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Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water

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Abstract

The decomposition of trihaloacetic acids [bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), tribromoacetic acid (TBAA)], and the formation of the corresponding trihalomethanes [bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM)] were studied. Like TBAA, the two mixed chlorobromo-species, BDCAA and DBCAA, were found to decompose to form BDCM and DBCM, respectively, via a decarboxylation pathway. The decomposition of BDCAA, DBCAA and TBAA in water at neutral pH follows a first-order reaction, with rate constants of 0.0011, 0.0062 and 0.040 day⁻¹ at 23°C, respectively; and 0.000028, 0.00014 and 0.0016 day⁻¹ at 4°C, respectively. The activation energies for the decomposition reaction of BDCAA, DBCAA and TBAA in water at neutral pH were found to be 35.0, 34.5 and 29.2 kcal/mol, respectively. The effect of pH in the range of 6–9 and the effect of a drinking water matrix on the decomposition of BDCAA, DBCAA, and TBAA in water were found to be insignificant. Measurement and health implications due to decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes were discussed. By applying the technique of quantitative structure–activity relationships (QSAR), the decomposition rate constants of six iodinated trihaloacetic acids were estimated. \bigcirc 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Decomposition; Haloacetic acids; Trihalomethanes; Drinking water; Disinfection by-products; Quantitative structureactivity relationships

1. Introduction

Haloacetic acids (HAAs) and trihalomethanes (THMs) are major chemical by-products of chlorination of drinking water [1,2]. There are a total of nine HAA species containing chlorine or bromine, of which trihaloacetic acids (THAAs) including trichloro-, bromodichloro-, dibromochloro-, and tribromoacetic acid (TCAA, BDCAA, DBCAA, and TBAA) were found to constitute a significant mole fraction of the total HAA concentration formed from chlorination of humic substances or raw waters in the presence of bromide ion [3]. Accordingly, more attention should be paid to the measurement of THAAs in chlorinated drinking water. Heller-Grossman et al. [4] found that TBAA undergoes decomposition to form bromoform in aqueous solution at 25°C while TCAA does not decompose. Pourmoghaddas et al. [5,6] questioned the stability of BDCAA and DBCAA, thus Cowman and Singer [3] suggested that some research was needed to determine the degree to which species persist in water distribution systems. Since THMs and five of HAAs are regulated by US EPA in Stage I of the disinfectants/disinfection byproducts (D/DBP) rule, and all the nine HAAs are likely to be included in Stage II of the D/DBP rule [7,3], the stability of THAAs is an important question that may impact the measurement of THAAs, the sampling locations, the extent of conversion to THMs, and

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possible health implications. In this work, the kinetics of decomposition of BDCAA, DBCAA, and TBAA, and the formation of corresponding THMs in water were studied.

The characteristic medicinal odors in drinking waters have frequently been associated with the formation of iodinated THMs [8], in particular iodoform, which has an organoleptic threshold concentration of about 1 µg/ L. Iodinated THMs can be produced via a reaction of natural organic matter with HOI, which is derived from the oxidation of I⁻ by the commonly used disinfectants such as chlorine or chloramine [9]. The total iodine (mainly as I^- and IO_3^-) level in raw waters is in the range of $0.5-10 \,\mu\text{g/L}$, but it can reach $50 \,\mu\text{g/L}$ in certain groundwaters near the sea coast [10,11]. Though some researchers observed the presence of iodinated THMs including iodoform, dichloroiodomethane, bromochloroiodomethane and dibromoiodomethane in drinking waters [12,13], no one has reported the formation of iodinated THAAs. Also, the fact that no iodinated THAA standards are available makes the direct study of kinetics of the decomposition of iodinated THAAs very difficult. Therefore, another goal of this work was to set up a quantitative relationship between structure and decomposition rate constants of THAAs to estimate the decomposition rate constants of iodinated THAAs.

2. Experimental methods

High purity single standards of 1000 mg/L of BDCAA, DBCAA or TBAA in methyl-tert-butyl ether (MtBE), EPA 552.2 acids calibration mixture of 200–2000 mg/L each in MtBE, EPA 501 trihalomethanes calibration mixture of 2000 mg/L each in methanol, 2000 mg/L of fluorobenzene in methanol (internal standard for THMs) and 1000 mg/L of 1,2,3-trichloropropane in MtBE (internal standard for HAAs) were purchased from Supelco and kept at -15° C. Analytical grade MtBE was purchased from Fluka. Nanograde pentane was purchased from VWR. MilliQ water (mqw) was supplied by a Millipore MR3 purifier system. Tap water (tapw) was collected locally.

MilliQ water and tap water, unless otherwise specified, were buffered to pH 8.0 with 5 mM phosphate, then adjusted to pH 6.0 or 7.0 with HCl, or to pH 9.0 with NaOH if necessary. THAA stock solutions were quickly injected with a syringe (the needle below water surface of 3–4 cm) into the bulk water in volumetric flasks, which were capped immediately, shaken vigorously, and diluted to prepare 2–5 L solutions of 30, 10 or 5 μ g/L just before the kinetic studies. For each set of kinetic studies, at least 16 aliquots of the above solutions were collected headspace-free in 68-mL glass vials and sealed with polypropylene screw caps and Teflon-lined septa. Those aliquots were stored in a refrigerator or a water bath at a given temperature in the absence of light. Two aliquots were analyzed, one for THAAs and one for THMs, after a designated time period. THAAs were measured immediately after extracted and quantified with a fresh calibration curve. THMs were extracted immediately and kept in a freezer and measured together quantified with a calibration curve prepared once a week. (Since THMs were demonstrated to be the only decomposition products of THAAs from the first part of the experiment, only THMs were analyzed for the balance of the experiments so that the concentrations of THAAs could be deduced.) The same samples as above without adding THAAs were prepared and measured as controls.

Gas chromatography with an electron capture detector (GC-14A, Shimadzu) was used for determining HAAs and THMs by using and slightly modifying EPA Methods 552.2, 551.1 [14,15]. THMs were extracted with pentane, HAAs were extracted with MtBE and derivatized with acidic methanol. Two series of DBPs were well separated with the same DB-1701, fused silica capillary column $(30 \text{ m} \times 0.32 \text{ mm i.d.}, 0.25 \mu\text{m film})$ thickness) under two different procedures. The procedure for the analysis of HAAs was: carrier gas, nitrogen; inlet pressure, 0.75 kg/cm²; 35°C for 12 min, ramp to 135°C at 5°C/min, ramp to 220°C at 20°C/min. The procedure for the analysis of THMs was: carrier gas, nitrogen; inlet pressure, 0.30 kg/cm²; 35°C for 18 min, ramp to 145°C at 5°C/min, ramp to 220°C at 20°C/min. Recently, Brophy et al. [7] systematically studied the effect of quenching agents and derivatizing agents on the quantification of nine HAAs, which aided in establishing a reliable analytical method for HAAs.

Total organic carbon and inorganic carbon were determined with a carbon analyzer (TOC-500, Shimad-zu), pH was measured with a pH meter (Accumet 930, Fisher Scientific), conductivity was measured with a conductivity meter (Model 152, Fisher Scientific), chlorine residue was measured by the iodometric method [16] with a spectrophotometer (DU 7400, Beckman).

3. Results and discussion

3.1. Decomposition of THAAs and Formation of THMs

Fig. 1 illustrates decomposition of THAAs and formation of the corresponding THMs in MilliQ water at pH 7 and 23°C. TBAA decomposed relatively fast to form tribromomethane (TBM or bromoform). This was expected as previously reported in the literature [4]. The two mixed chlorobromo-species, BDCAA and DBCAA were demonstrated to decompose to form bromodichloromethane (BDCM) and dibromochloromethane (DBCM), respectively. The classical mechanism for



Fig. 1. The decomposition of THAAs and the formation of THMs in MilliQ water buffered at pH 7 and 23°C with an initial concentration of $30 \,\mu$ g/L of (A) TBAA, (B) DBCAA, (C) BDCAA, respectively.

haloform formation consists of a series of reactions involving enolizable compounds from a precursor molecule such as methyl ketone [17]. Based on Fig. 1, it can be seen that three of the four typical THMs can be produced to some extent by the decomposition of THAAs, which constitutes a complementary pathway for the formation of THMs in drinking waters.

Mass balances for decomposition of THAAs and formation of the corresponding THMs were examined. For this set of experiments, the initial concentration for each THAA was $30 \,\mu\text{g/L}$. Fig. 1 shows that there was a slight fluctuation for the total molar concentration of THAA + THM, but it was within the range of measurement deviation, which means that the loss of THAA was equivalent to the formation of the corresponding THM. Because the analysis of HAAs involves derivatization with acidic methanol to form esters, it is more timeconsuming and has larger relative standard deviations than that of THMs. Moreover, the decarboxylation of THAAs is believed to be the only pathway that can chemically occur under other conditions [18,4]. Accordingly, the mass balance was very beneficial to the other parts of the study: the concentration of THAA could be deduced by measuring that of the corresponding THM.

3.2. Rate law

The decomposition of THAAs in MilliQ water at pH 7 and 23°C was carried out under three different initial concentrations: 30, 10 and $5 \mu g/L$ of each species. Fig. 2 describes the case with an initial concentration of $30 \,\mu g/$ L. The good linear relationship of ln(concentration) versus t shows that the decomposition of THAAs complies with a first-order reaction. The rate constants and correlation coefficients under different initial concentrations are given in Table 1. For different initial concentrations, the decomposition rate constants of TBAA, DBCAA and BDCAA in MilliQ water at pH 7 and 23°C were very close to one another, with an average of 0.040 ± 0.002 , 0.0062 ± 0.0006 and $0.00113 \pm 0.00006 \text{ day}^{-1}$, respectively. This also confirms that the decomposition of THAAs follows first order.



Fig. 2. The decomposition of THAAs in MilliQ water buffered at pH 7 and 23°C with an initial concentration of $30 \,\mu\text{g/L}$ of each species.

Table 1 Decomposition of THAAs in water at pH 7

	23°C 30 μ g/L ^a k (day ⁻¹) ^b	R^{2c}	23°C $10\mu\text{g/L}$ $k~(\text{day}^{-1})$	<i>R</i> ²	$23^{\circ}C$ $5 \mu\text{g/L}$ $k (\text{day}^{-1})$	R^2
BDCAA	0.0012	0.969	0.0011	0.976	0.0011	0.995
DBCAA	0.0068	0.994	0.0062	0.998	0.0056	0.993
TBAA	0.0412	0.988	0.0400	0.998	0.0379	0.985
	$4^{\circ}C$ $30 \mu\text{g/L}$ $k (\text{day}^{-1})$	R^2	$36^{\circ}C$ $30 \mu\text{g/L}$ $k (\text{day}^{-1})$	R^2	50°C $30 \mu\text{g/L}$ $k (\text{day}^{-1})$	R^2
BDCAA	0.000028	0.982	0.0165	0.990	0.234	0.994
DBCAA	0.000135	0.989	0.0783	0.997	1.02	0.999
TBAA	0.00158	0.990	0.344	0.988	3.02	0.988

^aInitial concentration.

^bRate constants.

^cFirst order correlation coefficients.



Fig. 3. Arrhenius plot of the decomposition of THAAs in MilliQ water buffered at pH 7.

The data were also tested for second-order fits which yielded negative results.

3.3. The effect of temperature

The first-order rate constants for the decomposition of THAAs in MilliQ water at 4°C, 36°C and 50°C are also shown in Table 1. An Arrhenius plot is shown in Fig. 3, where k values are the decomposition rate constants in MilliQ water at pH 7, T is temperature in K. The activation energies (the product of-slope and the ideal gas constant) for the decomposition reaction of BDCAA, DBCAA and TBAA at neutral pH were found to be 35.0, 34.5 and 29.2 kcal/mol, respectively. Brown [18] studied the thermal decomposition of TCAA and



Fig. 4. The effect of pH on the decomposition of THAAs in MilliQ water buffered with 5 mM phosphate at 23° C.

TBAA, and reported the activation energies of 36.2 and 32.9 kcal/mol, respectively. The activation energy for the decomposition of THAAs seems to be in the order of TCAA > BDCAA > DBCAA > TBAA, which is opposite to that of decomposition rate constant of THAAs.

3.4. The effect of pH and drinking water matrix

Four pHs typical of natural waters were tested. The results show that effect of pH in the range of 6–9 on the decomposition of BDCAA, DBCAA and TBAA is not significant (Fig. 4). Brown [18] studied the thermal decarboxylation of carboxylic acids and pointed out that trichloro- and tribromo-acetic acids decompose as the anions:

$$X_3 CCO_2^- \rightarrow X_3 C^- + CO_2 \tag{1}$$

Also since X_3CCO_2H is a strong acid (p K_a is estimated to be <2.0 based on the book by McMurry [19]) and X_3C^- is a strong base, the other two steps should be: $X_3CCO_2H \rightarrow X_3CCO_2^- + H^+$ and $X_3C^- + H^+ \rightarrow X_3CH$. Because acid dissociation or basic association reactions generally are very fast, Eq. (1) should be the rate-controlling step. Moreover, when the pH of water is much higher than the p K_a of X_3CCO_2H , almost all the X_3CCO_2H is present in the form of $X_3CCO_2^-$ (99.99% at pH 6, 99.99999% at pH 9). Accordingly, a pH in the range of 6–9 does not affect the decomposition of THAAs significantly.

To determine the effect of a drinking water matrix on the decomposition of THAAs, a local tap water was employed. The water quality parameters were measured as follows: pH, 7.9; total organic carbon, 1.9 mg/L as C; inorganic carbon, 28.8 mg/L as C; chlorine residue, 0.6 mg/L as Cl₂; conductivity, $805 \mu \text{mho/cm}$ at 23° C. Fig. 5 shows the comparison of THM levels formed in MilliQ water and the tap water without buffer at 23° C with an initial concentration of $30 \mu \text{g/L}$ of each THAA.



Fig. 5. The formation of THMs in MilliQ water and tap water without buffer at 23° C with an initial concentration of $30 \,\mu$ g/L of each THAA (control subtracted).



Fig. 6. Formation of THMs in MilliQ water and tap water with or without buffer at 50° C with an initial concentration of $30 \,\mu$ g/L of each THAA after 11 h (control subtracted).

THM concentrations in the tap water control sample were subtracted at each point. For either TBM, DBCM or BDCM, the solid line and the dashed line, which indicates THM levels in MilliQ water and the tap water, respectively, were very close to each other. Fig. 6 shows the comparison of THM levels produced in MilliQ water and the tap water with or without 5mM phosphate buffer at pH 7.9 (except for the sample in MilliQ water without buffer, $pH \cong 7.0$) and $50^{\circ}C$ with an initial concentration of 30 µg/L of each THAA. The reaction time was 11h. THM concentrations in the tap water control sample were subtracted. Within the range of experimental errors, there was no apparent difference for the formation of THMs in MilliQ water and the tap water with or without phosphate buffer. Consequently, the drinking water matrix does not affect the formation of THMs, i.e. the decomposition of THAAs significantly. Heller-Grossman et al. [4] compared the decomposition of tribromoacetic acid in distilled water and chlorinated lake water, and reported that tribromoacetic acid decomposes spontaneously in aqueous solutions at 25° C and that there was no effect of bromide, organic matter or chlorine on its decomposition. These studies appear to support the mechanism described in Eq. (1). The intramolecular electron transfer during decomposition is supposed to be

$$X_{3C} \xrightarrow{\uparrow} C \xrightarrow{\downarrow} C \xrightarrow{\circ} C \xrightarrow{\circ} X_{3C} + O = C = O$$

3.5. Measurement and health implications

According to the data of Table 1 and Fig. 3, the decomposition rate constants of THAAs in water at any temperature can be obtained. Also, since the decomposition of THAAs in water follows first order, the conversion of THAAs to the corresponding THMs with time (t) can be estimated:

Conversion = $(1 - e^{-kt}) \times 100\%$.

Assuming that the storage temperature in a refrigerator is 4° C, 0.04% of BDCAA, 0.2% of DBCAA and 2.2% of TBAA in a stock water solution will be converted to THMs if the solution is refrigerated for 2 weeks. This indicates that the storage in a 2-week period in a refrigerator has little influence on the concentrations of BDCAA, DBCAA and TBAA in a stock water solution.

Assuming that the typical condition in a water distribution system in summer is 23°C and pH 8, then 0.4% of BDCAA, 3.4% of DBCAA and 19.7% of TBAA formed in a water treatment plant will be transformed to THMs in tap water if the water stays up to 5 days in a water distribution system. This implies that sampling location in a distribution system affects the levels of THAAs and THMs. In reality, THMs continue to form in a chlorinated distribution system due to continued reaction of the chlorine residual and THM precursors, and the decomposition of a wide range of other halogenated species to yield THMs. Xie and Reckhow [20] found that brominated trihaloacetaldehydes decomposed to form THMs via hydrolysis, with rate constants at pH 9.0 and 20°C ranging from 0.9 to $37.6 \times 10^{-5} \text{ s}^{-1}$. It appears that trihaloacetaldehydes could represent a more significant source of THMs in alkaline waters under normal distribution-system detention times, but their levels are generally lower than those of THAAs [21].

It is of interest that if the tap water is boiled at 100°C for 3 min before drinking (a practice in some Asian countries for preparation of tea water), another 48% of

BDCAA, 93% of DBCAA and 93% of TBAA will be converted to the corresponding THMs. If iodinated THAAs were considered, a higher percentage would be converted to the corresponding iodinated THMs because iodinated THAAs generally decompose much faster than chlorinated or brominated THAAs as is discussed later.

Kargalioglu et al. [22] recently quantitatively compared the cytotoxic and mutagenic properties of some known disinfection by-products, and found that TBM and TCM have much higher cytotoxicity and mutagenic potency than their counterparts TBAA and TCAA. If this were true for all the species, then the conversion of THAAs to THMs in water distribution pipes would increase adverse effects to human health. In addition, the unpleasant odor and taste linked to the iodinated THMs would increase. Since teapots are generally open systems, the actual concentration of THMs will be lower due to volatilization, but the effects of airborne THMs on human health should then be considered.

3.6. Estimation of decomposition rate constants of iodinated THAAs

For the purpose of estimation of decomposition rate constants of iodinated THAAs, a quantitative structure– activity relationship (QSAR) between structure of THAAs and their decomposition rate constants can be established. A very useful tool to set up the QSAR is the Hammett equation and Taft's model. Hammett [23] gave an equation to describe the electronic effect of substituents on a rate constant:

$$\log(k_x) = \rho \sigma + \log(k_{\rm H}),\tag{2}$$

where k_x is a rate constant, $k_{\rm H}$ is the rate constant for the parent unsubstituted compound, ρ is a measure of the sensitivity of a reaction to the electronic effect of the substituents X, σ is the parameter for electronic effect.

Taft separates the electronic and steric properties of substituents by making use of either the hydrolysis of esters of substituted acetic acids (XCH₂COOR) or the reverse esterification reaction [24]:

$$\sigma^* = 0.403[\log(k_x/k_{\rm H})_{\rm B} - \log(k_x/k_{\rm H})_{\rm A}],\tag{3}$$

where σ^* is the inductive-field effect of X, k_x is the rate constant for the hydrolysis of XCH₂COOR, k_H is that for the hydrolysis of the parent CH₃COOR ($\sigma^* = 0$ for CH₃, where X = H), B and A indicate hydrolysis in basic or acid solution, respectively.

Earlier studies of the Hammett equation showed that the electronic effect of substituents on acid hydrolysis was nil, but the effect of substituents on basic hydrolysis of benzoate esters was significant. Taft defines the second term in Eq. (3) as a steric parameter: $E_s = \log(k_x/k_H)_A$. Substituting E_s into Eq. (3):

$$\sigma^* = 0.403[\log(k_x/k_{\rm H})_{\rm B} - E_{\rm s}]$$

or

$$\log(k_x)_{\rm B} = E_{\rm s} + 2.48\sigma^* + \log(k_{\rm H})_{\rm B}.$$
 (4)

Most possibly based on Eqs. (4) and (2), Hansch and Leo [25] presented an equation for the general approach to correlating rate constants that involve steric and electronic effects:

$$\log(k) = aE_{\rm s} + b\sigma + d,\tag{5}$$

where $\sigma = \sigma_{I} + \sigma_{R}$, σ_{I} and σ_{R} represent inductive and resonance components of electronic effect. *k* is reaction rate constant. *a*, *b* and *d* are constants.

In trihaloacetic acids, since substituents (F, Cl, Br, I) do not accept or donate a pair of electrons that are in direct conjugation with the reaction center, σ_R values are negligible. The values of σ_I (F 0.45, Cl 0.42, Br 0.45, I 0.42) were given by Hansch and Leo [25]. Since they are very close to one another, σ_I may be considered as a part of *d*. Therefore, Eq. (5) is simplified to Eq. (6):

$$\ln(k) = mE_{\rm s} + n,\tag{6}$$

where m and n are constants.

The values of E_s for substituents of F, Cl, Br and I were also given in Hansch and Leo [25] as -0.46, -0.97, -1.16 and -1.40, respectively. If E_s for a THAA is assumed to be the sum of E_s of three single substituents (Xi) in it:

$$E_{\rm s}({\rm THAA}) = \Sigma E_{\rm s}({\rm Xi})$$
 Xi = F, Cl, Br, or I. (7)

Thus, $E_{\rm s}$ for each THAA can be calculated as shown in Table 2.

Decomposition rate constants of Cl₃CCOO⁻ (TCAA) in water at 90°C, 80°C, 70°C, 60°C and 50°C were 3.11×10^{-4} , 7.70×10^{-5} , 1.71×10^{-5} , 3.48×10^{-6} and

Table 2	
Decomposition rate constants of THAAs in water (23°C

	$k (\mathrm{day}^{-1})$	Es ^a	$\ln(k)$	$t_{1/2}$ (day)
TFAA	$6.16 \times 10 - 11$	-1.38	-23.51	1.12×1010
TCAA	0.00032	-2.91	-8.06	2190
BDCAA	0.0011	-3.10	-6.81	630
DBCAA	0.0062	-3.29	-5.08	112
TBAA	0.040	-3.48	-3.22	17
DCIAA ^b	0.012	-3.34	-4.42	57
BCIAA ^b	0.076	-3.53	-2.58	9.1
DBIAA ^b	0.48	-3.72	-0.74	1.4
CDIAA ^b	0.78	-3.77	-0.25	0.89
BDIAA ^b	4.9	-3.96	1.59	0.14
TIAA ^b	50	-4.20	3.91	0.014

^a Steric parameter.

^bPossible disinfection by-products with the predicted values.

 $6.18 \times 10^{-7} \text{ s}^{-1}$, respectively [26]. According to the Arrhenius rate law, a linear relationship of $\ln(k)$ versus 1/T is plotted, and the decomposition rate constant of Cl₃CCOO⁻ in water at 23°C ($k_{\text{TCAA},\text{H}_2\text{O}}$) can be obtained as $3.66 \times 10^{-9} \text{ s}^{-1}$ or 0.00032 day^{-1} .

To obtain the decomposition rate constant of F₃CCOO⁻ (TFAA, which is not a disinfection byproduct) in water at 23°C ($k_{\text{TFAA},\text{H}_2\text{O}}$) is a little more complicated since this compound does not decompose apparently even if heated to 100°C in water. Auerbach et al. [27] conducted the thermal decarboxylation of F_3CCOO^- by using ethylene glycol (EG) as solvent, and obtained the following decomposition rate constants: $1.78 \times 10^{-3} \text{ min}^{-1}$ (170.0°C), $4.29 \times 10^{-3} \text{ min}^{-1}$ $(177.8^{\circ}C)$, $1.27 \times 10^{-2} \text{ min}^{-1}$ $(188.8^{\circ}C)$ and $2.54 \times$ 10^{-2}min^{-1} (196.5°C). By plotting of ln(k) versus 1/T, the decomposition rate constant of TFAA in EG at 23°C ($k_{\text{TFAA,EG}}$) can be obtained as $1.99 \times 10^{-10} \text{ day}^{-1}$. For comparison, Auerbach et al. [27] also reported the decomposition rate constants of Cl₃CCOO⁻ in EG: $1.49 \times 10^{-4} \text{ min}^{-1}$ (55.5°C), $1.12 \times 10^{-3} \text{ min}^{-1}$ (68.7°C), $2.84 \times 10^{-3} \text{ min}^{-1}$ (76.7°C). Similarly by plotting $\ln(k)$ versus 1/T, the decomposition rate constant of TCAA in EG at 23°C ($k_{\text{TCAA,EG}}$) can be obtained as 1.02×10^{-3} day^{-1} . Obviously, k_{TCAA,H_2O} is very close to $k_{TCAA,EG}$, which means that solvents do not affect the decomposition of THAA very much if the THAA is present predominantly as the anion in both solvents. This seems to be in agreement with Eq. (1). But a safe way is to assume that different solvents affect the decomposition rate constants of different compounds in a same way, i.e. the following relationship can be assumed to be effective:

$k_{\text{TCAA},\text{H}_2\text{O}}/k_{\text{TCAA},\text{EG}} = k_{\text{TFAA},\text{H}_2\text{O}}/k_{\text{TFAA},\text{EG}}.$

Then, $k_{\text{TFAA},\text{H}_2\text{O}}$ can be estimated as $6.16 \times 10^{-11} \text{ day}^{-1}$. By now, the decomposition rate constants of BDCAA, DBCAA, TBAA, TCAA and TFAA in water at 23°C have been obtained experimentally or



Fig. 7. Plot of $\ln(k)$ versus E_s for the decomposition of THAAs in MilliQ water at 23°C.

theoretically. Based on Eq. (6), plot $\ln(k)$ versus E_s as Fig. 7, which shows a very good linear relationship $(R^2 = 0.9987)$:

$$\ln(k) = -9.684E_{\rm s} - 36.76,\tag{8}$$

where k is the decomposition rate constant of a THAA in water at 23°C, E_s is the value of steric effect of the THAA calculated according to Eq. (7).

Since Eq. (8) fits well for fluorinated, chlorinated and brominated THAAs, it should be applicable to iodinated THAAs. By substituting E_s of each iodinated THAA into this equation, the decomposition rate constant and half-life of the corresponding iodinated THAA can be estimated as shown in Table 2.

Accordingly, the decomposition rate of THAAs in water should be in the order of Cl₃CCOOH < BrCl₂-CCOOH < Br₂ClCCOOH < Cl₂ICCOOH (DCIAA) < $Br_3CCOOH < BrClICCOOH (BCIAA) < Br_2ICCOOH$ $(DBIAA) < ClI_2CCOOH$ $(CDIAA) < BrI_2CCOOH$ (BDIAA) < I₃CCOOH (TIAA). Compared to the chlorinated and brominated THAAs, iodinated THAAs generally decompose very fast in water under ambient temperature, especially for DBIAA, CDIAA, BDIAA and TIAA, with an estimated half-life of only 1.4, 0.89, 0.14 and 0.014 days, respectively. In addition to the generally low level of iodide in raw waters, these short half-lives provide another important reason why iodinated THAAs have yet to be reported in drinking waters. For two of iodinated THAAs, DCIAA and BCIAA, however, the estimated decomposition rate constants are 0.012 and 0.076 day⁻¹, respectively, which are roughly the same as that of TBAA (0.040 day⁻¹), a disinfection by-product infrequently reported to be present in drinking water.

4. Conclusions

HAAs are formed during disinfection of water with chlorine and generally are the second major group of disinfection by-products in drinking water after THMs (but HAAs exceed the formation of THMs in many waters). This work describes the quantitative study of the spontaneous chemical decomposition of THAAs and the formation of the corresponding THMs. Rate constants at different temperatures were measured for the bromine containing acids and calculated for the iodine containing acids. This information contributes to the understanding of the chemical reactions that take place in the water distribution system and even more important enables quantifying the different reactions. Thus, the following has been demonstrated by this research:

• Two mixed chlorobromo-haloacetic acids, BDCAA and DBCAA were found to decompose to form

BDCM and DBCM, respectively, in water under ambient temperature. Considering that TBAA can decompose to form TBM under ambient temperature, three of four commonly known THMs in drinking water can be produced via decarboxylation of the corresponding THAAs, which constitutes a complementary pathway for the formation of trihalomethanes in drinking water.

- The decomposition of BDCAA, DBCAA and TBAA in water at neutral pH follows a first-order reaction, with rate constants of 0.0011, 0.0062 and 0.040 day⁻¹ at 23°C, respectively; and 0.000028, 0.00014 and 0.0016 day⁻¹ at 4°C, respectively. The activation energies for the decomposition reaction of BDCAA, DBCAA and TBAA in water at neutral pH were found to be 35.0, 34.5 and 29.2 kcal/mol, respectively.
- The effect of pH in the range of 6–9 and the effect of one drinking water matrix on the decomposition of BDCAA, DBCAA and TBAA in water were found to be insignificant.
- The quantitative structure-activity relationship demonstrated that the steric properties of halogen substituents play a pivotal role in determining the decomposition rate constants of THAAs. The decomposition rate constants of six iodinated THAAs were estimated accordingly. Compared to chlorinated and brominated THAAs, iodinated THAAs generally decompose very fast in drinking water under ambient temperature, which appears to support the fact that iodinated THAAs have yet to be reported in the literature.

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