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FORMATION OF COMPLEX ORGANOCHLORINE SPECIES IN WATER DUE TO CAVITATION

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ABSTRACT

Sonication at 900 kHz was carried out on aqueous solutions of chloroform in the concentration range 25 to 500 mg/L. The formation of chlorinated hydrocarbons was detected by means of GC/MS analyses. For instance, carbon tetrachloride, chlorinated ethanes, and chlorinated ethenes were formed after 10 min of sonication. The greatest concentration of any product was 6 mg/L. Sonication of aqueous chloroform with phenol present produced chlorophenols, and with benzene present produced phenol, chlorobenzene and chlorophenols. These results are significant for the evaluation of sonication as a method of eliminating chlorinated organic compounds from water. They also have significance in supporting the notion that some complex organochlorines may be formed naturally in the environment. Some chloroform and methyl chloride are produced in nature and could react with other organic compounds to form more complex organochlorines through natural processes which have an action similar to cavitation, e.g. waterfalls and breaking waves.

INTRODUCTION

Sonochemical reactions of aqueous solutions of organochlorine compounds (OCs) received intensive study in the 1950s (1). Lately, there has been renewed interest in such reactions, partly motivated by attempts to remove OCs and other pollutants from water supplies (2-4). When sonication is used for this purpose, it is of importance to ensure that sonication of organochlorines in water does not result in species which may be even more toxic than the initial pollutants. For example, sonication of aqueous chlorobenzene solutions results in the formation of traces of chlorinated biphenyls (5), some of which have the potential to cause harmful biological effects (6).

The presence of chloroform and other OCs in drinking water is of some concern because of their potential impact on human health (7). A thorough sonochemical study of neat chloroform was reported in 1984 (8). Traces of more complex OCs such as hexachloroethane were detected after sonication. To improve understanding of the fate of OCs, sonication was carried out of aqueous solutions of chloroform alone, as well as with phenol and benzene present.

The results are of relevance in assessing the ultility of sonication in removing OCs from water. They are, however, also of interest in determining the origins of OCs in nature. Chloroform is produced naturally (9), and natural phenomena such as waterfalls and breaking waves produce effects similar to cavitation (10), which also occurs in sonication of water. The chemical effects of cavitation often resemble "accelerated aging". Alcoholic liquors can be artificially aged by cavitation caused by rotating vanes (11), and sonication of diesel fuels results in the formation of products similar to the gums formed during long-term storage (12). Thus, it is possible that some more complex OCs are formed by reactions of naturally formed compounds such as chloroform and methyl chloride in cavitation-like natural phenonmena.

This paper reports an investigation of the effect of sonication of water containing selected organic compounds. The formation of organochlorine reaction products was monitored in sonicated aqueous solutions of chloroform, and chloroform together with benzene or phenol. A determination was also made of the effects on the formation of reaction products of the initial chloroform concentration and the duration of sonication.

EXPERIMENTAL

Reagents

Aqueous solutions of known composition were prepared by spiking deionized water with the appropriate chemicals: chloroform (Caledon Laboratories Ltd. Ont., Canada, spectro grade), phenol (J.T. Baker, Baker analyzed reagent), and benzene (Fisher Scientific Co., ACS).

Three stock standard solutions were prepared in methyl-*t*-butyl ether (MTBE) (Fisher Scientific, Ont., Canada, HPLC grade) for analytical purposes. The first solution contained chloroform, trichloroethene (Fisher Scientific Co., ACS), carbon tetrachloride (J.T. Baker, Baker analyzed reagent), tetrachloroethene (Fisher Scientific Co., ACS), pentachloroethane, 1,1,2,2-tetrachloroethane, hexachloroethane, 1,1,2,3,4,4-hexachloro-1,3-butadiene (all from Aldrich Chemical Co., all 98+%) to give 74 mg/L of hexachloroethane and 500 mg/L of the rest of the compounds.

A second MTBE stock solution was prepared to contain 628 mg/L of 2-chlorophenol (Supelco Inc., phenol kit 4-4570, 98+%) and 780 mg/L of 4-chlorophenol (Aldrich Chemical Co., 99+%). The third stock solution in MTBE contained 691 mg/L of phenol, 498 mg/L of chlorobenzene (Fisher Scientific Co., ACS) and 500 mg/L of benzene.

The standard solutions used to calibrate the GC-MSD response were prepared by diluting measured aliquots of the stock solutions with MTBE. The nominal concentrations of individual compounds in the series of composite solutions were 0 (blank), 0.5, 1, 5, 10, 25 and 50 mg/L, except for compounds occurring in the stock solution at a concentration other than 500 mg/L. For extraction recovery tests, a standard solution in acetone (Caledon Laboratories, HPLC grade) was prepared to contain 500 mg/L of each of trichloroethene, carbon tetrachloride, chloroform, tetrachloroethene, pentachloroethane, 1,1,2,2-tetrachloroethane, and 1,1,2,3,4,4-hexachloro-1,3-butadiene, and 97 mg/L of hexachloroethane.

Sonication

The 900 kHz apparatus, consisting of a temperature control bath, a holder device and a power amplifier, is described elsewhere in detail (13,14). The glass bath is cylindrical with double walls; a transducer, covered by protective resin (RTV 11 white), is mounted at the bottom of the bath. As some chemicals may affect the resin, the sonication takes place indirectly. One hundred mL of water is placed into the bath as an acoustically conducting medium. The water was kept at constant temperature (3 ± 1 °C) by passing aqueous ethylene glycol solution between the double walls.

A 125 mL Erlenmeyer flask with a flat bottom was used as the reaction vessel. The flask was mounted inside the bath by the aid of the holder device to ensure a reproducible geometry (14). The acoustic power transmitted into the flask was 20 watts, as measured by the rate of decomposition of carbon tetrachloride in an aqueous solution (14). Fifty mL of sample was transferred into the flask, which was immediately sealed with a cork wrapped with fresh aluminum foil. The contents of the flask was exposed to ultrasound for the desired duration, i.e., 10, 30, 60 or 120 minutes.

Separate experiments were performed under the following conditions:

(a) Aqueous chloroform solutions (500 mg/L and 100 mg/L), sonicated for 10, 30, 60 and 120 min.

(b) Aqueous chloroform solutions (100, 200, 300, 400 and 500 mg/L) sonicated for 30 min.

(c) Aqueous solutions containing phenol (500 mg/L) and chloroform (500 mg/L) together, sonicated for 10 and 30 min.

(d) An aqueous solution of phenol (500 mg/L) and chloroform (100 mg/L), sonicated for 30 min.

(e) An aqueous solution of 500 mg/L of benzene, sonicated for 30 min.

(f) An aqueous solution of benzene (500 mg/L) and chloroform (500 mg/L), sonicated for 30 min.

After sonication, the contents of the reaction flask was transferred into a 125 mL separatory funnel. The flask was rinsed with one mL of MTBE which then was added to the separatory funnel. Also, 10 mL of MTBE was added to the funnel, which was then stoppered and shaken for 5 min. The liquid phase was allowed to separate for 5 min before the organic phase was collected into a preweighed vial, which was then weighed to determine the amount of MTBE recovered. A one mL aliquot of the extract was transferred to a 1.5 mL glass vial for analysis by GC-MSD.

For sonication experiments (c) to (f), the samples in the funnel were acidified with H_2SO_4 to pH 2 prior to extraction. This procedure of rinsing the flask with MTBE fails to completely recover all the phenolic products remaining in the reaction vessel. Mutual miscibility between water and MTBE was observed by measuring the amount of MTBE recovered into the preweighed vial. It was estimated that about 25 % of the MTBE remained in the aqueous phase. This is consistent with the published solubility value (15) for MTBE in water (4.8 g/100 g). Although it is likely that some water also was dissolved in the MTBE extract (solubility, 1.5 g/100 g MTBE)(15), this had no noticeable effect on the GC-MSD analyses.

To determine the reliability of the results of the above experiments, additional tests were done as follows:

(a) Fifty mL of deionized water was extracted with MTBE.

(b) Fifty mL of deionized water was sonicated for 10 or 30 min and extracted with MTBE.

(c) Fifty mL of deionized water was spiked with 0.100 mL of the standard solution in acetone. The solution was allowed to equilibrate for 5 min, and then extracted with MTBE. This was done in order to make an estimate of extraction recoveries.

For the additional tests, all MTBE extractions were done using 11 mL MTBE in a separatory funnel; the extracts were analyzed by GC-MSD, as for the sonication experiments.

Analysis

Aliquots (one μL setting) of extracts and standard solutions were automatically injected (splitless; solvent delay 4 min; injection port purge after 1 min) by means of a Hewlett-Packard (HP) autoinjector (model 7673) into a gas chromatograph (GC; HP 5890, series II)-mass selective detector (MSD; HP 5972) equipped with a J&W DB-624 capillary column (length 60 m, i.d. 0.32 mm, film thickness 1.8 μm; Chromatographic Specialties, Brockville, Ont.). The GC oven temperature program was: held at 40 °C for 4 min after injection, then increased to 220 °C at 10 °C/min, then to 250

°C at 20 °C/min, then held for 6 min. The total analysis time was 29.50 min.

To identify sonication reaction products, the MSD was operated in the scan mode (50 - 550 amu). The mass spectra of sample chromatogram peaks were compared with spectra in the HP Mass Spectral Database (NIST/EPA/NIH, 75 K), and the reaction products were considered tentatively identified if the match quality was better than 80 %. To confirm the identity of products listed in Table 1, a standard solution containing these compounds at 50 mg/L was analyzed, and the mass spectra for the appropriate peaks at the same retention time in the chromatogram were compared with those from extract analyses, as well as those obtained in the mass spectral library search.

Table 1. List of compounds quantified by GC/MSD. Retentition times, quantification (Q) and confirmation (C) ions.

RT (min)	Compound	Q	C1	C2	C3
11.4	Chloroform	83	85	87	
12.0	Carbon Tetrachloride	117	119	121	
12.3	Benzene	78	51	77	
13.2	Trichloroethene	130	132	95	
15.8	Tetrachloroethene	166	164	129	
17.1	Chlorobenzene	112	114	77	
18.8	1,1,2,2-Tetrachloroethane	83	85	95	168
19.9	Pentachloroethane	167	117	119	
20.7	2-Chlorophenol	128	130	64	63
20.9	Phenol	94	66	65	
21.6	Hexachloroethane	201	117	119	
23.6	Hexachlorobutadiene	225	227	223	190
24.9	4-Chlorophenol	128	130	65	63

To quantify the reaction products, and to further confirm their identity, the MSD was operated in the selected ion monitoring (SIM) mode for reanalyses of extracts and standard solutions. The occurrence of one quantification (Q) and at least two confirmation (C) ions were monitored for each target compound (Table 1). A retention time window of ± 0.1 min, and a tolerance of ± three standard deviations about the mean values for the abundance ratios of Q and C ions were the confirmation criteria. The standard deviation was calculated from results of analyses of replicate standard solutions (n=3).

The external standard method based on the analytical results for the series of standard solutions of concentrations ranging up to 50 ng/μL was used to determine the concentrations of the quantification ions in the extracts. The internal standard method was not used since the products formed in the sonolysis were unknown, and as internal standards may contribute to interferences in such complex samples.

RESULTS AND DISCUSSION

Analysis

Detection limits for the compounds listed in Table 1 were typically ca. 10 pg injected for GC-MSD-SIM analyses. Thus, reaction products occurring at concentrations above ca. 10 pg/μL in MTBE could be detected and identified. The detection limits for scan analyses were estimated to be ca. 1 ng/μL of analytes in MTBE. These were determined by noting the lowest concentrations of standard solutions which gave a response at least three times the noise level.

Based on the results of MTBE extraction of standards in water (1 mg/L), the extraction efficiency for all seven test compounds was better than 70 %. The recovery values were used to calculate the actual amounts of the seven analytes recovered in the sonication tests. For the remaining six compounds, 70 % recovery was assumed. If we assume that only 50 % of the analyte in the aqueous phase was recovered by the MTBE extract, then it was possible to detect analytes occurring at ca. 5 μg/L in the aqueous reaction mixture in the SIM mode, and 0.5 mg/L in the scan mode.

The identity of reaction products was carefully confirmed, first by use of the HP Mass Spectral Database (NIST/EPA/NIH, 75 K), and then by comparison of analytical results for extracts with those for standard solutions. Due to the unavailability of appropriate standards, the occurrence of pentacyclopropane and pentachloro-1-propene was only determined by use of the mass spectral library; no quantitative data are available for these compounds. Although no target compounds were detected in extracts of deionized water, the occurrence of chlorobenzene, chlorophenols, phenol and benzene was not monitored.

Low concentrations of some analytes were however detected by GC-MSD-SIM analysis in extracts of deionized water which had been sonicated for 30 min. Levels of hexachlorobutadiene, phenol and benzene, respectively, were calculated to be 0.01, 1.4 and 0.1 mg/L in the sonicated water. This suggests that the hexachlorobutadiene may be a contaminant in the system rather than a compound formed from the sonication of aqueous chloroform solutions.

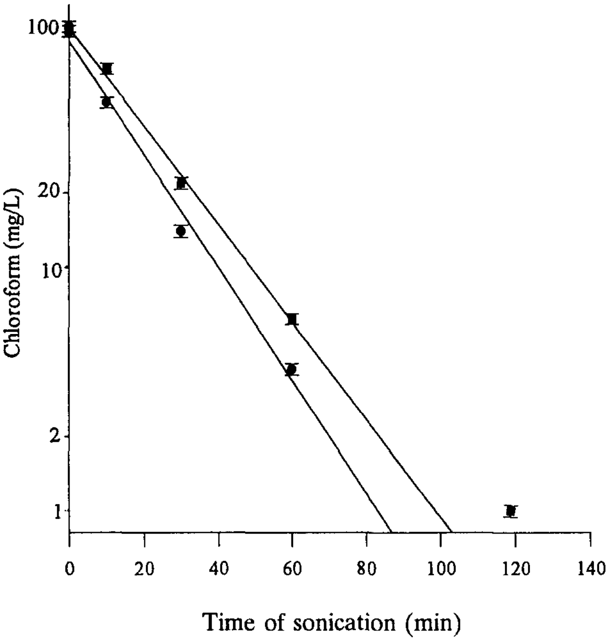
Effect of time of sonication

Experiments were performed in order to obtain the amount of products formed as a function of time of sonication. Solutions with 100 mg/L of chloroform were sonicated for 0, 10, 30, 60 and 120 min. This was done twice in order to test the reproducibility of the results.

Figure 1 shows the logarithm of amount of chloroform remaining in solution after sonication for the two separate experiments with 100 mg/L chloroform at time 0. Each of the two sets of data gives a linear correlation ($r^2 > 0.99$) from 0 to 60 min of sonication. The slopes of the two lines are -0.054 and -0.045, i.e. they agree to within 20%. However, the values at 120 min were not used in this linear regression analysis. The difference in the two slopes is likely to be due to the difficulty in accurately controlling the ultrasonic power from one experiment to another.

These results suggest first order kinetics for the sonochemical reaction of chloroform in water. The rate constant would be expected to be dependent on parameters such as bulk temperature and ultrasound intensity and frequency. Variations in the rate constant were not investigated in these experiments.

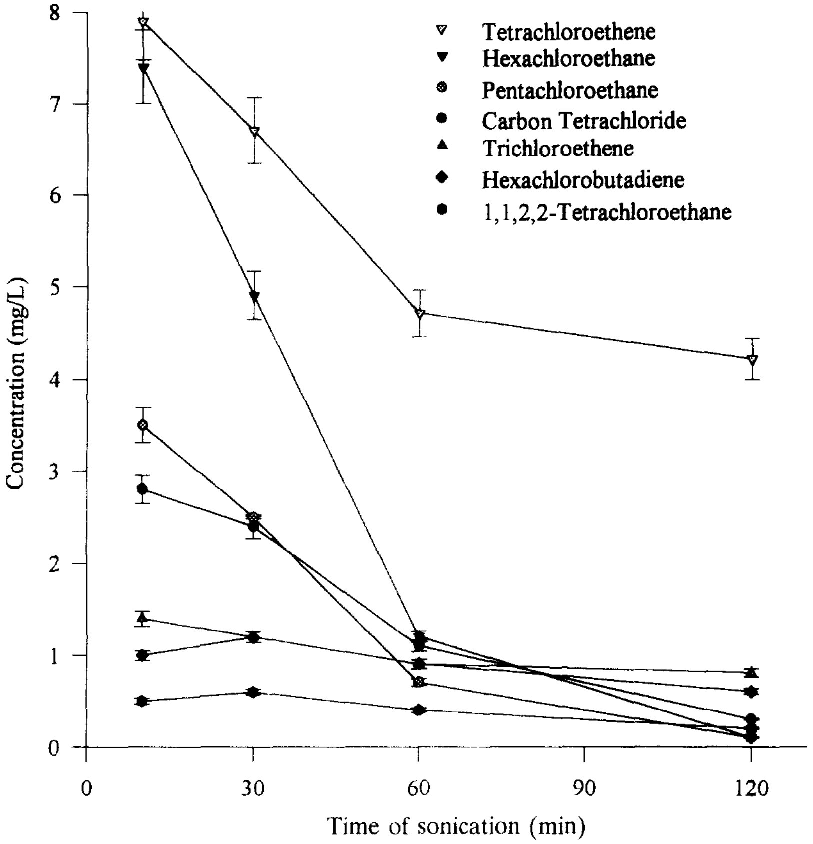
Figure 1. Plot of the logarithm of the concentration of chloroform present as a function of time of sonication. The estimated uncertainty in the analysis is shown.



Solutions with 500 mg/L were sonicated for 0, 10, 30, 60 and 120 min. The chloroform concentration also decreased exponentially with time in this case. The correlation coefficient was 0.997, and the slope -0.055, in good agreement with the 100 mg/L experiments shown in Figure 1.

The concentrations of the products formed are shown in Figure 2. The organochlorines observed are essentially the same as those observed in the sonication of neat chloroform (8). In those experiments, carbon tetrachloride, tetrachloroethene and pentachloroethane were the three main OCs found after 1.5 hr of sonication with 300 kHz ultrasound. The concentrations of hexachlorobutadiene detected for aqueous chloroform (0.6 - 1.2 mg/L, Figure 2) were well above the levels found after sonication of deionized water (0.01 mg/L). No C_4 compounds were reported in neat chloroform (8).

Figure 2. Products formed after sonication of chloroform solutions (500 mg/L) as a function of time of sonication.



As seen in Figure 2, the amount of products detected decreased with time after 10 min. Tetrachloroethene and hexachloroethane were the major products after 10 min in the 500 mg/L solution; tetrachloroethene persisted for the longest time. In experiments with 100 mg/L chloroform solutions, tetrachloroethane was the most persistent OC.

It is not surprising that tetrachloroethane is a major product. The C-Cl bond has the smallest bond energy, approximately 330 kJ/mol, as compared to 410 kJ/mol for the C-H bond and 470 kJ/mol for O-H (16). The C-Cl bond of chloroform would be expected to be the most likely to rupture in the "hot spots" caused by cavitation, forming $CHCl_2$ radicals. These can then combine to form tetrachloroethane.

The temperature of the "hot spots" has been estimated to be of the order of 5200 K (17). At such high temperatures, there is also a significant chance of the breaking of C-H in chloroform and O-H bonds in water. Carbon tetrachloride can thus be formed by the cleavage of the C-H bond in chloroform, with subsequent attack by a Cl atom.

It is possible to have some control over the effective temperature reached in the "hot spots". The presence of gas bubbles can moderate the temperature and lead to cleavage of only the weakest bonds, as in the case of initiating polymerization (18); the nature of the gas present is of importance (8, 19). The presence of a liquid solute which is more volatile than the solvent can also reduce the rate of sonochemical reaction (19).

The types of reactions observed in the aqueous chloroform system have some similarity to those observed in sonication of water with ethyne present (20); the solute in that case was a gas rather than a liquid. In the sonication of water with ethyne, the products detected were similar to those found in flames and shock tubes, including aromatic compounds and even soot particles (20). In sonication of aqueous chloroform, the major initial reaction is likely to be cleavage of the C-Cl and C-H bonds in chloroform. In sonication of aqueous ethyne, it is suggested (20) that the decomposition of water to form H and OH is the primary reaction. It is possible that compounds formed through the attack of OH are also significant in sonicated aqueous chloroform, but that they are not detected through an analytical method using MTBE for extraction.

Effect of the initial chloroform concentration.

In order to obtain the effect of the initial chloroform concentration in the production of OCs, solutions containing, 100, 200, 300, 400 and 500 mg/L of chloroform were sonicated for 30 min. As seen in Table 2, over 18 % of the initial chloroform remained in all cases after this time. A solution with 25 mg/L chloroform was also sonicated for 30 min; any OCs produced were in concentrations below the detection limit of the analytical method.

As seen in Table 2, the effect of the initial concentration of chloroform in the formation of carbon tetrachloride approximately follows a linear response from 100 to 500 mg/L. At the lowest initial concentration, carbon tetrachloride was the most abundant product. However, as the initial chloroform concentration increased, compounds such as tetrachloroethene and hexachloroethane become more abundant than carbon tetrachloride. It might be expected that more complex OC products are formed at higher chloroform concentrations, as the collapsing cavities, the "hot spots", would contain more chloroform molecules and more radicals formed from the thermal decomposition of chloroform. There would thus be more likelihood of bimolecular reactions between chloroform and various chlorinated methyl and methylene radicals.

Table 2. Effect of initial chloroform concentration on levels (mg/L) of organochlorine compounds present after 30 min sonication. ND, not detected.

RT (min)	Compound	Initial chloroform concentration (mg/L)				
		100	200	300	400	500
11.4	Chloroform	40	37	77	71	114
12.0	Carbon Tetrachloride	0.2	0.5	1.6	1.8	3.3
13.2	Trichloroethene	ND	0.1	0.3	0.5	1.2
15.8	Tetrachloroethene	0.1	0.5	2.0	3.0	8.0
18.6	1,1,2,2-Tetrachloroethane	0.06	0.08	0.2	0.3	0.6
19.9	Pentachloroethane	ND	0.2	0.8	1.2	3.2
21.5	Hexachloroethane	ND	0.1	1.0	1.7	7.0
23.7	Hexachlorobutadiene	ND	0.03	0.2	0.4	1.2

Effects of the presence of phenol and benzene

After samples containing 500 mg/L of phenol and chloroform were sonicated, extracted and analyzed, the products shown in Table 3 were identified by the library search and by comparison with spectra of standards.

Table 3. Concentrations (mg/L) of compounds identified after sonication of aqueous solutions of phenol and chloroform.

RT (min)	Compound	[Phenol] + [Chloroform] (mg/L)		
		500+500		500+100
		Sonication duration (min)		
		10	30	30
11.4	Chloroform	210	132	96
12.0	Carbon Tetrachloride	1.8	1.1	ND
12.3	Benzene	ND	ND	ND
13.2	Trichloroethene	1.8	2.1	ND
15.8	Tetrachloroethene	7.9	7.7	ND
17.1	Chlorobenzene	0.01	0.04	ND
18.8	1,1,2,2-Tetrachloroethane	0.4	0.6	ND
19.9	Pentachloroethane	3.1	3.4	ND
20.7	2-Chlorophenol	7.7	10.9	0.05
20.9	Phenol	329	317	377
21.6	Hexachloroethane	3.1	2.6	ND
23.6	Hexachlorobutadiene	0.4	0.4	0.1
24.9	4-Chlorophenol	3.1	4.6	ND

After 30 min of sonication, with 500 mg/L of both phenol and chloroform present, the major products are seen to be tetrachloroethene, followed by 2-chlorophenol and hexachloroethane. Similar results were obtained after only 10 min of sonication, although the amounts of carbon tetrachloride and hexachloroethane were significantly greater for this experiment. When there was initially only

100 mg/L of chloroform, then after 30 min, the only products detected were 2-chlorophenol (0.05 mg/L) and the hexachlorobutadiene (0.1 mg/L). There may have been other compounds formed which were not extracted effectively by MTBE.

Sonication was also carried out on a solution initially with 500 mg/L of benzene and 500 mg/L of chloroform. This solution became yellow and turbid after 30 min of sonication. A brown precipitate formed which was insoluble in MTBE, ethyl ether and acetone. Further analysis of this precipitate was not pursued. Table 4 shows the compounds identified in the analysis of the MTBE extract. It is interesting to note that there was significantly less carbon tetrachloride than in the previously described experiments, and that some chlorobenzene and phenol were formed.

Table 4. Concentrations (mg/L) of compounds identified after 30 min sonication of aqueous solutions of benzene and chloroform.

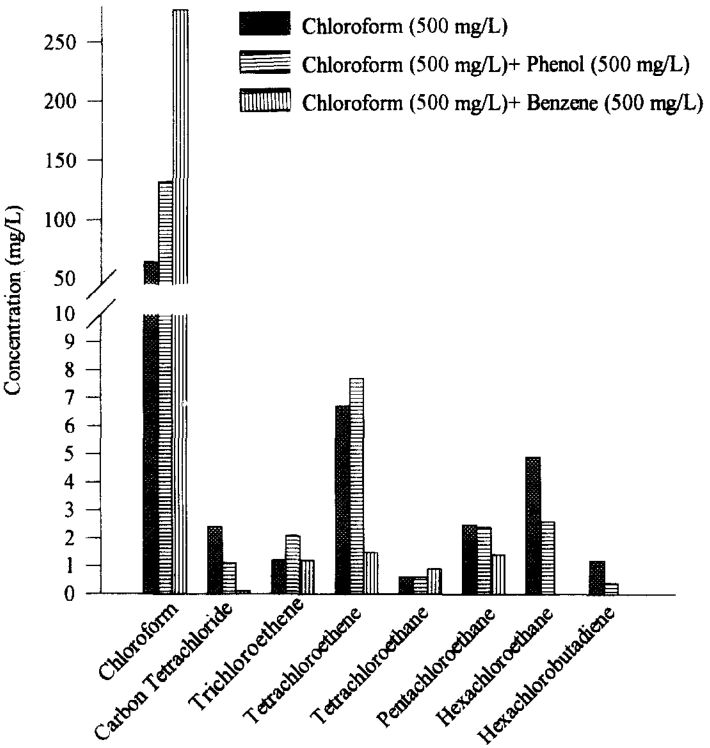
RT (min)	Compound	[Benzene] + [Chloroform]		[Benzene]
		500 + 500 mg/L	500 + 100 mg/L	500 mg/L
11.4	Chloroform	277	82	ND
12.0	Carbon Tetrachloride	0.1	ND	ND
12.3	Benzene	331	317	331
13.2	Trichloroethene	1.2	ND	ND
15.8	Tetrachloroethene	1.5	ND	ND
17.1	Chlorobenzene	5.3	1.1	ND
18.8	1,1,2,2-Tetrachloroethane	0.9	ND	ND
19.9	Pentachloroethane	1.4	ND	ND
20.7	2-Chlorophenol	0.9	ND	ND
20.9	Phenol	5.7	5.4	2.0
21.6	Hexachloroethane	ND	ND	ND
23.7	Hexachlorobutadiene	ND	ND	ND
24.9	4-Chlorophenol	0.3	ND	ND

The presence of chlorobenzene and phenol was confirmed by the comparison of the sample mass spectra against spectra of standards and the library search. Chlorophenols were also observed after sonication of aqueous chlorobenzene solutions (5). This indicates that there is a significant contribution to the sonochemical activity from the OH and H radicals formed in the dissociation of water in the cavitation process.

As shown in Figure 3, the presence of a compound such as phenol or benzene thus has an effect in the final amount of chloroform and the products formed. This is contrary to the conclusions drawn from experiments on the sonochemical degradation of nitrophenol in pure and natural waters (4). However, the degradation of the nitrophenol in water is assumed to be due to reactions with OH radicals formed from the thermal decomposition of water (4), while here radicals formed from the decomposition of chloroform are likely to important in the reactions forming the OCs.

The amount of chloroform remaining is considerably greater when benzene is present. The presence of a compound with a high vapour pressure such as benzene is expected to result in a higher pressure inside the cavities formed in sonication, and hence a lower temperature in the collapse of the cavities (19). There is also significantly diminished production of carbon tetrachloride, tetrachloroethene and pentachloroethane in the presence of benzene; no hexachloroethane and hexachlorobutadiene were detected. There is however no reduction in tetrachloroethane, the product expected from thermal cleavage of the C-Cl bond, the weakest bond in chloroform.

Figure 3. Effect of the presence of phenol and benzene in the formation of organochlorine compounds. Samples were sonicated for 30 min.



Naturally formed OCs such as chloroform are present in water together with compounds with aromatic groups in natural substances such as humic and fulvic acids. In natural phenomena such as waterfalls, rapids, and breaking waves there is thus the possibility for these substances to react and form more complex OCs. The concentrations of chloroform present in nature are much less than in the experiments reported here. The background level in the troposphere has been measured to be on 8.5 pptv on the average (9). This corresponds to an equilibrium concentration of 2.3 μmol m^{-3} (22). Nevertheless, there is a large amount of activity in natural waters which resembles cavitation, and trace amounts of some more complex OCs found in water could have such a natural chemical source.

CONCLUSIONS

Chlorinated hydrocarbons were detected after sonication in aqueous chloroform solutions. The formation of alcohols, aldehydes, etc. may also be possible. The formation of phenols was observed when samples containing benzene and chloroform were sonicated. However, due to the fact that the alcohols likely to be formed from chloroform are water soluble and with a low boiling point, their presence could not be proven with the extraction and detection methods used in this work.

Sonication of aqueous benzene/chloroform solutions also resulted in the formation of phenol and a precipitate. Precipitate formation has also been noted in the sonication of neat benzene (21) and diesel fuels (12).

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