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Photochemical transformation of benzotriazole, relevant to sunlit surface waters: Assessing the possible role of triplet-sensitised processes

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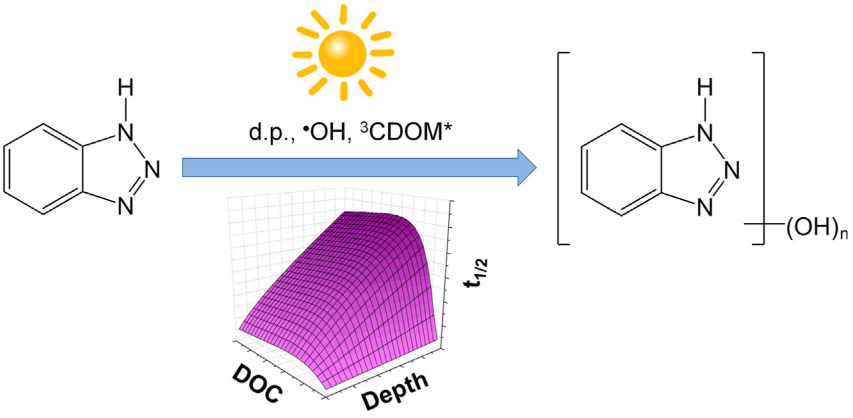
HIGHLIGHTS

- Triplet sensitisation can be important for the photodegradation of benzotriazole.
- Anionic benzotriazole reacts fast with excited triplet states.
- Neutral benzotriazole needs very reactive triplet states to undergo fast reaction.
- Lifetimes in sunlit surface waters might be highly affected by triplet reactivity.
- Hydroxyderivatives are formed as intermediates in all tested conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

The corrosion inhibitor 1H-benzotriazole ($pK_a = 8.4$) can exist in two different forms in natural waters, and photochemical transformation is a potentially significant attenuation pathway for both of them. Depending on conditions, the modelled half-life times range from some days/weeks to several months. In sunlit water bodies, the acidic (neutral) form would undergo direct photolysis (accounting for up to 7% of total phototransformation) and, most notably, reaction with the hydroxyl radicals ($^{\cdot}OH$) and the triplet states of chromophoric dissolved organic matter ($^3CDOM^*$). The basic (anionic) form would undergo significant transformation with $^{\cdot}OH$ and $^3CDOM^*$. The $^{\cdot}OH$ reactions would be more important at low dissolved organic carbon (DOC) and the $^3CDOM^*$ processes at high DOC. In the presence of highly reactive triplet-state model compounds, the two benzotriazole forms react with similar rate constants. In this case, they would show comparable half-life times in surface-water environments. With less reactive triplet states, the rate constant of the anionic form can be a couple of orders of magnitude higher than that of the neutral one. Under these circumstances, the neutral form could be

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1H-benzotriazole
Photochemical attenuation

considerably more photostable than the anionic one at high DOC. Therefore, depending on ^{3}CDOM* reactivity, the solution pH may or may not play an important role in the photoattenuation kinetics of 1H-benzotriazole in sunlit natural waters, especially at high DOC. Both forms of benzotriazole yield hydroxyderivatives as their main transformation intermediates under all the relevant photochemical reaction pathways. These intermediates could be formed via $^{\cdot}$OH-induced hydroxylation, or upon electron abstraction followed by reaction with water. Differently from UVC irradiation data reported in previous studies, the concentration of aniline upon excitation of 1H-benzotriazole under environmentally significant UV wavelengths was always below the detection limit of the analytical method used in this work (5 μmol L^{-1}).

1. Introduction

Benzotriazole (1H-benzotriazole or 1,2,3-benzotriazole, hereafter BZT) is a heterocyclic compound acting as an effective corrosion inhibitor, particularly for copper and its alloys. This property accounts for the widespread BZT use, not only in the direct protection of metal surfaces but also as an additive for several substances and materials that could come in contact with metals during use. A partial list of products that can contain BZT includes lacquer and varnishes, waxes and polish, packing papers, lubricants, brake fluids, sealants, detergents for metals, as well as aircraft de-icing fluids. BZT is also used as an additive in recirculating water for engine cooling, air conditioning, heating systems, and industrial equipment (Allam et al., 2009; Finsgar and Milosev, 2010; Copper Development Association, 2016). Moreover, the biological activity of BZT and its derivatives makes them a useful library of potential drug precursors (Briguglio et al., 2015).

Unfortunately, BZT is quite persistent in the environment which, combined with its widespread use, has resulted in the non-surprising detection of this compound in a variety of environmental matrices including soil, sediment, surface and ground water, and snow (Giger et al., 2006; Alotaibi et al., 2015; Careghini et al., 2015). In particular, the occurrence of BZT in wastewater is mainly due to its inclusion in household detergent formulations, and dishwashers effluents account for the majority of BZT emissions to wastewater (Vetter and Lorenz, 2013). The biorefractory nature of BZT and related compounds accounts for their incomplete removal by wastewater treatment plants (Morasch et al., 2010; Reemtsma et al., 2010; Herzog et al., 2014; Acero et al., 2015; Molins-Delgado et al., 2015), with consequent release to the receiving water bodies. An additional source is caused by the use of BZT in aircraft de-icing formulations, with possible contamination of soil and groundwater near airports (McNeill and Cancilla, 2009; Sulej et al., 2013).

Biodegradation of BZT is possible but it is rather slow, with reported half-life times ranging from one month to almost one year and, sometimes, no degradation at all (Liu et al., 2011; Liu et al., 2013; Alotaibi et al., 2015). Photodegradation is a potentially competitive transformation pathway for BZT in surface waters (Matamoros et al., 2010; Janssen et al., 2015). Photoinduced transformation is usually divided into direct photolysis, where a contaminant absorbs sunlight and undergoes transformation as a consequence (Aguera, 2012), and indirect photochemistry. In the latter, sunlight is absorbed by photoactive molecules called photosensitisers, which in surface waters include chromophoric dissolved organic matter (CDOM), nitrate and nitrite. Irradiated photosensitisers produce reactive transients species such as hydroxyl radicals ($^{\cdot}$OH), singlet oxygen ($^1O_2$) and CDOM triplet states (^{3}CDOM*), which are involved in pollutant transformation (Takeda et al., 2004; Nakatani et al., 2007; Lee et al., 2013; Vione et al., 2014; Chiwa et al., 2015). The combination of direct and indirect photochemistry can induce effective pollutant degradation in a variety of environmental conditions, but it can also generate harmful transformation intermediates (DellaGreca et al., 2004; Carlos et al., 2012; Wang and Lin, 2012; Anger et al., 2013).

In the case of BZT phototransformation, an issue of considerable concern is the detection of aniline upon BZT direct photolysis (Hem et al., 2003; Benitez et al., 2013). Aniline has been detected upon UVC irradiation, and it is thus very important to check whether its formation from BZT is also possible under conditions that are representative of sunlit surface waters. The concern related to the possible formation of aniline is due to its being classified as a probable carcinogen for humans, based on its ability to induce spleen cancer in rats (EPA, 2000). The carcinogenicity of this compound has been the object of debate, and the link between aniline exposure and cancer development is probably not accounted for by primary genotoxicity, but rather by hematotoxicity and cell damage/proliferation effects (Bomhard and Herbold, 2005; Wang et al., 2015).

Another key issue connected with BZT phototransformation is that, while its direct photolysis quantum yields and reaction rate constants with $^{\cdot}$OH and $^1O_2$ are reported in the literature (Naik and Moorthy, 1995; Benitez et al., 2013; Janssen et al., 2015), no data are available concerning the BZT reactivity with ^{3}CDOM*. Unfortunately, natural CDOM is a very complex mixture of compounds and the experimental measurement of substrate reactivity with ^{3}CDOM* is very challenging. To simplify the experimental system, in this work we have used two CDOM proxies that behave as triplet sensitisers under irradiation. The chosen proxies are anthraquinone-2-sulphonate (AQ2S) and 1-nitronaphthalene (1NN). The main reasons for choosing AQ2S are the following: (*i*) quinones are photoactive CDOM components (Cory and McKnight, 2005; Fimmen et al., 2007; Clark et al., 2014) and (*ii*) AQ2S photochemistry is well known and it does not involve additional transient species such as $^{\cdot}$OH or $^1O_2$ (Bedini et al., 2012). Unfortunately, the AQ2S triplet state (^{3}AQ2S*) is often more reactive than average ^{3}CDOM* and it may represent an upper limit of triplet-sensitised photoreactivity induced by CDOM (De Laurentiis et al., 2014). Although 1NN bears little resemblance with CDOM functional groups, its triplet state (^{3}1NN*) is less reactive than ^{3}AQ2S*; the standard reduction potentials of these triplet states are in fact 2 and 2.6 V, respectively (Loeff et al., 1993; Brigante et al., 2010; Sur et al., 2011; De Laurentiis et al., 2012). Therefore, results obtained with 1NN can be used to check for the AQ2S ones and provide a control for the rate constants of triplet sensitisation. Moreover, 1NN is easy and convenient to use in laser flash photolysis experiments because its triplet state, absorbing radiation at both 380 and 620 nm, can be monitored in different wavelength intervals to overcome possible problems of spectral interferences (Brigante et al., 2010).

Based on previous considerations, the present work has the following goals: (*i*) predicting the kinetics of BZT photochemical transformation in surface-water bodies, as a function of the environmental variables, and (*ii*) assessing the possible formation of aniline upon BZT phototransformation. To reach these goals, it was essential to get insight into the triplet-sensitised reactivity of BZT.

2. Experimental

2.1. Reagents and materials

The chemicals used in this study were of at least analytical grade and used as received, without further purification. Organic solvents were of HPLC grade (Aldrich). Water used was of Milli-Q quality (resistivity > 18.2 MΩ cm, total organic carbon <2 ppb).