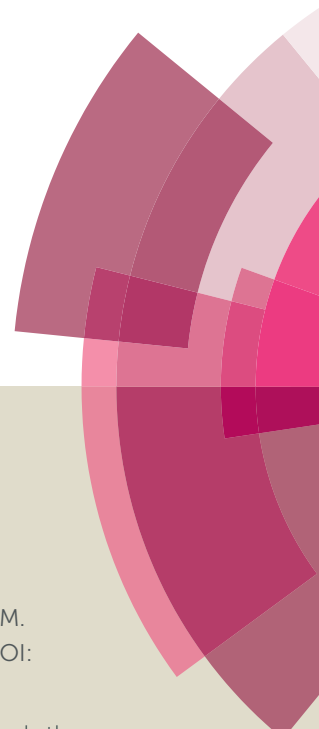


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## A Mn(III) Polyoxotungstate in the Oxidation of Organosulfur Compounds by H<sub>2</sub>O<sub>2</sub> at Room Temperature: An Environmentally Safe Catalytic Approach

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### Abstract

The tetrabutylammonium (TBA) salt of a Keggin-type polyoxometalate (POM), with the chemical formula TBA<sub>4</sub>H<sub>2</sub>[BW<sub>11</sub>Mn(H<sub>2</sub>O)O<sub>39</sub>]·H<sub>2</sub>O, **TBABW<sub>11</sub>Mn**, was evaluated as catalyst in the oxidation by hydrogen peroxide of several organosulfur compounds, namely benzothiophene (BT), 2-methylbenzothiophene (2-MBT), 3-methylbenzothiophene (3-MBT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-diethyldibenzothiophene (4,6-DEDBT), in acetonitrile at room temperature. All compounds were oxidized to the corresponding sulfones with high conversion and selectivity. Following the excellent results achieved, the **BW<sub>11</sub>Mn**/H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CN system was tested in the oxidation of model fuels (MF) consisting of a mixture of BTs and DBTs in hexane (**MF1** containing mainly BTs and **MF2** containing predominantly DBTs). In both cases the organosulfur compounds from the model fuels were fully converted into the corresponding sulfones. Envisaging developing a promising desulfurization procedure, the extraction of the sulfur compounds from **MF2** was attempted after the catalytic oxidation process. More than 98 mol % was removed using an ethanol/H<sub>2</sub>O mixture.

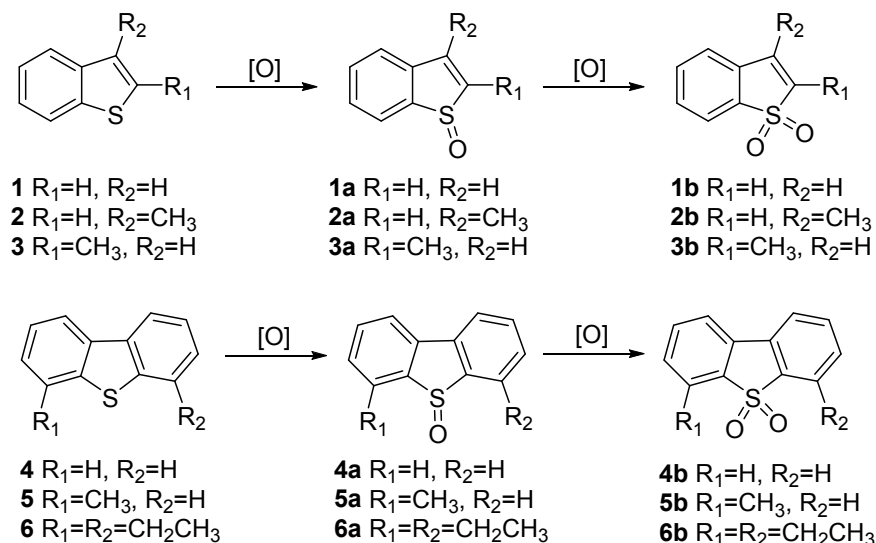
## 1. Introduction

The search for new and efficient catalytic systems for the oxidation of organosulfur compounds into the corresponding sulfoxides and sulfones is a research area of great relevance nowadays. Firstly, sulfoxides and sulfones, besides being important intermediates in organic synthesis, are also known biological active molecules.<sup>1-5</sup> Secondly, the oxidative desulfurization (ODS) of fuels constitutes a process with very high potential, in terms of efficiency and environmental sustainability, thus gathering the interest of the scientific community.<sup>6-12</sup>

Polyoxometalates (POMs) are a class of metal-oxygen cluster anions that have been applied in several fields, namely catalysis, medicine and materials science.<sup>13-19</sup> This derives from the high diversity of the known structures, and the large range of physical and chemical properties that make them fit for a wide domain of applications.<sup>20-23</sup> One of the most important fields in which these metal-oxygen cluster anions have been applied is oxidative catalysis.<sup>13,14,24-27</sup> POMs evidence an all set of important properties, like strong Brønsted acidity, good redox properties under mild conditions, tunable solubility in different solvents (according to the counter-ion) and, not less important, high thermal and oxidative stability, which make them very interesting catalysts. The so-called Keggin-type polyoxometalates, namely  $[XM_{12}O_{40}]^{n-}$  ( $M = Mo, W; X = P, Si, B, \text{etc.}$ ), the lacunary  $[XM_{11}O_{39}]^{n-}$ , and other related species, are among the most studied in catalysis. In particular, in the case of the transition metal monosubstituted Keggin-type polyoxometalates  $[XM_{11}M'(H_2O)O_{39}]^{n-}$  ( $M' = \text{transition metal}$ ), their success as catalysts is associated also with the easy tuning of structure and properties, as the POM properties can be modulated by the introduction of diverse  $M'$  and varying the X atoms. In our previous work, the transition metal monosubstituted Keggin-type polyoxometalates were used successfully as catalysts in the oxidation of diverse types of organic compounds with  $H_2O_2$ .<sup>28-36</sup>

Several recent reviews mentioned the role of polyoxometalates in ODS related processes.<sup>7,9,14,18,19</sup> Among others, the catalytic efficiency of the lacunary and transition metal-substituted Keggin-type polyoxotungstates in the oxidation of S-compounds has already been demonstrated in several reports.<sup>27,37-46</sup> Our previous experience with the use of the undecatungstoboromanganate(III) anion,  $[BW_{11}Mn(H_2O)O_{39}]^{6-}$  (**BW<sub>11</sub>Mn**), in oxidative catalysis has shown that it is an efficient and robust catalyst for the oxidation with  $H_2O_2$  of several types of substrates,<sup>28,31,47-49</sup> suggesting that it could be a good candidate to be used for the oxidation of organosulfur compounds. Moreover, our research group has developed a

catalytic oxidation system of organosulfur derivatives under mild conditions using metalloporphyrin complexes.<sup>50-52</sup> Thus, based on our experience on the catalytic oxidation of recalcitrant organosulfur compounds and on the catalytic applications of POMs, and taking advantage of the fact that manganese POMs have been poorly studied in this context,<sup>45</sup> the oxidation, by the environmentally safe oxidant H<sub>2</sub>O<sub>2</sub>, of several benzothiophenes and dibenzothiophenes (Figure 1), namely benzothiophene **1** (BT), 3-methylbenzothiophene **2** (3-MBT), 2-methylbenzothiophene **3** (2-MBT), dibenzothiophene **4** (DBT), 4-methyldibenzothiophene **5** (4-MDBT), and 4,6-diethyldibenzothiophene **6** (4,6-DEDBT), is studied in the presence of the tetrabutylammonium (TBA) salt TBA<sub>4</sub>H<sub>2</sub>[BW<sub>11</sub>Mn(H<sub>2</sub>O)O<sub>39</sub>]·H<sub>2</sub>O (**TBABW<sub>11</sub>Mn**). Furthermore, the potential of this **BW<sub>11</sub>Mn**/H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CN catalytic system for ODS is demonstrated using two distinct model fuels (**MF**), mixtures of four BTs and DBTs in hexane. Finally, in order to evaluate the potential of this desulfurization procedure, the ultimate removal of the sulfones is also assessed under green and sustainable conditions.



**Figure 1.** Benzothiophenes and dibenzothiophenes studied and the corresponding oxidation products.

## 2. Experimental Section

### 2.1. Reagents and synthetic procedures

Acetonitrile (Panreac), 30% (w/w) aqueous hydrogen peroxide (Sigma-Aldrich) and all other reagents and solvents obtained from commercial sources were used as received or distilled and dried using standard procedures. TBA<sub>4</sub>H<sub>2</sub>[BW<sub>11</sub>Mn(H<sub>2</sub>O)O<sub>39</sub>]·H<sub>2</sub>O was prepared and characterized according to previously described procedures.<sup>48</sup> The obtained compound was

characterized by elemental analysis (C, H, N, W, Mn), thermogravimetry and infrared spectroscopy and the results were in agreement with those previously published.<sup>47,48</sup>

## 2.2. Typical procedure for the oxidation reactions

The **TBABW<sub>11</sub>Mn** catalyzed oxidation reactions were carried out as follows: the substrate (0.3 mmol); the catalyst, corresponding to the appropriate substrate/catalyst (S/C) molar ratio 150 or 300; the required amount of 30% (w/w) aqueous H<sub>2</sub>O<sub>2</sub> (61 μL, 0.6 mmol for a H<sub>2</sub>O<sub>2</sub>/substrate (O/S) molar ratio equal to 2; 122 μL, 1.2 mmol for a H<sub>2</sub>O<sub>2</sub>/substrate (O/S) molar ratio equal to 4; 183 μL, 1.8 mmol for a H<sub>2</sub>O<sub>2</sub>/substrate (O/S) molar ratio equal to 6); 2.0 mL of acetonitrile and the internal standard (chlorobenzene, 0.3 mmol) were stirred in a close vessel at room temperature (22-24°C) for 3 hours in the absence of light. To monitor the sulfoxidation reactions, small aliquots from the reaction mixture were directly injected into the GC-FID apparatus at regular intervals. The reactions were stopped after 3 h of reaction, or when a conversion plateau was reached. Blank reactions were performed for all the substrates, confirming that almost no oxidation occurs in the absence of catalyst (conversion below 5% for all the substrates, except for DBT that gives 12% of conversion) after 3 hours.

Experiments done to mimic the oxidation of model fuels (**MF**) were performed as follows: four substrates (0.03 mmol of each organosulfur compound, a total of 0.12 mmol) and the catalyst were dissolved in 500 μL of CH<sub>3</sub>CN, and the total reaction volume was completed with 1.5 mL of hexane. Addition of H<sub>2</sub>O<sub>2</sub> and the completion of the reaction were done as indicated above. Experiments designated as **MF1** contain substrates **1-4** and **MF2** contain substrates **3-6**, both **MF** with 3.8x10<sup>3</sup> ppm of sulfur.

## 2.3. Instruments and Methods

The GC-FID and GC-MS analyses were performed as previously described.<sup>51,52</sup> The conversion and selectivity values were estimated from the corresponding chromatographic peak areas, using chlorobenzene as internal standard. To confirm the structure of the achieved products, the retention times in the GC-FID were compared with those of authentic samples identified previously,<sup>51,52</sup> and the reaction mixtures were also injected in the GC-MS.

## 3. Results and Discussion

### 3.1. Oxidation of the organosulfur compounds in acetonitrile

The catalytic performance of the tetrabutylammonium salt of a Keggin-type undecatungstoboromanganate(III) anion,  $\text{TBA}_4\text{H}_2[\text{BW}_{11}\text{Mn}(\text{H}_2\text{O})\text{O}_{39}]\cdot\text{H}_2\text{O}$ , was evaluated in the sulfoxidation of recalcitrant benzothiophenes and dibenzothiophenes by  $\text{H}_2\text{O}_2$  under homogeneous conditions at room temperature. The catalytic tests were performed with substrates **1-6** (Figure 1) and the results obtained after 3h (except when indicated) are summarized on Table 1. For all the substrates, only the corresponding sulfones are observed at the end of the reactions. Sulfoxides could only be detected in some cases at the beginning of the reactions (up to 30 min). From the results obtained, it is possible to conclude that good to excellent conversions, ranging from 90 to 100%, were attained with most of the substrates for both S/C molar ratios tested (150 and 300). As expected, the use of a higher amount of **TBABW<sub>11</sub>Mn** catalyst (S/C molar ratio = 150) affords the best results for each substrate. In particular, the full oxidation of DBT **4** and 4-MDBT **5** are attained after 60 min for S/C = 150. Furthermore, for BT **1** and 4,6-DEDBT **6**, a significant difference between the two S/C ratios was observed. It must be emphasized that this is a rare example of a Keggin-type polyoxotungstate catalyst efficiently used at room temperature in a sulfoxidation process of recalcitrant sulfur compounds. Usually the use of these POMs as catalysts in sulfoxidation processes requires temperatures around 50-80 °C, or even higher. Mizuno and collaborators have obtained quite good results in the homogeneous oxidation of various kinds of sulfides at room temperature with  $\text{H}_2\text{O}_2$  in the presence of  $[\gamma\text{-PW}_{10}\text{O}_{38}\text{V}_2(\mu\text{-OH})_2]^{3-}$ , but the sulfoxidation of dibenzothiophene was only obtained at 50 °C.<sup>41</sup> A similar situation was reported quite recently, with hybrid composite materials based on the parent Keggin anions as catalysts.<sup>53</sup> Also, the mono-lacunary polyoxotungstate  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  showed high catalytic activity on the oxidation of BT in an emulsion at 30 °C, but the corresponding transition metal  $[\text{PW}_{11}\text{MO}_{39}]^{n-}$  anions (M = Ti, Mn, Fe, Co, Ni, Cu) had much lower activity.<sup>45</sup> Thus, the efficiency demonstrated here by **BW<sub>11</sub>Mn** at room temperature is quite remarkable. Noteworthy, **BW<sub>11</sub>Mn** is especially efficient with the recalcitrant DBTs **4** and **5**. In fact, this constitutes a very promising result, since the most difficult or the most recalcitrant organosulfur compounds to treat through an ODS procedure are DBTs. Besides, all the previous studies indicate that the catalyst is stable, either under similar conditions or under more drastic conditions than that used in the present work (e. g.,  $\text{H}_2\text{O}_2$ /substrate molar ratio up to 7, at 80 °C).<sup>48</sup>

Figure 2 illustrates the kinetic profile of the reaction for each substrate in the catalytic assays with **BW<sub>11</sub>Mn** for S/C molar ratio of 300. This puts in evidence the higher efficiency of **BW<sub>11</sub>Mn** for the oxidation of DBTs. Considering the results at 30 or 60 min of reaction,

the higher conversion values were attained for DBTs **4**, **5** and **6**, decreasing in this order, whereas the worst result was for the unsubstituted BT **1**.

**Table 1. Results obtained for the oxidation of substrates (1-6) with H<sub>2</sub>O<sub>2</sub> catalyzed by the manganese polyoxometalate (BW<sub>11</sub>Mn).<sup>a</sup>**

Substrate	S/C molar ratio	Conversion (%) <sup>b</sup>	Product	Time (min)
<b>1</b> <b>(BT)</b>	300	47		180
	150	97	<b>(1b)</b>	180
<b>2</b> <b>(3-MBT)</b>	300	90		180
	150	100	<b>(2b)</b>	180
<b>3</b> <b>(2-MBT)</b>	300	93		180
	150	100	<b>(3b)</b>	180
<b>4</b> <b>(DBT)</b>	300	100		120
	150	100	<b>(4b)</b>	60
<b>5</b> <b>(4-MDBT)</b>	300	98		180
	150	100	<b>(5b)</b>	60
<b>6</b> <b>(4,6-DEDBT)</b>	300	72		180
	150	98	<b>(6b)</b>	180

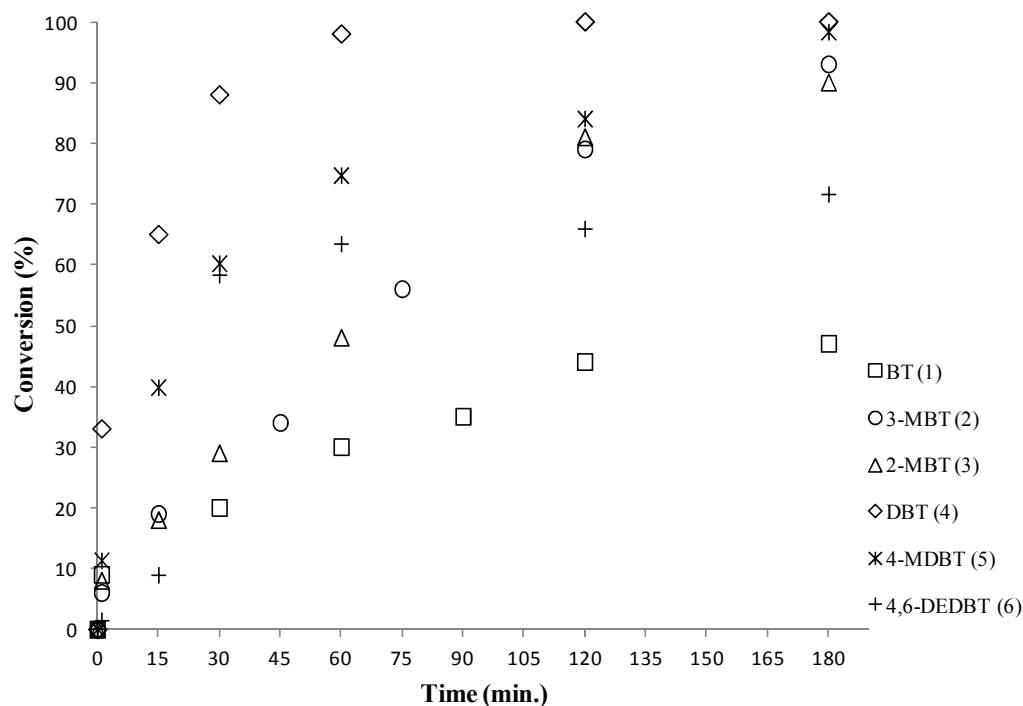
<sup>a</sup>Reaction conditions: the substrate (0.3 mmol), the catalyst corresponding to a substrate/catalyst (S/C) molar ratio of 150 and 300, the internal standard (chlorobenzene, 0.3 mmol) and the 30% (w/w) H<sub>2</sub>O<sub>2</sub> (6 equiv.) were stirred in 2.0 mL of CH<sub>3</sub>CN at room temperature. <sup>b</sup>Conversion values determined by GC-FID.

This shows that the results may only be partially related to the increase of the electron density at the S atom, which varies in the order 3-MBT < BT < 2-MBT < DBT < 4-



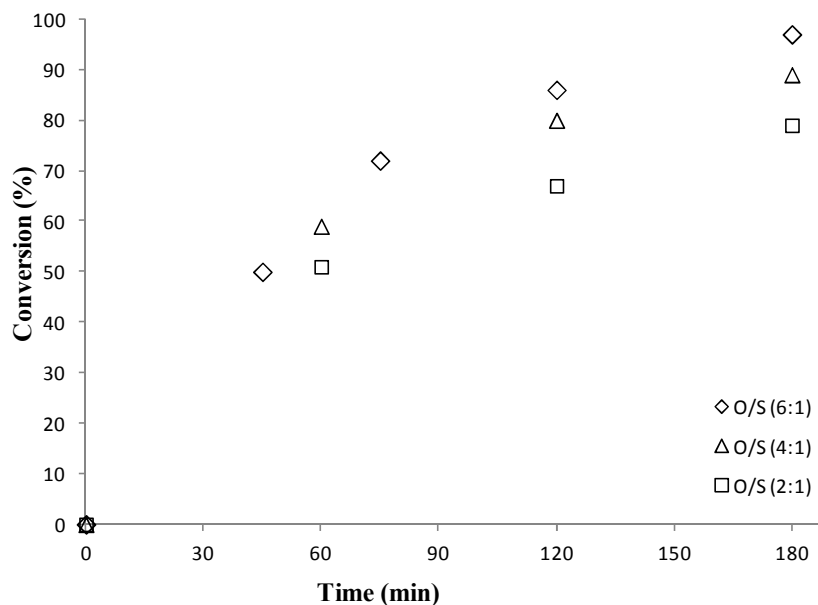
MDBT.<sup>54,55</sup> Yet, the distinction between BTs and DBTs is clear. In the case of benzothiophenes the presence of the methyl substituents seems to have a positive effect in the course of the sulfoxidation reactions, independently of its position (**2** and **3** are easily oxidized if compared with **1**). Moreover, when the kinetic profile of the oxidation of BT (**1**) is compared for different O/S molar ratios (Figure 3), the 6:1 molar ratio gives rise to higher conversion than 4:1 and 2:1 after 180 min of reaction. Based on this results for the most recalcitrant substrate studied here, the O/S 6:1 molar ratio was used for all the organosulfur compounds (**1-6**). This slight excess is not unusual in the oxidation of this kind of substrates by hydrogen peroxide and catalyzed by POMs, since O/S molar ratios of 50:1,<sup>56</sup> 23:1,<sup>57</sup> 12:1,<sup>58,59</sup> 11:1,<sup>60</sup> 10:1,<sup>61</sup> 8:1,<sup>62,63</sup> or 6:1,<sup>53</sup> can be found in the very recent literature.

In the case of DBTs the steric hindrance appears as the main factor affecting the catalytic results. Despite the differences in conversion at the beginning of the reaction, the presence of a methyl substituent does not affect significantly the results attained after 180 min for **5** if compared with **4**; in the case of **6**, possessing two ethyl substituents, a significant lower conversion after 3 hours of reaction is detected, when a S/C molar ratio of 300 is used.



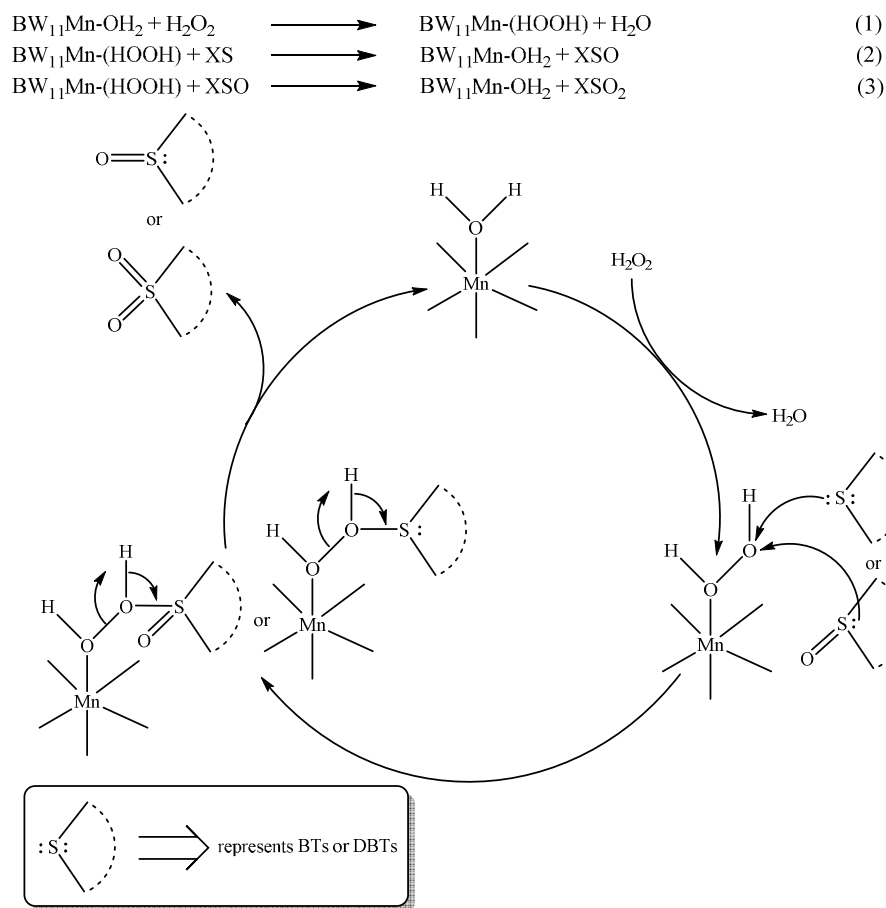
**Figure 2.** Kinetic profile (conversion vs time) of the oxidation reactions with  $\text{H}_2\text{O}_2$  for all the organosulfur compounds tested (**1-6**) in the presence of  $\text{BW}_{11}\text{Mn}$  (S/C molar ratio of 300) at room temperature in  $\text{CH}_3\text{CN}$ .





**Figure 3.** Kinetic profile (conversion vs time) of the oxidation of BT (**1**) with different H<sub>2</sub>O<sub>2</sub>/substrate (O/S) molar ratios in the presence of **BW**<sub>11</sub>**Mn** (S/C molar ratio of 150) at room temperature in CH<sub>3</sub>CN.

Recently, our group has demonstrated the efficiency of Mn(III) porphyrin complexes in the oxidation of this type of substrates by hydrogen peroxide.<sup>52</sup> The experiments using the Mn(III) porphyrins and the **BW**<sub>11</sub>**Mn** anion were carried out using similar reaction conditions. Thus, in both cases the reaction solvent was CH<sub>3</sub>CN, the oxidant was aqueous H<sub>2</sub>O<sub>2</sub> and the assays were carried out at room temperature (22-24 °C). It is important to refer that for Mn(III) porphyrins the oxidant is previously diluted and added to the reaction in small aliquots (half of the substrate amount at each 15 min) to protect the Mn(III) porphyrin catalyst from the oxidation conditions. For the studies employing **BW**<sub>11</sub>**Mn**, and due to its higher chemical resistance, 30% (w/w) hydrogen peroxide is used directly and added all at once at the beginning of the reactions. This may explain differences in the observation of intermediate sulfoxides in the course of reactions with porphyrins when compared with this study. Comparatively, Mn(III) porphyrins proved to be more efficient for BTs sulfoxidation by H<sub>2</sub>O<sub>2</sub>, whereas the MnPOM evidences better performance for DBTs.



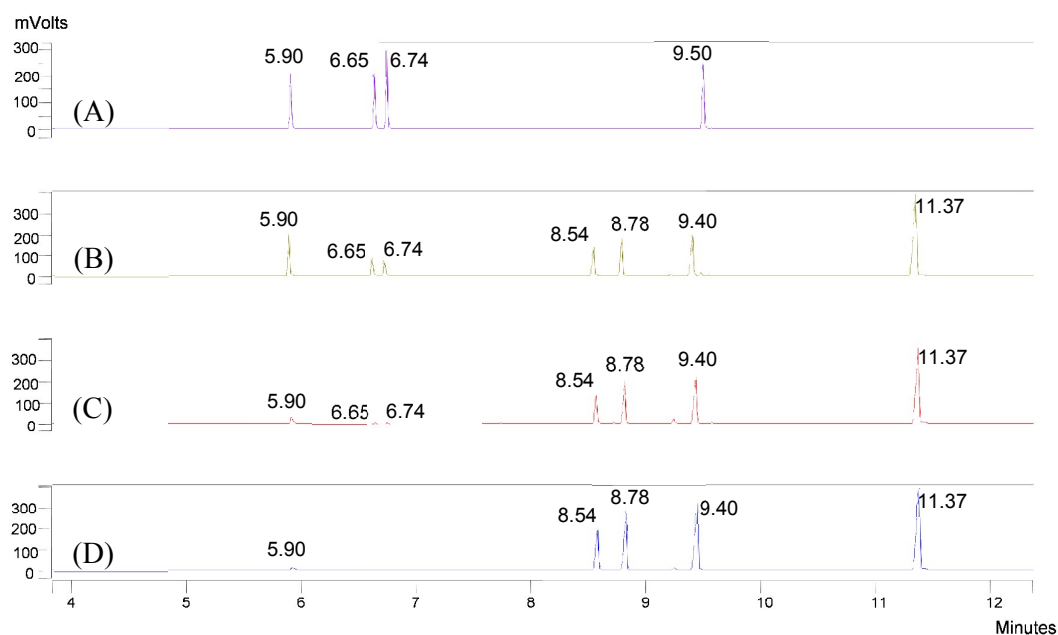
Scheme 1

Based on our previous studies with the  $\text{BW}_{11}\text{Mn}/\text{H}_2\text{O}_2$  system in the oxidation of anthracene to 9,10-anthraquinone<sup>31</sup> and on what is known for oxidations with polyoxotungstates,<sup>14</sup> we suggest a possible mechanism for the oxidation of the studied sulfur compounds, translated by equations (1)-(3), Scheme 1. Equation (1) represents the formation of a complex, by the reaction of hydrogen peroxide with the POM, whereas equations (2) and (3) correspond to the successive sulfoxidation reactions of a generic substrate XS. The exact type of complex formed is unknown (in scheme 1 is shown the simplest possibility) but, as in the case of the oxidation of anthracene<sup>31</sup> it seems to be prone to a nucleophilic attack, in this case by the S atoms of BTs and DBTs. The possible formation of a peroxocomplex through coordination at a W atom (suggested in many other cases<sup>26,31</sup>) cannot be ruled out, but, as the reactions took place at room temperature, its formation seems less plausible (in view of the W coordinative saturation, it needs the breaking of, at least, one POM W–O bond). It has been shown that the oxidation of  $\text{BW}_{11}\text{Mn(III)}$  favors the formation of a  $\text{Mn(IV)-OH}$  derivative.<sup>64</sup> For this reason we have not considered a  $\text{Mn(V)=O}$  containing species, even if they have been

identified in the oxidation of other POMs in different conditions.<sup>65,66</sup> Also, the reactivity of Mn and other metal substituted POMs often seems to be more in accordance with a peroxy or hydroperoxy intermediate than with an oxo complex.<sup>14,24,67</sup> Peroxy or hydroperoxy complexes with  $d^0$  metals are electrophilic in nature, contrarily to complexes with  $d^8$  metals, which are nucleophilic.<sup>68</sup>  $BW_{11}Mn(III)$ , with a  $d^4$  configuration, is possibly intermediate in character, and it is reasonable to consider it liable to a nucleophilic attack. The presence of protons in the catalyst chemical formula (protonation) may increase its nucleophilic character, as reported for  $Ti(IV)$  POMs.<sup>14</sup>

### 3.2. Oxidation of the organosulfur compounds and desulfurization of the model fuels

Based on the promising results achieved for the recalcitrant organosulfur compounds described above, the catalytic performance of  $BW_{11}Mn$  was evaluated for the oxidation of two model fuels (**MF**), consisting of a mixture of substrates **1-4** (**MF1**) and **3-6** (**MF2**), in hexane. The reactions occurred in homogeneous conditions in a  $CH_3CN$ /hexane (1:3) medium. The solvent mixtures are very common in this type of studies, as can be profusely found in the literature.<sup>38,40,57-59,61-63,69-71</sup>

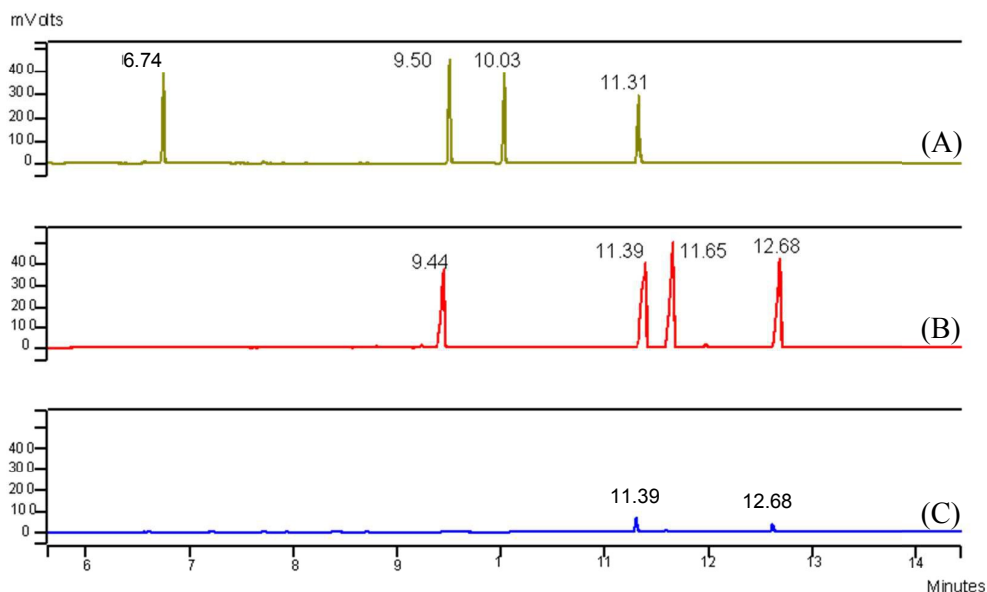


**Figure 4.** Typical GC-FID chromatograms illustrating **MF1** oxidation reaction profile with  $H_2O_2$  in the presence of  $BW_{11}Mn$  for a S/C molar ratio of 150. (A) Initial reaction mixture before the addition of  $H_2O_2$ ; (B) After 60 min of reaction; (C) After 120 min of reaction; (D) After 180 min of reaction. The model fuel **MF1** is a solution of **1** ( $R_t = 5.90$  min), **2** ( $R_t = 6.65$  min), **3** ( $R_t = 6.74$  min), and **4** ( $R_t = 9.50$  min) in hexane (0.03 mmol each).

Figure 4 illustrates the GC-FID monitoring profile for the oxidation of **MF1** by  $\text{H}_2\text{O}_2$  in the presence of **BW<sub>11</sub>Mn**, after 60, 120 and 180 min of reaction. The disappearance along the time of the four original signals (corresponding to the initial compounds) was accompanied by the appearance of four new peaks, indicating that the only products were the sulfones **1b** ( $R_t = 8.54$  min), **2b** ( $R_t = 8.78$  min), **3b** ( $R_t = 9.40$  min), and **4b** ( $R_t = 11.37$  min).<sup>52</sup> Only a minor amount of **BT 1** ( $R_t = 5.90$  min) remains in solution after 180 min of reaction. More than 99% of the starting **MF1** is fully converted into the corresponding oxidized products and, in accordance to the above-mentioned results, the **BW<sub>11</sub>Mn** catalyst seems to be more efficient for the DBTs oxidation. In fact, after 60 min of reaction, the DBT **4** ( $R_t = 9.50$  min) is hardly observed in the corresponding chromatogram (Figure 4B), whereas all the BTs are still present. The different rates of sulfone formation follow closely the described in 3.1.

The course of the oxidation of model fuel **MF2**, composed by three DBTs (**4**, **5** and **6**) and one BT (**3**), is illustrated on Figure 5. The chromatogram registered before  $\text{H}_2\text{O}_2$  addition shows four peaks that correspond to the initial compounds (Figure 5A), and the chromatogram obtained after 3 hours of reaction (Figure 5B) shows four different peaks that match the corresponding sulfones.<sup>52</sup> Due to the partial overlap of some of the starting peaks with those corresponding to the oxidized products, the chromatograms on Figure 5 may not demonstrate clearly the total conversion of the starting substrates in **MF2**. Therefore, the unambiguous identification of each peak was performed by GC-MS: the peak at 9.44 min corresponds to the sulfone **3b** ( $M^{+} = 180$ ); the peak at 11.39 was identified as the product **4b** ( $M^{+} = 216$ ); finally the peaks at 11.65 and 12.68 were assigned to the sulfones **5b** ( $M^{+} = 230$ ) and **6b** ( $M^{+} = 272$ ), respectively.

The oxidation of hexane did not take place in the model fuels. It is important to note that polyoxometalates may be good catalysts for the oxidation of several types of organic compounds, including hydrocarbons.<sup>14,26</sup> In particular, the **BW<sub>11</sub>Mn**/ $\text{H}_2\text{O}_2$  system in acetonitrile has been used in the oxidation of cycloalkanes,<sup>49</sup> *cis*-cyclooctene,<sup>47</sup> anthracene,<sup>31</sup> styrene,<sup>28</sup> and indene,<sup>36</sup> among others. However, none of these reactions occurs at room temperature. This point may need consideration in studies with real fuels at higher temperatures.

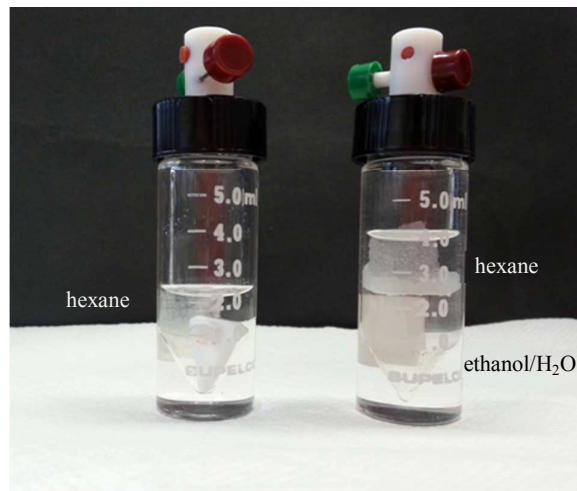


**Figure 5.** Typical GC-FID chromatograms illustrating **MF2** oxidation reaction profile with  $\text{H}_2\text{O}_2$  in the presence of **BW<sub>11</sub>Mn** for a S/C molar ratio of 150. (A) Initial reaction mixture before the addition of  $\text{H}_2\text{O}_2$ ; (B) After 180 min of reaction; (C) After the extraction procedure. The model fuel **MF2** is a solution of **3** ( $R_t = 6.74$  min), **4** ( $R_t = 9.50$  min), **5** ( $R_t = 10.03$  min), and **6** ( $R_t = 11.31$  min) in hexane (0.03 mmol each).

Liquid phase oxidative desulfurization is basically a two stage process, in which sulfur compounds are firstly oxidized to their corresponding sulfones, and subsequently removed from the solution by extraction or other separation method.<sup>9,12</sup> Proven the high efficiency of the use of **BW<sub>11</sub>Mn** in the oxidation methodology, the next step studied was the extraction of the oxidized products, in order to develop a promising desulfurization procedure. This was performed with model fuel **MF2**. After a few attempts using different extraction solvents, namely methanol, acetone, ethyl acetate, ethanol, water, and ethanol/ $\text{H}_2\text{O}$  (2:1) or (1:1) mixtures, the successful elimination of S-compounds from the hexane solution was achieved using a mixture of ethanol/ $\text{H}_2\text{O}$  (1:1).

In a typical procedure, 2 mL of the ethanol/ $\text{H}_2\text{O}$  (1:1) mixture are added at the end of the catalytic step to the reaction mixture, the system is stirred for 10 min and left to rest for another 10 min. At the end, it is possible to observe that the addition of ethanol/ $\text{H}_2\text{O}$  causes a phase separation with the concomitant precipitation of sulfones in the interface of the two phases (Figure 6). The GC-FID analysis of the hexane fraction after the described procedure clearly put in evidence the success of the separation methodology (Figure 5C), since more than 98 mol% of the organic compounds were removed. This process, besides being efficient

and simple, using only ethanol and water as solvents, respects the environmental and safety issues required to ODS.



**Figure 6.** Reactors used during the desulfurization procedure of **MF2**, before extraction (left) and after extraction (right)

#### 4. Conclusions

In conclusion, with the catalytic experiments involving  $\text{TBA}_4\text{H}_2[\text{BW}_{11}\text{Mn}(\text{H}_2\text{O})\text{O}_{39}]\cdot\text{H}_2\text{O}$ , the  $\text{BW}_{11}\text{Mn}/\text{H}_2\text{O}_2$  in  $\text{CH}_3\text{CN}$  catalytic system, a new environmentally friendly and efficient oxidation procedure for BTs (**1-3**) and DBTs (**4-6**) at room temperature is disclosed. As far as we know, this is the first example of a POM as catalyst operating at room temperature (22–24°C) with such efficiency in the oxidation of recalcitrant S-compounds. Under very mild conditions, excellent organosulfur compounds conversion values were obtained (97–100% for S/C molar ratio of 150). The high potential of  $\text{BW}_{11}\text{Mn}$  for application in ODS processes was verified through the results achieved in the oxidation of two model fuels by  $\text{H}_2\text{O}_2$ : one mainly composed by BTs (**1-4**) and the other mainly by DBTs (**3-6**), both with conversions close to 100%, attained after 3 hours of reaction. Envisaging the simulation of the entire ODS procedure, a simple, efficient and environmentally sustainable removal approach of the sulfones from model oil (**MF2**) was also developed, using an ethanol/ $\text{H}_2\text{O}$  (1:1) mixture to successfully remove the sulfones from hexane. The GC-FID analysis after 20 min of extraction showed that more than 98 mol% of the organosulfur compounds were removed from the organic layer, corresponding to a decrease from  $3.8 \times 10^3$  to 76 ppm of sulfur. In a near future we intend to develop our studies by using POM-based heterogeneous catalysts in the oxidation of this kind of recalcitrant compounds, also in real fuel samples.

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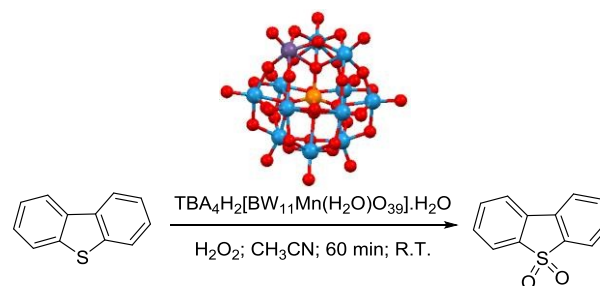
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A manganese monosubstituted Keggin-type polyoxometalate as catalyst in the oxidation of recalcitrant organosulfur compounds by hydrogen peroxide at room temperature.