

OXIDATIVE DESULFURIZATION OF FUELS THROUGH TAML[®] ACTIVATORS AND HYDROGEN PEROXIDE

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Introduction

The removal of sulfur from petroleum is necessary for both industrial and environmental reasons. Sulfur in petroleum products poisons catalytic converters, corrodes parts of internal combustion engines and refineries because of the formation of oxyacids of sulfur,¹ and air pollution due to exhaust from diesel engines is a major concern to the public.²⁻⁴ The U. S. Environmental Protection Agency (EPA) has mandated reduction of sulfur content of diesel fuel and gasoline. The requirement will decrease the sulfur content of diesel fuel and gasoline to 15 ppm by 2006 and to 30 ppm by 2004, respectively.^{5,6}

The conventional method for reducing sulfur is catalytic hydrodesulfurization (HDS). In the HDS method, hydrogen and the organic sulfur compound react together at high temperature and high partial pressure of hydrogen.⁷ The effectiveness of the HDS process depends on the type of sulfur compound. The complete removal of sulfur present in petroleum as sulfides, disulfides and mercaptans is relatively easy and an inexpensive process. However, benzothiophenes and dibenzothiophenes (DBTs) are difficult to remove by this process.⁸ Particularly, the sterically hindered ones, 4-Methylthiobenzothiophene and 4,6-dimethylthiobenzothiophene are the most resistant to the current HDS process and they retard the rate of HDS.⁹ Most of the sulfur contamination in petroleum can be traced to the dibenzothiophene derivatives. In order to remove these compounds by HDS, it would require more hydrogen capacity and the maintenance of high temperatures and pressures for longer time periods. This would increase operating costs and enhance the likelihood that saturation of olefins and aromatics will occur resulting in a lower-grade fuel and additional processing steps.¹⁰ Thus, it is likely that HDS processing has reached a stage where increasing temperature and pressure are just not enough to remove the residual sulfur without affecting the octane number. This process also produces increased volumes of hydrogen sulfide. Although HDS processes have dominated desulfurization of petroleum in the past, their cost and the requirements of strict fuel specifications combine to motivate the development of innovative process technologies.

An oxidative desulfurization (ODS) approach to sulfur removal serves as an alternative to the HDS process. An ODS process has the significant advantage over HDS in that the sulfur compounds that are the most difficult to reduce by HDS are the most reactive for ODS. In effect, the ODS

process has the reverse order of reactivity as compared to the HDS process. This effect arises because the reactivity of sulfur compounds for oxidation is augmented with an increase of electron density on the sulfur atom. The electron donating properties of methyl groups on the aromatic rings positively influences DBT derivatives and the one with the most electron rich sulfur atom will react fastest.⁹ Of significant importance is that this increased electron density at sulfur upon methyl incorporation overshadows their steric effects. The oxidation of thiophenes to sulfones increases their polarity, and molecular weight.¹¹ The enhanced polarity makes it easier to remove them by adsorption on a solid material such as silica, alumina, clay or activated carbon.¹² It also facilitates their separation by extraction,¹³ distillation¹¹ or alkali treatment.¹⁴ Several peroxy organic acids (formic, acetic, propionic etc.) and Caro's acid (peroxysulfuric acid) have been used for selective oxidation of organic-sulfur compounds.^{11,13,15-18} The other oxidative processes involve nitrogen dioxide,² transition metal-based catalysts in conjunction with hydroperoxide as oxidant, and photo-^{19,20} or ultrasound-induced²¹ oxidation. The catalysts reported include mixed molybdenum/tungsten oxides^{4,14}, tungstophosphoric acid (TPA)¹² and methyl trioxorhenium.²² However, reaction selectivity, safety and cost are the important concerns for the selection of oxidant, catalyst and operating conditions for ODS processing. The peroxyacids are generated *in situ* at operating conditions of 200-250 °F near atmospheric pressure. The catalytic systems reported are toxic and expensive. While these are significant technologies, there are still issues relating to ultimate fuel quality and economy of the process that need to be determined. Thus there is a need for a new technology that can perform the oxidation reaction under mild conditions and one that can selectively oxidize the sulfur compounds.

We have developed a series of iron (III) complexes called TAML[®] (for Tetra Amido Macrocyclic Ligand) activators that enhance the oxidizing ability of hydrogen peroxide at low catalyst concentration and mild reaction conditions.²³ These peroxide activators are finding uses in many different areas including the pulp and paper industry, the textile and laundry industries, mineralization of organohalogenes, and others. Their versatility as oxidants lead to their use in the current study where it was found that they are capable of rapidly oxidizing the dibenzothiophene derivatives that are of concern to the petroleum industry. The general structure of TAML[®] activators is shown in Figure 1. The R and X groups are used to control activator reactivity, selectivity and lifetime. The activator used for this study has R = H and X = F and is referred to as FeF₂B. The FeF₂B form of the activator is particularly active in neutral pH water. Fe-TAML[®] activators, which have been developed over twenty years to be long-lived activators of hydrogen peroxide, can be used under different reaction conditions including variable pH, temperature and solvent composition.²⁴ They are non-toxic and are most effective at very low concentrations (1 – 5 μM; 0.5 – 2 ppm). Here we report a practical system using Fe-TAML and H₂O₂ as catalyst and oxidant, respectively. We show that micromolar concentrations of FeF₂B activate H₂O₂ to convert greater than 99% of millimolar solutions (>7000:1 substrate: catalyst concentrations) of dibenzothiophene

derivatives to the corresponding sulfones under mild conditions. The choice of dibenzothiophene derivatives was based on their relative abundance in petroleum.

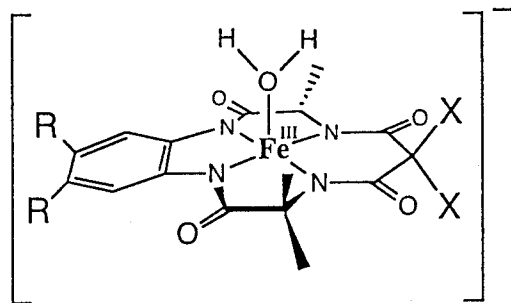


Figure 1: Structure of TAML activators

Experimental Section

General Materials and Methods.

Dibenzothiophene, 4-Methyldibenzothiophene and 4,6-Dimethyldibenzothiophene, 2-Methyl dibenzothiophene, 1,2-Benzophenylenesulfide, Benzothiophene, 3-Methylbenzothiophene, tert-butanol and hydrogen peroxide were purchased from Aldrich and Acros and used without further purification. Deuterated solvents for NMR spectroscopy were supplied from Cambridge Isotope labs. All aqueous solutions were made with doubly distilled water. H_2O_2 (30%) was diluted with water as necessary. UV-visible spectra were obtained on a Hewlett Packard 8453 Diode Array Spectrophotometer. The kinetic oxidation reactions were maintained at 40 °C. Quartz cuvettes of 1 cm optical path were used. Infrared spectra were obtained on a Mattson Galaxy 5000 FT-IR spectrophotometer. ^1H NMR spectra were measured at 300 MHz on a IBM NR/300 spectrometer. Gas Chromatography-Mass Spectroscopy (GC-MS) data were recorded on a Agilent 6890 Series Gas Chromatography and 5973 Network Mass Selective detector spectrometer. Gas Chromatography-Atomic Emission Detector (GC-AED) data were measured on an Agilent 6890 GC and 2350A AED. Midwest Microlabs of Indiana performed elemental analyses of the dibenzothiophenes and corresponding sulfones.

General Procedure for Bulk Oxidation of Dibenzothiophenes.

A procedure is given for dibenzothiophene. Dibenzothiophene (20 mg, 0.11 mmol) was dissolved in tert-butanol (2 mL, 54.3 mM) and the resulting solution added to 8 mL of a 50% pH 7 KH_2PO_4 buffer:50% tert-butanol solution with stirring (10.9 mM final concentration). Then, FeF_2B (3 μL , 1.5 μM final concentration) and H_2O_2 (50 μL , 30 vol% solution, 44 mM final concentration) were added. The mixture was stirred for 20 min at 60 °C. Upon cooling, a white solid precipitated from solution. The solid was recovered by filtration, washed, dried and fully characterized as dibenzothiophene sulfone.

General Procedure for the Kinetics of Oxidation of Dibenzothiophene.

In a typical case, dibenzothiophene (1.8 mg) was dissolved in tert-butanol (1 mL, 9.8 mM) and then added to 3 mL of a pH 7 KH_2PO_4 buffer solution (25 μL , 83 μM final concentration). The FeF_2B activator (7.35 μL , of 0.1 mM solution, final concentration 0.25 μM) was added and then the reaction was initiated by the addition of H_2O_2 (3.4 μL , 1 mM final concentration). The reaction was maintained at 40 °C and was determined to be complete when there were no further changes in absorbance.

Results and Discussion

A wide range of benzothiophenes and dibenzothiophenes are rapidly oxidized by hydrogen peroxide at atmospheric pressure in the presence of the Fe-TAML activator FeF_2B , Figure 1, in water/tert-butanol to give the corresponding sulfone. Table 1 lists the DBT derivatives that we have examined thus far. The ones that are of prime interest for an ODS process, dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene, have been the ones most extensively investigated. The products of these reactions were fully characterized by the techniques indicated in the table. The reaction product is the corresponding sulfone with 99% isolated yield. These conversions, which generally require less than one hour, are accomplished with molar ratios of substrate to catalyst of approximately 7000:1 and a reaction temperature of 60 °C. Since the sulfones are, like the starting DBTs, very insoluble in water rich mixtures, they precipitate from solution upon cooling to near room temperature.

The data presented in Table 2, which are preliminary kinetic measurements, reflect reactions carried out at 40 °C. These conditions are chosen to facilitate the ongoing kinetic studies and the ability to obtain high quality data. The data correspond to the reaction times to achieve greater than 95% conversion of the DBT derivative to the sulfone as determined by UV/visible spectroscopy. The differences between the starting DBT derivative and its corresponding sulfone are significant enough that this is readily determined. The overall efficiency of the oxidation process, the reaction rates, and the reaction pathways are still under investigation. It is worthwhile to note that increasing the temperature to 60 °C and raising the FeF_2B concentration to 1.5 μM (0.25 μM for kinetic studies), results in the oxidation of 4,6-Dimethyldibenzothiophene (approx. 80 μM , 17 ppm) in less than 1 minute as determined by UV/vis measurements. Thus the oxidation of the thiophenes is extremely rapid with this catalyst system.

The oxidation reaction with Fe-TAML/ H_2O_2 is flexible with respect to the type of the medium in which it is performed. For example, the kinetic studies described above were carried out in essentially pure water with only enough tert-butanol to solubilize the dibenzothiophene derivatives (the KH_2PO_4 buffer (see Experimental section) can be eliminated from the reaction mixture but was used to maintain constant ionic strength). When bulk reactions are performed to produce sufficient product for full characterization, the reaction medium was 50% water/50% tert-butanol; the higher

concentrations of tert-butanol are required for solubility of the starting dibenzothiophene derivatives. The concentration of tert-butanol could be raised to 70% without negatively impacting the oxidation process. These observations indicate that the Fe-TAML/H₂O₂ system is amenable to variations in operating conditions and determining the breadth of reaction conditions under which this oxidation can take place is part of the ongoing investigation.

Each table should have a number and heading, formatted as follows above the table:

Table 1. Dibenzothiophene derivatives investigated and the characterization techniques applied to reactants and products

Compound	Benzothiophenes	Benzothiophene sulfones
DBT	UV-vis, NMR, IR, GC-MS, GC-AED, elemental analysis	UV-vis, NMR, IR, GC-MS, GC-AED, elemental analysis
4-MethylDBT	UV-vis, NMR, GC-MS, GC-AED, elemental analysis	UV-vis, NMR, GC-MS, GC-AED, elemental analysis
4,6-dimethylDBT	UV-vis, NMR, GC-MS, elemental analysis	UV-vis, GC-MS, NMR, GC-AED, elemental analysis
2-MethylDBT	UV-vis	UV-vis
1,2-BenzoPS	UV-vis	UV-vis
BT	UV-vis	UV-vis
3-MethylBT	UV-vis	UV-vis
DBT : Dibenzothiophene 1,2-BenzoPS : 1,2-Benzophenylenesulfide BT : Benzothiophene		

Table 2. Reaction times of DBT derivatives at 40°C.^a

Compounds ^b	Reaction Time (sec) >95% conversion
Dibenzothiophene	200
4-Methyldibenzothiophene	1500
2-Methyldibenzothiophene	800
4,6-dimethyldibenzothiophene	150
1,2-Benzophenylenesulfide	>8000

^aFe₂B concentration 0.25 μM

^bCompound concentrations approximately 80 μM

Conclusions

A new method to reduce sulfur content in petroleum is needed to meet future regulations. The results presented here indicate that the Fe-TAML activators of H₂O₂ are capable

of rapidly oxidizing the dibenzothiophene derivatives present in fuels under mild reaction conditions. The results further indicate that an ODS process with Fe-TAML activators is a promising technology for decreasing sulfur content in fuels especially since these are non-corrosive.

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