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Investigation of the behaviour of haloketones in water samples

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Abstract

The behaviour of the haloketones (HKs) 1,1-Dichloropropanone (1,1-DCP), 1,1,1-Trichloropropanone (1,1,1-TCP) and 1,3-Dichloropropanone (1,3-DCP) in ultrapure water solutions and in fortified drinking water samples was investigated. Their concentrations were determined at regular time intervals by the use of a gas chromatography–electron capture detector (GC–ECD) method. Two different temperatures were studied. The results have shown that HKs decompose both in ultrapure water solutions and in drinking water samples. The decomposition rates are higher in the drinking water samples, especially at higher temperature. 1,1,1-TCP is the compound which decomposes fastest followed by 1,3-DCP and 1,1-DCP. Chloroform was formed both in the ultrapure water solutions and in the drinking water samples, probably due to the decomposition of 1,1,1-TCP. In the drinking water samples, formation of chloral hydrate was also observed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Haloketones; 1,1-dichloropropanone; 1,1,1-trichloropropanone; 1,3-dichloropropanone

1. Introduction

Trihalomethanes were the first class of chlorination by-products to be identified in drinking water (Bellar et al., 1974; Rook, 1974; Golfinopoulos et al., 1998), followed by haloacetic acids (Quimby et al., 1980; Christman et al., 1983; Miller and Uden, 1983; Reckow and Singer, 1984; Krasner et al., 1989) and haloacetonitriles, haloketones (HKs), and chloropicrin at lower concentrations (Trehy and Bieber, 1980; Oliver, 1983; Krasner et al., 1989; Williams et al., 1997; Nikolaou et al., 1999, 2000). HKs belong to the volatile chlorination by-products and have been found to be subject to base-catalyzed hydrolysis and reactions with residual chlorine (Krasner et al., 1989; Singer, 1994). The main HKs identified as chlorination by-products are 1,1-dichloropropanone, 1,1,1-trichloropropanone and 1,3-dichloropropanone (Lekkas, 1996). They have been detected at concentrations an order of magnitude lower than trihalomethanes and haloacetic acids (Nieminski et al., 1993; LeBel et al., 1997; Williams et al., 1998; Simpson and Hayes, 1998) and they have been reported to diminish at high pH, decrease with contact time and further degrade throughout the distribution system (Arora et al., 1997). 1,1,1-trichloropropanone decomposes to form chloroform (Stevens et al., 1989; Koch et al., 1991; Singer, 1994; Chen and Weisel, 1998).

1,1-dichloropropanone and 1,1,1-trichloropropanone have been found to have carcinogenic and mutagenic effects on mice (Bull and Robinson, 1986). The concentration of these compounds in drinking water has not yet been regulated.

In the present paper, the behaviour of HKs in ultrapure water solutions and in fortified drinking water samples is investigated. The kinetics of HKs decomposition and simultaneous chloroform formation are also determined.

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2. Experimental

2.1. Glassware

All glassware used during analysis were prepared as follows: washed with detergent, rinsed with tap water, ultrapure water (Millipore: Milli-Ro 5 plus and Milli Q plus 185), acetone (Mallinckrodt Chemical Works, St. Louis) and placed in an oven at 150°C for 2 h.

2.2. Standard solutions

Stock solutions were prepared in Methyl-tert-butyl-ether (MTBE) (Merck, for organic trace analysis) by the addition of 1,1-dichloropropanone, 1,1,1-trichloropropanone and 1,3-dichloropropanone (Chemservice, purity > 99%). The concentrations of the stock solutions were calculated by the volumetric flask weight change. These stock solutions were used to prepare a solution with the three HKs (100 mg/l) in MTBE, known volumes of which were injected into ultrapure water (Millipore: Milli-Ro 5 plus and Milli Q plus 185) in order to obtain standard solutions with final concentrations 0.25, 1.00, 4.00, 10.00, 25.00, 50.00 and 100.00 μg/l for system calibration. The stock solution of 100 mg/l HKs was also used for preparation of standard solutions 50 μg/l in ultrapure water and in drinking water These solutions were divided and stored in 40 ml glass vials capped with PTFE-faced silica septum (Pierce 13075). The vials were carefully filled just to overflowing without trapping air bubbles in the sealed vial. Two different temperatures were tested: 21°C (ambient) and 30°C (in a water bath).

2.3. Sample preparation

A modification of EPA Method 551.1, which includes liquid–liquid extraction (LLE) with MTBE (EPA, 1998) was performed. 6 g of anhydrous sodium sulfate (Merck) and 2 ml of MTBE were added to 35 ml of HKs solution in a 40-ml vial. The vial was sealed and shaken by hand for 1 min and left undisturbed for 2 min. 1 μl of the ether phase was then injected into the gas chromatograph. Each solution was analyzed every half an hour in order to observe the effect of time on HKs concentrations.

2.4. Apparatus

The instrumentation used included a Hewlett Packard Gas Chromatograph 5890 Series II with a ^{63}Ni Electron Capture Detector and a Hewlett Packard Mass Selective Detector 5971. The system was supported by HP G1034C system software. The carrier gas used was Helium and the make-up gas, nitrogen. The column used for gas chromatography–electron capture detector (GC–ECD) analysis was fused silica DB-1, 30 m × 0.32 mm i.d. × 0.25 μm film thickness. A fused silica capillary HP-VOC column (60 m × 0.32 mm × 1.8 μm) was also used for gas chromatography–mass spectrometer (GC–MS) verification. The injection technique was split/splitless and the carrier gas flow 1.6 ml/min.

Table 1
GC–ECD conditions

Carrier gas flow	1.6 ml/min
Oven temperature	39°C (12 min)
Injector temperature	175°C
Split ratio	1:25
Detector temperature	300°C

Table 2
GC–MS conditions

Carrier gas flow	1.3 ml/min
Oven temperature	35°C (9 min) to 40°C (3 min) at 1°C/min to 148°C at 6°C/min
Injector temperature	175°C
Split ratio	1:25
MS conditions	
Solvent delay	12 min
MS temperature	280°C
EMV	2200
Scan/s	1.9
MS scan programme	35–265

2.5. Analytical conditions

The analytical conditions of the gas chromatograph and the mass spectrometer are presented in Tables 1 and 2.

3. Results and discussion

The recoveries of the GC–ECD method for HKs determination have been estimated at six concentration levels and are given in Table 3.

The recoveries of the method ranged from 66.2% to 121.6%. The lowest value was observed for 1,1,1-TCP at a concentration of 1.0 μg/l. 1,3-DCP was not recovered at concentrations below 1.0 μg/l and the relative SD for this compound was high.

The detection limits were calculated as follows:

$$\mathrm{DL} = t \times S, \tag{1}$$

where DL is the detection limit (μg/l), t the Student's t value for a 99% confidence level and an SD estimate with $n-1$ degrees of freedom ($t = 3747$ when $n = 5$) and S is the SD of the replicate analyses.

Table 3
Mean recovery (%), relative SD (%, in parenthesis) and detection limits (DLs) of HKs at six concentration levels ($n = 5$)

Concentration levels (μg/l)							DL (μg/l)
HKs	0.5	1.0	2.0	5.0	10.0	20.0	
1,1-DCP	120 (2.6)	79 (2.4)	83.7 (5.6)	112.48 (1.7)	107.0 (4.5)	102.54 (6.1)	0.06
1,1,1-TCP	108 (7.29)	66.2 (11.2)	75.8 (5.6)	111.32 (5.3)	111.7 (1.3)	105.49 (4.9)	0.15
1,3-DCP	[a]	121.6 (35.1)	100.7 (13.0)	98.4 (15.8)	88.0 (20.9)	97.35 (3.2)	0.98

[a] Not recovered.

The concentrations of HKs versus time in a fortified water sample at 21°C, in a fortified water sample at 30°C and in an ultrapure water solution at 30°C are plotted in Figs. 1(a)–(c), respectively.

The rate of the decomposition was determined for each compound by the use of linear regression after the concentration values were ln-transformed. The logarithms of the concentration values plotted versus time give a linear curve, the slope of which represents the rate k of the reaction. Representative $\ln C$–t plots are presented in Figs. 2(a)–(c) for HKs concentrations in a fortified drinking water sample at 21°C. The decomposition rates are presented in Table 4, while the linear regression equations that best describe the reactions in each case and the corresponding confidence intervals are shown in Table 5.

The fact that the zero value is not included in the estimated confidence intervals for k at 95% confidence

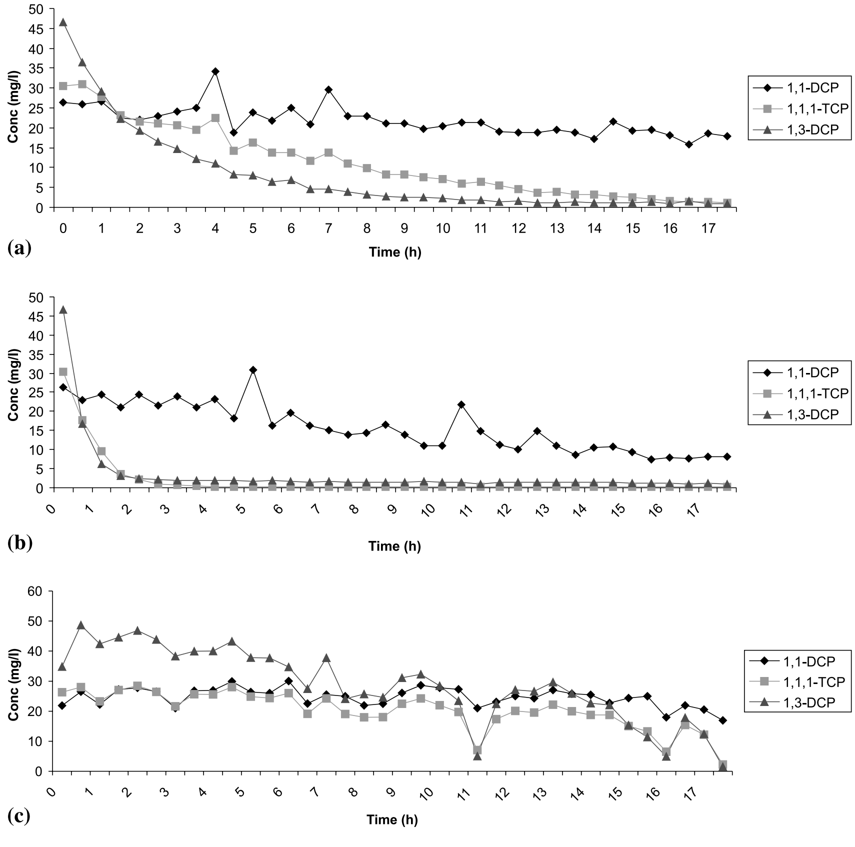

Fig. 1. Decomposition of HKs in: (a) fortified water sample at 21°C; (b) fortified water sample at 30°C; (c) ultrapure water solution at 30°C.

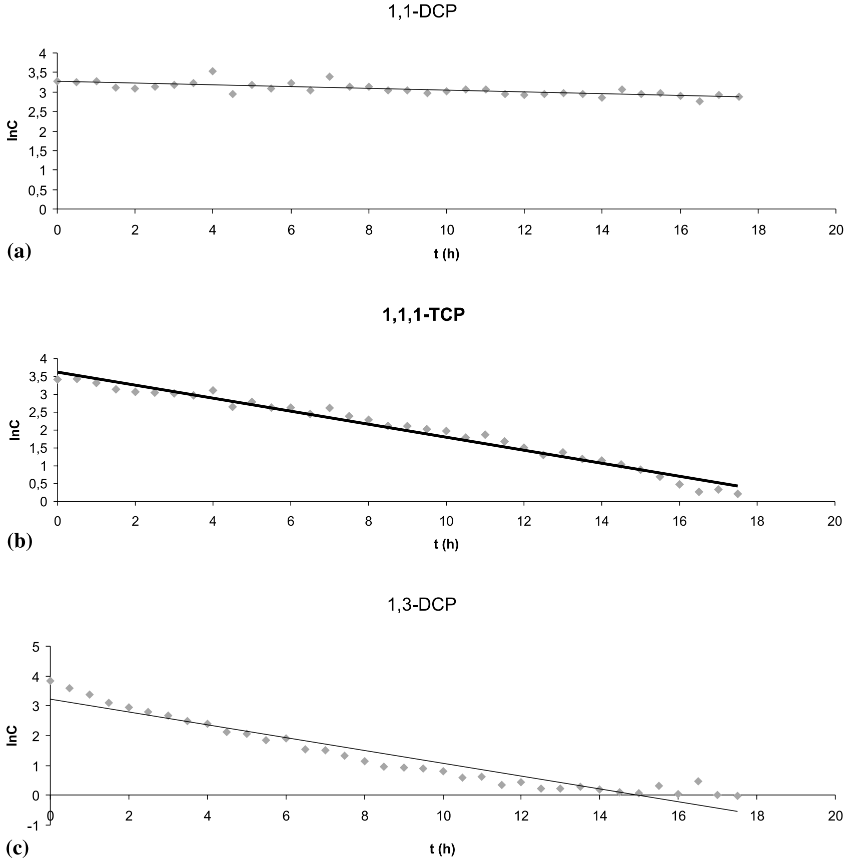

Fig. 2. Decomposition of HKs in fortified drinking water at 21°C.

Table 4
Decomposition rates of HKs

	Water sample		Ultrapure water, 30°C
	21°C	30°C	
1,1-DCP	0.022	0.071	0.010
1,1,1-TCP	0.182	1.393	0.062
1,3-DCP	0.220	0.099	0.098

level statistically confirms that the concentrations of HKs are dependent on time.

In ultrapure water solutions at 30°C and in fortified drinking water samples at 21°C, the compound which decomposes fastest is 1,3-DCP, followed by 1,1,1-TCP and 1,1-DCP. However, in fortified water samples at 30°C the highest decomposition rate is that of 1,1,1-TCP followed by the rates of 1,3-DCP and 1,1-DCP decomposition. The three HKs studied have higher decomposition rates in fortified drinking water samples than in ultrapure water solutions. 1,1-DCP and 1,1,1-TCP decompose faster at 30°C than at 21°C. On the contrary, 1,3-DCP shows a higher decomposition rate in fortified drinking water sample at 21°C.

Chloroform formation was observed during the decomposition of HKs, as is presented in Fig. 3 for a fortified drinking water sample at 21°C. The kinetic equations describing chloroform formation have been estimated using the procedure described above for HKs and are shown in Table 6.

Chloroform is formed faster in ultrapure water solutions than in drinking water samples. This fact indicates that HKs decomposition in drinking water may lead to other products as well in addition to chloroform. A faster chloroform formation rate in drinking water sample was observed at 21°C than at 30°C.

Chloral hydrate formation was also observed in fortified water samples only. Chloral hydrate concentration versus time in a fortified drinking water sample at 21°C is plotted in Fig. 4.

The formation of chloral hydrate only in fortified drinking water samples and not in ultrapure water solutions suggests that chloral hydrate is not produced directly from the decomposition of HKs but can be

Table 5
Equations describing the decomposition of HKs ($\ln C = \ln C_0 - kt$)

	Equation	n	$tn - 2; a/2$	Confidence interval for $\ln C_0$	Confidence interval for k	Confidence level (%)
Fortified water sample, 21°C						
1,1-DCP	$\ln C = 3.264 - 0.022t$	36	1.645	(3.235–3.293)	(0.021–0.023)	95
1,1,1-TCP	$\ln C = 3.621 - 0.182t$	36	1.645	(3.580–3.662)	(0.181–0.183)	95
1,3-DCP	$\ln C = 3.248 - 0.220t$	35	1.645	(3.156–3.340)	(0.218–0.222)	95
Fortified water sample, 30°C						
1,1-DCP	$\ln C = 3.299 - 0.071t$	36	1.645	(3.252–3.346)	(0.070–0.072)	95
1,1,1-TCP	$\ln C = 3.499 - 1.393t$	6	1.943	(3.406–3.592)	(1.366–1.420)	95
1,3-DCP	$\ln C = 1.490 - 0.099t$	35	1.645	(1.333–1.647)	(0.096–0.102)	95
Ultrapure water solution, 30°C						
1,1-DCP	$\ln C = 3.286 - 0.010t$	36	1.645	(3.253–3.319)	(0.009–0.011)	95
1,1,1-TCP	$\ln C = 3.469 - 0.062t$	36	1.645	(3.365–3.573)	(0.060–0.064)	95
1,3-DCP	$\ln C = 4.049 - 0.098t$	36	1.645	(3.910–4.188)	(0.096–0.100)	95

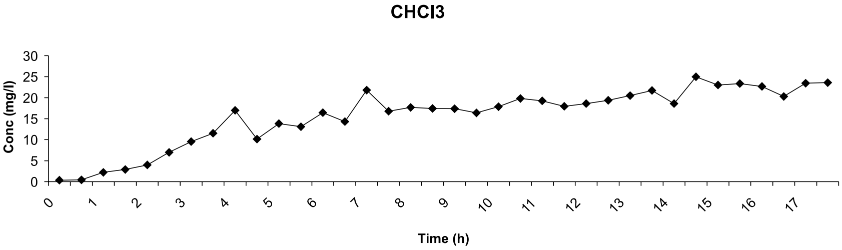

Fig. 3. Formation of chloroform in a water sample fortified with HKs at 21°C.

Table 6
Equations describing the formation of chloroform ($\ln C = \ln C_0 + kt$)

	Equation	n	$tn - 2; a/2$	Confidence interval for $\ln C_0$	Confidence interval for k	Confidence level (%)
Fortified water sample, 21°C						
$CHCl_3$	$\ln C = 1.846 + 0.092t$	34	1.645	(1.740–1.952)	(0.090–0.094)	95
Fortified water sample, 30°C						
$CHCl_3$	$\ln C = 2.942 + 0.009t$	35	1.645	(2.875–3.009)	(0.008–0.010)	95
Ultrapure water solution, 30°C						
$CHCl_3$	$\ln C = 0.123 + 0.134t$	29	1.703	(0.009–0.237)	(0.132–0.136)	95

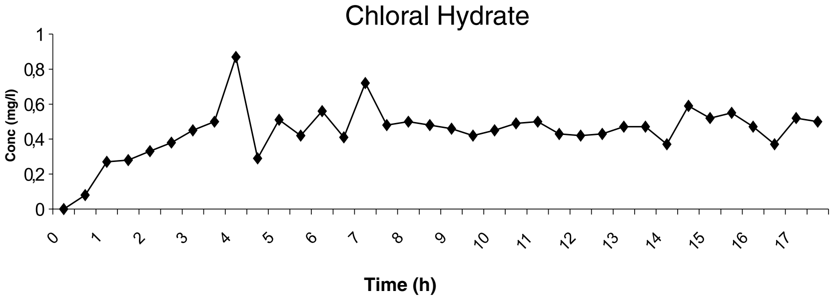

Fig. 4. Chloral hydrate formation in a fortified water sample at 21°C.

formed through another pathway when natural organic matter is present.

4. Conclusions

The behaviour of the HKs 1,1-DCP, 1,1,1-TCP and 1,3-DCP in ultrapure water solutions and fortified drinking water samples was investigated at two different temperatures. The reaction kinetics of HKs decomposition and simultaneous chloroform formation were determined in each case. The results have shown that the decomposition rates of HKs are higher in fortified water samples than in ultrapure water solutions. In ultrapure water solutions at 30°C and in fortified drinking water samples at 21°C, the highest decomposition rate is that of 1,3-DCP, followed by 1,1,1-TCP and 1,1-DCP. However, in fortified water samples at 30°C 1,1,1-TCP decomposes faster than 1,3-DCP and 1,1-DCP. While the rates of 1,1-DCP and 1,1,1-TCP decomposition are higher at 30°C than at 21°C, the rate of 1,3-DCP decomposition is higher at 21°C. Chloroform formation is faster at 21°C than at 30°C and faster in ultrapure water solutions than in drinking water samples. The latter indicates that HKs decomposition in drinking water may lead to other products as well in addition to chloroform. Chloral hydrate formation was also observed only in fortified water samples and not in ultrapure water solutions, which suggests that chloral hydrate is not produced directly from the decomposition of HKs but can be formed through another pathway in the presence of natural organic matter.

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