1982), the reaction rate of ozone with hydroxide ion at various temperatures and and the frequency factor can be calculated (See Table 7.1. and Appendix). Since the parameters other than the rate constant for both ozone with NOM and OH radical with NOM have been determined, the R_{CT} value can be predicted if the values of $k_{O3,NOM}$ and $k_{NOM,OH}$ at the different temperatures are known.

Table 7.1. Activation energy and frequency factor of bicarbonate and ozone

	Activation energy (kJ mole^{-1})	log A
Bicarbonate†	21.2	12.8
Ozone††	70.5	72.1

Reference: †Buxton et al. 1988,

††Hewes and Davison, 1971

Based upon the literature values, the R_{CT} value was calculated at the temperatures at the various temperatures and compared to the R_{CT} values obtained in this study. Due to two unknown parameters ($k_{O3,NOM}$, $k_{NOM,OH}$), the calculation was attempted with the equation which is eliminated $k_{O3,NOM}$ term. Calculation of the rate constant of NOM with OH radical always resulted in negative values, (See Appendix) which increased as temperature increased. Thus, it appears that the role of NOM as a promoter of molecular ozone decomposition is more significant for OH radical production rather than is the role of NOM as an OH radical scavenger. Comparing the activation energy for the reactions occurring during ozonation in the water sources, temperature had the greatest effect on the rate constant of NOM with OH radical and on that for NOM with ozone were the most significantly increased as temperature increased (See Appendix).As a result, the OH radical production rate can be calculated if the characteristics (rate of promotion and inhibition) of the reaction of NOM with ozone and OH radical can be determined experimentally.

The experiments for R_{CT} were conducted in the batch reactor at temperature ranging from 5 to 35 °C (See Figure 7.1). Each experiment was maintained with constant temperature.

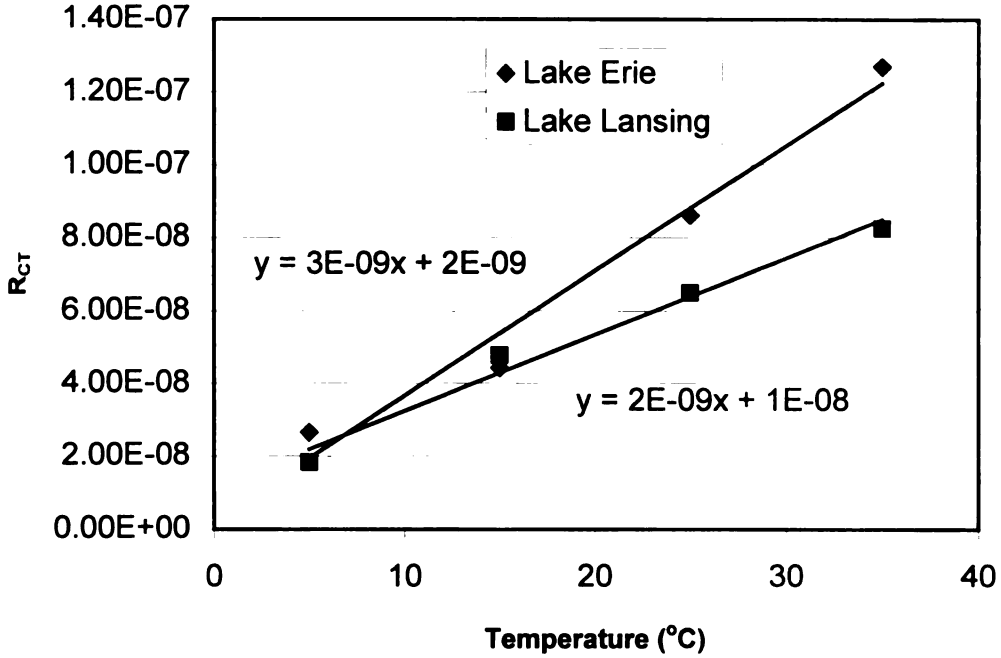


Figure 7.1. The effect of temperature on R_{CT} values (Ozone dosage: 1 mg O_3/mg C).

During ozonation, the OH radical concentration increased as temperature increased due to the acceleration of ozone decomposition with temperature (See Figure18). This result indicates that the denominator term of Eq. 7.2 does not increase as much as the numerator of Eq. 7.2 increases. As shown in Figure 7.1, the R_{CT} values for both water sources increased linearly as temperature increased. The increase of R_{CT} value of Lake Erie was greater than that of Lake Lansing. It is thought that either the activation energy of the OH radical with NOM of Lake Erie is less than that of Lake Lansing or that the promotion of the OH radical by NOM of Lake Lansing is less than that of Lake Erie.

7.2. Formation of ketoacids for temperatures.

Based on the R_{CT} values obtained from the batch reactor, experiments to determine the formation of ketoacids, AOC and DBPs were conducted in a CSTR at temperatures ranging from 5 to 35 °C at a fixed ozone dosage of 1 mg O_3/mg C and a HRT of 12.5 minute.

As shown in Figure 7.2, the formation of ketoacids appears to increase as temperature increased. Comparing the formation of ketoacids with R_{CT} values, the formation of ketoacids increased as R_{CT} values increased (See Figure 7.1 and Figure 7.2). The increase of the concentration of ketoacids follows the same order of magnitude increase with the increase of R_{CT} values. This result contradicts the hypothesis that AOC is formed preferentially by molecular ozone over the OH radicals, the results show different trend. The result indicates that the ozone molecule dose not always drive the formation of ketoacids.

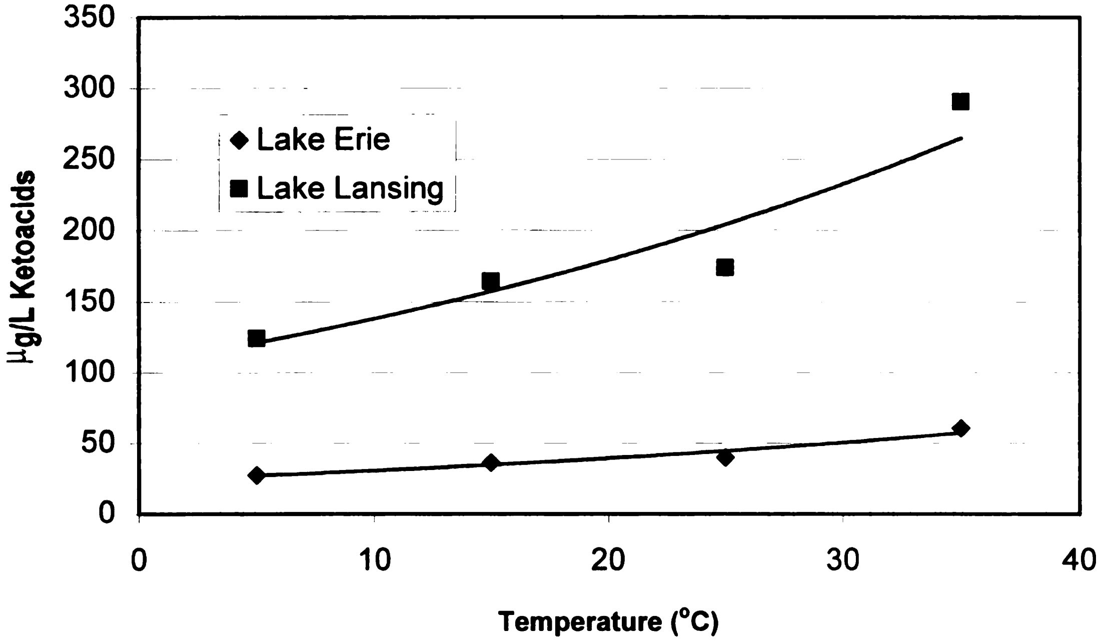


Figure 7.2. Formation of ketoacids for temperature (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min).

7.3. Formation of AOC for temperatures.

The concentration of AOC did not change as temperature increases as shown in Figure 7.3. Moreover, the formation of AOC in Lake Lansing decreased as temperature increased within the range 20 –35 ^{o}C in statistically at 95 % confidence interval. The formation of AOC in Lake Lansing water was unrelated to R_{CT} values. Although at high temperatures the rapid decomposition ozone results in the predominance of OH radical reactions, the complexity of ozone reactions with NOM results in less significant changes than expected.

As temperatures increased, ozone decomposition is accelerated so that higher concentrations of OH radical are expected, and were observed (Figure 7.1.). However, the reaction rates of the OH radical with both NOM and OH radical scavengers are also increased. Therefore, there may be competition reactions of OH radical with either NOM or OH radical scavengers. Regardless of their concentrations, each reaction obviously affects the overall ozone reaction since the specific increases in the reaction rate constant with respect to temperature is different.

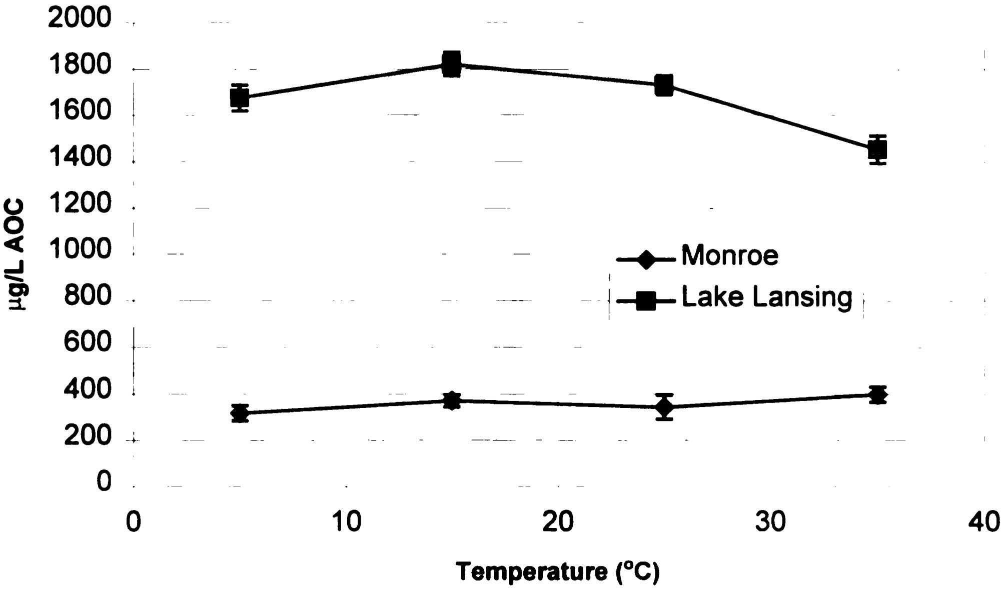


Figure 7.3. Formation of AOC for temperature (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5).

7.4. Formation of THM and HAA for temperatures.

The effects of temperature on the formation of THMs and HAAs are presented in Figures 7.4 and 7.5. The formation of THM and HAAs were independent of R_{CT} values, which increased as temperature increased. The reason is that as temperature changes, even though R_{CT} values change, the rate constant of molecular ozone with NOM and of OH radical with NOM also change. Hence, the reaction activity of NOM with molecular ozone and OH radical is difficult to compare at the each temperature. It may be possible to explain the formation of AOC at different temperature with same reason. The results also show that THM and HAAs can not be controlled by changing the water temperature.

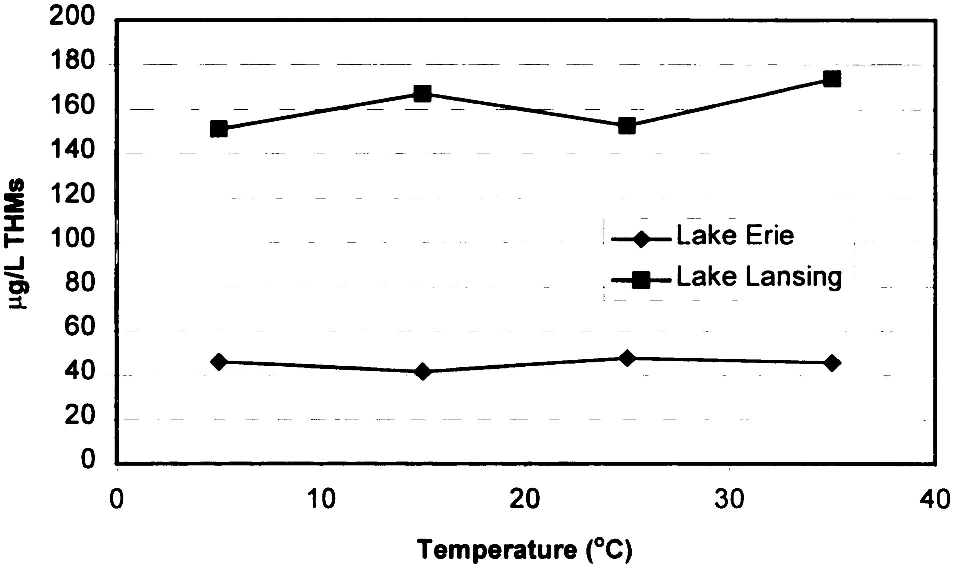


Figure 7.4. Formation of THMs for temperature (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5).

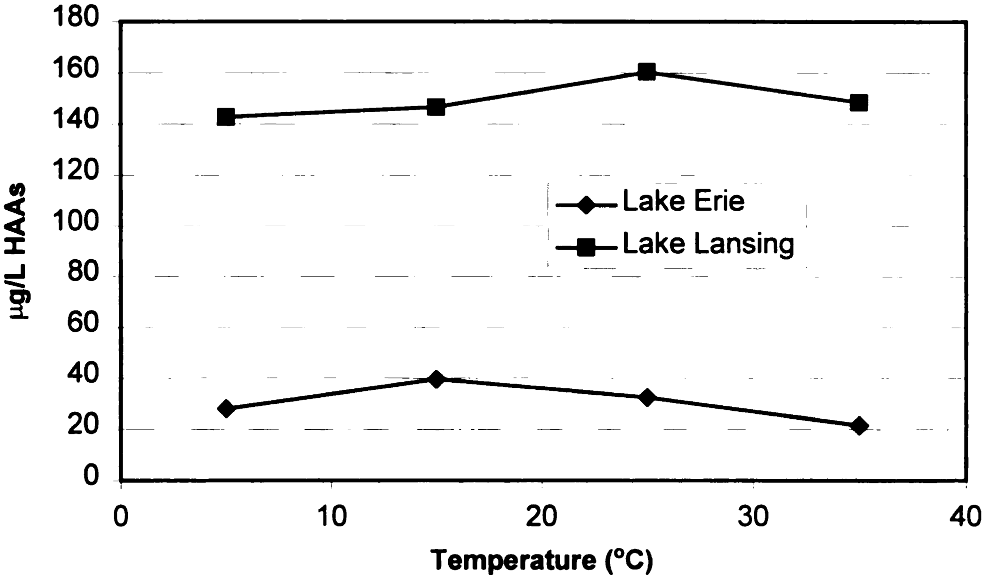


Figure 7.5 Formation of HAAs for temperature (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5).

8. EFFECT OF pH

8.1. R_{CT} values for pH

Varying the pH affects the ozone decomposition rate not only because the hydroxide ion concentration changes but also because the OH radical scavenging rate is altered since the concentrations of bicarbonate, carbonate ions and other radical species (ionic scavenging) are pH dependent. As such, the OH radical scavenging rate changes with pH even if the alkalinity is held constant. In order to maintain the same OH radical scavenging rate at the different pHs (from 2 to 10) to investigate the effect of pH on ozonation, the OH radical scavenging rate was calculated considering the alkalinity of raw water samples, the pH and calibrated by adding bicarbonate and phosphate ions, which are well characterized OH radical scavengers at each pH (Eq. 8.1). The pH was fist controlled within the range from 2 to 10 by adding sodium hydroxide and hydrochloric acid. The OH radical scavenging species were, then, added to water samples to achieve the desired OH radical scavenging rate. Based on the Eq. 8.1, the total scavenger capacities were set as $2.34 \times 10^5\ s^{-1}$, $3.38 \times 10^5\ s^{-1}$ in Lake Erie and Lake Lansing water, respectively.

$$\{Scavenging\,Capacity\} = k_{H_2CO_3,OH}[H_2CO_3] + k_{HCO_3^-,OH}[HCO_3^-] + k_{CO_3^{2-},OH}[CO_3^{2-}]$$
$$+ k_{H_3PO_4,OH}[H_3PO_4] + k_{H_2PO_4^-,OH}[H_2PO_4^-]$$
$$+ k_{HPO_4^{2-},OH}[HPO_4^{2-}] + k_{PO_4^{3-},OH}[PO_4^{3-}]$$

Eq. 8.1.

Where, $k_{H2CO3,OH} = 1.0\ M^{-1}s^{-1}$, $k_{HCO3^-,OH} = 8.5\ x10^{-6}\ M^{-1}s^{-1}$, $k_{CO3^{2-},OH} = 3.9\ x\ 10^{-8}\ M^{-1}s^{-1}$,

$k_{H3PO4,OH} = 2.7\ x\ 10^{-6}\ M^{-1}s^{-1}$, $k_{H2PO4^-,OH} = 2.0\ x\ 10^{-4}\ M^{-1}s^{-1}$,

$k_{HPO4^{2-},OH} = 1.5x10^{-5}\ M^{-1}s^{-1}$, $k_{PO4^{3-},OH} = 1.0\ x\ 10^{-7}\ M^{-1}s^{-1}$.

The R_{CT} values were investigated at different pH values in solutions having the same scavenging capacity. As shown in Figure 8.1, The R_{CT} values increased as pH increased in both water sources. However, the R_{CT} values in these results were low compared to the results obtained under uncontrolled (no added scavenging capacity) conditions. This shows that the production of the OH radical is restricted and OH radicals are consumed by the scavenging species added.

The larger R_{CT} values in Lake Erie compared to Lake Lansing is due to the lower scavenging capacity ($2.34\ x\ 10^5\ s^{-1}$) in Lake Erie compared to that in Lake Lansing ($3.38\ x\ 10^5\ s^{-1}$). In order to compare the OH radical scavenging rate by scavenging species and NOM, the rate of OH radical reacting with NOM also calculated (Eq. 8.2). The rate constant of the OH radical and the molecular weight of NOM were used obtained from previous research ($k_{NOM,OH} \approx 3.6\ x\ 10^8$ mol $C^{-1}\ s^{-1}$, 12 g C per mol C) (Westerhoff et al., 1999). In both Lake Erie and Lake Lansing waters, the ratios of OH radicals reacting with NOM and scavengers were calculated to be 0.77, 1.28, respectively. The results indicate that scavengers were able to compete with NOM for OH radicals. Therefore, the effect of NOM on the ozone reactions is less that what would otherwise be expected, especially in Lake Erie water.

$$[\text{Scavenging Capacity}] > k_{NOM,OH}[NOM]$$

$(k_{NOM,OH} \approx 3.6 \times 10^8 \text{ mol C}^{-1} \text{ s}^{-1}$, 12 g C per mol C) (Westerhoff et al., 1999) Eq. 8.2.

As pH increased, the formation of the OH radical increased (See Figure 8.1). This is not unexpected since the ozone decomposition rate at low pH is significantly lower than that at high pH, due to the restricted initiation step of ozone decomposition at low pH.

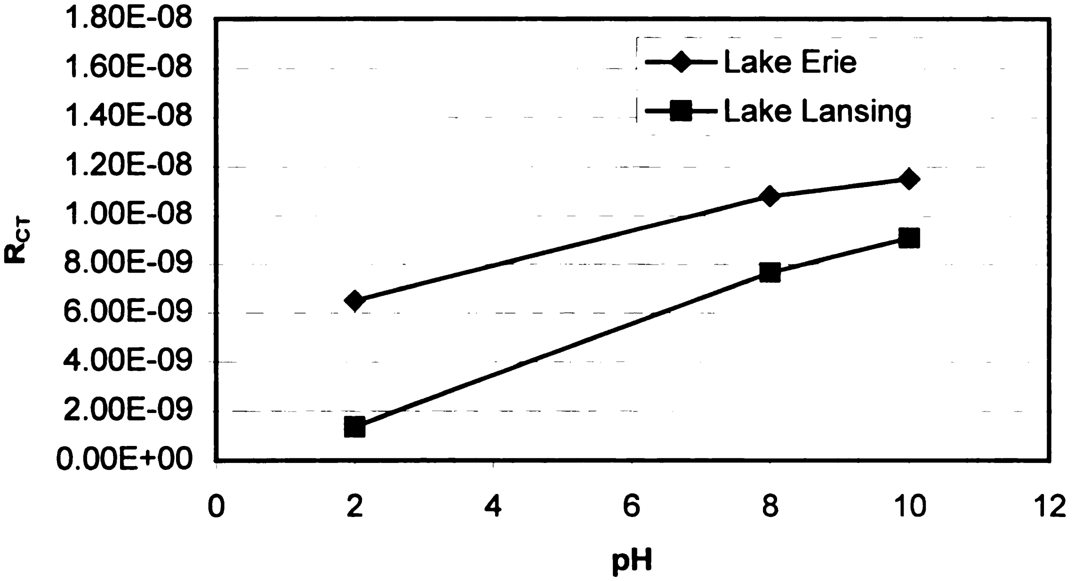


Figure 8.1. The effect of pH on R_{CT} values (Ozone dosage: 1 mg O_3/mg C, Temperature: 25 °C).

8.2. Formation of ketoacids for pH

As shown in Figure 8.2, the concentration of ketoacids decreased as pH increased for both water sources. This result also indicates that the formation of ketoacids occurs preferentially by a molecular ozone reaction as compared to an OH radical mediated reaction. This is consistent with the original hypothesis. An increase in pH resulted in a greater in the concentration of ketoacids in Lake Lansing water as compared to that in Lake Erie. The lower reaction rate of OH radical with NOM from Lake Erie water as compared to that with Lake Lansing may be the cause of this phenomenon.

Comparing the concentrations of ketoacids produced in the uncontrolled conditions (no additional buffer), it was observed that the concentration of ketoacids in buffered water was greater (See Figure 5.2 and 8.3). This was due to the greater concentration of ozone that is maintained in waters having a greater scavenging capacity since the reaction of the scavenging species with OH radical consumes OH radical without producing superoxide anion (O_2-), thereby slowing down the decomposition of ozone (Langlais et al. 1991). The decomposition of ozone in the buffered and unbuffered water is presented in the Figure 8.3. Consequently, the concentration of ketoacids was increased at the high pH under the presence of molecular ozone dominant.

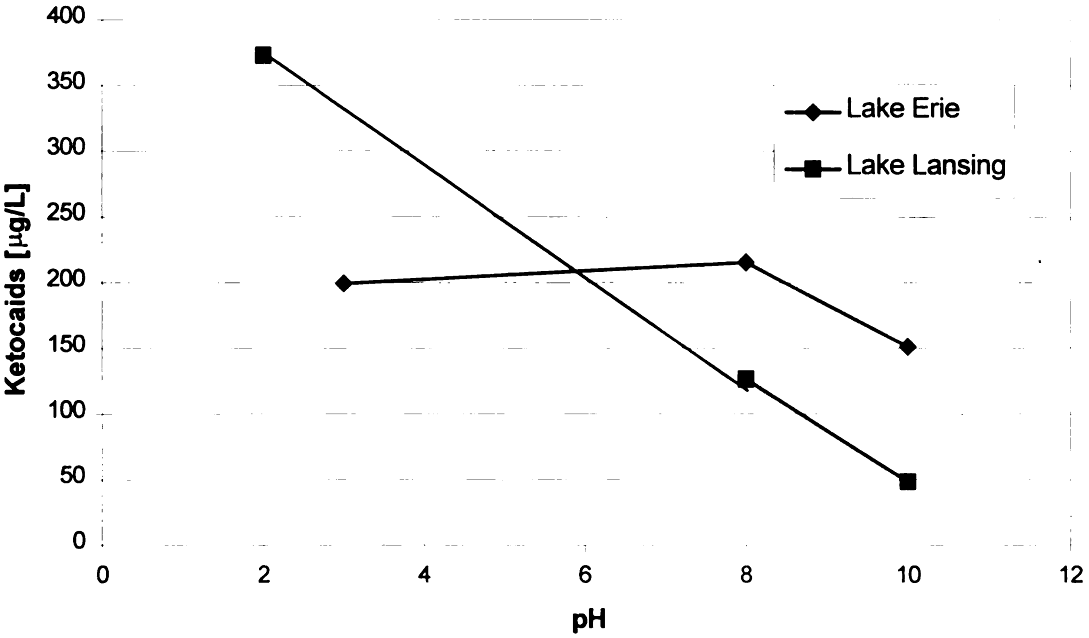


Figure 8.2. Formation of ketoacids for pH (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

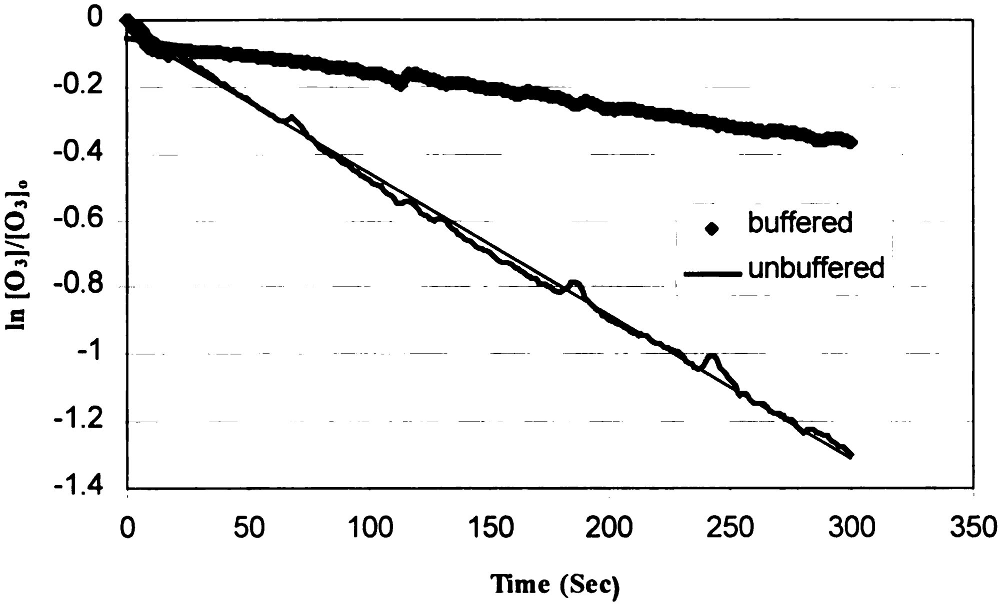


Figure 8.3. Decomposition of ozone in the raw water and buffered water (Lake Erie water, Ozone dosage: 2mg/L, pH 8, Temperature 25 °C).

8.3. Formation of AOC for pH

Prior to the inoculation of bacteria into the samples for AOC determination, the pH of samples was adjusted to neutral (pH=7) using sodium hydroxide and/or hydrochloric acid. In order to minimize the volume of sodium hydroxide and hydrochloric acid, the concentration of the solutions used as 4 M. The formation of AOC is expected to decrease as pH increased since the reaction of molecular ozone with NOM is more favorable than is the OH radical for the formation of AOC. The concentrations of AOC in both Lake Erie and Lake Lansing water decreased at high pH. The concentrations of AOC produced in Lake Lansing were higher than that in Lake Erie water. This was due to not only higher concentration of NOM but also the low concentrations of OH radical in Lake Lansing (See Figure 8.4).

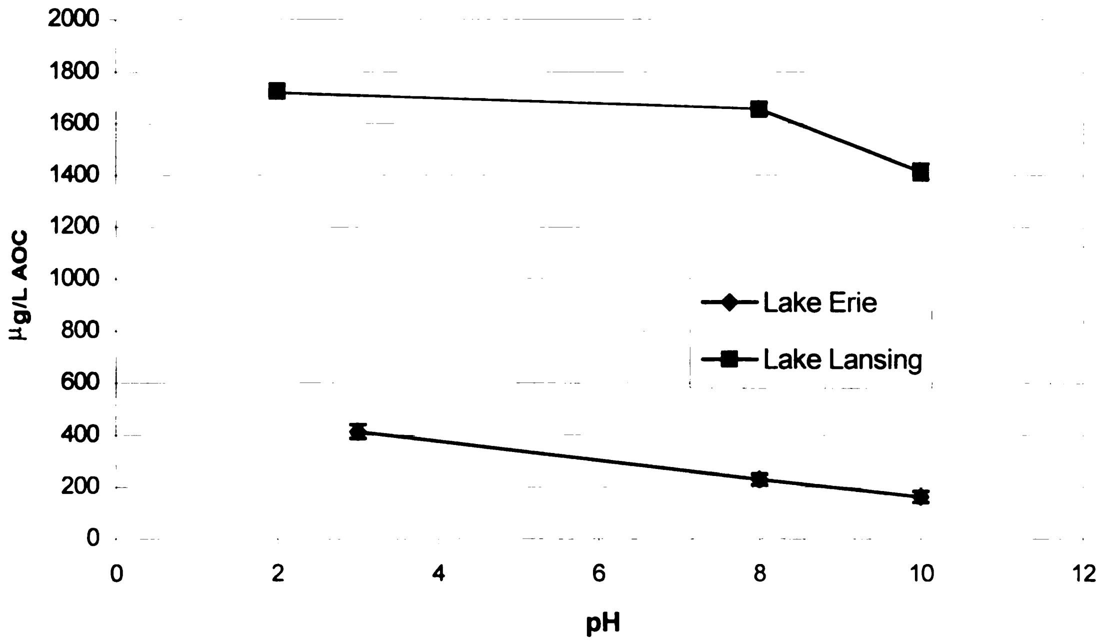


Figure 8.4. Formation of AOC for pH (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

8.4. Formation of THMs and HAAs for pH

The formation of THMs and HAAs following ozonation at pH from 2 to 10 is shown in Figures 8.5 and 8.6. Prior to adding chlorine to the ozonated samples, the pH values of the samples were adjusted to neutral (pH=7) using sodium hydroxide and/or hydrochloric acid. After that, the phosphate buffer was added into the samples as usual chlorination procedure.

The concentrations of THMs in both water sources decreased as pH increased. This can be explained by the presence of higher concentrations of molecular ozone at lower pH. The concentration of THMs was greatest at the lowest. This conflicts with our hypothesis that the predominance of the molecular ozone reaction would result in a decrease the formation of DBPs. This result may also be due to the significant role the scavengers play a significant role in the ozone reaction. The buffering was controlled with bicarbonate at high pH and phosphate at low pH since the bicarbonate ion present as H_2CO_3 at low pH (pH <6.3) has little buffering capacity. The bicarbonate and carbonate ion produce the secondary oxidants, the bicarbonate radical and carbonate radical ($HCO_3\cdot$ /$CO_3\cdot^-$), which can oxidize some inorganic and organic compounds. Although the fate of carbonate radicals in drinking water is not entirely determined, carbonate radicals have been found to react through self-reaction (Eq. 7.1) or with NOM (Eq. 7.2) (Acero and von Gunten, 2000).

$CO_3\cdot^- + CO_3\cdot^- \rightarrow CO_2 + CO_4^{2-}$ $k=2\times10^7\ M^{-1}s^{-1}$ Eq. 7.1.

$CO_3\cdot^- + NOM \rightarrow CO_3^{2-} + \text{Products}$ $k=1\times10^7\ M^{-1}s^{-1}$ Eq. 7.2.

Therefore, at the high concentration of bicarbonate and carbonate that exist at the higher pH values, the concentration of carbonate radicals would also increase, significantly affecting the reaction of ozone with NOM.

Although the concentration of HAAs in Lake Erie did not change with pH, the concentration of HAAs in Lake Lansing decreased as pH increased. These trends are similar to those for the THMs

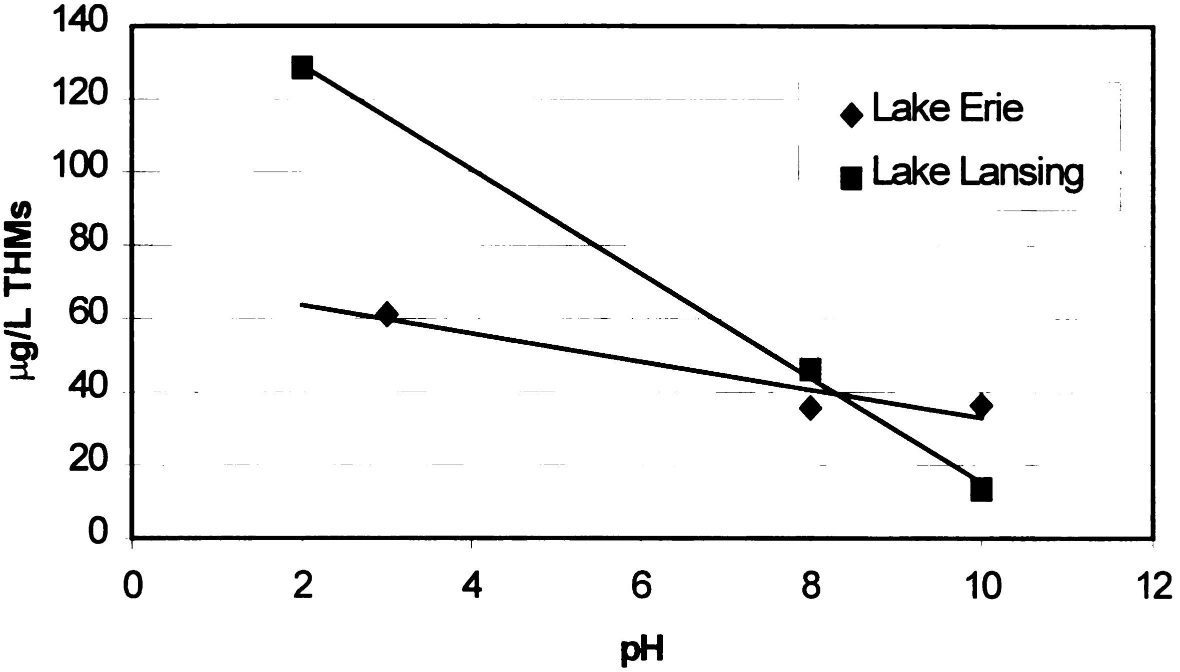


Figure 8.5. Formation of THMs for pH (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

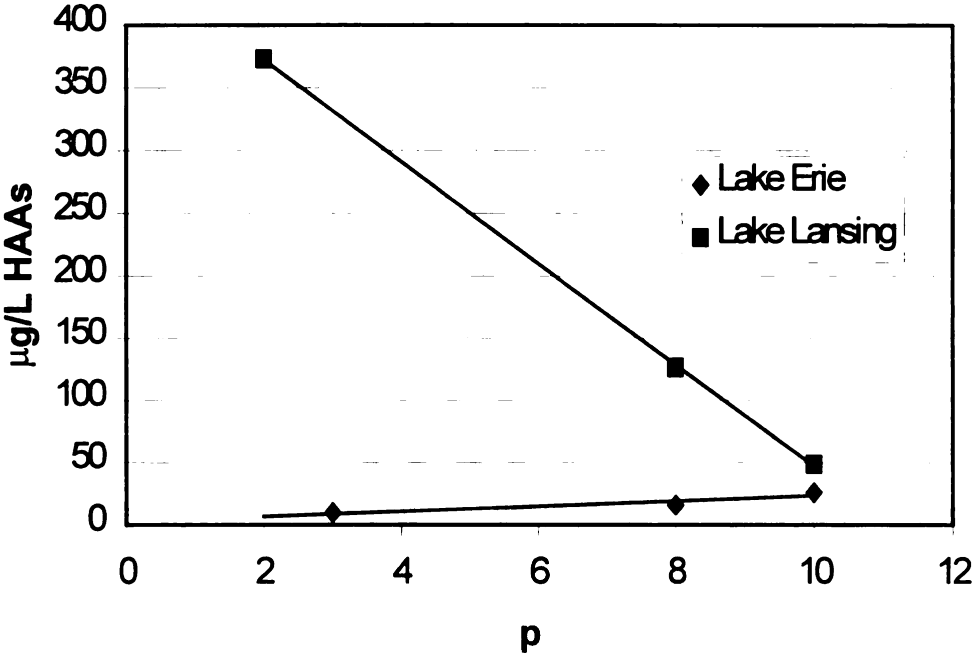


Figure 8.6. Formation of HAAs for pH (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

9. EEFFECT OF BICARBONATE

9.1. R_{CT} values in solutions containing bicarbonate ions

Scavenging reactions consume OH radicals without producing superoxide ions. Although there are various additives that could have been used as scavengers, nontoxic inorganic additives were used for this study so as to avoid problems associated with the influence of the organic scavenging compounds on AOC and TOC analysis. Since residual organic additives will affect the measurement of TOC measurement, these compounds were avoided. The organic additives and their ozonation by-products may also influence the formation of AOC, providing another reason for using inorganic scavengers.

Staehelin and Hoigné (1982) found that carbonate and bicarbonate ions have the ability to stabilize molecular ozone. This has been confirmed by many other researchers (Yuteri and Gurol, 1988; Reckhow et al., 1986; Forni et al., 1982). The presence of the OH radicals, bicarbonate and carbonate ions, which are ubiquitous in most natural waters, will result in relatively low OH radical concentration in these waters. This is especially true when the bicarbonate ion is dissociated into carbonate ion at pH > 10.3 (pKa = 10.3) (Snoeyink and Jenkins, 1980). The reaction rate of carbonate with OH radical is greater than that of bicarbonate. As such, bicarbonate and carbonate ions may serve to consume OH radicals, thereby stabilizing molecular ozone. The bicarbonate ion inhibits the radical chain reaction, hence increasing the concentration of molecular ozone. As such, the presence of radical scavengers could result in the predominance of reactions involving the ozone molecule, resulting in preferential reactions involving the ozone molecule and the aromatic moieties of fulvic acid, a component of humic substance.

According to previous research conducted on the effect of alkalinity on ozonation (alkalinity ranging from 0 to 1.5 mM) in Lake Zűrich water (Elovitz et al. 2000), R_{CT} values were seen to decreased five-fold when the alkalinity was increased from 0 to 1.5 meq/L. The concentration range of bicarbonate applied in our study was to 10 mM. As shown in Figure 9.1, the R_{CT} values in Lake Erie decreased as the concentration of bicarbonate increased while the R_{CT} values in Lake Lansing increased as bicarbonate increased. However, the R_{CT} values in Lake Lansing water remained relatively constant at bicarbonate concentrations greater than 4 mM. The addition of bicarbonate (to 10 mM) resulted in an increase in the pH values in Lake Erie water from 7.8 to 8.2, and from 8.0 to 8.9 in Lake Lansing water. The pH increase is expected to lead to higher concentrations of OH radicals due to an increase in the ozone decomposition rate. However, the change of R_{CT} values in Lake Erie was 75 % and in Lake Lansing was 37 % comparing at bicarbonate concentration of 0 and 10 mM. Increase in the pH led to higher concentration of OH radicals. As a result, the impact of the pH which resulted in an increase in the concentration of OH radicals and the addition of bicarbonate which decreased the concentration of OH radicals counteracted one another.

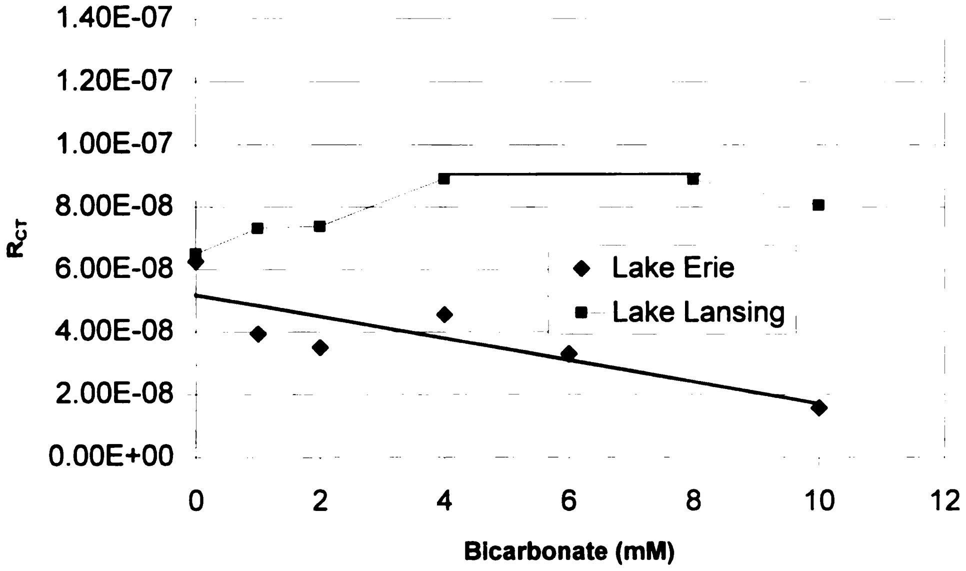


Figure 9.1. The effect of bicarbonate on R_{CT} values (Ozone dosage: 1mg O_3/mg C, Temperature: 25 °C).

9.2. Formation of ketoacids in solutions containing bicarbonate ion

The effect of bicarbonate addition on the concentration of ketoacids is shown in Figure 9.2. While increasing the bicarbonate concentration in Lake Erie water had no effect on the concentration of ketoacids, the ketoacids concentration in Lake Lansing did decrease with increasing bicarbonate concentration in Lake Lansing water. Although bicarbonate and carbonate ions are effective OH radical scavengers, they produce the secondary oxidants, the bicarbonate radical and carbonate radical ($HCO_3\cdot$ /$CO_3\cdot^-$), which can oxidize some inorganic and organic compounds. Although the fate of carbonate radicals in drinking water is not entirely determined, carbonate radicals have been found to react through self-reaction (Eq. 9.1) or with NOM (Eq. 9.2) (Acero and von Gunten, 2000).

$$CO_3\cdot^- + CO_3\cdot^- \rightarrow CO_2 + CO_4^{2-} \qquad k=2\times10^7\ M^{-1}s^{-1} \qquad \text{Eq. 9.1.}$$

$$CO_3\cdot^- + NOM \rightarrow CO_3^{2-} + \text{Products} \qquad k=1\times10^7\ M^{-1}s^{-1} \qquad \text{Eq. 9.2.}$$

Therefore, as the concentration of bicarbonate increases, the concentration of carbonate radicals would also increase, significantly affecting the reaction of ozone with NOM. This may cause a decrease in the concentrations of ketoacids at the high concentrations of bicarbonate since the radical species can directly attack NOM to inhibit the formation of ketoacids.

The results regarding the effect of bicarbonate on the formation of ketoacids have been plotted along with the concentration of carbonate ion. (See Figure 9.3).

Considering the amount of bicarbonate added and pH in water, the concentration of carbonate ion in water was calculated (Snoeyink and Jenkins, 1980). The total alkalinity, including added bicarbonate, can be expressed as Eq. 9.3

$$\left[Total\,alkalinity\right] = C_{T,CO_3}(\alpha_1 + 2\alpha_2) + \frac{K_W}{[H^+]} - [H^+] \qquad \text{Eq. 9.3.}$$

The ionization fractions obtained from the exact equations for diprotic acid are

$$\alpha_0 = \frac{[H^+]^2}{E} = \frac{[H_2CO_3]}{C_{T,A}} \qquad \text{Eq. 9.4.}$$

$$\alpha_1 = \frac{[H^+]^C K_{a,1}}{E} = \frac{[HCO_3^-]}{C_{T,A}} \qquad \text{Eq. 9.5.}$$

$$\alpha_2 = \frac{{}^C K_{a,1}\,{}^C K_{a,2}}{E} = \frac{[CO_3^{2-}]}{C_{T,A}} \qquad \text{Eq. 9.6.}$$

Where $E = [H^+]^2 + [H^+]^C K_{a,1} + {}^C K_{a,1}\,{}^C K_{a,2}$

For bicarbonate and carbonate ions, $K_{a,1} = 10^{-6.3}$, $K_{a,2} = 10^{-10.3}$.

Using the Eq. 9.3 through 9.6 and constants ($K_{a,1}$, $K_{a,2}$), $C_{T,CO3}$ (concentration of total inorganic carbon) can be obtained from Eq. 9.3. Thus, the concentration of bicarbonate ion and carbonate ion can be calculated based on the Eq. 9.7 and 9.8.

$$[HCO_3^-] = C_{T,CO3} \cdot \alpha_1 \qquad \text{Eq. 9.7.}$$

$[CO_3^{2-}] = C_{T,CO3} \cdot \alpha_2$ Eq. 9.8.

The calculated values of carbonated concentration in Lake Erie and Lake Lansing are presented in Table 9.1.

Table 9.1. Concentrations of carbonate ion including added bicarbonate in Lake Erie, and Lake Lansing.

Added amount of bicarbonate ion (mM)	pH (Lake Erie and Lake Lansing)	$[CO_3^{2-}]$ in Lake Erie (M)	$[CO_3^{2-}]$ in Lake Lansing (M)
0	7.8, 8.0	5.692E-06	1.403E-05
1	7.9, 8.1	8.854E-06	1.904E-05
2	8.0, 8.3	1.201E-05	3.028E-05
4	8.0, 8.6	2.309E-05	8.800E-05
6	8.1, 8.7	3.105E-05	1.394E-04
8	8.2, 8.7	4.911E-05	2.712E-04
10	8.2, 8.9	5.914E-05	5.095E-04

The concentrations of ketoacids on the effect of bicarbonate were plotted according to the concentration of carbonate ion in Figure 9.3.

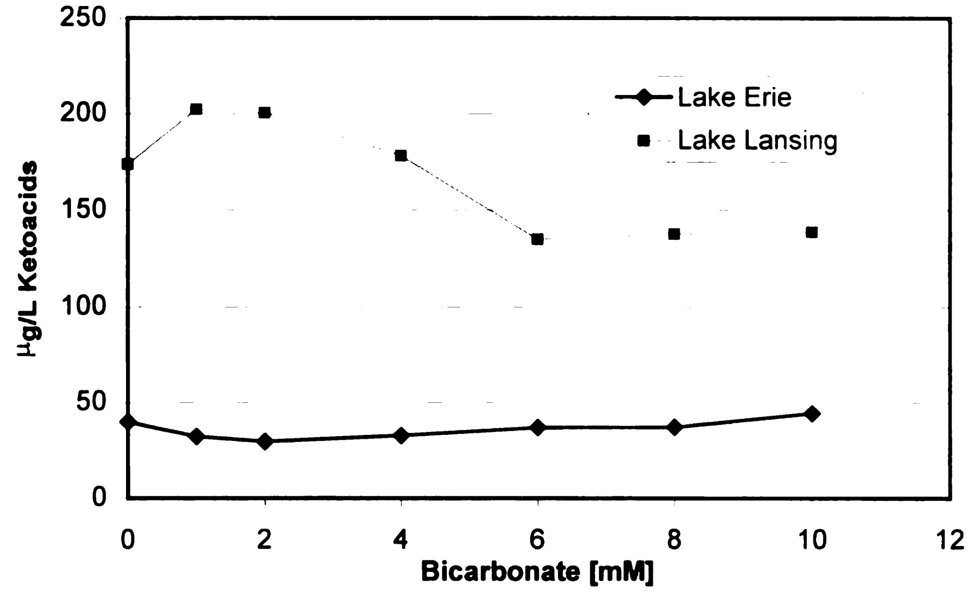


Figure 9.2. Formation of ketoacids on bicarbonate (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

As shown in Figure 9.2, the concentration of ketoacids in Lake Lansing increased until approximately 6.0×10^{-5} M of carbonate concentration. The concentrations of ketoacids were decreased at the carbonate ion concentration greater than approximately 6.0×10^{-5} M. (See Figure 9.2.) Therefore, due to increases of the carbonate radical concentration, the formation of ketoacids seems to be restricted otherwise increased by prevalent molecular ozone concentration.

Comparing the results presented in Figure 9.2 with those in Figure 9.3, the concentration of ketoacids in Lake Erie did not change significantly while the concentration of Lake Lansing changed over the bicarbonate range from 0 to 10 mM (Figure 9.2). However, when considering the concentration of carbonate ion as shown in Figure 9.3, it is apparent that the carbonate ion concentration in Lake Erie water is significantly smaller than that in Lake Lansing water, even though the addition of bicarbonate was equivalent (0 to 10 mM of bicarbonate) in both waters. Thus, the effect of carbonate radical would be expected to be less significant in Lake Erie water.

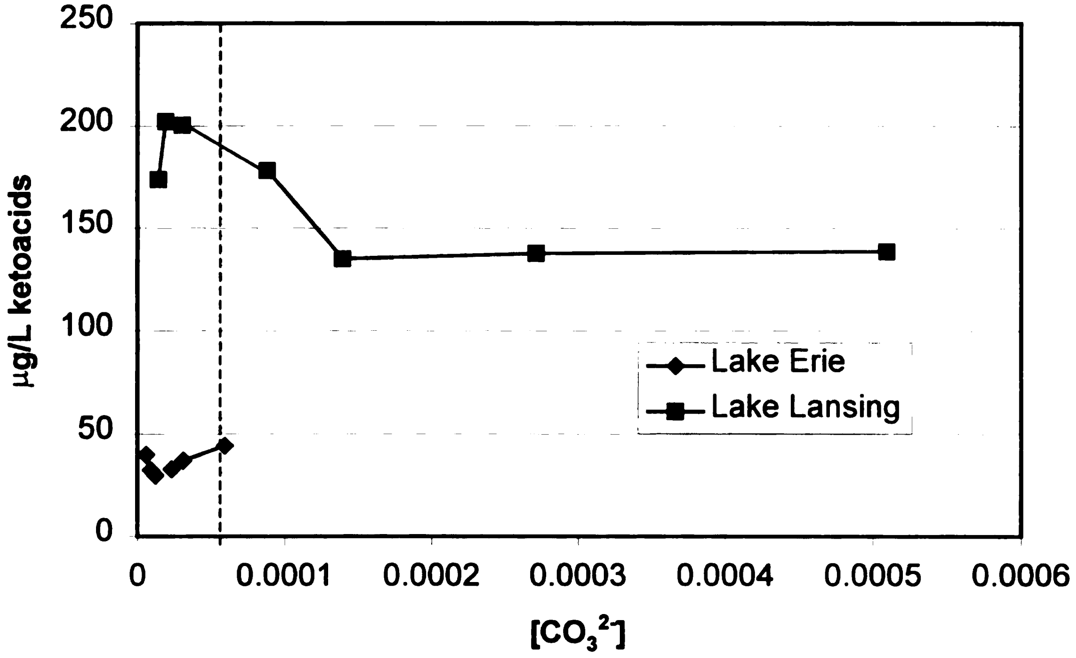


Figure 9.3. Formation of ketoacids on bicarbonate (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

9.3. Formation of AOC in solutions containing bicarbonate ions

The addition of bicarbonate was expected to increase AOC formation since as an OH radical scavenger its presence would result in molecular ozone reaction predominating. As shown in Figure 9.1, although the R_{CT} values measured in Lake Erie water decreased as the concentration of bicarbonate increased, the concentration of AOC was essentially unchanged. This is consistent with the previous results, that is, the rate of reaction of the OH radical with NOM from Lake Erie is slow. In Lake Lansing water, the concentration of AOC increased as bicarbonate concentration increased (within the range from 0 to 4 mM). At bicarbonate concentrations greater than 4 mM, the concentration of AOC decreased with increasing bicarbonate concentration. This may be due to the reaction of radical species (bicarbonate radicals and carbonate radicals) produced as secondary oxidants. These radical species also seem to affect the concentration of AOC differently that the OH radical does. The relationship between the concentration of AOC and the concentration of carbonate ion is shown in Figure 9.5. As was shown in Figure 9.3 (with ketoacids), the concentration of AOC also decreased as the concentration of carbonate ion, increased above approximately 6.0×10^{-5} M (See Figure 9.4). The radical reaction involving carbonate and bicarbonate radicals seems to effectively react with NOM. This indicates that higher concentrations of carbonate ion during ozonation will promote carbonate radicals, increasing the reactivity with NOM that otherwise might react with OH radicals.

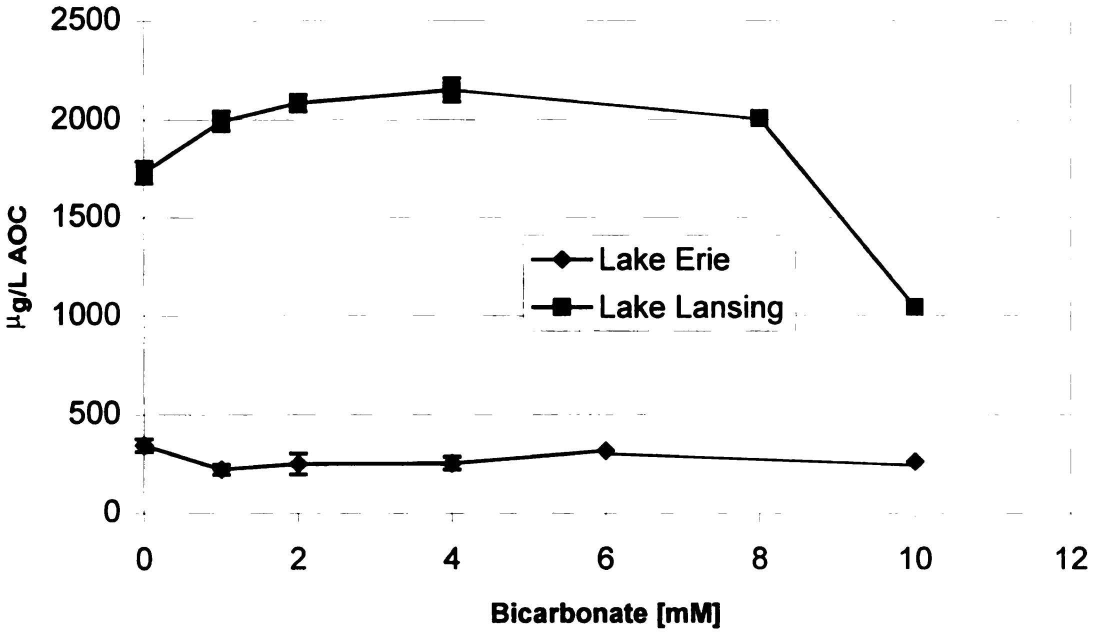


Figure 9.4. The effect of bicarbonate on the formation of AOC (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

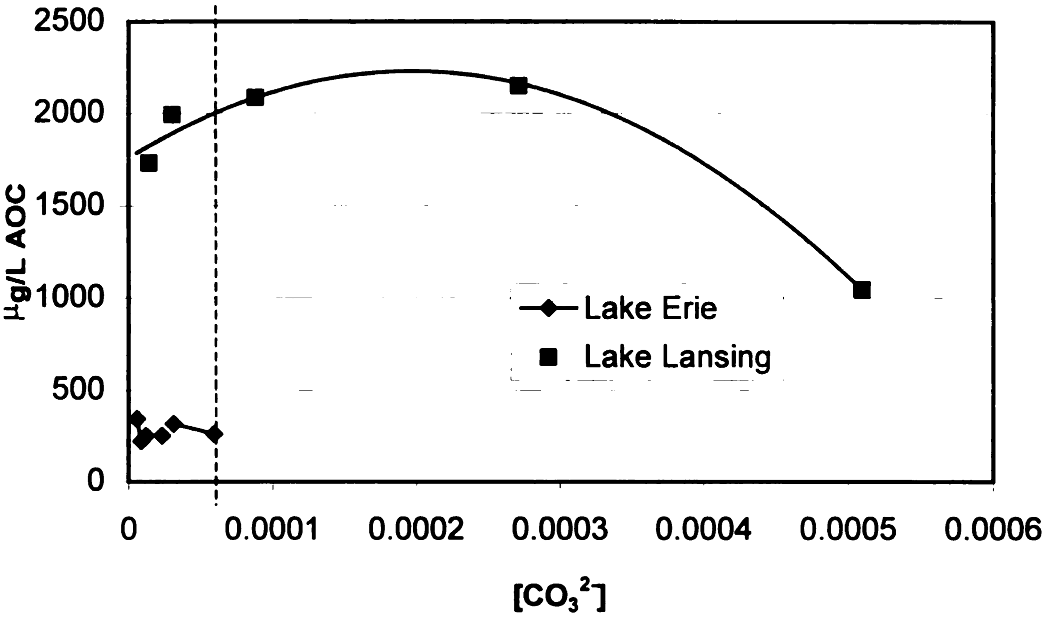


Figure 9.5. Formation of AOC on bicarboante (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

9.4. Formation of THMs and HAAs in solutions containing bicarbonate ions

The effects of bicarbonate on the formation of THMs and HAAs are shown in Figures 9.6 and 9.7. The addition of 1 mM bicarbonate to Lake Lansing water resulted in a decrease in the THMs concentration approximately from 260 μg/L to 190 μg/L. No further decreases were observed even at a bicarbonate concentration of 10 mM. The concentration of THMs in Lake Erie water did not change (with in a 95 % confidential interval) with increase in the concentration of bicarbonate ranging from 0 to 10 mM. This result indicates that small amounts of bicarbonate are effective at reducing the formation of THMs in Lake Lansing water, but that the effective of bicarbonate is maximized at some bicarbonate concentration of 4 mM (in this case). Further work would need to be a accomplished to determine if this concentration is consistent. Due to the slow reaction rate of the OH radical with NOM in Lake Erie, bicarbonate is less effective for the control of the formation of THMs and HAAs in this water source. A similar trend for the decrease in the HAA concentration with increasing bicarbonate concentration is in Figure 9.7. This result is consistent with the findings of Reckhow et al. (1986). They observed that comparing to no addition of bicarbonate, the concentration of THMs and HAAs decreased from 1mM of bicarbonate and no significant changes until 10 mM of bicarbonate in extracted fulvic acid from Black Lake near Elizabethtown, NC. Consequently, both Reckhow et al (1986) and our results supports the hypothesis that the precursors of THMs and HAAs are preferentially formed by the reaction of OH radical with NOM.

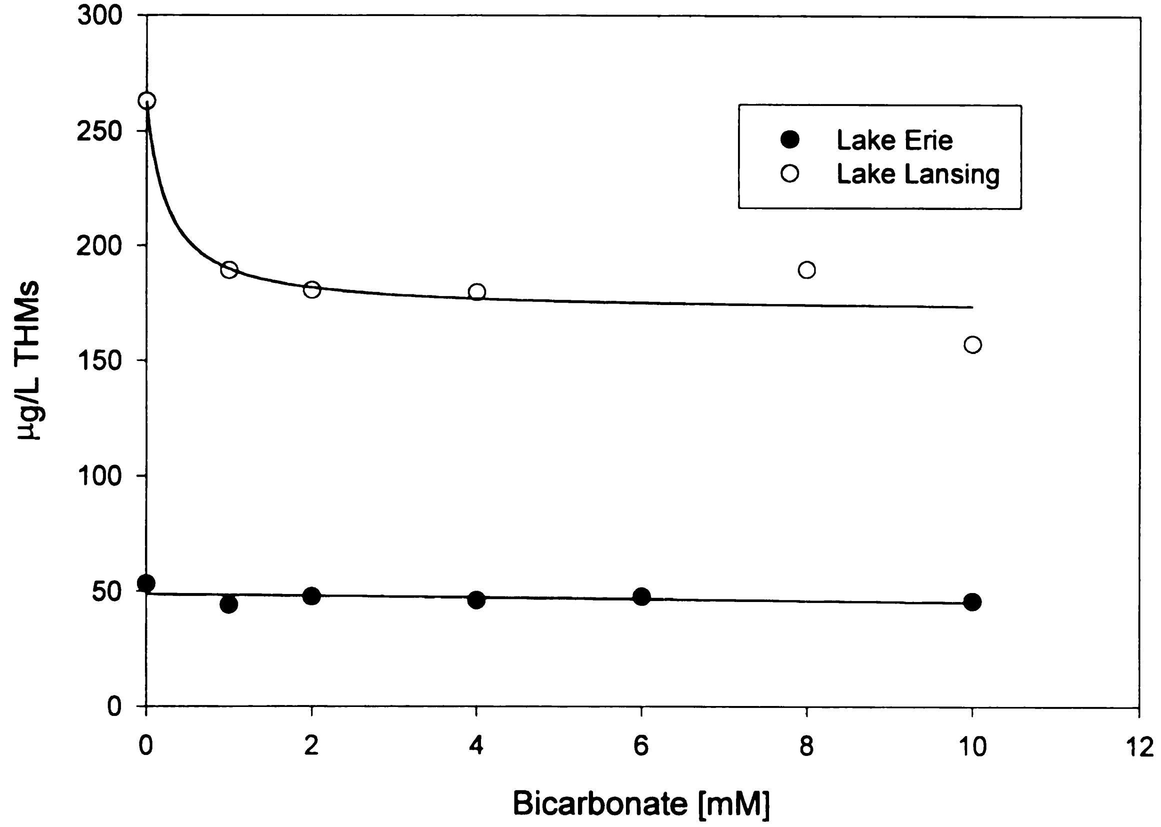


Figure 9.6. Formation of THMs on bicarbonate (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

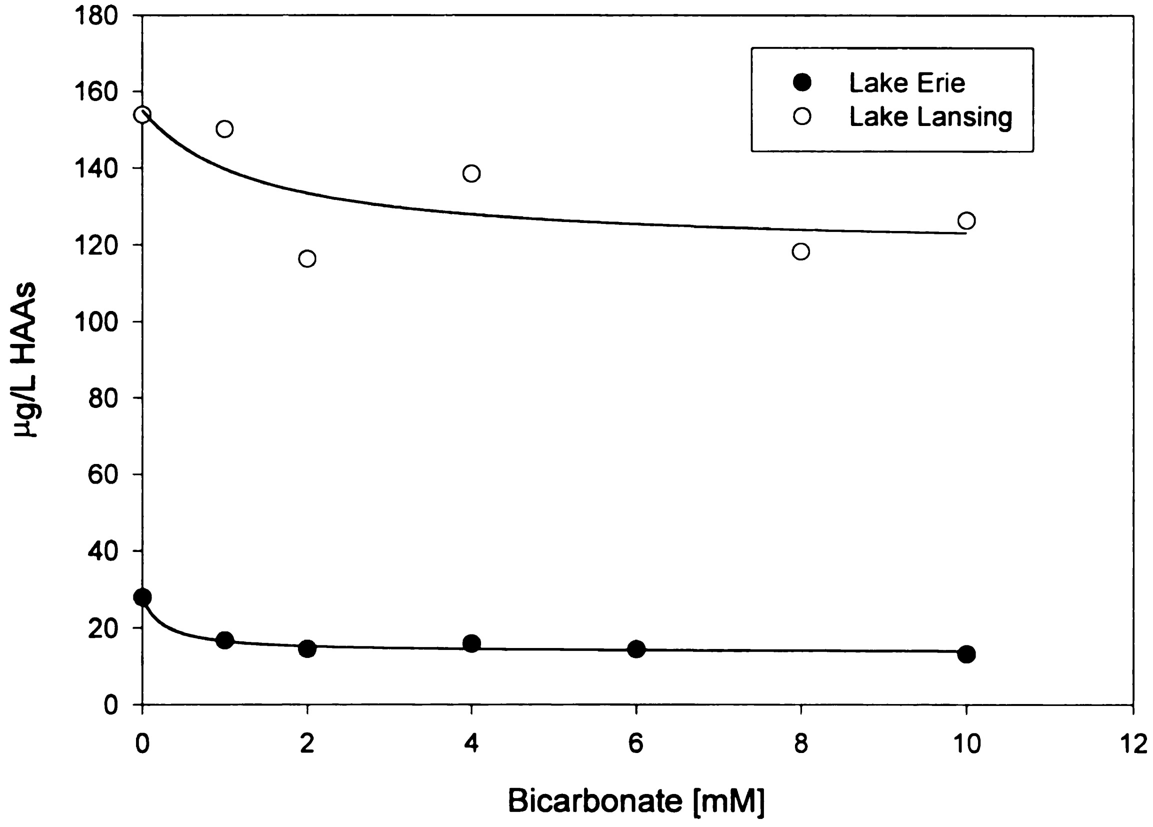


Figure 9.7. Formation of HAAs on bicarbonate (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

10. EFFECT OF HYDROGEN PEROXIDE

10.1. R_{CT} values for hydrogen peroxide

The combination of hydrogen peroxide with ozonation can enhance OH radical production because the decomposition of the ozone molecule is accelerated by superoxide ion (HO_2^-), producing OH radicals (Masten et al., 1997; Glaze et al., 1987; Duguet et al. 1985; Brunet et al., 1984, Staehelin and Hoigné, 1982). However, competition reactions occur at high pH since hydroxide ions are more effective at initiating molecular ozone than is hydrogen peroxide (See Figure 10.1 and Table 10.1) and at high pH OH radicals are also consumed by bicarbonate and carbonate ions. (Eq. 10.1 and 10.2) The OH radical concentration is also influenced by the composition of water sources and types and the concentrations of OH radical scavengers. Also, OH radical concentrations will increase with increasing hydrogen peroxide up to a certain dosage. Beyond this dosage, the concentration of OH radical decreases due to the recombination reaction of OH radicals. (Eq. 10.3)

Table 10.1. Rate constant for the H_2O-O_3 and Aqueous H_2O_2-O_3 Systems (Staehelin and Hoigné, *ES&T*. 1982).

H_2O $k_n = < 5 \times 10^{-6}\ s^{-1}$ $k_{O3,H3O+} = < 4 \times 10^{-4}\ M^{-1}s^{-1}$ $k_{O3,OH-}^{measd} = 210 \pm 20\ M^{-1}\ s^{-1}$

H_2O_2 $k_{O3,H2O2} = < 10^{-2}\ M^{-1}s^{-1a}$ $k_{O3,HO2-}^{measd} = (5.5 \pm 1.0) \times 10^{6}\ M^{-1}s^{-1}$

$k_{HO2-} = 5.5 \times 10^{6}[H_2O_2]_{tot}10^{pH-pK}\ s^{-1b}$

[a]For Ionic strength I= 0.05 M. [b]Taube, H and Bray, W.C., J. Am. Chem. Soc. 1940

$\cdot OH + HCO_3^- \rightarrow CO_3^{\cdot -} + H_2O$ $8.5 \times 10^{8}\ L\ mol^{-1}\ s^{-1}$ Eq. 10.1. (Buxton et al., 1988)

$\cdot OH + CO_3^{-2} \rightarrow OH^- + CO_3^{\cdot -}$ $3.9 \times 10^{9}\ L\ mol^{-1}\ s^{-1}$ Eq.10.2. (Buxton et al., 1988)

$\cdot OH + \cdot OH \rightarrow H_2O_2$ $2k = 1.1 \times 10^{10}\ L\ mol^{-1}\ s^{-1}$ Eq.10.3. (Buxton et al., 1988)

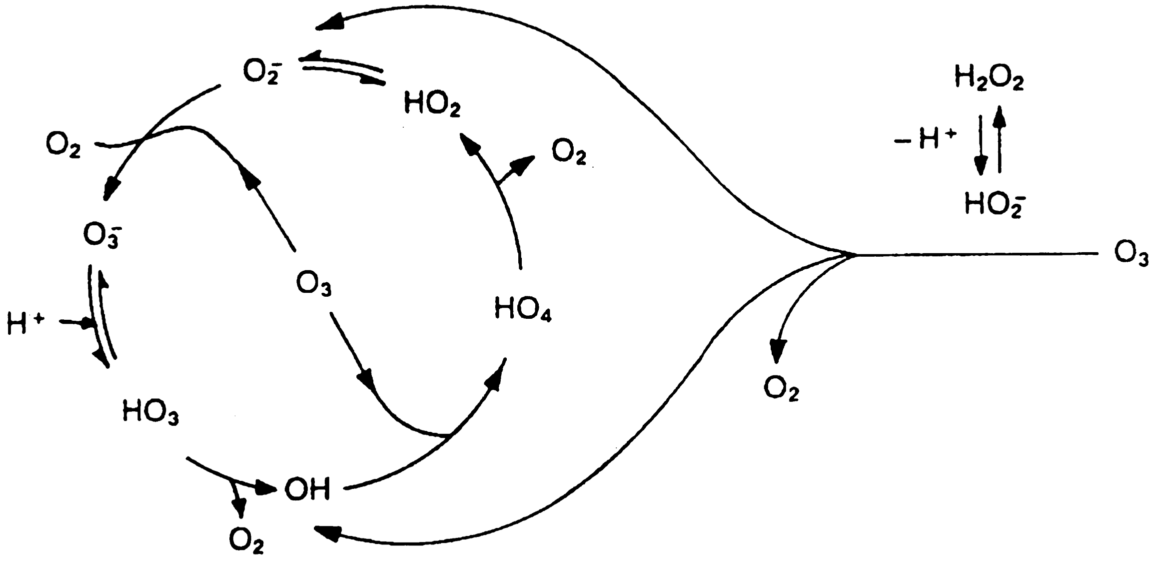


Figure 10.1. Diagram of ozone decomposition by hydrogen peroxide ions (Langlais et al., 1990).

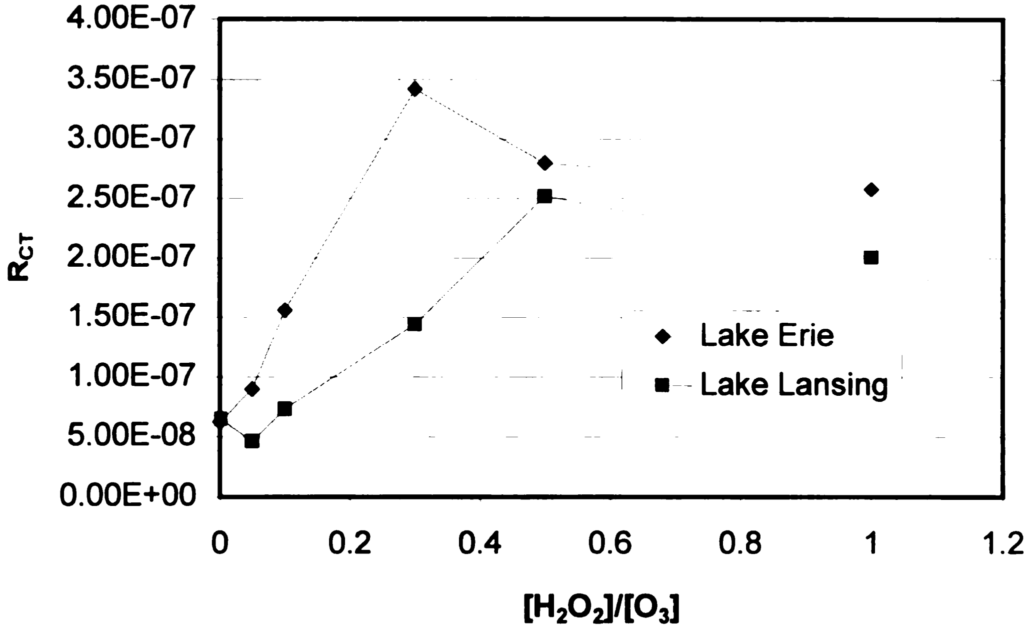


Figure 10.2. The effect of hydrogen peroxide on R_{CT} values (Ozone dosage: 1 mg O_3/mg C, Temperature: 25 °C).

The peroxide concentrations applied in this study were varied from 0 to 1.0 $[H_2O_2]/[O_3]$ (wt/wt) with a fixed ozone dosage (1 mg O_3/mg C). As shown in Figure 10.2, over the range of $[H_2O_2]/[O_3]$ ratio of 0.3- 0.5, the R_{CT} values increased as peroxide concentration increased. However, the R_{CT} values decreased at the high peroxide dosages greater than an $[H_2O_2]/[O_3]$ ratio of 0.5. The results indicate that the production of OH radical can be maximized at a certain dosage (0.3 - 0.5) and higher concentrations of H_2O_2 actually have a negative effect on the production of OH radicals. This is due to OH radical scavenging effects at high concentrations of H_2O_2. These results are consistent with that of previous researcher (Glaze et al., 1987; Duguet et al. 1985).

At a particular ozone dosage and $[H_2O_2]/[O_3]$ ratio, greater OH radical concentrations were produced in Lake Erie water as compared to that in Lake Lansing water. It is thought that the OH radicals in Lake Lansing water may be consumed by high alkalinity in Lake Lansing water. Also, due to the high concentration of NOM in Lake Lansing, the NOM plays a greater role as scavenger than as a promoter of OH radicals. As stated previously in the section on the effect of ozone dosage, the properties of the NOM in Lake Erie make it effective at promoting OH radical from ozone.

10.2. Formation of ketoacids for hydrogen peroxide

As peroxide concentration is increased, the production rate of OH radical increased up to a certain dosage (See Figure 10.2). However, the formation of ketoacids decreased as peroxide concentration increased (Figure 10.3). This result shows that the reaction of molecular ozone with NOM preferentially produces ketoacids over the OH radical reaction. Comparing the formation of ketoacids in Lake Lansing water and Lake Erie water, the OH radical is more effective at reducing the ketoacids concentration in Lake Lansing water. However, decreases both about 50 % increase in concentration of OH radical more than 7 fold. This result shows good agreement with the previous conclusion made in the section on the effect of ozone dosage that the reaction of OH radical with NOM in Lake Erie is slower than that with Lake Lansing NOM.

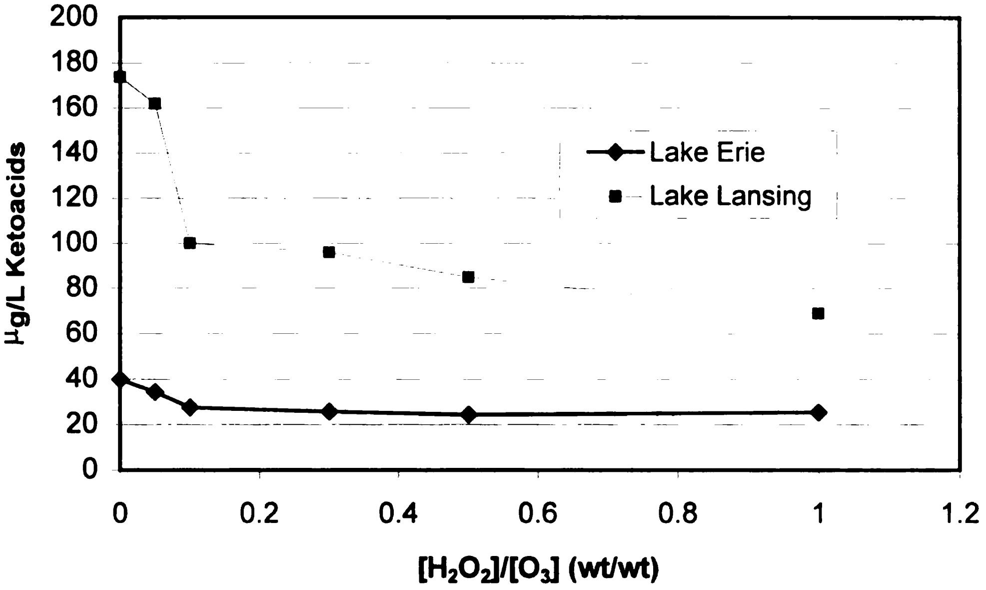


Figure 10.3. Formation of ketoacids for hydrogen peroxide (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

10.3. Formation of AOC in the hydrogen peroxide/ozone treatment

The formation of AOC during ozone/hydrogen peroxide treatment is expected to be hindered by the reactions involving OH radicals, which are produced from the reaction of ozone with hydrogen peroxide. Therefore, it is predicted that low concentrations of AOC will result during ozone/hydrogen peroxide treatment as compared to that resulting during ozonation.

The concentration of AOC decreased as the concentration of hydrogen peroxide increased, following a similar trend as that observed with the formation of ketoacids (See Figures 10.3 and 10.4). This result also indicates that the formation of AOC is also related to the reaction of molecular ozone with NOM. The concentration of AOC in Lake Lansing at a peroxide ratio of 0.01 $[H_2O_2]/[O_3]$ (wt/wt) resulted in a higher value of AOC as compared to the AOC concentration produced at other $[H_2O_2]/[O_3]$ ratios. Although the experimental error ranges are small as shown in Figure 10.4, the datum apprears to be an artifact.

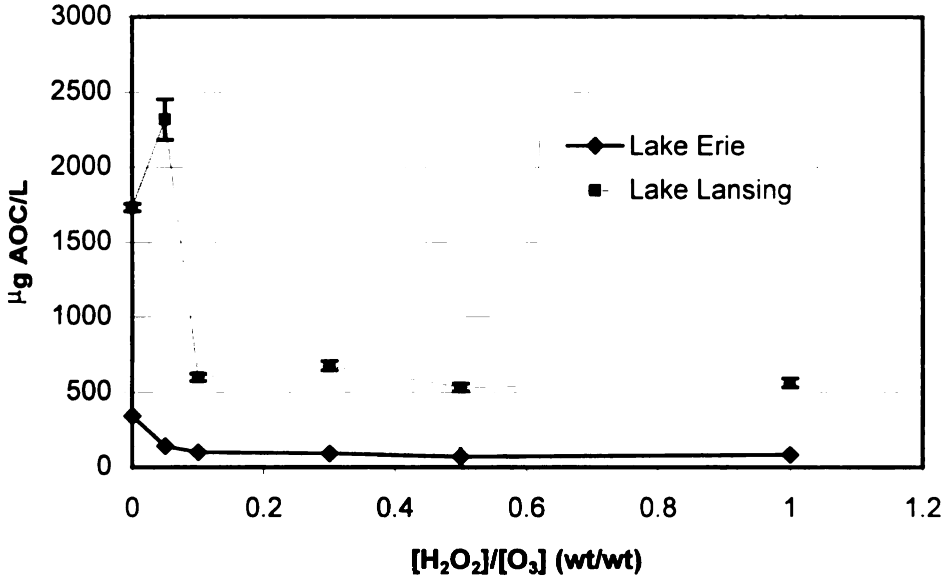


Figure 10.4. Formation of AOC for hydrogen peroxide (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

10.4. Formation of THMs and HAAs for hydrogen peroxide/ozone treatment

The relationship between the concentrations of THMs and HAAs and the peroxide/ozone ratio (0 - 1.0 $[H_2O_2]/[O_3]$ wt/wt) also was determined (Figures 10.5 and 10.6). As shown in Figure 10.5, the concentration of THMs decreased as the concentration of peroxide was increased. Although there was no significant difference (at 95 % confidential interval) in the concentrations of THMs in Lake Erie at different $[H_2O_2]/[O_3]$ ratios, the concentration of THMs in Lake Lansing decreased as the concentration of peroxide increased. These results also indicate that increased OH radical concentrations compared to ozone only may further oxidized NOM that would react with chlorine in Lake Lansing water. Reckhow et al. (1986) explained the formation pathway of DBP precursors on ozonation. Since both ozone and aqueous chlorine can act as strong electrophiles in such systems (Decoret et al., 1984; Morris, 1975), molecular ozone would destroy nucleophilic centers otherwise attacked by chlorine (e.g. highly activated aromatics such as dihydroxy benzenes). In contrast, OH radicals are more non-selective than are molecular ozone and chlorine. Hence, it presumed that molecular ozone alters moieties in the humic molecule which react with chlorine to produce THMs to a far greater extent than does the OH radical (Reckow et al 1986). The results excluding that for THMs in Lake Lansing show good agreement with this proposed mechanism.

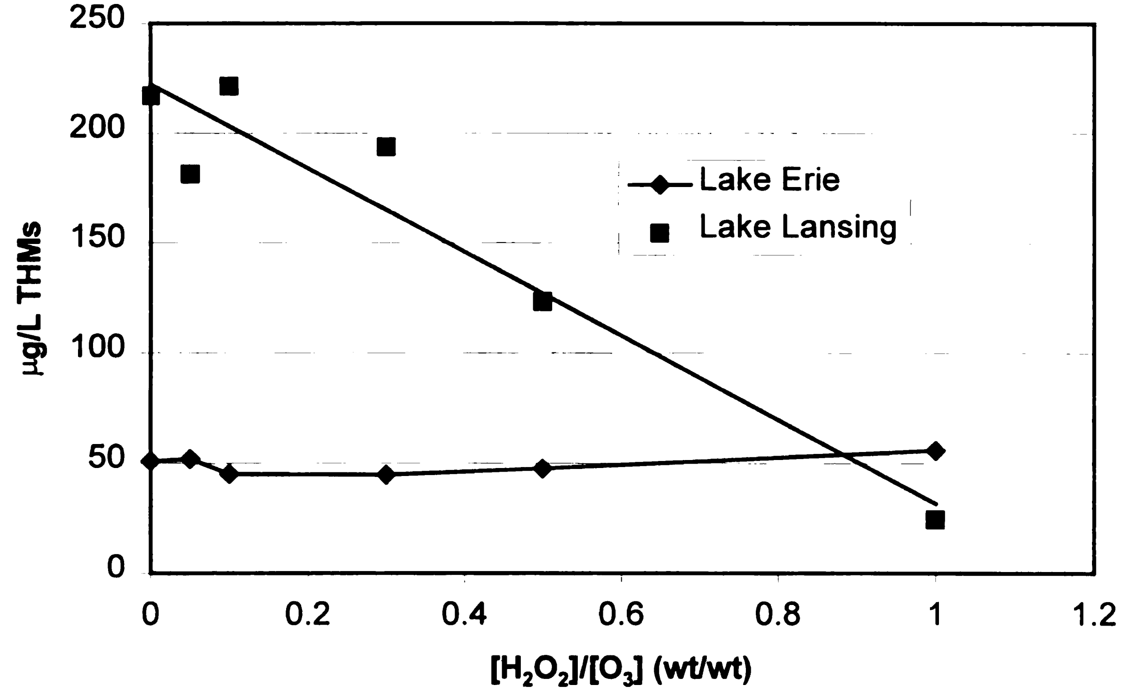


Figure 10.5. Formation of THMs for hydrogen peroxide (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

The formation of HAAs is shown in Figure 10.6. The formation of HAAs follows the trend for OH radical cocentration. As the concentration of OH radical increases, the formation of HAAs also increases. As the concentration of OH radical decreases at the high ratio of [H_2O_2/O_3], the formation of HAAs also decreases in Lake Lansing water and the increases in HAAs concentrations were less significant in Lake Erie water since the reaction rate of the OH radical with NOM in Lake Erie water is rather slow. The concentration of THM and HAA were maximized at a [H_2O_2/O_3] (wt/wt) of 0.1 even though the concentration of OH radical was maximized at 0.3 [H_2O_2/O_3] (wt/wt). According to Acero and von Guten, (2000), carbonate radical produced by OH radical with bicarbonate exert to promote ozone decomposition. The carbonate radical recombination takes place to produce CO_2 and CO_4^{2-} ($k = 2 \times 10^7$ $M^{-1}s^{-1}$). Thus, at peroxide/ozone ratios greater than 0.3, these reactions may result in low concentrations of molecular ozone and OH radical available react to NOM. The lack of variability in THMs and HAAs concentration resulting in treated Lake Erie water seems to indicate that the reaction of NOM with OH radical is too slow for these factors to influence the formation of DBPs.

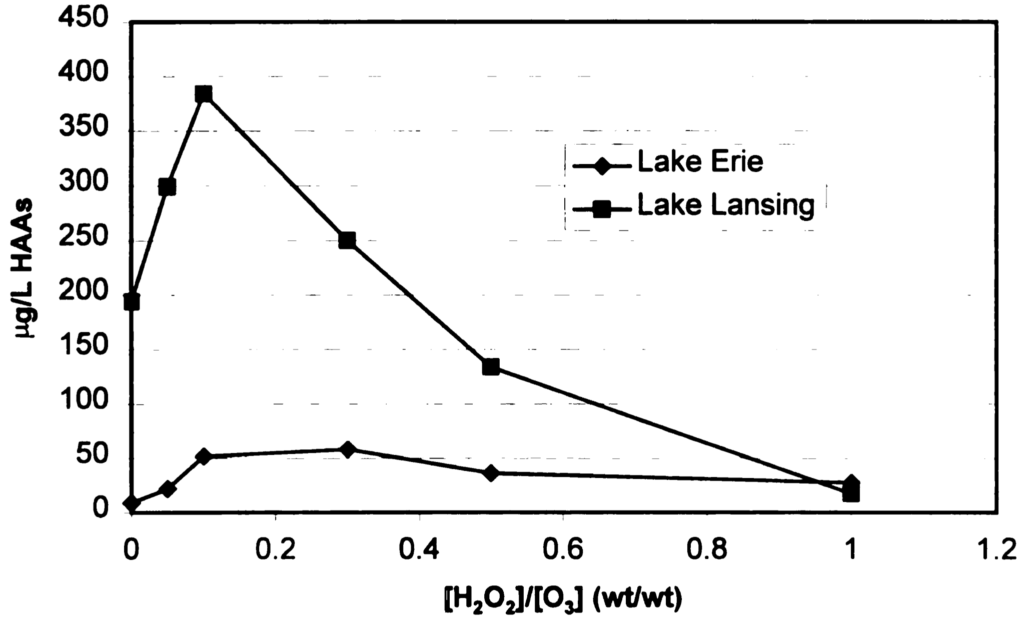


Figure 10. 6. Formation of HAAs for hydrogen peroxide (Ozone dosage: 1 mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

11. EFFECT OF PHOSPHATE

11.1. R_{CT} values in solutions containing phosphate ions

In order to more thoroughly investigate the influence of OH radical reactions on the formation of AOC, THMs and other by-products during the ozonation of NOM, phosphate (range from 0 to 10 mM) was used in this study. The phosphate ion is well documented as a promoter of OH radicals during the decomposition of ozone (Hoigné and Bader, 1985). Therefore, it was expected that the R_{CT} values would increase as the concentration of phosphate increased since the phosphate ion generates the superoxide anion (O_2^-) from oxygen. In the presence of the phosphate ion and organic alcohols, the superoxide anion is formed by the following mechanism (See Figure 11.1). Superoxide (O_2^-) can react with O_3^- to produce the OH radical. At very high phosphate concentrations, (e.g., in buffer solutions) the phosphate ions can act as an inhibitor of the OH radical (Hoigné and Bader, 1985).

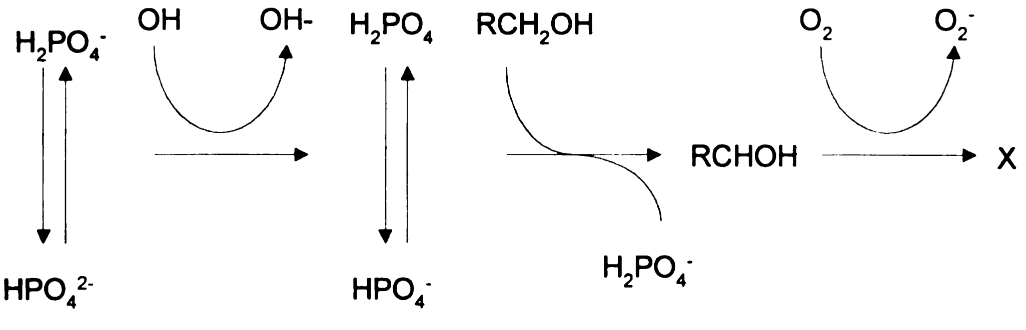


Figure 11.1. Schematic drawing of the proposed set of typical reactions, resulting in the conversion of OH· to O_2^- radicals due to the action of phosphate ions as promoters. (Hoigné and Bader, 1985)

The effect of phosphate concentration on R_{CT} values is shown in Figure 11.2. As expected, the R_{CT} values increased with increasing phosphate concentration in both Lake Erie and Lake Lansing water. Also as expected, the R_{CT} value decreased at high concentrations of phosphate (10 mM). At the lower concentrations of phosphate, the phosphate ion acted as a promoter, increasing the OH radical concentration while at high concentrations the inhibition reactions predominated, resulting in a decrease in the concentration of OH radicals. The result substantiates the well-established theory by Hoigné and Bader (1985).

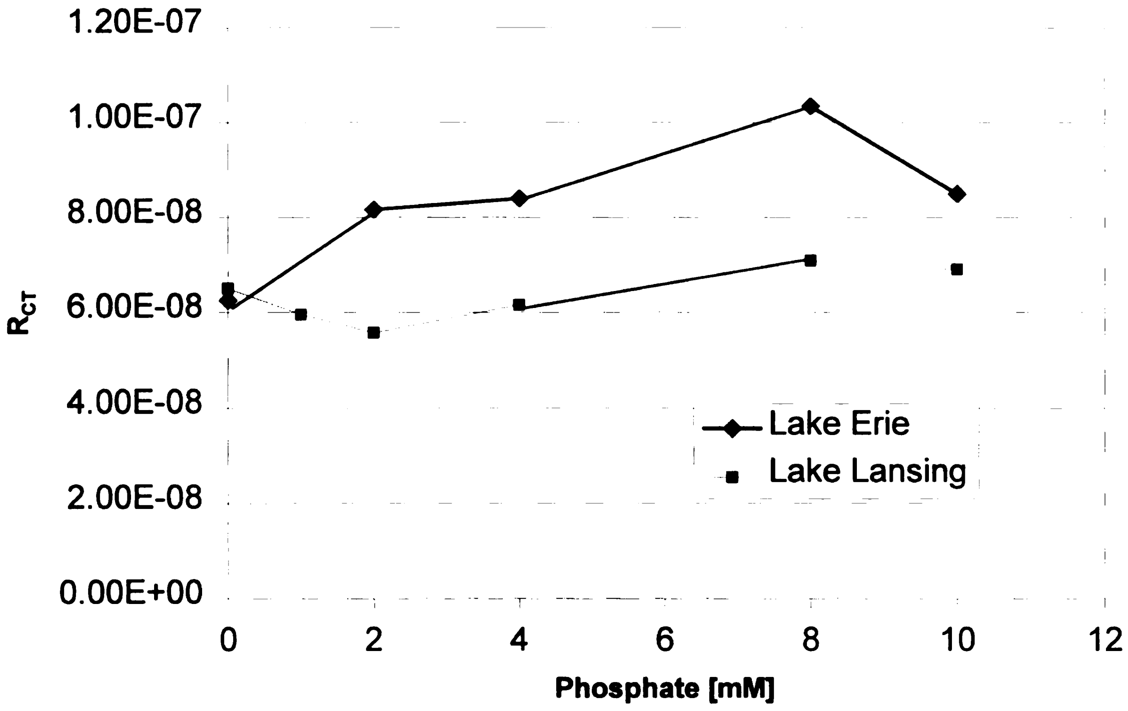


Figure 11.2. The effect of phosphate on R_{CT} values (Ozone dosage: 1mg O_3/mg C, Temperature: 25 °C).

11.2. Formation of ketoacids in solutions containing phosphate

The concentration of ketoacids formed in the presence of phosphate is shown in Figure 11.3. Based upon our hypothesis that the predominance of molecular ozone reactions would increase the formation of ketoacids, it was expected that the concentration of ketoacids would decrease as the concentration of phosphate increased since the concentration of OH radical is increased due to the promotion reaction of phosphate.

As observed in Figure 11.3, the concentration of ketoacids increased at low concentrations of phosphate ion (<2mM). However, the concentration of ketoacids decreased as the concentration of phosphate increased above this threshold value. The result confirms the hypothesis that the formation of ketoacids is hampered under conditions where the OH radical reaction predominates. It also substantiates the hypothesis that promoters and scavengers play a role greater than just reacting with ozone and OH radicals. It appears that as with bicarbonate, the relationship between R_{CT} and by-product concentration is much more complex than originally hypothesized. As with bicarbonate/carbonate radicals, the phosphate radicals may react with the NOM present in solution.

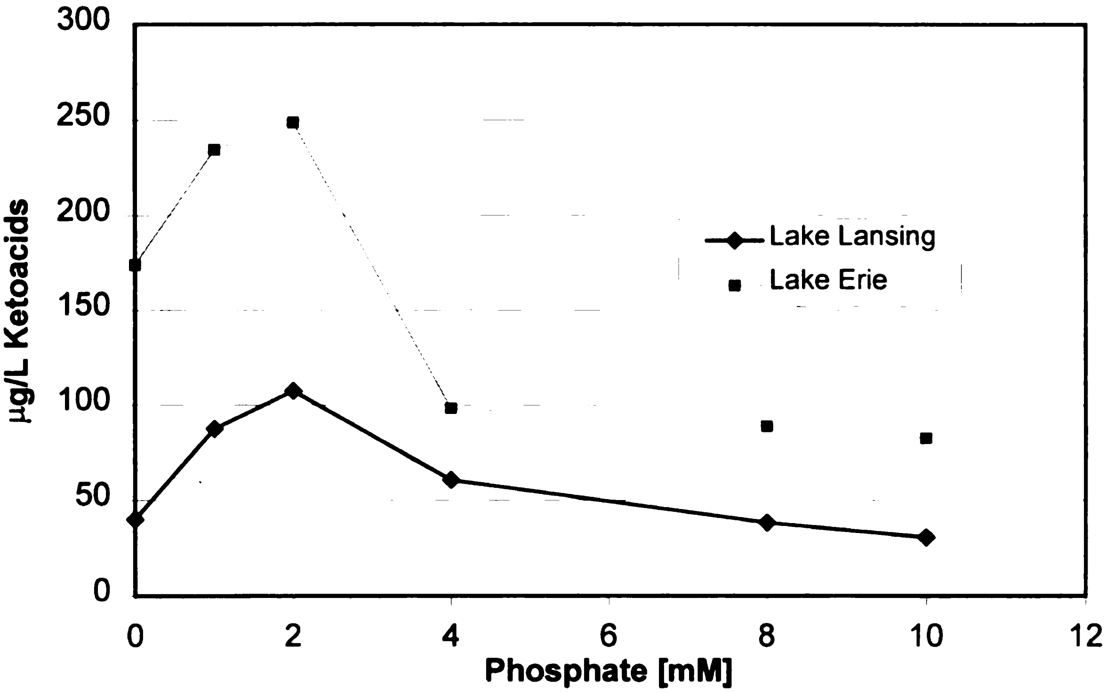


Figure 11.3. The effect of phosphate on the formation of ketoacids (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 ^oC).

11.3 Formation of AOC in solutions containing phosphate ions

Since the formation of AOC occurs by reactions involving molecular ozone, the concentrations of AOC are expected to decrease as the concentration of phosphate increases, since OH radical reactions will predominate at high concentration of phosphate. As shown in Figure 11.4, the concentration of AOC decreased as the concentration of phosphate was increased in both Lake Erie and Lake Lansing water (See Figure 11.4). This result also confirms the hypothesis that the reaction of molecular ozone with NOM is the predominant source of AOC rather than OH radical reaction. The addition of phosphate (10mM) before ozonation resulted in 77% and 22% lower concentrations of AOC in Lake Erie and Lake Lansing than that of the raw water.

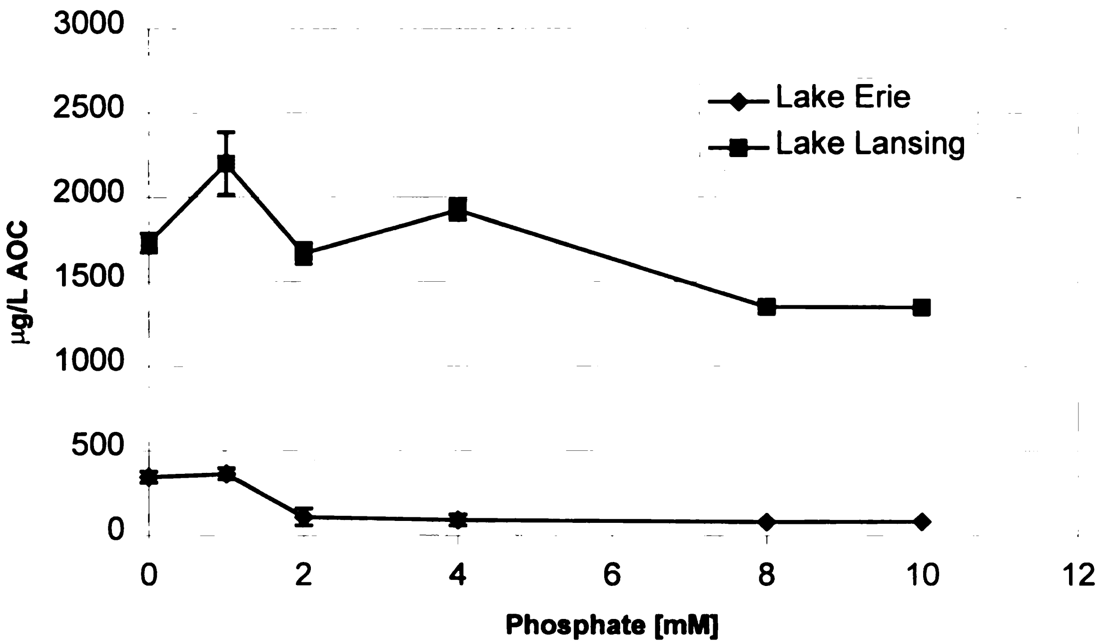


Figure 11.4. The effect of phosphate on the formation of AOC (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

11.4. Formation of THMs and HAAs in solutions containing phosphate ions

Since phosphate is a promoter of OH radicals, the formation of THMs and HAAs in the presence of phosphate ions is expected to increase due to the increased prevalence of the OH radical reaction. The results obtained for THMs and HAAs in both Lake Erie and Lake Lansing water are consistent with that observed with AOC and ketoacids, (See Figure 11.5 and Figure 11.6) and the hypotheses put forth in this work. In general, the concentration of HAAs increased as the concentration of phosphate increased. This result is consistent with the hypothesis that the formation of THMs and HAAs occurs, predominately, as a result of the reaction of OH radicals with NOM. However, as with R_{CT} and AOCs, the concentrations of THMs and HAAs leveled off at high phosphate concentrations. This result further supports the hypothesis that at high concentrations, the phosphate ion acts as an inhibitor, thereby decreasing the concentration of OH radicals and the importance of the OH radical reaction compared with the molecular ozone reaction.

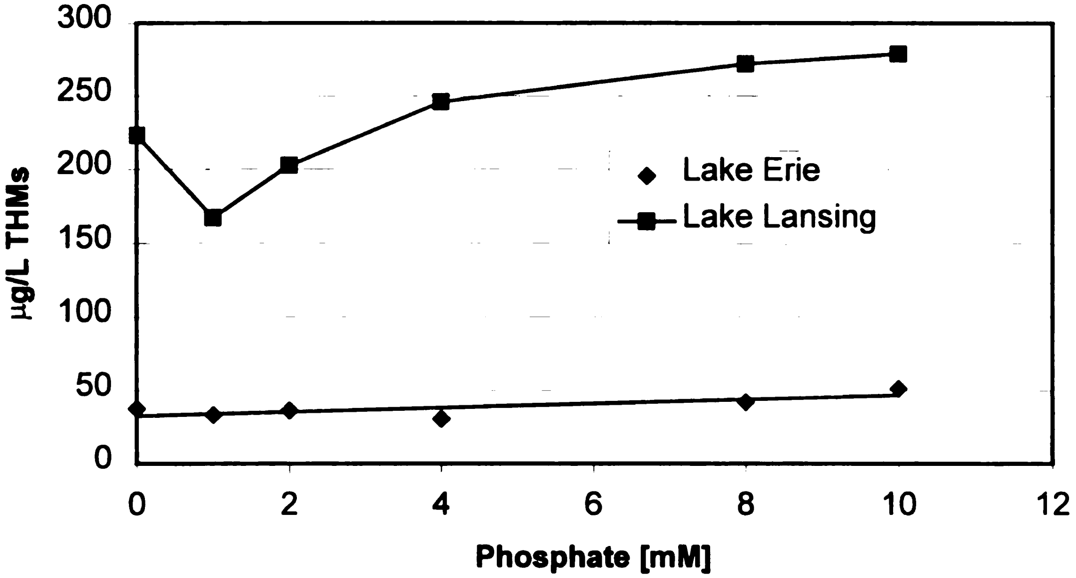


Figure 11.5. Effect of phosphate on the formation of THMs (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

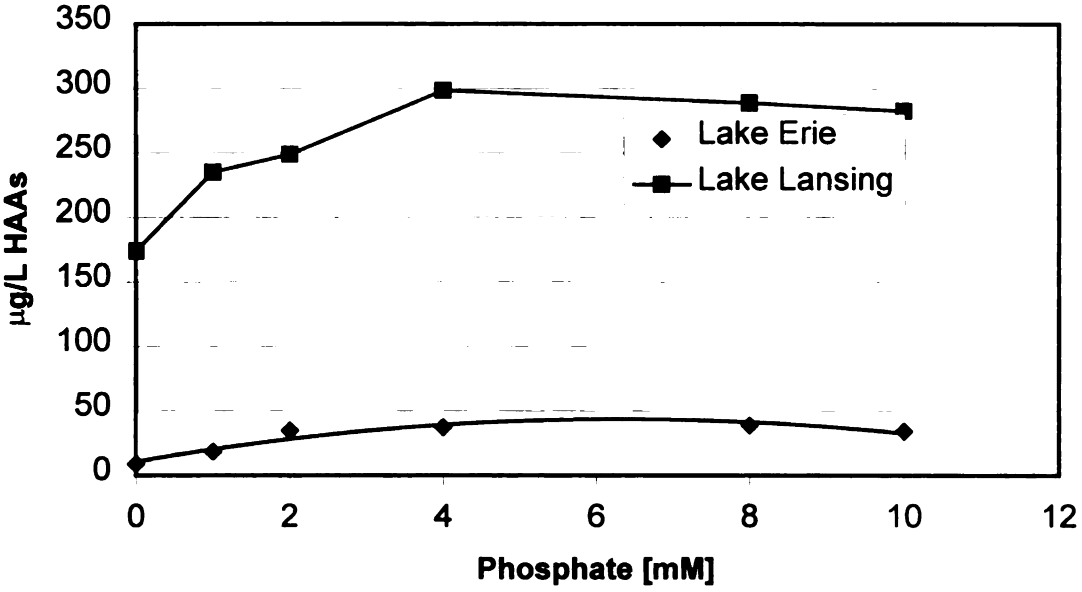


Figure 11.6. Effect of phosphate on the formation of HAAs (Ozone dosage: 1mg O_3/mg C, HRT: 12.5 min, Temperature: 25 °C).

12. COMPARISON OF WATER CHARACTERISTICS

The results obtained in this study were used to calculate the rate constants for the reaction of OH radical with NOM ($k_{OH,NOM}$) based upon the methodology developed by Haag and Yao (1993). The rate constant for the OH radical reaction with NOM was determined by using the Ω concept developed by Haag and Hoigné (1985). The Ω value is defined as the amount of ozone that is necessary to degrade one log unit removal (37 %) of an OH radical probe compound. The Ω value was determined from the slope of a plot of ln {[PCBA]/[PCBA]$_o$} vs. dosed initial ozone concentrations, such that:

$$\Omega_{PCBA} = \frac{-\ln \frac{[PCBA]}{[PCBA]_0}}{[O_3]_{added}} \qquad \text{Eq. 12.1}$$

If PCBA is present at a low aqueous concentration relative to that of NOM and the OH radical is consumed only by NOM, the assumption can be made:

$$k_{OH,PCBA}[PCBA] <<<< k_{OH,NOM}[NOM] \qquad \text{Eq. 12.2}$$

Then, the steady-state concentration of the very short lived OH radicals can be determined by Eq. 12.3:

$$[OH\cdot]_{SS} = -\eta \frac{\Delta[O_3]}{\Delta t} \times \frac{1}{\Sigma k_{OH,NOM}[NOM]} \qquad \text{Eq. 12.3.}$$

where η is stoichiometric yield of OH radicals from ozone decomposition. A value of 0.67 is usually selected for η based on the based-catalyzed OH radical yield without promotion (Westerhoff et al. 1999). This OH radical concentration can be applied to the PCBA degradation equation (Eq. 12.4), such that:

$$-\frac{d[PCBA]}{dt} = k_{OH,PCBA}[PCBA][OH\cdot]_{ss} = k_{\text{exp}eriment}[PCBA] \qquad \text{Eq. 12.4.}$$

Thus, the OH radical concentration at steady-state can be described as Eq. 12.5.

$$[OH]_{SS} = \frac{k_{\text{exp}\,eriment}}{k_{OH,PCBA}} \qquad \text{Eq. 12.5.}$$

Integration of equation 12.4 and then substitution of Eq. 12.3 into Eq. 12.4 yields Eq. 12.6.

$$-\ln\frac{[PCBA]}{[PCBA]_0} = \eta \cdot \frac{k_{OH,PCBA}}{\Sigma k_{OH,NOM}[NOM]} \cdot \int_0^t d[O_3] = k_{\text{exp}eriment} \times t \qquad \text{Eq. 12.6.}$$

When ln[PCBA]/[PCBA]$_o$ =1 (PCBA is degraded 37 %), the amount of ozone consumed until this time represents the Ω value. Thus, Eq. 12.6 can be rewritten as:

$$\eta \cdot \Omega_{PCBA} = \frac{k_{OH,NOM}}{k_{OH,PCBA}} \qquad \text{Eq. 12.7.}$$

The determination of Ω and η values for the raw water tested can give the rate constant for the reaction of OH radical with NOM. These values can be used in the analysis to understand the pathways for the ozonation of NOM in various water sources. When the concentration of either ozone or promoter is much less than that of NOM and the rate of reaction of OH radical with NOM is slower than that of OH radicals with ozone or ozone decomposition intermediates, the OH radicals might be consumed during ozone decomposition, even though the formation of the OH radical is enhanced.

The values for DOC, alkalinity, Ω_{PCBA}, R_{CT}, and rate constant of OH radical with NOM obtained in this study were compared to that obtained in other U.S. surface waters (Table 12.1). The ratios of [OH·]/[O_3] were quite constant, ranging from 0.76 to 1.56 for all waters except Lake Lansing water (value of 0.06) and Eno River water (Durham, NC) (value of 2.66). As such, the ratio of [OH·]/[O_3] appears to be independent of the DOC concentration.

The relationship between Ω_{PCBA} and DOC is plotted in Figure 12.1. The results indicate that Ω_{PCBA} is linearly correlated with the DOC. The equation describing this relationship is (0.519 ± 0.04) DOC - 0.286 when data for Lake Erie and Lake Lansing water are included. This resulted in a lower slope compared to the equation (Ω_{PCBA} =

(0.57± 0.05)·DOC - 0.42; r^2= 0.989) obtained by Haag and Yao (1993). However, using the F test (See Appendix, Park J.H. 2000, Anderson R.L. 1987), yielded F values for the results of 0.25 and the F value based on the degree of freedoms (n) is 8.18 for a confidence interval of 99%. Therefore, the slope obtained by us and Haag and Yao (1993) are not statistically different at a 99 % confidential interval. These results are important since they allow for the estimation of ozone consumption in U.S. surface waters, along with estimating OH radical concentrations based upon DOC concentrations.

The rate constant for the reaction of the OH radical with NOM in Lake Lansing water is quite low compared to that obtained using Lake Erie water. This result contrasts with the previous results that indicated that the rate constant for the reaction of OH radical with NOM in Lake Erie water (in Chapter 5) is greater than that obtained using Lake Lansing water. In order to determine the rate of reaction for the OH radical with NOM, a value of 0.67 was used for the stoichiometric yield, η, of OH radicals from ozone decomposition. This value does not consider the promotion or inhibition roles of NOM (Westerhoff et al. 1999). As such, the difference in the rate constants obtained using this calculation and that obtained from experiments indicates the importance of promotion and inhibition reactions. As expected, this difference also indicates that the influence of these reactions varies with water source.

Table 12.1. Characteristics of U.S. surface waters

Water sample	DOC mg/L	Alkalinity meq/L	Ω_{PCBA} mg/L Ozone	10^7 [OH]/[O_3]	$10^{-4}k_{OH,DOC}$ L·s/(m DOC)
Hetch Hetchy Res. Yosemite Park, CA	1.4	0.0065	0.7	1.56	3.49
***Lake Erie, Monroe, MI**	**2.0**	**1.8**	**1.02**	**1.13**	**3.56**
L.Crystal Springs Res. Hillsborough, CA	2.1	0.39	0.68	1.26	2.26
San Andreas Res. Millbrae,CA	2.4	0.41	0.72	1.11	2.09
San Antonio Res, Sunol, CA	2.6	0.6	0.84	0.81	2.25
Potomac River Reston, VA	3.3	0.68	1.34	1.09	2.83
Calaveras Res. Milpitas, CA	3.7	1.25	2.12	0.76	4.00
Eno River Durham, NC	4.8	0.19	2.18	2.66	3.17
Lake Hennessey Napa, CA	5.6	1.33	2.77	1.05	3.45
***Lake Lansing, Haslett, MI**	**9.5**	**2.5**	**3.59**	**0.06**	**2.64**
Virginia Key Wastewater Miami, FL	14.1	2.13	7.62	1.08	3.77
			Averages:	1.14 ± 0.63	3.05 ± 0.66
Aldrich Humic Acid	4.8	0	2.75		4.0

*Obtained from this research †Reference: Haag and Yao (1993)

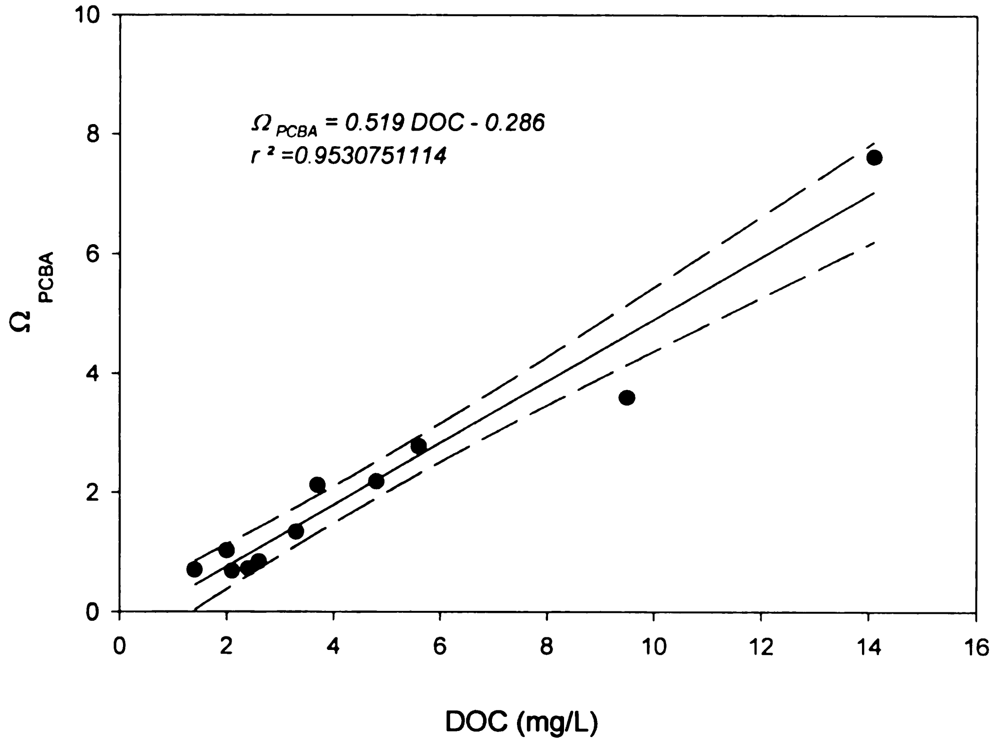


Figure 12.1. Correlation between DOC and Ω_{PCBA} in U.S. surface water (Dashed line: 95 % confidence interval).

It was attempted to correlate ketoacids and AOC concentrations on formed upon ozonation of Lake Erie and Lake Lansing water. Since the ketoacids as biodegradable compounds, the ketoacids would be portion of AOC. However, as shown in Figure 12.2, no correlation between ketoacids and AOC was found. This result indicates that the portion of ketoacids concentration in AOC is significantly smaller than expected. Not only the variability of the biodegradable organic carbon formed upon ozonation but also small portion of ketoacids in AOC would result in insignificant correlation (r^2 = 0.499) between ketoacids and AOC.

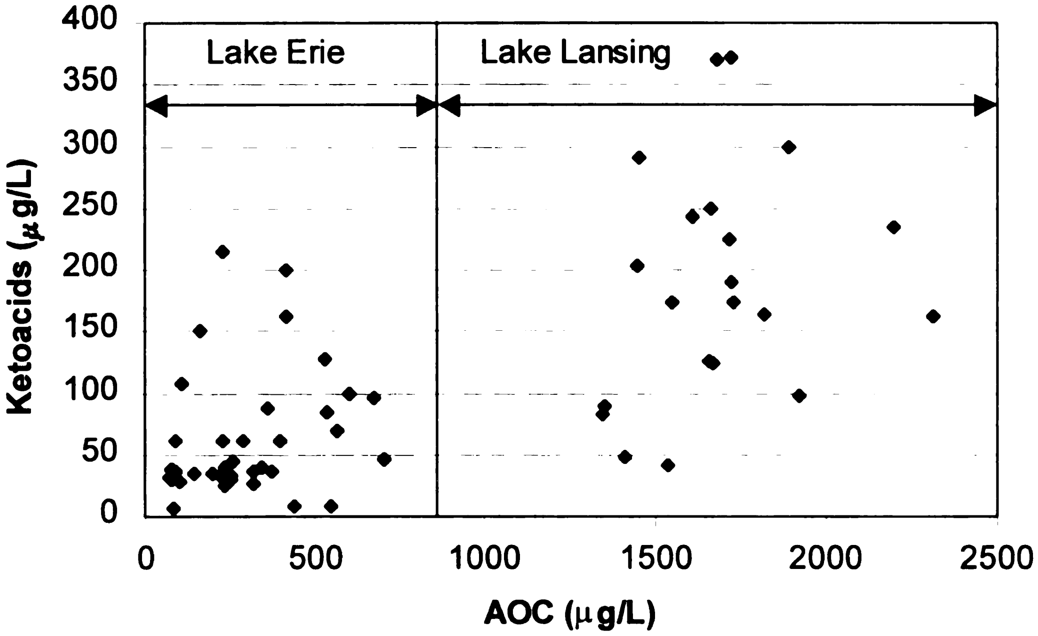


Figure 12.2. Correlation between ketoacids and AOC in Lake Erie and Lake Lansing water.

13. CONCLUSIONS

1. The R_{CT} values obtained experimentally allowed us to not only determine the ratio of OH radical to molecular ozone concentration at the various ozonation conditions but also indicated the reaction rate of OH radical with NOMs tested. The NOM of Lake Erie reacts with OH radicals more slowly than does the NOM present in Lake Lansing and the NOM of Lake Erie has a capability to promote more OH radical formation than does that of Lake Lansing.

2. The OH radical concentration was calculated based on R_{CT} values. During the ozonation time, the R_{CT} values were constant even though the ozone decomposes continuously. The formation of DBPs on ozonation was influenced by the ratio of the concentration of OH radical and molecular ozone rather than reaction time.

3. The R_{CT} values at various temperatures (ranges from 10 to 40 °C) linearly increased as temperature increased. However, due to the changes in the reaction rate of OH radical and molecular ozone with NOM on the temperature, the formation of ketoacids, AOC and DBPs are independent of R_{CT} values.

4. Ozonation at various pH (2 to 10) significantly changed the R_{CT} values, the R_{CT} did not affect the reaction of ozonation with NOM due to high concentration of scavenging capacity of the OH radical. The secondary radical species produced from

OH radical reaction with scavenging species also affected the reaction of NOM with ozone.

5. Bicarbonate ion inhibited the reaction of the OH radical with NOM. However, carbonate radicals produced from the reaction of OH radical with carbonate ion resulted in oxidation of NOM otherwise oxidized by OH radicals.

6. OH radical concentrations increased with increasing hydrogen peroxide up to the ratios $[H_2O_2/O_3]$ of 0.3 to 0.5 [Wt/Wt] in both water sources. The higher the concentration of OH radical formed, the lower the concentration of ketoacids, AOC and DBPs produced.

7. Phosphate ion plays a promoter role in ozonation increasing OH radical. Ozonation in the presence of phosphate ion (0 to 10 mM) the concentration of AOC resulted in 77% and 22% lower concentration of AOC in Lake Erie and Lake Lansing than that of the raw water.

8. The Ω_{PCBA} obtained from Lake Erie and Lake Lansing was compared with that of other surface water in U.S. A correlation between DOC and Ω_{PCBA} for surface water including Lake Erie and Lake Lansing was predicted. The results using Lake Erie and Lake Lansing water were not statistically different at a 99 % confidential interval included within a confidence interval of 99% obtained by us and Haag and Yao (1993). The rate constants of OH radical with NOMs were determined in Lake Erie

and Lake Lansing, 3.56×10^{-4} and 2.64×10^{-4} L·s/(M of DOC), respectively. Since the calculation excluded the promotion role of NOM on ozonation, it showed difference from the R_{CT} value obtained in this study. The calculation of the rate constant including promotion role of NOM on ozonation is recommended for future research.

9. The concentration of ketoacids and AOC were not correlated since the ketoacids has smaller potion of AOC thereby, giving more variability than expected.

10. The formation of AOC indicates that the reaction of molecular ozone with NOM is the predominant source of AOC rather than OH radical reaction and that the formation of DBPs decreased under the molecular ozone predominant condition. However, the NOM characteristics and background characteristics affecting ozone decomposition also need to be considered for predicting the formation of AOC and DBPs.

11. These results would important for water treatment industry to not only control the concentration of AOC and DBPs but also understand ozone reaction with NOM on ozonation.

12. The followings are recommended for a future research.

- The rate constants of NOM with OH radical and ozone considering the promotion effect is needed to predict the concentration of AOC and DBPs.
- More water sources in U.S. need to be tested to confirm the correlation obtained in this study.
- Prior to application of controlling AOC and DBPs for the fields, the cost estimation needs to be calculated.
- The computer modeling work including the mechanisms suggested in this research need to be tested by the field operators if the results would be incorporated with the results in the fields.

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APPENDICES

Calculation of rate constant of $k_{NOM,OH}$

Reaction rate of OH radical with bicarbonate

Temperature	lnA			$k_{HCO3,OH}$
278	12.8	0.009172359	12.79082764	358910.2517
288		0.008853874	12.79114613	359024.5773
298		0.008556764	12.79144324	359131.2629
308		0.008278947	12.79172105	359231.0496

Reaction rate of ozone with hydroxide

	$k_{O3,OH-}$
278	69.89062148
288	69.96478778
298	70.03404744
308	70.09887174

Determination of A for O_3OH^-

	0.971434034
A=	72.05841834

Temperature	R_{CT}	Calculated	$k_{O3,OH-}$	Denominator 2*k*OH
5	2.65E-08	2.47E-08	69.89062148	1.39781E-05
15	4.42E-08	4.43E-08	69.96478778	1.3993E-05
25	8.61E-08	8.61E-08	70.03404744	1.40068E-05
35	1.27E-07	1.27E-07	70.09887174	1.40198E-05

$k_{HCO3,OH}$	$k_{NOM,OH}$	Numerator
3.5891E+05	-275805.71202	5.66E+02
3.5902E+05	-1838904.14493	3.16E+02
3.5913E+05	-2799017.37871	1.63E+02
3.5923E+05	-3126882.90438	1.10E+02

R_{CT}x10^8	Calculatedx10^8	Substract
26.5000000	24.6955249	3.2561304
44.2000000	44.2651054	0.0042387
86.1000000	86.1001841	0.0000000
127.0000000	127.0004653	0.0000002
	3.2603694	Sum

F test[2]

A variance ratio test used to decide whether two independent estimates of variance can reasonably be accepted as being two estimates of the variance of a single normally distributed universe.

$$F = \frac{S_A^2}{S_B^2}$$

Where

S_A^2 = the larger variance estimate
S_B^2 = the smaller variance estimate

F test for a group of sets[3]

$$F = \frac{(RSS_{12} - RSS_1 - RSS_2)/(df_{12} - df_1 - df_2)}{RSS_{12}/df_{12}}$$

where

RSS = $\Sigma(yi\text{-}\hat{}yi)^2$: Residual sum of square
SST= $\Sigma(yi\text{-}\bar{}yi)^2$: Total sum of square
yi = datum point
^yi = predicted point by equation
¯yi= mean of data
RSS_1= Residual sum of square at first set
RSS_2 = Residual sum of square at second set
RSS_{12}= Residual sum of square at combined set

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[2] Anderson R.L., 1987

[3] Park J.H., 2000