Trihalomethane hydrolysis in drinking water at elevated temperatures

Xiao-lu Zhang, Hong-wei Yang, Xiao-mao Wang, Tanju Karanfil, Yuefeng F. Xie

State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Court, Anderson, SC 29625, USA

Environmental Engineering Programs, The Pennsylvania State University, Middletown, PA 17057, USA

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Abstract
Hydrolysis could contribute to the loss of trihalomethanes (THMs) in the drinking water at elevated temperatures. This study was aimed at investigating THM hydrolysis pertaining to the storage of hot boiled water in enclosed containers. The water pH value was in the range of 6.1–8.2 and the water temperature was varied from 65 to 95 °C. The effects of halide ions, natural organic matter, and drinking water matrix were investigated. Results showed that the hydrolysis rates declined in the order following CHBrCl2 > CHBr2Cl > CHBr3 > CHCl3. THM hydrolysis was primarily through the alkaline pathway, except for CHCl3 in water at relatively low pH value. The activation energies for the alkaline hydrolysis of CHCl3, CHBrCl2, CHBr2Cl and CHBr3 were 109, 113, 115 and 116 kJ/mol, respectively. No hydrolysis intermediates could accumulate in the water. The natural organic matter, and probably other constituents, in drinking water could substantially decrease THM hydrolysis rates by more than 50%. When a drinking water was at 90 °C or above, the first order rate constants for THM hydrolysis were in the magnitude of 10^−3–10^−1 1/h. When the boiled real tap water was stored in an enclosed container, THMs continued increasing during the first few hours and then kept decreasing later on due to the competition between hydrolysis and further formation. The removal of THMs, especially brominated THMs, by hydrolysis would greatly reduce one’s exposure to disinfection by-products by consuming the boiled water stored in enclosed containers.

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1. Introduction

Chemical disinfection acts as the cornerstone unit operation of water treatment processes that secure drinking water safety (Crittenden et al., 2012; Ohar and Ostfeld, 2014). One side effect of disinfection is the formation of disinfection by-products (DBPs). DBPs are produced from the reactions of the disinfectants (e.g. free chlorine and chloramines) with natural organic matter (NOM) and/or bromide that are ubiquitous in natural waters (Xie, 2003; Krasner et al., 2006; Yang et al., 2012; Hua et al., 2014). Previous toxicological and environmental studies have revealed that DBPs are potential human health threats (Krasner et al., 2006; Landis et al., 2013; Shamsuzzoha et al., 2014). The occurrence and fate of DBPs are determined by the chemical composition of drinking water and the performance of water treatment processes (Xie, 2003; Krasner et al., 2006; Yang et al., 2012; Hua et al., 2014).
epidemiological studies have reported the linkage of carcinogenic and developmental effects to exposure to DBPs in drinking water (Richardson et al., 2007). DBPs can generally be classified as either volatile or non-volatile, determined by their Henry’s law constants. Trihalomethanes (THMs) and haloacetic acids (HAAs), which in most cases have the highest occurrence levels in the disinfected drinking waters and are currently regulated in a number of countries (Wang et al., 2014), belong to volatile and non-volatile DBPs, respectively.

Boiling the tap water (i.e. drinking water) for the preparation of hot beverages becomes increasingly popular all around the world. Boiling could have a great effect on the DBP levels in the boiled water (Li and Sun, 2001; Krasner and Wright, 2005). Consumption of the boiled drinking water, not only cold water, should therefore be taken into consideration when collecting information of exposure to DBPs in drinking water (Krasner and Wright, 2005). Previous studies showed that the boiling effect was greatly dependent on the volatility and chemical stability of the DB, the heating duration, and the free and combined chlorine residuals in the water. Generally, when the heating duration was sufficiently long (e.g. 5 min), the levels for THMs, trihaloacetic acids (THAAs) and several non-regulated DBPs (including halogenated aldehydes, ketones and acetonitriles) would be reduced, while the levels for dihaloacetic acids (DHAAs) would be increased or keep unchanged in chlorinated and chloraminated water, respectively. THMs and other volatile DBPs were removed mainly by volatilization, while THAAs and other non-volatile DBPs were degraded primarily by hydrolysis. The hydrolysis of THAAs and other trihalogenated DBPs (e.g. chloral hydrate) would lead to the formation of THMs, on the other hand volatilization of THMs would be largely reduced. THM hydrolysis becomes important.

Table 1 – Hydrolysis rate constants (unit: 1/h) for the four THMs at various water temperatures, calculated by using the correlation equations given in previous studies. THM was either dissolved in 66.7% dioxane-water solution at ~0.1 mol/L (Hine et al., 1956), or in water at ~10 mmol/L (Fells and MoelwynHughes, 1959) or at concentration close to saturation (1%–10%) (Jeffers et al., 1989). The calculated hydrolysis rates for chloroform differed in different studies. Only alkaline hydrolysis rate could be obtained for CHBrCl₂, CHBrCl₃ and CHBr₃ (Hine et al., 1956). The pH values correspond to that for 25°C.

<table>
<thead>
<tr>
<th>Heating temperature (°C)</th>
<th>pH 6.5</th>
<th>pH 7.5</th>
<th>pH 8.5</th>
<th>CHBrCl₂</th>
<th>CHBrCl₃</th>
<th>CHBr₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>(0.74–2.3) × 10⁻⁸</td>
<td>(0.74–1.2) × 10⁻⁷</td>
<td>(0.74–1.1) × 10⁻⁶</td>
<td>2.0 × 10⁻⁶</td>
<td>9.2 × 10⁻⁷</td>
<td>3.6 × 10⁻⁷</td>
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<tr>
<td>65</td>
<td>(1.6–2.0) × 10⁻⁵</td>
<td>1.7 × 10⁻⁴</td>
<td>(8.8–9.0) × 10⁻⁴</td>
<td>3.5 × 10⁻³</td>
<td>2.0 × 10⁻⁴</td>
<td>6.5 × 10⁻⁴</td>
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<tr>
<td>75</td>
<td>(7.9–8.8) × 10⁻⁵</td>
<td>(7.2–8.0) × 10⁻⁴</td>
<td>(3.2–3.6) × 10⁻³</td>
<td>1.6 × 10⁻²</td>
<td>9.2 × 10⁻⁵</td>
<td>3.0 × 10⁻⁵</td>
</tr>
<tr>
<td>85</td>
<td>(2.9–3.4) × 10⁻⁴</td>
<td>(2.5–3.4) × 10⁻³</td>
<td>(0.99–1.4) × 10⁻²</td>
<td>6.4 × 10⁻²</td>
<td>3.9 × 10⁻²</td>
<td>1.2 × 10⁻²</td>
</tr>
<tr>
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<td>(5.2–6.8) × 10⁻³</td>
<td>(4.4–6.9) × 10⁻³</td>
<td>(1.6–2.5) × 10⁻²</td>
<td>0.12</td>
<td>7.5 × 10⁻²</td>
<td>2.3 × 10⁻²</td>
</tr>
<tr>
<td>95</td>
<td>(0.91–1.3) × 10⁻³</td>
<td>(0.74–1.3) × 10⁻²</td>
<td>(2.6–4.6) × 10⁻²</td>
<td>0.22</td>
<td>0.14</td>
<td>4.2 × 10⁻²</td>
</tr>
</tbody>
</table>

2. Theory of THM hydrolysis

2.1. THM hydrolysis pathways

The hydrolysis mechanism of chloroform, which was at very high concentrations (in g/L level), has been well studied (Hine et al., 1956; Jeffers et al., 1989; Chen, 2011). However, THM hydrolysis rates can be substantially enhanced to the magnitude of 10⁻²–10⁻¹ 1/h when the water temperature approaches the boiling point. It indicates that THMs can significantly be hydrolyzed in a time scale of hours. It is unusual to boil a drinking water for hours. However, in many places of the world, especially East Asia, the hot boiled water is stored in thermo bottles for many hours for the ease of preparation of hot beverages. In addition, electrical boilers were also installed in many public buildings in the world. In the enclosed containers like thermo bottles, on one hand the hydrolysis of trihalogenated DBPs would lead to the formation of THMs, on the other hand the volatilization of THMs would be largely reduced. THM hydrolysis becomes important.

This study was conducted to investigate the THM hydrolysis kinetics that pertains to the storage of boiled drinking water in enclosed containers. All four THMs, which are chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl) and bromoform (CHBr₃), were included in the investigation. A water temperature range from 65 to 95 °C was adopted, below which THM hydrolysis becomes negligible. The pH value of the water was slightly changed within the circum-neutral range (from 6.1 to 8.2), which can also be used to investigate the effect of water pH on the rate of THM hydrolysis. The sum of the four THM concentrations in a typical drinking water is usually in tens of μg/L level (Obolensky et al., 2007; Ding et al., 2013), and the THM speciation is critically dependent on the bromide ion concentration (Obolensky and Singer, 2005; Roccaro et al., 2014). A drinking water also contains NOM usually in mg/L level and mineral ions (e.g. chloride) usually in tens to hundreds of mg/L level. The effect of these water “impurities” on THM hydrolysis rates was also investigated. The purpose of this study is to draw one's attention to the significance of THM hydrolysis in assessing the health risks posed by DBPs contained in cool and boiled drinking water.
et al., 1956; Fells and Moelwyn-hughes, 1959). It was not the intention of this study to investigate the hydrolysis mechanism of THMs which are at fairly low concentrations (in tens of μg/L order). Rather, we assumed that the same hydrolysis mechanism stands, regardless of the THM species and their concentrations in water.

THMs hydrolyze in two separate pathways. The neutral hydrolysis pathway (by reacting with water molecule) involves the formation of dihalomethanol, which then rapidly breaks down into carbon monoxide and formic acid (Reactions (1) and (2)).

$$\text{CH}_X + H_2O \rightarrow \text{CH}_XOH + HX$$ (1)

$$\text{CH}_XOH \rightarrow HCOX + HX$$ (2a)

$$(x+y)\text{HCOX} + yH_2O \rightarrow x\text{CO} + y\text{HCOOH} + (x+y)\text{HX}$$ (2b)

The rate-limiting step is the substitution of the first halide atom by hydroxyl group (Reaction (1)). As such, the hydrolysis rate by the neutral pathway can be described by,

$$\frac{dC}{dt} = -k_1C$$ (3)

where C is the THM concentration. The alkaline hydrolysis pathway (by reacting with hydroxide ion) involves the formation of carbon trihalide anion and carbon dihalide, the latter of which quickly breaks down into carbon monoxide and formic acid (Reactions (4–6)).

$$\text{CH}_X + OH^- \rightarrow k_3 \rightarrow \text{CX}_3 + H_2O$$ (4)

$$\text{CX}_3 \rightarrow k_4 \rightarrow \text{CX}_2 + X^-$$ (5)

$$(x+y)\text{CX}_2 + (2x+3y)\text{OH}^- \rightarrow x\text{CO} + y\text{HCOO}^- + 2(x+y)X^- + (x+y)\text{H}_2\text{O}$$ (6)

The equilibrium between THM and carbon trihalide anion (Reaction (4)) can be rapidly established, and the breakdown of carbon trihalide anion to carbon dihalide (Reaction (5)) is the rate-limiting step. As such, the hydrolysis rate by the alkaline pathway can be described by,

$$\frac{dC}{dt} = \frac{-k_1[OH^-]C}{k_3 + k_4[OH^-]}.$$ (7)

The observed hydrolysis rate is the sum of that for neutral hydrolysis and that for alkaline hydrolysis, i.e.

$$\frac{dC}{dt} = -(k_1 + k_3[OH^-])C = -k_{obs}C.$$ (8)

Equation (8) shows that, at a fixed water temperature, the THM hydrolysis follows pseudo-first order kinetics as long as the water pH is buffered. (Note that both $k_3$ and $k_4$ depend on the water temperature.)

2.2. Theoretical calculation for hydroxide ion concentration

The pH value and the hydroxide ion concentration ([OH⁻]) were calculated based on the water dissociation constant ($K_w$) and the phosphate dissociation constants ($K_{a1}$, $K_{a2}$ and $K_{a3}$) according to

$$K_w = [H^+] [OH^-]$$ (9)

$$K_{a1} = [H^+] [H_2PO_4^-] / [H_3PO_4]$$ (10)

$$K_{a2} = [H^+] [HPO_4^{2-}] / [H_2PO_4^-]$$ (11)

$$K_{a3} = [H^+] [PO_4^{3-}] / [HPO_4^{2-}]$$ (12)

$$[Na^+] + [K^+] + [H^+] = 3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-] + [OH^-]$$ (13)

The $pK_{a1}$, $pK_{a2}$ and $pK_{a3}$ values at 25 °C are 14.00, 2.12, 7.21 and 12.67, respectively. All the above dissociation constants are dependent on the water temperature. According to the literature (Haynes, 2013), the $pK_w$ values are 12.90, 12.69, 12.50, 12.42 and 12.34 at 65, 75, 85, 90 and 95 °C, respectively. The $pK_w$ values for phosphate at other temperatures were calculated by using the van’t Hoff equation (Stumm and Morgan, 1996),

$$\ln \left( \frac{K_w}{K_w} \right) = -\frac{\Delta H_f^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$ (14)

where $\Delta H_f^o$ is the standard enthalpy change for the dissociation reaction, $R$ the gas constant, $T$ the absolute temperature and subscripts 1 and 2 for the two temperatures. The $\Delta H_f^o$ values at 25 °C for the dissociation of $H_3PO_4$, $H_2PO_4^-$ and $HPO_4^{2-}$ are $-8.0, 4.2$ and $14.7$ kJ/mol, respectively. Table 2 gives the calculation results for the hydroxide concentrations. It shows that hydroxide ion concentration substantially increased with the increase of the temperature of the same phosphate buffered water.

3. Materials and methods

3.1. THM solutions and heating treatment

The THM solutions were individually prepared by spiking an appropriate volume of each commercial concentrated solution (Sigma–Aldrich, USA) into either deionized (DI) water, an aqueous solution containing sodium halides (100 mg/L chloride and 100 μg/L bromide), an aqueous solution containing humic acid (2.0 mg/L as TOC), or a drinking water matrix. In most cases, the final THM concentration was 100 μg/L; while the THM concentration was increased to 5 μmol/L when the solution was used for mass balance test. The pH of each THM solution was buffered by adding 0.4 mmol/L phosphate. In most cases, the pH was buffered at 7.5 (calculated for room temperature (25 °C) and $[H_2PO_4^-]/[HPO_4^{2-}] = 33.8/66.2$; while the pH value might be varied among 6.1 ($[H_2PO_4^-]/[HPO_4^{2-}] = 92.8/7.2$), 6.9 ($[H_2PO_4^-]/[HPO_4^{2-}] = 67.0/33.0$), 7.4 ($[H_2PO_4^-]/[HPO_4^{2-}] = 39.1/60.9$), 7.5, 7.8 ($[H_2PO_4^-]/[HPO_4^{2-}] = 20.4/79.6$), 8.0 ($[H_2PO_4^-]/[HPO_4^{2-}] = 13.9/86.1$), and 8.2 ($[H_2PO_4^-]/[HPO_4^{2-}] = 9.2/90.8$) for the investigation of pH effect on hydrolysis rates. The above theoretically calculated values were basically identical to that measured by pH meter, which were 6.12, 6.89, 7.38, 7.52, 7.77, 7.98, and 8.23, respectively. The concentrations of chloride and...
bromide ions, and humic acid, if added, were typical of that in drinking water, and were added to investigate the effects of halide ions and natural organic matter, respectively. The drinking water matrix was a grab sample collected from a local water treatment plant at the point just prior to primary disinfection. The plant treated raw surface water following a treatment process that consisted of prechlorination, clarification, sand filtration, granular activated carbon filtration and primary disinfection. Therefore, the collected water sample was not a finished drinking water but a well-pretreated raw surface water. It had a TOC concentration of 1.0 mg/L, UV254 absorbance at 0.016 1/cm, and non-detectable residual chlorine. Very low DBP levels were detected in the water sample before THM spiking.

Each THM solution was dispensed into a number of amber glass vials (40 mL in volume, each equipped with a Teflon septa and a screw cap) with no headspace left. In this way, the THM volatilization from the solution could be effectively prevented. The vials were then transferred into a hot water bath. The water bath temperature was varied among 65, 75, 85, 90 and 95 °C for the investigation of the temperature effect on hydrolysis kinetics. The heating duration was up to 216 h, depending on the hydrolysis rate. After a preset heating duration, the vials were quickly transferred into a cool water bath at 20 °C. The cooled samples were then determined for the residual THM concentration and, if required, the formed halide concentrations. All heating treatment and THM analysis were conducted in duplicate for each solution and condition.

3.2. Boiling and storage of real tap water

A real tap water sample was collected from a household tap located at Clemson, SC, USA. The collected water sample had a pH at 7.1, TOC concentration at 1.0 mg/L, UV254 absorbance at 0.016 1/cm, and residual chlorine at 1.0 mg/L. The concentrations of DBPs (including THMs, HAAs and other common species) in the water sample were measured as the already formed DBPs levels before heating treatment.

The tap water was fast heated (in 6 min) to just boiling in an electrical kettle. A volume of the boiled water was quickly cooled down to 20 °C for the determination of the DBP levels after boiling. The remaining boiled water was quickly dispensed into a number of 40 mL amber glass vials with no headspace left, which were then immediately transferred to a water bath set at 90 °C. They were kept at that temperature for up to 72 h. After preset storage durations, appropriate vials were quickly cooled down to 20 °C. The DBP levels were then determined to investigate the effect of storage.

3.3. Analytical methods

Both THMs and HAAs were analyzed by using a gas chromatograph equipped with an electron capture detector (GC 7890A, Agilent, USA) after the micro liquid–liquid extraction by using methyl tert-butyl ether as the extraction agent (and, additionally, esterification for HAAs by using diazomethane). More details could be found by referring to the USEPA Method 551.1 (1995) and APHA et al (2005), respectively. The detection limits were approximately 0.1 μg/L for each THM, chloral hydrate (CH), dichloroacetoniitrile (DCAN) and 1,1,1-tri-chloropropanone (TCPN), and 0.5 μg/L for each HAA, respectively.

Chloride and bromide were analyzed by using an ion chromatograph (761, Metrohm, Switzerland). The detection limit was 5 μg/L for both chloride and bromide. The TOC and UV254 were analyzed by using a TOC analyzer (TOC-V CPH, Shimadzu, Japan) and an ultraviolet spectrophotometer (UV-1800, Shanghai Aoxi, China), respectively.

4. Results and discussions

4.1. THM hydrolysis at elevated water temperatures

THM was dissolved in DI water and pH-buffered at 6.1, 6.9, 7.5, 7.8, 8.0 or 8.2 by using 0.4 mmol/L phosphate. The THM solution was then heated at 65, 75, 85, 90 or 95 °C. The hydrolysis kinetics was analyzed by plotting the THM concentration (C) versus heating time (t) and fitted by using Equation (8) (Fig. 1). Because hydroxide ion concentration would not change during heating, it was expected that the THM hydrolysis followed the pseudo-first order kinetics, as was the case for all four THMs under all conditions investigated. The obtained hydrolysis rate constants (kobs) (Table 3) were compared with that calculated by using correlation equations given in previous studies (Table 1) (Hine et al., 1956; Fells and Moelwynhughes, 1959; Jeffers et al., 1989). It appears that initial THM concentration had minimal effect on the hydrolysis rate. The THM concentration was 100 μg/L in this study, while it was from g/L to tens of g/L in previous studies. The hydrolysis rate constant determined when the THM concentration was low (in this study) was only slightly higher than that determined when the THM concentration was high (in previous studies).

The pH value of the THM solution (calculated for and measured at 25 °C) was varied to obtain the neutral (k0) and the alkaline (kφ) hydrolysis rate constants for the four THMs at both 90 °C and 65 °C (Equation (8)). As expected, the observed hydrolysis rate constant (kobs) for each THM was in a linear

<table>
<thead>
<tr>
<th>pH at 25 °C</th>
<th>6.1</th>
<th>6.5</th>
<th>6.9</th>
<th>7.4</th>
<th>7.5</th>
<th>7.8</th>
<th>8.0</th>
<th>8.2</th>
<th>8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>65</td>
<td>0.130</td>
<td>0.324</td>
<td>0.813</td>
<td>2.54</td>
<td>3.14</td>
<td>5.98</td>
<td>8.72</td>
<td>11.9</td>
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The determined hydrolysis rate constants (unit: 1/h) for the four THMs of trace amount in the water at elevated temperatures and typical drinking water pH values.

<table>
<thead>
<tr>
<th>Water matrix (all buffered by phosphate)</th>
<th>Heating T (°C)</th>
<th>pH (at 25 °C)</th>
<th>CHCl3</th>
<th>CHBrCl2</th>
<th>CHBr2Cl</th>
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<td>65</td>
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<td>1.0 × 10⁻³</td>
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<td>5.5 × 10⁻³</td>
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<td>1.8 × 10⁻³</td>
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<tr>
<td>100 mg/L chloride and 100 μg/L bromide solution</td>
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<td>7.5</td>
<td>7.8 × 10⁻³</td>
<td>6.1 × 10⁻²</td>
<td>4.5 × 10⁻²</td>
<td>2.0 × 10⁻²</td>
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<td>2.0 mg/L (as TOC) humic acid solution</td>
<td>90</td>
<td>7.5</td>
<td>3.5 × 10⁻³</td>
<td>3.1 × 10⁻²</td>
<td>2.3 × 10⁻²</td>
<td>1.1 × 10⁻²</td>
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<td>Drinking water matrix</td>
<td>90</td>
<td>7.5</td>
<td>3.5 × 10⁻³</td>
<td>3.1 × 10⁻²</td>
<td>2.3 × 10⁻²</td>
<td>1.1 × 10⁻²</td>
</tr>
</tbody>
</table>
brominated THMs) but in actuality differed only slightly (Haynes, 2013). In contrast, the pre-exponential factors \( A \) differed greatly among \( \text{CHCl}_3 \), \( \text{CHBrCl}_2 \), \( \text{CHBr}_2\text{Cl} \) and \( \text{CHBr}_3 \), which were \( 8.03 \times 10^{16} \), \( 3.46 \times 10^{20} \), \( 5.61 \times 10^{20} \) and \( 2.54 \times 10^{20} \) L/mol h, respectively. According to the alkaline hydrolysis mechanisms (Reactions (4–6)), the concentration of carbon trihalide anion \( (\text{CX}_3^-) \) could be a critical factor in controlling the hydrolysis rate. A higher carbon trihalide anion concentration corresponded to a higher hydrolysis rate (and a larger pre-exponential factor value).

After the breakdown of \( \text{CX}_3 \) to \( \text{CX}_2 \), the ensuing steps in which \( \text{CX}_2 \) hydrolyzes to carbon monoxide and formic acid are very rapid (Reaction (6)). Complete dehalogenation could therefore be expected along with the loss of THMs. Mass balance for halide ions and THMs were established as

\[
C_0 - C = \left( [\text{Cl}^-] + [\text{Br}^-] \right) / 3
\]

where all species are in molar concentration, \( C_0 \) is the initial THM concentration before heating, and \( C \) is the measured THM concentration after heating. The initial THM concentration was set at 5 \( \mu \text{mol/L} \) for the better measurement of the released halogen ions. Results showed that Equation (16) stood for all the four THMs (Fig. 4). The verification of this hydrolysis pathway is important under the drinking water condition. It indicates that no potentially hazardous halogen-containing intermediates would accumulate during the hydrolysis of any THM.

4.2. Effects of water chemistry on THM hydrolysis

Typical drinking water is a solution that contains natural organic matter (NOM) in mg/L level, chloride ion in tens to hundreds of mg/L level, bromide ion in tens to hundreds of \( \mu \text{g/L} \) level, and other molecules and ions in various levels. In contrast, the THM concentrations are in tens of mg/L level. Therefore, it is important to investigate the effect of water matrix on the THM hydrolysis.

Reaction (5) could be reversible, and the increase of halide ions might slow down the THM hydrolysis rate. The results by dosing 100 mg/L chloride and 100 \( \mu \text{g/L} \) bromide into the phosphate-buffered deionized water indicated that halide concentrations at the typical levels in drinking water had negligible effect on THM hydrolysis rates (Fig. 5). The differences were within 5% for all four THMs when the THM solution was heated to 90 \( ^\circ \text{C} \). A plausible reason was that the rate constant for the reversal of Reaction (5) was very low compared with that for the forward reaction.

To explore the effects of NOM on THM hydrolysis rates, commercial humic acids were dosed into DI water to a final TOC concentration at 2.0 mg/L, which was then pH-buffered at 7.5 (25 \( ^\circ \text{C} \)). Humic substances are the major organic components in most natural surface waters. Results demonstrated that humic acid could substantially decrease the hydrolysis rates for all THMs (Fig. 5). When the water contained 2.0 mg/L humic acids as TOC (pH \( = 7.5 \), 25 \( ^\circ \text{C} \)), the hydrolysis rate constants for \( \text{CHCl}_3 \), \( \text{CHBrCl}_2 \), \( \text{CHBr}_2\text{Cl} \) and \( \text{CHBr}_3 \) at 90 \( ^\circ \text{C} \) were decreased to 0.0078, 0.0612, 0.0453 and 0.0198 1/h, respectively, by 55% on average (Table 3). According to the hydrolysis mechanisms and Equation (8), the plausible reason for the reduction of hydrolysis rate was the decrease of the hydroxide ion concentration in solution when humic acids were present under otherwise identical conditions. Humic acids are weak acids which could also participate in the acid–base equilibria as Equations 9–13 show.
In addition to halide ions and humic substances, drinking water also contains other mineral ions, dissolved organic substances and colloidal particles. The THM hydrolysis in a locally sampled drinking water matrix was consequently investigated. The collected water sample was a well-pretreated raw surface water but with no primary disinfection (and as such contained non-detectable residual chlorine and negligible background DBPs) and had a pH value of 7.6, which was phosphate-buffered to 7.5 (at 25 °C) and spiked with each THM at 100 μg/L before heated at 90 °C. Similar to the effect of humic acids, the hydrolysis rate constants for CHCl₃, CHBrCl₂, CHBr₂Cl and CHBr₃ at 90 °C were decreased to 0.0035, 0.0309, 0.0228, and 0.0111 1/h, respectively, by 77% on average (Fig. 5) (Table 3). A direct comparison of the hydrolysis rate constants in the humic acid-containing water and the real drinking water might not be appropriate. Though the effect of NOM on THM hydrolysis kinetics was evident, the effects of other components in the drinking water could not be excluded. In addition to NOM, drinking water also contains a number of dissolved chemicals, colloids, microorganism metabolites, suspended solids and etc. Moreover, the NOM properties of various water sources could be very different (Reckhow et al., 1990). The specific effects of various drinking...
water ingredients on THM hydrolysis rates need to be further investigated.

### 4.3. The significance of THM hydrolysis for drinking water

Tap water normally contains the already formed DBPs, DBP precursors and disinfectant residual. During heating of tap water to the boiling point, the THM concentrations might substantially increase due to the further and enhanced reactions between the precursors and free chlorine and the enhanced hydrolysis of trihalogenated DBPs, such as trihaloacetic acids, trihaloacetaldehydes and trihalopropanones (Zhang and Minear, 2002; Hua and Reckhow, 2012; Pan and Zhang, 2013; Zhang et al., 2013; Liu and Reckhow, 2013). The extent of concentration increase depends on the free chlorine level in the heated tap water (Li and Sun, 2001; Krasner and Wright, 2005). For the particular example of this study, during heating of the real tap water (with a free chlorine residual at 1.0 mg/L) to the boiling point, the CHCl₃, CHBrCl₂ and CHBr₂Cl concentrations were increased from 7.3 to 14.0 µg/L, from 4.2 to 6.1 and from 2.0 to 2.7 µg/L, respectively (Table 4). (No CHBr₃ was detected in either water sample.) Simultaneously, the TCPN concentration was decreased from 0.9 to 0.4 µg/L, while the TCAA and CH concentrations were increased from 4.9 to 5.9 µg/L and from 3.6 to 5.3 µg/L, respectively. (All DHAA and DCAN concentrations were increased.)

Although THMs are volatile compounds (the Henry's constants at 95 °C for CHCl₃, CHBrCl₂, CHBr₂Cl and CHBr₃ are 57.9, 28.1, 20.5 and 10.9 L·bar/mol, respectively), volatilization of THMs into the atmosphere is only favored by continuous agitation (e.g. by boiling). Therefore, in practice, the THM concentration remains quite high in the boiled water, unless the water is let for continuous boiling for at least several minutes.

If the hot boiled water were then stored in an enclosed container for sufficient long time, the THM concentrations would be firstly increased and then decreased. In such an enclosed container, THM volatilization into the atmosphere is greatly reduced. Nevertheless, on one hand, THM can be further formed, e.g. from hydrolysis of the above-mentioned trihalogenated DBPs. The pseudo-first order rate constants (at 95 °C) for the hydrolysis of bromodichloroacetic acid, dibromochloroacetic acid and tribromoacetic acid were determined to be ca. 5.2, 24.9 and 27.6 1/h, respectively (Zhang and Minear, 2002). On the other hand, THM hydrolysis could be substantial. The hydrolysis rate constants determined in this study for the four THMs in a typical drinking water at or near the boiling point were in the magnitude of 10⁻²⁻¹⁻¹⁻¹ 1/h (Table 3). For the particular example of this study, keeping the boiled tap water at 90 °C led to the depletion of TCPN, CH and TCAA in 0.5, 2 and 8 h, respectively. In the mean time, the concentrations for CHCl₃, CHBrCl₂ and CHBr₂Cl continued increasing during the first 8 h and then kept decreasing later on (Table 4). This way of hot water storage is therefore effective to remove trihalogenated DBPs including THMs from the water.

Brominated DBPs are believed more toxic than their chlorinated analogs. This study showed that under otherwise identical conditions, CHBrCl₂ and CHBr₂Cl hydrolyze in a faster rate than CHBr₃ and CHCl₃. The THM speciation in chlorinated waters depends on both the bromide concentration and the chlorine dosage. However, unless bromide concentration is very high, CHCl₃ and CHBrCl₂ are normally the major THM species. Therefore, when the conditions are favorable for THM hydrolysis, the THM that eventually remains in the highest level should be CHCl₃, which is the least toxic among the four regulated THMs. For the particular example of this study, in the first 8 h, the concentration increase rate for CHCl₃ was much higher than that for CHBrCl₂ and CHBr₂Cl. After 8 h of storage, the concentration decrease rate for CHCl₃ was much lower than that for CHBrCl₂ and CHBr₂Cl. Both observations could be partly explained by the higher hydrolysis rates of CHBrCl₂ and CHBr₂Cl than CHCl₃. (One other possible explanation was the slower formation rates of CHBrCl₂ and CHBr₂Cl than CHCl₃ when bromide ion concentration was low.) In addition, the limiting step of both neutral and alkaline hydrolysis is the cleavage of the first halogen atom (Reactions (1) and (5)). It indicates that no potentially toxic intermediates will accumulate after THM hydrolysis. Heating water therefore has an additional impact on reducing the health effect posed by THMs, although toxicity (e.g. cytotoxicity and genotoxicity) measurement need be conducted for a better illustration.

If the boiled water were let open to the atmosphere, the water temperature would gradually decrease to the room temperature in a couple of hours. In this case, THM hydrolysis would be firstly increased and then decreased. In such an enclosed container, THM volatilization into the atmosphere is greatly reduced. Nevertheless, on one hand, THM can be further formed, e.g. from hydrolysis of the above-mentioned trihalogenated DBPs. The pseudo-first order rate constants (at 95 °C) for the hydrolysis of bromodichloroacetic acid, dibromochloroacetic acid and tribromoacetic acid were determined to be ca. 5.2, 24.9 and 27.6 1/h, respectively (Zhang and Minear, 2002). On the other hand, THM hydrolysis could be substantial. The hydrolysis rate constants determined in this study for the four THMs in a typical drinking water at or near the boiling point were in the magnitude of 10⁻²⁻¹⁻¹⁻¹ 1/h (Table 3). For the particular example of this study, keeping the boiled tap water at 90 °C led to the depletion of TCPN, CH and TCAA in 0.5, 2 and 8 h, respectively. In the mean time, the concentrations for CHCl₃, CHBrCl₂ and CHBr₂Cl continued increasing during the first 8 h and then kept decreasing later on (Table 4). This way of hot water storage is therefore effective to remove trihalogenated DBPs including THMs from the water.

<table>
<thead>
<tr>
<th>DBPs</th>
<th>Before boiling</th>
<th>0 h</th>
<th>0.5 h</th>
<th>2 h</th>
<th>4 h</th>
<th>8 h</th>
<th>16 h</th>
<th>24 h</th>
<th>48 h</th>
<th>72 h</th>
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<tbody>
<tr>
<td>CHCl₃</td>
<td>7.3</td>
<td>14.0</td>
<td>29.5</td>
<td>29.3</td>
<td>36.1</td>
<td>42.3</td>
<td>40.1</td>
<td>34.7</td>
<td>26.2</td>
<td>/</td>
</tr>
<tr>
<td>CHBrCl₂</td>
<td>4.2</td>
<td>6.1</td>
<td>9.2</td>
<td>8.2</td>
<td>9.2</td>
<td>9.8</td>
<td>7.3</td>
<td>7.4</td>
<td>3.1</td>
<td>1.7</td>
</tr>
<tr>
<td>CHBr₂Cl</td>
<td>2.0</td>
<td>2.7</td>
<td>3.4</td>
<td>3.1</td>
<td>3.1</td>
<td>3.5</td>
<td>3.0</td>
<td>2.8</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>DCAA</td>
<td>1.9</td>
<td>3.5</td>
<td>3.9</td>
<td>3.3</td>
<td>3.3</td>
<td>3.7</td>
<td>3.6</td>
<td>3.2</td>
<td>3.2</td>
<td>1.7</td>
</tr>
<tr>
<td>BCAA</td>
<td>3.0</td>
<td>4.0</td>
<td>4.0</td>
<td>3.8</td>
<td>3.4</td>
<td>3.6</td>
<td>3.4</td>
<td>3.1</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>DBAA</td>
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<td>2.0</td>
<td>1.9</td>
<td>2.1</td>
<td>1.8</td>
<td>1.8</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>TCAA</td>
<td>4.9</td>
<td>5.9</td>
<td>4.1</td>
<td>2.7</td>
<td>1.9</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>3.6</td>
<td>5.3</td>
<td>1.2</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>TCPN</td>
<td>0.3</td>
<td>0.4</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>DCAN</td>
<td>0.4</td>
<td>0.6</td>
<td>0.4</td>
<td>0.0</td>
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<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
can be negligible, considering the short time period and the lowered water temperature. For example, the hydrolysis rate constants at 65 °C for the four THMs in a typical drinking water are in the magnitude of \(10^{-4} - 10^{-3}\) 1/h (Table 3), indicating the half-lives ranged from days to months. However, some water utilities adjust the pH of their finished water a bit higher in order to comply with the Lead and Copper Rule (USEPA, 2007). At alkaline conditions, the THM hydrolysis is substantially enhanced. In a water at pH 9.0 (measured at 25 °C) and 65 °C, the THM hydrolysis rate constants could be in the magnitude of \(10^{-2} - 10^{-1}\) 1/h and THM hydrolysis becomes considerable.

A number of epidemiological studies have been conducted to investigate the exposure risks posed by DBPs. It is well-known that the DBP concentrations vary spatially and temporally in the water distribution systems (Williams et al., 1997; Rodriguez et al., 2004; Symanski et al., 2004). Attention was also paid to the DBP variations in the plumbing systems and the residential hot water tanks (Dion-Fortier et al., 2009; Chowdhury et al., 2011). The effect of boiling water on THM levels was also investigated, focusing on further formation (from the precursors and the decomposition of other DBPs) and volatilization of the THMs (Li and Sun, 1997; Wu et al., 2001; Krasner and Wright, 2005). Recently, the heating effect on DBP levels in the waters of different water ages was systematically investigated by taking into account the disinfectant residual variation with water age in water distribution systems (Liu and Reckhow, 2013). The current study stepped further into the THM hydrolysis in the heated water stored for a relatively long duration. The results might help raise water professionals’ concerns on the fate and transformation of THMs and other conceived thermally stable DBPs in hot drinking waters when conducting epidemiological studies and regulatory estimations.

5. Conclusions

Hydrolysis of the four regulated THMs pertaining to storage of hot boiled drinking water in enclosed containers was investigated by varying the water temperature and the water pH value and by using various water matrices. It revealed that all four THMs underwent considerable hydrolysis in the water at the temperature range from 65 to 95 °C with an initial pH within 6.1 and 8.2. When the water was pH buffered, the THM hydrolysis followed pseudo-first order kinetics, regardless of the water pH, temperature and matrix. Under otherwise identical conditions, the hydrolysis rates showed a declining order following CHBrCl2 > CHBrCl > CHCl3 > CHCl2. At circum-neutral pH ranges for most drinking water, the alkaline pathway predominated over the neutral pathway, except for CHCl3 in water of relatively low pH value. Regarding the alkaline pathway, cleavage of the first halogen atom was the rate-limiting step. The activation energies for the alkaline hydrolysis of the four THMs were unusually high and differed only slightly, which were 109, 113, 115 and 116 kJ/mol for CHCl3, CHBrCl2, CHBrCl and CHCl2, respectively. The difference of THM hydrolysis rates could be due to its reactivity with hydroxide ion and the product’s reactivity with water. The normal occurrence level of halogen anions (tens to hundreds of mg/L for Cl\(^-\), tens of μg/L for Br\(^-\) ) could not affect THM hydrolysis kinetics. The commercial humic substances (TOC = 2 mg/L and natural organic matter (and probably other constituents) in drinking water substantially decreased THM hydrolysis rates, by 55% and 77% on average, respectively. It was likely due to the reduction of hydroxide ion concentration by the enhanced ionization of organic acids and by carbonate precipitation with cations at elevated temperature in drinking water matrix. When a drinking water was at 90 °C or above, the THM hydrolysis rate constants were all in the magnitude of \(10^{-2} - 10^{-1}\) 1/h, which indicated that all four THMs could be largely removed by hydrolysis in the magnitude of hours. When the boiled real tap water was stored in an enclosed container at 90 °C, THMs continued increasing during the first 8 h and then kept decreasing later on due to the competition between hydrolysis and further formation. The least stable CHBrCl2 and CHBrCl could be almost eliminated after storage for 3 d. The benefit margin of boiling/storing drinking waters was unclear so far unless the overall DBP toxicity was considered. In the situation while volatilization of THMs is largely blocked, the role of THM hydrolysis can be significantly enhanced. These results on THM hydrolysis at elevated water temperatures could help water professionals to better assess the health risks posed by DBPs due to cool and boiled tap water consumption.

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References


