



# Transformation pathways and acute toxicity variation of 4-hydroxyl benzophenone in chlorination disinfection process



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## HIGHLIGHTS

- 7 transformation products in 4HB chlorination disinfection system were identified.
- Transformation pathways of 4HB during chlorination disinfection were proposed.
- Acute toxicity increased after chlorination due to the formation of 3,5-dichloro-4HB.
- The transformation mechanisms of 4HB can be repeated in ambient water matrices.

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## ABSTRACT

Benzophenones compounds (BPs) are widely used as UV filters, and have been frequently found in multiple environmental matrices. The residual of BPs in water would cause potential threats on ecological safety and human health. Chlorination disinfection is necessary in water treatment process, in which many chemicals remained in water would react with disinfectant chlorine and form toxic by-products. By using ultra performance liquid phase chromatography quadrupole time of flight mass spectrometer (UPLC-QTOF-MS), nuclear magnetic resonance (NMR), the transformation of 4-hydroxyl benzophenone (4HB) with free available chlorine (FAC) was characterized. Eight major products were detected and seven of them were identified. Transformation pathways of 4HB under acid, neutral, and alkaline conditions were proposed respectively. The transformation mechanisms involved electrophilic chlorine substitution of 4HB, Baeyer-Villiger oxidation of ketones, hydrolysis of esters and oxidative breakage of benzene ring. The orthogonal experiments of pH and dosages of disinfectant chlorine were conducted. The results suggested that pH conditions determined the occurrence of reaction types, and the dosages of disinfectant chlorine affected the extent of reactions. Photobacterium assay demonstrated that acute toxicity had significant increase after chlorination disinfection of 4HB. It was proved that 3,5-dichloro-4HB, one of the major transformation products, was responsible for the increasing acute toxicity after chlorination. It is notable that, 4HB at low level in real ambient water matrices could be transformed during simulated chlorination disinfection practice. Especially, two major products 3-chloro-4HB and 3,5-dichloro-4HB were detected out, implying the potential ecological risk after chlorination disinfection of 4HB.

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## 1. Introduction

With the increasing concern about the effects of ultraviolet (UV) irradiation, more and more UV filters especially organic types with better sun protection factors, higher photo stability, and better water resistance have been produced and used throughout the last decades. Besides cosmetics such as lotions, shampoos, and lipsticks in personal care products, UV-filters are also widely used in

insecticides, agricultural chemicals, pharmaceuticals and material preservatives, e.g. textiles and numerous other products (Christin et al., 2007; Roelandts et al., 1983; Stenback, 1977; Tomson et al., 1981). Benzophenones (BPs), one class of commonly used UV-filters, have wide absorption wavelength range at 200–400 nm. BPs are effectively used in preventing some skin diseases even skin cancer, for reducing the harms of UVA (320–400 nm) and UVB (290–320 nm) to human body completely (Moloney et al., 2002). In addition, BPs are also used as agricultural chemicals, flavor ingredients and UV stabilizers in plastic surface coatings for food packaging and in the manufacture of cosmetics and other personal care products due to their low cost (Suzuki et al., 2005; Zenker et al., 2008). The maximum authorized concentration of 2-hydroxy-4-methoxy-BP (BP-3) in sunscreens is 10% in EU, 6% in USA, 2,2'-dihydroxy-4-methoxy-BP (BP-8) is 3% in Korea (EEC, 1983; FDA, 1999; Jeon et al., 2006). 2-Hydroxy-4-methoxy-5-sulfonic acid BP (BP-4) is permitted for use in cosmetics at a maximum concentration of 10% in Japan and Australia (SJP, 1985; TGA, 2003). As a result, a large amount of residual BPs and their metabolites enters into the aqueous environment via washing off from skin and clothes, or discharging of sewage and swimming pool waters (Kim and Choi, 2014). The concentration of BP-4 ranged from 237 to 1481 ng L<sup>-1</sup> in wastewater from Galicia (NW Spain) (Rodil et al., 2008). 2,4-Dihydroxy-BP (BP-1) was detected with the mean concentration of 47 ng L<sup>-1</sup> in 25 rivers in Korea, and benzhydrol, a major metabolite of benzophenone was detected with the highest concentration of 204 ng L<sup>-1</sup> as well. Meanwhile, the concentration of BP-3 and BP-8 ranged from 730 to 3880 and 500–4170 ng kg<sup>-1</sup> in soil samples, respectively (Jeon et al., 2006). It has been proved that human bodies would absorb and accumulate BPs after skin administration. BP-3 was detected up to 445 ng g<sup>-1</sup> lipid in human breast milk samples (Hany and Nagel, 1995), up to 40 µg L<sup>-1</sup> in urine samples (Zwiener et al., 2007). BP-1, a metabolite of BP-3, has also been detected in urine after application of commercially available sunscreen products to the skin (Felix et al., 1998).

BPs are bioaccumulative in organisms due to their hydrophilicity, which would make adverse biological effects. For example, BPs exhibited both estrogenic and anti-androgenic properties in a variety of organisms, exerted auterotropic effect *in vivo* test, stimulated cell proliferation of human breast cancer cell line MCF-7 (Michigan Cancer Foundation7) and increased the secretion of tumor marker pS2 (an estrogen-induced protein) *in vitro* (Balmer et al., 2005; Ma et al., 2003; Schlumpf et al., 2001; Schreurs et al., 2005; Zenker et al., 2008). Moreover, some BPs such as benzophenone, BP-3 and BP-8, 2,3,4-trihydroxy-BP (BP-20) have been reported to have potential genotoxic effects (Fluck et al., 1976; French, 1992; Jeon et al., 2007; Mortelmans et al., 1986; Zeiger et al., 1987). Some BPs have also been observed obvious genotoxic effects at high milligram per liter level (Zhao et al., 2013). A current epidemiological survey suggested that male exposure to 2,2',4,4'-tetrahydroxy-BP (BP-2) or 4-hydroxyl benzophenone (4HB) may diminish couples' fecundity by about 30 percent, resulting in a longer time to pregnancy (Louis et al., 2014).

Disinfection is one of necessary processes for producing tap water, reclaimed water, and swimming pool water. Chlorine is still one of the most popular disinfectants in the world due to its high efficiency, convenience and low cost. However, except for killing pathogens, chlorine may react with the residual chemicals and natural organic matter in water, and generate some unintended toxic disinfection by-products (DBPs). More than 600 DBPs have been identified in drinking water, and many of them are mutagenic or carcinogenic (Richardson, 1998; Richardson et al., 2007). During

chlorination of BP compounds, halogenated aromatic DBPs might be formed. And recent studies have shown that halogenated aromatic DBPs were significantly more toxic than the regulated trihalomethanes and haloacetic acids (Yang and Zhang, 2013; Pan et al., 2016; Liu and Zhang, 2014). The formation mechanisms and potential ecological or health risk of DBPs should be paid more attention, which would provide scientific reference for optimizing disinfection operating parameters. The substitution and cleavage of two benzene rings of BP-3 and BP-4 in chlorination disinfection have been reported (Negreira et al., 2008, 2012; Xiao et al., 2013). Bromoform was found to be generated from BP-3 during the chlorination of seawater swimming pools (Manasfi et al., 2015). However, the toxicity changes after chlorination disinfection of BPs, identification and formation pathways of toxic products have not been disclosed systematically. It is well known that lots of chemical reactions occur in chlorination disinfection system, and the components in chlorinated solution are quite complex. Furthermore, the target chemicals selected in the previous literature usually had complex molecular structures, which increased the difficulty in identifying products structures and analyzing transformation mechanisms. If a model chemical with simple structure and similar reactivity is selected, it will be quite easier to disclose common transformation characteristics of pollutants comprehensively. Therefore, the present paper focused on the chlorination disinfection of 4HB, identified the main transformation products, and proposed the plausible transformation pathways under acid, neutral and alkaline conditions, respectively. Moreover, the acute toxicity variation of 4HB after chlorination treatment under different conditions was monitored to screen transformation products with high toxicity. The results of this study would throw more light on the transformation mechanism of BPs in water disinfection treatment, and provide scientific basis to the risk evaluation of this kind of compounds.

## 2. Methods and materials

### 2.1. Reagents and instruments

4HB (>97.5% purity) was purchased from Sigma-Aldrich (St Louis, MO, USA) which was used directly without further purification. Salts including HOAc (acetic acid), NaOAc (sodium acetate), Na<sub>2</sub>CO<sub>3</sub> (sodium carbonate), Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O for preparing buffer (pH = 4.6, 7.5 and 11.0 with the concentration of 0.02 M), KH<sub>2</sub>PO<sub>4</sub>, NaCl and Na<sub>2</sub>SO<sub>3</sub> for toxicity test medium and quenching solutions, were purchased from Sigma-Aldrich (St Louis, MO, USA). Yeast extract, tryptone and glycerol were obtained from BD (Franklin Lakes, NJ, USA). Methanol and acetone for HPLC analysis were obtained from Fisher Sci (Fair Lawn, NJ, USA). Dimethylsulfoxide (DMSO) was purchased from Amresco (Solon, OH, USA). The NaClO (8%) aqueous solution was purchased from Wako Co (Tokyo, Japan). The test bacteria *Photobacterium phosphoreum* T3 Straus was provided as freeze-dried powder by the Institute of Soil Science, Chinese Academy Sciences, Nanjing, China. The ultrapure water used in solution preparation and dilution was produced by a Milli-Q purification system (Millipore, Billerica, MA, USA). An Ultimate3000 UPLC (Dionex, USA) and QTOF-MS (microTOF QII, Bruker, Germany) were used to separate and identify the main transformation products of 4HB after chlorination in different buffer system.

### 2.2. Chlorination experiments

Considering the relative distribution and properties of free

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