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Transformation mechanism of benzophenone-4 in free chlorine promoted chlorination disinfection

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ARTICLE INFO

Article history:
Received 20 April 2013
Received in revised form
16 July 2013
Accepted 26 July 2013
Available online 6 August 2013

Keywords:
UV-filters
Benzophenone
Chlorination
Genotoxicity

ABSTRACT

The UV-filter BP-4 (2-hydroxy-4-methoxybenzophenone-5-sulfonic acid) has been frequently observed in the environment, showing high potentials to invade drinking water, swimming water, or wastewater reclamation treatment systems. With the help of high performance liquid chromatography-high resolution mass spectrometry and nuclear magnetic resonance spectroscopy, 10 new products from free chlorine-promoted BP-4 disinfection have been disclosed and their possible transformation routes have been investigated. The first route is chlorine substitution of BP-4 and its transformation products, forming mono-, di-, and tri-chlorinated BP-4 analogs. The second is Baeyer–Villiger-Type oxidation, converting diphenyl ketone to phenyl ester derivatives. The third is ester hydrolysis, generating corresponding phenolic and benzoic products. The fourth is decarboxylation, replacing the carboxyl group by chloride in the benzoic-type intermediate. The fifth is desulfonation, degrading the sulfonic group through an alternative chlorine substitution on the benzene ring. Orthogonal experiments have been established to investigate the species transformed from BP-4 at different pH values and free available chlorine (FAC) dosages. The reaction pathways are strongly dependent on pH conditions, while an excessive amount of FAC eliminates BP-4 to the smaller molecules. The initial transformation of BP-4 in chlorination system follows pseudo-first-order kinetics, and its half-lives ranged from 7.48 s to 1.26 × 10^2 s. More importantly, we have observed that the FAC-treated BP-4 aqueous solution might increase the genotoxic potentials due to the generation of chlorinated disinfection by-products.

1. Introduction

UV filters are widely used in sunscreens and some other personal care products, such as cosmetics, lotions, shampoos, and lipsticks, to protect the skin from sun radiation, and they are also used as chemical ingredients of insecticides, agricultural chemicals and pharmaceuticals (Roelandts et al., 1983; Stenback, 1977; Tomson et al., 1981; Richardson and Ternes, 2011; Diaz-Cruz et al., 2008; Fent et al., 2010). Because UV filters are basic ingredients in personal care products, they are primarily discharged by point sources after having been washed off skin and clothing, and they eventually

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0043-1354/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2013.07.043

end up in wastewater treatment plants with low degradation efficiency and high residue in activated sludge (Kupper et al., 2006; Liu et al., 2012). However, these chemicals are also directly released into surface waters through swimming, bathing, and leaching of land and house coatings (Poiger et al., 2004; Giokas et al., 2007; Plagellat et al., 2006).

With the increased use of sunscreens, considerable concerns have been raised regarding the long-term environmental impact of sunscreen ingredients. Benzophenone-type (abbreviated as BP) chemicals, which are one of the primary components in the UV-filter family, have been classified as "chemicals suspected of having endocrine disrupting effects" by the Japanese Ministry of Environment (MOE, 2000). It has been reported that BP-type UV-filters exhibited many biological risks, such as exerting uterotrophic effects *in vivo*, showing estrogenic activity in the yeast two-hybrid assay (Kawamura et al., 2003), stimulating the proliferation of MCF-7 breast cancer cells, and increasing the secretion of the tumor marker pS2 *in vitro* (Schlumpf et al., 2001). Furthermore, some studies have suggested that BP-type UV-filters were displaying mutagenic effects in *Salmonella* (Zeiger et al., 1987), and inducing sister chromatid exchanges and chromosomal aberrations in Chinese hamster ovarian cells (French, 1992).

BP-4 (2-hydroxy-4-methoxybenzophenone-5-sulfonic acid) is one of the most popular UV-filters used in cosmetics at a maximum concentration of 10% (Japan), 10% (Australia), 6% (USA), 5% (EU), and 5% (China) (MHLW, 2000; TGA, 2003; FDA, 1999; EC, 1976; MOH, 2007). A survey on the UV-filter ingredients of 329 sunscreen products available in the UK market revealed that the prevalence of BP-4 in all skin products and children's products were 2.9% and 4.8%, respectively (Wahie et al., 2007). However, studies on the detection and biological effects of BP-4 were rarely reported until a novel analytical method for BP-4 in environmental water samples was established in 2008 (Rodil et al., 2008). It was thus surprising to observe that the concentration of BP-4 from UV-filters were ranging from 237 to 1481 ng L^{-1} in examined wastewater samples, whereas the elimination efficiency was quite limited in wastewater treatment plants (Rodil et al., 2008). Furthermore, hundreds of ng L^{-1} of BP-4 has also been detected in river water and sea water, and it exhibited higher concentrations in July than in January or March (Rodil et al., 2008). Following the introduction of a special polar organic chemical integrative sampler (POCIS) for improving the extraction ratio of UV-filters (Alvarez et al., 2004), a high level of BP-4 (0.43–1344 ng $(POCIS)^{-1}$) has been discovered in natural water samples (Zenker et al., 2008). The highest residual level of UV-filters in river water, among the studied cases, was reported from an investigation in Switzerland. Using POCIS method, BP-4 concentration was measured as 0.27–24.0 μg $(POCIS)^{-1}$ (Fent et al., 2010).

UV-filters are often inert in traditional wastewater treatment processes, and thus have the potential to contaminate the reclaimed water system, natural water bodies, and even drinking water resources. Disinfection with free available chlorine (FAC, $HOCl/OCl^-$) to reduce pathogenetic risk is a common practice for the treatment of drinking water, swimming pool water and in wastewater reclamation. During this process, residual UV-filters are able to react with the added disinfectant to form chlorinated, oxidized, and fragmented by-products (Deborde and von Gunten, 2008; DellaGreca et al., 2009; Yang and Shang, 2004; Dodd and Huang, 2004; Pinkston and Sedlak, 2004; Hu et al., 2003; Buth et al., 2007). For example, Sakkas and coworkers identified mono-chlorinated by-products of octyl-dimethyl-*p*-aminobenzoic acid in swimming pool water (Sakkas et al., 2003).

Negreira et al. (2012) investigated the stability of BP-4 in free chlorine-containing water using liquid chromatography quadrupole time-of-flight mass spectrometry (LC–QTOF-MS). At neutral pH, in excess of chlorine, the degradation of BP-4 was noticeable and 3 products including chlorinated and ester products were detected. The study indicated the importance of the chlorination process of BP-4 in the environment. However, on one hand, some nucleophilic agents (e.g., OCl^-) in the chlorination system (Jencks and Carriuolo, 1960), could further react with active functional groups such as sulfonic acid, ester to form more products. These products need to be explored and the transformation behaviors of BP-4 under different operating conditions (various pH values and doses of FAC) should be investigated as well. On the other hand, the changes of biological effect in chlorination treatment should be of concerns. Based on the above consideration, the goal of this study was to explore the comprehensive reaction mechanisms of BP-4 with FAC in aquatic media. The transformation products even those with low responses were separated and carefully recognized using both HPLC and GC, and their structures were elucidated based on MS and NMR spectra. Cases under different pH values and with different doses of FAC were studied to verify and complete the mechanism. In addition, in order to obtain an overall transformation characteristics of BP-4 in chlorination process, genotoxicity changes during chlorination process were screened and transformation kinetics was recorded as well.

2. Materials and methods

2.1. Chemicals and solutions preparation

BP-4 was purchased from Sigma–Aldrich. The sodium hypochlorite (8%) aqueous solution was obtained from Wako Co. (Japan). Methanol (for HPLC analysis) was purchased from Fisher Scientific (USA). Formic acid (for HPLC analysis) was purchased from Acros Organics (USA). All other chemicals were of reagent grade and used without further purification. Ultrapure water generated using a Millipore Purification System (Milli-Q water) was used throughout the analytical experiments. All stock solutions were prepared and diluted with Milli-Q water without adding any organic co-solvent. The concentration of FAC stock solution was standardized using iodometric titration method according to the recommended procedure (APHA, 1998).

2.2. Chlorination experiments and samples preparation

The experiments were performed in a 1000 mL borosilicate glass conical flask, which was wrapped with aluminum foil and placed in a water bath with a magnetic stirring apparatus to maintain the reaction temperature at 25 ± 0.5 °C. Based on the relative distribution of FAC species at different pH values