Oxidative Desulfurization of Diesel Oil with Hydrogen Peroxide in the Presence of Acid Catalyst in Diesel Oil/Acetic Acid Biphasic System

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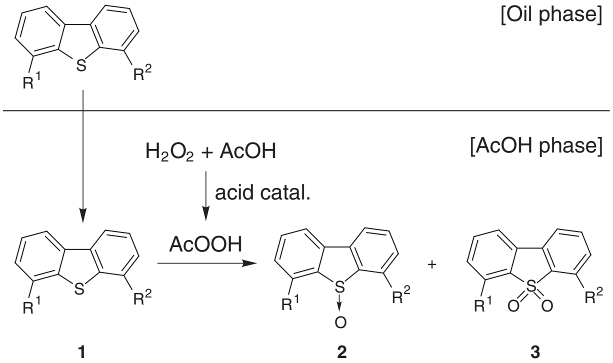
Dibenzothiophenes are oxidized effectively with H_2O_2 in the presence of acid catalysts in a tetradecane/AcOH biphasic system. The oxidation proceeds in the AcOH phase and most of the oxidation products stay there, resulting in the successive removal of the dibenzothiophenes from the tetradecane phase. Using this biphasic oxidation system can effectively reduce the sulfur content in diesel oil.

Air pollution due to diesel exhaust gas has been a major concern of the public. It is necessary to decrease NO_x and particulates in the exhaust gas in order to reduce the sulfur content in diesel oil since the sulfur causes the damage to exhaust after-treatment devices (e.g., exhaust catalysts and diesel particulate filters). Thus new regulations in Japan and Europe will limit the sulfur content to 10 ppm maximum from 2007 and 2009, respectively. The US EPA will also regulate the sulfur in on-road diesel oil to below 15 ppm from mid-2006. The development of a novel desulfurization process, therefore, has been expected to remove alkylated dibenzothiophenes from diesel oil since they are resistant to conventional hydrodesulfurization because of their steric hindrance.[1,2] Oxidative desulfurization would be the most likely candidate since the dibenzothiophenes in fuel oil have been effectively oxidized by using H_2O_2–formic acid,[3] H_2O_2–Ti-containing molecular sieve,[4] H_2O_2–tungstophosphoric acid (TPA)–ultrasonication,[5] *t*-BuOOH-Mo/Al_2O_3,[6] and O_2–Co salts–aldehydes,[7] and the oxidation products would be easily removed from the oil by extraction and adsorption. We have demonstrated that dibenzothiophenes are effectively oxidized with H_2O_2 catalyzed by TPA in an organic biphasic system using AcOH as a polar solvent and that this oxidation system is useful for the oxidative desulfurization of diesel oil.[8] We have also observed that even without TPA dibenzothiophenes are slowly oxidized by peracetic acid (AcOOH) formed from H_2O_2 and AcOH. Recently, the addition of a strong acid, e.g. H_2SO_4, in the biphasic system has been found to accelerate the oxidation of dibenzothiophenes. Here we report a new oil/AcOH biphasic oxidation system of dibenzothiophenes using H_2O_2 and strong acids as an oxidant and acid catalysts, respectively. This biphasic oxidation was applied to the oxidative desulfurization of diesel oil.



a, $R^1 = R^2 = H$; **b**, $R^1 = R^2 = Me$

Scheme 1.

Figure 1a shows the oxidation of dibenzothiophene (**1a**) and 4,6-dimethyldibenzothiophene (**1b**) with H_2O_2 in AcOH in the presence or absence of acid catalysts. For a typical run, 50 mL of 5 mM **1a** in AcOH containing 10 mM H_2SO_4 (1 mequiv.) was heated to 50 °C with stirring, and then 0.5 mL of 35 wt % H_2O_2 (5.8 mmol) aqueous solution was added. Concentrations of the substrate and the oxidation products were determined by HPLC as reported previously.[9] Major products are the corresponding sulfoxides and sulfones (Scheme 1). The addition of H_2SO_4 promotes the oxidations of **1a** and **1b**, since the rate of AcOOH formation can be accelerated by the addition of a strong acid.[10] In addition, **1b** underwent faster oxidation than **1a** under the same conditions, suggesting that **1b** would be more oxidizable by AcOOH than **1a**. The oxidation of **1b** by using H_2O_2–formic acid[3] and H_2O_2–trifluoroacetic acid[11] has been reported to proceed faster than that of **1a**. The oxidation rates increase with increasing reaction temperature and H_2SO_4 concentration, possibly owing to the increase of the rates of AcOOH formation. Furthermore, a strong acid cation exchange resin, Amberlyst 15DRY (Organo Co., Ltd., 3.0 meq/g-dry resin), is applicable as an acid catalyst, although the catalytic activity is lower than that of H_2SO_4 under similar conditions (Figure 1a). Ion exchange resins also promote the formation of AcOOH.[12]

Tetradecane solutions of **1a** and **1b** were used as model diesel oils. Tetradecane and AcOH are immiscible under the

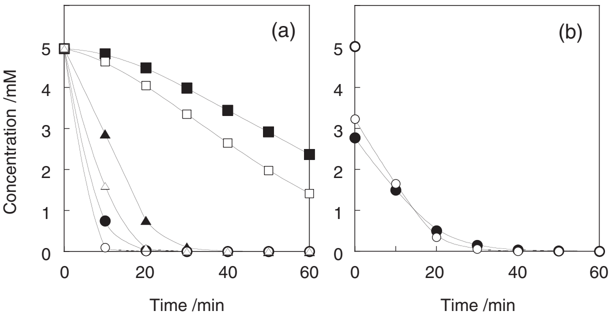


Figure 1. The disappearance of **1a** (solid) or **1b** (open) during the oxidation with H_2O_2 in the presence of an acid catalyst at 50 °C in (a) AcOH and (b) tetradecane in tetradecane/AcOH biphasic system. Acid catalyst: ●, H_2SO_4; ▲, Amberlyst 15DRY; ■, none.

conditions employed; they form a biphasic system. The oxidation of **1a** or **1b** in a tetradecane/AcOH biphasic system was done as follows: 50 mL of 5 mM **1a** in tetradecane was mixed with 50 mL of AcOH containing 10 mM H_2SO_4 (1 mequiv.) This biphasic mixture was heated to 50 °C with stirring, and then 0.5 mL of 35 wt % H_2O_2 (5.8 mmol) aqueous solution was added. Concentration of **1a** in tetradecane was similarly determined by HPLC. Figure 1b shows that **1a** and **1b** are also consumed by the oxidation in this biphasic system; 45% of **1a** or 34% of **1b** is extracted from the tetradecane to the AcOH and the oxidation of **1a** or **1b** proceeds in the latter, resulting in the successive removal of **1a** or **1b** from the tetradecane phase (Scheme 1). This oxidation mechanism is similar to those in other biphasic oxidation systems.[8,13] Further, most of the oxidation products resides in the AcOH phase owing to their polarity (e.g., the oxidation of **1b** for 1h gave **2b** and **3b** in 18 and 82% yield, respectively, and 97% of **2b** and 92% of **3b** resided in the AcOH phase), indicating that most sulfur compounds can be removed from model diesel oils only by separation of the model oils and the AcOH after oxidation.

This oxidation treatment was applied to diesel oil containing 333 ppm sulfur as follows: 50 mL of diesel oil was mixed with 50 mL of AcOH containing 20 mM H_2SO_4 or 667 mg of Amberlyst 15DRY (each 2 mequiv.) This biphasic mixture was heated to 60 °C with stirring, and then 0.5 mL of 35 wt % H_2O_2 (5.8 mmol) aqueous solution was added. After 1 h of oxidation, the oil phase was separated, washed with water, and dehydrated with $CaCl_2$. Then its sulfur content was measured using a Horiba SLFA-UV21 analyzer. It is insufficient for desulfurization of diesel oil to simply extract sulfur compounds with AcOH (entry 4, Table 1). The oxidation with H_2O_2 in the presence of H_2SO_4 and Amberlyst 15DRY, however, can reduce the sulfur contents to 63 and 64 ppm, respectively (entries 1 and 2, Table 1). The complete oxidation of the sulfur compounds has been confirmed by using sulfur-specific GC analysis as reported previously:[8] the sulfur compounds in an unoxidized oil disappeared owing to the oxidation and they were replaced by new sulfur-containing products having higher boiling points in an oxidized oil (Figure 2). Thus the sulfur contents can be decreased to below 10 ppm by extraction with an equal volume of MeOH two times. The oxidation without acid catalysts also lowers the sulfur content to 85 ppm (entry 3, Table 1), but the oxidation of the sulfur compounds is incomplete since unoxidized sulfur compounds remain (Figure 2). The sulfur content is consequently lowered only to about 40 ppm by the same extraction mentioned above. These results have indicated that the addition of acid catalysts is effective for the complete oxidation of sulfur compounds in diesel oils and that the complete oxidation is essential for an oxidative desulfurization. Furthermore the availability of a heterogeneous acid catalyst would provide some advantages, e.g., ease of recovery.

Table 1. Oxidative desulfurization of diesel oil[a] for 1 h at 50 °C

Entry	35%H_2O_2 / mL	Acid Catalyst	Sulfur Content / ppm		
			After Oxidation	After Extraction with MeOH	
				One time	Two times
1	0.5	H_2SO_4	63	18	6
2	0.5	Amberlyst 15DRY	64	16	6
3	0.5	—	85	55	36
4	0	—	284	267	244

[a] Initial sulfur content of diesel oil was 333 ppm.

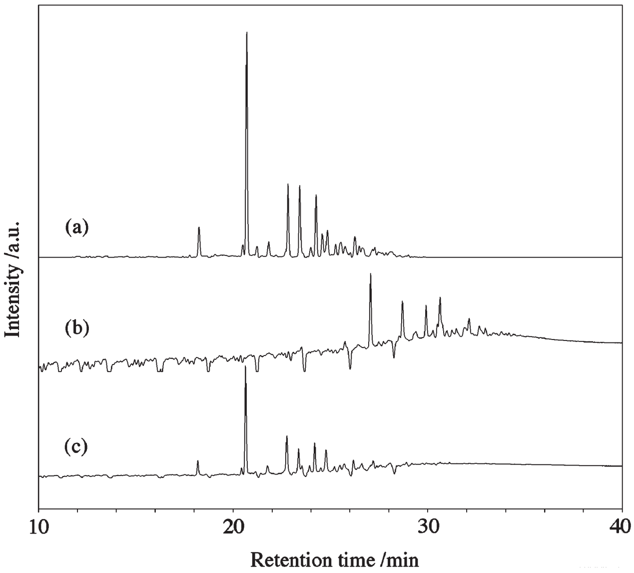


Figure 2. Sulfur-specific GC of (a) unoxidized, (b) oxidized in the presence of H_2SO_4, and (c) oxidized diesel oil in the absence of H_2SO_4.

In conclusion, dibenzothiophenes are effectively oxidized with H_2O_2 in the presence of acid catalysts in an oil/AcOH biphasic system. This oxidation system is useful for the oxidative desulfurization of diesel oil.

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