

A Study for Chloroform Formation in Chlorination of Resorcinol

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Abstract

In this study, resorcinol, chosen as a model humic acid, is chlorinated with sodium hypochlorite in aqueous medium. The effects of some factors, such as initial concentrations of resorcinol and chlorine, as well as their ratios, temperature, time and pH on chloroform formation, are investigated and discussed. Correlations with accuracies of $\pm 10\%$ are obtained to predict the formed chloroform concentration in terms of time, initial total organic carbon (TOC), initial chlorine to initial TOC ratio, reaction temperature and reaction pH.

In the chlorination of water containing total organic carbon due to the presence of humic acids at a certain concentration, the necessary optimum chlorination time for each applied chlorine dosage, ensuring the maximum permissible chloroform concentration in the drinking water, can be determined from these correlations.

Key Words: Chlorination, humic acid, resorcinol, haloform reaction, trihalomethane, chloroform, disinfection, drinking water.

Resorsinolun Klorlanmasında Oluşan Kloroformun Formasyonu üzerine bir Çalışma

Özet

Bu çalışmada model hümitik asit olarak seçilen resorsinol, sulu ortamda sodyum hipoklorit ile klorlanmıştır. Resorsinol ve klorun başlangıç derişimleri ve bunların oranları, sıcaklık, zaman ve pH gibi bazı faktörlerin kloroform oluşumuna etkileri incelenmiş ve tartışılmıştır. Oluşan kloroformun derişimini zaman, başlangıç toplam organik karbon derişimi, başlangıç klor derişiminin başlangıç toplam organik karbon derişimine oranı, reaksiyon sıcaklığı ve reaksiyon pH'sı cinsinden önsezinleyen $\pm 10\%$ hassasiyette korelasyonlar elde edilmiştir.

Hümitik asitlerin varlığı nedeniyle belli bir derişimde toplam organik karbon içeren suyun klorlanmasıyla oluşacak kloroformun tolere edilebilir en yüksek derişimi aşmamasını garanti eden gerekli optimum klorlama süresi, uygulanacak herbir klor dozu için, bu korelasyonlardan saptanabilir.

Anahtar Sözcükler: Klorlama, hümitik asit, resorsinol, haloform reaksiyonu, trihalometan, kloroform, dezenfeksiyon, içme suyu.

Introduction

The formation of chlorinated organics and especially of trihalomethanes (THMs) during the disinfection of water with chlorine is emerging as a persistent problem associated with the maintenance of potable water quality due to the fact that high concentrations of THMs in drinking water may have carcinogenic effects in the long-term, according to the information published by the National Cancer Institute of the U.S.A. (1976). Therefore, the water industry now faces a regulation proposed by the Environmental Protection Agency (EPA) to limit the long-term average exposure of the public to THMs up to 100 $\mu\text{g}/\text{l}$ via the drinking water supply.

The humic substances naturally present in water constitute the dominant precursors of THMs among which chloroform is known to be the by-product occurring at the highest concentrations. Therefore, the conditions controlling the formation of chloroform have to be optimized to keep the THM concentrations within the permissible ranges, while efficiently disinfecting water by chlorination. Also, to establish a reaction pathway for the formation of chloroform and the chlorinated acids, knowledge of the structure of humic material is necessary. Leer et al. (1985) reported that the possibility of 1,3-dihydroxybenzene structures as the precursor fragment for chloroform formation from humic material remained to be proven, although Rook (1977, 1980) proposed a mechanism for the reaction between chlorine and resorcinol (1,3-dihydroxybenzene). Leer et al. (1985) also emphasized the necessity for the identification of reaction intermediates to understand the mechanism of the chlorination reaction between chlorine and resorcinol, being a model precursor fragment for chloroform formation.

Boyce and Hornig (1983) conducted a series of experiments showing that the derivatives of resorcinol were highly effective precursors of THMs at neutral and alkaline pH. They identified and reported the chlorination intermediates of resorcinol at different conditions. The distribution of products was found to be strongly dependent on both the pH and the relative initial concentrations of chlorine and resorcinol in solution. They used phosphate buffer for adjusting the desired pH in the solution and their study was directed to elucidate the mechanism rather than the kinetics. An investigation of the aqueous chlorination of resorcinol was also reported by Heasley et al. (1989) at different pH values and varying per-

centages of chlorination: 2-chloro- ; 4-chloro- ; 2,4-dichloro-; 4,6-dichloro- and 2,4,6-trichloro-resorcinol. They identified the intermediates in the absence of phosphate buffer which might participate in the reaction and alter the structure of the products. Only the relative rates of chlorination were determined for resorcinol and several of the chlorinated resorcinols.

Based on the above-given information from the literature, resorcinol was chosen as a model humic substance and its chlorination in aqueous medium deprived of any halogen ions, ammonia and additional organic substances is investigated in this work. The effects of some factors such as initial concentrations of resorcinol and chlorine as well as their ratios, temperature, time and pH are studied and discussed. Developing equations for predicting the chloroform formation rate and kinetics as a function of these factors is considered to be advantageous, because they will allow more adequate design formulations of treatment plants that minimize the formation of THMs and better prediction of the influence of environmental parameters on the plant performance.

Experimental

Reagents: Resorcinol, 4-chloro-resorcinol and 4,6-dichloro-resorcinol were obtained in high purity from Aldrich Chemical Company. Sodium hypochlorite (NaOCl) solution (5% by wt) was directly used as a stock solution during the experiments. The solutions of resorcinol, 4-chloro-resorcinol and 4,6-dichloro-resorcinol were prepared by weighing appropriate amounts of each and diluting them with ultrapure water to the desired molarities. Ultrapure water of 18 M Ω -cm resistivity was used for all stock solution preparations and also for cleaning and rinsing all the glassware during the experiments.

Reaction vessel: In order to reduce any photolytically induced reactions, 50 ml-amber glass bottles covered with teflon-septum headings were used without stirring.

Residual chlorine analysis: Based on the literature survey, the DPD (diethyl-p-phenyl-diamine) method was chosen for the residual chlorine analysis as the most appropriate technique (Wilde, 1991) giving very quick and reproducible results.

Haloform analysis: The reaction was quenched by the addition of excess sodium thiosulfate to the solution, before the analysis of the unreacted reactants and the formed products. The analyses were carried out by direct aqueous injections of 0.1 μl sam-

ples to a Hewlett-Packard 5890 Gas Chromatograph (GC) with a flame ionization detector (FID). Preliminary runs were performed to choose the most suitable column and the detector in the present experimental work. A high performance, cross-linked methyl silicone gum capillary column (called HP-1 after its trade name) with a length of 25 m and an outside diameter (OD) of 0.32 mm was decided to be used at a constant temperature of 120°C throughout the analyses. The electron capture detector (ECD) was best in the detection of chloroform after its extraction from the aqueous medium into an organic solvent, namely, n-pentane with an extraction efficiency of 99%, whereas extracted resorcinol samples gave unsatisfactory results due to the low extraction efficiency of resorcinol in n-pentane (about 1%). In the present study, a common organic solvent for extracting both the reactants and the by-products from the aqueous medium with high extraction efficiencies could not be found either at the end of a thorough literature survey, or after a tedious trial and error procedure involving preliminary laboratory work. It was found by Mukhopadhyay and Sohani (1989) that 99% recovery of resorcinol from the aqueous phase could be achieved only with a mixed solvent of 40% butanol and 60% butyl acetate in three stages. This procedure was not practical for the present study. Therefore, it was decided to use the direct aqueous injections of 0.1 μ l samples to the GC with an FID, which would make possible the detection of chloroform, resorcinol, and the intermediates; namely chloro-resorcinols in the same chromatogram. Very small sample sizes used with capillary columns required a detector having high sensitivity and fast response. The hydrogen-flame unit of FID used in this work showed a linear response over a dynamic range of about a million to one, thereby making it very suitable for the analysis of mixtures having constituents of widely varying proportions. Its noise level was also very low compared to that of the ECD, the lower limit of detectability being on the order of 10^{-12} moles. The present FID was relatively insensitive to the fluctuations of carrier gas flow and/or changes in temperature.

Nitrogen was used as a carrier gas at a flow rate of 5 ml/min. The temperatures of the injector and the detector were 250°C and 300°C, respectively. The selection of the isothermal operation of the column at 120°C avoided the changes in the flow rate of the carrier gas. Also, the best peaks for resorcinol, chloroform and the intermediates were achieved at this

constant temperature of 120°C. 0.1 μ l samples were injected to the GS using 1 μ l gas-tight Hamilton syringes with sensitivities of $\pm 0.001 \mu$ l and at least three injections of this volume were repeated for each specific measurement. Each experimental run was also repeated three times to check the accuracy and the reproducibility of the results. The syringes were cleaned after each experiment with detergents and ultrapure water, rinsed with pure alcohol and dried in an oven at 100°C.

Standard solutions: The standard solutions of resorcinol and chloro-resorcinols were prepared at different concentrations in ultrapure water. Only chloroform was injected in its pure form as a 0.1 μ l standard sample into the GC. The internal standard chosen to be para-chlorophenol, as it did not interfere with the products of analysis, could be easily detected and its retention time as well as its position with respect to the intermediate products was found in the literature (Heasley et al., 1989).

Experimental set-up and procedure: The experimental set-up as well as the sequential flow of the procedure is shown in Figure 1. The reaction vessels used were all 50 ml and amber-colored with a specially designed teflon-septum heading. Stock solutions of resorcinol and sodium hypochlorite (NaOCl) were added at appropriate volumes to each bottle and its duplicate so as to obtain the desired molar ratio of reactants (R/C = initial resorcinol-to-initial chlorine) ranging from 1/1 to 1/20. The concentration of NaOCl to be used was determined according to the chosen initial resorcinol to initial chlorine ratio. Immediately after mixing the reactants, the reaction in each bottle was terminated by injecting 10 ml of sodium thiosulfate ($Na_2S_2O_3$) into the bottle, in excess amounts to remove the excess chlorine (Cl_2) present in the reaction mixture. The stoichiometric amount of $Na_2S_2O_3$ necessary to stop the chlorination at any desired reaction time was calculated according to the reaction stoichiometry of $Na_2S_2O_3$ with NaOCl. The concentration of the injected $Na_2S_2O_3$ to terminate the reaction was not less than half the resorcinol's concentration to provide the required excess amount of $Na_2S_2O_3$. Just before the injection of $Na_2S_2O_3$, an equal volume of reaction mixture (10 ml) was withdrawn from the reaction bottle for the residual chlorine analysis by the DPD method. In the experiments, the injection time of NaOCl was noted carefully for each bottle since this was the start of the chlorination reaction in each reaction-bottle. The reaction was ter-

minated at any desired time interval ranging from 0–12 hours. The reaction mixture was analyzed for the unreacted resorcinol and the reaction by-products by the GC-method and for the residual chlorine (Cl_2) by the DPD-method. The temperature of the reaction medium was kept constant by keeping the bottles in

a water-bath having a sensitivity of $\pm 0.05^\circ\text{C}$ and the pH of the solutions was kept at the desired level by buffer solutions for the experiments involving the effect of pH on the results (e.g. pH values of 4, 7, and 10). Further details are given elsewhere (Şahinalp, 1994).

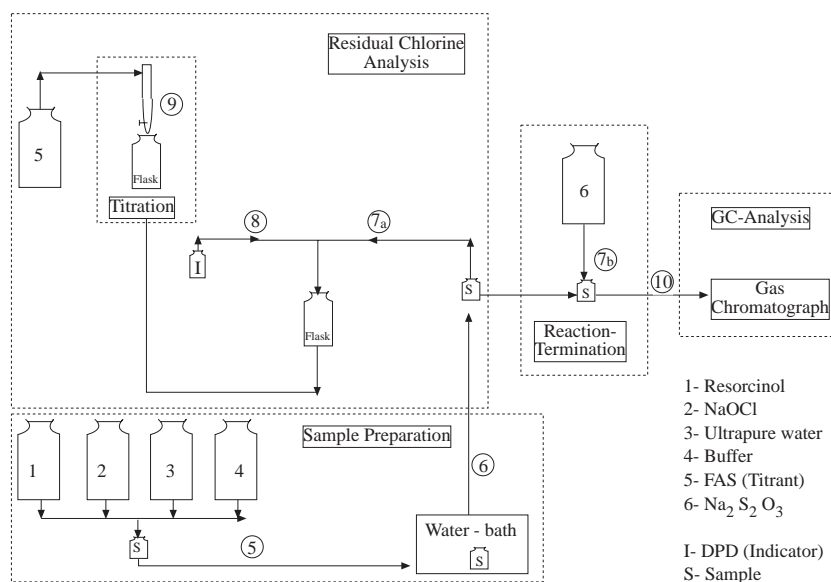


Figure 1. Experimental set-up and procedure

Results and Discussion

Effects of time and initial (R/C) molar ratio: The general rate curves for resorcinol and chlorine consumptions as well as chloroform (trichloromethane = TCM) formation are shown in Figure 2 for an initial R/C ratio of 1/3 ($R=62.7 \text{ mMole/l}=\text{mM}$ and $C=190 \text{ mM}$), at $\text{pH}=7$ and $T=20^\circ\text{C}$. These curves are characterized by a rapid formation of chloroform and the rapid consumptions of resorcinol and chlorine at the beginning of the chlorination reaction, but the rates of the reactants and those of the products decrease with time. The behaviour of such rate curves is crucial, because it explains the nature of the reaction that occurs at any time, as well as the nature and reactivity of the precursor involved in the chlorination process. Figure 2 is therefore specific to resorcinol only, and the other precursors might differ in reactivity as well as in chloroform formation potential. This is in accordance with the rate curves obtained for the other precursors in the literature which show different behaviour than that of resorcinol in terms of reactivity and percent yield (Boyce and Hornig, 1983). At

the initial molar ratio of $R/C=1/3$, the concentration versus time data of both the reactants (resorcinol and chlorine) and the by-product (chloroform) could be simultaneously observed. It is seen in Figure 2 that the concentration of resorcinol decreases very fast with time so that its detection during the chlorination process becomes quite difficult, even for the ratios at which the reaction is chlorine-controlled (e.g. $R/C=1/2, 1/1$ etc.). The consumption data of chlorine shows that the chlorine is also consumed as fast as resorcinol but its consumption is observed more easily for the ratios at which resorcinol is reaction controlling, (e.g. $R/C=1/5, 1/8, 1/10$ etc.). The decrease in chlorine concentration with time for various initial R/C ratios is presented in Figure 3.

Effect of initial resorcinol concentration: In order to determine the effect of different initial resorcinol concentrations on the chloroform yield at a constant initial chlorine dose of 190 mM, the reaction mixtures prepared for six different initial R/C molar ratios of 0.05, 0.1, 0.125, 0.200, 0.250 and 0.333 were analyzed for their chloroform yields and the results are shown in Table 1. This data shows clearly

that the amount of resorcinol initially present in the reaction-medium determines the percent yield of chloroform, once sufficient and/or abundant chlorine is available for the reaction to achieve completion. As the initial resorcinol concentration increases at a constant initial chlorine dose, the chloroform yield decreases due to the formation of other by-products.

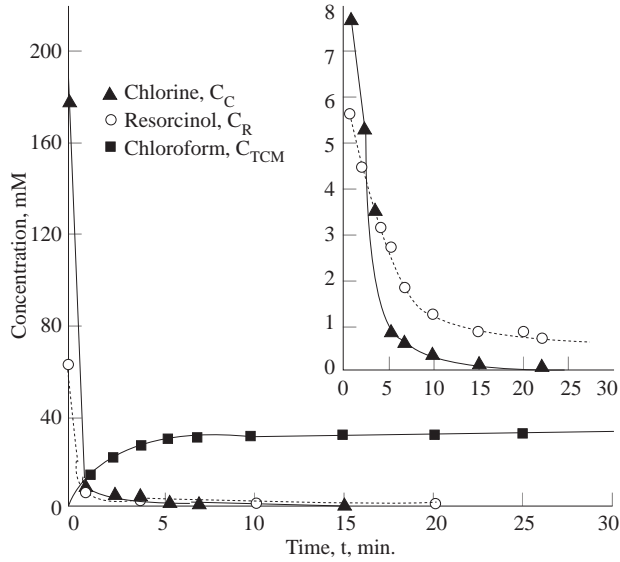


Figure 2. Consumption of reactants and formation of chloroform at R/C=1/3, pH=7, T=20°C

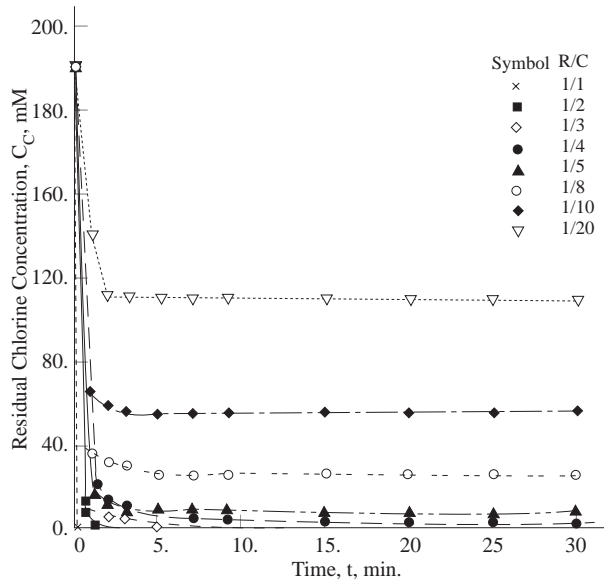


Figure 3. Residual chlorine concentrations as a function of R/C at C=190mM, pH=7, T=20°C

Table 1. Chloroform-yield as a function of initial resorcinol concentration at a constant initial chlorine dose of C=190 mM, T=20°C and pH=7.

R(mM)	R/C	% Yield (TCM/R)
9.5	0.050=1/20	84
19.0	0.100=1/10	82
23.7	0.125=1/8	82
38.0	0.200=1/5	79
47.5	0.250=1/4	76
62.7	0.333=1/3	50

$$\% \text{ Yield (TCM/R)} = \text{Chloroform formed (mM)} / \text{Resorcinol consumed (mM)}$$

The corresponding rate curves of chloroform formation in the form of chloroform concentration versus time are given in Figure 4, for each R/C ratio. These curves definitely indicate that there is an increase in the chloroform concentration with an increase in the initial resorcinol concentration, provided that the residual chlorine still exists in the solution for longer times, which is called “long-term residual chlorine”, and therefore the reaction is not chlorine limited. This behaviour accounts for a strong dependency of chloroform yield on the initial precursor concentration.

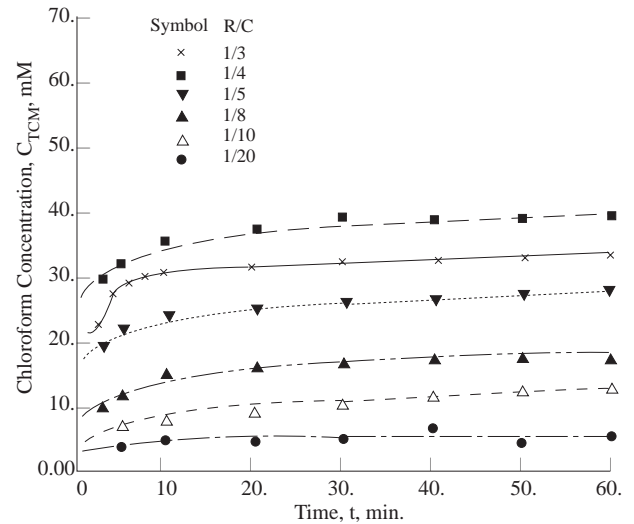


Figure 4. Effect of initial resorcinol concentration on chloroform formation at C=190 mM, pH=7, T=20°C

Effects of initial and residual chlorine concentrations: The effect of initial chlorine dose on the chloroform yield is observed at four different initial chlorine doses of 47.5, 95, 143 and 190 mM by keeping the initial resorcinol concentration constant at 9.5 mM. The curves obtained from data are shown in Figure 5 and the yields are given in Table 2. No chloroform is detected at R/C ratios of 1/2 and 1/1. In Figure 5, it is seen that the chloroform formation increases in progressing from R/C ratio of 1/2 to 1/20 at a constant value of initial resorcinol concentration and the ultimate chloroform concentration is not much affected by the initial chlorine dose as long as the maintained long-term residual corresponds to the R/C ratios of (1/15) to (1/20).

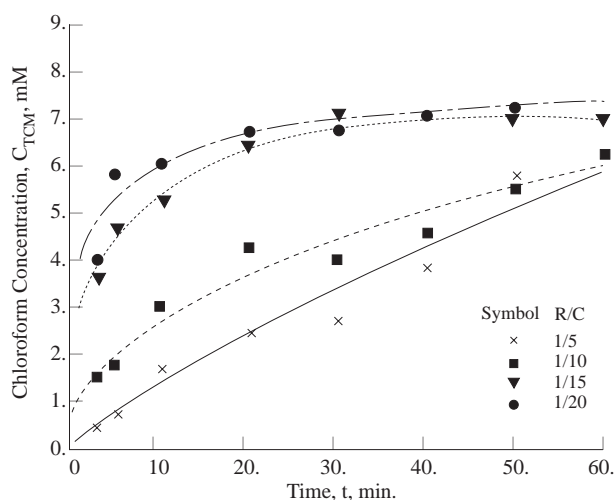


Figure 5. Effect of initial chlorine dose on chloroform formation at R= 9.5 mM pH=7, T=20°C

Table 2. Chloroform-yield as a function of initial chlorine dose at a constant initial resorcinol concentration of R=9.5 mM, T=20°C and pH=7.

C(mM)	R/C	% Yield (TCM/R)
47.5	0.200=1/5	81
95.0	0.100=1/10	82
142.5	0.067=1/15	84
190.0	0.050=1/20	84

Independent experiments were performed in order to identify any stoichiometric relation or ratio between resorcinol and chlorine consumptions. For this purpose, the residual chlorine values were measured at different R/C ratios providing excess chlo-

rine so that residual chlorine still remained in the reaction mixture after the chlorination reaction was completed. The consumed chlorine (Cl₂) in the chlorination reactions was measured at different R/C ratios smaller than 1/10 (e.g. 1/15 - 1/26) keeping the initial resorcinol concentration at 5 mM and 10 mM; the results are given in Tables 3 and 4, respectively.

Table 3. Consumed chlorine for initial resorcinol concentration of R=5 mM, at R/C of 1/18, 1/22 and 1/26

Time(h)	Cl ₂ (mM)	Cl ₂ (mM)	Cl ₂ (mM)
0	90	110	130
12	55	75	95
Consumed	35	35	35

Initial resorcinol (mM)/Consumed Chlorine (mM)= 1/7

Table 4. Consumed chlorine for initial resorcinol concentration of R=10 mM, at R/C of 1/10, 1/15 and 1/20

Time(h)	Cl ₂ (mM)	Cl ₂ (mM)	Cl ₂ (mM)
0	100	150	200
1	30	80	130
Consumed	70	70	70

Initial resorcinol (mM)/Consumed Chlorine (mM)= 1/7

Tables 3 and 4 indicate a consistency in the consumption of chlorine with respect to resorcinol which is completely used up during the reactions, and the consumed chlorine per mole of reacted-resorcinol remains constant at around 7 moles of chlorine per mole of resorcinol. This kind of relation between the two reactants is not observed at R/C ratios greater than 1/7 (i.e. 1/5, 1/4 etc.) and it is only valid for the reaction conditions remaining in the long-term residual chlorine range, not for all reaction conditions.

Effect of temperature: Experiments performed at different reaction temperatures produced different yields of chloroform at any specific R/C ratio and at any time, keeping all other parameters constant. These are shown in Table 5 and the curves are given in Figure 6.

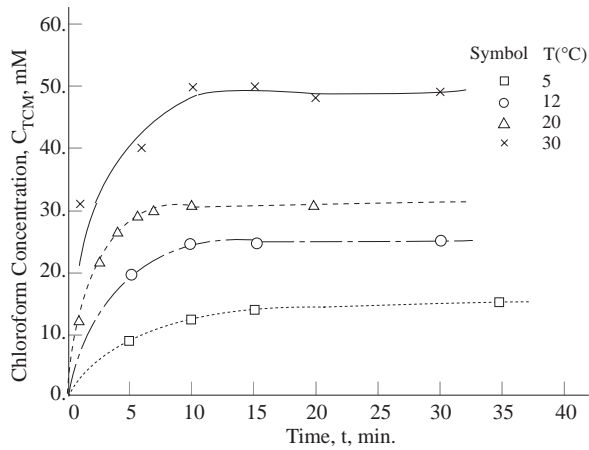


Figure 6. Effect of temperature on chloroform formation at R/C=1/3, C=190 mM, pH=7

Table 5. Chloroform-yields as a function of temperature at pH=7, R/C=1/3 and R= 62.7 mM

T(°C)	% Yield (TCM/R)
5	22
12	35
20	50
30	81

The results clearly indicate that for an increase of 25°C, chloroform concentration increases nearly four times as much at R/C=1/3 and consequently the yield increases proportionally from 22% to 81%. The range of temperature applied in this study is not uncommon if summer and winter conditions are taken into consideration and the necessity for close temperature control during the determination of chloroform formation within the water distribution system becomes inevitable. The consumptions of chlorine at 20°C and 30°C justify an increase in chloroform formation and no residual chlorine remains in the reaction mixture within a short time after the reaction is completed, while long-term chlorine residuals are observed at the lower temperatures of 5°C and 12°C.

Effect of pH on chloroform yield: The THM formation rate has been shown to increase with an increase in pH level by a number of researchers (Rook, 1980; Stevens et al., 1976). In this study, the same result is observed, related to an increase in chloroform concentration at the higher pH levels. This increase is expected since the haloform reaction is base-catalyzed and more of the haloform is formed as pH increases. The chloroform yields studied at

different values of pH and R/C molar ratios are summarized in Table 6.

Table 6. Percent chloroform-yields (TCM/R) at different pH and R/C values at the initial chlorine dose of C=190 mM and T = 20°C

R/C	pH = 4	pH = 7	pH = 10
1/1	None	None	Not studied
1/3	None	50	95
1/10	32	82	Not studied

As seen in Table 6, pH is the dominant factor in determining the conversion of resorcinol to chloroform during its chlorination in the aqueous medium, and the effect of R/C ratio seems less than that of the pH. A chloroform yield of 50% at R/C = 1/3 and pH = 7 increases to 95% with a change of pH from 7 to 10, while a lower percentage increase in yield is possible in varying the R/C ratio from (1/3) to (1/10) keeping the pH at 7.

The change in pH seems to have less effect on the residual chlorine consumption, indicating that chlorine will be used up rapidly at any pH, but the reaction products will change. In this study, a strong effect of pH on the halogenated intermediates is observed. The pH medium affects not only the formation of total chloroform, but also the relative proportions of the intermediates (chloro-resorcinols) as well as those of the other products (e.g. straight-chain ketones, chlorinated acids, etc.) formed as a result of ring-opening steps during the chlorination reaction. The effect of pH on the intermediates can be used further to elucidate the reaction mechanism, which may be the topic of a future publication. The research on the chlorination of water is going on. A recent publication by Heasley et al. (1999), emphasizing the reactions of resorcinol and its chlorinated derivatives with monochloramine in ether and aqueous solution (pH=7) to identify the intermediates and products, is worth mentioning here.

Correlation attempts

The present experimental data gives a best-fit to the following general predictive model (equation 1) proposed by Engerholm and Amy (1983):

$$C_{TCM} = K (TOC)^x (C/TOC)^y t^z \tag{1}$$

where K is the overall reaction constant and given by

$$K_{T^{\circ}C} = (k_1)(k_2) \quad (2)$$

where k_1 is a constant related to pH, and k_2 is another constant related to the temperature. In equation (1), x and y are constants; but exponent z varies with temperature. The model formulated by equation (1) will predict the chloroform concentration (C_{TCM}) as a function of time (t) for a given set of experimental parameters, such as, initial total organic carbon concentration (TOC), ratio of initial chlorine concentration to initial total organic carbon concentration (C/TOC), reaction pH, and reaction temperature.

The following correlations are obtained by applying the chlorination data of resorcinol to the model given in equation (1) with the regression methods (Marquardt, 1963):

$$C_{TCM} = K_{5^{\circ}C}(R)^{0.945} (C/R)^{1.01} t^{0.0404} \quad (3)$$

$$C_{TCM} = K_{12^{\circ}C}(R)^{0.945} (C/R)^{1.01} t^{0.0454} \quad (4)$$

$$C_{TCM} = K_{20^{\circ}C}(R)^{0.945} (C/R)^{1.01} t^{0.0550} \quad (5)$$

$$C_{TCM} = K_{30^{\circ}C}(R)^{0.945} (C/R)^{1.01} t^{0.0679} \quad (6)$$

where C_{TCM} is the concentration of trichloromethane or chloroform (TCM); R is the initial concentration of resorcinol; (C/R) is the molar ratio of initial chlorine to initial resorcinol and t is time (min). All the concentrations in the above equations (3-6) have the unit of 'Mole/l' and equations (3-6) are found to apply at pH=7 for the C/R ratio of 3 and at different temperatures of 5, 12, 20 and 30°C, respectively. Each of the overall reaction constants in equations (3-6) were delineated according to equation (2) given by Engerholm and Amy (1983) who arbitrarily assigned a value of 1 to k_1 for a pH value of 7, thus equating k_2 to $K_{T^{\circ}C}$. Since the same basic conditions are applied in this study, the same assumption of accepting $k_1 = 1$ (at pH=7) can be used as well. In order to obtain k_2 constants at four different temperatures, four separate regressions were carried out taking x and y values pertaining to the base condition of pH=7 and using all concentration versus time data for the operating conditions of $C/R=3$ and pH=7 at the temperatures of 5, 12, 20 and 30°C. These regressions yield the values of z for the temperatures at the above-stated conditions as being 0.0404, 0.0454, 0.055 and 0.0679, respectively. The corresponding values of $K_{T^{\circ}C}$ are found to be 0.0507, 0.0928, 0.1000 and 0.1358 respectively. Since k_1 is accepted as 1 at pH = 7, these $K_{T^{\circ}C}$ values are

equal to the values of k_2 . As anticipated, the values of k_2 and z indicate that chloroform yield increases with temperature.

A separate regression is conducted with the data obtained at pH = 10, $T = 20^{\circ}C$ and $C/R = 3$, which yields the following correlation with a constant $K'_{20^{\circ}C}$ given in equation (7).

$$C_{TCM} = K'_{20^{\circ}C}(R)^{0.945} (C/R)^{1.01} t^{0.0550} \quad (7)$$

Since k_2 is determined previously as a function of temperature, regardless of any change in pH, k_1 can be calculated at a pH of 10 from $K'_{20^{\circ}C}$ by assuming a direct proportionality between $K_{T^{\circ}C}$ and k_1 at a constant temperature of 20°C. The value of k_1 thus estimated being equal to 1.8 at a pH of 10, shows that the chloroform yield increases as pH increases. This is in accordance with the observations made during the experiments. The estimated values of the above-mentioned constants are summarized in Table 7. The experimental and the calculated values of chloroform concentrations are plotted on a logarithmic paper and given in Figures 7 and 8; they show a scattering around the 45°- diagonal with an accuracy of $\pm 10\%$.

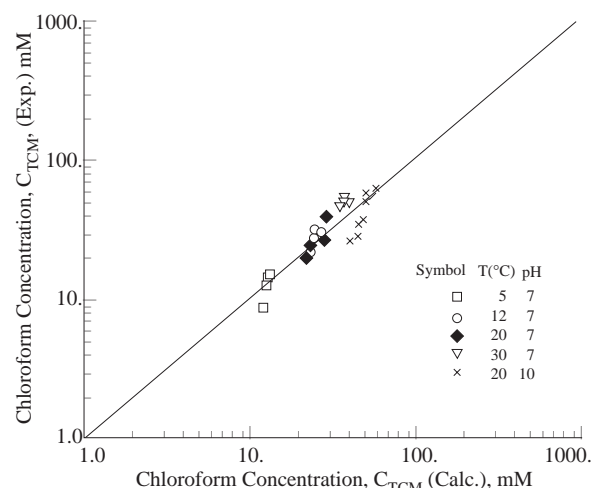


Figure 7. C_{TCM} (Exp.) vs C_{TCM} (Calc.) as a function of temperature and pH at $R/C=1/3$ and $R=62.7$ mM

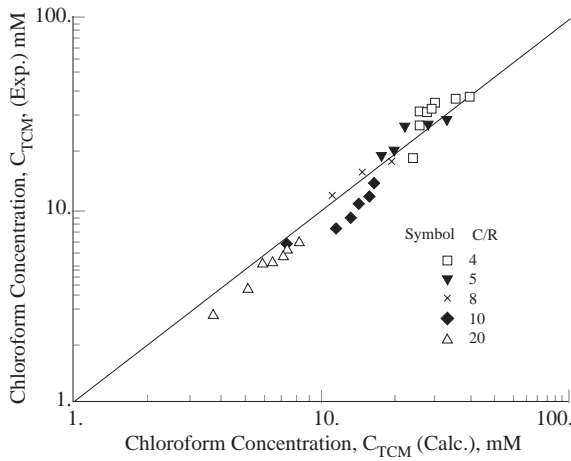


Figure 8. C_{TCM} (Exp.) vs C_{TCM} (Calc.) as a function of C/R at C=190 mM, pH=7 and T=20°C

Table 7. Summary of constants appearing in the model equations representing the chlorination of resorcinol at an initial molar ratio of (C/R)=3 and initial chlorine concentration of C=0.19 M.

T (°C)	5	12	20	30	20
pH	7	7	7	7	10
x	0.945	0.945	0.945	0.945	0.945
y	1.010	1.010	1.010	1.010	1.010
$K_{T^{\circ}C}$	0.0507	0.0928	0.1000	0.1358	0.1800
k_1	1.0	1.0	1.0	1.0	1.8
k_2	0.0507	0.0928	0.1000	0.1358	0.1000
z	0.0404	0.0454	0.0550	0.0679	0.0550

Experimental data obtained at the higher initial molar ratios of C/R between 4-20 at pH=7 and T=20°C are also correlated to predict the chloroform concentrations (Mole/l) as a function of time (min), initial resorcinol concentration in (Mole/l), and the initial molar ratio of chlorine to resorcinol. They are given in the following equations (8 and 9), one in terms of resorcinol concentration, and the other one in terms of total organic carbon concentration, equivalent to the concentration of resorcinol respectively, since 1 mole of resorcinol corresponds to 6 moles of total organic carbon according to its chemical formula:

$$C_{TCM} = 0.77(R)^{1.5} (C/R)^{0.55} t^{0.2} \quad (8)$$

$$C_{TCM} = 0.1404 (TOC)^{1.5} (C/TOC)^{0.55} t^{0.2} \quad (9)$$

The constants of 0.77 and 0.1404 in equations (8) and (9), respectively have the same unit of

$[(l^{0.5}/(\text{mole}^{0.5} \text{ min}^{0.2}))]$; the intervals of the parameters are (0.0095 - 0.0475 M) for R, (4-20) for C/R ratio and (0-60 minutes) for t in equation (8), and (0.057-0.285 M) for TOC, $[(2/3)-(10/3)]$ for (C/TOC) ratio and (0-60 minutes) for t in equation (9).

The correlations obtained (equations 3-9) are not valid for (C/R) ratios of 1 and 2, which are already not representative ratios for a successful disinfection. The proposed correlations can be used to predict the contact times between the reactants (chlorine and total organic carbon) such that an efficient disinfection is provided and the chloroform concentration does not exceed its maximum permissible limit value of 30 ppb.

Conclusions

Based on the results, it can be concluded that the chloroform formation is strongly organic precursor-controlled (for the cases such as R/C = 1/8, 1/10 etc.) except for the cases where chlorine is the reaction limiting reactant (i.e. R/C = 1/5, 1/3 etc.). Residual chlorine is rapidly used up for R/C ratios above 1/3; but for R/C molar ratios lower than 1/8 (e.g., 1/20), the relative molar ratio between the reacted-resorcinol and the consumed-chlorine remains constant at around 1/7. In other words, almost 7 moles of chlorine react with one mole of resorcinol, provided that the molar R/C ratios are lower than 1/8.

At neutral pH, the effect of temperature on the chloroform yield is enormous, such that for every 12°C increase, the percent yield in chloroform is doubled. The effect of pH on the chloroform yield is significant, such that an increase in pH from 7 to 10 raises the chloroform yield from 50% to 95% even for the R/C ratio of 1/3.

The correlations obtained predict the chloroform concentrations as a function of time, initial resorcinol concentration, and initial molar ratio of chlorine to resorcinol with accuracies of $\pm 10\%$ on a log-log scale.

The correlation obtained (equation 9) in terms of total organic carbon concentration equivalent to resorcinol concentration from the known chemical formula of this humic acid, namely resorcinol, is especially important for generalizing the applicability of the present results to the chlorination of all humic substances containing organic carbon. Also in practice, it will be useful in predicting the optimum necessary chlorination time for a given initial total

organic carbon concentration, initial molar ratio of chlorine to total organic carbon at each applied chlorine dosage in such a way that the maximum permissible concentration of chloroform will not be exceeded.

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