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Identification of halogenated photoproducts generated after ultraviolet-irradiation of parabens and benzoates in water containing chlorine by solid-phase microextraction and gas chromatography–mass spectrometry[☆]

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ABSTRACT

This work presents a new solid-phase microextraction (SPME)-based approach to investigate the formation of halogenated by-products generated by the UV-induced photodegradation of parabens and their congener benzoates in water containing chlorine. Degradation of parent species, and further identification of their transformation by-products were monitored by gas chromatography coupled to mass spectrometry (GC/MS). In order to improve detectability, SPME was applied as a preconcentration step after UV-irradiation of target preservatives. Experiments performed with dechlorinated water, ultrapure water, and tap water showed that under UV-light, the presence of even low levels of free chlorine, increases the photodegradation rate of target preservatives, enhancing the formation of halogenated photoproducts. Monobrominated, dibrominated and bromochlorinated hydroxybenzoates were identified, and the transformation of benzoates into halogenated parabens was also confirmed. Bromination is expected to occur when free chlorine is present, due to the presence of traces of bromide in water samples. Five halogenated phenols (mainly brominated) were detected as breakdown photoproducts from both families of target preservatives. On the basis of the appearance of the aforementioned by-products, a tentative transformation pathway, consistent with the photoformation–photodecay kinetics of the by-products, is proposed herein for the first time.

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1. Introduction

Benzotates and parabens, alkyl esters of benzoic acid and para-hydroxybenzoic acid, respectively, are structurally related chemicals that are widely used as preservatives in cosmetics and personal care products (PCPs), as well as in canned food and pharmaceuticals [1–3]. Although no harmful effects on consumer health have been attributed to the use of benzoates or their salts in cosmetics [4], some studies indicate that most benzoic acid derivatives may exhibit toxicity and cause serious public health and environmental problems [2]. In fact, sodium and potassium benzoic acid salts have been shown to be clastogenic, mutagenic

and cytotoxic to human lymphocytes in vitro [5]. Parabens are suspected endocrine disrupting compounds with oestrogenic- and antiandrogenic-like properties [6,7]. Moreover, recent studies suggest a potential relationship between the application of paraben-containing products and some types of allergies [8] and even breast cancer [9]. The continuous release of PCPs into the environment, has raised scientific concern about the effects that these ubiquitous compounds and their transformation products might have on human health and on aquatic organisms. The efficient removal of these compounds in conventional wastewater treatment plants is a challenge for drinking water production [10]. UV light is an established method of drinking water disinfection and a developing method for wastewater purification, which can be used in combination with strong antioxidants in the so-called Advanced Oxidation Processes (AOPs) [11].

Although literature about photodegradation of parabens and benzoates is rather scarce, some studies dealing with photolytic or photocatalytic processes applying AOPs have been reported. Thus, direct photolysis of butylparaben (BuP) [11] was found to be

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inefficient due to low quantum yield. Although other oxidative processes such as ozonation are reported to be more effective than photolysis [12], degradation of BuP using combined action of UV radiation and H₂O₂ occurred rapidly and effectively [13]. In this respect, photooxidation with additives such as H₂O₂ or TiO₂ was found to enhance methylparaben degradation [14], whereas the combination of two or more simple oxidation systems increased the reactivity by a synergic effect [15]. Heterogeneous TiO₂-mediated photocatalysis has also been used to degrade benzylparaben [16] and benzoic acid [17]. In the latter two studies, several photoproducts were identified, such as hydroxylated benzoates and phenols, as in other ozonation studies about parabens [10].

On the other hand, it is well known that compounds containing phenolic hydroxyl groups, such as parabens, can react readily with free chlorine in chlorinated water (0.4–5 mg Cl₂ L⁻¹) yielding chlorinated by-products [18,19]. In fact, several chlorinated parabens, which are eventually released into aquatic environments, have been detected in water samples from public swimming pools [20] and from raw sewage water samples [19]. Toxicity studies reveal that the resulting chlorinated by-products generate more acute toxicity responses than the parent compounds in the *Daphnia magna* and *Vibrio fischeri* tests [21]. Moreover, evidence has shown that brominated parabens and phenols are generally significantly more cytotoxic and genotoxic than their chlorinated analogs [22–24]. Nowadays, the use of chlorophenols, has been restricted or widely banned in many countries due to possible adverse health effects, even at low concentrations [25].

To our knowledge, the photochemical behavior of parabens and their congener benzoates under UV light in water containing chlorine has not yet been investigated. Photohalogenated derivatives and halogenated breakdown photochemical by-products are suspected to be generated. Thus, in this work, a reliable methodology based on solid-phase microextraction coupled to gas chromatography mass-spectrometry (SPME-GC/MS) was developed and applied in order to tackle the following aims: (i) to investigate the photodegradation of parabens and benzoates in water samples containing chlorine, (ii) to identify their potential degradation and transformation by-products on the basis of their mass spectra, information reported in the literature and the NIST Mass Spectral Database, (iii) to monitor their photoformation-photodegradation kinetics, and (iv) to propose the transformation pathways for the preservatives under study. We suggest herein the implementation of SPME-GC/MS as highly valuable tool, which allow, for the first time, the monitorization of photohalogenated by-products from the target emerging pollutants.

2. Experimental

2.1. Reagents and materials

Methylbenzoate (MeBz; 99%), ethylbenzoate (EtBz; 99%), and butylbenzoate (BuBz) were supplied by ChemService (West Chester, USA). Methylparaben (MeP; 99%), ethylparaben (EtP; 99%), propylparaben (PrP; 99%), butylparaben (BuP; 99%), isopropylparaben (iPrP; ≥99%) and isobutylparaben (iBuP; ≥97%) were acquired from TCI Europe (Belgium). The retention times and the selected quantification and identification ions of the target preservatives are included in Table 1. For confirmation purposes, 3,5-dibromomethylparaben (3,5-DBrMeP) was obtained from Sigma-Aldrich.

Acetone (99.9%) and sodium thiosulphate (>98%) were provided by Merck (Darmstadt, Germany) and sodium chloride (99.7%) was supplied by Prolabo (VWR, Fontenay-sous-Bois, France). All solvents and reagents were of chromatographic grade.

Individual stock solutions of each compound were prepared in acetone. Further dilutions and mixtures in the same solvent were

prepared by convenient dilution of the stock solution to spike water samples. Stock and working solutions were stored in a freezer at –20 °C protected from light.

Commercially available fibers housed in manual SPME holders were obtained from Supelco (Bellefonte, PA, USA): 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS/DVB), 75 μm carboxen-polydimethylsiloxane (CAR/PDMS). The fibers were conditioned as recommended by the manufacturer.

2.2. Water samples

Three different water samples containing different amounts of free chlorine were tested for photodegradation studies with the target preservatives: dechlorinated ultrapure water (TH-W), ultrapure water (MQ-W), and tap water (TP-W). Use of the *N,N*-diethyl-*p*-phenylenediamine procedure with photometric detection [26] confirmed the presence of free chlorine in tap water (0.6 mg L⁻¹) and also in ultrapure water. In the case of MQ-W, free chlorine was not possible to quantify, since the concentration was below the LOQ (0.1 mg L⁻¹). The pH of the samples was similar, ranging from 6.4 to 7.1. Dechlorinated water was obtained by removing the available free chlorine from ultrapure water with sodium thiosulphate (1 mM).

2.3. Photodegradation and solid-phase microextraction procedure

Two aliquots of water (3 ml each) previously spiked with the target preservatives (at 50 ng mL⁻¹) were placed in two quartz cuvettes. Irradiation experiments were conducted in a laboratory-made photoreactor equipped with two low-pressure mercury lamps (8 and 10 W, 254 nm). Quartz cuvettes were placed inside the photoreactor box at a distance of 9 cm from the lamps, and irradiated with UV light (254 nm) at 8 or 18 W-UV (depending on the experiment) for the designated time (2–60 min). In the control experiment (0 min of UV irradiation), the water samples were immediately extracted by SPME.

Irradiated solutions (6 ml of water) were transferred to 10 ml vials with addition of sodium chloride at 20% (w/v). Vials were sealed with aluminum caps furnished with PTFE-faced septa and immersed in a water bath maintained at the working temperature (25 or 100 °C). Samples were let to equilibrate for 5 min before placing the SPME device. Afterwards, the fiber was exposed to the headspace over the sample (HS-SPME) or immersed into the sample (SPME) for 15 min. Three different fiber coatings (PDMS, PDMS/DVB, and CAR/PDMS) were compared to evaluate the capability of SPME to extract the parent compounds and photochemical by-products. After extraction, the fibers were thermally desorbed at 270 °C in the GC injector port for 5 min, for GC-MS analysis. Under the final optimized conditions, target compounds were extracted at 25 °C for 15 min in direct sampling mode, using a CAR/PDMS fiber over the stirred samples, with addition of 20% (w/v) of sodium chloride.

Dark test were performed by placing the cuvettes in the photoreactor box, maintaining the lamps switched off for a certain time (0–60 min), and covering the whole device with aluminum foil. The SPME procedure was then applied.

2.4. Gas chromatography-mass spectrometry analysis

The GC-MS analysis was performed with a Thermo Scientific Trace 1310-GC gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 8000; Thermo Scientific; San Jose, CA, USA). The system was operated by Xcalibur 2.2 and Trace Finder TM 3.0.

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