

Original

Serdechnova, M.; Ivanov, V.L.; Domingues, M.R.M.; Evtuguin, D.V.;
Ferreira, M.G.S.; Zheludkevich, M.L.:

**Photodegradation of 2-mercaptobenzothiazole and 1,2,3-
benzotriazole corrosion inhibitors in aqueous solutions and
organic solvents**

In: Physical Chemistry Chemical Physics (2014) Royal Society of Chemistry

DOI: [10.1039/c4cp03867c](https://doi.org/10.1039/c4cp03867c)



Cite this: *Phys. Chem. Chem. Phys.*,
2014, **16**, 25152

Photodegradation of 2-mercaptobenzothiazole and 1,2,3-benzotriazole corrosion inhibitors in aqueous solutions and organic solvents

Maria Serdechnova,^{*a} Vladimir L. Ivanov,^b M. Rosario M. Domingues,^c
Dmitry V. Evtuguin,^d Mario G. S. Ferreira^a and Mikhail L. Zheludkevich^{ae}

The photochemical degradation of 2-mercaptobenzothiazole (MBT) and 1,2,3-benzotriazole (BTA) inhibitors was studied in the present work in aqueous and in organic solutions. The extent of photodegradation was assessed by UV-Vis spectroscopy and the main reaction products were identified by tandem electrospray ionization mass spectrometry (ESI-MS/MS). The analysis of degradation products upon UV irradiation revealed the predominant formation of dimeric compounds from MBT and oligomeric structures from BTA, which were further converted into aniline. The increase of the quantum yield of MBT and BTA photodegradation reactions under aerobic conditions both in aqueous and organic solvents was explained by an increase of the spin-orbit conversion of the singlet radical pairs into the triplet radical pairs in the presence of oxygen. These triplet pairs further dissociate into free radicals, or convert to the parent compounds. At the early stage of UV irradiation, free radical coupling leads essentially to dimer formation in the case of MBT and to the formation of oligomers in the case of BTA irradiation.

Received 28th August 2014,
Accepted 3rd October 2014

DOI: 10.1039/c4cp03867c

www.rsc.org/pccp

Introduction

The utilization of inhibitors for minimizing metal corrosion attracts increasing interest.^{1,2} The area of self-healing protective coatings, involving the anti-corrosion inhibitors, is developing very fast in the last decade due to the strong industrial demand.^{3–5} One of the main strategies is based on the incorporation of inhibitor compounds into polymer, hybrid or inorganic layers.^{6,7} The concept has been well known for decades when different inhibitor pigments were used to confer active protection to the polymer paints. The most effective inhibitor pigments were composed of moderately-soluble chromate-based salts such as strontium chromate.^{8,9} However, the strong oxidizing potential of chromate, which is responsible for its unique inhibiting potential, is also the reason for the high toxicity and carcinogenicity of this compound. While exploring the new environmentally friendly alternative inhibitors much attention was paid to the organic heterocyclic compounds.^{10–12} For example

triazole and thiazole derivatives are widely considered as potential inhibitors to be added to the technological medium¹³ and recently to the active protective coatings as well.¹⁴ The mechanism of action of such inhibitors is not fully understood; however, the adsorption properties are expected to explain their anticorrosion effect.^{15–18}

1,2,3-Benzotriazole (BTA) and 2-mercaptobenzothiazole (MBT) are the most widely used corrosion inhibitors for copper,¹⁹ aluminum²⁰ and other metals.^{21–24} The attention to them is fast growing in recent years, thanks to their efficiency as standalone inhibitors,^{17,18} or as a part of synergistic mixtures.^{13,25,26} They have a wide number of applications in aeronautic, automotive and shipbuilding industries.

The high industrial demand of anti-corrosion inhibitors stimulates their application also under atmospheric conditions, where they undergo degradation induced by solar irradiation.^{27–29} The photodegradation of anticorrosion additives results in loss of their protective properties and environmental hazards.^{30,31}

Up to now only a few studies on the behavior of MBT and BTA under irradiation have been performed. Thus, it was shown that in the 2-mercaptobenzothiazole structure, the C–S bond is relatively weak and renders the homolytic cleavage under UV irradiation.³² It was proposed³³ that MBT decomposition under irradiation occurs *via* both singlet and triplet excited states and decomposes very faster in the presence of oxidizing agents (like O₃, ref. 34). However, the products of the photodegradation reaction, proposed in the literature, and mechanisms of their

^a CICECO/Department of Material Engineering and Ceramics, University of Aveiro, 3810-193 Aveiro, Portugal. E-mail: serdechnova@mail.ru; Fax: +351-234-425-300

^b Department of Chemistry, Lomonosov Moscow State University, Leninskiye gory 1, 119991, Moscow, Russia

^c Mass Spectrometry Centre, Organic Chemistry and Natural Products Research Unit/Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

^d CICECO/Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

^e Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Strasse 1, 21502 Geesthacht, Germany

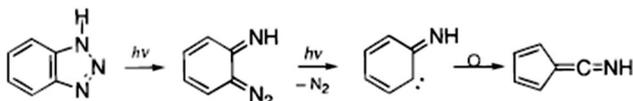


Fig. 1 The proposed photolysis mechanism of 1,2,3-benzotriazole.³⁵

formation are quite different and sometimes contradict each other. For example, it was notified that BTA is surprisingly stable to the UV irradiation in aqueous solution.³⁵ However, in other studies, the formation of different BTA degradation products such as 6-diazo-2,4-cyclohexadien-1-imine,³⁶ iminocarbene³⁷ and 6-iminofulvene³⁸ has been reported (Fig. 1).

The aim of this work is to perform a systematic study of MBT and BTA photodegradation reactions on a mechanistic level identifying the products of their photodegradation and kinetics of the respective processes. The final goal is to understand if these inhibitive compounds are able to sustain under intensive UV light exposure without sufficient degradation.

Materials and methods

Materials

2-Mercaptobenzothiazole, $C_7H_5NS_2$, (97%) was supplied by Sigma-Aldrich Chem. Comp. (USA). 1,2,3-benzotriazole, $C_6H_5N_3$, (>99%) was purchased from Sigma-Aldrich Chemie GmbH (Germany). The inhibitors were used as received without any further purification. Borate and acetate standard buffers (pH 9.2 and 4.0 respectively) were prepared using commercially available PA grade chemicals. Milli-Q water was used for the preparation of aqueous solutions. The PA grade organic solvents (iso-propanol, methanol and hexane) and 96% ethanol supplied by Sigma-Aldrich Chemie GmbH (Germany) were used.

UV irradiation assays

The solutions of MBT and BTA (concentration $ca. 3 \times 10^{-4} \text{ mol L}^{-1}$) were irradiated employing a high pressure mercury lamp DRSh-500 using quartz cells ($10 \times 10 \text{ mm}$). Spectrally clean argon was used for the deaeration of the solutions. The quantum yield of the reaction was defined as a ratio between the amount of decomposed original compound and the amount of light absorbed by this compound.

The concentration changes of the original MBT and BTA compounds were defined *via* the change of the optical density of the solution at a specific wavelength. The intensity of the absorbed light was defined by the photocell system F-4, calibrated with a ferrioxalate actinometer.³⁹ The quantum yield of the reaction was calculated using the “Mathcad-15” software.

Analyses

The absorption spectra were recorded on a spectrophotometer Shimadzu UV-2101 PC (Shimadzu, Japan). The electrospray mass spectra (ESI-MS) and tandem mass spectra (ESI-MS/MS) were acquired using a LXQ linear ion trap mass spectrometer (ThermoFinnigan, San Jose, CA, USA). For the analysis previously prepared samples (original and irradiated) were diluted hundred times with ultra-pure methanol. Positive ion ESI-MS and MS/MS spectra were acquired using the following conditions: nitrogen sheath gas 30 psi, spray voltage 5 kV, heated capillary temperature 275 °C, capillary voltage 1 V, and tube lens voltage 40 V. The flow rate was set to $8 \mu\text{L min}^{-1}$ and the voltage applied was 5 kV. Nitrogen was used as nebulizing and drying gas. Full scan mass spectra ranging from m/z 100 to 1500 were acquired. In the MS^n experiments, collision energy varied between 15 and 25 of normalized collision. Data acquisition was carried out using an Xcalibur data system.

Results

The MBT irradiation was performed using a mercury lamp using a light filter Hg313 to separate off the intensive line of mercury emission at 313 nm. In the case of BTA the irradiation of the sample was carried out with the full light range of the lamp.

Photolysis of MBT and BTA in aqueous solution

The changes in the absorption spectra of aqueous BTA and MBT solutions during the irradiation are evidenced in Fig. 2.

Fairly a significant decrease of optical density in solution of MBT at 320 nm and in solution of BTA at 256 nm revealed the decomposition of heterocyclic inhibitors under irradiation. The evolution of spectra is in good agreement with previously published results obtained in the air-saturated medium.³³ A significant increase

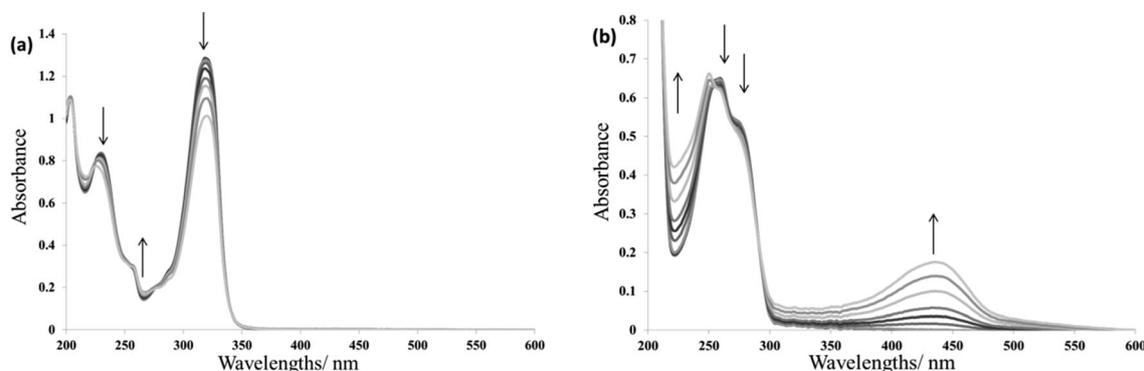


Fig. 2 UV-Vis absorption spectra of MBT (a) and BTA (b) in aqueous solution upon irradiation: 0 s, 60 s, 360 s, 1260 s, 2160 s, 4160 s and 5940 s respectively.

of optical density at around 350–500 nm has been observed in BTA solution, similarly to that previously reported for BTA irradiated in basic media³⁵ and at 77 °C³⁶ yielded a so-called “yellow intermediate”.³⁶ In both absorption spectra (MBT and BTA) the isosbestic points have been detected. The presence of the isosbestic points indicates that the ratio between photodegradation products remains constant up to a very deep level of the photolysis.

The quantum yields of the photodegradation reaction in the aqueous solution were determined as $(4.5 \pm 0.5) \times 10^{-3}$ for MBT and $(5 \pm 1) \times 10^{-3}$ for BTA. It should be noted that a significant decrease of the decomposition rate and the quantum yield of the reaction occurs in the case of irradiation of de-aerated solutions. Hence the presence of oxygen promotes the photodegradation of MBT and BTA under realistic conditions when these inhibitors are used in active coatings and oxygen from air can provide an accelerating effect on the photolysis processes.

Photodegradation of MBT and BTA at variable pH

The photodegradation reaction of MBT and BTA was studied both in basic and acidic media. The irradiation of both inhibitors was performed in borate buffer at pH 9.2 and in sodium acetate buffer at pH 4.0. The absorption spectra of MBT and BTA (Fig. 3a and 3b, respectively) irradiated under basic conditions were significantly different to those acquired in neutral medium, because they deal with the anionic forms of aforementioned compounds.

A decrease of optical density of MBT solution at 310 nm and of BTA solution at 275 nm evidenced the decomposition of heterocyclic inhibitors in their anionic form. In the case of BTA, the irradiation in basic solution leads to only a minor increase of the optical density between 350 and 500 nm in comparison with the irradiation in neutral medium.

The quantum yield of the MBT photodegradation reaction in basic aqueous solution is close to 0.03. The absorption spectra of MBT and BTA in the acidic aqueous solution were similar to the spectra without pH adjustment. The quantum yield of the MBT photodegradation in an acidic environment is equal to $(2 \pm 0.2) \times 10^{-4}$. BTA photodegradation both under acidic and basic conditions during the irradiation occurs much slower in comparison with neutral solution (quantum yield is less than 10^{-4}).

Products of photodegradation reaction in aqueous solution

Electrospray ionization (ESI-MS) mass spectra of original and irradiated MBT and BTA aqueous solutions were registered in order to evaluate the primary reaction products.

Organic inhibitors were dissolved in water, irradiated for about 1 hour and further diluted 100 times with ultra-pure methanol before being injected into the electrospray source.

Comparison of ESI-MS spectra obtained before and after the irradiation of MBT and BTA allowed the identification of newly formed molecular ions. As an example, Fig. 4 shows the ESI-MS spectrum of the original aqueous BTA and solution after UV irradiation. The essentially protonated $[M + H]^+$ adducts derived from BTA were observed in ESI-MS spectra. The molecular ion $[M + H]^+$ of non-modified BTA at m/z 120 and the new ion assigned to the dimerization product of BTA at m/z 213 were detected (Fig. 4a). At the same time, no significant amounts of low molecular products below 120 Da have been observed. The ESI-MS/MS (MS^2) spectrum of the molecular ion at m/z 213 and the MS^3 spectrum of the ion at m/z 185 are presented in Fig. 4c and 4d, respectively, thus confirming the proposed structures.

It was evident that BTA degradation by photolysis leads to the cleavage of the triazole cycle followed by nitrogen release and the dimerization of the formed aniline radical with BTA cation-radical *via* coupling.

The detailed MS/MS fragmentation patterns of MBT and BTA and their oligomeric irradiation products are listed in Table 1. The structural analysis clearly confirmed the formation of dimers during MBT irradiation and the formation of dimers and conjugated oligomeric structures during UV irradiation of BTA. Interestingly, the detected oligomers undergo further transformations when the storage solution is exposed to daylight with the formation of low molecular weight products. These transformations might include autoxidation steps.

The analysis of photodegradation products during the irradiation of MBT and BTA in the aqueous solutions with adjusted pH (acidic and basic) was not performed due to the inconvenience of mass spectrometry analysis of solutions rich in inorganic ions.

Photolysis of MBT and BTA in organic solvents

In order to better understand the photodegradation pathways for MBT and BTA, the photolysis was carried out also in iso-propanol

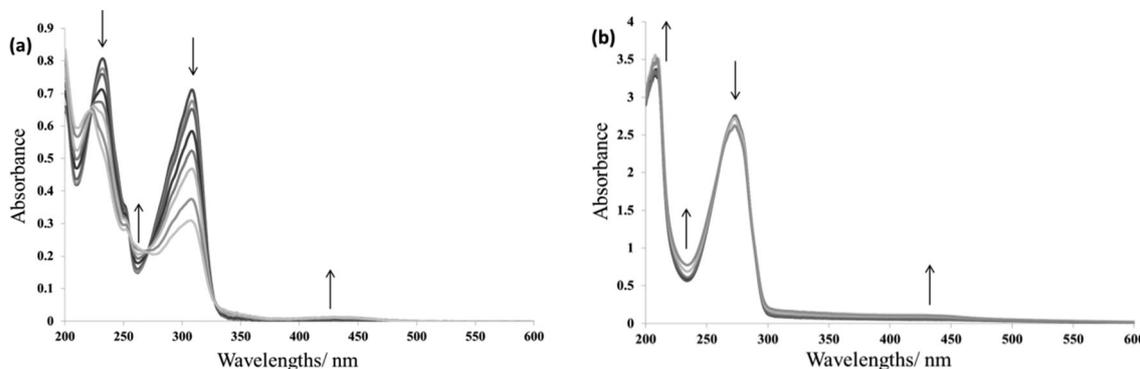


Fig. 3 UV-Vis spectra of MBT (a) and BTA (b) irradiated under basic conditions: 0 s, 60 s, 360 s, 960 s, 2160 s, 3960 s and 5760 s respectively.

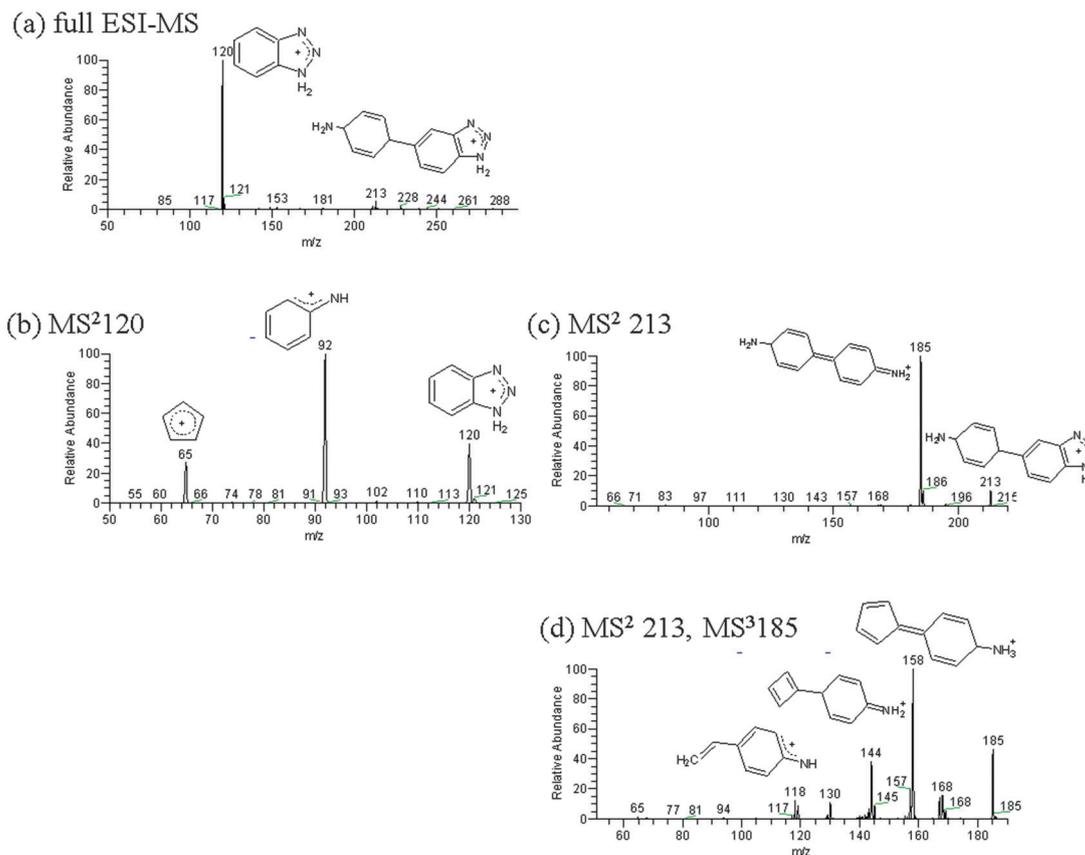


Fig. 4 Proposed fragmentation of BTA and the dimer formed during irradiation in the aqueous solution: (a) full ESI-MS spectrum of BTA after irradiation, (b) MS² of the [M + H]⁺ at *m/z* 120 corresponding to the non-modified BTA, (c) MS² of the [M + H]⁺ ion at *m/z* 213 corresponding to the newly formed dimer, (d) MS³ of the ion at *m/z* 185.

solution. iso-Propanol was chosen for several reasons: (1) it does not contain any aqueous impurities, (2) it is polar and (3) it has a low energy C–H bond. This facilitates the radical reaction between the organic inhibitory compound and the solvent molecule (in comparison with aqueous media) and can help in the elucidation of reaction pathways. The changes in absorption spectra of MBT in iso-propanol solution are quite similar to those registered in aqueous solution for the non-dissociated molecular form of the substrate. The quantum yield of reaction was $(3.6 \pm 0.5) \times 10^{-3}$. The quantum yield of the MBT photodegradation was significantly decreased when carried out in the de-aerated iso-propanol solution (less than 10^{-4}).

The significant difference occurs in the case of BTA irradiation in iso-propanol and aqueous solutions. Firstly, the absence of the optical density increase between 350 and 550 nm was observed in organic medium (the optical density slightly increases at around 300–400 nm). The photolysis of BTA was monitored using the characteristic band at about 250 nm (Fig. 5). The optical density of solution decreases due to the photodegradation of BTA during the first 30–40 min, being further increased up to *ca.* 100 min of photoirradiation and fall down in the period of 100–250 min (Fig. 5).

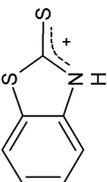
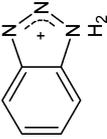
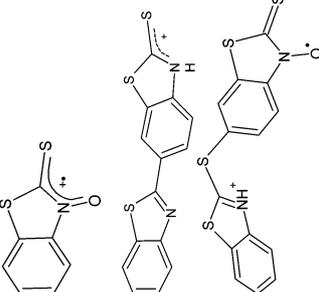
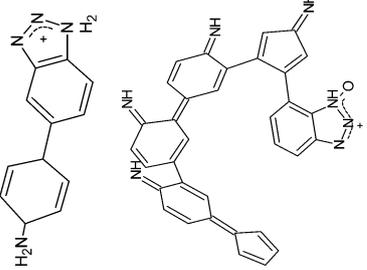
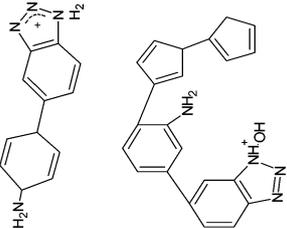
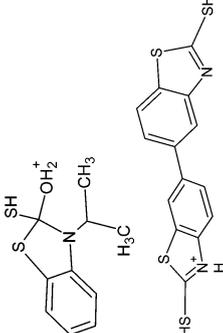
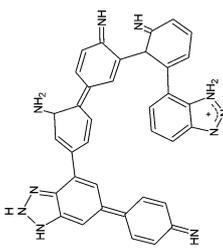
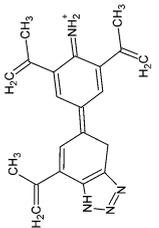
This behavior can be explained by the formation of the intermediate product, which absorbs the UV light in the similar

region as original BTA and undergoes further photodegradation under irradiation. The contribution of autoxidation reactions with reactive oxygen species to the degradation of these intermediate compounds may be proposed by analogy to aerobic photolysis of pesticides structurally similar to BTA.⁴⁰ The formation of this intermediate was not observed in the case of de-aerated solution. The final reaction product had the maximum absorbance at around 275 nm.

The proposed structures for the intermediate and final products of BTA and final MBT photodegradation products in iso-propanol solution were identified by ESI-MS/MS using an ion trap mass spectrometer (Table 1). The examples of ESI-MS and MS/MS spectra of the original MBT ([M + H]⁺ at *m/z* 168) and the dimer formed during the photolysis in the iso-propanol solution are presented in Fig. 6. The obtained results indicate that similarly to BTA the dimerization of MBT occurs *via* coupling of phenyl radicals.

Following the experiment with iso-propanol solution as a solvent, *n*-hexane, which is less polar in comparison with iso-propanol and contains C–H bonds with higher energy than energy of the C–H bond of the tertiary carbon atom in iso-propanol, was chosen. Fig. 7 shows the changes in MBT (Fig. 7a) and BTA (Fig. 7b) absorption spectra in hexane under UV irradiation.

Table 1 The detailed MS/MS fragmentation patterns of MBT and BTA and their oligomeric irradiation products

2-Mercaptobenzothiazole		1,2,3-Benzotriazole	
Proposed structure	<i>m/z</i> values of the proposed compound [M + H] ⁺ and product ions observed in the ESI-MS/MS spectra	Proposed structure	<i>m/z</i> values of the proposed compound [M + H] ⁺ and product ions observed in the ESI-MS/MS spectra
	<i>m/z</i> of [M + H] ⁺ is 168 136 (-S), 135 (-SH), 124 (-SC), 109 (-SCNH), 92 (-S ₂ CH)		<i>m/z</i> of [M + H] ⁺ is 120 92 (-N ₂), 65 (-N ₃ CH)
Original compound		Original compound	
Irradiated aqueous solution	Irradiated aqueous solution	Irradiated aqueous solution	Stored aqueous solution
	<i>m/z</i> of [M + H] ⁺ is 185 167 (-H ₂ O), 153 (-S), 139 (-SCH ₂), 121 (-SCOH ₄) <i>m/z</i> of [M + H] ⁺ is 301 268 (-SH), 166 (-C ₇ H ₄ SN) <i>m/z</i> of [M + H] ⁺ is 348 330 (-H ₂ O), 304 (-SC), 272 (-S ₂ C), 229 (-C ₆ H ₆ SN), 181 (C ₇ H ₅ S ₂ N), 167 (-C ₇ H ₃ S ₂ NO)		
	<i>m/z</i> of [M + H] ⁺ is 213 185 (-N ₂), 158 (-N ₃ CH), 144 (-N ₃ C ₂ H ₃), 142 (-N ₃ C ₂ H ₅), 118 (-N ₃ C ₄ H ₅) Derivatives with <i>m/z</i> of [M + H] ⁺ from about 550 to 600 Fragmentation due to: -H ₂ O -C (benzene ring transformation) -N ₂ (BTA to aniline transformation) -C ₆ N (formation of shorter oligomer structures)		<i>m/z</i> of [M + H] ⁺ is 213 185 (-N ₂), 158 (-N ₃ CH), 144 (-N ₃ C ₂ H ₃), 142 (-N ₃ C ₂ H ₅), 118 (-N ₃ C ₄ H ₅) Derivatives with <i>m/z</i> of [M + H] ⁺ from about 350 to 450 Fragmentation due to: -H ₂ O -C (benzene ring transformation) -N ₂ (BTA to aniline transformation) -C ₆ N or C ₅ H ₅ (formation of shorter oligomer structures)
Irradiated iso-propanol solution	Irradiated iso-propanol solution	Irradiated iso-propanol solution	Prolonged irradiation of iso-propanol solution
	<i>m/z</i> of [M + H] ⁺ is 228 211 (-OH), 210 (-H ₂ O), 193 (-SH ₃), 175 (-SOH ₅) <i>m/z</i> of [M + H] ⁺ is 333 257 (-CS ₂), 224 (-CS ₃ H), 197 (-C ₂ S ₃ NH ₂), 167 (-C ₂ S ₂ NH ₆)		
	Derivatives with <i>m/z</i> of [M + H] ⁺ from about 590 to 730 Fragmentation due to: -C (benzene ring transformation) -N ₂ (BTA to aniline transformation) -C ₆ N (formation of shorter oligomer structures)	Derivatives with <i>m/z</i> of [M + H] ⁺ from about 590 to 730 Fragmentation due to: -C (benzene ring transformation) -N ₂ (BTA to aniline transformation) -C ₆ N (formation of shorter oligomer structures)	Derivatives with <i>m/z</i> of [M + H] ⁺ from about 300 to 350 Fragmentation due to: -3C, 5H (iso-propanol radical) -2N (BTA to aniline transformation) -C, -4H (parts of iso-propanol)

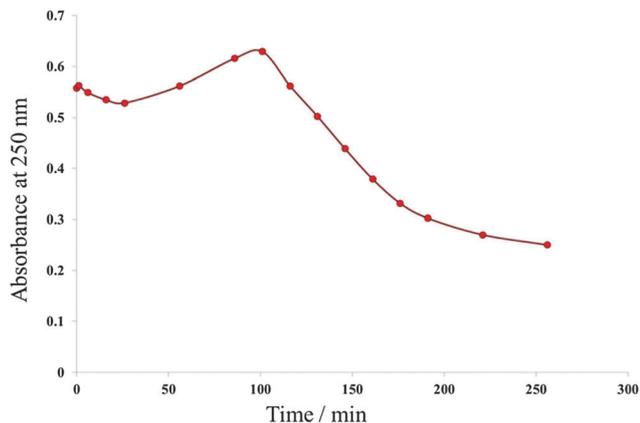


Fig. 5 The optical density of the BTA solution at 250 nm during the irradiation experiment.

The changes of the absorption spectra of MBT in the hexane solution are very similar to the irradiation of the molecular form of MBT in aqueous solution (Fig. 7a). The quantum yield of the reaction was $(4.5 \pm 0.5) \times 10^{-3}$. The irradiation of the BTA in the hexane solution leads to the formation of the product with maximum absorbance at *ca.* 240 nm. No increase of optical density between 350 and 550 nm was observed (Fig. 7b).

Discussion

The formation of intermediate short-living products during the MBT and BTA photolysis, which were previously described in the literature,³⁵ and a great number of radical recombination products, which we have found during this work, indicates that the initial stage of the photochemical reaction is the photodissociation of the N–N bond in the case of the BTA compound and C–S in the case of the MBT compound. The dissociation energy of the C–S bond is equal to $84.9 \text{ kcal mol}^{-1}$ and the S–H bond is equal to $76.2 \text{ kcal mol}^{-1}$.⁴¹ The energy of the light at 313 nm is equal to $91.35 \text{ kcal mol}^{-1}$.

Since the energy of UV light at 313 nm is higher than the energy of both chemical bonds, their dissociation is energetically feasible. The photodissociation of bonds in organic molecules occurs after the formation of radical pairs in a singlet state. Radical pairs in the singlet state have very short lifetime due to the high rate of recombination of the parent molecules.

The dissociation of the chemical bonds and the formation of free radicals occur from the triplet radical pairs, which are formed as a result of the spin–orbit conversion of singlet radical pairs.⁴² This fact explains very low quantum yields of the photochemical reactions. It is well-known that paramagnetic oxygen quenches both singlet and triplet excited states of molecules.⁴²

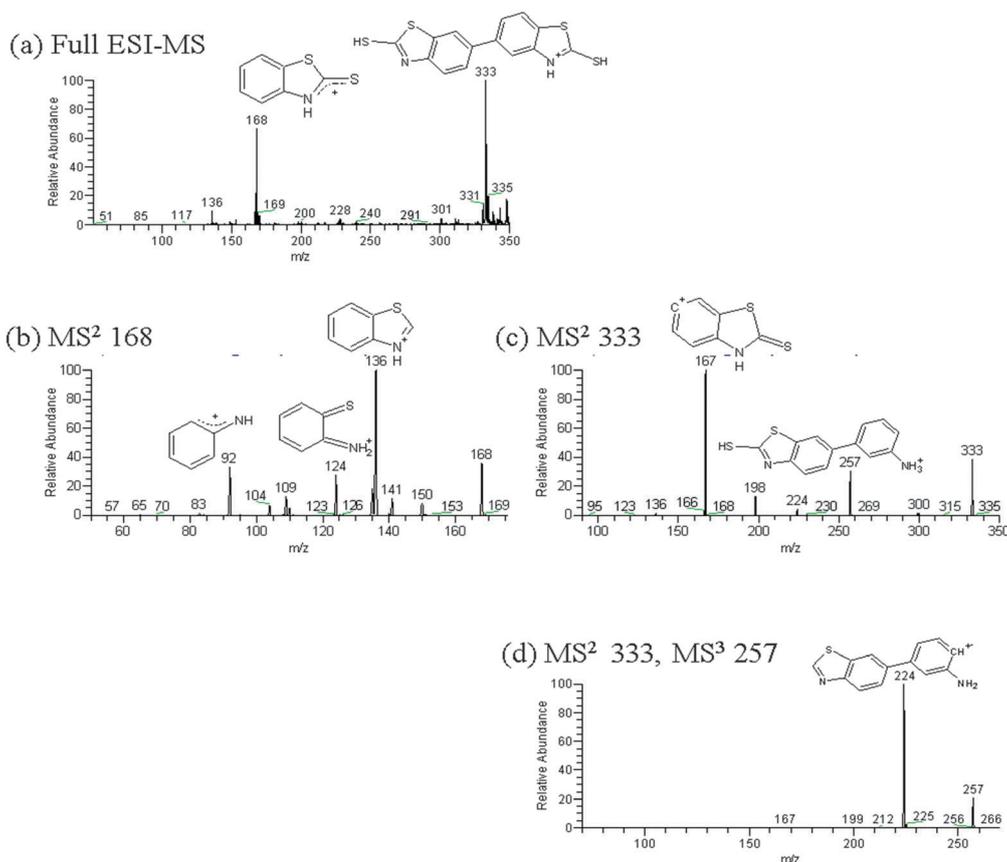


Fig. 6 Proposed fragmentation of MBT and the dimer formed during its irradiation in the iso-propanol solution: (a) full ESI-MS spectrum of MBT after irradiation, (b) MS^2 of the $[\text{M} + \text{H}]^+$ ion at m/z 168 corresponding to the non-modified MBT, (c) MS^2 of the $[\text{M} + \text{H}]^+$ ion at m/z 333 corresponding to the formed dimer, and (d) MS^3 of the $[\text{M} + \text{H}]^+$ ion at m/z 257.

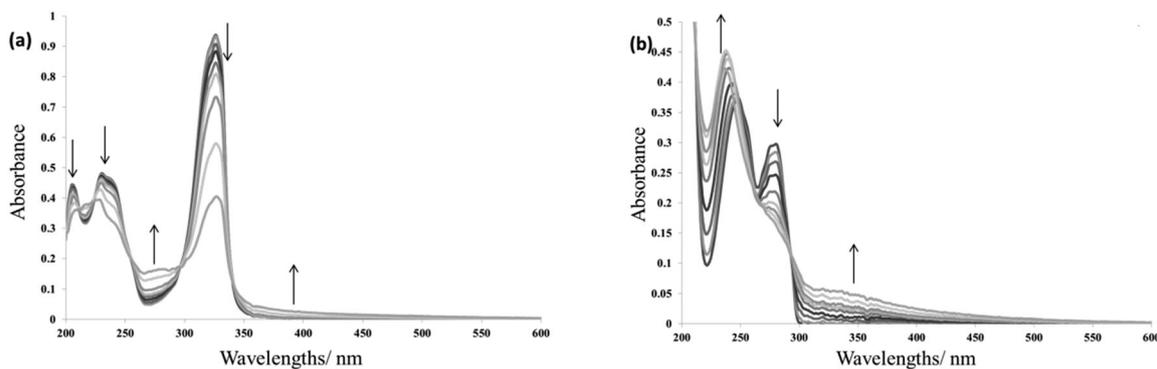


Fig. 7 The irradiation of MBT (a) and BTA (b) in hexane: 0 s, 60 s, 360 s, 960 s, 1260 s, 2460 s and 4260 s respectively.

In this work, we assume that oxygen increases the spin-orbit conversion of singlet radical pairs into triplet pairs. However, the dynamic interaction of dissolved oxygen with singlet radical pairs of the irradiated compound is hardly possible due to the low concentration of oxygen in the solution and a short lifetime of singlet radical pairs. More likely, oxygen forms a complex with the original BTA or MBT molecules, leading to a static spin-orbit interaction between oxygen and the radical pair, because these compounds are good electron donors while oxygen is a powerful electron acceptor. Triplet radical pairs further either convert back to the singlet radical pairs, which recombine under aerobic conditions by oxygen attack, or dissociate into a free radical form. The free radicals further participate in subsequent chemical reactions, mainly in coupling of mesomeric radical structures forming dimers (Table 1). The proposed mechanism of free radical formation by photolysis of the C-S bond in MBT is shown in Fig. 8. A similar mechanism can be proposed for the photodissociation of the S-H bond.

Despite the similar values of quantum yields of MBT and BTA photodegradations, the degradation of BTA occurs much slower than MBT under irradiation by a standard reference light source or under sunlight. This can be explained by the shift of BTA absorption spectra to the shorter wavelength UV region, where the radiation of lamps and energy of the sunlight near the Earth surface decreases. Taken into consideration that sunlight reaching the Earth's surface (mainly UV-A, with varying amounts of UV-B) contains only a very small amount of short wave-length UV radiation.⁴³ BTA looks more resistant to sunlight in comparison to MBT. However, the prolonged irradiation leads to the interesting reaction behavior of BTA related to the formation

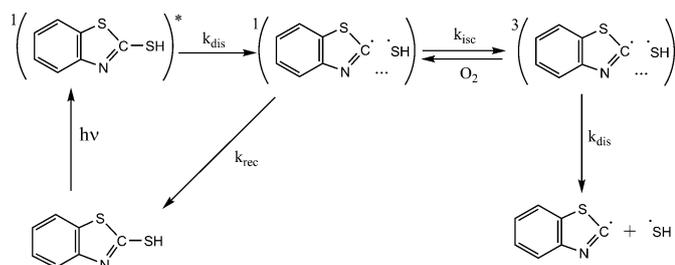


Fig. 8 The proposed mechanism of MBT photodegradation.

of a set of colored oligomers and even six-membered cyclic intermediate products that were registered by mass spectroscopy analysis of degradation products (Table 1). It should be mentioned that since the quantum yields of the photodegradation reactions and main products of the photolysis are practically independent of the solvent (water, isopropanol, *n*-hexane), we assume that the mechanism of the BTA and MBT photodestruction is determined by photophysical and photochemical properties of the substrates.

The initial step of BTA photodecomposition can be represented similarly to MBT and includes the photodissociation of the N-N bond (N-N bond energy in PhNH-NH₂ is about 41.2 kcal mol⁻¹, ref. 41) followed by the formation of a radical pair in the singlet state. This pair either further recombines to the original BTA compound or converts in the presence of oxygen to the triplet pair, which has longer lifetime and transforms into a diazo-compound (Fig. 9).³⁶

The formed diazo-compound undergoes further photodegradation under UV irradiation (Fig. 10).

As it was previously shown,³⁵ the intermediate cation (i) adsorbs light around 350–450 nm, and transforms into biradical (ii).

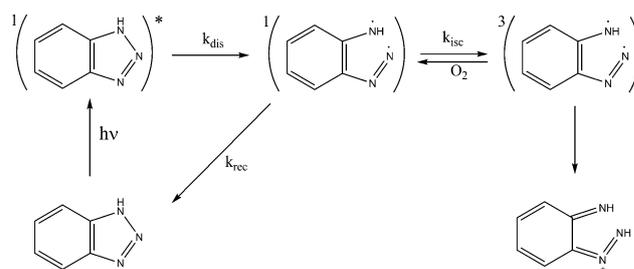


Fig. 9 The proposed mechanism of BTA photodegradation.

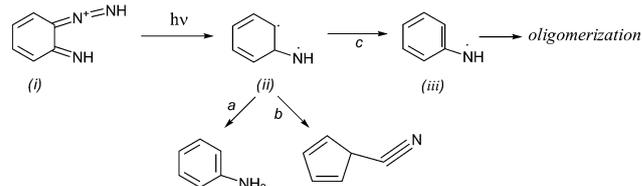


Fig. 10 The proposed mechanism of diazo-compound photodegradation.

This short lifetime biradical (ii) has several ways for its further transformation:

(a) undergoes the recombination reaction in the organic solvent medium to form aniline or its derivatives³⁶ (these were detected among degradation products, Table 1),

(b) undergoes the regrouping of the benzene ring thus forming a cyano-cyclopentadiene or its derivatives,

(c) emits a hydrogen atom and leads to oligomerization by reaction with extra BTA molecules (was detected among photodegradation products, Table 1).

Following the highly conjugated electron system of the formed oligomers that are responsible for the yellowish color of the BTA solution after the UV irradiation.

The formation of conjugated oligomeric systems was also observed for the BTA irradiation in iso-propanol. Unlike the aqueous solution these compounds are less stable and undergo further degradation under irradiation. The final products of the BTA photolysis carried out in iso-propanol indicate further transformation of oligomers into lower molecular weight compounds and their reaction with the solvent (Table 1).

The difference between oligomeric products released in the aqueous and iso-propanol solutions can be explained by the different degrees of conjugation in formed products and the possibility of the excited molecule to react with the solvent. In the iso-propanol solution, the reaction occurs easier than in water. This leads to the formation of less conjugated compounds, which absorb UV light at the shorter wavelength and easily undergo further excitation and photodegradation thus forming the reaction products as proposed in Fig. 10.

Conclusions

Photodegradation reactions of 2-mercaptobenzothiazole and 1,2,3-benzotriazole corrosion inhibitors in aqueous solutions and in organic solvents under UV irradiation have been studied. The primary products formed as a result of photodegradation reactions were determined by ESF-MS mass spectrometry. The analysis of degradation products upon UV irradiation revealed the predominant formation of dimeric compounds from MBT and oligomeric structures from BTA, which were further converted into aniline derivatives. Both reactions resulted in the decrease of inhibitor concentration in solution, which can be critical for the anti-corrosion protection.

The proposed photodegradation pathways of MBT and BTA include the photolysis of identified photolabile bonds (N–N bond in BTA and C–S or S–H bonds in MBT) promoted by the presence of oxygen. The role of oxygen consists in the spin-orbit interaction with radical pairs in the singlet state, which form during photodissociation thus converting them into the triplet state followed by dissociation into free radicals. Both MBT and BTA suffer polymerization *via* free radical coupling at the early stage of UV irradiation, whereas at a longer irradiation period the eventual conversion of oligomeric structures into low molecular products *via* photolytic/autoxidation mechanisms takes place.

Some general features concerning the MBT and BTA application in anti-corrosion formulations with relation to their photodegradation ability may be considered. Since the absorption maximum of MBT is around 320 nm and BTA is around 260 nm, the lower tolerance towards photodegradation of the former nearly the Earth's surface by sunlight (mainly UV-A) may be suggested. This fact poses more restrictions to MBT than to BTA. However, for example, for the external aeronautic applications the advantages of BTA over MBT in anti-corrosion formulations look not so evident, because at an altitude of 10 000–13 000 m above the ground the spectral range of sunlight (significant contribution of UV-B) imposes the same restrictions to BTA as to MBT. The obtained results suggest that the inhibition efficiency of “self-healing” coatings containing these inhibitors can be strongly affected under certain exploitation conditions, *e.g.* when subjected to UV irradiation.

The inhibitory effect of the products from MBT and BTA photolysis has to be assessed in the frame of future studies in order to understand if the photodegradation processes will have a detrimental impact on the long term performance of active self-healing coatings for external applications.

Acknowledgements

The authors would like to thank Fundação para a Ciência e a Tecnologia em Portugal (FCT grants PEst-C/QUI/UI0062/2013, PEst-C/CTM/LA0011/2013 and FCOMP-01-0124-FEDER-037296); European FP7 projects “PROAIR” (PIAPP-GA-2013-612415), SAR-ISTU “FP7-AAT-2011-RTD-1”, the Portuguese National Mass Spectrometry Network, project “RNEM” (REDE/1504/REM/2005).

References

- 1 M. Whelan, K. Barton, J. Cassidy, J. Colreavy and B. Duffy, *Surf. Coat. Technol.*, 2013, **227**, 75.
- 2 J. Zhang, *Corros. Sci.*, 2009, **51**, 1207.
- 3 I. J. Zvonkina and M. Hilt, in *Handbook of Smart Coatings Materials Protection*, ed. A. S. H. Makhlof, Woodhead Publishing, 2014, pp. 105–120.
- 4 W. Wang, L. Xu, X. Li, Y. Yang and E. An, *Corros. Sci.*, 2014, **80**, 528.
- 5 J. Carneiro, J. Tedim, S. C. M. Fernandes, C. S. R. Freire, A. J. D. Silvestre, A. Gandini, M. G. S. Ferreira and M. L. Zheludkevich, *Prog. Org. Coat.*, 2012, **75**, 8.
- 6 M. Samadzadeh, S. H. Boura, M. Peikari, S. M. Kasirihah and A. Ashrafi, *Prog. Org. Coat.*, 2010, **68**, 159.
- 7 M. Serdechnova, P. Volovitch and K. Ogle, *Surf. Coat. Technol.*, 2012, **206**(8–9), 2133.
- 8 I. Zin, R. Howard, S. Badger, J. Scantlebury and S. Lyon, *Prog. Org. Coat.*, 1998, **33**, 203.
- 9 I. Baghni, I. S. Lyon and B. Ding, *Surf. Coat. Technol.*, 2004, **185**, 194.
- 10 E. A. Noor, *Mater. Chem. Phys.*, 2009, **114**, 533.
- 11 S. Issaadi, T. Douadi and S. Chafaa, *Appl. Surf. Sci.*, 2007, **316**, 582.

- 12 A. Popova, M. Christov and A. Vasilev, *Corros. Sci.*, 2007, **49**, 3276.
- 13 S. Kallip, A. C. Bastos, K. A. Yasakau, M. L. Zheludkevich and M. G. S. Ferreira, *Electrochem. Commun.*, 2012, **20**, 101.
- 14 M. Serdechnova, S. Kallip, M. G. S. Ferreira and M. L. Zheludkevich, *Electrochem. Commun.*, 2014, **41**, 51.
- 15 M. M. Antonijević, S. M. Milić and M. B. Petrović, *Corros. Sci.*, 2009, **51**, 1228.
- 16 D. Zhang, L. Gao and G. Zhou, *Corros. Sci.*, 2004, **46**, 3031.
- 17 L. P. Kazansky, I. A. Selyaninov and Y. I. Kuznetsov, *Appl. Surf. Sci.*, 2012, **258**, 6807.
- 18 M. Finšgar and I. Milošev, *Corros. Sci.*, 2010, **52**, 2737.
- 19 N. K. Allam, A. A. Nazeer and E. A. Ashour, *J. Appl. Electrochem.*, 2009, **39**, 961.
- 20 M. A. Páez, J. H. Zagal, O. Bustos, M. J. Aguirre, P. Skeldon and G. E. Thompson, *Electrochim. Acta*, 1997, **42**, 3453.
- 21 K. Ramji, D. R. Cairns and S. Rajeswari, *Appl. Surf. Sci.*, 2008, **254**, 4483.
- 22 T. Kosec, I. Milošev and B. Pihlar, *Appl. Surf. Sci.*, 2007, **253**, 8863.
- 23 J. Zhang, Q. Zhang, H. Ren, W. Zhao and H. Zhang, *Appl. Surf. Sci.*, 2007, **253**, 7416.
- 24 N. Kovačević and A. Kokalj, *Mater. Chem. Phys.*, 2012, **137**, 331.
- 25 U. Rammelt, S. Koehler and G. Reinhard, *Corros. Sci.*, 2009, **50**, 1659.
- 26 D. Gopi, K. M. Govindaraju, V. Arun Prakash Collins, D. M. Angeline Sakila and L. Kavitha, *Corros. Sci.*, 2009, **51**, 2259.
- 27 J. Xu, L. Li, C. Guo, Y. Zhang and S. Wang, *Chem. Eng. J.*, 2013, **221**, 230.
- 28 R. Andreozzi, V. Caprio, A. Insola and G. Longo, *J. Chem. Technol. Biotechnol.*, 1998, **73**, 93.
- 29 A. Allaoui, M. A. Malouki and P. Wong-Wah-Chung, *J. Photochem. Photobiol., A*, 2010, **212**, 153.
- 30 J. E. Tietge, S. J. Degitz, J. T. Haselman, B. C. Butterworth, J. J. Korte, P. A. Kosian, A. J. Lindberg-Livingston, E. M. Burgess, P. E. Blackshear and M. W. Hornung, *Aquat. Toxicol.*, 2013, **126**, 128.
- 31 D. A. Pillard, J. S. Cornell, D. L. DuFresne and M. T. Hernandez, *Water Res.*, 2001, **35**, 557.
- 32 D. Vialaton and C. Richard, *J. Photochem. Photobiol., A*, 2000, **136**, 169.
- 33 M. A. Malouki, C. Richard and A. Zertal, *J. Photochem. Photobiol., A*, 2004, **167**, 121.
- 34 O. Fiehn, G. Wegener, J. Jochimsen and M. Jekel, *Water Res.*, 1998, **32**, 1075.
- 35 H. Wang, C. Burda, G. Persy and J. Wirz, *J. Am. Chem. Soc.*, 2000, **122**, 5849.
- 36 H. Shizuka, H. Hiratsuka, M. Jinguji and H. Hiraoka, *J. Phys. Chem.*, 1987, **91**, 1793.
- 37 H. Murai, M. Torres and O. P. Strausz, *J. Am. Chem. Soc.*, 1980, **102**, 1421.
- 38 H. Tomioka, N. Ichikawa and K. Komatsu, *J. Am. Chem. Soc.*, 1992, **114**, 8045.
- 39 W. D. Bowman and J. N. Demas, *J. Phys. Chem.*, 1976, **80**, 2434.
- 40 H. D. Burrows, L. M. Canle, J. A. Santaballa and S. Steenken, *J. Photochem. Photobiol., B*, 2002, **67**, 71.
- 41 J. D. Cox and G. Pilcher, *Thermochemistry of organic and organometallic compounds*, Acad. Press., New York, 1970.
- 42 S. P. McGlynn, T. Azumi and M. Kkinoshita, *Molecular spectroscopy of the triplet state*, Prentice-Hall International, Hemel Hempstead, 1969.
- 43 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, 1993.