An aerobic oxidation of dibenzothiophene and related compounds using a catalytic amount of ruthenium chloride in hydrocarbon solvents at 80°C for 20 h gave the corresponding sulfones in almost quantitative yields. The reaction might proceed via autoxidation of solvents to hydroperoxides and the reaction of sulfur compounds with the resulting hydroperoxides.

Keywords: oxidative desulfurization, ruthenium catalyst, molecular oxygen, dibenzothiophene

1. Introduction

From an increase of environmental concern, special interests had been paid for reduction of organosulfur compounds in transportation fuels, because these compounds are converted into sulfur oxide, i.e., SOx, during their combustion. Under these situations, many researchers are investigating developments of highly active catalysts for ultra deep hydrodesulfurization (HDS) of diesel fuels to meet these sulfur regulation. As another method for deep desulfurization, oxidative desulfurization (ODS) was proposed in 1990s [1,2]. In ODS process, oxidation of sulfur compounds is involved as a key step. Therefore, many papers concerning oxidation of sulfides have been published. Usually, peroxides (peracids or hydrogen peroxide) are used for oxidation of organic sulfides to sulfones because reactions proceed rapidly and selectively [2-5]. However, peroxides are somewhat dangerous reagents for a large scale usage and storage. Therefore a development of new oxidation system without peroxides is expected. In this study, the authors had found that dibenzothiophene (DBT) and related compounds could be oxidized to the corresponding sulfones by molecular oxygen in the presence of a ruthenium catalyst in hydrocarbon solvents under relatively mild conditions (eq. 1). The results were reported briefly.

\[ \text{DBT} + \text{O}_2 \xrightarrow{\text{RuCl}_3} \text{DBT-O}_2 \]
yield (Table 1). Other oxidized products from DBT such as a sulfoxide were not detected by GC analysis. In the reaction at 70°C, conversion of DBT was only 20%. Both manganese and cobalt salts were also examined as a catalyst of this reaction. Results are also shown in Table 1. Reactions hardly proceeded at 80°C, but increasing the temperature and extending the reaction duration gave sufficient conversion of DBT. DBT was not consumed in the absence of transition metal salts.

To obtain information concerning reaction mechanism, the reaction mixture was analyzed by GC-MS, the results indicating that several products from autoxidation of solvents such as 1-phenylethyl hydroperoxide (trace, A), 1-phenylethanol (trace, B), and acetonophenone (7%, C) were contained.

Hydrocarbons with labile hydrogens are known to be easily oxidized in the presence of transition metal salts under molecular oxygen to the corresponding hydroperoxides. Based on these results, plausible mechanism was as follows: first step is autoxidation of ethylbenzene to the hydroperoxide A (eq. 2), second step is oxidation of DBT with the peroxide A and/or Ru catalyst to afford the sulfone (DBT-O₂) and alcohol B (eq. 3), and third step is oxidation of B to C with oxygen, the peroxide A, and Ru catalyst (eq. 4).

Further investigation concerning the effects of reaction temperature and nitrogen ligands are now in progress.

4. Conclusion

In this study, we studied the oxidation reaction of dibenzothiophene and related compounds with transition metal catalysts in hydrocarbon solvents and found the following results.

1. Organic sulfides involving DBT could be oxidized in the presence of ruthenium chloride in ethylbenzene under molecular oxygen under relatively mild conditions (80°C and 20 h) and the corresponding sulfones were produced in almost quantitatively.

2. Both manganese and cobalt chlorides could be used instead of ruthenium chloride and both cumene and decalin were also used as reaction solvents.

3. Reaction proceeds via the following steps: autoxidation of solvents to hydroperoxides and the reaction of sulfur compounds with the resulting peroxides.

REFERENCES