



Enhanced formation of chlorinated disinfection byproducts in the UV/chlorine process in the presence of benzophenone-4



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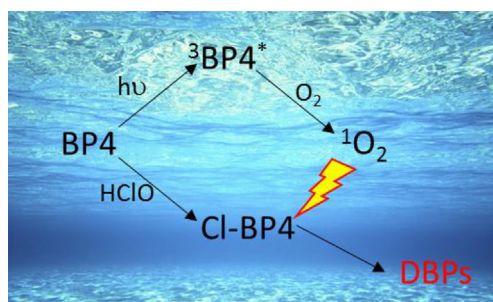
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HIGHLIGHTS

- BP4 was efficiently removed by chlorine, chloramine, and UV/chlorine treatment.
- Removal of BP4 by UV/chlorine was mostly arose from the reactions with $\cdot\text{OH}$ and $\text{Cl}\cdot$.
- Methanol in the UV/chlorine process suppressed BP4 removal but enhanced DBPs formation.
- $^3\text{BP4}^*$ and $^1\text{O}_2$ could be formed because of the photochemical activity of BP4.
- $^1\text{O}_2$ was responsible for DBP formation in the UV/chlorine/methanol process.

GRAPHICAL ABSTRACT



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ABSTRACT

Benzophenone-4 (BP4) is UV-filter that is widely in sunscreens and cosmetics to prevent skin damage from sunlight exposure. Washing off of BP4 from the human body in swimming pools represents a direct source of BP4 in the environment. In this study, we investigated the transformation of BP4 by free chlorine, chloramine, and UV/chlorine, which can be found in swimming pool water. It was found that BP4 can be rapidly removed by both chlorine and chloramine treatment, but only chlorination led to appreciable formation of chlorinated disinfection by-products (DBPs), such as dichloroacetic acid and trichloroacetic acid. However, chloramination of BP4 resulted in higher levels of chlorinated intermediates, which were relatively recalcitrant to further chlorination. The UV/chlorine process was significantly more efficient than the chlorine treatment alone for BP4 removal and resulted in trace chlorinated intermediates and formation of DBPs. Radical scavenger tests revealed that the removal of BP4 in the UV/chlorine process was mostly ascribed to reactions with the $\text{Cl}\cdot$ and $\cdot\text{OH}$ generated from HClO photolysis. The presence of methanol as a radical scavenger resulted in incomplete removal of BP4 in the UV/chlorine process and enhanced the formation of DBPs. The increase in DBP formation was because the residual BP4 can be excited to a triplet state ($^3\text{BP4}^*$) upon UV irradiation. $^3\text{BP4}^*$ subsequently reacted with O_2 to form $^1\text{O}_2$, a reactive oxygen species that generated DBPs by reacting with chlorinated intermediates in water. All benzophenone-type UV-filters may have similar photochemical activity and thus influence the transformation of other organics in sunlit surface water environments.

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1. Introduction

Due to their widespread presence in the environment and the risks associated with their presence, organic UV-filters are considered to be emerging contaminants [1–6]. Benzophenone (BP) has two benzene rings jointed by a carbonyl group. Depending on the number and types of the functional groups attached to the backbone, a total of 12 substituted derivatives of BP are commercially used as UV-filters. Among them, BP3 (2-hydroxyl-4-methoxyphenone) and BP4 (2-hydroxy-4-methoxybenzophenone-5-sulphonic acid) are the most widely known and have been approved for use in the EU, the U.S., China, Japan, and many other countries [7,8]. High levels of BP3 and BP4 have been detected in water used for recreational purposes [9–11].

Although BP3 and BP4 are relatively resistant to direct photodegradation and biodegradation, they are readily degraded by advanced oxidation, such as Fenton oxidation, TiO₂ catalyzed oxidation, activated persulfate oxidation, and sonication [12–15]. BP3 and BP4 are also highly unstable in the presence of chlorine [16–23]. Under typical water chlorination conditions, the half-lives of BP3 and BP4 range from seconds to a few minutes [7,16,20,21]. Free chlorine reacts with BPs via the electrophilic substitution mechanism, resulting in the stepwise incorporation of Cl atoms into the methoxyphenol moiety [7,16,17]. Cleavage of the chlorinated ring due to further chlorination/oxidation leads to the formation of a variety of chlorinated disinfection by-products (DBPs), such as chloroform and chloroacetic acids [16,17,20,22].

The reactions between chlorine and BPs have been well investigated. However, few studies have examined the reactions of BPs under swimming pool water conditions, where chlorine can be present in both free and combined forms. In addition, BPs in outdoor swimming pool water can be exposed to UV light. UV disinfection is also applied in swimming pool water treatment systems through which water is cycled and reused. Chlorine rapidly decomposes to Cl· and ·OH upon UV irradiation [24–26]. As a highly potent oxidant, ·OH reacts with a wide spectrum of organic compounds at nearly diffusion-controlled rates [27]. Cl· is also highly reactive to electron-rich compounds [24,28]. A synergistic effect between UV and chlorine was demonstrated during the degradation of contaminants, which were otherwise less reactive to UV or chlorine alone [29–31]. UV/chlorine has been developed as an advanced water treatment strategy to address micropollutants [24,28,32].

In the present study, we investigated the transformation of BP4 by chlorine, chloramine, and UV/chlorine, which are expected to be found in swimming pool water. We demonstrated that BP4 acted as a photosensitizer, leading to the increased formation of DBPs in the presence of UV irradiation. Such photochemical activity has not been previously reported. We assume that other BP-type UV-filters would have a similar property, which could affect the fate of organic compounds that are co-present in UV-based water treatment processes and sunlit environments.

2. Materials and methods

2.1. Materials

A BP4, 3,4,5-trimethylphenol (TMP), furfuryl alcohol (FFA), and haloacetic acid calibration mixture was obtained from Sigma-Aldrich (St. Louis, MO). Sodium hypochlorite (NaClO) and *N,N*-dimethyl-1,4-phenylenediamine monohydrochloride (DPD) were purchased from Aladdin (Shanghai, China). Stock solutions of BP4 and NaClO were prepared by dissolving the reagents in Milli-Q water and storing them in a refrigerator. Prior to use, the free chlorine concentration of the NaClO stock solution was measured using the DPD method [33]. The chloramine (NH₂Cl) solution was freshly prepared by adding a NaClO stock solution dropwise to the NH₄Cl solution to achieve a final NH₄Cl/NaClO molar ratio of 1.2:1 following Schreiber and Mitch's method

[34]. The entire process was performed in a cooler at 4 °C. This could maximally inhibited the formation of di- and trichloramine [34,35]. The chloramine concentration was calculated assuming that free chlorine had been completely converted to NH₂Cl. Swimming pool water was sampled from the Fitness Center of Nanjing City. The sample was filtered through a 0.45 μm membrane. The residual chlorine and DBPs were analyzed immediately after sampling.

2.2. Reaction kinetics

Chlorination and chloramination of BP4 were performed in 40 mL borosilicate glass vials with polypropylene screw caps as batch reactors. The initial BP4 concentration was 1.0 mg/L. The reaction was initiated by rapid mixing of the BP4 solution with chlorine or chloramine. Phosphate buffer (10 mM) was added to maintain pH 7, and the molar ratio of chlorine or chloramine to BP4 was fixed at 10:1. The reactors were kept in the dark at 20 °C. The same conditions were applied for the UV/chlorine treatment except quartz vials were used as the reactors and placed in a BL-GHX-V photoreactor (Bilang, Shanghai, China) equipped with a low-pressure mercury lamp (ozone free, 15 W) emitting dominantly at 254 nm. The average UV fluence rate through the reaction volume was determined to be 4.68×10^{-7} Einstein·L⁻¹·s⁻¹ using atrazine as an actinometer. The detailed experimental procedures can be found in a study by Canonica et al. [36]. A more detailed description of the apparatus used for the photo reaction can be found in Fig. S1 in the Supporting Data. Aliquots of the solution were withdrawn from each reactor and quenched immediately with 20 μL of 1 M Na₂S₂O₃. To determine the contribution of the free radicals to BP4 removal in the UV/chlorine treatment, a concurrent experiment was conducted in the presence of 1 mM methanol. All samples were kept in a refrigerator at 4 °C until analysis for residual BP4.

2.3. Identification of the transformation products of BP4

Experiments were performed in 250 mL flasks in the dark. The initial concentration of BP4 was 1 mg/L and pH buffered at 7. The reaction was initiated by rapid mixing of a BP4 solution with an appropriate quantity of chlorine or chloramine stock solution. After 2 h of reaction, excess Na₂SO₃ was added to quench the residual chlorine or chloramine, and 2 mL of 98% sulfuric acid was added to reduce the pH to < 2. Then, solid phase extraction (SPE) using HyperSep C18 cartridges (Thermo Scientific, Waltham, MA) was performed to purify and concentrate the transformation products. Additional details of the procedure are described in the Supporting Information. For UV/chlorine, the reaction was performed in quartz vials in a photoreactor. After 2 h, the solution was taken out and quenched with Na₂SO₃ before being extracted by SPE as described above. The transformation products produced by UV/chlorine in the presence of 1 mM methanol were also collected for comparison. The SPE eluents were analyzed using an Agilent 1200 HPLC coupled with an Agilent G6410B Triple Quad Mass spectrometer with an electron spray ionization (ESI) source operated in the negative mode. The detailed instrumental setup is provided in the Supporting Information.

2.4. Formation of chloroacetic acids (CAAs)

The formation of CAAs in the chlorination, chloramination, and UV/chlorine processes was investigated in a series of vials. The initial BP4 concentration was 1 mg/L, and the chlorine/BP4 M ratio was 10. The other conditions were identical to those of the kinetic study. At pre-determined time points, a vial was sacrificed by adding 1 mM Na₂S₂O₃ (1 mM) to quench the reaction. The quenched reaction solutions were kept in a refrigerator until further treatment and analysis for CAAs.

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