Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Photochemistry and Photobiology A: Chemistry 167 (2004) 121–126
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photolysis of 2-mercaptobenzothiazole in aqueous medium Laboratory and field experiments

Moulay Abderrahmane Malouki[a,b], Claire Richard[a,*], Abdennour Zertal[b]

[a] Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS-Université Blaise Pascal no. 6505, 63177 Aubière Cedex, France
[b] Laboratoire des Sciences et Technologies de l'Environnement, Université Mentouri, 25000 Constantine, Algeria

Received 8 January 2004; received in revised form 19 April 2004; accepted 21 April 2004

Abstract

We first investigated the direct photolysis of 2-mercaptobenzothiazole ($\mathrm{p}K_\mathrm{a} = 6.94 \pm 0.05$) using 313 nm radiation. The anionic form was found to be photoconverted into benzothiazole and 2-hydroxybenzothiazole when irradiated in aerated medium ($\Phi = 0.02$). Transient species assigned to the triplet excited state ($\lambda_{\max} = 510\,\mathrm{nm}$, $\tau = 0.2\,\mu\mathrm{s}$), the solvated electron and the benzothiazolyl radical ($\lambda_{\max} = 350\,\mathrm{nm}$, $\tau \approx 100\,\mathrm{ms}$) were detected by laser flash photolysis ($\lambda_{\mathrm{exc}} = 266\,\mathrm{nm}$). A mechanism is proposed to rationalise all these observations. In a second step, 2-mercaptobenzothiazole was dissolved either in Milli-Q purified water buffered at pH 8.0 or in a natural water sampled in a lake and exposed to solar light. Desulfurisation into benzothiazole was clearly favoured in the latter case and the disappearance of 2-mercaptobenzothiazole was found to be four-fold faster in the natural than in the Milli-Q water. It shows that sensitised reactions mediated by the chromophoric components of natural waters significantly contribute to the transformation of 2-mercaptobenzothiazole in the aquatic environment.

Keywords: 2-Mercaptobenzothiazole; Water; Photolysis; Transient species; Aquatic environment; Solar light

---

1. Introduction

Benzothiazoles are synthesised in an industrial scale. Some derivatives (benzothiazole, methabenzthiazuron) serve as pesticides while others such as 2-mercaptobenzothiazole as agents of tires vulcanisation. These compounds are rejected in the environment and are potential pollutants of the aquatic environment. Only a few publications have been devoted to their phototransformation. The herbicide methabenzthiazuron was found to be quite photostable when irradiated at $\lambda > 290\,\mathrm{nm}$; in contrast to 6-hydroxymethabenzthiazuron, its main biodegradation metabolite, that undergoes photooxidation and photodimerization in the same exposure conditions [1]. In concentrated organic solutions of benzene, toluene, alcohols or acetonitrile 2-mercaptobenzothiazole (BT-SH) was found to be photoconverted into dimers BTS-STB or $\mathrm{BTSO_2\text{-}O_2STB}$ and benzothiazole (BT-H) [2]. More recently, Browlee et al. [3] investigated the photolysis of the main photoproducts of 2-(thiocyanomethylthio)ben-zothiazole, among which appeared BT-SH. Irradiation of aqueous BT-SH at pH 7.0 using polychromatic light led to the formation of BT-H and 2-hydroxybenzothiazole (BT-OH). The authors observed that acidification of irradiated solutions led to additional production of BT-H.

Sulfur organic compounds show an interesting but rather complex photochemistry. The C–S bond is of weak energy rendering the homolytic cleavage possible under irradiation, however heterolytic cleavage may occur in water too [4]. In addition, the S atom is oxidizable. Photosensitised oxidation of sulfur compounds was the subject of several detailed studies [5,6]. Moreover, BT-SH bears a 2-mercaptothiazole moiety that is a tautomeric system. The tautomeric equilibrium is generally influenced by the environment [7]. In the case of BT-SH, it was found that the thione form predominates in water [8].

We investigated the photochemistry of BT-SH in pure water by means of product studies and laser flash photolysis experiments. In order to get a better insight of the fate of BT-SH in the aquatic environment, we also studied the phototransformation of BT-SH when dissolved (i) in a natural water and (ii) in Milli-Q purified water containing humic substances used to mimic the chromophoric moiety of the natural organic matter.

---

* Corresponding author. Tel.: +33-4-73-40-71-42;
fax: +33-4-73-40-77-00.
E-mail address: claire.richard@univ-bpclermont.fr (C. Richard).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.04.010

2. Materials and methods

BT-SH (98%), BT-H (96%) and BT-OH (98%) were provided by Aldrich. The other reagents were of the highest grade available. Water was purified using a Milli-Q (Millipore) device. The humic acids were standards of IHSS (International Humic Substances Society). The natural water was collected in a lake (damned River Loire near Roanne, France), filtered on 0.45 μm cellulose acetate filters and stored at 4 °C until use.

Monochromatic irradiations at 313 nm were carried out using a high pressure mercury lamp (Osram HBO 200 W) equipped with a Bausch and Lomb monochromator. Potassium ferrioxalate was used as a chemical actinometer. The photon fluence rate was found to be 7.8×10^{15} photon s^{-1} cm^{-2}. Irradiations in the presence of humic substances were performed using three "black-light" lamps emitting about 90% of the radiant energy at 365 nm. Irradiations in solar light were carried out in Clermont-Ferrand (latitude 46°N) in May 2002 in quartz reactors (approximately 20 ml) closed hermetically by a septum. Solutions of $BT\text{-}S^-$ in buffered Milli-Q water and in the natural water were exposed to solar light simultaneously so that they received the same global radiation. Sampling was done at selected intervals. The loss of BT-SH and the formation of photoproducts were followed by HPLC using a Waters apparatus equipped with two 510 model pumps and a C_{18} 4.6 cm × 250 cm spherisorb ODS column. The photodiode array detector was a Waters 996 model. The mobile phase was a mixture of acidified water 0.1% of orthophosphoric acid (A)/methanol (B) (45/55, v/v). UV-Vis absorption spectra were recorded on a Varian Cary 13 spectrophotometer.

The pH of solutions was measured using Orion pH-meter with a combined electrode. All mother solutions of substrate were prepared with ultra pure water or with the natural water. Buffered solutions were elaborated from solutions of $Na_2HPO_4 \cdot 12H_2O$ and KH_2PO_4 then adjusted with ultra pure water. Oxygenation or deoxygenation of solutions was achieved by oxygen or nitrogen bubbling for 20 min prior to irradiation, respectively. Laser flash photolysis experiments were carried out using the fourth harmonic of a Nd-YAG Quanta Ray GCR 130 laser. The experimental device was previously described [9].

3. Results and discussion

3.1. Spectral properties

As shown in Fig. 1, molecular and anionic forms of BT-SH show both an intense absorption band with a maximum at $\lambda > 300$ nm. The maximum of absorption of the molecular form is located at 315 nm and the molar extinction coefficient equal to $22800 \pm 500\,M^{-1}\,cm^{-1}$. The thiolate has a maximum of absorption at 302 nm with $\varepsilon = 17900 \pm 500\,M^{-1}\,cm^{-1}$. Unsubstituted benzothiazole shows a maximum of absorption around 290 nm and absorbs only poorly at $\lambda > 300$ nm. It means that the presence of the SH group affects the spectral properties strongly.

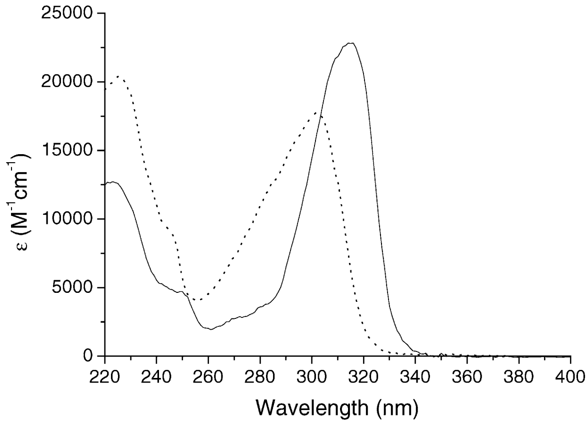


Fig. 1. Absorption spectrum of BT-SH in molecular form (solid line) and anionic form (dotted line).

3.2. pK_a measurement

To determine the pK_a, we recorded the spectrum of BT-SH solutions at several pH values ranging from 2 to 11, keeping constant the BT-SH concentration. In each case, we measured the absorbances at 330 nm and plotted it versus pH (see Fig. 2). We got a sigmoidal curve, the centre of which gave the pK_a value: 6.95 ± 0.05.

3.3. Laser flash photolysis

The laser flash photolysis of molecular BT-SH (3×10^{-5} M, pH = 5.0) yielded only very weak transient absorbances. On the other hand, the photolysis of the thiolate (3×10^{-5} M, pH = 8.3) produced several transient species at the end of the pulse. One disappeared within the first microseconds following the pulse in deoxygenated medium. Its transient spectrum was obtained by making the difference between absorbances at the pulse end and 1 ms after

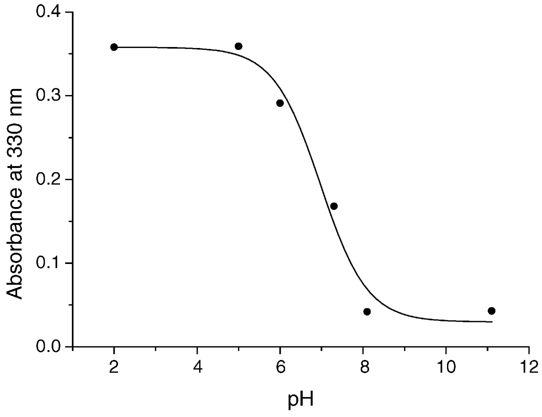


Fig. 2. Plot of the end-of-pulse absorbance at 330 nm vs. pH.

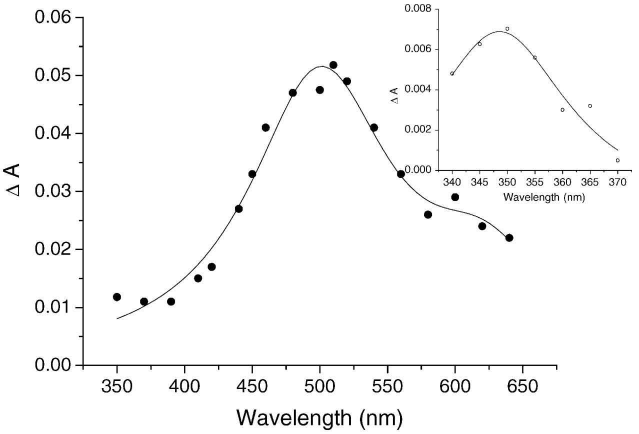


Fig. 3. Transient absorption spectrum from BT-SH (3×10^{-5} M, pH = 8.3). (●) Difference between absorbances measured at the end of the pulse and 1 μs after at $P = 0.37$ mJ per pulse and (○) absorbance measured 10 ms after the pulse end at $P = 0.5$ mJ per pulse.

measured (Fig. 3). It showed a broad band with a maximum at 510 nm. The absorbance decayed by a first order kinetics with $k = 4.1 \times 10^6\,\mathrm{s}^{-1}$. In suroxygenated medium, it was observed again, but the rate constant decay was enhanced to $7.1 \times 10^6\,\mathrm{s}^{-1}$. Lastly, in the presence of methyl acrylate (2×10^{-2} M) the disappearance was still faster with $k = 1.7 \times 10^7\,\mathrm{s}^{-1}$ (Fig. 4). The second transient had a maximum around 725 nm that is characteristic of the solvated electrons. It decayed by an apparent first order kinetics with $k = 2.5 \times 10^6\,\mathrm{s}^{-1}$ in deoxygenated medium and was found to be trapped by N_2O. The third transient species absorbed within the wavelength range 340–380 nm with a maximum at 350 nm (Fig. 3). The latter was long-lived with $\tau \approx 100$ μs.

We monitored the end-of-pulse absorbances at 510, 725 and 350 nm as a function of the energy pulse, P (Fig. 5). The increase of the 510 nm absorbance with P was linear indicating a monophotonic formation. In contrast, the absorbances at 350 and 725 nm increased in a quadratic manner with P showing mixed mono and biphotonic formations. The similarity of the curves indicates that the two transients were produced in the same processes. It can be concluded that the long-lived species is the benzothiazolyl radical that is produced simultaneously with the solvated electron via photoionisation.

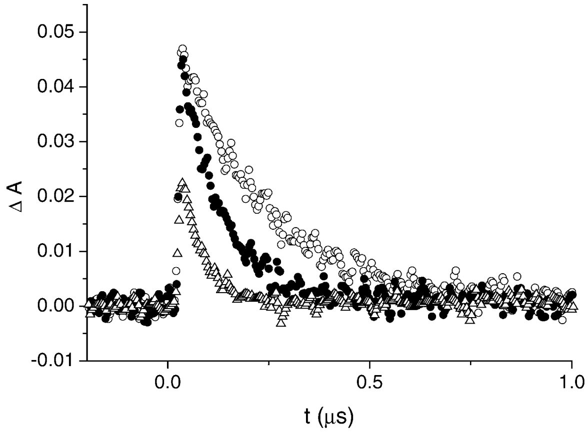


Fig. 4. Time course absorbance at 510 nm in deoxygenated medium (○), in suroxygenated medium (●), in the presence of methyl acrylate (2×10^{-2} M) (△).

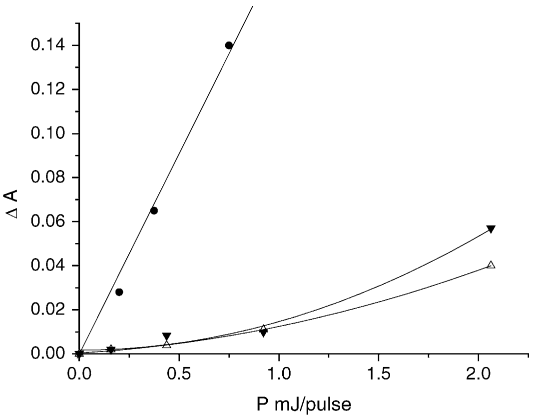


Fig. 5. Plot of the end-of-pulse absorbances at 510 nm (●), 725 nm (▼) and 350 nm (△) as a function of P, the energy pulse.

On the basis of oxygen and methyl acrylate quenchings, the 510 nm short lived species can be assigned to the triplet excited state. Aromatic thiones were reported to populate efficiently their triplet excited states [10,11]. Triplet–triplet absorptions were found to exhibit a broad bands with maximum between 430 and 520 nm.

3.4. Steady-state irradiation

In a first step, we monitored the UV-Vis absorbance changes in the course of irradiation. The intense band disappeared, but no new absorption bands appeared, as shown in Fig. 6 in the case of molecular BT-SH (3×10^{-5} M) irradiated in air-saturated medium.

Then, we measured the quantum yields of photolysis at 313 nm. In air-saturated solutions, we found $(1.9 \pm 0.3) \times 10^{-3}$ and $(1.9 \pm 0.3) \times 10^{-2}$ for the molecular

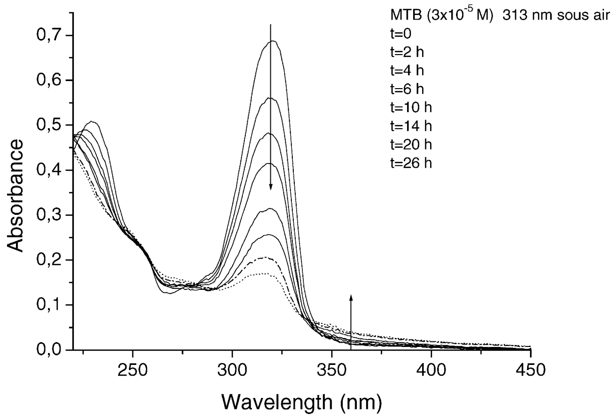


Fig. 6. UV-Vis absorbance changes in the course of the irradiation of BT-SH (3×10^{-5} M, pH = 5) in air-saturated medium.

and anionic forms, respectively. In argon-saturated medium, quantum yields were significantly lower, $(1.3 \pm 0.2) \times 10^{-3}$ for the thiolate and less than 5×10^{-4} for molecular BT-SH. These results show that the anionic form is much more photoreactive than the neutral one and that oxygen exhibits an accelerating effect on the reaction. In addition, we irradiated BT-S^- in N_2O-saturated solution. We found a quantum yield of photolysis equal to $(2.2 \pm 0.3) \times 10^{-3}$, i.e. slightly higher than in argon-saturated solution.

In a third step, we monitored the formation of photoproducts by analysing the irradiated solutions by HPLC. The irradiation of deoxygenated solution led to the sole formation of BT-H with a chemical yield higher than 90%. In aerated solution, BT-H and BT-OH were both detected. A third unidentified photoproduct showing a very short retention time was also observed.

3.5. Humic substances-mediated reaction

BT-SH (3×10^{-5} M) was dissolved in Milli-Q purified water containing humic acids ($50\,\mathrm{mg\,l^{-1}}$) and buffered at pH 6.5 using photophate buffers. BT-SH disppeared by an apparent first order kinetic with $k = 0.011\,\mathrm{min^{-1}}$. In an other set of experiments, BT-SH and the humic acids were irradiated in the presence of azide anions (5×10^{-3} M) used as oxygenated reactive species (singlet oxygen, hydroxyl radicals) quencher. The consumption of BT-SH was found to be slower with $k = 0.006\,\mathrm{min^{-1}}$.

3.6. Field experiments

BT-S^- (10^{-4} M) dissolved either in a buffered Milli-Q water (pH = 8.0) or in a natural water was exposed to solar light in the mid-day. The disappearance of BT-S^- and formation of BT-H and BT-OH were monitored by HPLC. Results are presented in Fig. 7.

In the Milli-Q purified water, the half-life of BT-S^- was approximately 250 min, whereas it was only 65 min in the lake water (Fig. 7a). It can be concluded that constituents of natural water photoinduced significantly the degradation of BT-S^-. The kinetics of formation of BT-H and BT-OH are presented in Fig. 7b. After a conversion extent of 30%, BT-H and BT-OH were formed with chemical yields of 13 and 6%, respectively, in the Milli-Q water. In the natural water, the formation of BT-H was definitively favoured compared to that of BT-OH, BT-H being produced with a chemical yield of about 25% while BT-OH only detected in traces. It shows that chromophoric components of the natural water not only accelerated the disappearance of BT-S^- but also supported the formation of BT-H.

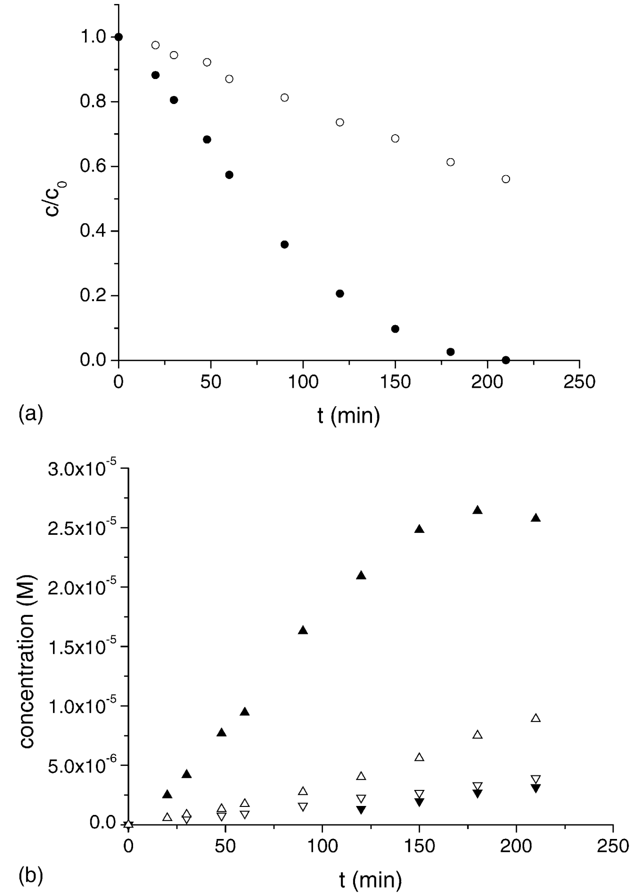


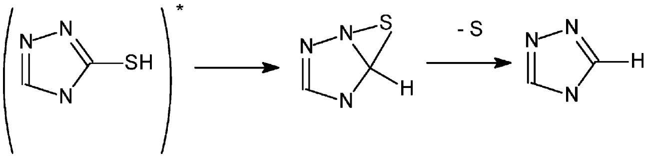
Fig. 7. Disappearance of BT-SH (10^{-4} M) when exposed to solar light in pH 8.0 buffered Milli-Q water (○) and in a natural water (●) and formation of BT-H (△, ▲) and BT-OH (△, ▼).

3.7. Mechanism of the reactions

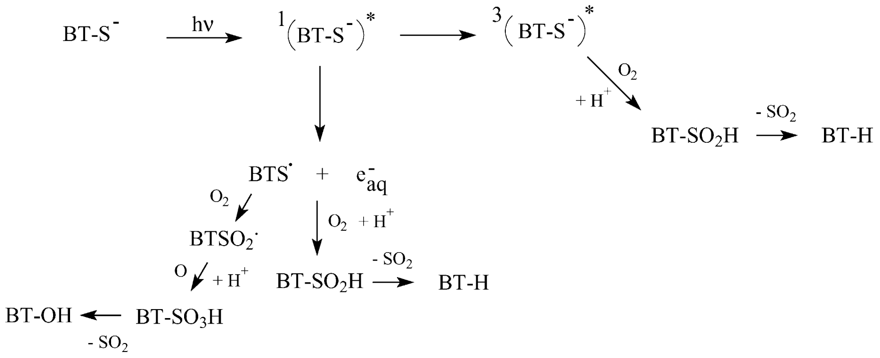
Laser flash photolysis experiments brought information on the primary steps of BT-S^- photolysis. They allowed the detection of the anionic triplet excited state and showed that BT-S^- undergoes photoionisation that yield solvated electrons and the benzothiazolyl radical. The increase of the quantum yield of BT-S^- photolysis in N_2O saturated medium confirms the production of solvated electrons, these latters being converted into highly oxidant hydroxyl radicals according to the process

$$e^-_{\mathrm{sol}} + \mathrm{N_2O} + \mathrm{H_2O} \rightarrow \mathrm{HO}^{\bullet} + \mathrm{N_2} + \mathrm{OH^-}$$

In deoxygenated medium, desulfurization of BT-S^- took place with the sole formation of BTH. Photodesulfurisation of thiones was already reported in the literature [10–14]. The intermediary formation of episulfide was proposed [13].



The desulfurisation might be spontaneous or photoinduced as described by Padwa et al. [15] in the case of dibenzoylstilbene episulfide. An analogous mechanism may be operative for BT-S^-.



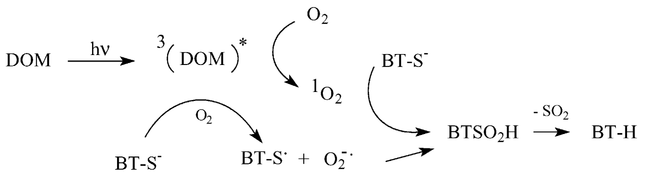
Scheme 1.

In aerated medium, the quantum yield of BT-S$^-$ photolysis was higher and BT-OH was formed along with BT-H. The triplet excited state and the species arising from photoionisation are likely to be involved in the phototransformation of BT-S$^-$. First, because the increase of the quantum yield of photolysis parallels the fact that the solvated electron and the benzothiazolyl radical react with oxygen. Second, molecular BT-SH that showed a very weak quantum yield of phototransformation did not yield measurable amounts of transient species (solvated electrons or triplet excited state) under excitation at 266 nm.

The oxidation of the triplet by oxygen might lead to sulfinic acid BT-SO$_2$H (see Scheme 1). The production of BT-SO$_2$H can also occur through photoionisation, subsequently to oxidation of solvated electrons by oxygen and addition of the superoxide anion radicals to the benzothiazolyl radical. The sulfonic acid might be formed too by further oxidation of the BTSO$_2^{\bullet}$ radical.

The formations of BT-H and BT-OH require a SO$_2$ extrusion. We could propose the intermediary formation of an “episulfoxide” by analogy to the episulfide proposed in deoxygenated solution. However, this hypothesis needs to be confirmed.

Experiments under conditions close to natural conditions were also undertaken to get a better insight into the fate of BT-SH in the aquatic environment. Solar light irradiation of BT-S$^-$ dissolved in Milli-Q purified water produced the same pattern of reactions than monochromatic irradiation. In contrast, the use of a natural water instead of Milli-Q purified water as a dissolving medium was found to affect the results. First, the rate of BT-S$^-$ loss was increased; second, the product distribution changed, the formation of BT-H being significantly favoured. The first point indicates that the phototransformation of BT-S$^-$ is mediated by the chromophores contained in the natural water and especially the coloured natural organic matter (DOM). Experiments conducted with humic acids confirm this result. It is now well-known that DOM produces reactive species under light absorption and especially singlet oxygen and oxidant triplet states [16–18]. These latters should be able to oxidize a sulfur compound such as BT-S$^-$ as they were found to react with a sulfur compound such as ethiofencarb for instance [19] (see Scheme 2).



Scheme 2.

Again, the efficient production of BT-H requires a SO$_2$ extrusion.

In conclusion, this study shows that 2-mercaptobenzothiazole is a special case in the benzothiazole series; it is much more photoreactive than most of them. The direct photolysis of 2-mercaptobenzothiazole in water involves the triplet excited state, the solvated electrons and the benzothiazolyl radical as primary intermediates. However, some work is still needed to clarify the desulfurisation steps. Episulfide or episulfoxide might be involved as intermediates. The phototransformation is photoinduced by chromophoric components of the natural waters. Again, desulfurisation occurs.

References

[1] M.A. Malouki, G. Giry, P. Besse, B. Combourieu, M. Sancelme, F. Bonnemoy, C. Richard, A.-M. Delort, Environ. Toxicol. Chem. 22 (2003) 2013.
[2] C. Parkanyi, A.O. Abdelhamid, Heterocycles 23 (1985) 2917.
[3] B.G. Brownlee, J.H. Carey, G.A. Macinnis, I.T. Pellizzari, Appl. Toxicol. Chem. 11 (1992) 1153.
[4] D. Vialaton, C. Richard, J. Photochem. Photobiol. A 136 (2000) 169.
[5] E. Robert-Banchereau, S. Lacombe, J. Olivier, Tetrahedron 53 (1997) 2087.
[6] D.J. Pasto, F. Cottard, L. Jumelle, J. Am. Chem. Soc. 116 (1994) 8978.
[7] P. Beak, J.B. Covington, J.M. White, J. Org. Chem. 54 (1980) 1347.
[8] B. Ellis, P.J.F. Griffiths, Spectrochim. Acta 22 (1966) 2005.
[9] F. Bonnichon, C. Richard, J. Photochem. Photobiol. A 136 (2000) 169.
[10] M.M. Alam, M. Fujitsuka, A. Watanabe, O. Ito, J. Chem. Soc., Perkin Trans. 2 (1998) 817.
[11] M.A. El-Kemary, M.E. El-Khouly, O. Ito, J. Photochem. Photobiol. A 137 (2000) 105.

[12] T. Nishio, J. Org. Chem. 53 (1988) 1323.
[13] A. Senthilvelan, D. Thirumalai, V.T. Ramakrishnan, Tetrahedron 60 (2004) 851.
[14] T. Nishio, N. Okuda, C. Kashima, J. Chem. Soc., Perkin Trans. 1 1 (1991) 141.
[15] A. Padwa, D. Crumrine, A. Shubber, J. Am. Chem. Soc. 88 (1966) 3064.
[16] S. Canonica, U. Jans, K. Stemmler, J. Hoigné, J. Environ. Sci. Technol. 29 (1995) 1822.
[17] W.R. Haag, J. Hoigné, Environ. Sci. Technol. 20 (1986) 341.
[18] J.P. Aguer, C. Richard, F. Andreux, J. Photochem. Photobiol. A: Chem. 103 (1997) 163.
[19] D. Vialaton, C. Richard, Aquat. Sci. 64 (2002) 207.