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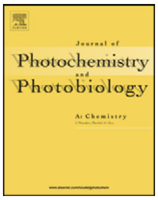

Homogeneous photodegradation study of 2-mercaptobenzothiazole photocatalysed by sodium decatungstate salts: Kinetics and mechanistic pathways

A. Allaoui[a,b], M.A. Malouki[a], P. Wong-Wah-Chung[c,*]

[a] *Laboratoire des Sciences et Technologies de l'Environnement, Université Mentouri, 25000 Constantine, Algeria*
[b] *Clermont Université, Laboratoire de Photochimie Moléculaire et Macromoléculaire, BP 10448, F-63000 Clermont-Ferrand, France*
[c] *Clermont Université, ENSCCF, Laboratoire de Photochimie Moléculaire et Macromoléculaire, BP 10448, F-63000 Clermont-Ferrand, France*

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ABSTRACT

The photochemical degradation of a benzothiazole derivative, 2-mercaptobenzothiazole (MBT) has been studied in aqueous solution in the presence of a polyoxometalate (POM): sodium decatungstate salts $Na_4W_{10}O_{32}$ (DTA). In aerated conditions, the photodegradation rate of MBT clearly increased in the presence of DTA by a factor six when compared with the direct photolysis with $k_{MBT} = 0.25\,h^{-1}$ and $t_{1/2}(MBT) = 2.8\,h$. For the total comprehension of the degradation mechanism, the oxygen influence has been investigated. Oxygen appeared essential for DTA regeneration, its absence induced a three times inhibition of MBT disappearance and completely stopped the photocatalytic cycle. The main photoproducts were identified with LC–ESI-MS and LC-DAD techniques and using some calculations obtained by B3LYP/6–21G method in Gaussian 4.1 software. All the results allowed to propose a mechanistic pathway. Electron transfer and H atom abstraction processes involving $W_{10}O_{32}{}^{4-*}$ excited state species were involved in the degradation. In the primary step of the degradation, the hydroxylation of the aromatic ring leading to four OH-MBT isomers and the formation of disulfide form of MBT were observed. For longer irradiation time, a secondary electron transfer permitted the oxidation of OH-MBT isomers and the formation of sulfoxide derivatives. For prolonged exposure (around 100 h), the complete mineralization was noticed in the presence of sodium decatungstate salts.

1. Introduction

The pollution of the environment by organic compounds is always of great concern because the occurrence of these compounds and their increasing concentration pointed out the toxicity risks for aquatic organisms and human. As a consequence, many researchers have focused their studies on different purposes: (i) the pollution assessment in a large wide of compartments (rivers, soils, lakes, . . .), (ii) the organic pollutants fate in natural environment, their impacts on different populations, (iii) the elimination processes' or advanced oxidized processes' (AOPs) improvement. Among the organic pollutants, the benzothiazole derivatives and particularly 2-mercaptobenzothiazole (MBT) is on great interest regarding all previous studies.

MBT is widely used in industries as rubber vulcanization accelerator, fungicide, bactericide, conservator or corrosion inhibitor [1,2]; this leads the Environmental Protection Agency of United States (EPA) to estimate that over 450 tons of MBT (3% of the US production) may be lost annually into the environment [3]. As a consequence, MBT has been measured in different compartments and was found in surface waters, in roads dusts and in wastewater effluents from tanneries, sewage treatment plants and rubber additive manufactories. This obviously confirms the prospective pollution of environmental compartments [4]. Moreover, many previous studies have proved that MBT is a strong pollutant of aquatic compartments, allergen and potentially mutagen for human that means a non-negligible impact of MBT on environment and on human health [5,6].

Some studies on the environmental behavior and the biodegradation of MBT showed that it is rather recalcitrant and it is not completely mineralized [7]. The biodegradation studies put in evidence the formation of different metabolites. Among them, 6-hydroxybenzothiazole (6-OH-MBT), dihydroxybenzothiazole, demethylated MBT (2-methylthiobenzothiazole) and the diacid derivative of MBT have been identified [8]. Other studies focused on the direct phototransformation proved that MBT is photoreactive under irradiation at 313 nm with a quantum yield equal to 0.02 and photostable under sunlight irradiation with a quantum yield equal to 0.002 [9,10]. The main degradation products

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[*] Corresponding author. Tel.: +33 473407172.
E-mail address: pascal.wong-wah-chung@univ-bpclermont.fr (P. Wong-Wah-Chung).

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observed were benzothiazole (BT) and 2-hydroxybenzothiazole (OBT) and the process occurred from the triplet and singlet excited states through the formation of $BTS^\bullet$ radical.

All these results demonstrating that MBT was very stable in environmental conditions, lead many researchers to work on its elimination. For example, the ozonation process and the photoinduced degradation (in the presence of iron oxides/UV irradiation, TiO_2, ...) were tested to reach the total elimination of MBT. In the presence of O_3, MBT disappearance was effective in less than 10 min, the mineralization was partial and the formation of BT, benzothiazole-2-sulfite ($BTOSO_2$) and OBT was observed [11]. In addition, systems combining iron-oxalate complexes and UVA irradiation showed that MBT is adsorbed on the support and photo Fenton reactions are responsible of MBT induced degradation. The authors put into evidence that the degradation rate depends on different parameters: the oxalate and iron oxides concentrations and the photonic flux intensity [12]. In more recent studies, titanium dioxide doped with neodymium, cerium or lanthanum allowed the efficient elimination of MBT under irradiation by $OH^\bullet$ radical attack with the formation of BT, OBT, $BTOSO_2$ and aniline sulfonate (ASA) as degradation products [13,14].

Regarding the remaining of MBT in natural compartments, its established toxicity and its low biodegradability, we focused our study on the potential elimination of this benzothiazole derivative under UV irradiation in the presence of a polyoxometalate (POM): the decatungstate anion $W_{10}O_{32}{}^{4-}$ (DTA). The system using decatungstate anion and UV irradiation was considered because of DTA photocatalytic activity and its efficient induced degradation of many organic pollutants in water (chlorinated phenols, pesticides, aromatic and aliphatic alcohols, alkenes, ...) [15,16]. It is well known that the DTA reactivity under irradiation comes from the formation of a very oxidative specie in the excited state $W_{10}O_{32}{}^{4-*}$, which allows the degradation of organic pollutants by H atom abstraction or by electron transfer. DTA reduced species ($W_{10}O_{34}{}^{5-}$) is then regenerated in the presence of oxygen and the obtained catalytic cycle could also lead to the continuous degradation of organic molecules and to their total elimination [17–20]. Papaconstantinou and Mylanos put into evidence, for the first time, the total decomposition of chlorinated phenols into CO_2 and chlorine in the presence of inorganic POMs under irradiation [15]. The total mineralization was reached in 600 min under irradiation in aerated aqueous solution. During the photocatalytic degradation of chlorinated phenol, Mylanos et al. supposed that the disappearance occurs through $OH^\bullet$ radical formation, dechlorination, hydroxylated compounds oxidation, open ring reaction regarding the photoproducts detected [21]. All the mechanistic pathways described by Mylanos and coworkers have also been confirmed in different studies realized on the organic pollutants' degradation in the presence of DTA (chlorinated phenol, atrazine, metsulfuron methyl, ...) but some authors described also demethylation reaction and bound scission [19,20]. Moreover, the same authors, who worked on 4-nitrophenol degradation in the presence of POMs, showed that the decatungstate anion leads to a higher 4-nitrophenol disappearance than with $PW_{10}O_{40}{}^{3-}$ and $SiW_{12}O_{32}{}^{4-}$ [21]. Nevertheless, in almost all studies realized on the photoinduced degradation of organic pollutants, the authors established that titanium dioxide catalyst is generally a more powerful candidate than POMs [22,23]. Only a few studies demonstrated that POMs and particularly $W_{10}O_{32}{}^{4-}$ is more capable to mineralize organic pollutants and more precisely small molecules like acetic acid, 1,1,2-trichlorinated ethane or formulated compounds such as the pesticide imidachloprid [24,19]. Moreover, like DTA polyoxoanions absorbs in the UV region, it has been considered with great interest in water detoxification processes because of the large overlap of its absorption spectrum with that of the solar UV emission spectrum and its low toxicity [25]. In fact, some experiments with solar irradiation showed the potential applications of DTA in the degradation of many compounds among them chlorinated phenol, imidachloprid or atrazine [19,26].

Regarding the decatungstate salts properties and the environmental stability of MBT, the present work is dealing with its photodegradability in the presence of DTA under UV irradiation and in aqueous solution. Our purpose was to evaluate the photodegradation of 2-mercaptobenzothiazole through the determination of disappearance kinetics, the initial rate constants and the quantum yields considering the influence of oxygen. In addition, with reference to the photoproducts' identification, the mechanistic pathways involved in the degradation will be proposed in order to have a better insight into the MBT degradation scheme.

2. Materials and methods

2.1. Materials

Sodium decatungstate $Na_4W_{10}O_{32}$ was prepared and purified according to the published procedure [27]. The decatungstate ion obtained after recrystallisation gave an UV–vis absorption maximum at 323 nm in acetonitrile and the IR spectrum, realized by diffuse reflexion, showed main vibration bands at 1004, 962, 912 and 800 cm^{-1} in agreement with the literature values [17,27].

2-Mercaptobenzothiazole (benzothiazolethiol, m.p. 178–181 °C) was purchased from Fluka (99% purity) and was used without further purification. Titanium dioxide TiO_2 Degussa P25 was 80:30 anatase:rutile with a surface area of 44 m^2/g. Methanol was from Carlo Erba (HPLC grade) and the other chemicals were of purest grade commercially available and used without further purification.

Solutions were prepared with water purified by a Millipore Milli-Q device and the pH was adjusted with NaOH or HCl and controlled with an ORION pHmeter to 0.1 pH unit. The ionic strength was not controlled.

The deaeration and the oxygenation of the solutions were accomplished respectively by bubbling N_2 and O_2 for a maximum of 30 min at room temperature prior to irradiation and all along the irradiation period.

2.2. Procedures

Two irradiation setups with emission at 365 nm were used all along the study. The quantum yields were calculated from the results obtained after monochromatic irradiation at 365 nm. These irradiations were conducted with a xenon lamp (1000 W) equipped with a LOT Oriel grating monochromator. The beam was parallel and the reactor was a quartz cell of 1 cm or generally 2 cm path length. The photonic flux at 365 nm measured by ferrioxalate actinometry was equal to $2.4 \times 10^{14} \pm 0.2 \times 10^{14}$ photons $cm^{-2}\,s^{-1}$ [28].

The kinetics' establishment and the photoproducts' identification were realized by using a cylinder reactor made in stainless steel. The container was equipped with three high-pressure mercury lamps (black lamp, Mazda MAW 125 W) emitted selectively at 365 nm (97% of the emission) and symmetrically installed in the down part of the cylinder. The reactor, a water-jacketed Pyrex tube (Ø = 2.8 cm) containing a maximum of 100 mL solution, was located in the centre. The solutions were continuously stirred during irradiation experiments by a magnetic stirrer. This irradiation set up allowed us to determine the initial rate constants and the half-life times; these values were exclusively determined in aerated and oxygen saturated conditions in the presence of DTA because in these conditions the kinetics were corresponding to first order kinetics.

The concentration evolutions of the initial and the degradation products were determined by HPLC experiments using a Waters liquid chromatography system equipped with two Waters 510 pumps, an automatic injector model Waters 717 and a Waters 996 diode array detector. An Agilent reverse phase column (Eclipse XDB-C8, 5 μm, 250 mm × 4.6 mm) and mixtures of water with 0.1% of H_3PO_4 and methanol (45/55, v/v) were used to obtain a correct elution of MBT. The flow rate was 1 mL min^{-1} and the injected volume was 30 μL.

Absorption spectra were recorded on a Cary 3 double beam spectrophotometer. Ions were measured by ionic chromatography (Dionex DX320, column AS11 for anions, eluent KOH; Dionex ICS1500, column CS16 for cations, eluent hydroxymethanesulfonate), while the mineralization was monitored by total organic carbon measurements with a Shimadzu TOC 5050 equipped with an automatic sample injector. The concentration in total organic carbon was obtained from three injections and accordingly to a calibration curve established the day of the measurements.

The photoproducts' identification were carried out by LC–MS studies realized with a Waters HPLC system (Alliance 2695) coupled to a Q-ToF mass spectrometer equipped with a pneumatically assisted electro spray ionization source (ESI). The HPLC system was also coupled with a Waters 996 diode array detector. The chromatographic separation was reached by using an elution program from 95% water (with 0.2% acetic acid) and 5% methanol to 5% water (with 0.2% acetic acid) and 95% methanol after 15 min; the obtained isocratic conditions were maintained during 10 min. The flow rate was 0.2 mL min^{-1}, the injected volume 30 μL and the column was distributed by Waters (Xterra MS C18, 3.5 μm, 100 mm × 2.1 mm). The electro spray source parameters were in positive mode: capillary voltage 3000 V (2100 V in negative mode), cone voltage 35 V, extraction cone voltage 2 V, desolvation temperature 250 °C, source temperature 100 °C, ion energy 2 V and collision energy 10 eV (7 eV in negative mode).

3. Results and discussions

3.1. Degradation of 2-mercaptobenzothiazole under direct irradiation

First, the degradation of MBT (1.0×10^{-4} M) was studied in the absence of $W_{10}O_{32}{}^{4-}$ upon irradiation at 365 nm in order to evaluate the direct photodegradation process. This contribution has to be considered for the precise determination of the decatungstate photocatalytic efficiency and mechanism.

2-Mercaptobenzothiazole may exist under three different forms in the environmental pH range: two molecular tautomer forms (thiol or thione) and an anionic form (S^-). Their presence depends on the pH ($pK_a = 6.95 \pm 0.05$). Studies on the tautomeric equilibrium of MBT gave the evidence that the thione form of MBT is the prevailing species [29]. Moreover, differences have been evidenced previously in the behavior of MBT forms in terms of photodegradation and primary species [9]. This points out the main role of the pH in the study. In our experimental conditions, the molecular form is the dominant form present in the solutions because the pH was around 4.4.

At very low pH, the UV-visible absorption spectrum of the molecular form presents a maximum at 320 nm ($\varepsilon = 26{,}500 \pm 200\ M^{-1}\ cm^{-1}$) and since the molecular form is the main form present in the solutions, this implies a minor recovery with the emission spectrum of the solar light.

Nevertheless, the direct elimination could be assumed with the irradiation device because of the MBT basic form tail beyond 365 nm and because of the two incompletely filtered rays of the mercury lamps at lower wavelengths (313 and 334 nm). As a consequence, the MBT direct degradation was evaluated and the kinetics obtained are represented in Fig. 1. We observed a weak disappearance equal to 25% for MBT after 8 h under direct irradiation.

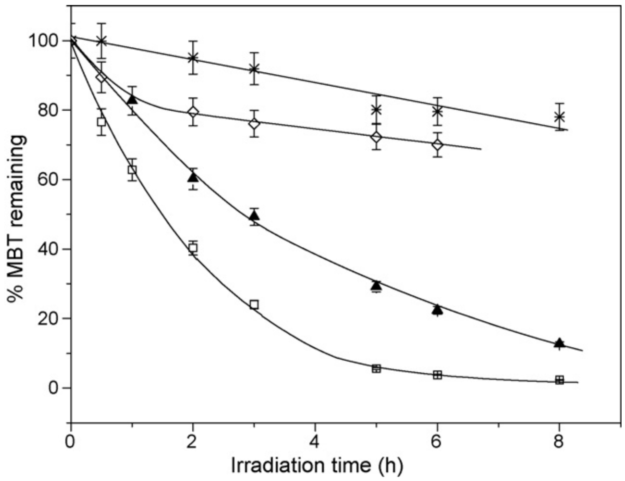


Fig. 1. Evolution of MBT (1.0×10^{-4} M) concentration in water under irradiation at 365 nm: (*) without $W_{10}O_{32}{}^{4-}$, in the presence of $W_{10}O_{32}{}^{4-}$ (2.0×10^{-4} M): (▲) aerated solution, (◊) deoxygenated solution, (□) oxygen saturated solution.

The kinetics obtained for the direct degradation of MBT under irradiation at 365 nm is in agreement with the previous quite low quantum yield determined when studying the MBT direct photolysis under irradiation at 313 nm [9]. The initial rate constants were exclusively determined in aerated and oxygen saturated conditions in the presence of DTA because in these conditions the kinetics were corresponding to first order kinetics. In addition, the low rate constant and the high half-life time value, determined in this study under direct irradiation at 365 nm, confirm the low direct photodegradability of MBT and it suggests that MBT could be present for long period of time in the environmental water compartments.

3.2. Degradation kinetics of 2-mercaptobenzothiazole in the presence of decatungstate salts

The degradation of MBT (1.0×10^{-4} M) was studied in the presence of $W_{10}O_{32}{}^{4-}$ (2.0×10^{-4} M) under irradiation at 365 nm in different conditions: aerated, oxygenated and deoxygenated solutions. During the study, the degradation of MBT was evaluated by the initial quantum yields determination in all experimental conditions and under monochromatic irradiation at 365 nm. The results are gathered in Table 1.

The pH was controlled to confirm that the main species in solution is $W_{10}O_{32}{}^{4-}$. In fact, the stability and the speciation of polytungstates in aqueous solution is very pH dependent. It has been showed for a pH between 6.9 and 4.2 that the decatungstate ions photoactivity was preserved and entirely inhibited at higher pH. This has been attributed to the formation of species like Keggin-type POMs ($H_2W_{12}O_{46}{}^{6-}$) with an absorption at lower wavelength ($\lambda = 260$–265 nm) and also a weak photoactivity under our irradia-

Table 1
Initial rate constants, half-life times and quantum yields of MBT (1×10^{-4} M) degradation in the presence of DTA (2.0×10^{-4} M) under irradiation at 365 nm in different experimental conditions.

Conditions	k (h^{-1})	$t_{1/2}$ (h)	Φ
Direct photolysis	0.03	23	0.02[a]
Aerated	0.25	2.8	0.032
Oxygen saturated	0.47	1.5	0.047
Deoxygenated	–	–	0.022

[a] Under irradiation at 313 nm [9].

tion conditions [20,30]. The pH measured for solutions of MBT-DTA was equal to 4.4 implying that the conditions involved optimal photocatalyst efficiency.

In aerated conditions (Fig. 1), MBT differently disappeared with a conversion of 90% after 8 h irradiation. This demonstrates that the photocatalysis process increases by a factor of 4 the MBT degradation when compared to the direct photodegradation.

Moreover, it is worth noting that the initial degradation rate is 6 times faster in the presence of DTA (Table 1). These results put into evidence the major catalytic role in the primary step of the degradation and also suppose a minor involvement of direct photolysis in the 2-mercaptobenzothiazole elimination under our experimental conditions. The remarkable decrease of the half-life times clearly illustrated the influence of DTA. In fact, the MBT half-life time is divided by a factor of 8 in aerated conditions (Table 1). In addition, the photocatalyst efficiency is evidenced by the quantum yields determined in aerated solutions compared to those measured in the absence of decatungstate and cited in the literature: the quantum yields are almost 2 times higher in the presence of $W_{10}O_{32}{}^{4-}$ whatever the experimental conditions are [9]. Nevertheless, the efficient photocatalysis reaction with DTA appeared to be very dependent on several parameters among them oxygen concentration.

3.2.1. Effect of oxygen on 2-mercaptobenzothiazole degradation

As shown in Fig. 1, 2-mercaptobenzothiazole degradation was significantly inhibited in deaerated conditions (around 50%) while in oxygen saturated solution the total degradation was reached in 8 h. The presence of oxygen increased the photocatalytic effect of decatungstate salts.

In the absence of oxygen, the degradation inhibition could be explained by the limited reoxidation of the reduced catalyst. This well known behavior occurs by the accumulation of the reduced species $W_{10}O_{32}{}^{5-}$ in the solution leading to the catalytic cycle opening and justifies the observation of the blue coloration during the irradiation of the mixture. Nevertheless, in the first step of the reaction, the availability of DTA salts could explain the initial fast degradation of MBT until a plateau is reached. This plateau value is reached after the total consumption of initial DTA and residual oxygen and it is also corresponding to the remaining MBT concentration noted with the direct photolysis process. Concerning the degradation in the oxygen saturated conditions, the oxygen concentration increase is in favor of $W_{10}O_{32}{}^{5-}$ reoxidation and also improves the photocatalytic degradation. The half-life time is divided by a factor of 2 and the initial rate constant is multiplied by a factor of 2 with higher oxygen concentration (Table 1).

Moreover, the oxygen effect is underlined by the considerable increase of the quantum yields as a function of oxygen concentration according to the decrease order: deoxygenated < aerated < oxygen saturated. These results confirm the major role of oxygen in the reoxidation process of reduced decatungstate $W_{10}O_{32}{}^{5-}$ and also its significant involvement in the photocatalytic reaction.

4. Kinetics and identification of 2-mercaptobenzothiazole photodegradation products in the presence of decatungstate salts

Solutions of decatungstate salts and 2-mercaptobenzothiazole were analyzed by HPLC all along the irradiation period in order to detect the degradation products formation, to establish their kinetics and to allow their identification. The study has been realized in the three experimental conditions previously cited (aerated, deoxygenated and oxygen saturated). The main degradation products have been identified by LC–ESI-MS analysis in positive and negative modes after convenient irradiation times. The degradation products are listed in Table 3.

Table 2

Maximum of absorbance and dipole moment calculated with B3LYP/6–21G method in Gaussian 4.1 software for MBT and hydroxylated MBT.

Name	MBT	4-OH	5-OH	6-OH	7-OH
λ_{max} (nm)	299.3	297	310.9	305.2	298.5
μ (D)	5.11	6.57	5.79	6.20	6.47

4.1. Identification of 2-mercaptobenzothiazole photoproducts

Aerated solutions of MBT and decatungstate salts irradiated 2 and 4 h correspond to a conversion extent of 40% and 60%, respectively have been analyzed by LC–ES-MS in positive and negative modes. The obtained photoproducts have been considered as degradation products essentially resulting from MBT induced degradation in the presence of $W_{10}O_{32}{}^{4-}$. This process is predominant because of a negligible MBT direct photodegradation (10% of conversion after 4 h) and particularly because of the competitive absorbance between MBT and DTA at 365 nm favorable for DTA ($\varepsilon_{DTA} = 1800 \pm 100\,M^{-1}\,cm^{-1}$ and $\varepsilon_{MBT} = 10 \pm 1\,M^{-1}\,cm^{-1}$).

Some calculated results obtained by B3LYP/6–21G method in Gaussian 4.1 software are gathered in Table 2. It is worth noting that the presence of an OH group on the aromatic ring generally modified the maximum of absorbance in the UV region and the polarity when compared to MBT.

A bathochromic effect was observed for the hydroxylated MBT attributed to the decrease of the π^* excited state energy due to the electronic delocalization growth favored by the presence of an electron doublet on the oxygen atom. This is clearly noted for 5 and 6-OH-MBT. Nevertheless, for 4 and 7-OH-MBT isomers, almost the same maximum of absorbance is observed compared to the one of MBT. This is probably due to the presence of intramolecular hydrogen bound between the hydroxyl function and S atom or between the amine and the hydroxyl group.

In addition, the presence of the OH group on the aromatic ring confers an additional polarity to the initial molecule. The dipole moment increase after the hydroxylation of MBT clearly indicates that the elution order should be controlled by the hydroxylation level. Moreover, considering the monohydroxylated MBT, it appears that the dipole moment increases as following: 5-OH < 6-OH < 7-OH < 4-OH. Nevertheless, it is worth noted that 4-OH and 7-OH-MBT present quite similar calculated polarities.

During the degradation of MBT in the presence of DTA, six products have been clearly detected and identified (Fig. 2). Among them, four hydroxylated MBT (**1**, **2**, **3** and **4**) have been put in evidence (Table 3). These compounds evidently correspond to the different isomers expected for OH-MBT. The OH-MBT assignment was based on the LC–MS-ESI analysis in negative and positive mode with a ratio *m*/*z* respectively equal to 182 and 184 which match with the molecular anion ($[M-H]^-$) and cation ($[M+H]^+$). In addition, hydroxylated MBT have already been observed in the biological degradation of MBT in the presence of *Rhodococcus rhodochrous* by Haroune and coworkers and the results obtained for the identification of those compounds confirm our hypothesis [7]. Correlations between calculated and experimental retention times allowed us to attribute the photoproducts **1**, **2**, **3** and **4** to respectively 5-OH, 6-OH, 7-OH and 4-OH-MBT.

An additional oxidized compound (**5**) have been observed with a lower retention time and a ratio *m*/*z* equal to 200 and to 198 respectively in positive and negative modes. The compound **5** was considered to be a sulfoxide derivative of OH-MBT. The hypothesis of such a structure was done according to the retention time and to the UV-spectrum shape (located at 336 nm) which imply an

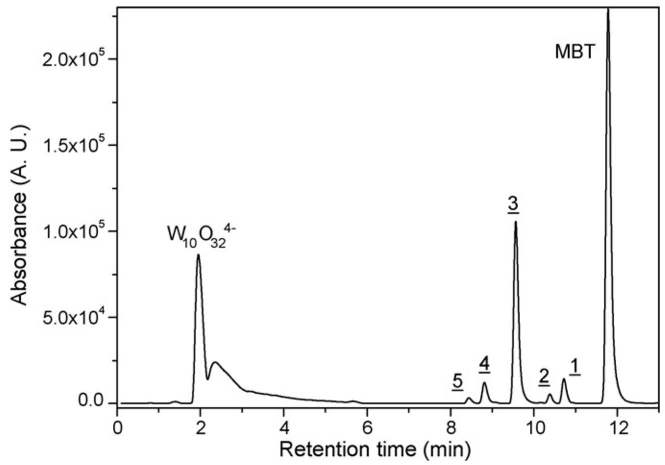


Fig. 2. Chromatogram of MBT and DTA irradiated 2 h at 365 nm in aerated solution, λ_{det} = 340 nm, [MBT] = 1.0 × 10^{-4} M, [$W_{10}O_{32}^{4-}$] = 2.0 × 10^{-4} M, LC–MS-DAD analysis conditions.

increase of the polarity and a monohydroxylation of the aromatic ring. The presence of an O atom on the benzothiazole part has been considered because we rejected the possibility of two OH groups on the aromatic ring. In fact, it has been shown that compounds with two OH groups on the aromatic ring could rapidly lead to an open ring derivative which is not detected in our experiments [8]. Another product, with a high retention time and a ratio *m*/*z* equal to 333 in positive mode, has been attributed to the MBT dimer. The low polarity of the product is in agreement with a retention time equal to 19.1 min (isocratic elution mode with 95% of MeOH) and the exclusive detection of this product in positive mode confirms also the attribution.

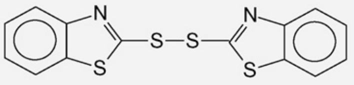
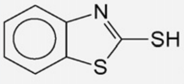
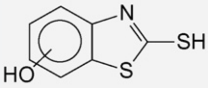
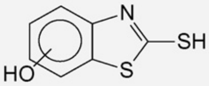
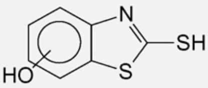
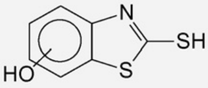
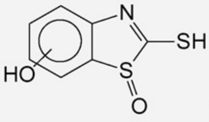
4.2. *Kinetic of 2-mercaptobenzothiazole photoproducts*

The photoproducts occurrence and kinetics clearly showed the major consequence of experimental conditions and put in evidence the main involvement of induced degradation.

In oxygenated conditions, four main products are detected during the irradiation of MBT and they have been attributed to hydroxylated MBT and to product **5** according to their retention time as well as their UV-spectrum. All the kinetics are represented in Fig. 3. No more than three kinetics of OH-MBT isomers have been established because of the really close polarity of 7 and 4-OH-MBT which did not permit their correct separation by HPLC. It is worth noting that the hydroxylation of MBT takes place at the beginning of the irradiation. The formation of OH-MBT isomers are followed by their disappearance after different irradiation times as a function of OH-MBT isomers. 5-OH-MBT is degraded after 1 h under irradiation and the degradation of the other isomers occurs later (2 or 3 h). The product **5** appears after 1 h under irradiation implying that it is a secondary product and is obviously formed from OH-MBT isomers degradation.

In aerated solutions, the same kinetics have been observed for hydroxylated MBT but on a higher time scale. Their disappearance

Table 3
Proposed structures for MBT photoproducts by LC–ESI-MS analysis.

Retention time (min)	Molecular weight (g/mol)	Observed ion *m*/*z* (abundance %) in positive mode	Observed ion *m*/*z* (abundance %) in negative mode	Proposed structure
19.1	332	333 (100): [M+H]$^+$		 Dimer (disulfide form)
11.8	167	168 (100): [M+H]$^+$	166 (100): [M–H]$^-$ 134 (10): 166-32 [–S]$^-$	 MBT
10.8	183	184 (100): [M+H]$^+$	182 (100): [M–H]$^-$	 **1**
10.4	183	184 (100): [M+H]$^+$	182 (100): [M–H]$^-$	 **2**
9.9	183	184 (100): [M+H]$^+$	182 (100): [M–H]$^-$	 **3**
9.6	183	184 (100): [M+H]$^+$	182 (100): [M–H]$^-$	 **4**
8.9	199	200 (100): [M+H]$^+$	198 (100): [M–H]$^-$	 **5**

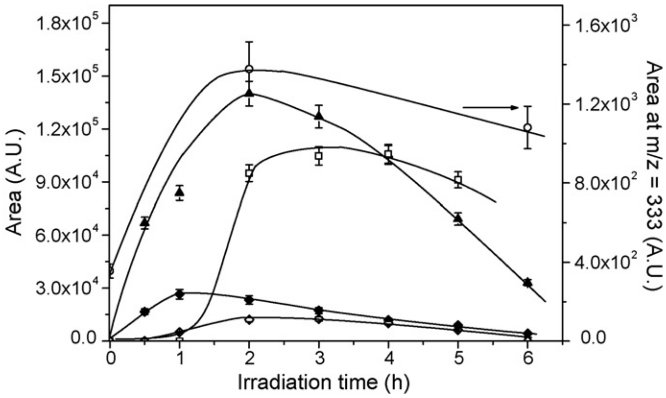


Fig. 3. Kinetics of MBT (1.0×10^{-4} M) photoproducts in the presence of DTA (2.0×10^{-4} M) and under irradiation at 365 nm: (▲) 7 and 4-OH-MBT, (●) 5-OH-MBT, (◊) 6-OH-MBT, (□) product **5** in oxygenated and LC-DAD analysis conditions, and (○) MBT dimer in aerated and LC–MS analysis conditions.

occurred two times later than in oxygen saturated conditions. This can be explained by the continuous reoxidation of reduced DTA in oxygenated conditions which permits the more efficient oxidation of MBT and of its primary photoproducts. As a consequence, the formation of product **5** was negligible in aerated conditions. In deoxygenated conditions, product **5** was not detected and the appearance of OH-MBT isomers took place on longer time. After 6 h under irradiation, their concentrations are always increasing probably because of residual diffused oxygen. The results obtained by LC–MS analysis showed that the disulfide form seems to be present in the first step of the irradiation and disappears for higher time in aerated conditions (Fig. 3). No other photoproduct was observed within the irradiation time implying that the direct degradation was negligible.

According to MBT photoproducts identification and kinetics and the oxygen role, a mechanism described in Fig. 4 has been proposed. The mechanism described below implies, in a first step, two concomitant processes. First, an electron transfer process with $W_{10}O_{32}^{4-*}$ excited state to give rise to a MBT radical cation located on the aromatic ring and second, a H atom abstraction with $W_{10}O_{32}^{4-*}$ excited state leads to another MBT radical located on the S atom of the thiol group (–S•).

In a second step, the formation of OH-MBT isomers can be attributed to a successive reaction of MBT radical cation with oxygen present in the solution. Such OH-MBT formations have been previously put in evidence in different previous studies [8,13,14]. Simultaneously, the MBT dimer formation could occur by the radical recombination of MBT radicals (–S•). This result is relevant considering previous studies on the oxidation of mercaptothiazoles in the presence of hydrogen peroxide and on the MBT photolysis in organic solutions [31,32].

In a third step, similar reactions have been expected. An electron transfer process involving DTA excited state and an electron doublet of S atom on benzothiazole ring takes place and a radical cation ($S^{+\bullet}$) is formed. A further reaction with superoxide or hydroxide ion in aqueous solution gives then rise to the sulfoxide derivative (product **5**) as described in the literature [33]. In our conditions, the reaction with $O_2^{\bullet-}$ could be favored because of its formation through the reoxidation reaction involving the reduced DTA and dissolved oxygen.

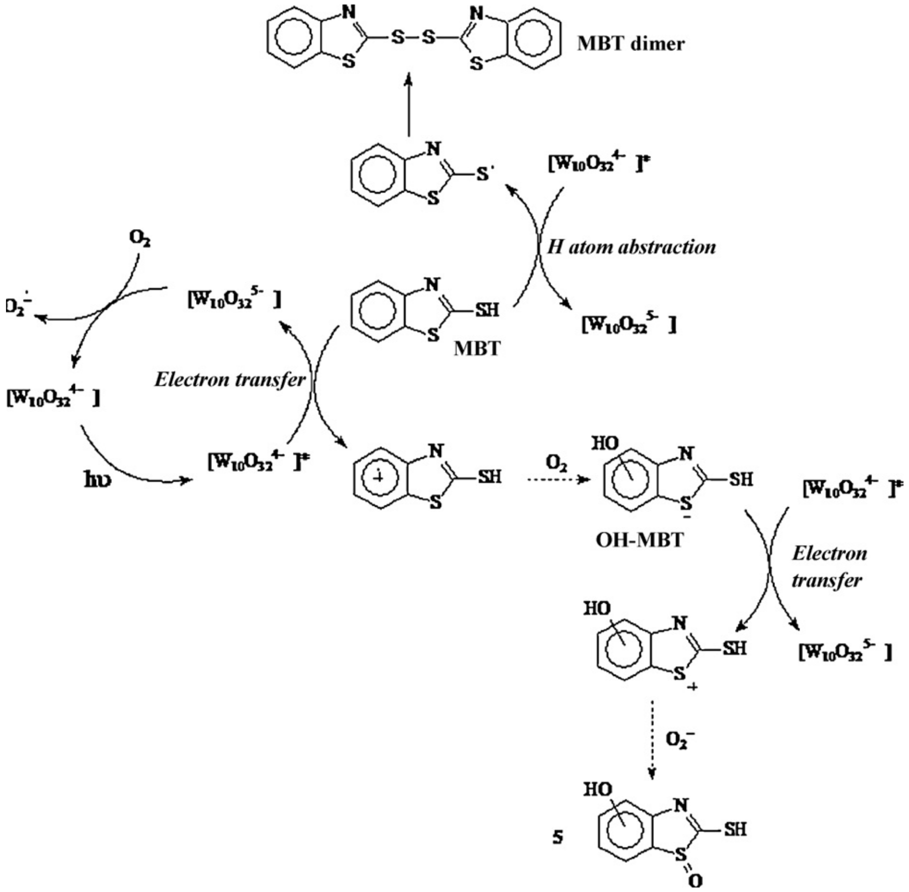


Fig. 4. Degradation mechanism of MBT in the presence of DTA under irradiation at 365 nm.

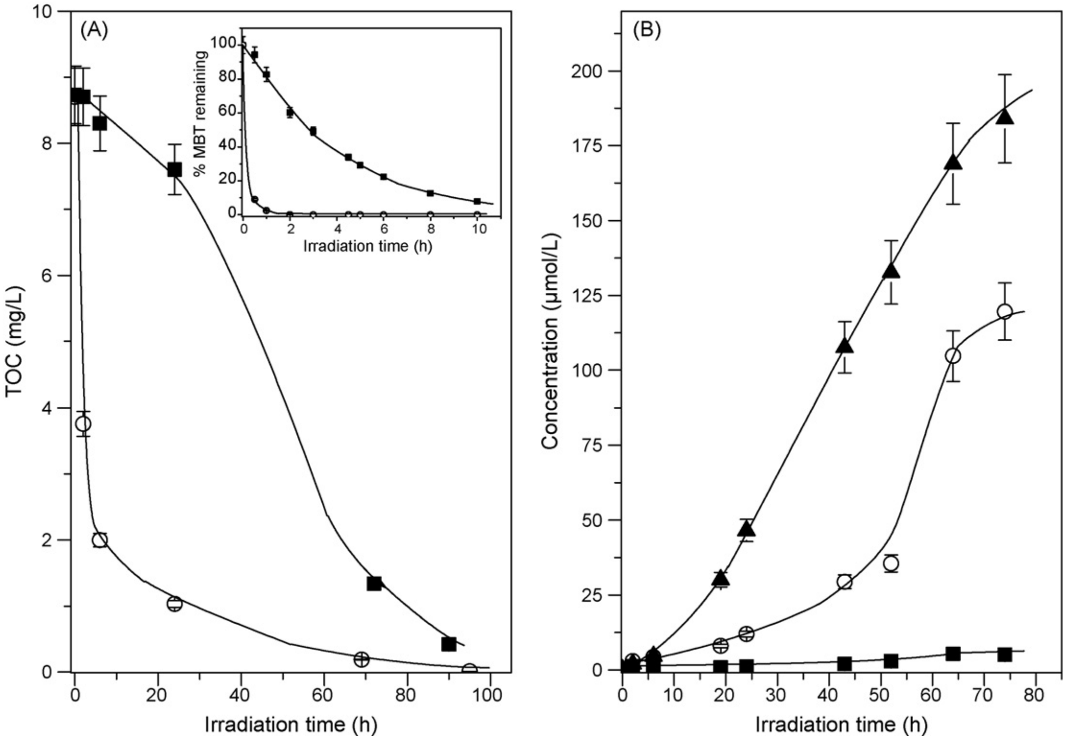


Fig. 5. (A) TOC evolution and degradation of MBT (insert) in the presence of DTA (■) and in the presence of TiO_2 (○); (B) formation of inorganic ions upon irradiation of MBT in the presence of DTA: sulphate (▲), nitrate (■) and ammonium ions (○) [MBT] = 1.0×10^{-4} M, [DTA] = 2.0×10^{-4} M, [TiO_2] = 0.2 g/L; aerated conditions, λ_{irr} = 365 nm.

5. Mineralization

The mineralization of MBT has been determined by dissolved organic carbon (or total organic carbon, TOC) measurements and the formation of inorganic ions has been quantified as a function of time in aerated solutions and under irradiation at 365 nm. This set of experiments was done in order to put into evidence the photocatalyst efficiency and also the potential application of $W_{10}O_{32}^{4-}$ in the elimination of this benzothiazole derivative. The mineralization and the degradation kinetics are represented in Fig. 5A.

As shown in Fig. 5A, the organic compounds degradation takes place on a shorter time scale than the mineralization. The total disappearance of MBT is effective in 20 h when its total mineralization is observed after 100 h under irradiation. This result indicates that the mineralization is initiated by the MBT photoproducts' elimination and the presence of a short induction period during the formation of inorganic species (SO_4^{2-}, NH_4^+ and NO_3^-) confirms this hypothesis (Fig. 5B). The correlation between the decrease in organic dissolved carbon concentration and the formation of inorganic ions is evidenced by the corresponding kinetics presented in Fig. 5A and B. After 90 h upon irradiation, the mineralization of MBT is almost total (92% of disappearance) and the concentration of sulphate ions is equal to 1.9×10^{-4} M, which corresponds to 95% of the sulphur atom present in the molecule also very similar to the expected value of 1.84×10^{-4} M. For the same irradiation time, the concentration of ammonium ions reaches a value around 1.1×10^{-4} M which is comparable to the nitrogen atoms expected value (0.92×10^{-4} M); the nitrate ions were detected in very low concentration (maximum equal to 5×10^{-4} M). All the results are in complete agreement with the total mineralization of MBT in the presence of DTA.

Moreover, compared with the results obtained during the biodegradation of MBT in the presence of *R. rhodochrous*, the presence of DTA enhanced the elimination of MBT. In fact, the authors put into evidence that only 30% of MBT is mineralized after 128 h of incubation, this is four times less efficient than with DTA [7]. More recent studies realized with doped titanium dioxides like photocatalyst put in evidence that around 50% of MBT are mineralized in less than 80 min [34]. In order to compare the efficiency of DTA and TiO_2 in the same conditions, we also realized some degradation and mineralization experiments with Degussa P25, a conventional TiO_2 photocatalyst, at a concentration equal to 0.2 g/L. The results presented in Fig. 5A show that the degradation of MBT in the presence of titanium dioxide is five times more efficient than with DTA (insert Fig. 5A) and the mineralization is reached in less than 70 h also about two times more efficiently than with DTA.

Nevertheless, we can also conclude that DTA seems to be a good candidate for the induced elimination of 2-mercaptobenzothiazole in aqueous homogeneous solutions.

6. Conclusion

All along the study, we demonstrated the decatungstate salts were efficient in the degradation of 2-mercaptobenzothiazole in aqueous homogeneous conditions under UV irradiation. In fact, the MBT disappearance and TOC kinetics, the rate constants and also the quantum yields clearly illustrated the more important degradation and the possible total elimination of MBT when compared to direct and/or biological degradations.

The whole process revealed to be oxygen dependent because of the restricted $W_{10}O_{32}^{5-}$ reoxidation step. The degradation of 2-mercaptobenzothiazole occurred by electron transfer and H atom abstraction processes with the very oxidative specie $W_{10}O_{32}^{4-*}$ and the main photoproducts formed were monohydroxylated products, sulfoxide derivatives and the dimer of MBT. The calculations by Gaussian 4.01 software allowed us to confirm MBT photoproducts identification considering their dipole moment and their UV–vis absorption spectrum. The total MBT mineralization was reached in the presence of DTA attesting the potential applications for the elimination of different organic pollutants and particularly benzothiazole derivatives.

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