



A Theoretical study on the degradation of 2-mercaptobenzothiazole and 2-mercaptobenzimidazole by $\cdot\text{OH}$ *in vacuo* and aqueous media

Kgalaletso P. Otukile^{a,b}, Liliana Mammino^c, Mwadham M. Kabanda^{a,b,*}

^a Department of Chemistry, Faculty of Natural and Agriculture Sciences, North-West University, Private Bag X2046, Mmabatho 2735, South Africa

^b Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Natural and Agriculture Sciences, North-West University, Private Bag X 2046, Mmabatho 2735, South Africa

^c Department of Chemistry, University of Venda, Thohoyandou, South Africa

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ABSTRACT

The hydrogen atom transfer mechanism for the reaction between 2-mercaptobenzothiazole (MBT) and $\cdot\text{OH}$ and between 2-mercaptobenzimidazole (MBZ) and $\cdot\text{OH}$ has been investigated theoretically for the first time for the purpose of understanding the degradation pathway for MBZ and MBT to thiyl radical species. The objectives of the work have been to elucidate the geometries of the species involved in the reaction and to characterise them with respect to their energetic, geometric, electronic and reaction-kinetic properties. More importantly, the study compares and contrasts the two hydrogen transfer mechanisms through which the degradation of MBZ and MBT could be achieved: the direct hydrogen atom transfer (hydrogen abstraction) and the $\cdot\text{OH}$ addition followed by water elimination (addition–elimination). The study has been performed *in vacuo* and in aqueous solution using the DFT/ $\omega\text{B97X-D}$ and DFT/M06–2X methods in conjunction with the 6-311++G(3df,2p) basis set. The results of the study indicate that the geometry of the considered species only minimally depends on the medium and is similar in the results of both calculation methods. The pre-reactive complexes for the direct H atom transfer mechanism and for the addition–elimination mechanism are significantly different. The activation energy depends on the medium; for instance, it is often greater in aqueous solution than *in vacuo*; the calculated values of the activation energy depend also on the calculation method. In water solution, the direct hydrogen atom abstraction mechanism is kinetically preferred to the addition–elimination mechanism, suggesting that the studied reactions most likely proceed through the direct hydrogen atom abstraction mechanism. The estimated rate constant for the MBZ + $\cdot\text{OH}$ reaction is also in close agreement with the experimentally determined value. The spin density distribution on the thiyl species is significantly delocalized away from the centre of H atom abstraction. The S–H bond dissociation enthalpy (BDE) is slightly higher for MBT than for MBZ, although both values are below the experimentally determined S–H BDE value.

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1. Introduction

2-mercaptobenzimidazole (MBZ) and 2-mercaptobenzothiazole (MBT) are important members of the benzimidazoles and benzothiazoles groups of heterocyclic aromatic compounds respectively, considered largely to be xenobiotic. MBZ and MBT (Fig. 1) have various useful applications including as rubber antioxidants [1–4] and corrosion inhibitors [1–6]; their anticorrosion properties allow them to be utilised in chemical decontaminant formulations for

* Corresponding author at: Department of Chemistry, Faculty of Natural and Agriculture Sciences, North-West University, Private Bag X2046, Mmabatho 2735, South Africa.

E-mail address: mwadham.kabanda@nwu.ac.za (M.M. Kabanda).

reducing the corrosion of base metals (e.g., copper and aluminium) of structural materials [7,8]. MBZ and MBT also possess various biological activities such as antibacterial and antifungal [3,4]. However, their positive effects are largely masked by their negative effects in the environment; for instance, studies have shown that once MBT and MBZ enter the environment from various sources that produce or use them and from products containing them, they tend to be toxic to aquatic organisms, to hamper wastewater treatment, to induce tumours and to be allergenic [9]. For these reasons, much attention has focused on finding ways for the removal of these substances from the environment [10–13]. The most frequently utilised approach for this removal utilises the degradation induced by exposure to the super-oxide radical ion $\text{O}_2^{\cdot-}$ and the hydroxyl radical ion $\cdot\text{OH}$ [4–6,14–16]. These two radical species

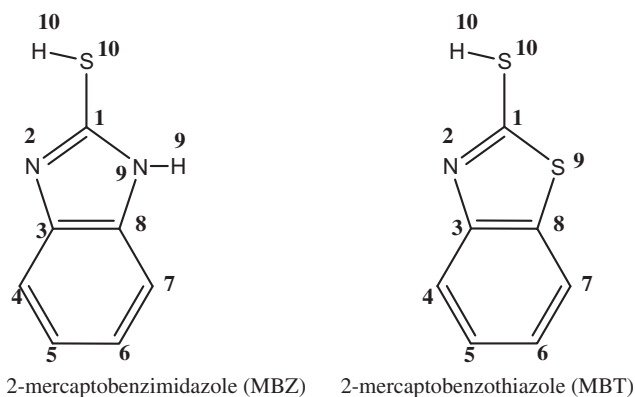
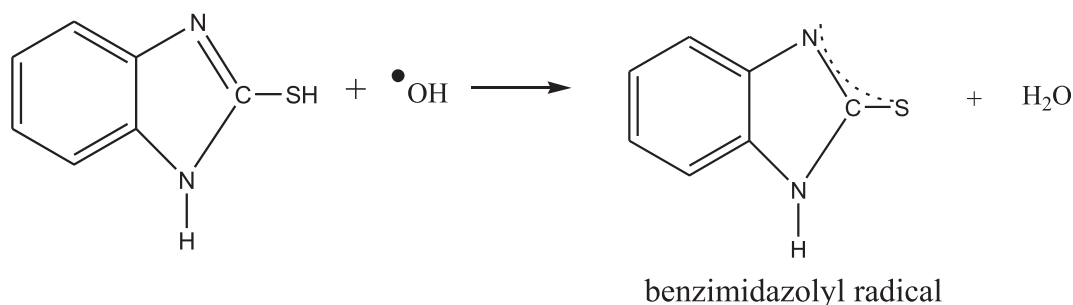
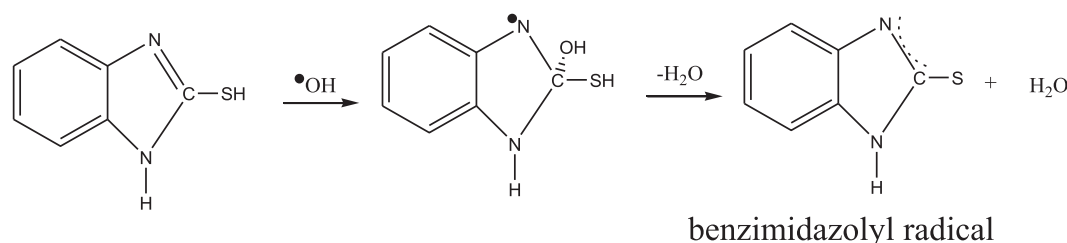


Fig. 1. Schematic representation of the structures 2-mercaptobenzimidazole (MBZ) and 2-mercaptobenzothiazole (MBT), with the atom numbering utilised in this work. The O and H atoms on the radical species are referred to with the number 11 in the text.

can be generated through various reactions, including the use of photocatalysts, the Fenton reaction system and the radiolytic reaction. For instance, through the use of modern photocatalytic technologies, environmentally friendly photocatalysts (e.g., spinel ferrites [4]) can be designed and imprinted on the surface of a polymer; after improving its activity through the use of a conductive polymer [17], the imprinted photocatalyst can be radiated with visible light, resulting in the generation of electrons (e^-) and holes (h^+). The generation of more e^- / h^+ triggers the formation of the very reactive O_2^- and $\cdot OH$ species [4]. The Fenton reaction system is extensively utilised in the degradation of organic pollutants because it involves hydrogen peroxide, which is an important source for the generation of $\cdot OH$ radicals [18–21]. Radiolytic reactions can also be considered as a source for the generation of $\cdot OH$ species because the products of such reactions (which often take place in aqueous medium) include hydrated electrons and $\cdot H$ and $\cdot OH$ radicals [1,2].



Scheme 1. Reaction pathway for the direct hydrogen atom abstraction mechanism for the degradation of 2-mercaptobenzothiazole by the $\cdot OH$ radical.



Scheme 2. Reaction pathway for the $\cdot OH$ addition reaction mechanism for the degradation of 2-mercaptobenzothiazole by the $\cdot OH$ radical.

If the surface of nuclear reactors in which the radiolytic reactions take place is coated with corrosion inhibitors to protect it from the effects of the corrosiveness of the species present within the reactors, then it is likely that the corrosion inhibitors would interact with the products of radiolysis and consequently react with some of the species resulting from the irradiated aqueous medium. Since MBT and MBZ derivatives are known to act as effective corrosion inhibitors, they may be present in chemical decontaminant formulations coated on the surface of nuclear reactors. The generated $\cdot OH$ can then react with either MBT or MBZ resulting in their degradation [4–6,14–16].

Experimental findings have shown that the degradation of MBT and MBZ through reaction with $\cdot OH$ may proceed through either the direct hydrogen atom abstraction mechanism or the addition-elimination mechanism [1,2]. In both cases, the outcome is an H transfer from the molecule to the $\cdot OH$ radical. In the direct H atom abstraction mechanism (scheme 1), $\cdot OH$ abstracts the H atom from the S–H group resulting in the formation of the benzimidazolyl radical species and a water molecule. The benzimidazolyl radical is a resonance-stabilised neutral radical species.

In the addition-elimination mechanism (scheme 2), the $\cdot OH$ radical adds to the C=N double bond, giving rise to an intermediate structure; the water molecule is then eliminated from the intermediate structure so that the end products are again the benzimidazolyl radical species and a water molecule.

The degradation of MBT and MBZ to corresponding radical species can be considered as the first step in a chain of reactions leading to the total degradation of these species to carbon dioxide, water and sulphate ions [11]. As the first step of the mechanism, the formation of the radical species already plays a very important role because it leads to the breaking of the C=N and S–H bonds. The S–H bond, for instance, is known to be responsible for the odour problems associated with plants for the treatment of wastewater containing mercaptans derivatives such as MBZ and MBT [22].

The MBT + $\cdot OH$ and MBZ + $\cdot OH$ reactions have been reported to take place in very acidic (pH = 0), neutral (pH = 7) and very basic (pH = 13) environments [1]. For simplicity sake, the study reported here considers a situation in which the reactions take place in a neutral environment.

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