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The chlorination transformation characteristics of benzophenone-4 in the presence of iodide ions

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ABSTRACT

Benzophenone-type UV filters are a group of compounds widely used to protect human skin from damage of UV irradiation. Benzophenone-4 (BP-4) was targeted to explore its transformation behaviors during chlorination disinfection treatment in the presence of iodide ions. With the help of ultra performance liquid phase chromatograph and high-resolution quadrupole time-of-flight mass spectrometer, totally fifteen halogenated products were identified, and five out of them were iodinated products. The transformation mechanisms of BP-4 involved electrophilic substitution generating mono- or di-halogenated products, which would be oxidized into esters and further hydrolyzed into phenolic derivatives. The desulfonation and decarboxylation were observed in chlorination system either. Obeying the transformation pathways, five iodinated products formed. The pH conditions of chlorination system determined the reaction types of transformation and corresponding species of products. The more important was that, the acute toxicity had significant increase after chlorination treatment on BP-4, especially in the presence of iodide ions. When the chlorination treatment was performed on ambient water spiked with BP-4 and iodide ions, iodinated by-products could be detected.

Introduction

With the rapid deterioration of the global climate, the depletion of the ozone layer becomes an extremely serious problem. Consequently, the UV (ultraviolet) irradiation level to the earth and the exposure dose to human body has significant increased, which can cause skin darkening and injury or even skin cancer. In recent decades, UV filters have been widely used not only in personal care products, such as cosmetics, lotions, lipsticks and shampoos (Roelandts et al., 1983; Diaz-Cruz et al., 2008; Fent et al., 2010; Manová et al., 2013), but also in pharmaceuticals, insecticides, and agricultural chemicals. The permitted maximum content of some UV filters may be up to 10% of the product weight (SJP, 1985; TGA, 2003). With the routine activities of human beings, such as bathing, swimming, leaching of land, house coating and effluent discharging from wastewater treatment plants, UV filters enter into the environment (Kasprzyk-Hordern et al., 2008a; Poiger et al., 2004; Giokas et al., 2007). Benzophenone-type compounds (BPs), one of the major classes of UV filters, are able to protect human skin from the harms of UVA (ultraviolet A, 320–400 nm) and UVB (ultraviolet B, 290–

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320 nm) (Moloney et al., 2002). BP-3 (2-hydroxy-4-methoxy-BP) and BP-4 (2-hydroxy-4-methoxy-5-sulfonic acid-BP) have been approved as additives of sunscreens by the European Legislation (Shaath, 2007). The maximum concentrations of BP-4 permitted in cosmetics are 10%, 10%, 5% and 5% in Japan, Australia, China and EU respectively (SJP, 1985; TGA, 2003; EEC, 1983; MOH, 2007). It was reported that the residual concentrations of BP-4 were at hundreds of ng/L in river and sea water, and ranged from 237 to 1481 ng/L in wastewater samples (Rodil et al., 2008). On the other hand, BP-4 levels in the inlet and outlet streams of activated sludge sewage plants were over 5 and 4 μg/L, respectively (Kasprzyk-Hordern et al., 2008b). This result suggested that BP-4 was stable enough to survive from the conventional biodegradation processes (Rodil et al., 2008). The residue of benzophenones in the environment would pose potential risk to fish and other organisms (Zucchi et al., 2011). Many reports showed that BP-type chemicals exhibited multiple biological effects, such as exerting uterotrophic effect *in vivo* (Kawamura et al., 2003), increasing the secretion of the tumor marker pS2 *in vitro*, and stimulating the proliferation of MCF-7 breast cancer cells (Schlumpf et al., 2001). In particular, a current epidemiological survey showed that BP-2 (2,2′4,4′-tetrahydroxy-BP) and 4-HBP (4-hydroxy-BP) were associated with 31% and 26% reduction in fecundity, respectively (Louis et al., 2014). Therefore, BPs have been defined as "chemicals suspected of having endocrine disrupting effects" by the Japanese Ministry of Environment (MOE, 2000). In addition, some other studies showed that BPs could bioaccumulate in human body, exhibited genotoxicity and reproductive toxicity (Zhao et al., 2013; Krause et al., 2012).

Disinfection with free available chlorine (FAC, $HOCl/OCl^-$) is the most common method to kill harmful pathogens in water treatment process. Except for killing pathogens, FAC can also react with some residual chemicals in water. Many reports showed that the residual UV filters may undergo chlorination, oxidation and decarboxylation to generate some unintended poisonous disinfection by-products (DBPs) during chlorination disinfection treatment (Xiao et al., 2013; Deborde and von Gunten, 2008; DellaGreca et al., 2009; Dodd and Huang, 2004; Pinkston and Sedlak, 2004; Buth et al., 2007). Recent studies evidenced that some non-regulated DBPs, *e.g.*, halogenated aromatic transformation products, and some regulated DBPs, such as trihalomethanes and haloacetic acids with high toxicity could be formed during chlorination of BPs (Yang and Zhang, 2013; Pan et al., 2016; Liu and Zhang, 2014). Moreover, some inorganic ions in natural aquatic system, such as Br^- and I^-, would affect the formation of DBPs (Deborde and von Gunten, 2008). It has been reported that the concentration of I^- in natural water bodies generally ranges from 0.5 to 20 μg/L, even reaches 50 μg/L in offshore surface water and some special geographical regions of the world (Fuge and Johnson, 1986). During the oxidation and disinfection treatment, the disinfectant chlorine oxidizes I^- to hypoiodous acid (HOI) rapidly (Nagy et al., 1988). And HOI would further react with natural organic matter (NOM) or pollutants in water to form iodo-organic compounds. Many kinds of iodinated DBPs, such as iodinated trihalomethanes (Bichsel and von Gunten, 2000) and iodoacetic acid have been detected in drinking water treated with chlorine (Weinberg et al., 2002; Liu et al., 2017; Ye et al., 2013). More importantly, iodinated DBPs usually exhibit higher toxicity than brominated and chlorinated analogs. For example, the toxicity of iodoacetic acid on Chinese hamster ovarian cells is 3.2 and 287.5 fold higher than that of bromoacetic acid and chloroacetic acid, respectively (Plewa et al., 2004).

In our previous study on transformation characteristics of BP-4 in chlorination process, 13 products were identified (Xiao et al., 2013). In the presence of Br^-, 12 products containing bromine atom were found in the chlorination system (Xiao et al., 2014; Negreira et al., 2012). Especially, the toxicity of reaction mixture with bromide ions was much higher than reaction mixture without bromide ions (Xiao et al., 2014). Since very little is known about the impacts of iodide ions on the BP-4 chlorination, the objectives of this study were to investigate the formation of transformation products and the acute toxicity variation during chlorination of BP-4 in the presence of iodide ions. Ultra performance liquid phase chromatography in tandem with quadrupole time-of-flight mass spectrometry (UPLC-QTOF-MS) was used for separating and identifying the transformation products, and the possible formation pathways of iodinated products were proposed. Especially, photobacterium bioassay was used for tracing the acute toxicity changes of chlorinated BP-4 in the presence of iodide ions.

1. Materials and methods

1.1. Chemical reagents and instruments

BP-4 (2-hydroxy-4-methoxy-5-sulfonic acid-benzophenone) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Salts including HOAc, NaAc, Na_2CO_3, $NaHCO_3$, $Na_2HPO_4{\cdot}12H_2O$ and $KH_2PO_4{\cdot}5H_2O$ for preparing buffer solutions, NaCl and Na_2SO_3 for preparing toxicity test medium and quenching solutions, were purchased from Sigma-Aldrich (St Louis, MO, USA). The sodium hypochlorite (8%) aqueous solution was obtained from Wako Co. (Tokyo, Japan). The concentration of chlorine stock solution was determined using the N,N-diethyl-phenylenediamine ferrous titration method. Methanol (for high performance liquid phase chromatography (HPLC) analysis) was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Formic acid (for HPLC analysis) was purchased from Acros Organics (Belgium, WI, USA). All reagents were diluted with ultrapure water and used without further purification. The test bacteria *Photobacteria phosphoreum* T3 Straus was provided as freeze-dried powder by the Institute of Soil Science, Chinese Academy Science, Nanjing, China. The ultrapure water used in solution preparation and dilution was produced by a Milli-Q purification system (Millipore, Billerica, MA, USA). An Ultimate 3000 UPLC (Dionex, USA) and QTOF-MS (micrOTOF QII, Bruker, Germany) were used to separate and identify the transformation products of BP-4 during chlorination treatment in the presence of iodide ions.

1.2. Chlorination experiments

The experiments were performed in a 1000 mL of borosilicate glass screw-cap conical flask, which was wrapped with aluminum foil and placed in water bath with a magnetic