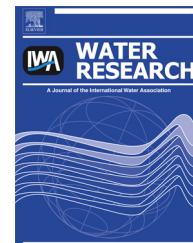




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# Photochemical transformation of ibuprofen into harmful 4-isobutylacetophenone: Pathways, kinetics, and significance for surface waters

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## ABSTRACT

The harmful compound 4-isobutylacetophenone (IBAP) can be formed photochemically from the anti-inflammatory drug ibuprofen (IBP), upon direct photolysis (yield  $25 \pm 7\%$ ,  $\mu \pm \sigma$ ), reaction with  $\cdot\text{OH}$  (yield  $2.3 \pm 0.1\%$ ) and reaction with triplet states of chromophoric dissolved organic matter,  ${}^3\text{CDOM}^*$  (yield  $31 \pm 4\%$ ). In the latter case, anthraquinone-2-sulphonate was used as CDOM proxy. The three processes would account for most of the photochemical transformation of IBP and IBAP in surface waters. IBAP formation from IBP involves the propanoic acid chain, which is more reactive than the aromatic ring as shown by quantum mechanical calculations. IBAP is expected to undergo slightly faster photochemical transformation than IBP in surface waters, with a modelled pseudo-first order rate constant that is higher by 1.5–1.9 times compared to IBP. Due to fairly high formation yields and depending on IBP emission scenarios, photochemical modelling suggests that IBAP could reach concentration values up to  $\sim 15\%$  of IBP in surface waters, thus being a potentially important transformation intermediate. This issue prompts for the need of field studies that provide information on IBAP environmental occurrence, which is virtually unknown at the present moment.

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## 1. Introduction

Ibuprofen (2-[4-(2-methylpropyl)phenyl] propanoic acid, hereafter IBP) is a non-steroidal anti-inflammatory drug (NSAID) that is widely used nowadays as the active principle of many “over the counter” pharmaceutical products, including analgesics and antipyretics (Kanabar et al., 2007). The widespread use of IBP is the main reason for its common

detection in both wastewater and surface water, at concentration levels of  $\text{ng L}^{-1}$  or even  $\mu\text{g L}^{-1}$  (Buser et al., 1999; Andreozzi et al., 2003; Tixier et al., 2003; Carballa et al., 2004; Castiglioni et al., 2006; Wu et al., 2009; Camacho-Munoz et al., 2010; Fernandez et al., 2010; Spongberg et al., 2011). This compound together with other NSAIDs is also a cause of concern for drinking water, where residues have been detected (at  $\text{ng L}^{-1}$  levels in the case of IBP; Mompelat et al., 2009).

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Bio- and photodegradation are the main transformation routes of IBP in surface waters (Packer et al., 2003; Lin et al., 2006; Peuravuori and Pihlaja, 2009; Kunkel and Radke, 2011; Jacobs et al., 2011). As far as IBP phototransformation is concerned, there is massive evidence that it can be carried out efficiently in technological systems under photocatalytic conditions (Molinari et al., 2006; Mendez-Arriaga et al., 2008; Achilleos et al., 2010; Miranda-Garcia et al., 2011; Choina et al., 2013). In the case of surface waters, it has been shown recently that the main pathways involved in IBP transformation would be photolysis, reaction with  $\cdot\text{OH}$  and with the triplet states of chromophoric dissolved organic matter ( $^3\text{CDOM}^*$ ) (Vione et al., 2011). Direct photolysis in surface waters takes place upon sunlight absorption by a dissolved substrate, which is then transformed via bond breaking, isomerisation or ionisation. The radicals  $\cdot\text{OH}$  are mainly produced upon irradiation of nitrite, nitrate and CDOM and they are mostly scavenged by dissolved organic matter (DOM, both chromophoric and not). Formation of  $^3\text{CDOM}^*$  involves radiation absorption by CDOM followed by intersystem crossing. Important sinks of  $^3\text{CDOM}^*$  are thermal deactivation and reaction with dissolved  $\text{O}_2$  to produce  $^1\text{O}_2$  (Canonica and Freiburghaus, 2001; Boreen et al., 2003; Richard et al., 2007; Al Housari et al., 2010; Page et al., 2011).

Among IBP transformation intermediates, 4-isobutylacetophenone (IBAP) is formed by several pathways and causes concern because of its adverse effects on connective tissue cells, red blood cells and the central nervous system (Castell et al., 1987; Miranda et al., 1991; Volonte et al., 2005; Cory et al., 2010; Sabri et al., 2012). Interestingly, IBAP formation has been detected via all the three main pathways of IBP photodegradation, namely direct photolysis and reactions with  $\cdot\text{OH}$  and  $^3\text{CDOM}^*$  (Vione et al., 2011). Unfortunately, very few data are reported on the environmental occurrence of IBAP (Zorita et al., 2007), and virtually no data are available on its persistence. At the present state of knowledge, it is extremely difficult to state if and to what extent IBAP is an IBP transformation intermediate of environmental concern.

This work has the goal of assessing the significance of IBP photochemical transformation into IBAP, thereby providing the first assessment of IBAP environmental importance. To this purpose we studied: (i) the reaction pathway, to explain why the detected IBP photo-intermediates are produced by transformation of lateral chains rather than the aromatic ring; (ii) the formation kinetics and yields of IBAP from IBP, via the main phototransformation processes that involve IBP in surface waters (direct photolysis and reaction with  $\cdot\text{OH}$  and  $^3\text{CDOM}^*$ ), and (iii) the transformation kinetics of IBAP via the photochemical processes that usually prevail in surface waters: direct photolysis and reaction with  $\cdot\text{OH}$ ,  $^3\text{CDOM}^*$ ,  $^1\text{O}_2$  and  $\text{CO}_3^{\cdot-}$  (Huang and Mabury, 2000; Boreen et al., 2003; Canonica et al., 2005). These data, combined with a photochemical model (Sur et al., 2012; De Laurentiis et al., 2012), allow an assessment of the photogeneration of IBAP from IBP, together with the identification of environmental conditions where the process could be most important. In this way, it is possible to get some insight into the otherwise unknown formation and reactivity of IBAP in surface waters.

## 2. Materials and methods

### 2.1. Reagents

Ibuprofen (IBP, purity grade 98%), anthraquinone-2-sulphonic acid, sodium salt (AQ2S, 97%), furfuryl alcohol (98%),  $\text{NaNO}_3$  (>99%),  $\text{NaHCO}_3$  (98%),  $\text{HClO}_4$  (70%) and  $\text{H}_3\text{PO}_4$  (85%) were purchased from Aldrich,  $\text{NaOH}$  (99%), methanol and 2-propanol (both gradient grade) from Carlo Erba, Rose Bengal (RB) and 4-isobutylacetophenone (IBAP, 97%) from Alfa Aesar.

### 2.2. Irradiation experiments

Solutions to be irradiated (5 mL) were placed inside cylindrical Pyrex glass cells (4.0 cm diameter, 2.3 cm height, 295 nm cut-off wavelength), closed with a lateral screw cap. Cells were magnetically stirred during irradiation, which occurred mainly from the top. The choice of lamps for irradiation depended on the experiments to be carried out, and on the need to excite some photoactive compounds as selectively as possible. In particular, a Philips TL 20W/01 RS UVB lamp was used for experiments of direct irradiation of IBP and IBAP, for exciting  $\text{H}_2\text{O}_2$  to produce  $\cdot\text{OH}$ , and for irradiating  $\text{NaNO}_3 + \text{NaHCO}_3$  to test reactivity between IBAP and  $\text{CO}_3^{\cdot-}$ . The lamp has emission maximum at 313 nm and  $13.0 \pm 0.6 \text{ W m}^{-2}$  UV irradiance (290–400 nm), measured with a power meter by CO.FO.ME.-GRA. (Milan, Italy). The incident photon flux in solution was  $P_0 = (8.53 \pm 0.39) \times 10^{-6} \text{ E L}^{-1} \text{ s}^{-1}$ , actinometrically determined with the ferrioxalate method (Kuhn et al., 2004). Irradiation of anthraquinone-2-sulphonate (AQ2S) as CDOM proxy to assess  $^3\text{CDOM}^*$  reactivity was carried out under a Philips TLK 05 UVA lamp, with emission maximum at 365 nm,  $31.4 \pm 1.0 \text{ W m}^{-2}$  UV irradiance, and  $P_0 = (2.38 \pm 0.11) \times 10^{-5} \text{ E L}^{-1} \text{ s}^{-1}$  incident photon flux. Irradiation of Rose Bengal as  $^1\text{O}_2$  source was carried out under a Philips TL D 18W/16 yellow lamp. The lamp had emission maximum at 545 nm and  $11 \pm 1 \text{ W m}^{-2}$  irradiance in the visible. Lamp spectra were measured with an Ocean Optics USB 2000 CCD spectrophotometer and were normalised to actinometry data. These spectra are reported in Fig. 1, together with absorption spectra of photoactive species, measured with a Varian Cary 100 Scan UV–Vis spectrophotometer.

AQ2S was chosen as CDOM proxy because quinones are important photoactive compounds in CDOM (Cory and McKnight, 2005). Furthermore, AQ2S does not yield (or yields to a low or negligible extent) interfering species such as  $^1\text{O}_2$  or  $\cdot\text{OH}$  upon irradiation. The reason is that  $^3\text{AQ2S}^*$  undergoes very fast reaction with  $\text{H}_2\text{O}$  to form water adducts, which evolve into ground-state AQ2S or into hydroxyderivatives. The fast reaction with the solvent prevents reaction between  $^3\text{AQ2S}^*$  and  $\text{O}_2$  to be significant (Loeff et al., 1983; Maddigapu et al., 2010). The lack of formation of  $\cdot\text{OH}$  and  $^1\text{O}_2$  is very important in this context. Indeed, while one can try to block reactivity of  $^1\text{O}_2$  and  $\cdot\text{OH}$  produced by triplet sensitisers (different from AQ2S) by addition of scavengers, it is not possible to exclude reactions of the triplet states themselves with the scavengers (Maddigapu et al., 2010; Vione et al., 2010; Bedini et al., 2012). Such reactions would bias the kinetic data. Therefore, although  $^3\text{AQ2S}^*$  may be more reactive than

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