



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Phototransformation of the sunlight filter benzophenone-3 (2-hydroxy-4-methoxybenzophenone) under conditions relevant to surface waters



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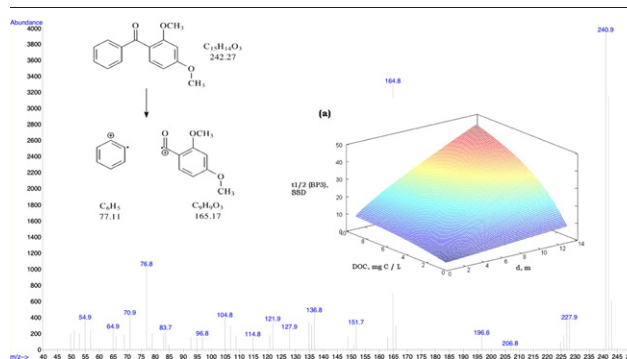
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HIGHLIGHTS

- Benzophenone-3 is mainly photodegraded by direct photolysis, $^{\bullet}\text{OH}$ and $^3\text{CDOM}^*$.
- Two methylated isomers, benzaldehyde and benzoic acid detected as intermediates.
- Phototransformation would be faster in shallow and DOM-poor water.
- Half-life times of benzophenone-3 are in the range of weeks to a couple of months.
- Transformation could be slower in sea-water due to $^{\bullet}\text{OH}$ scavenging by bromide.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 March 2013

Received in revised form 10 May 2013

Accepted 28 May 2013

Available online 26 June 2013

Editor: Adrian Covaci

Keywords:

Environmental modelling
Surface-water photochemistry
Indirect photolysis
Photosensitisers
Pharmaceuticals and personal care products

ABSTRACT

The UV filter benzophenone-3 (BP3) has UV photolysis quantum yield $\Phi_{BP3} = (3.1 \pm 0.3) \cdot 10^{-5}$ and the following second-order reaction rate constants: with $^{\bullet}\text{OH}$, $k_{BP3,^{\bullet}\text{OH}} = (2.0 \pm 0.4) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; with the triplet states of chromophoric dissolved organic matter ($^3\text{CDOM}^*$), $k_{BP3,^3\text{CDOM}^*} = (1.1 \pm 0.1) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$; with $^1\text{O}_2$, $k_{BP3,^1\text{O}_2} = (2.0 \pm 0.1) \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$, and with $\text{CO}_3^{\cdot-}$, $k_{BP3,\text{CO}_3^{\cdot-}} < 5 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$. These data allow the modelling of BP3 photochemical transformation, which helps filling the knowledge gap about the environmental persistence of this compound. Under typical surface-water conditions, direct photolysis and reactions with $^{\bullet}\text{OH}$ and $^3\text{CDOM}^*$ would be the main processes of BP3 phototransformation. Reaction with $^{\bullet}\text{OH}$ would prevail at low DOC, direct photolysis at intermediate DOC (around 5 mg C L^{-1}), and reaction with $^3\text{CDOM}^*$ at high DOC. If the reaction rate constant with $\text{CO}_3^{\cdot-}$ is near the upper limit of experimental measures ($5 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$), the $\text{CO}_3^{\cdot-}$ degradation process could be somewhat important for $\text{DOC} < 1 \text{ mg C L}^{-1}$. The predicted half-life time of BP3 in surface waters under summertime conditions would be of some weeks, and it would increase with increasing depth and DOC. BP3 transformation intermediates were detected upon reaction with $^{\bullet}\text{OH}$. Two methylated derivatives were tentatively identified, and they were probably produced by reaction between BP3 and fragments arising from photodegradation. The other intermediates were benzoic acid (maximum concentration $\sim 10\%$ of initial BP3) and benzaldehyde (1%).

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1. Introduction

Benzophenone-3 (2-hydroxy-4-methoxybenzophenone, hereafter BP3) can absorb sunlight in the UVA and UVB regions, with limited phototransformation. This property accounts for its use as sunlight filter in sunbathing lotions and in other cosmetic formulations, to protect either the skin or other formulation components from the effects of sunlight exposure (Rieger, 1997). BP3 is also employed as photostabiliser in packaging materials, to prevent polymer photochemical degradation and in the treatment of photodermatitis. An important consequence of the widespread use of BP3 is its frequent detection in human urine samples (up to 97% samples in the US; Calafat et al., 2008; Krause et al., 2012). BP3 may enter the body principally upon dermal exposure, while the oral intake is much less likely despite the rapid absorption by the gastrointestinal tract. Both phase I and phase II metabolism is observed, which is mostly carried out by liver and kidneys to produce compounds such as 2,4-dihydroxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone and 2,3,4-trihydroxybenzophenone. Both the primary compound and its metabolites are excreted in urine in the form of glucuronated derivatives (Okereke et al., 1993; Kadry et al., 1995; Calafat et al., 2008). BP3 has low acute toxicity (Okereke et al., 1995), but it shows estrogenic activity in several fish species, where it acts as vitellogenin inducer (Schlumpf et al., 2001; Schlenk et al., 2005; Kunz et al., 2006; Coronado et al., 2008). Therefore, BP3 has potential to cause feminisation of male fish.

BP3 can reach aquatic systems directly, due to its use as a sunscreen in recreational activities, or through wastewater because of its incomplete elimination in wastewater treatment plants (WWTPs; Balmer et al., 2005; Li et al., 2007). BP3 has been detected at levels of up to some $\mu\text{g L}^{-1}$ in raw wastewater, at tens to several hundreds ng L^{-1} in treated wastewater, and up to a hundred ng L^{-1} in lake water (Poiger et al., 2004; Balmer et al., 2005; Rodil et al., 2008). Moreover, it has been detected at ng g^{-1} levels in solid matrices and in biota (Meinerling and Daniels, 2006; Nieto et al., 2009). For these reasons, BP3 is considered as a personal care product of emerging environmental concern (Daughton and Ternes, 1999).

To date, very little is known about the environmental persistence of BP3. Its partial elimination in WWTPs (in the 68–96% range; Balmer et al., 2005; Li et al., 2007) suggests that biodegradation would be possible. Direct phototransformation is sufficiently slow to prevent the exploitation of photolysis as a removal technique of BP3 from aqueous solutions (Rodil et al., 2009). However, very little information is available on the photochemical behaviour of BP3 under conditions that are significant for surface waters. In addition to direct photolysis where transformation is induced by sunlight absorption, indirect photochemical pathways are also operational in sunlit water bodies. The latter processes involve reaction between the substrate and reactive transients, most notably $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and the excited triplet states of chromophoric dissolved organic matter, $^3\text{CDOM}^*$. These species are generated by sunlight irradiation of photosensitisers such as nitrate, nitrite and CDOM (Boreen et al., 2003; Al Housari et al., 2010). In the case of $\text{CO}_3^{\cdot-}$, the formation pathways include oxidation of bicarbonate and carbonate by $\cdot\text{OH}$ and of carbonate by $^3\text{CDOM}^*$ (Canonica et al., 2005).

This paper has the goal of assessing the photochemical transformation kinetics of BP3 via the main photochemical processes that are usually operational in surface waters, namely direct photolysis and reaction with $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$. This objective is pursued by combination of laboratory experiments (to determine photolysis quantum yields and second-order reaction rate constants) and of a modelling approach that makes use of kinetic parameters to assess phototransformation rates as a function of water chemical composition and depth. By adopting this methodology (Vione et al., 2010a, 2011; Maddigapu et al., 2011), it is possible to predict the photochemical behaviour of a compound in the environment under conditions that it would be difficult or even impossible to reproduce in the laboratory.

2. Experimental section

2.1. Reagents and materials

Benzaldehyde (purity grade 99%), anthraquinone-2-sulphonic acid, sodium salt (AQ2S, 97%), 1-nitronaphthalene (1NN, 99%), furfuryl alcohol (98%), NaNO_3 (>99%), NaHCO_3 (98%), anhydrous Na_2SO_4 (99%), NaCl (99.5%), $\text{Na}_2\text{HPO}_4 \cdot 2 \text{H}_2\text{O}$ (98%), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (98%), HClO_4 (70%) and H_3PO_4 (85%) were purchased from Aldrich, NaOH (99%), 2-propanol (LiChrosolv gradient grade) and dichloromethane (GC Suprasolv) from VWR Int., benzoic acid (97%) and methanol (gradient grade) from Carlo Erba, Rose Bengal (RB) and 2-hydroxy-4-ethoxybenzophenone (BP3, 98%) from Alfa Aesar.

2.2. Irradiation experiments

The kinetic parameters relevant to the main photochemical processes that would involve BP3 in surface waters (direct photolysis and reaction with $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$) were determined by laboratory measurements. These results allow the modelling of BP3 lifetime as a function of environmental variables (Vione et al., 2011; De Laurentiis et al., 2012b). AQ2S was used as CDOM proxy, to assess reactivity between BP3 and $^3\text{CDOM}^*$. Reasons for this choice are the widespread occurrence of quinones in CDOM and the fact that irradiation of AQ2S, unlike other triplet sensitisers, does not yield interfering transients such as $\cdot\text{OH}$ and $^1\text{O}_2$ (Cory and McKnight, 2005; Maddigapu et al., 2010). AQ2S initial concentration was 0.1 mM, to limit the additional complication represented by reaction between $^3\text{AQ2S}^*$ and ground-state AQ2S (Bedini et al., 2012a).

Solutions to be irradiated (5 mL) were placed inside Pyrex glass cells (4.0 cm diameter, 2.3 cm height, 295 nm cut-off wavelength) and magnetically stirred during irradiation. Irradiation of BP3 + nitrate and of BP3 + nitrate + bicarbonate to study reactions with $\cdot\text{OH}$ and $\text{CO}_3^{\cdot-}$ was carried out under a Philips TL 01 UVB lamp, with emission maximum at 313 nm. The lamp had $3.0 \pm 0.2 \text{ W m}^{-2}$ UV irradiance in the 300–400 nm range, measured with a power meter by CO.FO.ME.GRA. (Milan, Italy) equipped with a UV-sensitive probe. The incident photon flux in solution was actinometrically determined using the ferrioxalate method (Kuhn et al., 2004). By knowing, as a function of wavelength, the fraction of radiation absorbed by $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, the quantum yield of Fe^{2+} photoproduction and the shape of the lamp spectrum (measured with an Ocean Optics USB 2000 CCD spectrophotometer), it is possible to use the measured formation rate of Fe^{2+} to fix the value of the incident spectral photon flux density $p^\circ(\lambda)$. The photon flux of the TL 01 lamp between 300 and 500 nm was $P_0 = \int_{\lambda} p^\circ(\lambda) d\lambda = (2.0 \pm 0.1) \cdot 10^{-5} \text{ Einstein L}^{-1} \text{ s}^{-1}$.

BP3 direct photolysis and its transformation photosensitised by AQ2S were studied under a Philips TLK 05 UVA lamp, with emission maximum at 365 nm, $28 \pm 2 \text{ W m}^{-2}$ UV irradiance (300–400 nm), and $(2.1 \pm 0.2) \cdot 10^{-5} \text{ Einstein L}^{-1} \text{ s}^{-1}$ incident photon flux in solution. The photodegradation of BP3 sensitised by Rose Bengal (RB) via $^1\text{O}_2$ was studied under a Philips TL D 18 W/16 yellow lamp, with emission maximum at 545 nm and $11 \pm 1 \text{ W m}^{-2}$ irradiance in the visible, measured with the CO.FO.ME.GRA. power meter equipped with a probe sensitive to visible radiation.

The choice of the lamps had the purpose of exciting each photosensitiser as selectively as possible. The direct photolysis of BP3 was studied under UVA upon consideration of its absorption spectrum, measured with a Varian Cary 100 Scan UV-vis spectrophotometer. The same instrument was used to measure the absorption spectra of nitrate, AQ2S and RB. The various emission and absorption spectra are reported in Fig. 1. Unless otherwise reported, the initial concentration of BP-3 in the irradiation experiments was 20 μM and the solution pH was around 6.5.

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