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ARTICLES

Study of the Chlorination of Avobenzone in Sea Water by Gas Chromatography–High Resolution Mass Spectrometry

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Abstract—Disinfection is an important step in the purification of drinking and swimming pool water. The most common procedure includes chlorination, which efficiently eliminates microorganisms. However, the reaction of active chlorine with dissolved organic matter produces numerous organochlorine compounds posing a hazard to the environment and human health. UV filters belong to emerging contaminants, as their application to skin protection from UV irradiation becomes increasingly popular all over the world. Certain components of UV filters were detected in swimming pools and result in the emergence of new ecotoxicants. In the present study, 40 compounds, including numerous brominated derivatives, which result from the chlorination of avobenzone in sea water, were identified by gas chromatography–high resolution mass spectrometry. In addition, the applicability of photocatalysis to the destruction of chlorination products was studied. The procedure was found to be rather efficient and allows a decrease in the total amount of avobenzone transformation products by a factor of 10. The only compound class demonstrating stability under the applied conditions is exemplified by halogenated acetophenone derivatives.

Keywords: avobenzone, GC/HRMS, disinfection by-products, aquatic chlorination, photocatalysis, brominated compounds

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INTRODUCTION

Modern swimming pools are objects where disinfection by-products, resulting from the reaction between a disinfectant and an organic matter, are often detected [1, 2]. Decontamination of water using chlorine-based disinfectants was proved to afford more than 600 disinfection by-products [2, 3], resulting from the reaction of natural organic substances or other human-induced substrates, such as sweat and urea components, skin or hair species, and personal care products [4]. The thorough review [2] gives data on the presence of disinfection by-products in swimming pools, as well as emphasizes an urgent need in the study this problem.

Many commonly used personal care products contain organic and inorganic UV filters, protecting human skin from the harmful effect of solar radiation [5, 6]. As many other compounds, these products enter the aqueous medium upon washing off from the skin of swimmers.

Sea water swimming pools became popular in Europe, primarily, from considerations of health promotion (so called thalassotherapy), as well as for recreation purposes [7, 8]. Sea water pools are also used by hotels and SPA resorts practicing health tourism and recreational activities [9]. Bromination or chlorination of waters containing bromides (for example, sea water) is known to result in the formation of bromine-containing disinfection products [10–12] which have a higher toxicity compared to their chlorinated analogs [3, 13–15].

To date, another promising method for the decontamination of water is its UV irradiation. Because of its efficiency in the control of microorganisms, elimination of the need for storage and transportation of chemicals, and the absence of toxic disinfection by-products, UV decontamination finds increasingly wider application. Nevertheless, it has some drawbacks, associated with the high cost of equipment and its maintenance, as well as with the absence of afteraction, i.e., retention of disinfecting properties in water distribution facilities.

In the present work, we attempted to simulate real conditions of the disinfection of the sea water containing the most common UV filter avobenzone (4-*tert*-butyl-4'-methoxydibenzoylmethane). Disinfection was performed using a solution of sodium hypochlorite. As noted above, chemical disinfection, especially chlorination, results in a number of side products; toxicities of many of them have not been studied. Therefore, it is desirable to remove these compounds from water. As a destruction method, we chose UV irradiation. A combination of chlorination with UV irradiation allows one to perform the maximum efficient purification of sea water at the minimum residual amount of decontamination products therein.

Earlier, we have studied the chlorination of avobenzone. The formation of two primary products of NaClO chlorination in water, mono- and dichlorinated molecules, was confirmed by combined liquid chromatography–tandem mass spectrometry [16]. The structures of primary products obtained were confirmed by NMR spectroscopy and gas chromatography–mass spectrometry (**GC/MS**).

The combined action of active chlorine and UVC radiation results in the formation of 25 compounds (including acid chlorides and chlorophenols) which are not produced when these two disinfection methods are applied alone [17]. The primary chlorination products of avobenzone (2-chloro-1-(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione and 2,2-dichloro-1-(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione) were studied further for degradation at different pH, as well as for photostability [18].

In the present work, we focused on the chlorination of avobenzone in sea water. The data from this chlorination were combined with the data from a photocatalytic experiment using TiO_2 films in combination with UV-A irradiation. All products were identified by combined gas chromatography–high resolution mass spectrometry (**GC/HRMS**).

EXPERIMENTAL

Chlorination of avobenzone in sea water (Sample M1). Avobenzone (20 mg, 0.064 mmol) was dissolved in acetonitrile (40 mL) and mixed with sea water (2 L). NaClO (0.12 mmol) was added to the solution obtained. The reaction mixture was stirred for 24 h at room temperature and extracted with dichloromethane (30 mL). The extracts were dried over sodium sulfate, deuterated phenanthrene was added as an internal standard, and the sample was analyzed by GC/MS.

Photocatalytic decomposition of avobenzone chlorination products (Sample M2). Avobenzone (20 mg, 0.064 mmol) was dissolved in acetonitrile (40 mL) and mixed with sea water (2 L). NaClO (0.12 mmol) was added to the solution obtained. The reaction mixture was stirred for 24 h at room temperature and subjected to photocatalytic decomposition using TiO_2 films and UV-A irradiation for 2 h. The reaction mixture was passed through cartridges packed with a C18 stationary phase using acetonitrile as an eluent and the eluate were evaporated to dryness. The dry residue was dissolved in dichloromethane, deuterated phenanthrene was added as an internal standard, and the sample was analyzed by GC/MS.

GC/HRMS analysis. The data of GC/HRMS were obtained using a Pegasus GC-HRT time-of-flight mass spectrometer (LECO Corporation, United States) in combination with an Agilent 7890A gas chromatograph (Agilent, United States). The system was controlled using the ChromaTOF-HRT version 1.80 software (LECO Corporation), which was also used for data acquisition and processing. The data were acquired using 10 entire spectra (m/z 30–510) per second in the high-resolution mode (25 000 FWHH). The weight error was not higher than 0.5 ppm.

The chromatographic separation of samples was performed using a Rxi-5SilMS capillary column (30 m × 0.25 mm × 0.25 μm) purchased from Restek Corporation (Bellefonte, PA, United States) with a helium flow rate of 1 mL min^{-1}. The injected volume was 1 μL in splitless mode for 75 s and, afterwards, with a split ratio of 20 : 1. The injector, liner, and ion source temperatures were 270, 300, and 300°C, respectively. For all samples, 5 min delay prior to switching on the cathode was set for the escape of the solvent. Prior to experiments, the ion source and the ion beam-forming optics of the instrument were calibrated using an FC-43 standard calibration mixture. The temperature conditions of the column were as follows: 5 min at 40°C, temperature programming at a rate of 10 K min^{-1} up to 250°C and, then, at a rate of 6 K min^{-1} up to 300°C, and final keeping for 2 min at 300°C prior to cooling.

The levels of the transformation products were determined using deuterated phenanthrene as an internal standard. The response factor was calculated only for the starting avobenzone. For the remaining compounds, the response factor was taken equal to unity.

RESULTS AND DISCUSSION

An analysis of the reaction mixture (sample M1) showed the presence of several dozens of disinfection products. The room-temperature chlorination products of avobenzone with sodium hypochlorite in sea water coincided to a large extent with those found earlier for the analogous reaction in distilled water [16, 17]. A significant difference of the sea water reaction involved a considerable number of bromine-containing products (Table 1) because of the presence of bromides [19], which can be oxidized by active chlorine to hypobromites and initiate bromination [20], as well as can enter the molecules by nucleophilic substitution. In particular, the concentration of bromides in the Adriatic Sea water used in the experiment was 8 mg L^{-1}. This is in principle a key point from the environmental point of view, as the toxicity of bromine-containing compounds is usually significantly higher than that of chlorine-containing analogs [21–23].

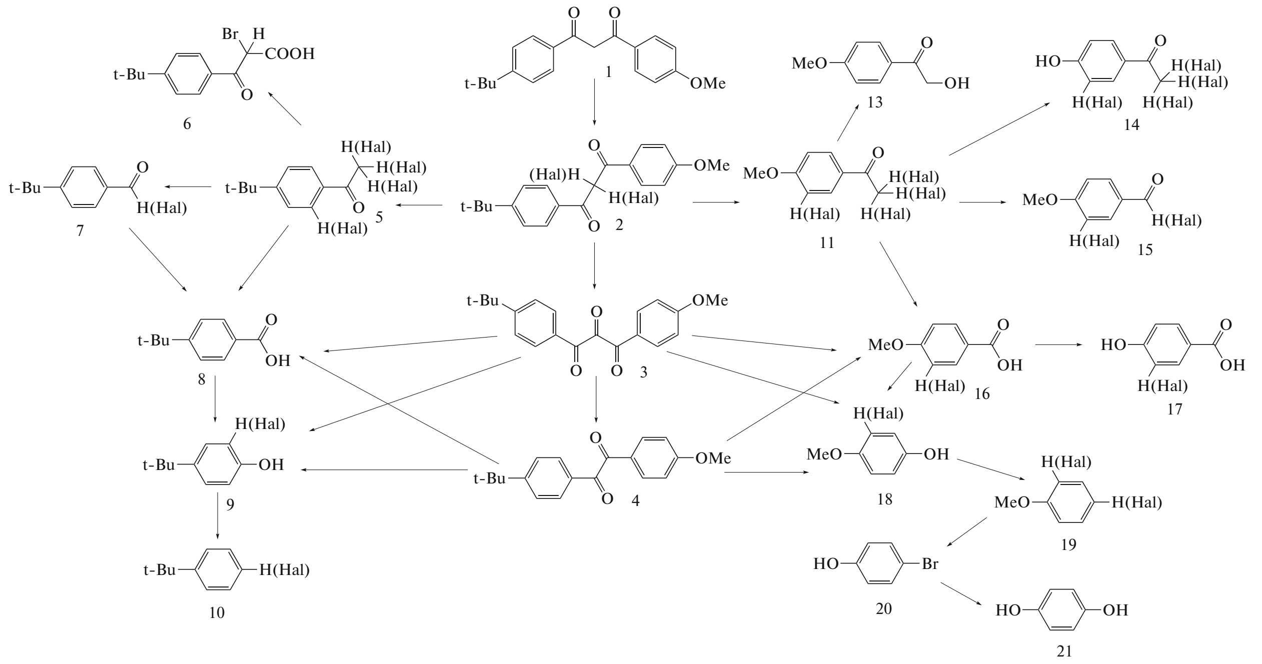
The reaction starts (Scheme 1) from the chlorination of the avobenzone (1) molecule by the methylene group to afford mono- (2a) and dichloro substituted (2b) molecules [16, 17]. It should be emphasized that there were no aromatic ring chlorination products as noted earlier [16, 17]. In addition to primary chlorination derivatives, bromo derivative (2c), resulting from the reaction between avobenzone and hypobromite or the nucleophilic substitution of chlorine for bromine was detected. The dichloroavobenzone (2b) molecule can be hydrolyzed to form triketone 3, followed by the release of CO by decarbonylation to form diketone 4. An important transformation under the experimental conditions was the $CO-CX_2$ bond cleavage on both sides from the methylene group. This resulted in two sets of similar products differing in the benzene ring substituent (*tert*-butyl or methoxy group). Among these products were acetophenones, aldehydes, acids, and phenols. In particular, the chloro substituted avobenzone (2a and 2b) can decompose into substituted acetophenones (5 and 11). Their sequential halogenation at the α position resulted in trihalogenated derivatives (not detected), which underwent the haloform reaction to form benzoic acids (8 and 16). In the case of the methoxy derivative, α-hydroxyacetophenone (13], resulting from hydrolysis of the corresponding monohalogenated product, was also detected. It appears that the lower stability of the analogous *tert*-butyl derivative did not allow us to detect this compound in the reaction mixture. Pairs of substituted aldehydes and acid chlorides (7 and 15) emerged, probably, upon the cleavage of the same $CO-CX_2$ bond in avobenzones 2. Analogous phenols (9 and 18) and halobenzenes (10 and 19) can form from any heavier molecules. The second halogen atom was introduced to the ring (19d) of the monobrominated derivative 19c.

Nevertheless, halogenation into the aromatic ring still proceeded, but as a result of secondary reactions with primary transformation products. As the methoxy group has a small volume and is an active type I orientating group, it favors the formation of halogenated derivatives (11, 15, 16, and 19) with halogen being in the *ortho* position relative thereto. The *tert*-butyl group is also a type I orientating group; however, the large volume of this substituent prevents electrophilic substitution at the *ortho* position of the benzene ring. As a result, only two products (5 and 9) were detected. One more group of secondary products is associated with the methoxy group cleavage to form hydroxy derivatives (14, 17, 20, and 21).

As the main objective of our study, besides the detection of chlorination products, was to check how the photocatalytic removal of these products from water is efficient, a portion of avobenzone chlorinated in sea water was subjected to photocatalytic decomposition using TiO_2 films and UV-A radiation for 2 h (sample M2). After this procedure, the concentration of disinfection by-products in water decreased about 10-fold, which, for sure, demonstrates the efficiency of the proposed approach. The residual amount of avobenzone itself and its chlorination products (2) was about 300-fold less and most of the other compounds were no more detected in the irradiated sample (Table 1). Against this dramatic decrease in the levels of almost all chlorination products, it comes under notice that the concentrations of some acetophenone derivatives (5 and 11) considerably increased. These compounds are, probably, more stable compared to other ones under photocatalysis conditions and their portion increased because of the decomposition of avobenzone itself and its primary chlorination products. As halogenated acetophenones are toxic products, the photocatalysis procedure should be improved to remove these compounds.

Table 1. Disinfection by-products of avobenzone in sea water

No.	Substance name	Retention time, s	M1, μg L^{-1}	M2, μg L^{-1}	Compound no.
1	Anisole	410.136	3.5	–	19a
2	Benzene, *tert*-butyl	495.648	11	3.3	10a
3	Benzene, 1-chloro-4-methoxy-	614.424	0.3	–	19b
4	Benzene, 1-bromo-4-methoxy-	697.92	0.9	–	19c
5	Anisole, 4-hydroxy-	714.72	2.9	–	18a
6	Benzaldehyde, 4-methoxy-	751.008	5.2	0.9	15a
7	Hydroquinone	761.448	0.3	–	21
8	Benzene, 1-bromo-4-*tert*-butyl-	767.976	1.6	–	10b
9	Phenol, 4-bromo-	775.704	0.1	–	20
10	Phenol, 4-*tert*-butyl-	779.904	12	0.8	9a
11	Benzaldehyde, 4-*tert*-butyl-	800.232	9.0	2.5	7a
12	Phenol, 3-bromo-4-methoxy-	806.616	0.2	–	18b
13	Anisole, 4-acetyl-	832.152	74	7.9	11a
14	Benzoyl chloride, 4-methoxy-	854.664	16	–	15b
15	Phenol, 2-bromo-4-*tert*-butyl-	866.76	0.3	–	9b
16	Benzoic acid, 4-methoxy-	880.375	450	5.0	16
17	Acetophenone, 4-*tert*-butyl-	882.384	45	27	5a
18	Benzoyl chloride, 4-*tert*-butyl-	895.32	17	1.9	7b
19	Acetophenone, 4-hydroxy-	897.00	2.1	–	14
20	Anisole, 2,4-dibromo-	924.452	11	–	19d
21	Benzoyl bromide, 4-methoxy-	936.984	100	–	15c
22	Benzoic acid, 4-*tert*-butyl-	943.199	573	59	8
23	Benzoic acid, 4-hydroxy-	946.392	5.2	–	17
24	Acetophenone, 2-chloro-4-*tert*-butyl-	968.4	3.4	273	5b
25	Benzaldehyde, 3-bromo-4-methoxy-	970.416	2.0	–	15d
26	Benzoyl bromide, 4-*tert*-butyl-	973.608	100	–	7c
27	Acetophenone, α-hydroxy-4-methoxy-	974.616	11	2.0	13
28	Acetophenone, 3-chloro-4-methoxy-	1001.33	10	310	11b
29	Acetophenone, 3-bromo-4-methoxy-	1037.78	15	1.2	11c
30	Acetophenone, α-chloro-4-*tert*-butyl-	1044.12	11	1720	5c
31	Acetophenone, α-bromo-4-methoxy-	1060.63	55	44	11d
32	Acetophenone, α,α-dichloro-4-*tert*-butyl-	1089.7	0.4	5.5	5d
33	Acetophenone, α-bromo-4-*tert*-butyl-	1100.78	36	186	5e
34	Acetophenone, α,α-dibromo-4-methoxy-	1187.47	2.9	–	11e
35	Acetophenone, α,α-dibromo-4-*tert*-butyl-	1220.54	3.2	2.4	5f
36	Acetophenone, α,α-dibromo,α-chloro-4-methoxy-	1288.94	0.6	–	11f
37	Acetophenon, α-bromo,α-carboxy-4-*tert*-butyl-	1341.7	1.0	–	6
38	ArCOCOAr'	1543.97	232	41.4	4
39	ArCOCOCOAr'	1611.34	680	0.9	3
40	Avobenzone	1666.78	2450	3.68	1
41	Chloro-avobenzone	1697.18	2800	4.12	2a
41	Dichloro-avobenzone	1697.18	1900	19.9	2b
41	Bromo-avobenzone	1697.18	185	–	2c



Scheme 1.

CONCLUSIONS

The transformation of the commonly used UV-radiation protector abovenzone in aquatic chlorination of sea water was studied. The chlorination afforded several dozens of disinfection by-products, including chlorine- and bromine-containing ones, which potentially pose a hazard to the human health. Among the main products are substituted halogenated aromatic aldehydes, acids, acetophenones, and phenols. To remove these compounds, photocatalysis by UV-A irradiation on titanium dioxide was applied. The irradiation demonstrated good results: the amount of transformation products decreased by a factor of 10. The exception was the group of substituted acetophenones, whose concentration increased due to the experiment. These molecules appear to be quite stable under the photocatalysis conditions and the additional amount of these molecules results from the decomposition of primary chlorination products.

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