Tungstophosphoric Acid-catalyzed Oxidative Desulfurization of Light Oil with Hydrogen Peroxide in a Light Oil/Acetic Acid Biphasic System

Kazumasa Yazu,* Takeshi Furuya, Keiji Miki, and Koji Ukegawa
Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8569

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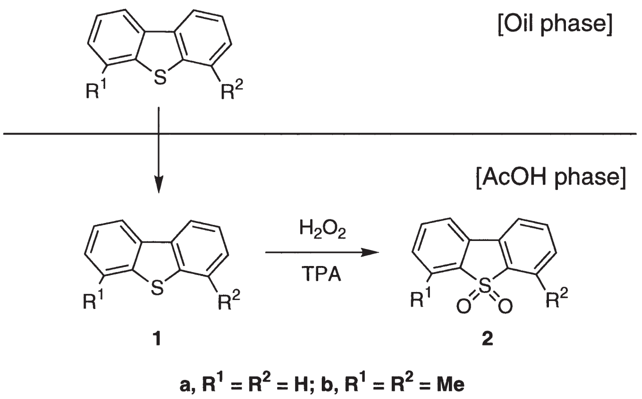
Dibenzothiophenes were oxidized effectively with H_2O_2 in the presence of 12-tungstophosphoric acid in the tetradecane/AcOH biphasic system to give their corresponding sulfones as the major products. The oxidation proceeded in the AcOH phase and most of the sulfones distributed there, resulting in the successive removal of the sulfur compounds from the tetradecane phase. This biphasic oxidation system can effectively reduce the sulfur content in light oil.

In order to decrease NO_x and particulates in diesel exhaust emissions it is necessary to reduce the sulfur content in light oil, and hence new legislation in Japan and Europe will limit the sulfur content to 50 ppm maximum by 2005. The development of a new desulfurization process has been expected to remove alkylated dibenzothiophenes from light oil since they are resistant to hydrodesulfurization because of their steric hindrance.[1,2] We have demonstrated that the sulfur content in light oil can be effectively reduced by oxidative desulfurization in the light oil/MeCN biphasic system using H_2O_2 and 12-tungstophosphoric acid (TPA) as oxidant and catalyst, respectively.[3] We have found that AcOH is applicable to this biphasic oxidation system instead of MeCN. AcOH would be a more desirable solvent than MeCN since it is nitrogen-free. Here we report a new biphasic oxidative desulfurization of light oil using AcOH as a polar solvent. Dibenzothiophenes were oxidized to the corresponding sulfones with H_2O_2 and TPA in the tetradecane/AcOH biphasic system. Furthermore, sulfur content in light oil was efficiently reduced by this biphasic oxidation system.

Dibenzothiophene (**1a**) and 4,6-dimethyldibenzothiophene (**1b**), one of the most unreactive sulfur compounds during hydrodesulfurization, were rapidly oxidized by H_2O_2 in the presence of TPA in AcOH to give the corresponding sulfones as the major products (Scheme 1). Conversion of the substrate and yields of the oxidation products were determined by HPLC as reported previously.[4] The rates of oxidation both in AcOH and in MeCN were pseudo-first-order in substrate concentration, C (Figure 1). The rate constants, k, were obtained from the equation, $\ln(C/C_0) = -kt$, where C_0 is the initial concentration of a substrate. The k values for **1a** and **1b** were almost identical in each solvent, indicating **1a** and **1b** have essentially the same oxidizability in the oxidation by H_2O_2 with TPA. For instance, those for the oxidation of **1a** (0.25 mmol) and **1b** (0.25 mmol) by 35 wt % H_2O_2 aqueous solution (0.5 mL, 5.8 mmol H_2O_2) with TPA (0.25 μmol) at 40 °C in AcOH (50 mL) were 2.2 and $2.3 \times 10^{-3}\,s^{-1}$, respectively, and those in MeCN (50 mL) were 4.7 and $5.4 \times 10^{-5}\,s^{-1}$, respectively; the oxidizabilities of **1a** and **1b** in AcOH were about 50-fold compared with those in MeCN. Under similar conditions, both substrates were completely consumed within 10 min with TPA (2.5 μmol) in AcOH. They were also oxidized without TPA due to the formation of peracetic acid by the reaction of AcOH with H_2O_2. In this case **1b** was oxidized faster than **1a** in a similar manner, as reported in the oxidation by H_2O_2 and trifluoroacetic acid.[5] The oxidation rates of **1a** and **1b**, however, were much smaller than those in TPA-catalyzed oxidations; the extent of conversion of **1a** and **1b** after 10 min oxidation was only 1 and 3%, respectively. These results indicated that the oxidation by peracetic acid should have little contribution to the overall oxidation under our experimental conditions.



Scheme 1.

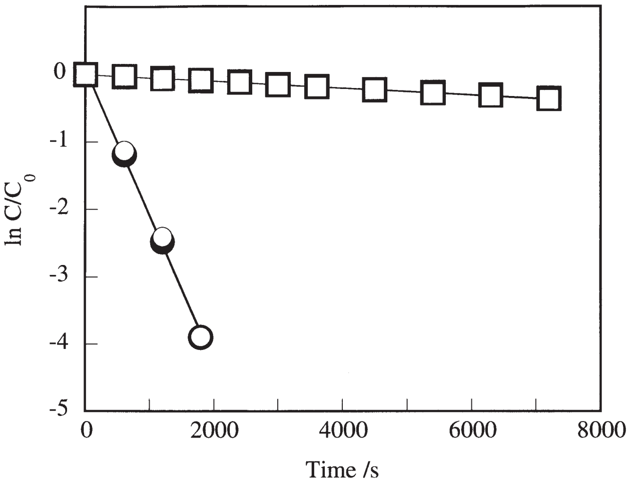


Figure 1. Pseudo-first-order plot for the oxidation of **1a** (solid) or **1b** (open) with H_2O_2 and TPA at 40 °C in AcOH or MeCN. ●, ○: in AcOH; ■, □: in MeCN.

AcOH and tetradecane form a biphasic system since they are immiscible. The oxidation of **1a** and **1b** with H_2O_2 and TPA also proceeded in the tetradecane/AcOH biphasic system. In a typical run, TPA (2.5 μmol) was dissolved in 35 wt % H_2O_2

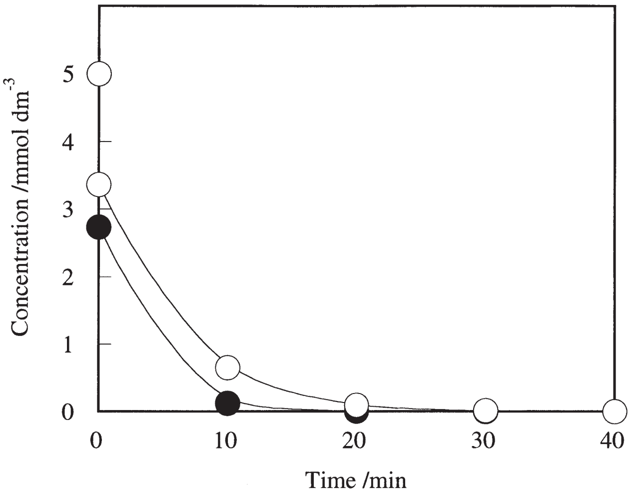


Figure 2. The disappearance of **1a** (●) or **1b** (○) in tetradecane during the oxidation with H_2O_2 and TPA at 40 °C in tetradecane/AcOH biphasic system.

aqueous solution (0.5 mL, 5.8 mmol H_2O_2) and mixed with AcOH (50 mL). Then, tetradecane solution (50 mL) of **1a** (0.25 mmol) was added and this biphasic mixture was heated to 40 °C with stirring. Concentration of **1a** in tetradecane was determined by HPLC. Figure 2 shows that **1a** and **1b** were smoothly removed from tetradecane phase by the oxidation. At a reaction time of zero, 45% of **1a** or 34% of **1b** was extracted from tetradecane with AcOH, and the oxidation proceeded in AcOH (Scheme 1) in the same way as in the biphasic one using MeCN.[3] Most oxidation products, **2a** (97%) and **2b** (92%), distributed in the AcOH phase, resulting in the successive removal of the sulfur compounds from the tetradecane phase. Accordingly, most of the oxidized sulfur compounds can be eliminated from tetradecane only by separating the two phases. In the tetradecane/MeCN system, 52% of **1a** or 31% of **1b** distributed in MeCN; the extractability of **1b** with AcOH is a little higher than that with MeCN, in contrast to that of **1a**. The rates of removal of **1a** and **1b** in the tetradecane/AcOH system were larger than those in the tetradecane/MeCN one as expected; e.g., **1b** was completely consumed within 40 min in the former (Figure 2), while the conversion was incomplete (ca. 57%) after 1 h oxidation in the latter. These results suggested that AcOH would be a more favorable polar solvent than MeCN.

This oxidation process was applied to light oil containing 318 ppm sulfur. Light oil (50 mL) was treated for 1 h at 40 °C in the acetic acid (50 mL) biphasic system with 35 wt % H_2O_2 aqueous solution (0.5 mL, 5.8 mmol H_2O_2) and TPA (2.5 µmol). 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. The sulfur content in the treated oil was effectively reduced to 58 ppm, while that without H_2O_2 and TPA was decreased to only 273 ppm; thus, extraction alone is not sufficient for desulfurization. MeCN extracts aromatics as well as sulfur-containing compounds from light oil in a light oil/MeCN system.[6,7] The light oil used contained 21 vol% aromatics and AcOH also extracted the aromatics in this biphasic system, indicating the need of the recovery of sulfur-free aromatics from the AcOH phase. Figure 3 shows the sulfur-specific GC of untreated and treated light oil. Sulfur-specific GC analysis was carried out using a DB-5MS capillary column (J&W Scientific) on a Shimadzu GC-2010 with a flame photometric detector. The major peaks in the GC of untreated and treated oil were identified as **1b** and **2b**, respectively, by comparison of their retention times. Sulfur compounds in untreated oil disappeared by the oxidation, and they were replaced by new sulfur-containing products having higher boiling points in treated oil; these products should be the oxidized ones of the sulfur compounds in untreated oil. Figure 3 also shows small amounts of oxidized sulfur products remained in treated oil, indicating that additional refining is necessary for further reduction of the sulfur content. For example, the sulfur content in the treated oil decreased to 17 and 2 ppm by extraction with an equal volume of MeOH one and three times, respectively. These results indicated that oxidized sulfur compounds can be readily removed from light oil.

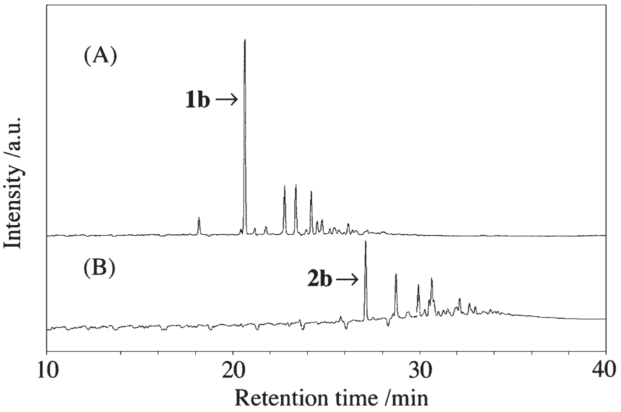


Figure 3. Sulfur-specific GC of (A) untreated and (B) treated light oil. **1b**, 4,6-Dimethyldibenzothiophene; **2b**, 4,6-dimethyldibenzothiophene 5,5-dioxide.

In conclusion, we have demonstrated effective oxidation of dibenzothiophenes with H_2O_2 and TPA in an organic biphasic system using AcOH as a polar solvent. This oxidation system was found to be effective for the oxidative desulfurization of light oil. We are currently undertaking a more detailed investigation to organize an overall process.

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