

FORMATION OF KETOACIDS AND AOC DURING OZONATION IN DRINKING WATER

Kyung-Hyuk Lee[†]

Water Research Center, Korea Institute of Water and Environment,
462-1 Jeonmin-Dong, Yuseong-Gu, Daejeon, Korea 305-730

Abstract : The reaction of ozone with NOM (Natural Organic Matter) can occur by two different pathways: that involving molecular ozone and by way of reactions with hydroxyl radicals which are produced from the decomposition of molecular ozone. As such, the formation of ketoacids and Assimilable Organic Carbon (AOC) can be controlled by controlling the pathway by which ozone reacts with NOM. The ratios of $[OH\cdot]/[O_3]$ (R_{CT} values) were determined under the various ozonation conditions. The R_{CT} values increased with increasing initial ozone concentration. The R_{CT} values (ranges from 10 to 35°C) increased linearly as temperature increased (within the range from 10 to 35°C). However, R_{CT} was independent of hydraulic retention time (HRT). Operational conditions were found to affect the formation of AOC. The conditions where the molecular ozone reaction predominated resulted in an increase in the formation of AOC.

Key Words : Ozonation, Ketoacids, AOC (Assimilable Organic Carbon), Molecular Ozone, Hydroxyl Radical

INTRODUCTION

In order to comply with more increasingly stringent regulations concerning Disinfection By-products (DBPs), many water treatment plants in the United States have replaced prechlorination with ozone. Although the use of ozone reduces the concentrations of THMs and HAA in the treated water^{7,8,14}, ozonation can result in other problems, such as an increase in the formation of Assimilable Organic Carbon (AOC), which can enhance the regrowth of bacteria in the distribution system.

Richardson et al.¹² and Gracia et al.⁵ 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. Comparing the concentrations

of these by-products, the concentrations of ketoacids, as a portion of the ozonation by-products, were observed to be much higher than that of aldehydes^{6,19}. The concentrations of the ketoacids (gloxalic acid, pyruvic acid and ketomalonic acid) increased with increasing ozone dose^{6,19}. The formation of ketoacids, those are easily biodegradable compounds, has been correlated with the formation of Biodegradable Organic Carbon (BDOC)⁶. This result implies that the ketoacids would be appropriate indicators of biological stability.

Masten et al.¹⁰ found that the reaction of molecular ozone with DEET (N,N-diethyl-m-toluamide), which has an aromatic ring, produced several hydrophilic by-products. Yao et al.²⁰ 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 the formation of various carboxylic acids and aldehydes. Determination of AOC is based on culturing

[†] Corresponding author
E-Mail: kh.lee@kowaco.or.kr
Tel: +82-42-860-0373, Fax: +82-42-860-0399

bacteria that utilize groups of specific compounds such as carboxylic acids or carbohydrates¹⁷⁾. Thus, if the ozone reaction pathways with Natural Organic Matter are controlled for the formation of AOC, the biological regrowth potential of the drinking water could also be controlled.

The aim of this study was to investigate the ozonation pathways that mitigate the formation of ketoacids and AOC. Since the characteristics of NOM, the initial $[O_3]/[NOM]$ concentration ratio, reaction temperature, reaction time affect the pathways by which ozone reacts with NOM the influence of these parameters on the formation of ketoacids and AOC were investigated.

MATERIAL AND METHODS

The water sources tested in this study were 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 2.5 and 10 ppm, respectively.

The experiments to determine $[OH\cdot]/[O_3]$ concentration ratio were conducted by using the method developed by Elovitz and von Guten⁴⁾ using PCBA (*p*-chlorobenzoic acid) as OH radical probe compound. The R_{CT} values were obtained on the various ozonation conditions in the batch type ozonation reactor (Figure 1). The saturated ozone solution was prepared in phosphate buffered D.I. water (1 L glass bottle) by providing gaseous ozone into the solution. A syringe type (headspace-free) batch reactor (250 mL) was used for ozonation experiments to prevent volatile losses of ozone from the solution. Prior to ozonation, the water samples were pre-filtered through a 0.45 μ m membrane filter to remove particulate matter. The solutions tested were prepared by adding stock solution of PCBA (approximately 100 ppb). When the desired concentration of ozone was achieved, an aliquot of the ozone stock solution was transferred immediately into the reactor. A magnetic stirrer

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 method¹⁵⁾. In order to investigate 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 ozone had completely decomposed, a sample also was taken to measure the residual additives and/or PCBA concentration.

A continuous semi-batch reactor (water-jacked glass reactor, 250 mL) was used for ozonation experiments in which the formation of AOC and ketoacids were monitored under various conditions. The ozone gas was dispersed in the reactor using a fritted glass diffuser. The residual ozone was quenched by sparging the solution with a high purity helium gas (99.999%). The concentration of generated gaseous ozone was measured at UV 254 nm with a UV/Vis spectrophotometer¹¹⁾. An extinction coefficient of 3,000 $M^{-1}cm^{-1}$ at 254 nm¹⁾ was used for calculating ozone concentrations.

TOC was measured with TOC analyzer (OI Analytical Model 1010, College Station, TX). PCBA (*p*-chlorobenzoic acid) was analyzed by HPLC (Perkin Elmer series 200, Norwalk, CT)

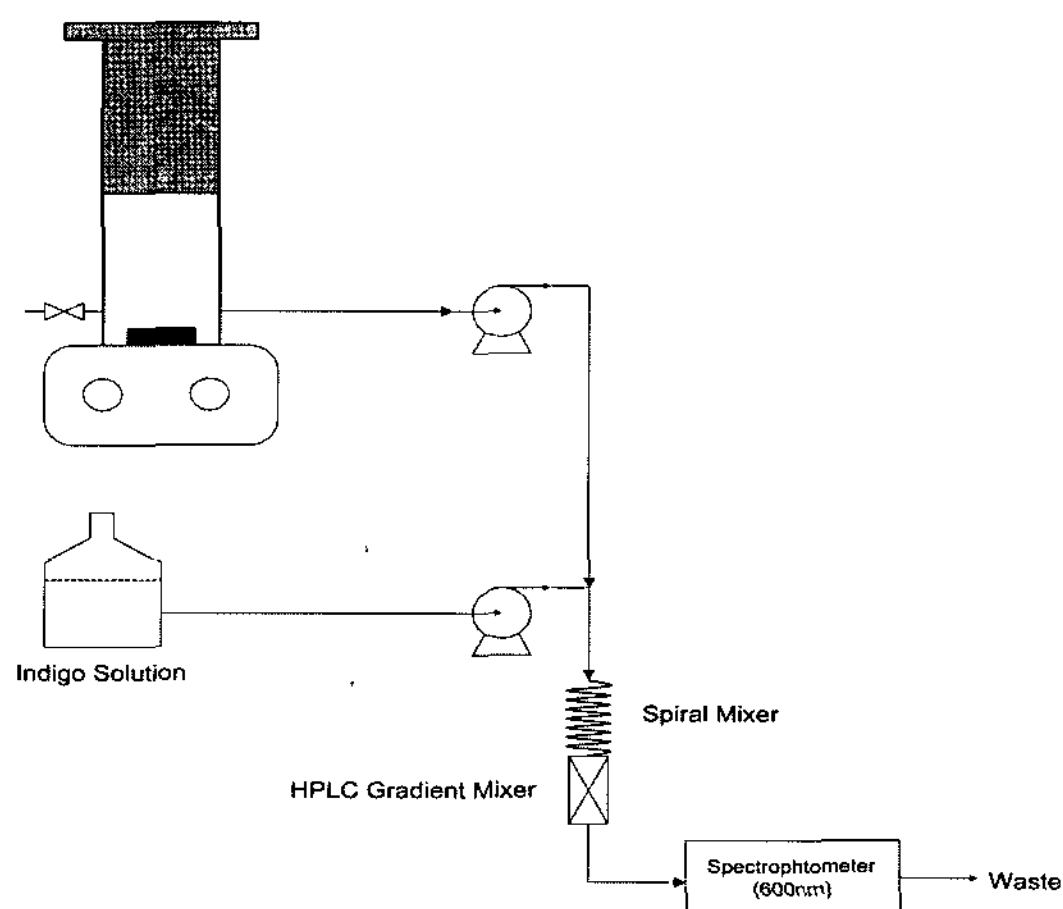


Figure 1. Schematic diagram of batch ozone reactor for determination of R_{CT}

with UV-vis detector (Waters 2487, Milford, MA) at 234 nm. Acetonitrile and D.I. Water mixture (60:40 wt %) were used as the HPLC eluent at a flow rate of 1.0 ml/min.

Ketoacids (Glyoxylic acid, pyruvic acid and ketomalonic acids), monitored as ozonation by-products, were determined by the PFBHA-diazomethane double derivatization procedure followed by GC/ECD equipped with DB-5 column (J&W Scientific). AOC was measured by the method developed by Van der Kooji et al.¹⁷⁾ and modified by adding inorganic nutrients, i.e., nitrate, phosphate, to the samples. A aliquot (100 μ L) of the nutrient solution containing 4.5 g $(\text{NH}_4)_2\text{SO}_4$, 0.2 g KH_2PO_4 , 0.1 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.2 g NaCl in 1,000 mL D.I. water was added into 100 mL samples, since nutrients, especially phosphorus, are often the limiting factor for microbial growth in treated drinking water¹¹⁾.

RESULTS AND DISCUSSION

R_{CT} Values on the Effect of Ozonation

In order to investigate the effect of the ratio of $[\text{O}_3]/[\text{OH}\cdot]$ on the formation of ketoacids, and AOC, the effect of ozone dosage on R_{CT} values were investigated in the batch reactor. As shown in Figure 2, the R_{CT} value increased with increasing ozone dosage. As the concentration of ozone increased, more ozone autocatalytically decomposed to form the OH radical. Differences in the characteristics of the NOM and/or in background electrolytes in the water sources also play a significant role in the formation of OH radicals and in the resulting R_{CT} value. Because NOM acts both as a promotor and inhibitor of ozone decomposition and the inorganics present in water can scavenge OH radicals, both NOM and inorganic species affect the production of the 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), thereby elimi-

nating the effects of carbonate and bicarbonate, both OH radical scavengers (see Figure 2). 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) water was greater than that in waters of high alkalinity (140 mg/L as CaCO_3). Thus, it can be concluded that the reaction of NOM with the OH radical is slow compared to the rate of reaction with the bicarbonate ion and the OH radical produced from ozone decomposition reacts predominantly with bicarbonate ions at the high ozone dosage.

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 CaCO_3). 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 R_{CT} 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, this phenomenon also contributes to the higher R_{CT} 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

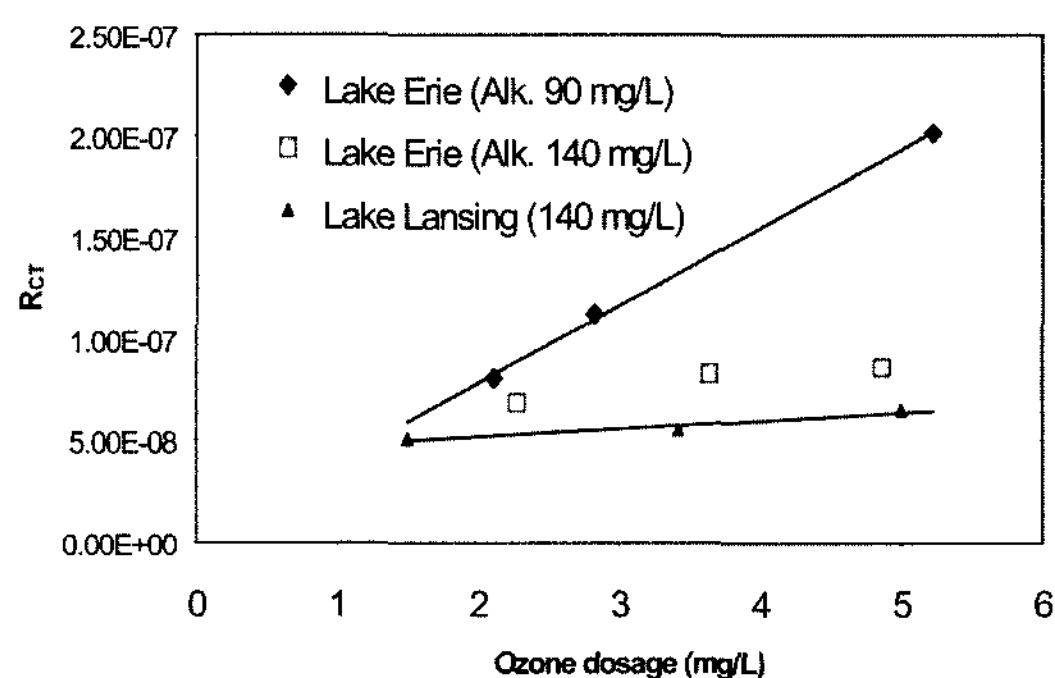


Figure 2. The effect of ozone dose on R_{CT} values (TOC: 2.0 mg/L for Lake Erie and 9.5 mg/L for Lake Lansing, Temperature 25°C).

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 from Lake Erie water has the capability to better promote OH radical formation than does that from Lake Lansing.

The effect of HRT on the R_{CT} values obtained for each water sources were investigated. The steady state 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. As shown in Figure 3 and Figure 4, 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.

The half-life of OH radical increased by a factor of approximately three over the course of a typical ozonation experiment (Table 1.), although the changes in the R_{CT} values with varying experimental conditions were small. Such small changes in the half-live of the OH radical may be critical. However, as expressed in Equation 1, if the value of $k_{O_3}[O_3][NOM]$ is greater than $k_{OH}[OH][NOM]$, the increased concentration of OH radical at high HRTs will not significantly

affect the ozonation reaction involving NOM.

$$k_{O_3}[O_3] \cdot [NOM] \geq k_{OH}[OH] \cdot [NOM] \quad (1)$$

k_{O_3} : Rate constant of ozone with NOM

k_{OH} : Rate constant of OH radical with NOM

As shown in Figure 3 and Figure 4, the ratio of $[OH]/[O_3]$ was essentially constant during the ozonation due to the significantly high concentrations of ozone compared to that of OH radical (a factor of 6 to 7). According to previous research¹⁸⁾, the rate constant for the reaction of OH radical with NOM is 3.6×10^8 L (mol C)⁻¹ s⁻¹ (assuming a mass of 12 g C per mole C), corresponding to values of 6.0×10^4 s⁻¹, and 3.0×10^5 s⁻¹ for Lake Erie water and Lake

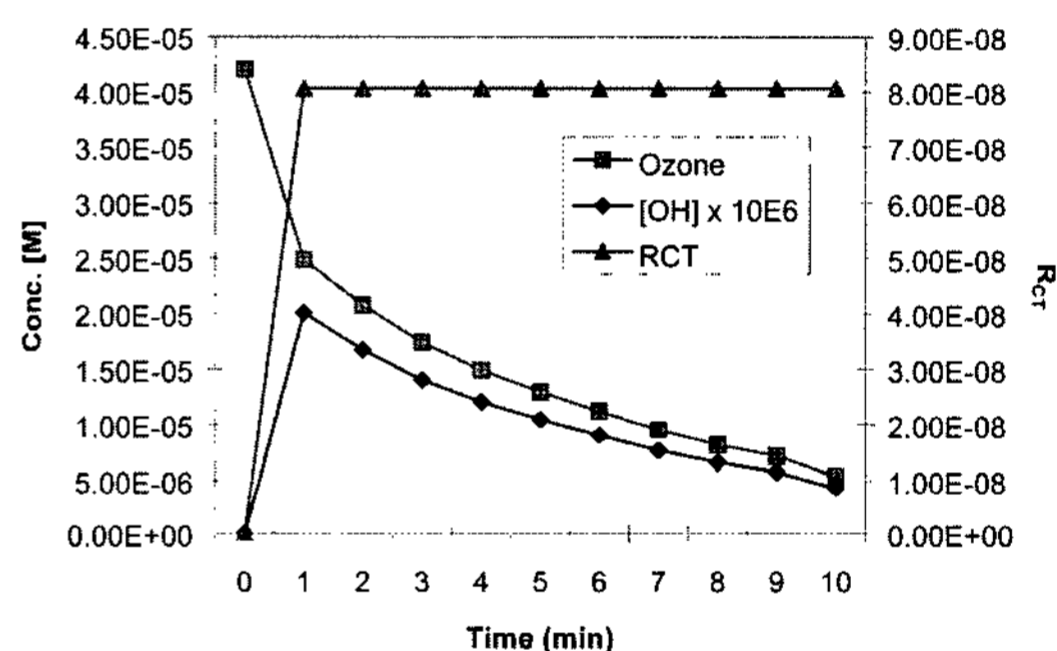


Figure 3. The effect of HRTs on Ozone, OH radical concentration and R_{CT} values in Lake Erie water (Ozone dosage: 1mg O_3 /mg C, Temperature: 25°C).

Table 1. Comparison of R_{CT} values and Half-life of OH radical in Lake Erie water and Lake Lansing water

Time	Lake Erie				Lake Lansing			
	Ozone (M)	[OH] x 10 ¹² (M)	R_{CT} x 10 ⁻⁸	Half-life of OH radical (time)	Ozone (M)	[OH] x 10 ¹² (M)	R_{CT} x 10 ⁻⁸	Half-life of OH radical (time)
0	4.2E-05	0	0		1.03E-04	0	0	0
1	2.49E-05	2.006	8.05999	3.45E-07	8.91E-05	4.280	4.79999	4.28E-05
2	2.08E-05	1.673	8.06000	4.14E-07	7.39E-05	3.546	4.79997	3.55E-05
3	1.74E-05	1.401	8.06000	4.94E-07	6.15E-05	2.950	4.79996	2.95E-05
4	1.49E-05	1.202	8.05999	5.77E-07	5.47E-05	2.624	4.79997	2.62E-05
5	1.3E-05	1.044	8.08475	6.64E-07	4.73E-05	2.269	4.80004	2.27E-05
6	1.12E-05	0.901	8.06000	7.69E-07	4.08E-05	1.959	4.80000	1.96E-05
7	9.51E-06	0.766	8.05999	9.04E-07	3.53E-05	1.693	4.80004	1.69E-05
8	8.17E-06	0.658	8.06000	1.05E-06	3.04E-05	1.460	4.79999	1.46E-05
9	7.14E-06	0.575	8.06000	1.20E-06				
10	5.36E-06	0.432	8.05999	1.60E-06				

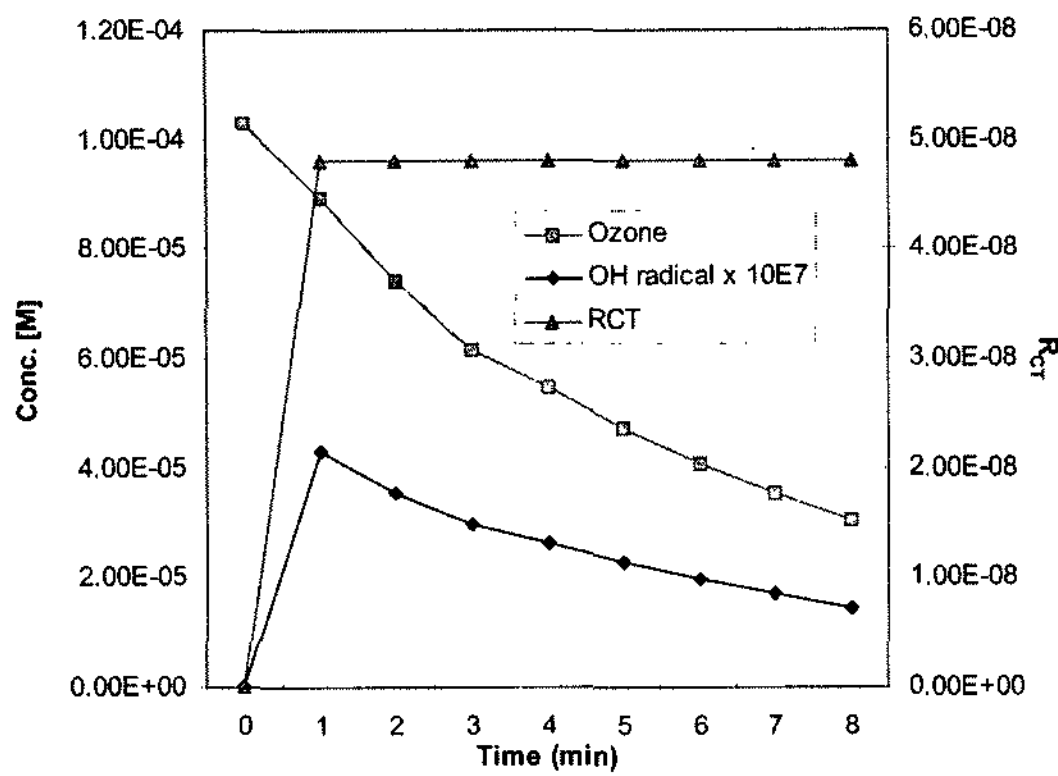


Figure 4. The effect of HRTs on Ozone, OH radical concentration and R_{CT} values in Lake Lansing water (Ozone dosage: 1mg O_3 /mg C, Temperature: 25°C).

Lansing water, respectively since 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.

The effect of temperature on R_{CT} was studied within the temperature range from 5 to 35°C (See Figure 5). Sotelo et al.¹³⁾ showed that while the ozone decomposition rate increased with temperature, the ozone initiation rate is negligible at pH values below 3 and at temperatures ranging from 10 - 40°C.

Based on the elementary reaction of ozone decomposition, the OH radical concentration at steady state conditions can be expressed by following equation (2).

$$[OH]_{ss} = \frac{2(k_{O_3,OH^-})_T [O_3]_T [OH^-]_{ss} + (k_{O_3,NOM})_T [NOM]_T}{(k_{HCO_3,OH})_T [HCO_3^-] + (k_{NOM,OH})_T [NOM]} \quad (2)$$

$[OH]_{ss}$: OH radical concentration at the steady state condition

$[OH^-]_{ss}$: Hydroxide ion concentration at the steady state condition

$(k_{NOM,OH})_T$: Rate constant of NOM with OH radical at temperature T

According to the Arrhenius law, elementary reaction rates increase with increasing temperature. Thus, the reaction rates that describe the initiation of ozone decomposition and the production of OH radicals, in the numerator of Equation 2, 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 Equation 2 is divided by $[O_3]$, the ozone concentration terms drop out of the numerator, and the resulting equation (3) is equivalent to R_{CT} :

$$\frac{[OH]_{ss}}{[O_3]} = \frac{2(k_{O_3,OH^-})_T [OH^-]_{ss} + (k_{O_3,NOM})_T [NOM]}{(k_{HCO_3,OH})_T [HCO_3^-] + (k_{NOM,OH})_T [NOM]} \quad (3)$$

$[OH]_{ss}$: OH radical concentration at the steady state condition

$[OH^-]_{ss}$: Hydroxide ion concentration at the steady state condition

$(k_{O_3,OH})_T$: Rate constant of ozone with hydroxide ion at temperature T

$(k_{O_3,NOM})_T$: Rate constant of ozone with NOM at temperature T

$(k_{HCO_3,OH})_T$: Rate constant of bicarbonate with OH radical at temperature T

$(k_{NOM,OH})_T$: Rate constant of NOM with OH radical at temperature T

The activation energy and frequency factor of the reaction of bicarbonate with the OH radical was determined by Buxton et al.²⁾ 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 determined¹⁶⁾, the reaction rate of ozone with hydroxide ion at various temperatures and the frequency factor can be calculated (see Table 2). 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 $k_{O_3,NOM}$ and $k_{NOM,OH}$ at the different temperatures are known.

Table 2. 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 for $k_{O_3,NOM}$ and $k_{NOM,OH}$ and the Arrhenius constants for the rate constants, the R_{CT} values can be calculated for the various temperatures used.

However, two parameters ($k_{O_3,NOM}$, $k_{NOM,OH}$) remained unknown. According to the Equation 3, if the $k_{O_3,NOM}$ term is assumed to be small compared to the hydroxide term, the R_{CT} value at steady state can be used to calculate the rate constant for the reaction of NOM with the OH radical. However, when this was done, a negative value was consistently obtained for the rate constant for the reaction of NOM with OH. The rate constant increased as temperature increased. Thus, it appears that the role of NOM for OH radical production is more significant as a promoter of molecular ozone rather than as an OH radical scavenger.

During ozonation, the OH radical concentration increased as temperature increased due to the acceleration of ozone decomposition with increasing temperature (See Figure 5). This result indicates that the denominator term of Equation. 3 does not increase as much as the numerator of Equation. 3 increases. As shown in Figure 5,

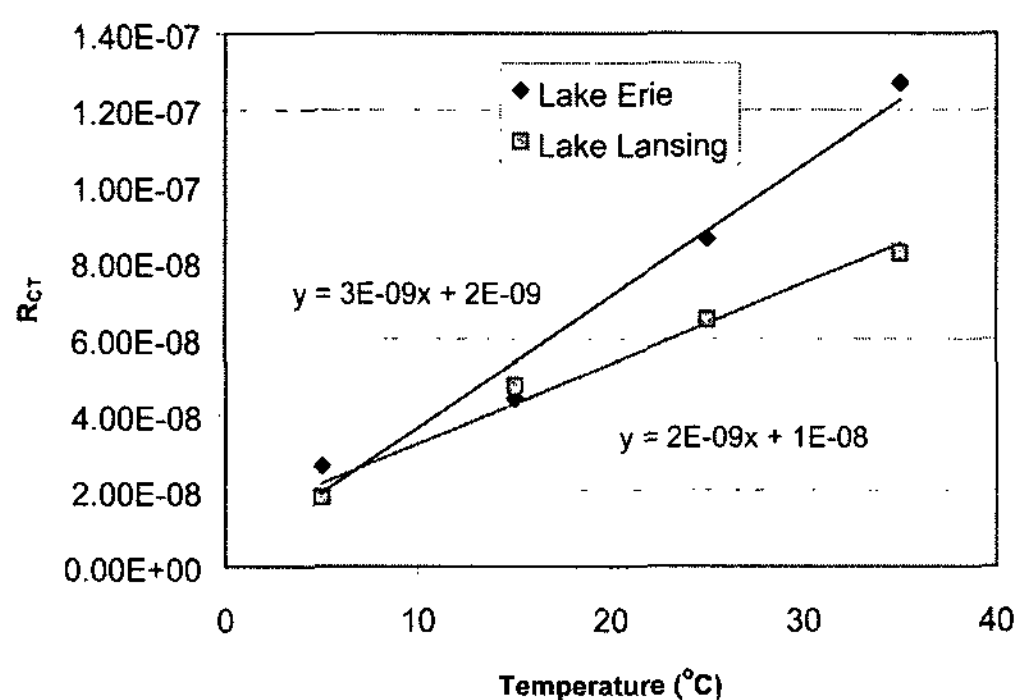


Figure 5. The effect of temperature on R_{CT} values (Ozone dosage: 1 mg O_3 /mg C).

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 for the reaction 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.

The Effects of Ketoacids Formation on the Ozonation

As shown in Figure 6, the formation of ketoacids significantly increased within increasing ozone dosage 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 Erie 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 2), the NOM of Lake Lansing water promoted the 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 more rapid reactions of the NOM from Lake Lansing with ozone at the early stages of ozonation (as compared to the NOM from Lake Erie water). After the initial reactivity of Lake Lansing 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.

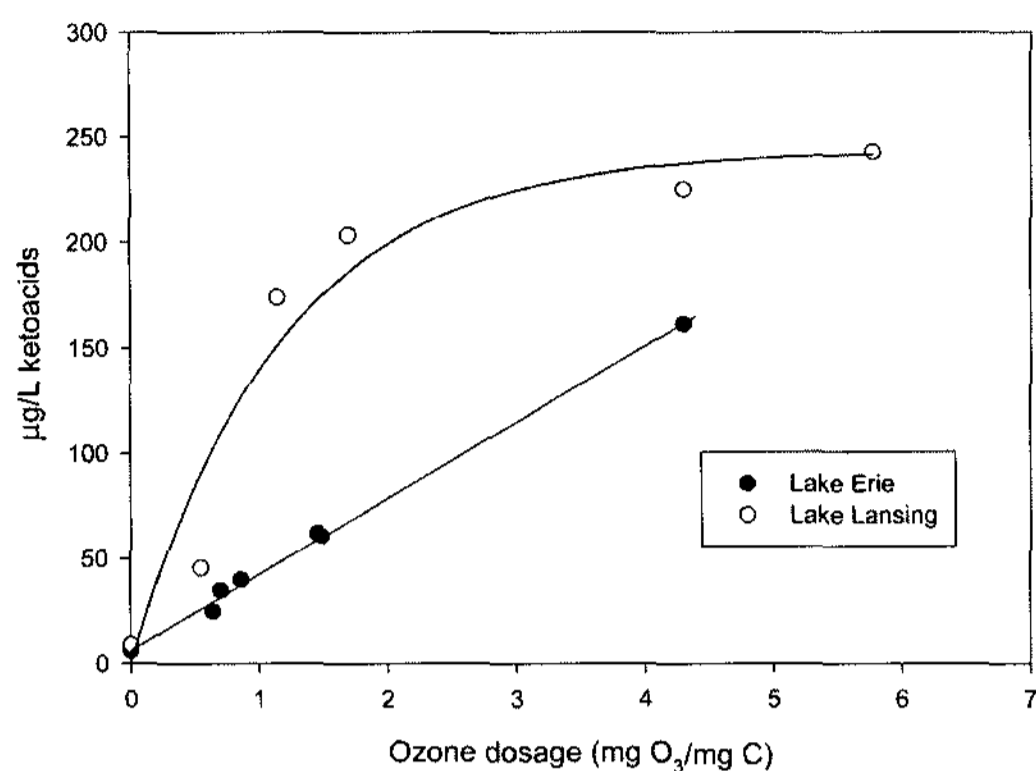


Figure 6. Formation of ketoacids for ozone dosages (TOC: 2.0 mg/L in Lake Erie, 9.5 mg/L in Lake Lansing, HRT: 12.5 min, Temperature: 25°C).

As shown in Figure 3 and Figure 4, the R_{CT} values were constant for the HRTs studied. However, the formation of ketoacids in both water sources increased unexpectedly as the HRT increased in CSTR (Figure 7). 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 (Figure 3 and Figure 4). The rate of formation of ketoacids in Lake Erie water was suppressed at short retention times due to high concentrations of the 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 small HRTs may play a role in suppressing the formation of ketoacids, as observed in Lake Erie water. The concentrations of ketoacids in Lake Erie are relatively low compared to that in Lake Lansing, even at low concentrations of OH radical (at long retention times) because of the low concentration of NOM in Lake Erie.

Experiments to determine the formation of ketoacids conducted in a CSTR at temperatures

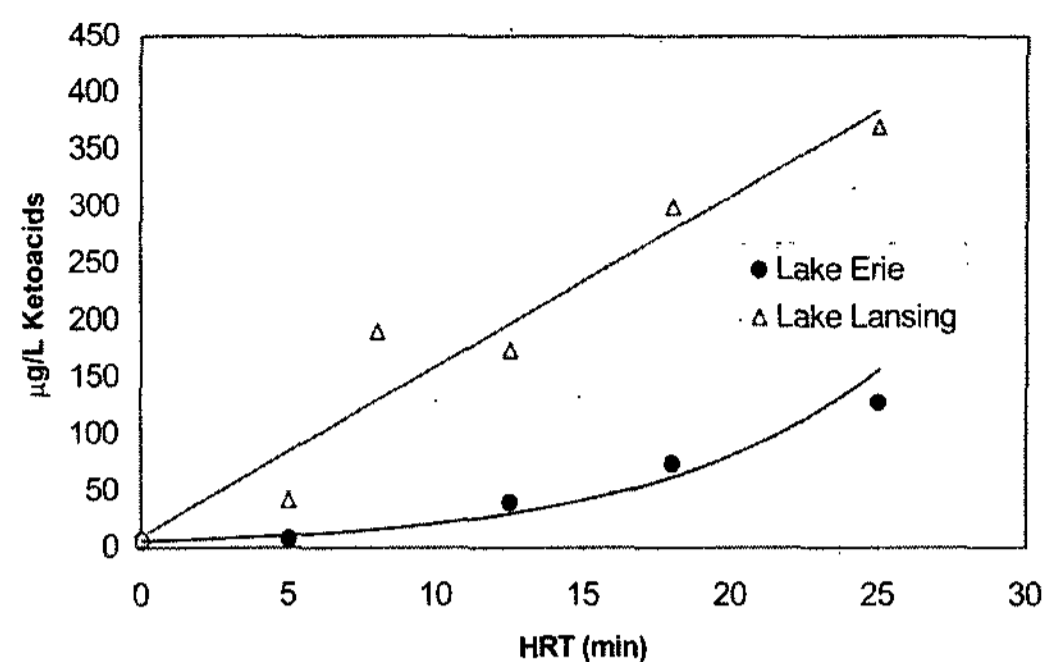


Figure 7. Formation of ketoacids for HRTs (Ozone dosage: 1 mg O₃/mg C, Temperature: 25°C).

ranging from 5 to 35°C at a fixed ozone dosage of 1 mg O₃/mg C and a HRT of 12.5 minute. As shown in Figure 8, the formation of ketoacids appears to increase as temperature increases. Comparing the formation of ketoacids with R_{CT} values, the formation of ketoacids increased as R_{CT} values increased (See Figure 8 and Figure 5). The increase of the concentration of ketoacids with temperature follows trends as the R_{CT} values, indicating that the reaction rate of the species, such as NOM, bicarbonate, and free radicals each others affect the formation of ketoacids.

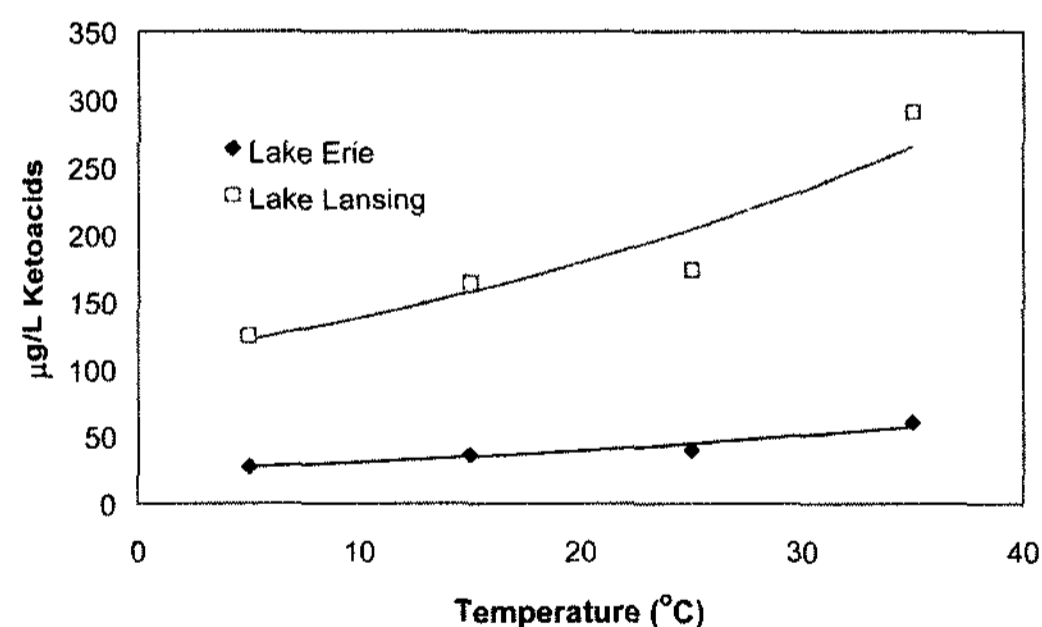


Figure 8. Formation of ketoacids for temperature (Ozone dosage: 1 mg O₃/mg C, HRT: 12.5 min).

The Effect of AOC Formation on Ozonation

The formation of AOC during ozonation is likely to result from the reaction of molecular ozone with the aromatic fraction of NOM, producing hydrophilic compounds. The AOC determination is based on culturing bacteria

(*Pseudomonas fluorescens* (P-17) and *Aquaspirillum* sp. (NOX)) that utilize groups of specific compounds such as carboxylic acids or carbohydrates¹⁷⁾. 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 acids³⁾.

As shown in Figure 9, the formation of AOC increased as ozone dosage increased. The formation of AOC in Lake Lansing water leveled off at high ozone dosages (approximately 2 mg ozone/mg C), whereas the formation of AOC in Lake Erie water gradually increased even at high concentrations of ozone, although there may be some leveling off at ozone dosages above approximately 5 mg ozone/mg C. The formation of AOC follows the same trends as those 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.

The concentration of AOC was expected to be constant with HRTs because the R_{CT} values were well correlated with HRT. As shown in

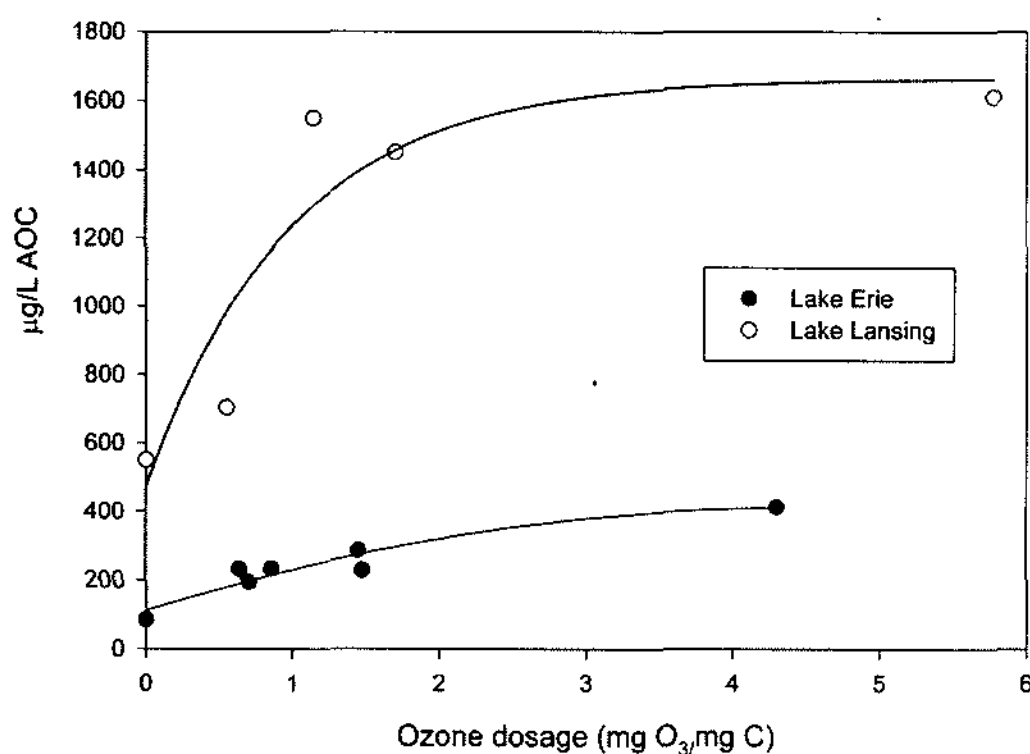


Figure 9. Formation of AOC for ozone dosages (TOC: 2.0 mg/L in Lake Erie, 9.5 mg/L in Lake Lansing, HRT: 12.5 min, Temperature: 25°C).

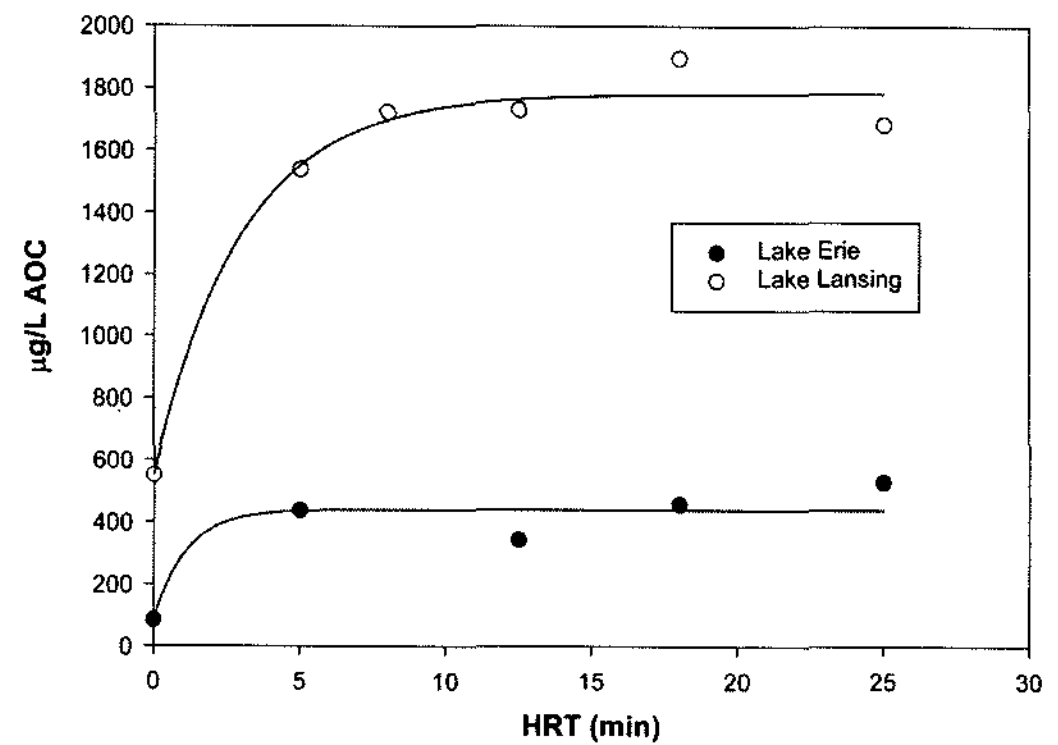


Figure 10. Formation of AOC for HRTs (Ozone dosage: 1 mg O₃/mg C, Temperature: 25°C).

Figure 10, the changes of AOC concentration with HRTs followed trends in OH radical concentration, suggesting that the formation of AOC depends on the R_{CT} values rather than the HRTs.

When the steady state AOC concentrations obtained in HRT experiments (Figure 10) are compared to those obtained when investigating the effects of ozone dosage (Figure 9), it is observed that much higher concentrations of AOC were obtained in the HRT experiments. With HRTs greater than 5 min, at an ozone dosage of 1 mg O₃/mg C, the concentration of AOC reached at 400 µg/L and 1,600 µg/L, in Lake Erie and Lake Lansing water, respectively. On the contrary, at a HRT of 12.5 min, and ozone dosages between 0.5 and 1.5 mg O₃/mg C, the AOC concentrations ranged from 200-300 mg/L. This apparent discrepancy in data for Lake Erie (but not for Lake Lansing) may have been the result of temporal changes in water quality. Variation of the HRT resulted in smaller changes in AOC formation than did increasing ozone dosage, indicating that ozone dosage is more effective at controlling the formation of AOC than HRTs.

The concentration of AOC did not change as temperature increased as shown in Figure 11. Moreover, the formation of AOC in Lake Lansing decreased slightly as temperature increased within the range 20 - 35°C. The temperatures differences are statistically significant at a 95%

confidence interval. The formation of AOC in Lake Lansing water was unrelated to R_{CT} values. Although at high temperatures the increasingly rapid decomposition of ozone results in the predominance of OH radical reactions (see Figure 5), the complexity of ozone reactions with NOM results in less significant changes than expected. At higher temperatures, 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 is different with respect to the temperature.

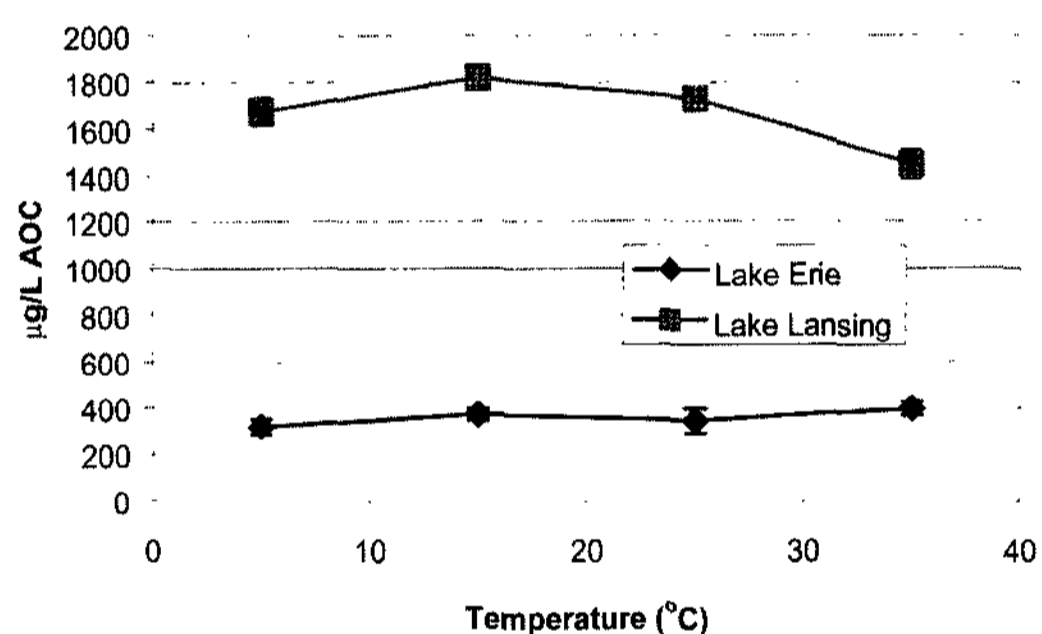


Figure 11. Formation of AOC for temperature (Ozone dosage: 1 mg O_3 /mg C, HRT: 12.5 min.).

CONCLUSION

1. The R_{CT} values obtained experimentally allowed us not only to determine the ratio of OH radical to molecular ozone concentration at the various ozonation conditions but also to indicate 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 with respect to HRTs. During the ozonation time, the R_{CT}

values were constant even though the ozone decomposes continuously. Based on the results, the high concentration of the OH radical present at short HRTs may play a role in suppressing the formation of ketoacids.

3. The R_{CT} values at various temperatures (ranges from 10 to 35°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 and AOC were independent of R_{CT} values. This may be due to 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.

4. The formation of AOC indicates that the reaction of molecular ozone with NOM is the predominant source of AOC rather than OH radical reaction under conditions where molecular ozone reactions predominate. However, the NOM characteristics and background ion concentrations also need to be determined to predict the formation of AOC. For the formation pathways of ketoacid were independent with the molecular ozone and OH radical concentrations at the various ozonation conditions such as temperature, ozone contact time and alkalinity.

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