

Advanced Oxidation Process  
Mid-year Report

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## ABSTRACT

The design of new, high efficiency and cleaner burning engines is strongly coupled with the removal of recalcitrant sulfur species, dibenzothiophene and its derivatives, from fuels. Oxidative desulfurization (ODS) wherein these dibenzothiophene derivatives are oxidized to their corresponding sulfoxides and sulfones is an approach that has gained significant attention. Fe-TAML® activators of hydrogen peroxide (TAML is Tetra-Amido-Macrocyclic-Ligand) convert in a catalytic process dibenzothiophene and its derivatives to the corresponding sulfoxides and sulfones rapidly at moderate temperatures (60 °C) and ambient pressure. The reaction can be performed in both an aqueous system containing an alcohol (methanol, ethanol, or *t*-butanol) to solubilize the DBT and in a two-phase hydrocarbon/aqueous system where the alcohol is present in both phases and facilitates the oxidation. Under a consistent set of conditions using the FeBF<sub>2</sub> TAML activator, the degree of conversion was found to be *t*-butanol > methanol > ethanol. In the cases of methanol and ethanol, both the sulfoxide and sulfone were observed while for *t*-butanol only the sulfone was detected. In the two-phase system, the alcohol may function as an inverse phase transfer agent. The oxidation was carried out using two different TAML activators. In homogeneous solution, approximately 90% oxidation of the DBT could be achieved using the prototype TAML activator, FeB\*, by sonicating the solution at near room temperature. In bi-phasic systems conversions as high as 50% were achieved using the FeB\* TAML activator and hydrogen peroxide at 100 °C. The sonication method yielded only ~6% conversion but this may have been due to mixing.

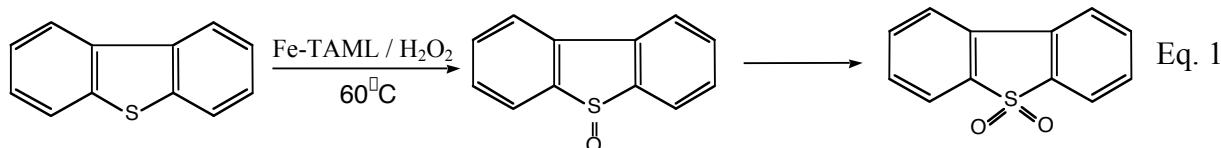
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## INTRODUCTION

The USEPA developed a regulatory plan for the petroleum industry targeted at lowering sulfur levels in gasoline and diesel fuels.<sup>2, 5</sup> The engine manufacturers need to design and build better engines and the petroleum industry must supply fuels substantially free of sulfur compounds in order to make engines cleaner burning. The petroleum industry needs to find and implement a desulfurization technology soon.<sup>3</sup> The future lies in the development of innovative technologies for removing the traces of sulfur compounds present after applying the standard hydrodesulfurization technology. This report describes the advances achieved by the Institute for Green Oxidation Chemistry (Institute) at Carnegie Mellon University in the area of oxidative desulfurization (ODS) using TAML® activators of H<sub>2</sub>O<sub>2</sub> while supported under **DOE Award No. DE-FC26-02NT41625** for the period September 26, 2003 – September 25, 2003.

The progress that has been achieved in the Institute for Green Oxidation Chemistry (Institute) relating to the desulfurization of diesel and gasoline fuels using the Fe-TAML® activators and hydrogen peroxide is described in this mid-year report. The project has focused on oxidizing the recalcitrant sulfur species, the benzothiophenes and dibenzothiophenes, Eq. 1, in diesel fuels that are present after hydrodesulfurization and subsequent treatments. These sulfur



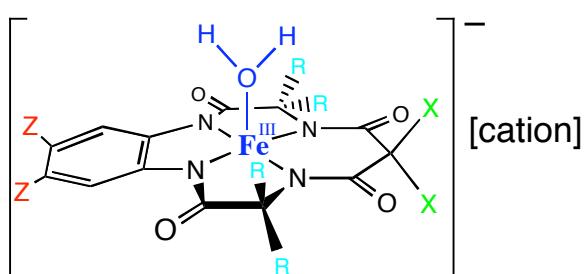
containing species are the primary cause of soot particles being emitted from diesel engines. Soot particles have been linked to many human health issues. The engine manufacturers, and advanced technologies for removing NO<sub>x</sub>, need low sulfur fuels in order to have engines that do not produce these pollutants.

The topics covered in this mid-year are:

- efficiency of H<sub>2</sub>O<sub>2</sub> usage
- exploration of TAML activator variants
- oxidation in bi-phasic systems
- influence of tertiary components

## EFFICIENCY OF H<sub>2</sub>O<sub>2</sub> USAGE

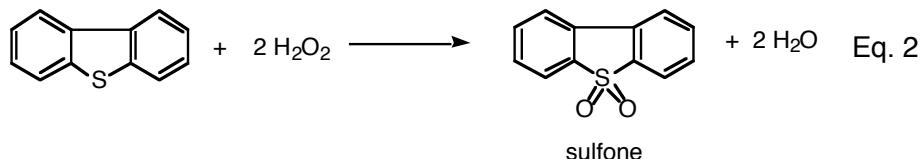
The desulfurization reactions performed prior to current support revealed complete oxidation of DBT derivatives at 60° C



within 30 min using the FeBF<sub>2</sub> activator, **Figure 1** (X = F, Z = H, and R = CH<sub>3</sub>), and a ten fold mole ratio excess of hydrogen peroxide with respect to DBT. An oxidative desulfurization technology based on hydrogen peroxide needs to be efficient with respect to peroxide use in order for it to be economically viable. Thus, it was significant to determine if

**Figure 1:** General structure depicting the TAML activator family of compounds

the oxidation could occur under stoichiometric conditions, that is 1 mol DBT:2 mol  $\text{FeBF}_2$  Eq. 2.



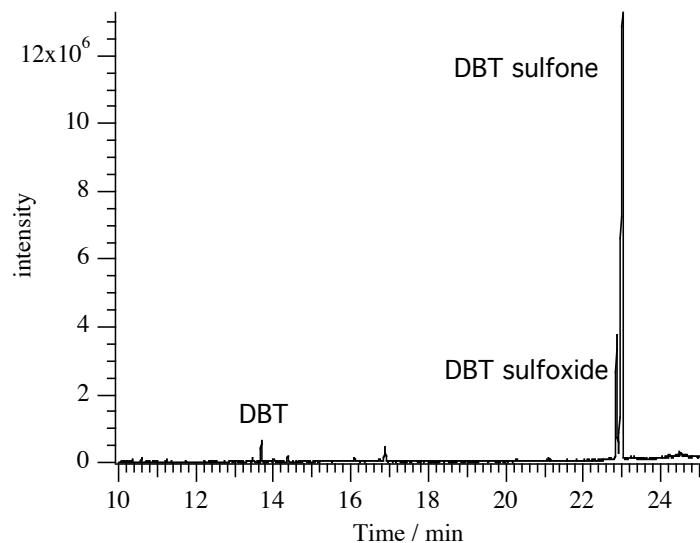
## Experimental

To a stirred  $\text{H}_2\text{O:t-BuOH}$  (7:3) solution of DBT ( $1.73 \times 10^{-3}$  M) at  $60^0$  C was added the  $\text{FeBF}_2$  activator ( $1.73 \times 10^{-6}$  M) and  $\text{H}_2\text{O}_2$  ( $3.46 \times 10^{-3}$  M) [TAML:DBT: $\text{H}_2\text{O}_2$  1:1000:2000]. The reaction mixture was stirred for 1 h and then the t-BuOH was removed in vacuo and the water layer extracted with diethyl ether. The ether layer was separated and analyzed by GC-MS.

## Results

Shown in **Figure 2** is the GC trace obtained from the ether extract using the reaction conditions described above. The majority, >95%, of the DBT was oxidized to its two oxidation products, the DBT-sulfoxide and the DBT-sulfone. This important result demonstrates that even at relatively low peroxide concentrations, DBT can be oxidized to a significant extent in a relatively short time period. Furthermore, this constitutes nearly 1000 turnovers of substrate in approximately 1 h using micromolar quantities of catalyst. It was found that approximately 80% of the conversion took place in the first 30 min of reaction. These results demonstrate the unprecedented reactivity and selectivity of the TAML activators.

It can be seen from the GC trace that the formation of the DBT-sulfone was much greater than the DBT-sulfoxide. Thus, even though the amount of peroxide is relatively low, DBT-sulfone is still the preferred oxidized product. This experiment also shows the stepwise conversion of the DBT to its oxidized products with the  $\text{FeBF}_2$  TAML activator. Previously only the sulfone had been observed using this catalyst. The explanation for this behaviour most likely resides in the fact that the reaction is slower overall because of the low peroxide concentration.



**Figure 2:** GC trace of the ether phase after reaction according to the conditions described above;  $\text{H}_2\text{O:t-BuOH}$  (7:3), DBT ( $1.73 \text{ mM}$ )  $\text{FeBF}_2$  activator ( $1.73 \mu\text{M}$ ) and  $\text{H}_2\text{O}_2$  ( $3.46 \text{ mM}$ ),  $T = 60^0$  C.

## TAML ACTIVATOR VARIANTS

We have previously observed that the Fe-TAML activator  $\text{FeBF}_2$  (**Figure 1**) in the presence of  $\text{H}_2\text{O}_2$  completely oxidizes DBT in a  $\text{H}_2\text{O:t-BuOH}$  (7:3) solvent system within 30 min at 60 °C. Currently, there are 20 variants of the TAML activators that could be applied to this chemistry. However, it was of most importance to demonstrate that the simplest TAML activator currently available,  $\text{FeB}^*$  ( $\text{X} = \text{F}$ ,  $\text{Z} = \text{H}$ , and  $\text{R} = \text{CH}_3$ ), was capable of oxidizing DBTs because this catalyst is undergoing scale-up to multi-tonne quantities. Furthermore, by observing and understanding how less active catalysts behave in this oxidation reaction, we gain insight into the design of more selective and reactive catalysts. Ultimately this results in developing the most efficient catalyst system. Here we describe the oxidation of DBT using  $\text{FeB}^*$ .

### General considerations

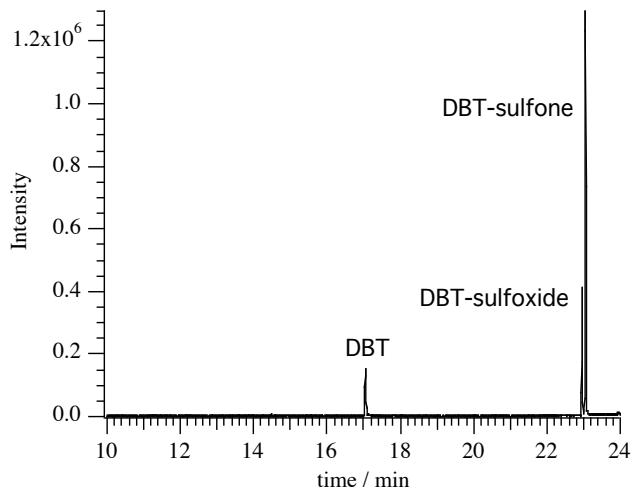
Along with the change in catalyst type, two additional modifications to the chemistry were examined. First, the reaction was performed using a standard laboratory sonicator system as an energy source rather than the typical application of heat. It is known that sound waves cause cavitations where local heat is high.<sup>1, 4</sup> These cavitations also activate  $\text{H}_2\text{O}_2$ . Thus it was reasoned that the combination of the TAML activator and sonication could lead to oxidation at ambient temperatures. The second modification was the use of 0.01 M pH 10 phosphate buffer (in water):t-BuOH (7:3) as the reaction medium. Previous work in the Institute with the  $\text{FeB}^*$  catalyst system has shown that it is most effective at pH 10. Interestingly, we previously examined the DBT oxidation process at pH 10 using an carbonate/bicarbonate buffer in 7:3  $\text{H}_2\text{O:t-BuOH}$  at 60 °C, but no oxidation was observed. Now with the change in the reaction medium to phosphate buffer, we do observe oxidation as detailed below. We are trying to determine if there is a specific interaction between one or more of the buffer components with the TAML activator that either activates or deactivates the oxidation reaction.

### Experimental

To a stirred 0.01 M pH 10 phosphate buffer:t-BuOH (7:3) solution of DBT (0.82 mM, 170 ppm) at ~30° C was added the  $\text{FeB}^*$  (8.22  $\mu\text{M}$ ) and  $\text{H}_2\text{O}_2$  (33 mM). The reaction mixture was sonicated for 1 h then the t-BuOH was removed in vacuo and the water layer extracted with diethyl ether. The ether layer was analyzed by GC-MS.

### Results

The GC trace of the ether layer is shown in **Figure 3**. Based on the area under the DBT peak, ~90% was oxidized. Both possible sulfur oxidation products, the DBT-sulfoxide and DBT-sulfone are detected. In the absence of the TAML activator, no oxidation occurs. This is a great advancement for a desulfurization technology based on TAML activators because we can synthesize this catalyst in high yields in our laboratory and commercially. Furthermore, since ~90% DBT oxidation could be achieved using the sonication method, which appears to be milder conditions even than heating to 60 °C with the  $\text{FeBF}_2$  TAML activator, the process becomes even more desireable. It is our intention to expand on this chemistry by examining the oxidation in bi-phasic systems.



**Figure 3.** GC trace of the solution after oxidation of DBT with FeB\* and H<sub>2</sub>O<sub>2</sub>.

## BI-PHASIC REACTIONS

Prior to current support, it was demonstrated that the oxidation of DBT in a bi-phasic system comprised of n-Octane/H<sub>2</sub>O/t-BuOH DBT sulfoxide and sulfone were produced using the FeBF<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system. The n-Octane is used to dissolve the DBT and act as a diesel mimic. Since the Fe-B\*/H<sub>2</sub>O<sub>2</sub> system could almost quantitatively oxidize DBT under homogeneous conditions in a 0.01 M pH 10 phosphate buffer H<sub>2</sub>O:t-BuOH (7:3) solvent system, the bi-phasic reaction was carried out with the same water:t-BuOH ratio. We have performed the reaction under heating and sonication conditions.

## Experimental

### Experiment 1:

A two-phase system consisting of 5.0 mL of 0.01 M pH 10 phosphate buffer:t-BuOH (7:3) and 1.0 mL of octane containing DBT ( $3.0 \times 10^{-3}$  M) was prepared. The mixture was heated with stirring to 100 °C and then Fe-TAML activator (2  $\mu$ M) and 47.0  $\mu$ L of H<sub>2</sub>O<sub>2</sub> (8 mM) were added. The reaction mixture was stirred for 1 h. Then a second and third portion of Fe-TAML activator (2  $\mu$ M) and H<sub>2</sub>O<sub>2</sub> (8 mM) were added every after 1 h. Total reaction time was 3 h. The n-Octane layer was separated from the aqueous phase and was analyzed by GC-MS.

### Experiment 2:

A two-phase system consisting of 5.0 mL of 0.01 M pH 10 phosphate buffer:t-BuOH (7:3) 1.0 mL of octane containing DBT ( $3.0 \times 10^{-3}$  M) was prepared. Then Fe-TAML activator (2  $\mu$ M) and H<sub>2</sub>O<sub>2</sub> (8 mM) were added. The reaction mixture was sonicated for 1 h at 40 °C. Then a second and third portion of Fe-TAML activator (2  $\mu$ M) and H<sub>2</sub>O<sub>2</sub> (8 mM) were added every after 1 h. Total reaction time was 3 h. The n-Octane layer was analyzed by GC-MS.

## Results

The GC trace obtained for the n-Octane phase using the conditions of **Experiment 1** revealed incomplete DBT removal. The degree of removal corresponds to nearly 50%. In the case of **Experiment 2**, only 6% conversion was obtained. As expected, the degree of DBT

oxidation is less in the bi-phasic system than in homogeneous solution. The very low conversion via the sonication method was somewhat surprising given the outstanding results in homogeneous solution. However, it is probable that mixing was not good because the mixture could not be simultaneously stirred and sonicated. Thus the 6% conversion is reasonable and warrants further investigation especially since it might be more cost effective to use sonication rather than heat for reactions on large volumes.

## TERTIARY COMPONENTS

We are in search of a agent other than t-BuOH to add to the water that will enhance the conversion of the DBT in bi-phasic systems. The initial approach was to examine solvent polarity and dielectric constant while still using alcohols. Here we used methanol (MeOH) and ethanol (EtOH). Ethanol is a desireable alcohol because it is a renewable resource. Both alcohols have very limited solubility in hydrocarbons thereby facilitating separation and simplifying processing. Since a H<sub>2</sub>O:t-BuOH (7:3) solvent system was found to be the optimum for t-BuOH, this was used for the other alcohols. The TAML activator for these studies is shown the Fe-BF<sub>2</sub> variant.

## Experimental

### Experiment 1:

To a stirred H<sub>2</sub>O:t-BuOH (7:3) solution of DBT (1.95x10<sup>-3</sup> M) at 60<sup>0</sup> C was added the FeBF<sub>2</sub> activator (1.95x10<sup>-6</sup> M) and H<sub>2</sub>O<sub>2</sub> (1.95x10<sup>-2</sup> M). The reaction mixture was stirred for 30 min and then the t-BuOH was removed in vacuo and the water layer extracted with diethyl ether. The ether layer was separated and analyzed by GC-MS.

### Experiment 2:

To a stirred H<sub>2</sub>O:MeOH (7:3) solution of DBT (1.94x10<sup>-3</sup> M) at 60<sup>0</sup> C was added the FeBF<sub>2</sub> activator (1.94x10<sup>-6</sup> M) and H<sub>2</sub>O<sub>2</sub> (1.94x10<sup>-2</sup> M). The reaction mixture was stirred for 30 min and then the MeOH was removed in vacuo and the water layer extracted with diethyl ether. The ether layer was separated and analyzed by GC-MS.

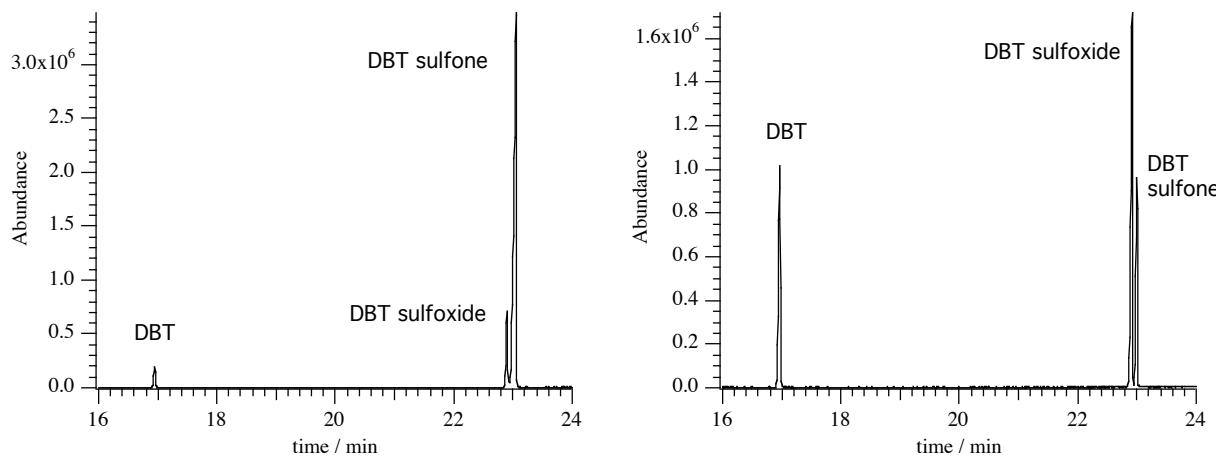
### Experiment 3:

To a stirred H<sub>2</sub>O:EtOH (7:3) solution of DBT (1.83x10<sup>-3</sup> M) at 60<sup>0</sup> C was added the FeBF<sub>2</sub> activator (1.83x10<sup>-6</sup> M) and H<sub>2</sub>O<sub>2</sub> (1.83x10<sup>-2</sup> M). The reaction mixture was stirred for 30 min and then the EtOH was removed in vacuo and the water layer extracted with diethyl ether. The ether layer was separated and analyzed by GC-MS.

## Results

As expected, the ether extract using the reaction conditions of **Experiment 1** contained only the DBT sulfone. In contrast, the ether extracts obtained using the conditions of **Experiments 2 and 3** showed residual DBT, **Figure 4**. This experiment shows the stepwise conversion of the DBT to its oxidized products and demonstrates that reaction medium will play a significant role in this chemistry. More significantly, both the DBT sulfoxide and DBT sulfone were formed and there is a distinct difference in extent of conversion when comparing the MeOH and EtOH samples. In the case of t-BuOH, a number of different ratios of t-BuOH to water were explored before finding the optimum one of 7:3 H<sub>2</sub>O/t-BuOH. Thus it might be that with further exploration of reaction conditions with MeOH and EtOH, better conversion can be found. We note that one possible explanation for the observed chemistry is that the FeBF<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> system is reacting with the MeOH and EtOH. This is an area of ongoing research. Nevertheless,

the results clearly demonstrate that it is possible to oxidize DBT to its corresponding sulfone and



**Figure 4.** GC traces of reactions performed in 7:3 H<sub>2</sub>O:MeOH (left) and 7:3 H<sub>2</sub>O:EtOH (right)

sulfoxide using simple alcohols like methanol and ethanol. This has a great economic advantage over t-BuOH especially since EtOH is a renewable resource and the alcohol can be readily separated from a hydrocarbon phase.

## SUMMARY

The program in the Institute designed to address the problem of residual sulfur species in fuel has made significant success during the funding period. Catalyst breadth has been achieved. Similarly, the variety of reaction conditions that can be used to remove the sulfur species has been expanded. Some of the challenges for the next few months will be to understand why the chemistry changes so much from aqueous to bi-phasic systems, sensitivity of fuel components to the oxidation conditions and improvement of the process overall.

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