MODELING BROMIDE EFFECTS ON THE SPECIATION OF TRIHALOMETHANES FORMATION IN CHLORINATED DRINKING WATER

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ABSTRACT

Speciation behavior of trihalomethanes formation in chlorinated waters due to the effects of bromide is mathematically modeled by a three-tier scheme. Equations for the mole fractions of the mono-, di-, and trihalo-intermediates at each tier level in terms of the initial bromide to chlorine molar ratio are derived and verified by comparison with results of other theoretical studies based on an assumption of constant bromination to chlorination reaction reactivity ratio. It is identified that the usage of applied chlorine concentration or available chlorine concentration for calculation of the relative initial bromide to chlorine concentration would yield different reactivity ratio and should be used consistently. The model equations are also tested by laboratory experiments done with source water at a local plant. It is found that equations with an overall bromination to chlorination rate constant ratio of 18.66 can capture the THM speciation behavior of all four tested incubation periods well.

KEYWORDS: Trihalomethanes; Speciation; Bromide effects; Kinetic model; Drinking water

1. INTRODUCTION

Chlorination is a common process used for disinfection of drinking water in the world. It is a process using chlorine to destroy pathogenic bacteria and algae in raw water. This process has only been considered as a life-saver until Rook (1974) and Bellar *et al*. (1974) showed that potent trihalomethanes (THMs) of four species can be formed as disinfection by-products in chlorination. They are Chloroform ($CHCl_3$), Bromodichloromethane ($CHBrCl_2$), Dibromochloromethane ($CHBr_2Cl$) and Bromoform ($CHBr_3$). Since then THMs have been researched intensively. It is known that the theoretical risk to humans varies among individual THM species, but the brominated ones are more toxic (U.S. EPA, 1992). Hence, the formation of brominated THMs during the disinfection process is of great concern. It is known that when there is bromide existing in raw water, the active halogen shifts from chlorine to bromine (Rook and Gras, 1978), which means that the reactions incorporating bromine into natural organic matters (NOM) are faster than those incorporating chlorine (Symons *et al*., 1993). Hence the potential for forming Br-THMs is higher if bromide exists. Studies indicate that Br-THMs could be produced even at a considerably low concentration of bromide relative to chloride concentration (Minear and

Bird, 1980; Luong *et al.,* 1982; Cooper *et al.*, 1985; Krasner *et al.*, 1994). Other studies also show that the distribution of chlorinated DBPs and brominated DBPs in treated water is affected by the ratio of HOCl/Br- (Rebhun *et al.,* 1990), Br-/NOM and Br-/free chlorine (Shukairy *et al.,* 1995).

The interests of the present study originated from the fact that many coastal cities including Macau have the problem of seawater intruding into their raw water intakes. Hence various levels of bromide concentration may exist in the drawn water source. Naturally the effects of bromine on the production of THMs in the finished water are of great interest to these cities. In this paper, detailed equations for estimation of THM speciation production based on an initial bromide to chlorine ratio are derived from a reaction scheme model. The equations are then tested with source water directly from an intake close to sea with controlled experiments in the laboratory.

2. THE MODEL

Considering the speciation of formed trihalomethanes relates mainly to the initial chlorine and bromide concentrations, Nokes *et al.* (1999) proposed a kinetic reaction scheme as shown in Fig. 1 and developed equations to estimate the relative concentrations of the four THMs. The model equations developed in the present paper, adopt the same reaction scheme with the goal of providing a complete set of equations at all tier levels. The results are expressed in terms of the relative bromination and chlorination reaction rates to reflect their effects. This also makes simplification of the equations easier for later comparison with other studies.
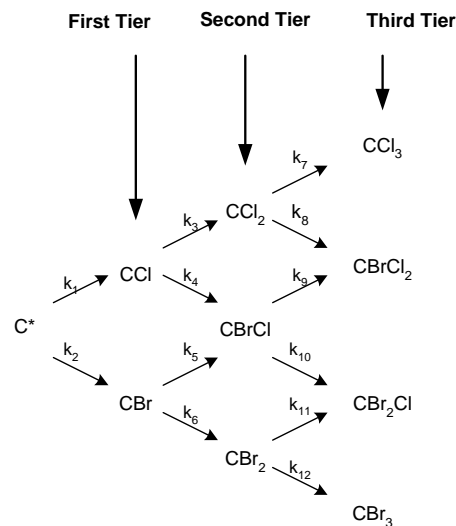

Figure 1. Reaction scheme by Nokes *et al.* (1999)

This kinetically controlled three tiers reaction scheme starts with activated carbon atoms, C^*, in the NOM. They must then go through halogen substitution to form the carbon of the THM molecules. In the first halogenation step, the activated carbon is either chlorinated to incorporate one chlorine atom, or brominated to incorporate one bromine atom. The two mono-halogenated reaction intermediates form the first tier of the scheme. Subsequently, these two intermediates in the first tier may each undergo either chlorination or bromination, and so this process continues until the trihalo-intermediates in the final or third tier, from which the THMs are eventually formed, are produced. The trihalogenated carbon atom of the final intermediate is assumed as part of a trihaloacetyl group, and base hydrolysis to be the final step leading to the THM (Peters *et al.,* 1980; Boyce and Hornig, 1983; Reckhow and Singer, 1985). In this three tiers scheme, there are twelve rate equations from the reaction stairs. It can be assumed that the rate of any step, A, in the reaction scheme is,

$$\text{Rate of } A = k_A \,[\text{HOX}][\text{intermediate}], \tag{1}$$

where [HOX] is the concentration of the reacting hypohalous acid, [intermediate] is the concentration of the intermediate (or C*) with which it reacts, and k_A is the reaction rate constant of the process. All concentrations concerned in Eqn. (1) are in molar. To derive the equations for the concentrations of the trihalo-intermediates, the reactions rates of the intermediates are assumed to be first order due to the concentration changes of bromide and chlorine in the period of the trihalo-intermediates formation are small. At the same time, it is known that the rates of change of the mono- and dihalogenated intermediate concentrations during the reaction are also small, hence steady-state approximation can be made and simplified expressions for these two types of intermediate can be derived. Based on these assumptions, the following expressions for the mole fractions of the mono-, di-, and trihalo-intermediates at each tier level are derived in the present study as follows:

Monohalogenated species

$$X_{CCl} = \frac{1}{1 + \dfrac{k_2[HOBr]}{k_1[HOCl]}} \tag{2}$$

$$X_{CBr} = \frac{\dfrac{k_2[HOBr]}{k_1[HOCl]}}{1 + \dfrac{k_2[HOBr]}{k_1[HOCl]}} \tag{3}$$

X_{CCl} is the mole fraction of the total monohalogenated species present as CCl, etc.

Dihalogenated species

$$X_{CCl_2} = \frac{1}{1 + \left(\dfrac{k_2}{k_1} + \dfrac{k_4}{k_3}\right)\dfrac{[HOBr]}{[HOCl]} + \dfrac{k_2 k_4 [HOBr]^2}{k_1 k_3 [HOCl]^2}} \, , \tag{4}$$

$$X_{CBrCl} = \frac{\dfrac{k_4[HOBr]}{k_3[HOCl]}}{1 + \dfrac{k_2[HOBr]}{k_1[HOCl]} + \dfrac{k_4[HOBr]}{k_3[HOCl]} + \dfrac{k_2 k_4 [HOBr]^2}{k_1 k_3 [HOCl]^2}} + \frac{\dfrac{k_2[HOBr]}{k_1[HOCl]}}{1 + \dfrac{k_2[HOBr]}{k_1[HOCl]} + \dfrac{k_6[HOBr]}{k_5[HOCl]} + \dfrac{k_2 k_6 [HOBr]^2}{k_1 k_5 [HOCl]^2}} \, , \tag{5}$$

$$X_{CBr_2} = \frac{\dfrac{k_2 k_6 [HOBr]^2}{k_1 k_5 [HOCl]^2}}{1 + \left(\dfrac{k_2}{k_1} + \dfrac{k_6}{k_5}\right)\dfrac{[HOBr]}{[HOCl]} + \dfrac{k_2 k_6 [HOBr]^2}{k_1 k_5 [HOCl]^2}} \, , \tag{6}$$

X_{CCl_2} is the mole fraction of the total dihalogenated species present as CCl_2, etc.

Trihalogenated species

$$X_{CCl_3} = \frac{1}{1 + \left(\dfrac{k_2}{k_1} + \dfrac{k_4}{k_3} + \dfrac{k_8}{k_7}\right)\dfrac{[HOBr]}{[HOCl]} + \left(\dfrac{k_2 k_4}{k_1 k_3} + \dfrac{k_2 k_8}{k_1 k_7} + \dfrac{k_4 k_8}{k_3 k_7}\right)\dfrac{[HOBr]^2}{[HOCl]^2} + \left(\dfrac{k_2 k_4 k_8}{k_1 k_3 k_7}\right)\dfrac{[HOBr]^3}{[HOCl]^3}} \, , \tag{7}$$

$$X_{CCl_2Br} = \left\{ \frac{\dfrac{k_2}{k_1}\dfrac{[HOBr]}{[HOCl]}}{1+\left(\dfrac{k_2}{k_1}+\dfrac{k_6}{k_5}+\dfrac{k_{10}}{k_9}\right)\dfrac{[HOBr]}{[HOCl]}+\left(\dfrac{k_2k_6}{k_1k_5}+\dfrac{k_2k_{10}}{k_1k_9}+\dfrac{k_6k_{10}}{k_5k_9}\right)\dfrac{[HOBr]^2}{[HOCl]^2}+\left(\dfrac{k_2k_6k_{10}}{k_1k_5k_9}\right)\dfrac{[HOBr]^3}{[HOCl]^3}} \right.$$

$$+ \frac{\dfrac{k_4}{k_3}\dfrac{[HOBr]}{[HOCl]}}{1+\left(\dfrac{k_2}{k_1}+\dfrac{k_4}{k_3}+\dfrac{k_{10}}{k_9}\right)\dfrac{[HOBr]}{[HOCl]}+\left(\dfrac{k_2k_4}{k_1k_3}+\dfrac{k_2k_{10}}{k_1k_9}+\dfrac{k_4k_{10}}{k_3k_9}\right)\dfrac{[HOBr]^2}{[HOCl]^2}+\left(\dfrac{k_2k_4k_{10}}{k_1k_3k_9}\right)\dfrac{[HOBr]^3}{[HOCl]^3}} , \quad (8)$$

$$\left. + \frac{\dfrac{k_8}{k_7}\dfrac{[HOBr]}{[HOCl]}}{1+\left(\dfrac{k_2}{k_1}+\dfrac{k_4}{k_3}+\dfrac{k_8}{k_7}\right)\dfrac{[HOBr]}{[HOCl]}+\left(\dfrac{k_2k_4}{k_1k_3}+\dfrac{k_2k_8}{k_1k_7}+\dfrac{k_4k_8}{k_3k_7}\right)\dfrac{[HOBr]^2}{[HOCl]^2}+\left(\dfrac{k_2k_4k_8}{k_1k_3k_7}\right)\dfrac{[HOBr]^3}{[HOCl]^3}} \right\}$$

$$X_{CBr_2Cl} = \left\{ \frac{\dfrac{k_2k_6}{k_1k_5}\dfrac{[HOBr]^2}{[HOCl]^2}}{1+\left(\dfrac{k_2}{k_1}+\dfrac{k_6}{k_5}+\dfrac{k_{12}}{k_{11}}\right)\dfrac{[HOBr]}{[HOCl]}+\left(\dfrac{k_2k_6}{k_1k_5}+\dfrac{k_2k_{12}}{k_1k_{11}}+\dfrac{k_6k_{12}}{k_5k_{11}}\right)\dfrac{[HOBr]^2}{[HOCl]^2}+\left(\dfrac{k_2k_6k_{12}}{k_1k_5k_{11}}\right)\dfrac{[HOBr]^3}{[HOCl]^3}} \right.$$

$$+ \frac{\dfrac{k_2k_{10}}{k_1k_9}\dfrac{[HOBr]^2}{[HOCl]^2}}{1+\left(\dfrac{k_2}{k_1}+\dfrac{k_6}{k_5}+\dfrac{k_{10}}{k_9}\right)\dfrac{[HOBr]}{[HOCl]}+\left(\dfrac{k_2k_6}{k_1k_5}+\dfrac{k_2k_{10}}{k_1k_9}+\dfrac{k_6k_{10}}{k_5k_9}\right)\dfrac{[HOBr]^2}{[HOCl]^2}+\left(\dfrac{k_2k_6k_{10}}{k_1k_5k_9}\right)\dfrac{[HOBr]^3}{[HOCl]^3}} , \quad (9)$$

$$\left. + \frac{\dfrac{k_4k_{10}}{k_3k_9}\dfrac{[HOBr]^2}{[HOCl]^2}}{1+\left(\dfrac{k_2}{k_1}+\dfrac{k_4}{k_3}+\dfrac{k_{10}}{k_9}\right)\dfrac{[HOBr]}{[HOCl]}+\left(\dfrac{k_2k_4}{k_1k_3}+\dfrac{k_2k_{10}}{k_1k_9}+\dfrac{k_4k_{10}}{k_3k_9}\right)\dfrac{[HOBr]^2}{[HOCl]^2}+\left(\dfrac{k_2k_4k_{10}}{k_1k_3k_9}\right)\dfrac{[HOBr]^3}{[HOCl]^3}} \right\}$$

$$X_{CBr_3} = \frac{\left(\dfrac{k_2k_6k_{12}}{k_1k_5k_{11}}\right)\dfrac{[HOBr]^3}{[HOCl]^3}}{1+\left(\dfrac{k_2}{k_1}+\dfrac{k_6}{k_5}+\dfrac{k_{12}}{k_{11}}\right)\dfrac{[HOBr]}{[HOCl]}+\left(\dfrac{k_2k_6}{k_1k_5}+\dfrac{k_2k_{12}}{k_1k_{11}}+\dfrac{k_6k_{12}}{k_5k_{11}}\right)\dfrac{[HOBr]^2}{[HOCl]^2}+\left(\dfrac{k_2k_6k_{12}}{k_1k_5k_{11}}\right)\dfrac{[HOBr]^3}{[HOCl]^3}} , \quad (10)$$

X_{CCl_3} is the mole fraction of the total trihalogenated species present as CCl_3, etc.

The current results are complete set of the formation equations describing the behaviors at all tier levels; in which Eqns. (7) to (10) can be used for estimation of the relative concentrations of the four THMs given that THM formation is complete when the measurements are made and the percentage of each trihalo-intermediate that is converted to its corresponding THM is the same for each intermediate as suggested by Nokes *et al.* (1999). It is noted that the equations given by Nokes *et al.* (1999) are only for the trihalo-intermediates which are counterparts of the current Eqns. (7) to (10). Comparison of the equations by Nokes *et al.* (1999) with Eqns. (7) to (10) reveals that the ones for CCl_3 (hence $CHCl_3$) and CBr_3 (hence $CHBr_3$) are identical while the ones for $CBrCl_2$ (hence $CHBrCl_2$) and CBr_2Cl (hence $CHBr_2Cl$) are quite different not just in appearance but also in terms of evaluated values with substituted values of [HOBr]/[*HOCl*] and reaction rate constants, k_i. These differences require further verification of the mole fraction equations derived in the present study through comparisons of them with results from other studies.

It is known that prior to Nokes *et al.* (1999), Cowman and Singer (1996) derived expressions for describing mole fraction distributions of individual HAA (haloacetic acids) species within the groupings of mono-, di-, and trihalogenated species in chlorinated

extracts through probability theory. Their results are based on the assumptions that the speciation of the HAAs is primarily a function of the ratio of the reactivity of HOBr to HOCl (which is accounted for by a single factor γ) for halogen substitution into natural organic material, all halogenated intermediates of the same group are formed through the same pathways, and the mole fraction of the total HAAs present as mono-, di-, or trihalogenated species remains constant over varying bromide concentration. Cowman and Singer (1996) also believed that their equations can be applied to THMs. They tested their equations with the THM experimental data of Bird (1979) and found good agreements. Later Chang *et al.* (2001) applied the approach of HAA by Cowman and Singer (1996) to THMs. They also found that the equations work well for THM mole fraction speciation. Now come back to the expressions for the halogenated intermediates mole fractions, Eqns. (2) to (10), derived in the present study. If the reaction reactivity ratio k_{2n}/k_{2n-1} between bromination and chlorination is taken as constant as assumed by Cowman and Singer (1996) along each tier of the reaction scheme and has the same value γ, i.e.

$$\gamma = \frac{k_{2n}}{k_{2n-1}}, \tag{11}$$

with n = 1, 2, 3, …, 12, Eqns. (2) to (10) can be simplified to the following forms.

Monohalogenated species

$$X_{CCl} = \frac{1}{1 + \gamma \frac{[HOBr]}{[HOCl]}}, \tag{12}$$

$$X_{CBr} = \frac{\gamma \frac{[HOBr]}{[HOCl]}}{1 + \gamma \frac{[HOBr]}{[HOCl]}}, \tag{13}$$

Dihalogenated species

$$X_{CCl_2} = \frac{1}{1 + 2\gamma \frac{[HOBr]}{[HOCl]} + \gamma^2 \frac{[HOBr]^2}{[HOCl]^2}}, \tag{14}$$

$$X_{CBrCl} = \frac{2\gamma \frac{[HOBr]}{[HOCl]}}{1 + 2\gamma \frac{[HOBr]}{[HOCl]} + \gamma^2 \frac{[HOBr]^2}{[HOCl]^2}}, \tag{15}$$

$$X_{CBr_2} = \frac{\gamma^2 \frac{[HOBr]^2}{[HOCl]^2}}{1 + 2\gamma \frac{[HOBr]}{[HOCl]} + \gamma^2 \frac{[HOBr]^2}{[HOCl]^2}}, \tag{16}$$

Trihalogenated species

$$X_{CCl_3} = \frac{1}{1 + 3\gamma \frac{[HOBr]}{[HOCl]} + 3\gamma^2 \frac{[HOBr]^2}{[HOCl]^2} + \gamma^3 \frac{[HOBr]^3}{[HOCl]^3}}, \tag{17}$$

$$X_{CBrCl_2} = \cfrac{3\gamma \cfrac{[HOBr]}{[HOCl]}}{1 + 3\gamma \cfrac{[HOBr]}{[HOCl]} + 3\gamma^2 \cfrac{[HOBr]^2}{[HOCl]^2} + \gamma^3 \cfrac{[HOBr]^3}{[HOCl]^3}}, \qquad (18)$$

$$X_{CBr_2Cl} = \cfrac{3\gamma^2 \cfrac{[HOBr]^2}{[HOCl]^2}}{1 + 3\gamma \cfrac{[HOBr]}{[HOCl]} + 3\gamma^2 \cfrac{[HOBr]^2}{[HOCl]^2} + \gamma^3 \cfrac{[HOBr]^3}{[HOCl]^3}}, \qquad (19)$$

$$X_{CBr_3} = \cfrac{\gamma^3 \cfrac{[HOBr]^3}{[HOCl]^3}}{1 + 3\gamma \cfrac{[HOBr]}{[HOCl]} + 3\gamma^2 \cfrac{[HOBr]^2}{[HOCl]^2} + \gamma^3 \cfrac{[HOBr]^3}{[HOCl]^3}}. \qquad (20)$$

These simplified equations are exactly the same as those given by Cowman and Singer (1996) for HAAs, while Eqns. (17) to (20) also agree with those used by Chang *et al.* (2001) for THMs. The agreements between the present results and other previous studies suggest that confidence can be placed on the complete equations developed here. In fact, Eqns. (17) to (20) are later used to study speciation of THM in Macau water. Before doing so, further manipulation of the derived equations are made so that direct estimation on the reaction reactivity ratio γ can be made by measurements of the molar ratio of the total concentrations of bromine and chlorine in THMs, and the molar ratio of the initial HOBr and HOCl concentrations. The molar concentrations of the brominated THMs (THM–Br) and chlorinated THMs (THM–Cl) can be calculated as

$$[THM-Br] = 1 \times [CHBrCl_2] + 2 \times [CHBr_2Cl] + 3 \times [CHBr_3], \qquad (21)$$

and

$$[THM-Cl] = 1 \times [CHBr_2Cl] + 2 \times [CHBrCl_2] + 3 \times [CHCl_3]. \qquad (22)$$

The ratio of Eqn. (21) to Eqn. (22) with the substitution of Eqns. (17) to (20) gives

$$\frac{[THM-Br]}{[THM-Cl]} = \gamma \frac{[HOBr]}{[HOCl]}. \qquad (23)$$

Hence a linear relation between the two mole ratios is expected.

It is noted that when using the derived equations, initial HOBr and HOCl concentrations would be used. The initial HOBr molar concentration is set equal to the spiked or applied Br^- concentration based on the assumption that the formation of HOBr from the reaction of Br^- with HOCl is rapid and occurs before reaction of the natural organic material with HOCl. As for the initial HOCl concentration, the difference between the applied HOCl concentration and the moles of HOBr produced from reaction with bromide can be used. This is similar to what Cowman and Singer (1996) used in their study. This choice of HOBr and HOCl concentration calculation is logical as the halogenation process is a competition between the available HOBr and HOCl. There are other studies (e.g. Chang *et al.*, 2001) in which the HOBr and HOCl concentrations are simply taken as the applied bromide and chlorine concentrations and it appears to work well too. However, it should be noted that the values of the reaction reactivity ratio γ estimated from the two different [HOBr]/[HOCl] calculation methods are different and should not be compared directly. In analyzing the results of the present experiments, both methods are used to calculate the

[*HOBr*]/[*HOCl*] ratio to see which one performs better. In order not to confuse the readers, notations of them are defined as follows,

[*HOBr*] = the applied Br^- molar concentration, (24)

[*HOCl*]$_0$ = the applied chlorine molar concentration, (25)

[*HOCl*]$_A$ = the available HOCl molar concentration = [*HOCl*]$_0$ − [*HOBr*], (26)

$$\gamma_0 = \frac{[THM-Br]}{[THM-Cl]} \bigg/ \frac{[HOBr]}{[HOCl]_0} \,, \tag{27}$$

$$\gamma_A = \frac{[THM-Br]}{[THM-Cl]} \bigg/ \frac{[HOBr]}{[HOCl]_A} \,. \tag{28}$$

The relation between them can be expressed as

$$\frac{[HOBr]}{[HOCl]_A} = \frac{\dfrac{[HOBr]}{[HOCl]_0}}{1 - \dfrac{[HOBr]}{[HOCl]_0}} \,, \tag{29}$$

where 0 < [*HOBr*]/[*HOCl*]$_0$ <1.   Note that [*HOBr*]/[*HOCl*]$_A$ is always larger than [*HOBr*]/[*HOCl*]$_0$. Hence for the same [*THM-Br*]/[*THM-Cl*] value, the γ_A value associated with [*HOBr*]/[*HOCl*]$_A$ is always smaller than the γ_0 associated with [*HOBr*]/[*HOCl*]$_0$ according to Eqns. (27) and (28). This may be the reason for the γ value estimated by Chang *et al.* (2001) is over two times larger than those from Cowman and Singer (1996).

3. EXPERIMENTS

The model equations of speciation behavior during THMs formation in chlorinated waters are tested by controlled experiments done in the Laboratory & Research Centre of the Macau Water Supply Co. Ltd., which is certified by the China National Accreditation Committee for Laboratories (CNAL) to meet the requirement of CNAL/AC01 (identical with ISO/IEC 17025).   The laboratory standard operation procedures collated from the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA and WEF, 1998) are strictly followed in this study. Water samples used in the study were directly collected from the source water of a treatment plant in Macau. The samples were stored in the dark under 4°C before chlorination in the laboratory. Characteristics of the raw water quality were indicated by a concentration of 1.8 mg l^{-1} in dissolved organic carbon, around 2.8 m^{-1} in UV254 reading and 7.8 in pH value.

To test the effects of bromide on THM formation, it is designed to spike the source water samples with five levels of bromide dosages (0.038 mg l^{-1}, 0.438 mg l^{-1}, 0.838 mg l^{-1}, 1.038 mg l^{-1} and 3.038 mg l^{-1}) to simulate various bromide conditions. For each bromide dosage, four levels of chlorine dosages (4.20 mg l^{-1}, 7.89 mg l^{-1}, 14.73 mg l^{-1} and 20.00 mg l^{-1}) are added to form a five by four matrix. Then each bromide-chlorine combination sample is subjected to four different incubation periods (1 hour, 6 hours, 24 hours and 72 hours) of chlorination before final THM concentrations are measured.

In the experiments, all water samples (50 ml each) spiked with bromide dosages were first buffered with phosphate at 7.0 ± 0.2. Chlorination of them was done by adding standardized hypochlorite solution prepared by iodometric method. The samples were then placed into organic free dark glass battles sealed with PTFE/silicon septa (Agilent, US), and stored at 25 ± 2°C for their prescribed incubation periods. At the end of their

incubation periods, water samples were quenched with sodium sulfite solution to stop chlorination. Concentrations of THMs in them were measured then.

The measuring instruments and reagents used are briefly introduced here. Measurement of dissolved organic carbon was done with a TOC analyzer (Shimadzu TOC-5000A) with the auto-sampler (Shimadzu ASI-5000A), while UV254 was detected by a UV-visible spectrophotometer (Shimadzu UV-2401). The pH value of water sample was measured by a TOA pH meter (Scientific HM-30S). Bromide concentration was determined by an ion chromatography system which includes mainly an analysis column (IonPac AS14), a gradient pump (Dionex GP50) and an absorbance detector (Dionex AD20). Concentrations of THMs were measured by uploading the water sample to the automatic headspace sampler (Pekin Elmer HS 40XL) of the gas chromatography system (Pekin Elmer Auto System XL). The GC column used in the system was a SPB-5 (30m×0.25mm, with id 2.5 µm). Reagent grade or higher quality chemicals were used throughout this study. Super-Q water (purified by reverse osmosis, deionization, and carbon adsorption) was used for preparation of reagents, sample blanks, and dilution water.

4. RESULTS AND DISCUSSIONS
The present paper mainly concentrates on the development of the mole fraction equations of the mono-, di-, and trihalo-intermediates formed during the chlorination of drinking water in terms of the relative initial bromide and chlorine concentrations. Hence the speciation of the corresponding disinfection byproducts, THMs, produced at the end can be modeled in fuller details if needed. The experiments designed here try to verify the derived equations simply by measuring the variations of the final THM species fraction concentrations with different relative initial [*HOBr*] and [*HOCl*] concentrations; i.e. Eqns. (17) to (20). At the same time, different incubation time periods after chlorination started are also set for the experiments so that the time effect on the THM speciation can also be clarified.

The key point in application of Eqns. (17) to (20) is to estimate the reaction reactivity ratio γ which is assumed constant in each tier of the reaction scheme. According to Eqns. (24) to (28), measurements of the molar concentrations of the brominated THMs (THM–Br), chlorinated THMs (THM–Cl), and the initial [*HOBr*], [*HOCl*]$_0$ and [*HOCl*]$_A$ concentrations can be used to estimate γ_0 and γ_A. Concentrations of these components from the experimental sets with 1 hour, 6 hours, 24 hours and 72 hours of incubation period are respectively plotted in Figs. 2 and 3. Least square line with forced intercept at zero [*THM-Br*]/[*THM-Cl*] fitted for each set of measurements with its prescribed incubation period is shown in the figures. The slopes of the fitted lines hence the corresponding reactivity ratios based on [*HOCl*]$_A$ and [*HOCl*]$_0$ together with their coefficients of determination are summarized in Table 1.

Table 1. The estimated reaction reactivity ratios based on Eqn. (23) in the controlled experiments

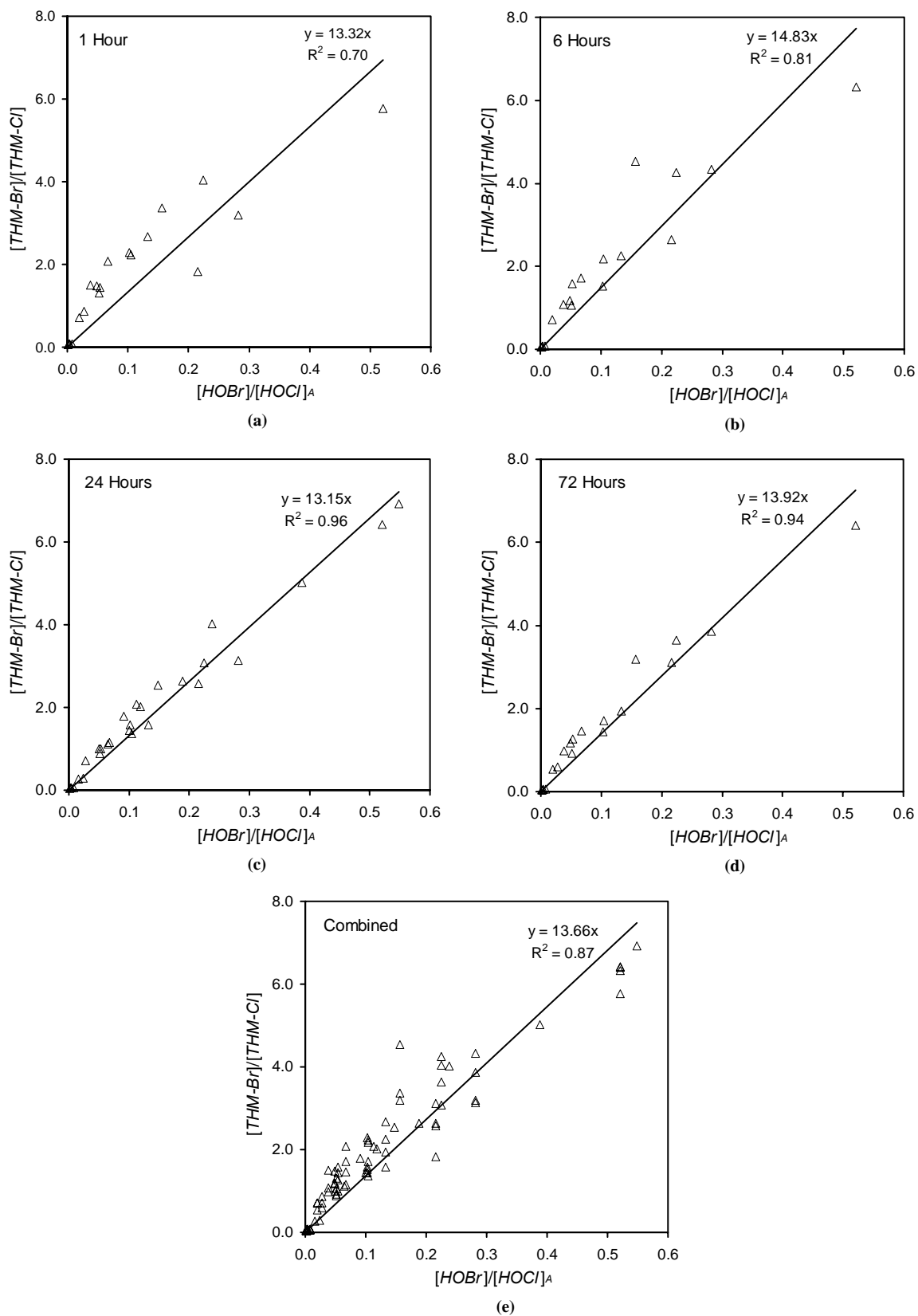| Incubation period	1 hour		6 hours		24 hours		72 hours		Combined	
Reaction reactivity ratio	γ_A	γ_0	γ_A	γ_0	γ_A	γ_0	γ_A	γ_0	γ_A	γ_0
	13.32	18.26	14.83	20.25	13.15	18.01	13.92	18.82	13.66	18.66
Coefficient of determination, R^2	0.70	0.81	0.81	0.90	0.96	0.97	0.94	0.98	0.87	0.92

Figure 2. Molar ratio of [*THM-Br*]/[*THM-Cl*] versus initial [*HOBr*]/[*HOCl*]$_A$ with incubation periods of (a) 1 hour, (b) 6 hours, (c) 24 hours and (d) 72 hours. All data from different incubation periods are combined in (e).
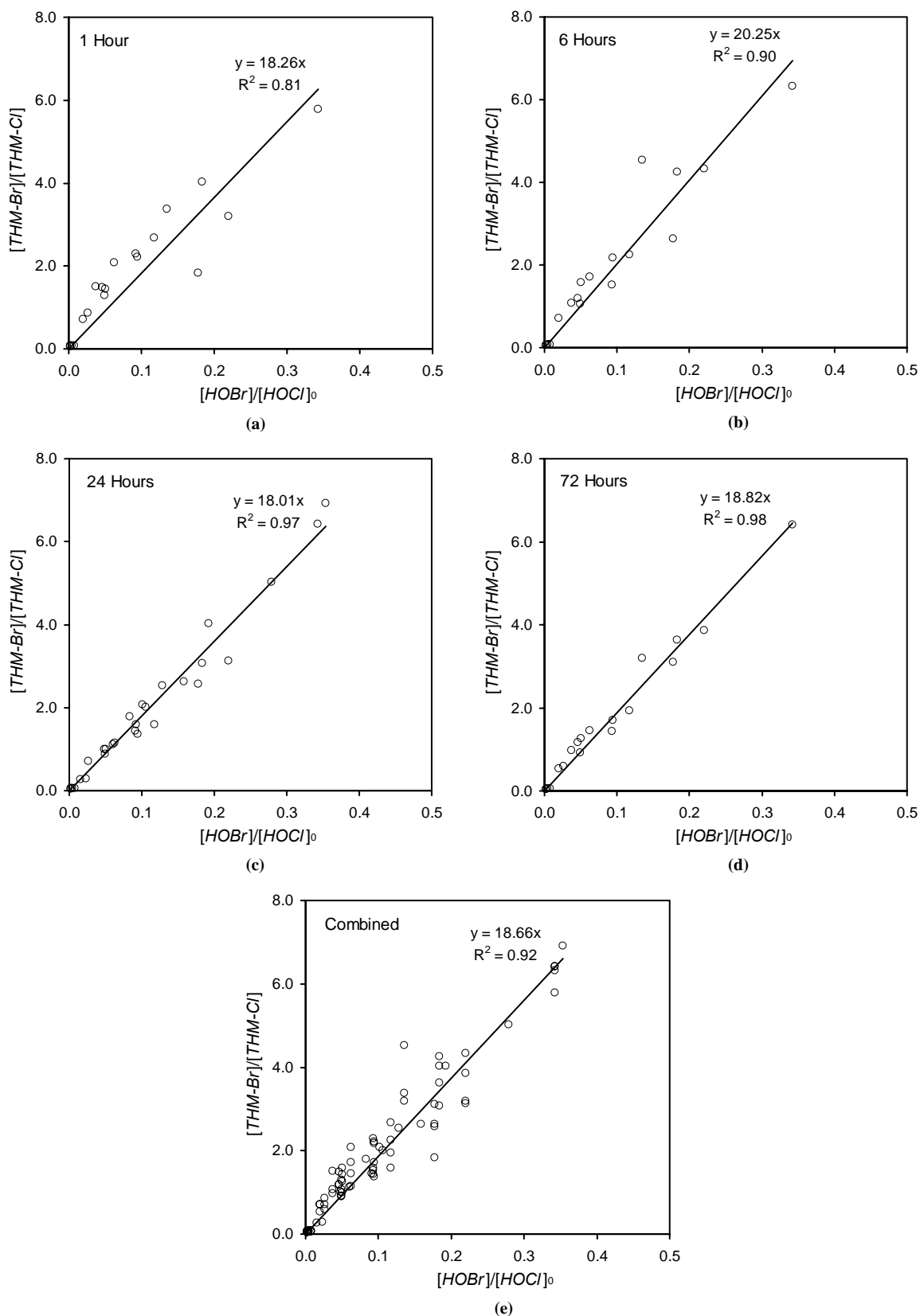
Figure 3. Molar ratio of [*THM-Br*]/[*THM-Cl*] versus initial [*HOBr*]/[*HOCl*]$_0$ with incubation periods of (a) 1 hour, (b) 6 hours, (c) 24 hours and (d) 72 hours. All data from different incubation periods are combined in (e).

It is clear that all data sets possess a relatively good linear relation by falling closely to the fitted lines and more importantly with good coefficients of determination. In general, the reaction reactivity ratio, obtained from either calculation method, is much larger than one indicating that bromination is much faster than chlorination as indicated in other studies (e.g. Symons *et al.*, 1993; Cowman and Singer 1996, Nokes *et al.*, 1999). It is found that the reaction reactivity ratio γ_0 obtained by using $[HOBr]/[HOCl]_0$ (i.e. applied chlorine) is consistently about 1.4 times larger than the γ_A obtained by using $[HOBr]/[HOCl]_A$ (i.e. available chlorine). This result confirms the theoretical analysis conclusion earlier based on Eqns. (24) to (29) and it gives a relation between the two for water in Macau. As for which one agrees better with the linear model, Eqn. (23), it is surprising to see that the one used $[HOBr]/[HOCl]_0$ consistently gives better performance, especially when incubation periods are shorter (6 hours and less) by showing a slightly larger coefficient of determination. However when the incubation periods becomes longer, the difference between the two is very small. This could be due to the stabilization of speciation occurs at a longer reaction time. This result also leads to a preliminary examination of the effect of incubation period on THM speciation. Overall the incubation time seems to make little difference; i.e. the estimated reaction reactivity ratio γ_A or γ_0 for all incubation periods tested here are within 1 to 8.5 % of their corresponding combined values. Fluctuations of this magnitude actually would not make much difference on the main trend of the modeled speciation behaviors as to be shown shortly. Actual effects would be seen by comparing concentrations of individual specie resulting from different incubation periods together with the model predictions.

With the estimated reactivity ratios given in Table 1, Eqns. (17) to (20) are used to model the speciation behaviors of THMs and compared to experimental results with different incubation periods. Similar to estimating the reaction reactivity ratio above, the speciation modeling is also done by plotting the predicted molar factions from a range of γ_A or γ_0 values against either $[HOBr]/[HOCl]_A$ or $[HOBr]/[HOCl]_0$ for visual observations. It is decided to use the minimum, the maximum and the combined reactivity ratios given in Table 1 to generate the concentration curves for the THM species. The THM speciation with variation of $[HOBr]/[HOCl]_A$ is given in Fig. 4, where the lines represent the model equations with γ_A values being 13.15, 14.83 and 13.66, and the points represent experimental data with different incubation periods. Similarly, Fig. 5 gives the modeled THM speciation with variation of $[HOBr]/[HOCl]_0$. In this figure, the model equations represented by the lines use 18.01, 20.25 and 18.66 as the γ_0 values and the experimental results are also plotted for comparison. Both Figs. 4 and 5 show relatively good agreements between the models and the THM speciation experimental data. Nevertheless, the model shown in Fig. 5 using $[HOBr]/[HOCl]_0$, hence ratio of applied bromide and chlorine, appears to perform a notch better by showing a slightly more compact data distribution around the model lines. Further discussions are focused on this case considering that similar comments can also be applied to that of Fig. 4.

It is noted that the lines representing the model equations shown in the plots of Fig. 5 are within very close proximity of each other showing that the variation of γ_0 estimated from measurements of $[THM\text{-}Br]$, $[THM\text{-}Cl]$, $[HOBr]$ and $[HOCl]_0$ with different incubation periods has very little effects on the modeled molar fraction distribution.This means that speciation can occur in short time and attention can be focused on investigating the variations of the relative concentrations of bromine and chlorine, $[HOBr]/[HOCl]_0$, on formation of individual THM specie. Generally the model states that with the increase of $[HOBr]/[HOCl]_0$ even at a very small amount (less than 0.02), the concentration fraction of chloroform declines sharply and the bromodichloromethane increases rapidly. This is a strong sign of bromination reactions taking its effects and is consistent with the large γ_0 value (18.66 for the combined one) observed in the experiments. It is noted that even chlorination is fighting for its position at this early stage; it is still in a relatively stronger

position. This can be viewed by the fact that in order to form bromodichloromethane, the activated carbon must go through one bromination and two chlorination steps hence chlorination is still the main halogenation process.
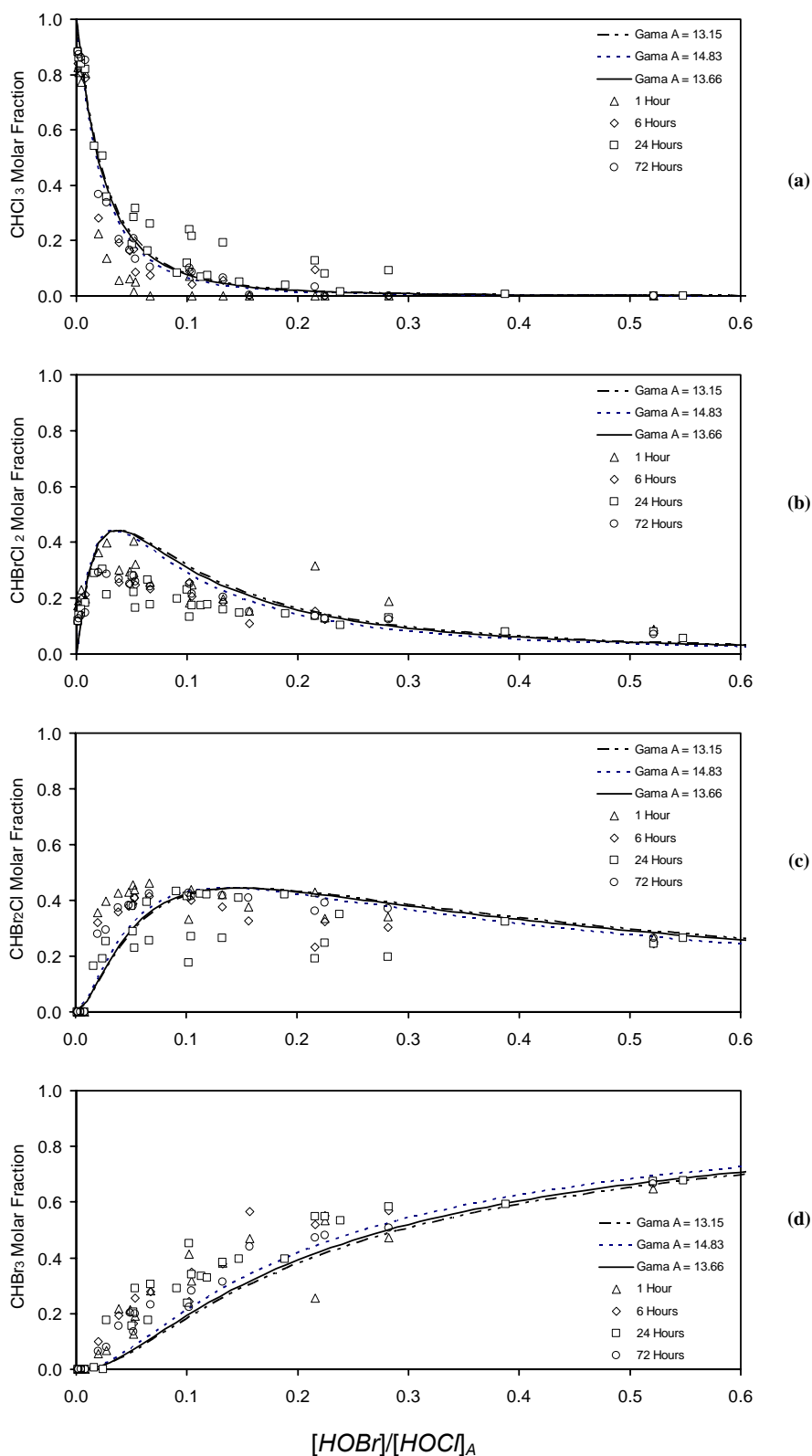

Figure 4. Modeling molar fractions of THM species with variation of initial $[HOBr]/[HOCl]_A$ with incubation periods of 1 hour, 6 hours, 24 hours and 72 hours; (a) $CHCl_3$, (b) $CHBrCl_2$, (c) $CHBr_2Cl$ and (d) $CHBr_3$.
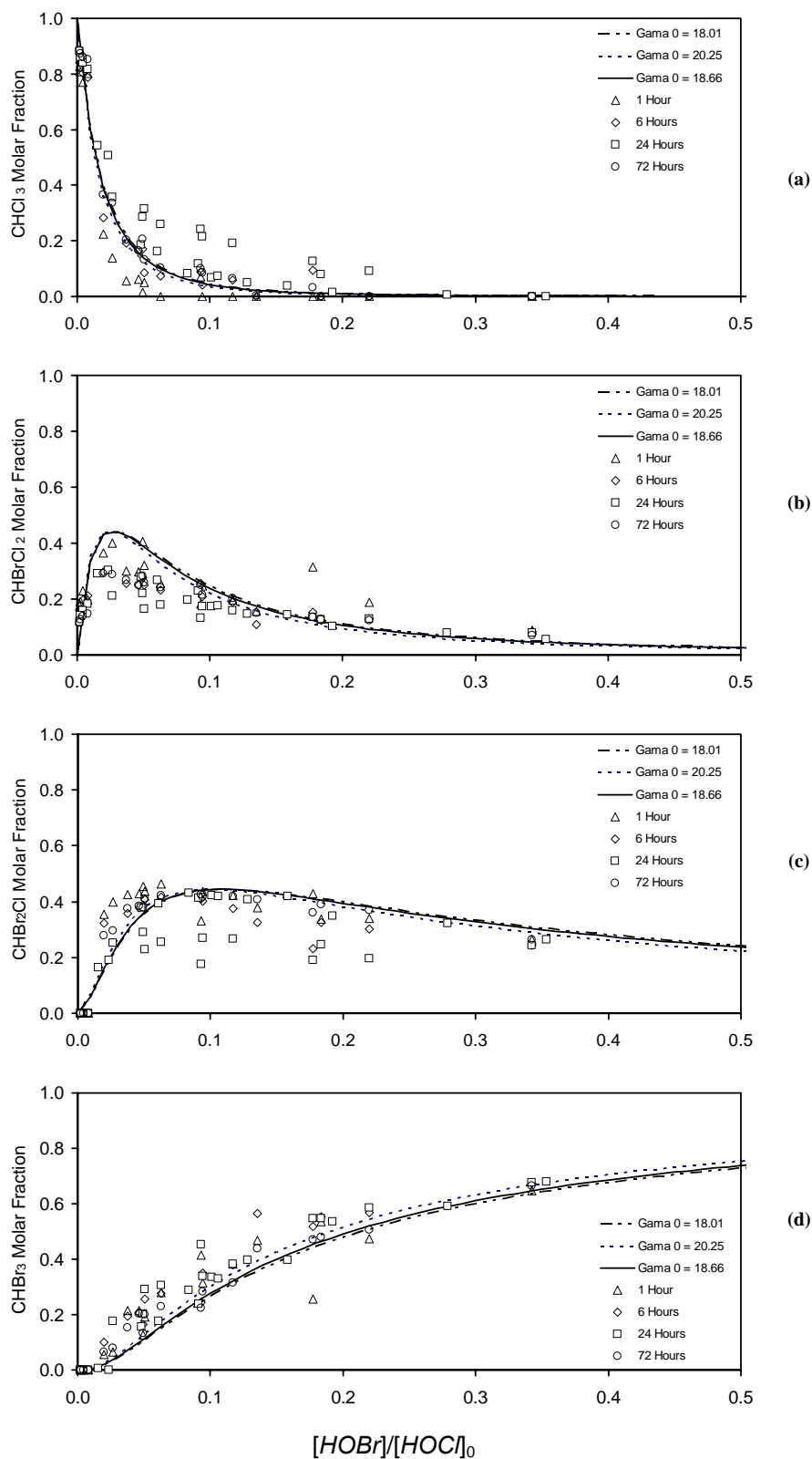
Figure 5. Modeling molar fractions of THM species with variation of initial $[HOBr]/[HOCl]_0$ with incubation periods of 1 hour, 6 hours, 24 hours and 72 hours; (a) $CHCl_3$, (b) $CHBrCl_2$, (c) $CHBr_2Cl$ and (d) $CHBr_3$.

However as the $[HOBr]/[HOCl]_0$ value increases further (larger than 0.03 here), the dominant THM specie is shifted to dibromochloromethane and later to bromoform. The

strength of bromination is completely revealed as it starts at a relatively low presence of bromine concentration; i.e. when $[HOBr]/[HOCl]_0$ is only larger than 0.16 for this case.

As for the performance of the model in comparison with experiments, it is found that even the experimental data in Fig. 5 show some scatterness, they appear to agree relatively well with the model calculations (shown as lines) indicating that the model can capture the main trends of THM speciation well. Chloroform concentration indeed decreases rapidly with the increase of bromine concentration while shifting of the dominating species to brominated THMs occurs with increasing bromine. This also means that the estimation of the reaction reactivity ratio by Eqn. (23) is satisfactory. Further examination of the plots in Fig. 5 shows that the model equation overpredicts bromodichloromethane when $[HOBr]/[HOCl]_0$ is less than 0.15 with differences being larger at $[HOBr]/[HOCl]_0$ of around 0.05 (Fig. 5b). At the same time, the model under predicts dibromochloromethane when $[HOBr]/[HOCl]_0$ is less than 0.07 and slightly overpredicts afterwards (Fig. 5c). As for bromoform, the model under predicts its concentration over the range of $[HOBr]/[HOCl]_0$ tested, and it is shown that larger deviations occurr at lower bromine concentrations (Fig. 5d).

The deviations between the experimental observations and the model predictions could be caused by many different factors. First of all, the larger differences occur at low bromine to chlorine ratios may be due to the halogen incorporation is not kinetically controlled there as suggested by Nokes *et al.* (1999). Nonetheless, the model equations are still considered of capable capturing the speciation trends relatively well. The larger amount of brominated THMs formed at low bromine to chlorine ratios than that predicted by the model also suggests that the reactivity of bromination may be stronger than the estimated γ_0. At the same time, the reaction reactivity ratio k_{2n}/k_{2n-1} at different tier level are expected to be different (Nokes *et al.*, 1999) hence the present assumption, Eqn. (11), could be the main contributor to the deviations between the two. Another factor would be the concentration of organic matters which is not accounted for in the present model equations. It is known that the rate at which the halogenation of activated carbon sites in organic matters occurs depends upon the structural features of the organic matters (Boyce and Hornig, 1983; Heller-Grossman *et al.*, 1993). Further study on their effect on THM speciation is suggested. Even the pH level in the present study is controlled at about 7.0, the importance of pH level variation should not be overlooked as studies showed that THM formation increases with increasing pH (e.g. Stevens *et al.*, 1976; Fleischacker and Randtke, 1983; Reckhow and Singer, 1985; Stevens *et al.*, 1989), hence the effect of pH on THM speciation may be important and need to be explored further. In addition, other factors, such as the variation in temperature and higher chlorine dosage may also impose effects.

5. SUMMARY AND CONCLUSIONS

The speciation of THM due to the effects of bromide is modeled based on a three-tier reaction scheme by Nokes *et al.* (1999). Complete model equations for the mole fractions of the mono-, di-, and trihalo-intermediates at each tier level are derived and they can be used to describe the detailed formation process based on an initial bromide to chlorine ratio. Comparison of the trihalo-intermediates fraction equations with those by Nokes *et al.* (1999) found that the ones for $CHBrCl_2$ and $CHBr_2Cl$ are different. Hence verification is through comparisons of the present results with other studies. By the assumption of the reaction reactivity ratio k_{2n}/k_{2n-1} between bromination and chlorination in any step being a constant, the present speciation equations reduce to the same equations given by Cowman and Singer (1996) and Chang *et al.* (2001). However, it is identified that the usage of the applied chlorine concentration or the available chlorine concentration for calculation of the relative initial bromide to chlorine concentration would yield different reactivity ratio. Even the usage of the available chlorine concentration would be more logical, the results from using the applied chlorine concentration show slightly better agreements with experiments. Results indicate that shifting of the dominant

THM specie from chlorinated one to brominated one occurs at very low bromide concentration reflecting the significant impact of bromide on THM production. Meanwhile the model equations with an overall bromination to chlorination rate constant ratio γ_0 of 18.66 captured the THM speciation behavior well for cases with incubation periods ranging from 1 hour to 72 hours. Small deviations between the model predictions and the experimental observations could be caused by different reaction rate at different halogination tier level and further study on this aspect for fine tuning the model is necessary. Other experimental parameters such as pH, temperature, chlorine dosages and organic matter concentrations in the source water may also need to be addressed later. However, the present study does provide significant framework for mathematically modeling THM speciation in chlorinated waters and for predicting their occurrence and speciation in finished drinking water.

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