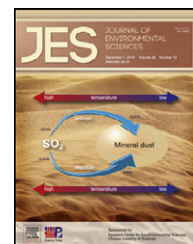


Available online at www.sciencedirect.com

ScienceDirect

www.journals.elsevier.com/journal-of-environmental-sciences

Formation pathways of brominated products from benzophenone-4 chlorination in the presence of bromide ions

Ming Xiao^{1,2}, Dongbin Wei^{1,*}, Liping Li¹, Qi Liu¹, Huimin Zhao¹, Yuguo Du^{1,2}

1. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: why1986@sina.com

2. University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 9 January 2014

Revised 19 March 2014

Accepted 10 April 2014

Available online 16 October 2014

Keywords:

UV-filters

Benzophenone

Chlorination

Brominated products

Acute toxicity

ABSTRACT

The brominated products, formed in chlorination treatment of benzophenone-4 in the presence of bromide ions, were identified, and the formation pathways were proposed. Under disinfection conditions, benzophenone-4 would undertake electrophilic substitution generating mono- or di-halogenated products, which would be oxidized to esters and further hydrolyzed to phenol derivatives. The generated catechol intermediate would be transformed into furan-like heterocyclic product. The product species were pH-dependent, while benzophenone-4 elimination was chlorine dose-dependent. When the chlorination treatment was performed on ambient water spiked with benzophenone-4 and bromide ions, most of brominated byproducts could be detected, and the acute toxicity significantly increased as well.

© 2014 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

UV filters are widely used in pharmaceuticals, insecticides, agricultural chemicals and personal care products (Roelandts et al., 1983; Stenback, 1977; Tomson et al., 1981). As main ingredients of these products, UV filters have a great chance to enter the environment through swimming, bathing, and leaching of land and house coating (Poiger et al., 2004; Giokas et al., 2007; Plagellat et al., 2006). Benzophenone-type chemicals (BPs) are a primary member in the UV filter family. BP-3 (2-hydroxy-4-methoxy-BP) and BP-4 (2-hydroxy-4-methoxy-5-sulfonic acid-BP) have been approved by the European Legislation to be used in sunscreens (Shaath, 2007). The maximum concentration range permitted for BP-4 in cosmetics is from 5% to 10% in Japan, Australia, USA, EU and China (MHLW, 2000; TGA, 2003; FDA, 1999; EC, 1976; MOH, 2007). Due to its higher polarity, BP-4 was mainly detected within the water phase (Zenker et al., 2008). The residual concentrations of BP-4 were at hundreds of ng/L level in river and sea water, and

ranged from 237 to 1481 ng/L in wastewater samples (Rodil et al., 2008). However, many studies showed that BP-4 had no significant deduction in conventional biodegradation processes (Rodil et al., 2008; Kasprzyk-Hordern et al., 2008), bringing the risks to fish and other aquatic organisms through interruption of their sexual hormone system (Zucchi et al., 2011). For example, BP-type chemicals exhibited multiple adverse biological effects, such as uterotrophic effects *in vivo*, 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). Benzophenone has been classified as “chemicals suspected of having endocrine disrupting effects” by Japanese Ministry of Environment (NIES, 1998).

Disinfection with free available chlorine (FAC, HOCl/OCl⁻) is a necessary process for drinking water, swimming pool water and wastewater reclamation treatment. During these processes, residual UV-filters may react with disinfectant to form chlorinated,

* Corresponding author. E-mail addresses: weidb@cees.ac.cn (Dongbin Wei), why1986@sina.com (Liping Li), why1986@sina.com (Qi Liu), why1986@sina.com (Huimin Zhao), why1986@sina.com (Yuguo Du).

oxidized, and fragmented byproducts (Deborde and 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). Negreira et al. (2008) studied the stability of three UV-filters under chlorination conditions and identified up to 8 byproducts for BP-3. Sakkas et al. (2003) detected mono-chlorinated byproducts of octyl-dimethyl-p-aminobenzoic in swimming pool water.

Except for dissolved organic materials, some inorganic ions, such as Br^- , I^- , and SO_3^{2-} in ambient water bodies, would also affect the chlorination process (Deborde and Gunten, 2008). It was reported that Br^- in natural water was around 100 $\mu\text{g/L}$ in the USA, and it could reach as high as 2000 $\mu\text{g/L}$ in some regions of the world (Richardson et al., 2003). Deborde and Gunten (2008) concluded the reaction of chlorine with bromide. During chlorination, bromide was oxidized by hypochlorous acid and hypochlorite, due to chlorine and bromide standard redox potentials. First, a BrCl -type intermediate would be formed via the transfer of Cl^{6+} from hypochlorous acid to the bromide (Br^-). Then the BrCl -type intermediate was hydrolyzed and lead to OBr^- (reactions (1) and (2)) (Kumar et al., 1986; Kumar and Margerum, 1987; Johnson and Margerum, 1991).



The small amount of chemically active bromine would be formed during traditional chlorination process (Gallard et al., 2003; Acero et al., 2005), leading to brominated byproducts (Gallard et al., 2003; Acero et al., 2005; Hu et al., 2006). Gallard et al. (2003) studied the kinetics of bromination based on *ortho*- and *para*-substituted phenols, and found that the reaction rate was about 1000-fold higher than that of chlorination in drinking water treatment conditions. Besides, brominated disinfection byproducts usually exhibited more significant toxicity than their chlorinated analogs (Richardson et al., 2007), causing more safety concerns in this regard (Xiao et al., 2012).

In our previous study on the transformation characteristics of BP-4 in chlorination process, 13 transformation products were identified, and the possible transformation mechanisms were proposed (Xiao et al., 2013). However, the influences of Br^- on BP-4 transformation were not involved. Negreira et al. (2012) preliminarily investigated the effects of Br^- on the transformation kinetics of BP-4 in chlorination system, and detected four brominated products (m/z : 384.9387, 400.9336, 478.8441, 434.8946). Theoretically, more brominated products would be formed, their molecular structures, and possible formation pathways in BP-4 chlorination system containing Br^- ions should be deeply explored. Therefore, in the present study, the brominated products were separated using gradient high performance liquid chromatography (or gas chromatography), and their structures were elucidated by mass spectrometry information. The possible formation pathways were proposed and verified by orthogonal experiments under different pH levels and FAC doses. Moreover, BP-4 chlorination experiments were conducted in ambient water matrices, to simulate its transformation characteristics in water treatment practices, and to confirm the formation of brominated products in bromide-containing chlorination disinfection system.

1. Materials and methods

1.1. Chemicals and solutions preparation

BP-4 (2-hydroxyl-4-methoxybenzophenone-5-sulfonic acid, purity >97%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). NaClO (8%) aqueous solution was obtained from Wako Co. (Tokyo, Japan). Methanol (for HPLC analysis) was purchased

from Fisher Scientific (Fair Lawn, NJ, USA). Formic acid (for HPLC analysis) was purchased from Acros Organics (Belgium, WI, USA). Potassium bromide and all other chemicals were of reagent grade and used without further purification. Ultrapure water (Milli-Q water) generated from Millipore Purification System (Billerica, MA, USA) was used throughout the analytical experiments. All stock solutions were prepared and diluted with Milli-Q water without adding any organic co-solvent.

1.2. Chlorination procedures

The experiments were conducted in a 1000 mL of borosilicate glass conical flask which was placed in a water bath with a magnetic stirring apparatus to maintain the reaction temperature at 25 ± 0.5 °C. In order to have a comprehensive understanding of the reaction, experiments were carried out under three different pH values (pH 4.6, 7.5 and 11). And the relative distributions of FAC and bromine species are shown in Appendix A Fig. S1. Considering the buffer capacity and adverse effects of excessive salts on instrumental detection and toxicity tests, the concentrations of buffer solutions were optimized. The 0.1 mol/L of acetate buffer (pH = 4.6), 0.02 mol/L of phosphate buffer (pH = 7.5) and 0.02 mol/L of carbonate buffer (pH = 11.0) were used to maintain pH within 0.1 unit of variance during the reaction period.

In order to permit the isolation of sufficient amounts of products for characterization by HPLC/MS and GC/MS, the chlorination experiments were conducted with a relatively high concentration of BP-4 and FAC. Reactions were initiated by adding appropriate volumes of FAC solution (molar equivalent ratio of $[\text{FAC}]_0:[\text{BP-4}]_0$ was set at 0.5:1, 1:1, 3:1, 5:1, 10:1 and 20:1) to 500 mL solutions containing 5 mmol/L of BP-4 and 5 mmol/L of KBr. Five milliliters of reaction mixture was subsequently taken at evenly-spaced time intervals and sodium sulfite solution was immediately added to quench residual FAC. The samples were then analyzed by ultra performance liquid chromatography and quadrupole-time of flight mass spectrometer (UPLC-QTOF-MS) or gas chromatography-mass spectrometer (GC-MS) to measure the loss of BP-4 and generation of transformation products.

For UPLC-QTOF-MS analysis, the quenched sample was directly injected after filtration through 0.22 μm glass fiber membrane. For GC-MS analysis, the sample is required to be anhydrous, so the aqueous reaction mixture after quenching was dehydrated. Specifically, 5 mL of aqueous sample was freeze-dried to remove solvent water, then 1 mL of methanol/acetone (1/1, V/V) solvents was added to extract transformation products. The extract was divided into two aliquots, one was for GC-MS analysis after filtrating through 0.22 μm glass fiber membrane, and the other was for acute toxicity test after a solvent conversion. The solvent methanol/acetone was dried with a gentle nitrogen gas stream (300 mL/min), and the solid was re-dissolved with 0.2 mL of DMSO. The DMSO was maintained at 0.1% in each exposing well.

1.3. Identification of transformation products

1.3.1. Ultra liquid chromatography-mass spectrometry method
To obtain MS^1 spectrum, an UPLC-QTOF-MS (Ultimate 3000, Dionex, Sunnyvale, CA, USA; microTOF QII, Bruker, Bremen,

Download English Version:

<https://daneshyari.com/en/article/4454314>

Download Persian Version:

<https://daneshyari.com/article/4454314>

[Daneshyari.com](https://daneshyari.com)