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## STUDIES ON AN AEROBIC OXIDATION OF DIBENZOTHIOPHENE AND RELATED COMPOUNDS USING RUTHENIUM CATALYST

### BADANIA UTLENIANIA AEROBOWEGO DIBENZOTIOfENU ORAZ ZWIĄZKÓW POKREWNYCH Z ZASTOSOWANIEM RUTENU JAKO KATALIZATORA

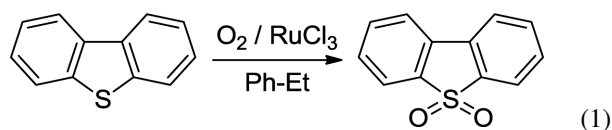
An aerobic oxidation of dibenzothiophene and related compounds using a catalytic amount of ruthenium chloride in hydrocarbon solvents at 80°C for 20 h gave the corresponding sulfones in almost quantitative yields. The reaction might proceed *via* autoxidation of solvents to hydroperoxides and the reaction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

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

Sulfony otrzymano metodą aerobowego utleniania dibenzotiofenu oraz związków pokrewnych w temperaturze 80°C przez 20 godz. Materiały te otrzymano przy użyciu katalitycznej ilości chlorku rutenu w rozpuszczalnikach wodorowęglowych. Można przypuszczać, że reakcja przebiega następująco: rozpuszczalniki samorzutnie się utleniają do wodoronadtlenków, które potem reagują ze związkami siarki.

### 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.* SO<sub>x</sub>, 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.



### 2. Experimental

GC and GC-MS analyses were conducted on a Shimadzu GC-14 (a CBP-1 column and a flame ionization detector) and on a Shimadzu GCMS-QP2010, respectively. All the reagents employed in this study were commercially available and used without further purification.

Typical procedures are as follows: A mixture of dibenzothiophene (184 mg, 1 mmol) and ruthenium chloride (10 mg, 0.05 mmol) in ethylbenzene (20 g) was stirred in an oil bath (typically at 80°C) for 20 h under a static pressure of oxygen. After completion of the reaction, the product mixture was analyzed by a gas chromatograph (GC) and gas chromatograph-mass spectrometer (GC-MS).

### 3. Results and discussion

First, we examined the oxidation of DBT. In this study, we employed three transition metal salts such as chlorides of ruthenium, manganese, and cobalt, because these are known to be popular catalysts for hydrocarbon oxidation. A mixture of DBT and ruthenium in ethylbenzene (EB) was stirred at 80°C for 20 h under molecular oxygen. After the reaction, a product mixture was analyzed by GC and GC-MS, indicating that DBT was consumed completely and the corresponding sulfone (DBT-O<sub>2</sub>) was produced in an almost quantitative

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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.

TABLE 1

Oxidation of DBT using transition metal salts

Catalyst	Temp. (°C)	Conv. of DBT (mol%)	
		20 h	70 h
RuCl <sub>3</sub>	70	20	
RuCl <sub>3</sub>	80	>99	
MnCl <sub>2</sub>	80	0	
MnCl <sub>2</sub>	100	44	>99
CoCl <sub>2</sub>	80	0	
CoCl <sub>2</sub>	100	27	>99
-	80	0	

A mixture of DBT (1 mmol), metal chlorides (0.05 mmol), and ethylbenzene (20 g) was stirred at 70–100°C for 20–70 h under a static pressure of oxygen. Conversion was determined by GC analysis.

TABLE 2

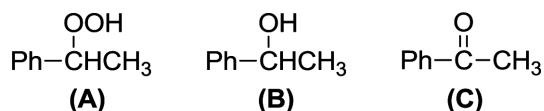
Oxidation of the sulfur compounds using ruthenium chloride in hydrocarbon solvents

Solvent	Substrate	Conv. (mol%)
cumene	DBT	>99
decalin	DBT	>99
tetralin	DBT	0
<i>n</i> -octane	DBT	0
toluene	DBT	0
EB	DMDBT	>99
EB	PhSMe	>99
EB	Ph <sub>2</sub> S	>99
EB	BT	0

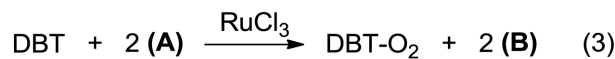
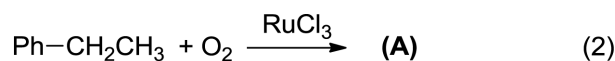
A mixture of sulfur compounds (1 mmol), ruthenium chloride (0.05 mmol), and hydrocarbon solvents (20 g) was stirred at 80 °C for 20 h under a static pressure of oxygen. Conversion was determined by GC analysis.

Several hydrocarbons such as cumene, decalin, tetralin, *n*-octane and toluene were also tested for the solvent of this reaction, the results being summarized in Table 2. Cumene and decalin could be used instead of EB. But, DBT was not consumed in the reaction in tetralin, *n*-octane, and toluene. The authors also examined the oxidation of other sulfur-containing compounds. 4,6-Dimethyldibenzothiophene (DMDBT), thioanisole (PhSMe), and diphenyl sulfide (Ph<sub>2</sub>S) were also oxidized to the corresponding sulfones in almost quantitative yields, while benzothiophene (BT) was not oxidized in this oxidation system.

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 acetophenone (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-O<sub>2</sub>) 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.

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