



Transformation of avobenzone in conditions of aquatic chlorination and UV-irradiation



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ABSTRACT

Emerging contaminants represent a wide group of the most different compounds. They appear in the environment at trace levels due to human activity. Most of these compounds are not yet regulated. Sunscreen UV-filters play an important role among these emerging contaminants. In the present research the reactions of 4-*tert*-butyl-4'-methoxydibenzoylmethane (avobenzone), the most common UV filter in the formulation of sunscreens, were studied under the combined influence of active chlorine and UV-irradiation. Twenty five compounds were identified by GC/MS as transformation products of avobenzone in reactions of aquatic UV-irradiation and chlorination with sodium hypochlorite. A complete scheme of transformation of avobenzone covering all the semivolatile products is proposed. The identification of the two primary chlorination products (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) was confirmed by their synthesis and GC/MS and NMR analysis. Although the toxicities of the majority of these products remain unknown substituted chlorinated phenols and acetophenones are known to be rather toxic. Combined action of active chlorine and UV-irradiation results in the formation of some products (chloroanhydrides, chlorophenols) not forming in conditions of separate application of these disinfection methods. Therefore caring for people «well-being» it is of great importance to apply the most appropriate disinfection method. Since the primary transformation products partially resist powerful UV-C irradiation they may be treated as stable and persistent pollutants.

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1. Introduction

Recently a new group of chemical compounds, known as emerging contaminants, and representing an extremely wide group including pharmaceuticals, nanomaterials, hormones, personal care products, flame retardants, etc. attracted the attention of the environmental scientists (Richardson, 2012; Lebedev, 2013). These compounds penetrate the environment due to extensive human activity usually at parts-per-billion and lower levels.

Although some rules and restrictions exist (Richardson and Ternes, 2011), the safe values for the vast majority of them have not been determined, and most of these compounds are not yet regulated.

Among these groups sunscreen UV-filters play an important role. During last 75 years they are intensively used in various sunscreen products and other formulations for the daily consumption (lotions, creams, shampoo, dyes and varnishes for hair, lipsticks, perfumes, etc.) The levels of certain UV-filters in sunscreens vary from 0.5 to 10%, sometimes reaching 25%. UV-filters penetrate the environment by several routes. They can be washed out directly from the skin of the swimmers, appear in the environment with waste water or swimming pool water, or due to leaching at the dump sites. Recently the data on their occurrence in different water compartments across the world (Ramos et al., 2015; Poiger and Buser, 2004) as well as at the wastewater plants (Ramos

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et al., 2016) have been published. The waste water treatment plants (WWTP) are not efficient dealing with emerging contaminants (Li et al., 2007; Gago-Ferrero et al., 2011; Zhang et al., 2011).

UV-filters are not always stable under the environmental conditions. Water in the natural reservoirs is always subjected to the sun irradiation, while swimming-pool water is required to be disinfected by chlorination, bromination, ozonation, or UV-irradiation (Chowdhury et al., 2014). Toxicity of the transformation products may be higher than that of the parent compound (Florentina et al., 2011; Bottoni et al., 2014). Therefore it is important to take into account not only the initial compounds, but their transformation products as well.

Our previous research dealt with aquatic chlorination reactions of benzophenone type UV-A filters (Grbović et al., 2013; Zhuang et al., 2013). The studies were combined with toxicity experiments, using marine bacteria *Vibrio Fischeri* (Zhuang et al., 2013) and microalgae *Desmodes subspicatus* (Grbović et al., 2015). Continuing our research we have focused on UV filters belonging to dibenzoylmethanes. The most common UV-A filter (400–320 nm) of this type in the formulation of sunscreens is 4-*tert*-butyl-4'-methoxydibenzoylmethane, known as avobenzone and sold under the trade names Parsol 1789 or Eusolex 9020. It is a constituent of numerous sunscreen products being one of UV-A filters permitted to be used by the European Commission on Health (The Encyclopedia of UV Filters, 2007).

Avobenzone exists in two tautomeric forms: enol and keto ones. In sunscreen formulations, avobenzone exists predominantly in the enol form, which has a maximum absorption at wavelengths ranging from 350 to 365 nm depending on the solvent used. Avobenzone photostability in organic solvents (methanol, acetonitrile and hexane) highly depends on the polarity and proticity of the solvent (Mturi and Martincigh, 2008; Vallejo and Gallardo, 2011). Recent studies (Santos et al., 2013; Crista et al., 2015) have dealt with the aquatic chlorination of avobenzone. Using LC/MS method the formation of two primary by-products in the reaction of avobenzone with sodium hypochlorite in water (a mono- and dichloro-substituted compounds) was demonstrated. Our recent LC/MS/MS experiments allowed elucidating the structures of these compounds being 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 (Kalister et al., 2016). The double bond of the enolic form was shown to be more reactive in conditions of aquatic chlorination, than the aromatic ring (Sinikova et al., 2014). Even activation of the aromatic moiety by methoxyl substituent did not change the situation and the reactive particle HOCl–H₃O⁺ (Lebedev et al., 2004) attacked exclusively the enolic fragment of avobenzone. The third product (2-chloro-1-(4-methoxyphenyl)ethanone) was formed due to the cleavage of CO–CH₂ bond in the aliphatic bridge of the original molecule.

The present study involves transformation of avobenzone under the combined influence of active chlorine and UV-irradiation. These conditions (usually combination of chlorination with UV-C disinfection) take place in the disinfection process when reprocessing water comes back to the swimming pools. The aim of the investigation deals with identification of all possible semi volatile transformation products. Additionally we have checked how stable all the products are. If they «resist» UV-C they are really persistent.

2. Experimental

2.1. Materials

The analytic standard of hexyl 4-*tert*-butyl-4'-methoxydibenzoylmethane (avobenzone) (99.0% purity); 10% sodium

hypochlorite (NaClO); acetonitrile and ethylacetate (HPLC grade) were purchased from Sigma Aldrich (UK). Anhydrous sodium sulfate and sodium sulfite were purchased from Fluka. Double deionized water (<18 MΩ cm) was prepared with the NANO pure water system (Barnstead, USA).

2.2. Reagent solutions preparation

The stock solution (1 g/L) of avobenzone (Solution 1) was prepared by dissolving of 200 mg of avobenzone in 200 mL of acetonitrile. The concentrated solution 0.5 g/L in water/acetonitrile (Solution 2) was prepared by adding of 50 mL of solution 1–50 mL of water. The diluted solution 1 mg/L in water/acetonitrile (solution 3) was prepared by diluting of 1 mL of solution 2–500 mL with water. Acetonitrile was used because avobenzone is not sufficiently soluble in water only.

2.3. UV-irradiation experiments

20 mL of solution (1, 2 or 3) in a 50 mL glass beaker was subjected to the irradiation with bactericidal lamp Philips TUV TL-D 30 W SLV (The Netherlands), producing UV photons with maximum at 253,7 nm and wavelength range 200–280 nm (UV–C). A sample aliquot was taken after 1, 2, and 4 h for further analysis.

2.4. Chlorination experiments

20 mL of avobenzone solution 2 was placed in a 50 mL glass beaker. Then, 12 and 120 μL (1 and 10 equivalents) of 10% sodium hypochlorite solution was added. In the case of solution 3 0.024 and 0.24 μL (2 and 20 equivalents) of 10% sodium hypochlorite solution was added. The reaction mixtures were maintained in a dark place at constant stirring. After 45 min the reaction was terminated by addition of sodium sulfite (Na₂SO₃) to eliminate the remaining active chlorine. Then 1 mL of the reaction mixture was subjected to triple extraction with ethylacetate, extracts were combined, dried over anhydrous sodium sulfate, and concentrated at 50°C to 200 μL. Dodecane was added as an internal standard. Its concentration in the sample ready for injection was 0.15 mg/μL.

The chlorination procedure, accompanied by UV-irradiation, was the same as in the case of chlorination. The only difference involves the fact that the reaction mixtures were placed in a special reactor and subjected to UV-C irradiation for 30 min.

2.4.1. Synthesis of mono chloro- and dichloroavobenzone

Chlorination of 1-(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione (Avobenzone).

- 1 equivalent of *tert*-BuOCl:** 310 mg (1.00 mmol) of avobenzone was dissolved in 5 mL dichloromethane, cooled in an ice bath and a solution of 120 mg (1.1 mmol) of *tert*-butyl hypochlorite in 2 mL of dichloromethane was added. After 15 min, the solvent was evaporated, the resulting oil (325 mg) was subjected to column chromatography (SiO₂, CH₂Cl₂: petroleum ether = 2: 1) and 226 mg (yield 66%) of 2-chloro-1-(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione was isolated as a colorless oil.
- 2 equivalents of *tert*-BuOCl:** the same procedure as in a), except the amount of *tert*-butyl hypochlorite was 230 mg (2.1 mmol). Several products were established in the reaction mixture. Chromatographic separation (SiO₂, CH₂Cl₂: petroleum ether = 2: 1) yielded 27 mg (yield 7%) of 2,2-dichloro-1-(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione as a colorless oil.

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