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Oxidation of sulfur components in diesel fuel using Fe-TAML® catalysts and hydrogen peroxide

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Abstract

Dibenzothiophene-derivatives are catalytically oxidized to their corresponding sulfone product in homogeneous and two-liquid phase systems by H_2O_2 with an iron containing tetraamidomacrocyclic ligand (TAML) catalyst, Fe-TAML®. The reaction medium is slightly caustic, pH 8, and uses *t*-BuOH as a co-solvent for solubilizing the dibenzothiophene starting compounds and their oxidation products. Fe-TAML® catalyst concentrations are in the low micromolar range. H_2O_2 consumption is nearly stoichiometric (two-equivalents) in homogeneous conditions and only slightly less efficient under two-liquid phase conditions. The catalytic process when applied to a sample of commercial diesel fuel occurs under mild conditions with respect to temperature (50 °C), pressure (1 atm), and time (3 h), to remove greater than 75% of the total sulfur content of the fuel after secondary treatment with silica. Both alkyl-benzothiophenes and alkyl-dibenzothiophenes compounds in the diesel fuel were oxidized by the Fe-TAML®/H_2O_2 system which facilitated their adsorption onto the silica. The mild reaction conditions result in no detectable over-oxidation of alkyl-dibenzothiophenes.

Keywords: Oxidative desulfurization; Dibenzothiophene; 4-Methyldibenzothiophene; 4,6-Dimethyldibenzothiophene; Oxidation; Fe-TAML® catalyst; Hydrogen peroxide; Two-liquid phase; Diesel

1. Introduction

The production of fuels containing less than 15 ppm total sulfur for the transportation sector has become an urgent challenge worldwide for both environmental and industrial reasons [1,2]. Most of the sulfur removed from petroleum currently is achieved by the catalytic hydrodesulfurization (HDS) process [3,4]. HDS is highly efficient at removing thiols, sulfides and disulfides, but it is less effective for aromatic thiophenes, especially the alkyl-dibenzothiophenes [5–7]. Operation at high temperatures and pressures is inevitably required to remove these recalcitrant sulfur species. This brings about a number of problems including high investment, high operating cost, reduction of the catalyst cycle length, and increase in the hydrogen consumption due to the hydrogenation of olefins and aromatics present in fuels [8–10]. Removal of the recalcitrant sulfur compounds from diesel fuel has received particular attention recently because of the human health and environmental issues associated with diesel exhaust [11–14]. Many diesel engine exhaust pollution problems could be eliminated by reduction of the recalcitrant sulfur compounds to very low ppm levels in the fuel. Dibenozothiophene (DBT), 4-methyl-dibenzothiophene (4-MDBT), and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) have become the challenge molecules for sulfur removal technologies as once these species have been removed, it is likely that the US EPA, European, and Japanese mandated sulfur levels in diesel fuels can be achieved [15].

Possible strategies [16,17] to realize ultra-low sulfur diesel (ULSD) other than hydrodesulfurization of the recalcitrant sulfur compounds include adsorption [18,19], bioprocesses

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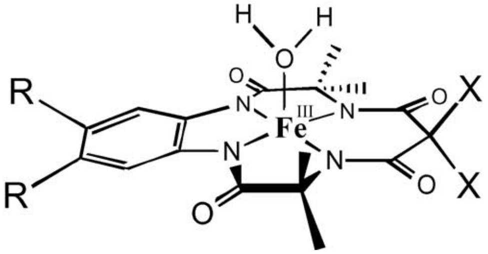

Fig. 1. General representation of the Fe-TAML® family of catalysts. The catalyst with X = F and R = Cl, FeDCBF$_2$, was used in this investigation.

[20,21], extraction [22], ultrasound [23], and oxidation [24–33] and oxidation using formic acid and H_2O_2 followed by adsorption such as in the UniPure ASR process [34–38]. Selective catalytic oxidation of the sulfur species to the corresponding sulfoxide or sulfone combined with extraction of these more polar, higher molecular weight products is one of the most promising desulfurization approaches. The main obstacles to the industrial application of the process at present include low-oxidation activity and low selectivity toward the sulfur species, difficulties in separation and recovery of the catalysts, low efficiency of H_2O_2 utilization, and the extraction of the oxidized sulfur species from diesel fuels.

Fe-TAML® catalysts (TAML is tetraamidomacrocyclic ligand), Fig. 1, are an expanding family of macrocyclic iron complexes that have been developed during the past 20 years to be long-lived activators of H_2O_2 in water [39–42]. These complexes are designed for use under a variety of working conditions, including variable pH, temperature, and solvent composition [41]. They are being used or have potential uses in a variety of different areas [43,44]. Their high inherent reactivity toward H_2O_2 and their selectivity toward substrates [45] make them ideal candidates for use in the oxidative desulfurization of refined fuels. In this contribution, we describe the application of the Fe-TAML® catalysts in a two-liquid phase system for the oxidation and removal of sulfur compounds from a commercial sample of diesel fuel.

The Fe-TAML® catalyst with X = F and R = Cl was used in this study. We refer to this compound as FeDCBF$_2$. Currently, it is one of the most reactive members of the Fe-TAML® catalyst family over a broad range of reaction conditions. This catalyst generally functions well in the pH 7–10 range under homogeneous reaction conditions. Furthermore, it reacts more rapidly with H_2O_2 than less reactive members of the Fe-TAML® catalyst family and results in faster and generally more complete reactions with substrates.

2. Experimental

2.1. General considerations

All reagents, components of the buffer solutions, and solvents were at least ACS reagent grade (Aldrich, Aldrich Sure-Seal, Fisher, Acros) and were used as received or purified in an appropriate manner [46]. Hydrogen peroxide was purchased from Fluka and standardized daily as described elsewhere [47]. The Fe^{III}-TAML catalyst, FeDCBF$_2$, was prepared as described previously [41]. Spectrophotometric measurements were performed using Hewlett Packard Diode Array spectrophotometer (model 8453) equipped with a thermostated cell holder and an automatic 8-cell positioner. The temperature was controlled by a Thermo digital temperature controller RTE17 within an accuracy of ±1 °C. Quartz cuvettes of the path length 1.0 cm were used for the investigation of the UV–vis spectral properties; extinction coefficients at 285 nm ($\varepsilon_{285\ \mathrm{nm}}$) in 7:3 H_2O:*t*-BuOH are in $M^{-1}\ cm^{-1}$ throughout. ^1H NMR spectra were measured using IBM NR/300 and a Brüker WM 300 FT-NMR spectrometers in *d*$_6$-DMSO unless stated otherwise–the δ scale is used throughout. Infrared data were obtained in KBr discs unless stated otherwise on a Mattson Galaxy 5000 FT-IR spectrophotometer; frequencies are in cm^{-1} throughout. Midwest Microlab, Indianapolis, IN performed elemental analyses. Sulfur analyses by ASTM D 5453 were performed by Southwest Research Institute, San Antonio, TX. Gas chromatography–mass spectroscopy (GC–MS) data were recorded on a Agilent 6890 Series Gas Chromatography and 5973 Network Mass Selective detector spectrometer. Also a Thermo Finnigan Trace GC equipped with flame photometric detector (FPD) and a Trace DSQ mass spectrometer were used for GC–MS studies. Gas chromatography–atomic emission detector (GC-AED) data were measured on an Agilent 6890 GC and 2350 A AED.

2.2. Oxidation of dibenzothiophene derivatives in a homogeneous medium

The oxidation reactions of the three dibenzothiophene derivatives were all performed in the same manner. Details are given for dibenzothiophene. DBT (5.94 mg, 3.2×10^{-5} mol) was dissolved in 10 mL of 7:3 (v/v) ratio of 0.01 M pH 8 phosphate buffer and *t*-BuOH. Then FeDCBF$_2$ (0.018 mg, 3.2×10^{-8} mol) and H_2O_2 (0.15 mL, 1.28×10^{-3} mol, 30 wt.%) were added and the reaction mixture was stirred for 30 min at 50° C. The FeDCBF$_2$:DBT mole ratio was 1:1000 (0.1%). When the reaction was complete, the *t*-BuOH was removed *in vacuo* and the water layer extracted with distilled diethyl ether. GC–MS analysis of the ether layer showed quantitative oxidation of DBT to dibenzothiophene sulfone (DBTO$_2$). Oxidized products of all three DBTs were isolated and characterized by elemental analyses, IR, NMR, GC–MS and GC–AED. UV–vis ($\varepsilon_{285\ \mathrm{nm}}$): DBT: 11,235; 4-MDBT: 10,330; 4,6-DMDBT: 9,980. DBTO$_2$: Isolated yield 97%. ^1H NMR: 8.21 (m, 2H), 7.99 (m, 2H), 7.82 (dt, 2H, *J* 7.5, 1.2), 7.67 (dt, 2H, *J* 7.5, 1.2). IR: 1288 and 1166. UV–vis ($\varepsilon_{285\ \mathrm{nm}}$): 5,075. Anal. Calcd. for $C_{12}H_8SO_2 \cdot 1/10H_2O$: C, 66.1; H, 3.79; S, 14.7. Found: C, 65.98; H, 3.87; S, 14.78%. 4-MDBTO$_2$: isolated yield 98%. ^1H NMR: 8.17 (d, 1H, *J* 7.8), 8.00 (d, 1H, *J* 7.8), 7.96 (d, 1H, *J* 7.8), 7.79 (dt, 1H, *J* 7.5, 1.2), 7.68 (m, 2H), 7.45 (d, 1H, *J* 7.5). IR: 1287 and 1161. UV–vis ($\varepsilon_{285\ \mathrm{nm}}$): 5,225. Anal. Calcd. for $C_{13}H_{10}SO_2$: C, 67.80; H, 4.38; S, 13.92. Found: C, 67.98; H, 4.44; S, 13.85%. 4,6-DMDBTO$_2$: isolated yield 95%. ^1H NMR: 7.96 (d, 2H, *J* 7.8), 7.66 (*t*, 2H, *J* 7.8), 7.44 (d, 2H, *J* 7.8). IR: 1283 and 1154. UV–vis ($\varepsilon_{285\ \mathrm{nm}}$): 5,720.

Anal. Calcd. for $C_{14}H_{12}SO_2\cdot 1/10H_2O$: C, 68.33; H, 5.0; S, 13.03. Found: C, 68.26; H, 4.82; S, 12.93%.

2.3. Oxidation of dibenzothiophene derivatives in a two-liquid phase system

The oxidations of DBT, 4-MDBT, and 4,6-DMDBT in a two-liquid phase system were performed in the same manner. Details for oxidation of DBT are described. A stock solution of DBT in *n*-decane or *n*-octane was prepared (2.7×10^{-3} M; 678 ppm DBT; 118 ppm S). A two-phase system consisting of 3.0 mL of 0.01 M pH 8 phosphate buffer H_2O:*t*-BuOH (7:3) and 1.0 mL of the DBT stock solution was prepared. The mixture was stirred at 50 °C and then 0.13 mL of $FeDCBF_2$ (2.0×10^{-4} M in 7:3 water:*t*-BuOH; 2.7×10^{-8} mol) and 30 μL of H_2O_2 (8.5 M; 2.7×10^{-4} mol) were added. The $FeDCBF_2$:DBT mole ratio was 1:100 (1.0%). The catalyst and H_2O_2 were added in six equal portions ($FeDCBF_2$ (0.022 mL) and H_2O_2 (5 μL)) at 30 min intervals for a total reaction time of 3 h. This addition methodology was used to reduce the deactivation rate of the activate catalyst species at higher concentration of catalyst and H_2O_2. The upper clear hydrocarbon solution was removed after separation by means of centrifugation and subjected to GC–MS and GC–FPD analyses. No DBT was detected in the hydrocarbon phase. The *t*-BuOH was removed in vacuo from the water:*t*-BuOH mixture and then the water layer was extracted with distilled diethyl ether. The ether layer was separated and analyzed by both GC–MS and GC–FPD and the product identified as the DBT sulfone.

2.4. Selectivity

A stock solution of DBT (2.7×10^{-3} M), fluorene (3.6×10^{-3} M) and toluene (470×10^{-3} M) in *n*-decane was prepared. A 1.0 mL portion of this solution was added to 3.0 mL of a 7:3 H_2O:*t*-BuOH 0.01 M pH 8 phosphate buffer solution. Then $FeDCBF_2$ (2.7×10^{-8} mol) and H_2O_2 (2.7×10^{-4} mol) were added to the mixture. The reaction mixture was stirred for 30 min at 50 °C. After cooling to room temperature, it was extracted with distilled diethyl ether. GC–MS analysis of the ether layer showed that quantitative oxidation of DBT to the dibenzothiophene sulfone. No oxidized products from fluorene or toluene were detected by GC–MS data and the concentrations of these two components were unchanged within experimental error.

2.5. Oxidation of sulfur in diesel

A commercially available sample of diesel fuel was used to determine the removal of sulfur compounds using $FeDCBF_2$ and H_2O_2. A two-phase system consisting of 3.0 mL of 0.01 M pH 8 phosphate buffer H_2O:*t*-BuOH (7:3) and 1 mL of diesel fuel was prepared. The total sulfur in the diesel sample was determined to be 348 mg/L by the ASTM D 5453 method (420 ppm S, $\rho = 0.83$ g/mL). The mixture was stirred at 50 °C and then 0.55 mL of $FeDCBF_2$ solution (2.0×10^{-4} M) in H_2O:*t*-BuOH (7:3) and 0.13 mL of H_2O_2 (8.5 M) were added ($FeDCBF_2$ 1.1×10^{-7} mol, H_2O_2 1.1×10^{-3} mol). The catalyst and H_2O_2 were added in six equal portions starting at time zero and then at each 30 min interval. After 3 h reaction time, the upper clear diesel solution was removed after separation by means of centrifugation and was then treated with silica to adsorb oxidized sulfur species. The total sulfur of the treated diesel sample was determined by both ASTM and rapid GC-AED methods [48].

3. Results and discussion

3.1. Homogeneous reaction conditions

The Fe-TAML® catalysts are most effective at activating H_2O_2 in aqueous solution. However, since DBT and its derivatives have very low solubilities in water, *tert*-butanol (*t*-BuOH) was used as a co-solvent. *t*-BuOH also solubilizes DBT oxidation compounds in water and no reactions have been observed between it and the Fe-TAML®/H_2O_2 system. Mixed-solvent systems of even highly miscible solvents like water and methanol [49–51] are complicated in terms of the structures that exist within the mixture [52]. This situation becomes more complex when a solute is present because it may have its own interactions with hydrophobic and hydrophilic groups on the solvent molecules. The interactions can have a profound impact on ensuing chemistry and reaction rates have been found to depend on factors such as hydrogen bonding, charge stabilization, and dipolar effects [53].

It was found in the present case, that the water/*t*-BuOH ratio was critical for the rate of the oxidation process. The oxidation of DBT with the Fe-TAML® catalyst/H_2O_2 system as monitored by UV–vis spectroscopy is shown in Fig. 2. It can be seen that the absorption band at 285 nm for DBT decreases and two isosbestic points are present. By monitoring the decrease in the absorption maximum at 285 nm, it was found that a 7:3 v/v H_2O:*t*-BuOH solvent composition gave the

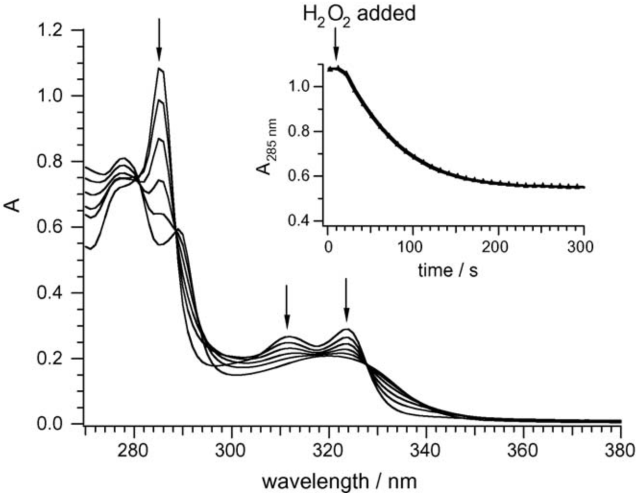

Fig. 2. Stacked plot of UV–vis traces taken every approx. 30 s showing the oxidation of DBT. The inset is the change in absorbance at 285 nm vs time. Reaction conditions: 100 μM DBT, 1.0 μM $FeDCBF_2$, 10 mM H_2O_2, $T = 50$ °C, pH 8 (0.01 M phosphate), 7:3 H_2O:*t*-BuOH.

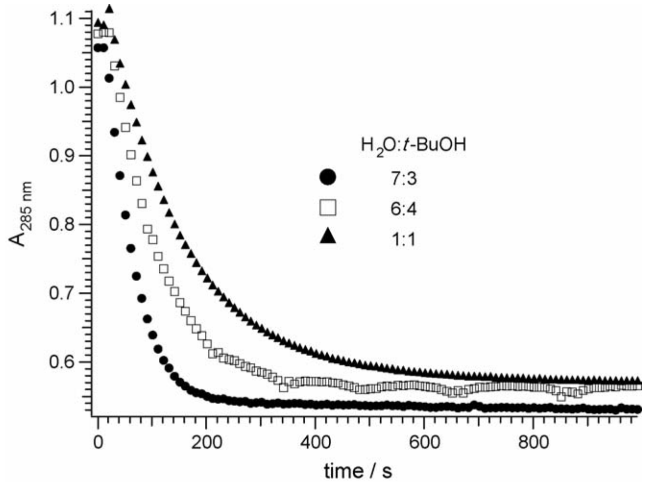

Fig. 3. Comparison of the oxidation rates of DBT, monitored by UV–vis spectroscopy at 285 nm, as a function of the H_2O:*t*-BuOH ratio. Reaction conditions: 100 μM DBT, 1.0 μM $FeDCBF_2$, 10 mM H_2O_2, $T = 50$ °C, pH 8 (0.01 M phosphate).

fastest reaction. Fig. 3 shows the decrease in absorbance at 285 nm for DBT as a function of the H_2O:*t*-BuOH ratio. An 8:2 v/v H_2O:*t*-BuOH ratio resulted in precipitation of the DBT. Strong solvent effects have been observed previously for the oxidation of sulfur compounds in organic matrices [54]. It was also found that when either methanol or ethanol was used as a co-solvent, oxidations were always slower than with *t*-BuOH as co-solvent. This behavior probably reflects *t*-BuOH as having the best balance between hydrophobic and hydrophilic properties with respect to the natures of the catalyst, H_2O_2 and DBT-derivative.

The oxidation reaction was also found to be sensitive to pH. In water, $FeDCBF_2$ activates H_2O_2 more rapidly at pH 10 than at pH 8. However, it was found that the oxidation of DBT was slower at the higher pH at all H_2O:*t*-BuOH ratios investigated. The times for 50% conversion of DBT at pH values between 7 and 11 are shown in Fig. 4. The data indicate a strong dependence on the solution pH. The increase in conversion rate from pH 7 to 8 was expected, but the decrease in rate with increasing pH was not. It is possible that the peroxide activation rate by $FeDCBF_2$ may be exhibiting different pH dependence in the mixed solvent system compared to water alone. Investigations are ongoing with substrates other than DBT to determine if this is the case. Alternatively, the caustic nature of the solvent system could alter the solvation properties of the DBT such that its oxidation reaction slows.

All three DBT compounds investigated showed the same type of reactivity toward $FeDCBF_2$ and H_2O_2 as monitored by UV–vis spectroscopy. The relative rates of oxidation of DBT, 4-MDBT, and 4,6-DMDBT are shown in Fig. 5 as changes in the absorbance at 285 nm versus time ($\varepsilon_{285\ \mathrm{nm}}$ for DBT is greater than for 4-MDBT and 4,6-DMDBT which accounts for the higher starting $A_{285\ \mathrm{nm}}$ seen in Fig. 5, see Section 2.2). Analysis of the data for the time to 50% conversion reveals the reactivity to be in the order DBT > 4-MDBT > 4,6-DMDBT (DBT 50 s, 4-MDBT 80 s, and 4,6-DMDBT 190 s). Initial rates for the DBT-derivatives were determined to be DBT 5.2×10^{-7} M s^{-1}, 4-MDBT 3.6×10^{-7} M s^{-1}, and 4,6-DMDBT 9.2×10^{-8} M s^{-1} under the following conditions: DBT-derivative 0.1 mM, 1 μM $FeDCBF_2$, 10 mM H_2O_2 and pH 8 (0.01 M phosphate). This trend in reactivity is opposite the generally observed behavior for oxidation of DBT-derivatives where the greater electron density of the sulfur-center of 4,6-DMDBT makes this derivative more susceptible to oxidation [55]. The reactivity pattern is however, in the same order as that observed for HDS of DBT-derivatives as well as for some metal catalyzed oxidation reactions [26,32]. In the HDS process, it has been shown that methyl groups in the 4- and 6-positions of DBT hinder approach of the DBT toward the metal surface [56–59]. It is possible that a similar situation is occurring in the present case where the reactive intermediate generated from reaction of $FeDCBF_2$ with H_2O_2 interacts directly with the DBT in order to transfer one or both of the oxygen atoms to the sulfur center.

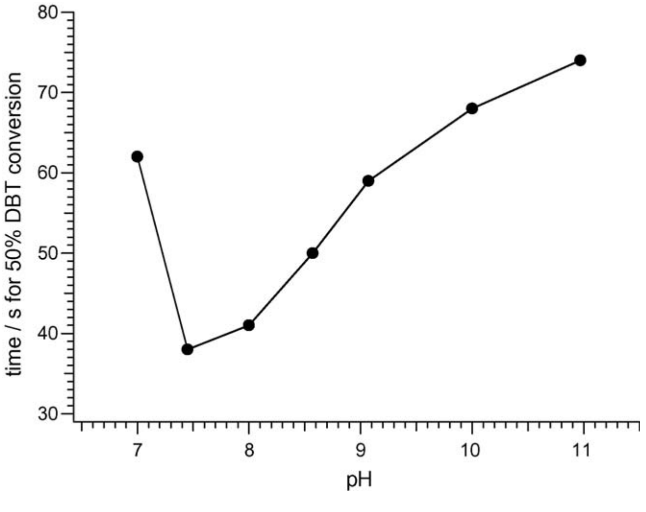

Fig. 4. Time for 50% conversion of DBT as a function of pH. Reaction conditions: 100 μM DBT, 1.0 μM $FeDCBF_2$, 10 mM H_2O_2, $T = 50$ °C (0.01 M phosphate), 7:3 H_2O:*t*-BuOH.

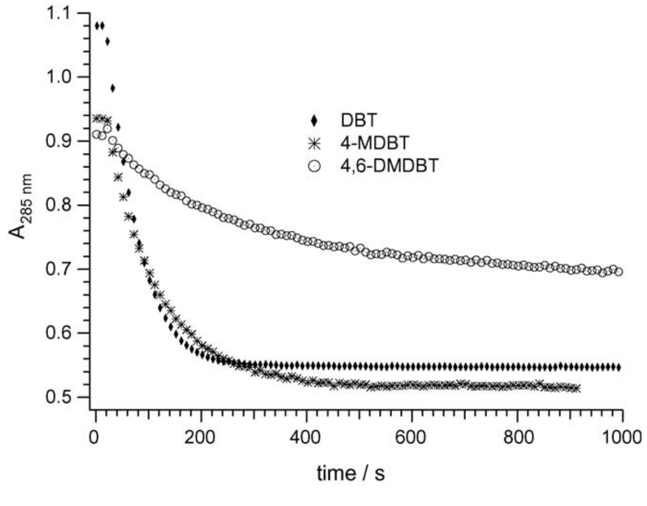

Fig. 5. Comparison of the oxidation rates of DBT, 4-MDBT, and 4,6-DMDBT as monitored by UV–vis spectroscopy at 285 nm. Reaction conditions: 100 μM DBT-derivative, 1.0 μM $FeDCBF_2$, 10 mM H_2O_2, $T = 50$ °C, pH 8 (0.01 M phosphate), 7:3 H_2O:*t*-BuOH.

In order to fully characterize the reaction products, sufficient quantities of the oxidized products were prepared and isolated for analysis by a variety of analytical techniques. A typical preparative scale reaction involved adding $FeDCBF_2$ and H_2O_2 to a solution of the appropriate DBT derivative in the H_2O/*t*-BuOH mixture followed by stirring for 30 min at 50° C. After removal of the *t*-BuOH *in vacuo* and extraction of the water layer with diethyl ether, GC–MS analysis of the diethyl ether extract showed quantitative conversion of the dibenzothiophene to its corresponding sulfone. The extraction efficiency of diethyl ether for the DBT-derivatives and their corresponding sulfones from water was independently determined to be >99%. None of the possible sulfoxide products were detected by GC–MS or GC–AED. In the case of 4,6-DMDBT, no other sulfur containing species were detected by GC–AED or GC–MS so the potentially oxidatively vulnerable CH_3-groups were not attacked by the system [28]. Combustion analysis, IR and NMR spectroscopy were also consistent with exclusive formation of the corresponding DBT-sulfone.

The oxidation reaction was performed using a 1:2 DBT:H_2O_2 stoichiometry. After the extraction procedure described above, it was determined by GC–MS that greater than 99% of the DBT was oxidized within 1 h and the majority (>80%) of the product was the sulfone, Fig. 6. The presence of the DBT-sulfoxide in this mixture clearly shows the stepwise conversion of the DBT to its sulfone. The highly efficient use of the peroxide in this transformation is a characteristic of the Fe-TAML® catalysts in a number of fields of use and it is consistent with a low catalase type reactivity under these reaction conditions. Quantitative oxidations of 4-MDBT and 4,6-DMDBT to their corresponding sulfones also were observed. We are in the process of determining if the catalase activity known for Fe-TAML® catalysts is suppressed in the mixed solvent system used here.

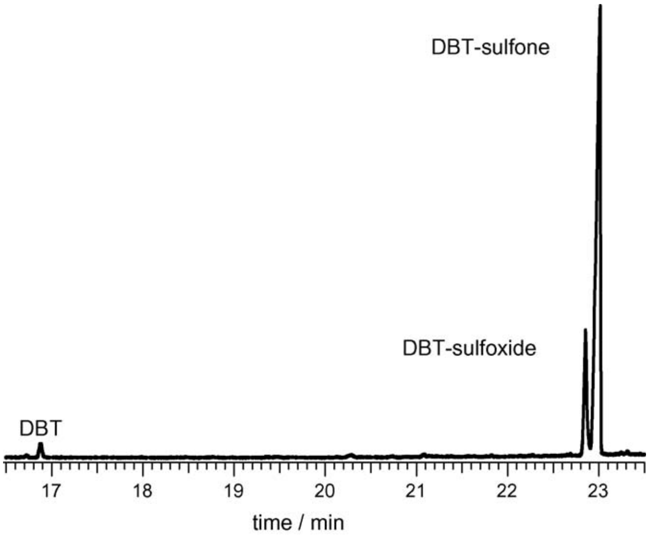

Fig. 6. GC trace (MS detection) of the products from the reaction of DBT with two molar equivalents of H_2O_2. Reaction conditions: 3 mM DBT, 3.0 μM $FeDCBF_2$, 6 mM H_2O_2, $T = 50$ °C, pH 8 (0.01 M phosphate), 7:3 H_2O:*t*-BuOH, 1 h.

3.2. Two-liquid phase reactions

Two-liquid phase systems employing H_2O_2 in catalytic and non-catalytic reactions have been used to oxidize DBT derivatives [26,27,60]. Schemes have been devised wherein the DBT is oxidized in the aqueous phase by using a co-solvent to extract it from the hydrocarbon into the aqueous layer or by using phase transfer agents where the oxidation takes place in the hydrocarbon. In this two-liquid phase approach, the chemistry and analysis procedures are substantially more complicated than in homogeneous solution, because the concentrations of the various components within the two phases can be different. For example, when CH_3CN is used as the co-solvent, the partitioning of DBT into the aqueous phase is substantially greater than that for 4,6-DMDBT [61]. This results in a higher overall oxidation rate for DBT even though 4,6-DMDBT often is easier to oxidize under homogeneous reaction conditions [55,62,63]. Given this complexity, we did not attempt to determine relative oxidation rates for the DBT-derivatives under two-phase conditions nor did we seek to compare the relative rates of reaction between homogeneous and two-phase reaction conditions. Rather the objective of the study under two-phase conditions was to ascertain how to achieve and maximize reactivity of the current Fe-TAML® catalyst under conditions that were not totally aqueous in nature. This information can then be used to design new Fe-TAML® catalysts that are more suited to the two-phase conditions.

The two-liquid phase reactions studied here, involved having the DBT or DBT-derivative dissolved in decane, an often-employed model for diesel, and the Fe-TAML® catalyst dissolved in the 7:3 H_2O/*t*-BuOH mixture (0.01 M phosphate buffer adjusted to pH 8). Unlike the "on-water" reactions, [53,64], there does not appear to be reaction without the *t*-BuOH. Prior to the reaction, the aqueous phase was analyzed by GC–MS and GC–FPD for the presence of DBT-derivatives (diethyl ether extraction) and the hydrocarbon phase for the presence of $FeDCBF_2$ (ESI–MS). Within the detection limits of these techniques, neither reaction component had been extracted out of the phase in which it was initially prepared at room temperature (DBT, log $P = 4.07$, ChemDraw [65,66]). *t*-BuOH was present in both phases as determined by ^1H NMR spectroscopy and GC–MS. However, the majority of the *t*-BuOH was in the aqueous layer. Despite not observing the DBT in the aqueous phase, we suspect that either the *t*-BuOH acts as an inverse phase transfer agent or it changes interfacial properties, or both.

Experimentally, the two-liquid phase system was developed by combining a 7:3 H_2O:*t*-BuOH mixture (pH 8) with the DBT-derivative dissolved in decane, heating with vigorous stirring to 50 °C, and then adding $FeDCBF_2$ and H_2O_2 in six equal portions over 3 h (1.62×10^{-7} mol $FeDCBF_2$ total and 1.62×10^{-2} mol H_2O_2 total). It was found that longer reaction times were needed for complete reaction under two-phase conditions compared to single-phase conditions probably because of partitioning effects. In all cases, the $FeDCBF_2$:DBT-derivative:H_2O_2 mole ratio of the mixture was approximately

1:100:10,000. The Fe-TAML® catalyst/H_2O_2 addition methodology was used to diminish the possibility of H_2O_2 disproportionation since DBT oxidation was slower under the biphasic conditions than in homogeneous solution. After the reactions were complete, analysis of both phases by GC–MS and GC–FPD (aqueous phase extracted with diethyl ether after *t*-BuOH removal) showed no DBT or DBT oxidation products in the hydrocarbon phase and only the DBT-sulfone was detected in the aqueous phase.

In order to ascertain the relative efficiency of peroxide usage for the oxidation process, an experiment was performed using a 1:100 mole ratio of DBT:H_2O_2 and then the residual peroxide was determined [47]. It was found that approximately 6% of the H_2O_2 was consumed whereas 2% was needed for complete conversion of DBT to the DBT-sulfone. This result indicates that H_2O_2 disproportionation was not significantly competitive, a result that is consistent with the efficient use of H_2O_2 in homogeneous solution for DBT oxidation.

The selectivity of the sulfur oxidation was probed by preparing a mixture of DBT, fluorene, and toluene in *n*-decane and reacting this mixture with $FeDCBF_2$ and H_2O_2 ($FeDCBF_2$:DBT:fluorene:toluene:H_2O_2 mole ratio was approximately 1:100:130:17,400:10,000). Toluene is one of the common aromatics in diesel fuel. Its oxidation would provide an indication that fuel degradation would occur with the Fe-TAML®/H_2O_2 treatment. Fluorene is structurally similar to DBT. More significantly, the weak C–H bond at the methylene position (74 kcal/mol) provides a means for testing if reactive intermediates form that are capable of H-atom abstraction reactions [67,68] under the current reaction conditions. GC–MS and GC–FPD measurements showed nearly complete conversion of the DBT to the DBT-sulfone. GC–MS data indicated that there was a <5% change in fluorene and toluene concentrations. Thus the Fe-TAML® catalyst and H_2O_2 system provides a very selective oxidant for sulfur containing compounds.

The 4-MDBT and 4,6-DMDBT both were completely oxidized and extracted into the aqueous phase using the method described above. This result indicates that despite the higher log *P* for 4,6-DMDBT (5.04 from ChemDraw) compared to DBT, the water/*t*-BuOH mixture was capable of supporting a relatively facile oxidation of all of the DBT-derivatives. No attempts were made to determine the relative rates of reactivity of the three DBT derivatives under the two-liquid phase conditions.

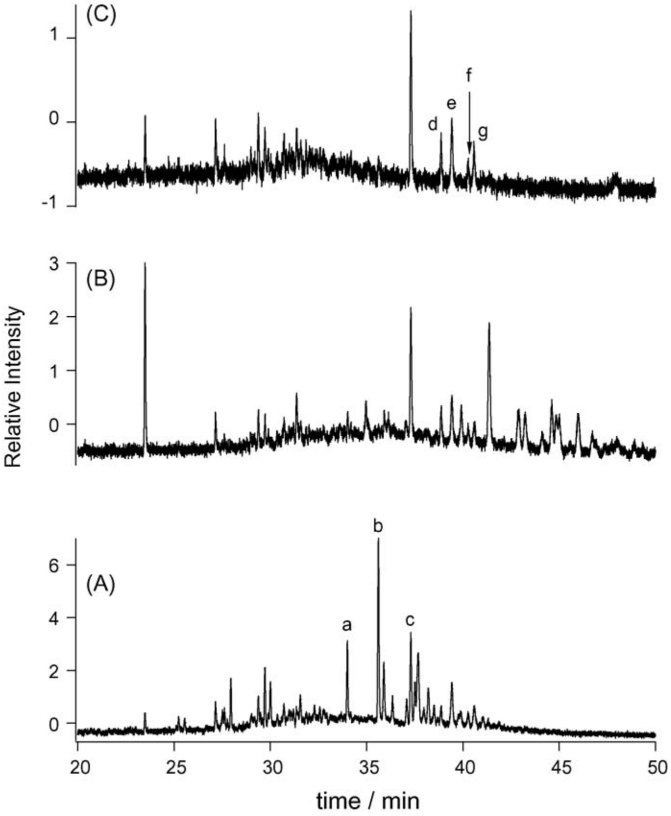

Fig. 7. GC–AED traces of (A) untreated commercial diesel; (B) $FeDCBF_2$/H_2O_2 treated diesel; (C) a sample from B after treatment with silica. The compounds identified are as follows: (a) DBT; (b) 4-MDBT; (c) 4,6-DMDBT; (d) 4-ethyl,6-MDBT; (e) 2,4,6-TMDBT; (f) 1,4,6-TMDBT; (g) 3,4,6-TMDBT. Reaction conditions: 1 mL diesel, 1.1×10^{-7} mol $FeDCBF_2$, 1.1×10^{-3} mol H_2O_2, $T = 50$ °C, 3 mL pH 8 (0.01 M phosphate), 7:3 H_2O:*t*-BuOH, $t = 3$ h.

3.3. Diesel fuel

A sample of diesel fuel from a local filling-station was examined for the $FeDCBF_2$/H_2O_2 oxidative desulfurization process. The GC–AED trace for the starting diesel fuel sample is shown in Fig. 7a. The trace is comparable to others in the literature in terms of the classes of sulfur compounds observed and their relative retention times [69]. The lower boiling alkyl-benzothiophene derivatives appear at earlier retention times than their dibenzothiophene counterparts. Many of the major and minor sulfur species in diesel fuels have been identified by others. We have directly identified the three DBT compounds used here by spiking them into the diesel fuel sample and these correspond to the peaks marked on the trace. Other substituted DBT compounds were then identified by comparison to data available in the literature [69]. The total sulfur in the sample was determined to be 348 mg/L (420 ppm S) by the ASTM D 5453 method and 393 ± 5 ppm by a rapid GC–AED method [48]. The close correspondence between the ASTM and the GC–AED methods for this fuel is consistent with previous results and we relied principally on the GC–AED method for quantification of sulfur from reactions with $FeDCBF_2$ and H_2O_2.

The reaction conditions and $FeDCBF_2$/H_2O_2 addition methodology used in the *n*-decane model system described above were used for treatment of the diesel sample. The GC–AED trace of the diesel after treatment with $FeDCBF_2$ (1.1×10^{-7} mol) and H_2O_2 is shown in Fig. 7b. A total sulfur analysis by the rapid GC–AED method gave 229 ± 4 ppm. The prominent features in the trace are the clear reduction in intensities of DBT and 4-MDBT peaks, the decrease in the total number of alkyl-benzothiophene compounds, and the appearance of new sulfur containing species at longer retention times than in the untreated sample. The species at longer retention times are consistent with oxidized sulfur compounds.

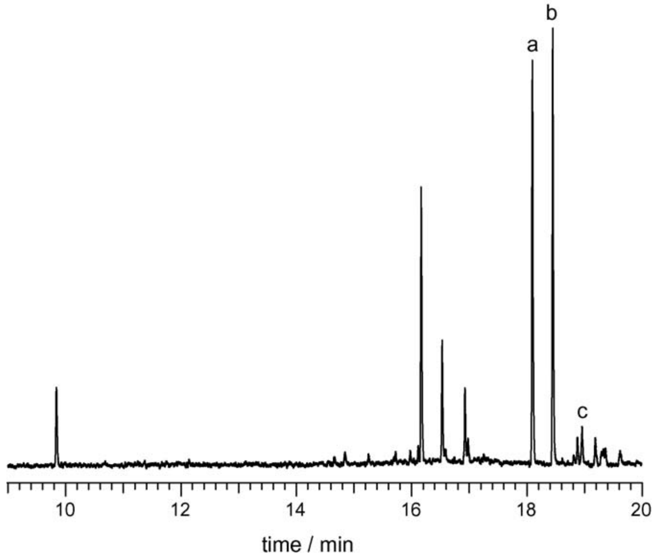

Fig. 8. GC–FPD of the aqueous layer (diethyl ether extract) after treatment of diesel with $FeDCBF_2$ and H_2O_2. The compounds identified are as follows: (a) DBT-sulfone; (b) 4-MDBT-sulfone; (c) 4,6-DMDBT-sulfone. Reaction conditions: 1 mL diesel, 1.1×10^{-7} mol $FeDCBF_2$, 1.1×10^{-3} mol H_2O_2, $T = 50$ °C, 3 mL pH 8 (0.01 M phosphate), 7:3 H_2O:*t*-BuOH, $t = 3$ h.

The removal of the benzothiophene compounds is noteworthy because they are harder to oxidize than the dibenzothiophene compounds [70]. Examination of the aqueous phase by GC–FPD shows clear evidence for the sulfone products of DBT, 4-MDBT and a small peak that likely corresponds to the 4,6-DMDBT sulfone, Fig. 8. The additional peaks have not been identified, but they must correspond to oxidized sulfur compounds because prior to treatment with $FeDCBF_2$ and H_2O_2, there are no sulfur species detected in the aqueous phase.

In other examples of ODS technologies, the removal of the oxidized sulfur species from treated diesel has been accomplished by adsorption either onto alumina or silica [29]. This type of treatment does not substantially change the sulfur content or the distribution of sulfur species in the diesel itself. This was confirmed for the diesel sample used in this study as the total sulfur content of an untreated sample of diesel passed down a silica column was found to be 379 ± 8 ppm, a decrease of about 15 ppm from the starting sample. The GC-AED trace of a sample of the $FeDCBF_2/H_2O_2$ treated diesel fuel that had been passed through a silica column is shown in Fig. 7c. The total sulfur in this sample was found to be 102 ± 2 ppm. Comparison of this trace to Fig. 7b, shows that all of the peaks at higher retention times that resulted from the $FeDCBF_2/H_2O_2$ treatment were removed by the silica column. In addition, the broad peak underlying the chromatogram from 25 min to 45 min is reduced overall and in particular the higher boiling species are removed. This broad peak is a composite of many unidentified sulfur compounds, which are present at low concentrations. Finally, the clearly identifiable alkyl-dibenzothiophenes are 4,6-DMDBT; 4-ethyl,6-MDBT; 2,4,6-TMDBT; 1,4,6-TMDBT and 3,4,6-TMDBT and they are lower in concentration than in the starting sample. Thus, overall the treatment of diesel with $FeDCBF_2$ and H_2O_2 resulted in a decrease in sulfur content of approximately 75%.

The 75% removal level of sulfur compounds appears to be the maximum attainable using the current methodology as a second treatment of treated diesel with the Fe-TAML® catalyst and H_2O_2 resulted in no further change in the sulfur level of the fuel. Since 4,6-DMDBT can be oxidized completely in the *n*-decane model system, it is likely that other hydrocarbon components in the diesel fuel are significantly better at solvating this species, and the other higher alkylated dibenzothiophene congeners, such that their reactivity becomes vanishingly small in the water/*t*-BuOH mixture. In support of this statement, we have performed experiments using the diesel fuel intentionally spiked with higher concentrations of DBT and it was completely removed from the diesel fuel. Thus, the solubility and the accessibility of the substrate to the Fe-TAML®/H_2O_2 derived reactive intermediate is an important issue for the two-phase oxidation process. This disparity in reactivity between model systems using simple hydrocarbons to dissolve DBT or it derivatives and diesel samples has been observed in other desulfurization approaches [54]. It is possible that other co-solvents can be used to complete the oxidation process and these are currently under investigation.

4. Conclusions

The Fe-TAML® catalyst and H_2O_2 combination can be very effective at oxidizing dibenzothiophene species under a wide variety of homogeneous and two-liquid phase reaction conditions. The principle advantages of the Fe-TAML® catalyst based approach over other ODS methods are the mild reaction conditions and small quantities of catalyst and H_2O_2 that are needed to achieve substantial desulfurization. In addition, since the oxidation process occurs in the aqueous phase, the diesel fuel does not become contaminated with the catalyst and the oxidant concentration in the diesel should be low. This is a significant consideration, as oxidant cannot be left in the fuel for reasons related to long-term storage stability. Thus, the Fe-TAML®/H_2O_2 system shows considerable promise for providing a technology to meet future needs for ultra-low sulfur diesel. Furthermore, the simplicity of the technology should allow it to be transferred to desulfurization of gasoline and jet fuel where the majority of the sulfur compounds remaining after refinement are alkyl-benzothiophenes rather than alkyl-dibenzothiophenes.

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