

Full Length Research Paper

Thermal degradation of haloacetic acids in water

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Haloacetic acids are commonly found in most natural waters. These are known as degradation products of some halogenated compounds such as C₂- chlorocarbons and CFC replacement compounds: hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs). While knowledge clarifying the particular sources of these compounds and precursor degradation mechanisms are progressing, there is less understanding of mechanisms for the environmental degradation resulting from haloacetic acids. In particular, increasing concentrations of trifluoroacetic acid (TFAA) and its stability to degradation have prompted concerns that it will accumulate in the environment. Here we present the results of experiments on the non-biological decomposition of aqueous haloacetic acids. The decarboxylation of trichloroacetic acid (TCAA) and tribromoacetic acid (TBAA) was investigated in the 1930's, so this process seemed a potentially important pathway for degradation of trihaloacetic acids (THAAs) in the environment. We have measured the rate of decarboxylation of TFAA, TCAA, and TBAA and also the hydrolysis rate constants for some mono-, di-, and mixed halogen haloacetic acids in water at temperatures above ambient. The results suggest long lifetimes in natural waters. Tri-substituted acids degrade through decarboxylation with half-lives (extrapolated) at 15°C for 103 days, 46 years and 40,000 years for TBAA, TCAA and TFAA respectively. The mono and di-substituted haloacetic acids degrade via hydrolysis with half-lives (extrapolated) of 2, 12, 15, and 68 years at 15°C for monobromo- (MBAA), dibromo- (DBAA), monochloro- (MCAA) and dichloro- (DCAA) acetic acids respectively. The mixed haloacetic acids, bromochloro- (BCAA) and chlorodifluoro- (CDFAA) degrade by hydrolysis with half-lives (extrapolated) of 6 and 83 years respectively at 15°C. The overall stability of nine haloacetic acids investigated in this study of thermal degradation regardless the process, is in the order: TFAA >> CDFAA > DCAA > DBAA > MCAA > BCAA > MBAA > TCAA > TBAA. We found no catalytic effect of iron, copper and manganese on the rate of decarboxylation in water.

Key words: Trifluoroacetic acid, trichloroacetic acid, decarboxylation, HFC, HCFC, hydrolysis, residence time.

INTRODUCTION

Halogenated acetic acids are widely distributed in the environment and have been detected in air, precipitation, surface water, groundwater and soil. The average measured concentrations of haloacetic acids in environmental reservoirs have been increasing over the last decades (Jordan and Frank, 1999; Wujcik et al., 1999; Berg et al., 2000; Cahill and Seiber, 2000; Martin et al., 2000; Martin

et al.2003; von Sydow et al., 2000; Römpf et al., 2001; Scott et al., 2002; Scott et al., 2005). These haloacetic acids originate from both natural and anthropogenic sources. Naturally occurring organohalogens have been identified as the main precursors of chlorinated and brominated acetic acids in terrestrial and marine environments (Asplund and Grimvall, 1991; Hoekstra and DeLeer, 1995; Hoekstra et al., 1998; Gribble, 1999; Keppler et al., 2000; LTURNUS et al., 2001; LTURNUS et al. 2005). There has been no confirmation of natural sources of trifluoroacetate (TFA) in the environment (Nielsen et

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al., 2001) although previous studies of Jordan and Frank (1999) and von Sydow et al. (2000) did suggest its production. Recent studies by O'Hagan et al. (2002) have shown that fluoroacetate, but not TFA, can be biosynthesised from s-adenosylmethionine in the presence of the enzyme fluorinase from *Streptomyces cattleya*.

Haloacetic acids are produced from volatile short-chain C₂-halocarbons used in anthropogenic activities as solvents, degreasers and dry cleaners agents (Tuazon et al., 1988; Midgley et al., 1995). Other anthropogenic processes which include the disinfection of drinking and swimming pool water, bleaching processes, anti-fouling applications and combustion processes (Plumacher and Schöder, 1994; Juuti et al., 1995; Creed et al., 1997; Chang et al., 2001; Chang et al., 2001; Nissinen et al., 2002) contribute significantly to the presence of chlorinated and brominated acetic acids in the environment. The photochemical transformations of HFC-134a, HCFC-123 and HCFC-124 used in domestic refrigeration, vehicle air conditioning units and foam blowing applications are anthropogenic precursors to fluorinated acetic acids (Wallington et al., 1992; Ravishankara and Lovejoy, 1994; Tromp et al., 1995; Frank et al., 1996). The use of the inhalation anaesthetics halothane and isoflurane (Boutonnet et al., 1999) and the thermolysis of widely used fluoropolymers (Ellis et al., 2001) have also been identified as a potential source of TFAA and CDFAA in the environment.

Haloacetic acids partition into water because of their large Henry's law constants (Bowden et al., 1998). However, the retention of haloacetic acids in soil depends on the chemical properties of the specific acid and the soil type. The adsorption of trifluoroacetic acid for example is favoured by low pH soils that are rich in iron and aluminium oxides (Key et al., 1997; Richey et al., 1997).

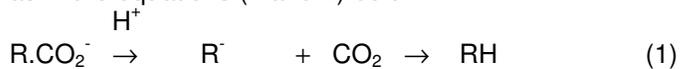
Haloacetic acids are often phytotoxic. Chloroacetates and trifluoroacetate (TFA) have been thought to play a role in forest decline (Frank et al., 1990; Jordan and Frank 1999). Chlorodifluoroacetate (CDFA) is assumed to have the same order of toxicity as TFA (Martin et al., 2000). More importantly, dibromoacetate (DBA) has been found to have direct effect on steroidogenesis and alter ovarian follicular progesterone secretion (Goldman and Murr, 2002). Some haloacetic acids have been reported to have a slight elevated risk on fetal growth (Porter et al., 2005). There is growing concern about the ecotoxicological effects of haloacetic acids, especially the very stable TFA (Lifongo et al., 2004) for which concentrations may exceed threshold limits over time.

Decarboxylation and hydrolysis are likely to be the main abiotic routes for the degradation of haloacetic acids in the environment. This paper reports a laboratory investigation of the thermal rates for these processes and establishes the likely balance of their importance in removing the acids from aqueous systems.

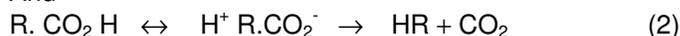
BACKGROUND

Traditional views of decarboxylation

Thermal decarboxylation of trihaloacetic acids occur readily at 100-150°C, either in the acid form as anions or as free acids in their zwitterionic form (Brown et al., 1951) as in the equations (1 and 2) below:



And



Where R = CCl₃; CBr₃; CFCl₂; CF₃

Decarboxylation reactions of haloacetic acids are influenced by the electronegativity of the halide group. This reaction can be regarded as the reverse of the addition of carbanions to carbon dioxide, although free carbanions are not always involved. The heterolytic fission of the carbon-bond in the acids is favoured by the presence of the electron-attracting groups (Auerbach et al., 1950; Brown et al., 1951; Clark, 1959). The kinetics of the decarboxylation reaction has been found to obey a first-order rate law.

Most carboxylic acids can be decarboxylated as the salt or the dissociated acid, but not the undissociated protonated acid although not all can be decarboxylated in water alone (March, 1992). The decarboxylation of trichloroacetate has been extensively studied in ethylene glycol, ethyl alcohol, aromatic amines, glycerol (Vehoeck, 1945; Auerbach et al., 1950; Clark, 1955; Clark, 1959; Clark, 1960) and in the solvent/water mixtures (Corchran and Verhoeck, 1947; Hall and Verhoeck, 1947). Trifluoroacetic acid was found to decarboxylate at temperatures greater than 170°C (Auerbach et al., 1950), but only in a mixture of ethylene glycol and boric acid and there was an indication of a decrease in rate constant with an increase in concentration at 188°C.

The products from the decarboxylation of THAAs are the corresponding trihaloform and carbon dioxide. However, side reactions involving the oxidation of trihaloform followed by hydrolysis would produce acid halides (Verhoeck, 1934; Fairclough, 1938; Johnson and Moelwyn-Hughes, 1940; Clark, 1960). Some of the haloacetic acids and mixed haloacetic acids (chlorodifluoroacetic acid and dichlorofluoroacetic acid) undergo hydrolysis or dehalogenation more readily than decarboxylation (Auerbach et al., 1950).

Hydrolysis of haloacetic acids

The hydrolysis of the haloacetic acids depends on the degree of ionisation of the C-halogen bond (Drushel and Simpson, 1917; Berhenke and Britton, 1933).



During the hydrolysis of monobromoacetic acid, it is mainly the undissociated acid, which partakes in the decomposition process (Senter, 1907a; Senter and Wood, 1915; Cowdrey et al., 1937). The hydrolysis rate constants determined for MCAA at 102°C is $8.0 \times 10^{-6} \text{ s}^{-1}$ and for NaMCA is $2.8 \times 10^{-5} \text{ s}^{-1}$ for a concentration of 0.1 mol dm^{-3} and $6.58 \times 10^{-5} \text{ s}^{-1}$ for 1.0 mol dm^{-3} solution (Senter, 1907a). The formation of glycollic acid (hydroxyacetic acid) during the hydrolysis has been reported to interact with both the bromoacetate and bromoacetic acid thereby, playing a significant role in the liberation of bromide ion (Brooke et al., 1936; Cowdrey et al., 1937). The hydrolysis rate constant for NaMBA at 52°C has been determined as $5.0 \times 10^{-6} \text{ s}^{-1}$ and for MBAA in water at 81°C as $2.5 \times 10^{-5} \text{ s}^{-1}$ (Senter, 1907b; Senter and Wood, 1915). However, Sutherland and Aston (1939) reported that three chlorine atoms would greatly facilitate cleavage of C-C bond and bromine atoms would further increase the rate despite the decrease in electronegativity.

EXPERIMENTAL PROCEDURE

Most of the chemicals used in this study were of high commercially available purity and were used as received. All aqueous solutions were prepared in MilliQ water (Bassett et al., 1978). The method used in this study was similar to that employed by Verhoek (1934) and Johnson and Moelwyn-Hughes (1940) for thermal decarboxylation of tribromo- and trichloroacetic acids. Approximately 250 cm^3 of 0.1 mol dm^{-3} solutions of individual haloacetic acids were prepared and then poured into 500 cm^3 conical flasks, sealed with thin plastic film and placed in a water bath (Grant SE 0 – 80°C) set to specified temperatures in a fume hood. At various time intervals, 10.0 cm^3 aliquots of acid samples were withdrawn from the flask and cooled in ice water before analysis by titration or ion chromatography. For longer term experiments, 600 cm^3 of 0.1 mol dm^{-3} and $0.001 \text{ mol dm}^{-3}$ solutions of CDFAA and TFAA were sealed in borosilicate glass and polypropylene bottles and placed in an oven (Genlab 30 - 250°C) for 7 and 100 days respectively at 90°C. For the degradation of CDFAA, aliquots of acid samples were withdrawn daily and weekly for TFAA.

In addition, metal salts used in the experiments in which potential metal catalysis were employed included cupric sulphate, zinc acetate, manganese (II) chloride tetrahydrate, ammonium ferrous sulphate, sodium metavanadate, sodium molybdate and titanium dioxide. The concentrations of these metal salts varied in the range of 0.001 – 0.02 mol dm^{-3} in a 0.1 mol dm^{-3} solution of trichloroacetic acid. Titanium dioxide was used as a suspension. The kinetic experimental procedure was the same as that of the decarboxylation of pure trichloroacetic acid solutions.

Cooled acid samples were titrated against a 0.1 mol dm^{-3} solution of sodium hydroxide using 0.5 cm^3 of bromocresol green indicator to a blue end-point to determine the amount of the unchanged acid. The sample solutions were further titrated with 0.01 mol dm^{-3} standard solution of silver nitrate using 0.5 cm^3 of potassium chromate as an indicator to a faint reddish-brown end-point to determine the halide ion concentration resulting from hydrolysis. The concentrations of the decomposing acids were obtained from the difference between the concentrations of total acid and halogen ion.

Haloacetate samples were further diluted to concentrations of 10^{-3}

or $10^{-4} \text{ mol dm}^{-3}$, filtered through $0.2 \mu\text{m}$ and analysed by ion chromatograph using Dionex DX-320/DX-600. The instrument was equipped with a GP50 Gradient Pump, EG40 Eluent Generator, ED50 Electrochemical Detector, AS50 Auto sampler and Ion Pac as 16 anion exchange column using potassium hydroxide as eluent. All the analyses were eluted from the column within a period of 30 minutes. The integrated peak area was found to be linear over the concentration range 10 – $1000 \mu\text{mol dm}^{-3}$ with $r^2 \geq 0.999$ for each species present. Calibration equations were used to make corrections for the concentrations of acid samples analysed. The haloacetate and halide ion concentrations were deduced from the peak areas and the equations derived from calibration curves.

RESULTS

The overall results obtained in this study of the thermal degradation of haloacetic acids indicated that decarboxylation process is faster for tri-halogenated acetic acids and hydrolysis predominates as the number of halogen atom decrease to di- and mono- substituted acids. The rate of the decarboxylation process is in the order of trihaloacetic acids > dihaloacetic acids > monohaloacetic acids. Conversely, the rate of hydrolysis is in the order mono > di- > tri-haloacetic acids. The results that support these observations are given below.

Decarboxylation of trihaloacetic acids

These acids decarboxylate as anions when subjected to thermal degradation at high temperatures and follow the first order rate equation:

$$\ln[C]_0/[C]_t = -kt \quad (4)$$

Where C_0 is the initial concentration of the acid, C_t is the concentration at time t and k is the rate constant.

Using the equation stated above, the plots of $\ln[C]_0/[C]_t$ versus time are linear ($r^2 > 0.9$) and the decarboxylation rate constants are deduced from the slope k . This study also confirms that the rates of decarboxylation of tribromoacetic acid and trichloroacetic acid are dependent on temperature and can be described according to the Arrhenius equation:

$$k = A \exp(-E_a/RT) \quad (5)$$

Where k is the decarboxylation rate constant, E_a is the activation energy for the reaction, R is the gas constant, T is the absolute temperature in Kelvin and A is the pre-exponential factor.

A plot of the natural logarithm of the rate constants ($\ln k$) as a function of the reciprocal of absolute temperature ($1/T$) is linear ($r^2 > 0.99$) with slope $-E_a/R$ and intercept $\ln A$. Figures 1 and 2 show that the Arrhenius plots for the

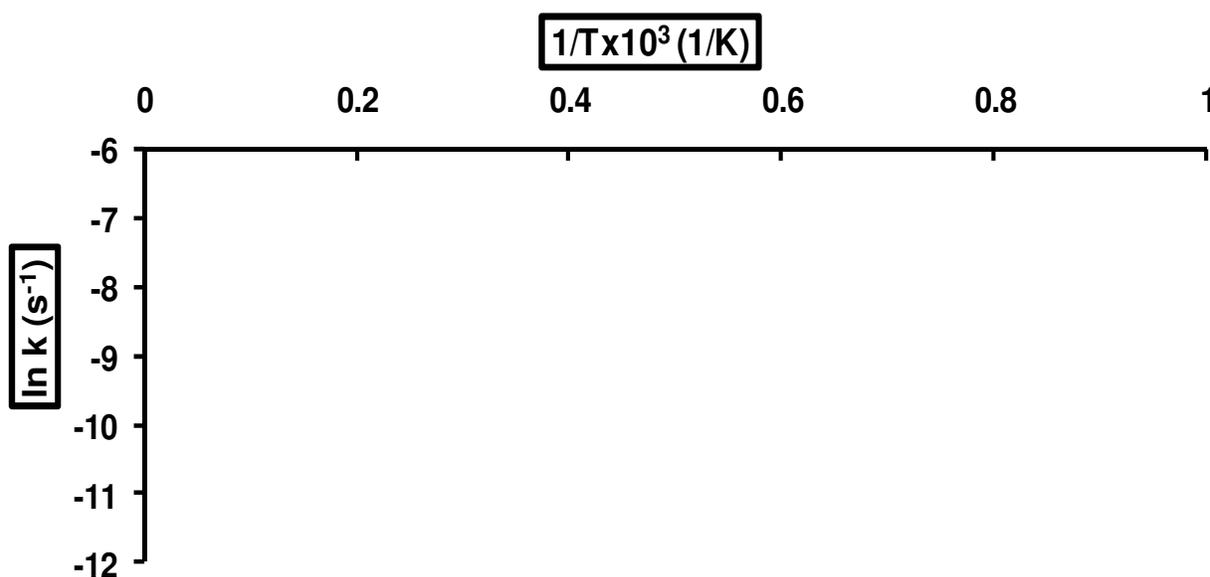


Figure 1. Arrhenius plots for the rate of decarboxylation of tribromoacetic acid in water. Activation energies, E_a in $\text{kJ mol}^{-1} \text{K}^{-1}$: *Triangles and fitted line* - This study TBAA 150.7, *Squares* - TCAA 138.5 (Johnson and Moelwyn-Hughes, 1940), *Diamonds* - NaTBA 102.4 (Fairclough, 1938).

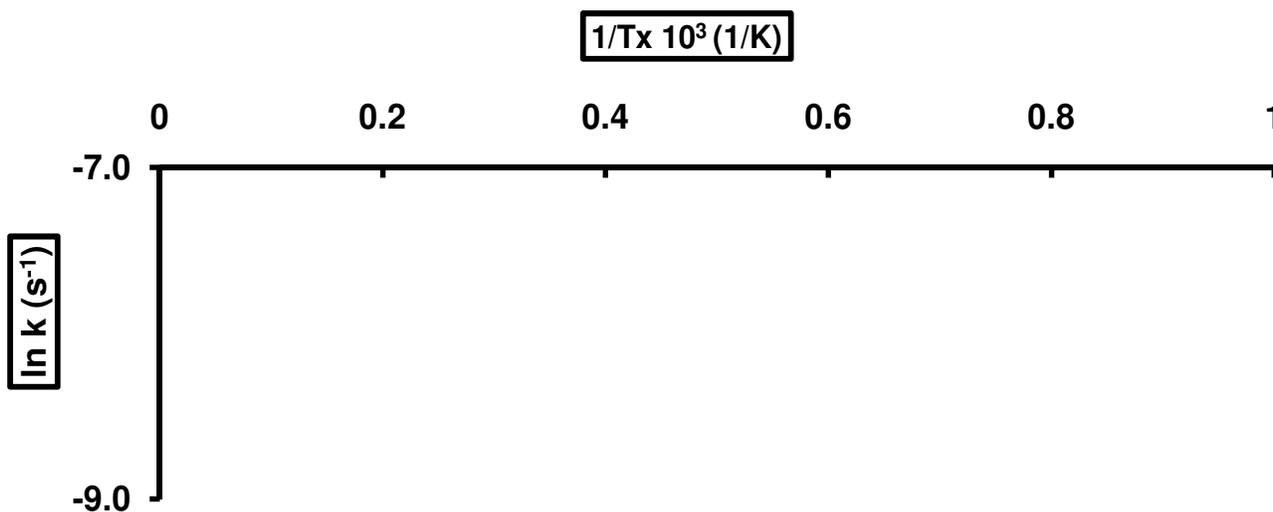


Figure 2. Arrhenius plots for the rate of decarboxylation of trichloroacetic acid. Activation energies, E_a in $\text{kJ mol}^{-1} \text{K}^{-1}$: *Triangles and fitted line* - This study TCAA 150.7, *Squares* - NaTCA 151.7 (Verhoek, 1934), *Diamond* - TCAA 150.9 (Johnson and Moelwyn-Hughes, 1940).

rate constants for tribromo and trichloroacetic acids obtained in this study are in reasonable agreement with those obtained in previous studies. The activation energy for the decarboxylation of tribromoacetic acid deduced from the slope $-E_a/R$ from this study is $139 \text{ kJ mol}^{-1} \text{K}^{-1}$, which is closer to $142 \text{ kJ mol}^{-1} \text{K}^{-1}$ from Johnson and Moelwyn-Hughes (1940) than $102 \text{ kJ mol}^{-1} \text{K}^{-1}$ from Fairclough (1938). The activation energy for the thermal

decarboxylation of trichloroacetic acid from this study is $151 \text{ kJ mol}^{-1} \text{K}^{-1}$ and is close to the $152 \text{ kJ mol}^{-1} \text{K}^{-1}$ of Verhoek (1934).

There is no evidence of decarboxylation of trifluoroacetic acid after 100 days at 90°C . Acid concentration increased slightly but no fluoride ion (evidence of fluoroform oxidation and hydrolysis) was detected either by titrimetric analysis or by ion chromatography. This stability

of TFAA has been attributed to the presence of the CF_3 group. Theoretically, fluorine atoms have strong electronegativity and could form carbanions, but do not have low-energy d-orbitals to accept electron density back from the carbon atom as is the case for tribromo- and trichloro- acetic acids. The strength of the C-C bond in trichloroacetic acid is greater than that in tribromoacetic acid due to the stability of the carbanion. Since the rate of decarboxylation depends on breaking of the C-C bond, hence there is higher activation energy for trichloroacetic acid ($150.7 \text{ kJ mol}^{-1} \text{ K}^{-1}$) compared to tribromoacetic acid ($138.7 \text{ kJ mol}^{-1} \text{ K}^{-1}$).

The present study confirms the rate of decarboxylation of trihaloacetic acid to follow the order $\text{TBA} > \text{TCAA} >> \text{TFAA}$. Decarboxylation reactions of trihaloacetic acids are slow and result in the formation of trihalomethane. A prominent side reaction is the oxidation of these haloforms followed by hydrolysis to produce the appropriate hydrogen halide. Since the thermal decarboxylation process depends on the heterolytic fission of the C-C bond in the trihaloacetic acid molecule, the presence of the electron attracting groups Br and Cl attached to the α -carbon atom weaken the C-C bond thus promoting decarboxylation reactions. Attempts to decarboxylate the mixed trihaloacetic acid, chlorodifluoroacetic acid and also the mono and di haloacetic acids was overwhelmed by the production of halide ions produced via hydrolysis of the haloacetic acid.

Hydrolysis of mono, di- and mixed haloacetic acids

The thermal degradation of haloacetic acids, especially the mono-, di-substituted and the mixed acids can occur through hydrolysis. The rate of hydrolysis depends on the degree of ionisation of the carbon-halogen bond. Nucleophilic attack of the α -carbon atom in an acid molecule by the oxygen atom of a water molecule is responsible for hydrolysis. The hydrolysis of these acids appears to obey the first order rate law, allowing the hydrolysis rate constants for the thermal degradation reactions to be readily determined. The hydrolysis rate constants for the acids examined in this study are listed in Table 1.

Ion chromatograms for the products of monobromo- and monochloroacetic acid hydrolysis indicate a small presence of glycollic acid (hydroxyacetic acid) and halide ions as reaction products although the quantities of glycollic acid produced were not measured quantitatively in this study. The presence of glycollic acid confirms the mechanism earlier established by Senter (1907a, b; 1915) and Dawson and Dyson (1933).

Assuming that the reaction mechanisms for the hydrolysis of dihaloacetic acids are similar to that for the mono haloacetic acids, the reaction products should also be glyoxalic acid and hydrogen halide as in the equation below:



Drushel and Simpson (1917) reported the presence of glyoxalic acid for the hydrolysis of sodium dichloroacetate. In our own experiments, peaks for glyoxalic acid were not observed in the chromatograms. A possible explanation might be that the amount of glyoxalic acid produced is below ($1 \mu\text{M}$) $1 \times 10^{-6} \text{ mol dm}^{-3}$, of the detection limit or not well separated.

Furthermore, the results from the ion chromatography indicate that for the mixed halogenated bromochloroacetic acid (BCAA), more bromide than chloride is released from the BCAA molecule. A comparison of the rate of hydrolysis of the di-substituted haloacetic acids gives the order $\text{BCAA} > \text{DBAA} > \text{DCAA}$. The presence of two halogens Br and/or Cl greatly facilitates cleavage and points to an inductive effect on the C-C bond which increases the rate. In the case for bromochloroacetic acid where a chlorine atom replaces a bromine atom (in comparison to dibromoacetic acid), the rate of hydrolysis increases due to the increased electronegativity of the chlorine atom.

In addition, the rate of hydrolysis of chlorodifluoroacetic acid (CDFAA) is greater than trifluoroacetic acid. These are both trihaloacetic acids and theoretically should undergo decarboxylation, the presence CF_3 (complete fluorine substitution) in TFAA makes it very stable for degradation, while the presence of a Cl atom in the CDFAA molecule promotes hydrolysis of this acid. Interestingly, higher concentrations of fluoride than chloride are detected by ion chromatograph for the hydrolysis of CDFAA even though one would expect the reverse since the chlorine atom is less electronegative than the fluorine atom.

Effect of concentration on the rate of thermal degradation

The rate of thermal degradation does not increase significantly with decreasing concentration of haloacetic acid. The values of the rate constants for decarboxylation and hydrolysis of some haloacetic acids at two different concentrations (Table 2) show a slight increase in rate constants. However, a more detailed investigation of the effect of concentration on the rate of decarboxylation of trichloroacetic acid and its sodium salt (pH ranges of 1.5-4.2 and 3.7- 5.5, respectively) did not show any significant change in rate of decarboxylation over a large range of concentrations (Figure 3).

Effect of metal catalysts on the rate of decarboxylation of trichloroacetic acid

There was no significant increase of the rate of decarbo-

Table 1. The hydrolysis rate constants for mono, di and mixed haloacetic acids.

Acid (0.1 mol dm ⁻³)	Temperature °C	Rate constant (s ⁻¹) titration	Rate constant (s ⁻¹) IC	95 % Confidence limit (titration)
Monobromoacetic acid (MBAA)	65	2.81x10 ⁻⁶	-	± 1.22
	70	-	2.11x10 ⁻⁶	-
	82	-	1.41x10 ⁻⁵	-
	83	2.32x10 ⁻⁵	-	± 0.68
Monochloroacetic acid (MCAA)	82	1.49x10 ⁻⁶	1.15x10 ⁻⁶	± 0.38
Dibromoacetic acid (DBAA)	70	-	3.2x10 ⁻⁷	-
	82	-	1.86x10 ⁻⁶	-
	83	2.96x10 ⁻⁶	-	±0.16
Dichloroacetic acid (DCAA)	70	1.53x10 ⁻⁷	-	± 1.15
	82	4.48x10 ⁻⁷	3.2x10 ⁻⁷	± 1.41
Bromochloroacetic acid (BCAA)	82	3.93x10 ⁻⁶	2.24x10 ⁻⁶	± 1.02
Chlorodifluoroacetic acid (CDFAA)	90	6.12x10 ⁻⁷	5.12x10 ⁻⁷	± 1.15

Table 2. Effect of concentration on the rate degradation (via hydrolysis or decarboxylation) some haloacetic acids.

Acid	Temperature °C	Rate constant (s ⁻¹) 0.1 mol dm ⁻³	Rate constant (s ⁻¹) 0.001 mol dm ⁻³
Monobromoacetic acid MBAA	82	1.41x10 ⁻⁵	2.33x10 ⁻⁵
Dibromoacetic acid DBAA	82	1.86x10 ⁻⁶	4.86x10 ⁻⁶
Chlorodifluoroacetic acid CDFAA	90	5.12x10 ⁻⁷	6.40x10 ⁻⁷

xylation of trichloroacetic acid at 70 and 80°C using individual salts of iron Fe(II), copper Cu(II), manganese Mn(II), molybdenum Mo(VI), titanium Ti(IV), vanadium V(V) and zinc Zn(II) (Figure 4). These results show that these metal ions do not catalyse the degradation reactions. However, slight variations of the rate constant values seem to be attributable to the colour affecting titration end point or the pH of the solutions as the concentrations of the metal catalysts are varied.

Overall observations

The overall stability of the nine haloacetic acids used in this study to thermal degradation (at 50°C) regardless the process (Figure 5) is in this order:

TFAA >> CDFAA > DCAA > DBAA > MCAA > BCAA > MBAA > TCAA > TBAA

For non-fluorine containing haloacetic acids, the di-

substituted haloacetic acid group are most stable. However, TFAA is most stable to degradation compared to the other haloacetic acids. The half-lives deduced from rate constants extrapolated to 15°C, show that tribromoacetic acid is the least stable while trifluoroacetic acid is the most stable of the haloacetic acids with respect to thermal degradation (Table 3).

The half-lives of some haloacetic acids undergoing thermal degradation reactions are comparable to the atmospheric lifetimes of chlorofluorocarbon (CFCs), the well known ozone depleting compounds. Interestingly, these have often been replaced by haloacetic acid precursors. The atmospheric lifetimes of the hydrofluorocarbon compound, HFC-134a and hydrochlorofluorocarbon compounds, HCFC-123 and HCFC-124 introduced as replacement compounds for CFC-12 used in refrigeration and automobile air conditioning systems are 14.6, 1.4 and 5.9 years respectively (Powell, 2002). Although these replacement compounds have short lifetimes relative to CFC-12 (atmospheric lifetime of 102

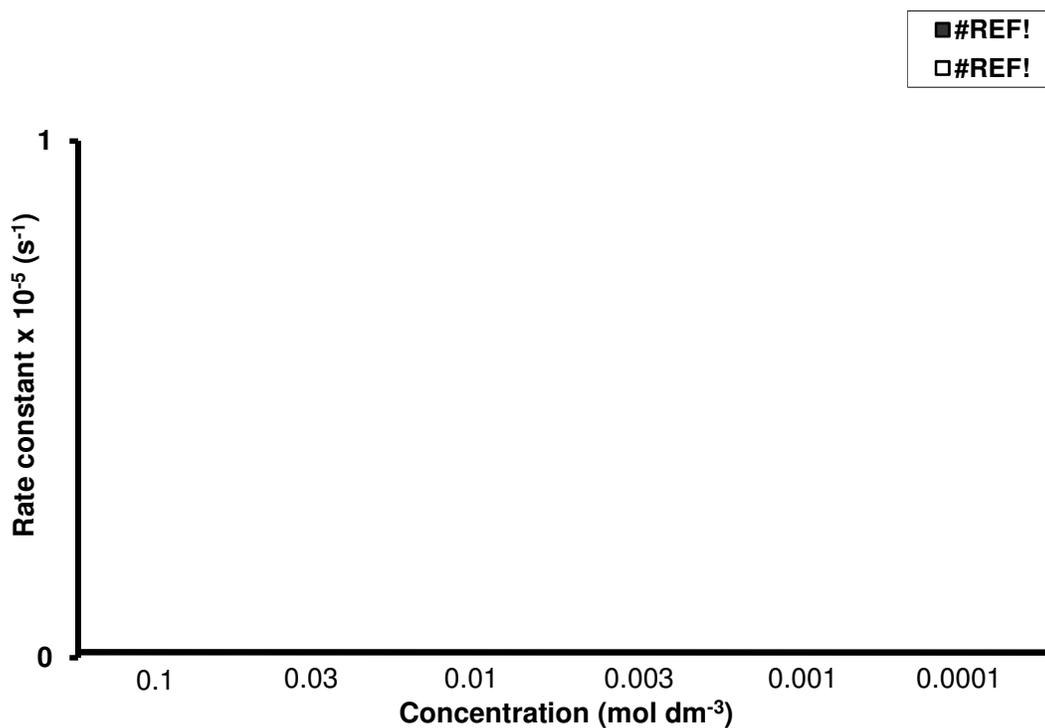


Figure 3. Effect of initial concentration on the rate of decarboxylation of trichloroacetic acid and its sodium salt at 80 °C using IC analysis

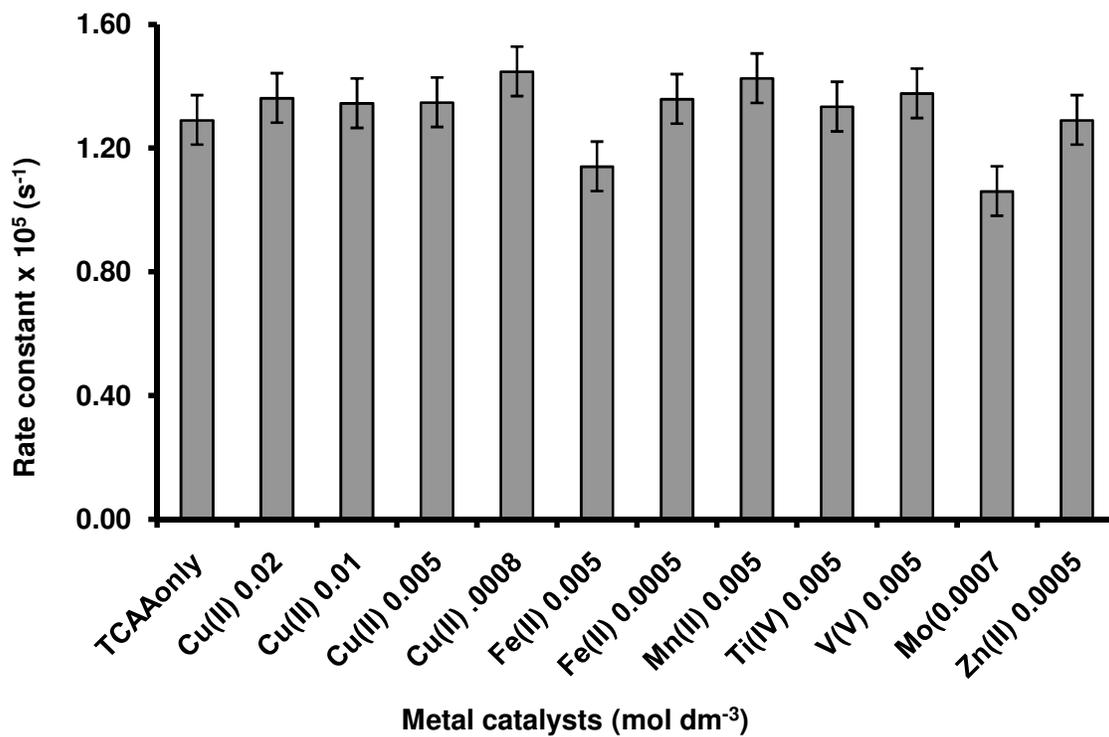


Figure 4. Effect of metal catalysis on the rate of decarboxylation of 0.1 mol dm^{-3} trichloroacetic acid at 71°C using titrimetric analysis.

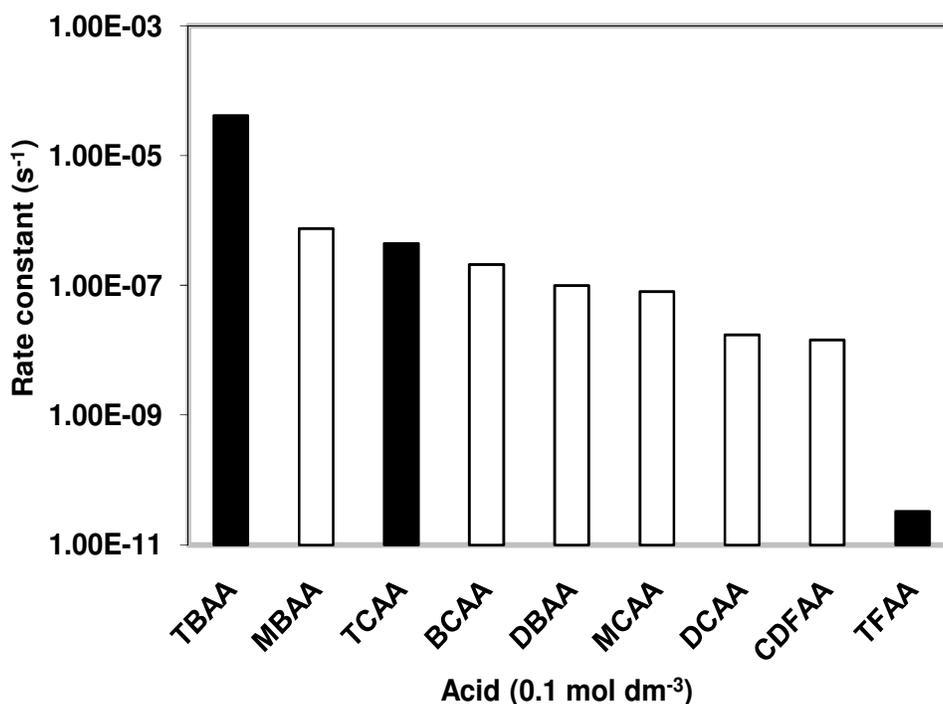


Figure 5. A summary of the thermal degradation of haloacetic acids at 50 °C from this study.

Table 3. Rate constants and half-lives of the haloacetic acids extrapolated to 15 °C from the thermal degradation experiments carried out in this study. Values for TFAA are deduced from an upper limit of $1.16 \times 10^{-9} \text{ s}^{-1}$ at 90 °C.

Acid	Rate Constant (s ⁻¹)	Half-life
TBAA	7.77×10^{-8}	103 days
DBAA	1.86×10^{-9}	12 yrs
MBAA	1.41×10^{-8}	2 yrs
TCAA	4.80×10^{-10}	46 yrs
DCAA	3.23×10^{-10}	68 yrs
MCAA	1.51×10^{-9}	15 yrs
TFAA	2.08×10^{-13}	40000 yrs
BCAA	3.92×10^{-9}	6 yrs
CDFAA	2.66×10^{-10}	83 yrs

years), they are the known precursors for trifluoroacetic acid in the atmospheric environment. The extrapolated thermal degradation half-life of trifluoroacetic in water at 15 °C, determined in this study is 40,000 years which implies it is more stable than CFC-12. Also the extrapolated half-lives from the thermal degradation of trichloro-, dichloro- and chlorodifluoroacetic acids at 15 °C in water of 46, 68 and 83 years respectively (Table 3) are similar to the estimated atmospheric lifetimes of CFC-11 and CFC-113 which are 50 and 85 years respectively (Powell, 2002).

Conclusion

According to the results from these laboratory experiments, most haloacetic acids particularly trifluoroacetic acids have a wide range of lifetimes with regard to thermal degradation. The half-lives of these acids, at ambient temperatures, range from a few days for brominated acids, years for chlorinated acids and thousands of years for trifluoroacetic acid. The rate of the thermal decarboxylation reactions is faster for trihaloacetic acids, while thermal hydrolysis is more important for the mono- and

dihaloacetic acids. Decarboxylation of haloacetic acids is in the order tri > di > mono- substituted acids, while the hydrolysis is in the order mono > di > tri-substituted acids. Decarboxylation reactions are very slow and the resulting products are carbon dioxide and trihalomethane. The reactions are temperature dependent, but there are first order and independent of the initial concentration of the acids.

The major product from hydrolysis of a haloacetic acid is the corresponding hydrogen halide, glycollic and glyoxalic acids which are either inorganic or biodegradable thus less harmful. Both mono- and di-substituted haloacetic acids probably degrade by similar reaction mechanisms. The brominated acids degrade faster than their corresponding chlorinated and fluorinated counterparts. Mixed haloacetic acids more readily undergo hydrolysis than decarboxylation and tend to behave more like the mono-substituted haloacetic acids, that is, the hydrolysis rate constant for bromochloroacetic acid is faster than that for dibromo and dichloroacetic acids and similar to monobromoacetic acid. The degradation of the mixed haloacetic acids cannot readily be predicted based on the nature of halogen atoms on the acid molecules as more bromide than chloride is released and more fluoride than chloride is released from bromochloro and chlorodifluoroacetic acids hydrolysis respectively. The rate of thermal degradation is not affected by the presence of potential trace metal catalysts such as iron, copper, zinc and manganese.

However, since the concept of residence time plays an essential role in the environmental chemistry of pollutants, the bromo-substituted haloacetic acids will not persist in the environment due to their relatively short half-lives. Conversely, the chloro-substituted haloacetic acids will have long-lived relative to their half-lives and TFAA, could accumulate to relatively high concentrations in aqueous reservoirs and would likely accumulate to toxic levels if their removal is solely by the thermal degradation pathway.

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[†] Footnote – HAA, that is, TFAA represents the free haloacetic acid and HA, that is, TFA - trifluoroacetate.

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