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OXIDATION OF SULFUR COMPOUNDS CATALYZED BY TITANOCENES

Miss Pipaporn Kanjanapipatkul



สถาบันวิทยบริการ

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เหมาะสม คือ ที่อุณหภูมิ 30 องศาเซลเซียส ปริมาณตัวเร่งปฏิกิริยา 0.27 มิลลิโมล สารออกซิไดซ์
2 มิลลิโมล เดิม โมเลกุลซัลไฟเป็นสารเติมแต่ง และใช้ไดคลอโรมีเทนเป็นตัวทำละลาย นอกจากนี้
ได้หาอัตราเร็วของการเกิดปฏิกิริยาพบว่าลำดับของอัตราเร็วเป็น ไดเอทิลซัลไฟด์ > ไทโอฟิน >
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In this work, the selective oxidation of sulfur compounds catalyzed with titanocene was studied. The sulfur compounds studied are diethyl sulfide, thiophene, benzothiophene, dibenzothiophene. The experimental results revealed that titanocene could catalyze the conversion of sulfur compounds to yield sulfoxide and sulfone in high activity and selectivity. Parameters affecting the reaction were investigated: amount of catalyst, amount of oxidizing agent, additive, solvent, time and temperature. The optimum condition for diethyl sulfide oxidation was at -20°C , 4 hrs, titanocene 0.136 mmol, oxidizing agent 1 mmol, with molecular sieve as an additive, and dichloromethane as solvent. For thiophene, benzothiophene and dibenzothiophene, the optimum condition was at 30°C , titanocene 0.27 mmol, oxidizing agent 2 mmol, with molecular sieve as additive, and dichloromethane as solvent. In addition, the rate of reaction was determined and found that the order of reaction rate was: diethyl sulfide > thiophene > benzothiophene > dibenzothiophene, which was due to the steric hindrance of catalyst.

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LIST OF ABBREVIATIONS

CAS	camphorsulfonic acid
°C	degree Celsius
CDCl ₃	deuteriochloroform
cm ⁻¹	unit of wavenumber
Cp	cyclopentadienyl
D ₂ O	deuterium oxide
Eq	equation
g	gram(s)
¹ H-NMR	proton nuclear magnetic resonance
hr	hour(s)
IR	Infrared
L	ligand
M	metal
ml	milliliter
mmol	millimole
m.s	molecular sieve
mtp	mercaptomethyl
TAML	tetraamidomacrocyclicligand
TBHP	<i>tert</i> -butylhydroperoxide
X	halogen
δ	chemical shift

CHAPTER I

INTRODUCTION

1.1 Introduction

Petroleum oils used as feedstocks for diesel oils are middle distillates in the 180-400°C boiling range. They include straight run gas oil, largely paraffinic, ranging from light gas oil to heavy gas oil that usually contain from 1 to 3 wt% sulfur. Various processes are used to upgrade heavier petroleum fractions to highly aromatic oils also in the middle distillate boiling range. The sulfur compounds present in the various oils are mostly aliphatic sulfides, benzothiophenes and dibenzothiophenes.

Sulfur compounds in fuels are a major source of pollution. The removal of sulfur from petroleum is necessary for both industrial and environmental reasons. Combustion of petroleum derived fuels leads to the atmospheric emission of sulfur oxides which are the major cause of acid rain. The main sources of $\text{SO}_{2(g)}$ emissions are the burning of fossil fuels (*e.g.*, power plants and mobile sources) and the smelting of ores rich in sulfur. In the atmosphere, $\text{SO}_{2(g)}$ can react with various oxidants (*e.g.*, O_2 , O_3 , H_2O , NO_x , OH radicals) to form sulfate aerosol, either as sulfuric acid droplets, or as neutralized particles such as ammonium sulfate, which play special role in acid rain and visibility degradation. Sulfur in petroleum products poisons catalytic converters, corrodes parts of internal combustion engines and refineries because of the formation of oxyacid of sulfur. The U. S. Environmental Protection Agency (EPA) has mandated reduction of sulfur content of diesel fuel and gasoline. The requirement will decrease the sulfur content of diesel fuel and gasoline to 15 ppm by 2006 and to 30 ppm by 2004, respectively. Recently, legislation has been introduced to reduce the level of permitted sulfur in diesel fuel (Table 1).

Table 1.1 Legislation on sulfur in diesel fuel

Country	Sulfur wt% (max)
Europe	0.2 (1994) to 0.05 (1996)
USA	0.3 (1993) to 0.05 (1996)
Japan	0.2 (1996) to 0.05 (1997)

The requirement to produce diesel fuels with very low levels of sulfur has stimulated much work in the area of hydrodesulfurization (HDS). The effectiveness of the HDS process depends on the type of sulfur compound. The complete removal of sulfur present in petroleum as sulfides, disulfides and mercaptans is relatively easy and an inexpensive process. However, benzothiophenes and dibenzothiophenes (DBTs) are difficult to remove by this process. Most of sulfur contamination in petroleum can be traced to the dibenzothiophene derivatives. In order to remove these compounds by HDS, it would require more hydrogen capacity and the maintenance of high temperature and pressure for longer time periods. This would increase operating costs and enhance the likelihood that saturation of olefins and aromatics will occur resulting in a lower-grade fuel and additional processing steps. Thus, it is likely that HDS processing has reached a stage where increasing temperature and pressure are just not enough to remove the residual sulfur without affecting the octane number. This process also produces increased volumes of hydrogen sulfide. Although HDS processes have dominated desulfurization of petroleum in the past, their cost and the requirements of strict fuel specifications combine to motivate the development of innovative process technology or alternative form of desulfurization.

An oxidative desulfurization (ODS) approach to sulfur removal serves as an alternative to the HDS process. An ODS process has the significant advantage over HDS in that the sulfur compounds that are the most difficult to reduce by HDS are the most reactive for ODS. Many different types of oxidants have been used, including HNO_3/AcOH , NO/NO_2 , NO_2 , HNO_3 , $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$, $t\text{BuOOH}$ and O_3 . The objectives of

oxidation have been varied in that some have been aimed at desulfurization while others have aimed at cetane number enhancement. Use of nitrogen oxides as oxidizing agent can have the double effect of oxidizing the sulfur compounds present in the oil: nitroaromatics are thought to have high cetane number. However, reaction selectivity, safety and cost are the important concerns for the selection of oxidant, catalyst and operating conditions for ODS processing. Advantages of the ODS process are low reaction temperature and pressure and that expensive hydrogen is not used in the process. Another feature of ODS is that the refractory sulfur compounds in HDS are easily converted by oxidation.

In the past few years, the synthesis of optically active sulfoxides through asymmetric oxidation of prochiral sulfides has constituted a very active research area, owing to the relevance of enantiopure sulfoxides as chiral auxiliaries, synthetic intermediates, and bioactive compounds. The conversion of organic sulfide to sulfoxides and sulfones holds interest from several points of view. Sulfide oxidation and sulfoxide reduction are the reverse of one another in oxygen atom transfer (OTA) reactions. Oxidation of sulfides is very useful route for preparation of sulfoxides. However, most of the existing methods use expensive, toxic or rare oxidizing reagents that are difficult to prepare. Many of these procedures also suffer from poor selectivity. Therefore, there is a need for a simple, less expensive, and safer method for conversion of sulfides to sulfoxides.

Metallocene complexes are catalysts of interest for several organic transformations as: Ziegler-Natta polymerization, Diels-Alder reaction, ketones reaction, pinacol coupling, allylation of carbonyl compounds. Their reactivity in processes of oxidation has been scarcely investigated. Titanocenes and zirconocenes have been employed in the epoxidation of unfunctionalized alkenes with *tert*-butyl hydroperoxide (TBHP), providing epoxides in low yields and when used as chiral complexes in low enantiomeric excesses. The asymmetric oxidation of prochiral sulfides is one of the most valuable methods for the preparation of enantiomerically enriched sulfoxides which are important intermediates in organic synthesis and pharmaceuticals. It was recently

discovered that some commercially available titanium and zirconium cyclopentadienyl chlorides catalyze diastereoselective epoxidation of allylic alcohols with TBHP in apolar solvents. The oxidation with *tert*-butyl hydroperoxide of sulfides to sulfoxides in the presence of transition metal give high enantioselectivity.

This thesis involved oxidation of sulfur compounds in the presence of titanocene as catalyst. The various reaction parameters, which may influence the catalytic efficiency of titanocene for oxidation of sulfur compounds have been investigated.

1.2 The Objectives of Thesis

The purposes of research can be summarized as follows:

1. To study optimization condition for the oxidation of sulfur compounds (diethyl sulfide, thiophene, benzothiophene, dibenzothiophene) using titanocene catalyst.
2. To study kinetics for oxidation of sulfur compounds (diethyl sulfide, thiophene, benzothiophene, dibenzothiophene).

CHAPTER II

THEORY AND LITERATURE

2.1 Theory

2.1.1 Sulfur compounds in crude oil

The chemical compositions of crude oil are uniform even though their physical characteristics vary widely. The elementary composition of crude oil usually falls within the following ranges in Table 2.1.

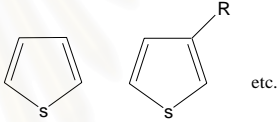
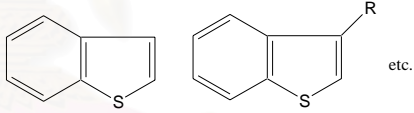
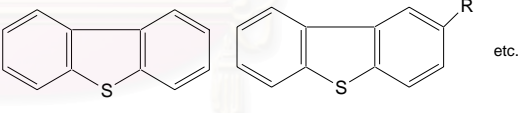
Table 2.1 Elementary composition of crude oil

Element	% By weight
Carbon	84 – 87
Hydrogen	11 – 14
Sulfur	0 – 3
Nitrogen	0 – 0.6

Sulfur content and API gravity are two properties, which have had the greatest influence on the value of crude oil, although nitrogen and metal contents are increasing in importance. The sulfur content is expressed as percent sulfur by weight and varies from less than 0.1% to greater than 5%. Sulfur is the heteroatom frequently found in crude oil. Sulfur concentration can range from 0.1% to greater than 8% by weight; moreover, this content is correlated with the gravity of the crude oil and, therefore, its quality (light or heavy oil).

The sulfur compounds found in petroleum or synthetic oils are generally classified into two types: heterocycles and nonheterocycles. The latter comprises thiols, sulfides and disulfides. Heterocycles are mainly composed of thiophenes with one to several rings and their alkyl or aryl substituents. Examples of sulfur compounds are shown in Table 2.2.

Table 2.2 Examples of the sulfur compounds found in petroleum

Compound class	Structure
Thiols (mercaptan)	RSH
Sulfides	RSR'
Disulfides	RSSR'
Thiophene	
Benzothiophene	
Dibenzothiophene	

International regulations on emission control will soon require reducing the sulfur content in fuels and distillates to less than 300 ppm. Under this incentive, intense research efforts are currently being directed to the development of more efficient or alternative routes to improve gasoline quality by reducing the content of sulfur without making significant changes in octane rating. Major source of aromatic sulfur compounds in gasoline are coking and cracking naphtha. In the latter, the content of sulfur may be as high as 1300 ppm with a 2:1 predominance of benzothiophene over thiophene.

2.1.2 Oxidizing agent

2.1.2.1 Air and ozone

Air, the cheapest oxidant, is rarely alone without irradiation and without catalysts. Examples of oxidations by air alone are the conversion of aldehydes into carboxylic acid (autoxidation). Usually, exposure to light, irradiation with ultraviolet light, or catalysts are needed.

Ozone, a blue gas or a dark blue liquid (bp. -106 , -116 or -125°C , depending on the source of data), is used in a mixture with oxygen. Ozonizations are carried out by passing ozone-containing oxygen through solution of organic compounds in solvent that do not react with ozone and liquid at low temperature. Cooling with dry ice-acetone bath (-78°C) is frequently needed to prevent the decomposition of ozone, some of which are unstable at room temperature. The most common solvents are pentane, cyclohexane, dichloromethane, chloroform, methanol, acetic acid, and ethyl acetate.

2.1.2.2 Hydrogen peroxide and its derivatives

Hydrogen peroxide, H_2O_2 , is commercially available in aqueous solution of 30% or 90% concentration. The 30% hydrogen peroxide is a colorless liquid (d 1.110) and is stabilized against decomposition, which occurs in the presence of traces of iron, copper, aluminum, platinum, and other transition metals. The 90% hydrogen peroxide is clear colorless liquid (mp. -11°C , bp. 140°C dec, d^{18} 1.393, n_D^{20} 1.3998. Although 90% hydrogen peroxide is stable at 30°C , it decomposes slowly at higher temperatures and rapidly with boiling at 140°C . All safety precautions should be taken when working with highly concentrated hydrogen peroxide.

Whereas 90% hydrogen peroxide is difficult to obtain commercially, 30% hydrogen peroxide is commonly available under the trade name of Perhydrol or Superoxol. The 30% hydrogen peroxide does not mix with non-polar organic compounds. When formic or acetic acid is used, the reacting species are the corresponding peroxy acid. Under such condition, the products of oxidation by hydrogen peroxide resemble

those obtained with peroxy acid. Transition metal catalysts not only increase the reaction rate but may also affect the oxidation, especially the stereochemistry of the product.

***Tert*-butyl hydroperoxide, $(\text{CH}_3)_3\text{COOH}$** , bp. 33-34 °C at 17 mm of Hg, is prepared from *tert*-butyl hydrogen sulfate and 27% hydrogen peroxide and is commercially available as a 70 or 90% solution containing water and *tert*-butyl alcohol. Anhydrous *tert*-butyl hydroperoxide is obtained from the 70% aqueous solution by azeotropic distillation with toluene. Anhydrous, as well as highly concentrated, *tert*-butyl hydroperoxide must be handled with most care, because it may decompose violently in the presence of strong acid and some transition metal, especially manganese, iron, and cobalt.

2.1.2.3 Organic peroxy acids

Peroxyformic acid (performic acid), HCO_3H , is always prepared *in situ* from hydrogen peroxide and formic acid. A much rare application of performic acid is the transformation of 2- or 4-dialkylaminoperhalopyridines into either amine oxides or *N,N*-dialkylhydroxylamines.

Peroxyacetic acid (peracetic acid), $\text{CH}_3\text{CO}_3\text{H}$, can be formed *in situ* from hydrogen peroxide with acetic acid. The most important applications of peroxyacetic acid are the epoxidation and *anti* hydroxylation of double bonds, of tertiary amines to amine oxide, of sulfides to sulfoxides and sulfones, of iodo compounds to iodoso or iodoxy compounds, of alcohol to ketones, and of lactams to imides.

2.1.2.4 Derivative of elements

Copper is used as a dehydrogenation catalyst for conversion of alcohols into aldehydes or ketone. Its efficiency is enhanced when it is applied on large-surface-area supports and in the presence of silver.

Copper oxide, CuO, is an oxidant for the conversion of alcohols into aldehydes or ketones and for the transformation of hydrazo compounds into azo compounds.

Nitric acid, HNO₃, is a very strong but not very selective oxidant. The advantages of its use are simple and usually clean-cut isolation of the products. The obnoxious fumes generated during the oxidations are a disadvantage. The main applications of nitric acid are the dehydrogenation of dihydropyridine.

2.1.3 Homogeneous and heterogeneous catalysts

A heterogeneous catalyst is the reaction which contains catalyst in another phase of reaction medium such as solid catalyst in liquid or aqueous solution. The disadvantage of heterogeneous catalyst is selectivity and using high temperature. Homogeneous catalyst in which catalyst is the same phase the reaction medium. On the other hand, homogeneous catalyst have been found to increase selectivity in the petrochemical industrial. Table 2.3 compares major differences between homogeneous and heterogeneous catalysis systems.

Table 2.3 Major differences between homogeneous and heterogeneous catalysts

Characteristic	Homogeneous catalyst	Heterogeneous catalyst
1. Catalyst composition and nature of active site	Discrete molecules with well-defined active site.	Nondiscrete molecular entities: active site not well-defined.
2. Determination of reaction mechanism	Relatively straightforward using standard techniques.	Very difficult.
3. Catalyst properties	Easily modified, often highly selective, poor thermal stability and mild conditions.	Difficult to modify, relatively unselective, thermally robust and vigorous reaction conditions.
4. Separation from product	Often difficult.	Relatively easy.

2.1.3.1 Catalyst composition and nature of the active site

The active sites on a heterogeneous catalyst are difficult to characterize because they are not discrete molecular entities. Instead, the active sites may be aggregations of solid support material (*e.g.*, silica gel or zeolites) coated with deposited metal atoms. Not all sites on the surface of catalyst have the same activity and physical or chemical characteristics. Analytical techniques (*e.g.*, Auger and ESCA spectroscopy) as well as scanning tunneling spectroscopy have been applied recently in attempts to determine the nature of catalytic surface. Homogeneous catalyst, on the other hand, are discrete molecules that are relatively easy to characterize by standard spectroscopic techniques, such as NMR, IR *etc.* The active site consists of the metal center and adjoining ligands.

2.1.3.2 Determination of the reaction mechanism

Because the construction of the active site of a heterogeneous catalyst is difficult to determine, the elucidation of reaction mechanism involving these catalysts can be troublesome indeed. The field of homogeneous catalysis, in contrast, has advanced rapidly over the last few decades because chemists have developed many techniques useful for studying reaction mechanisms. Elucidating the mechanism of a homogeneous catalyzed reaction means studying the mechanism of each individual step in a series of relatively elementary chemical reaction by conventional methods. Each step must be shown for a reaction involving several catalytic steps.

2.1.3.3 Catalyst properties

Because homogeneous catalysts are typically organotransition metal complexes, it is relatively easy to modify these compounds in order to increase selectivity. Homogeneous catalysts are often much less thermally stable than their heterogeneous counterparts. The use of homogeneous catalyst rather than a heterogeneous one requires milder conditions of temperature and pressure. If a sufficiently active homogeneous

catalyst can be found that can do the job of heterogeneous one, substantial savings in energy and initial capital cost accrue to the manufacturer that chooses to employ a homogeneously catalyzed process.

2.1.3.4 Ease of separation from reaction products

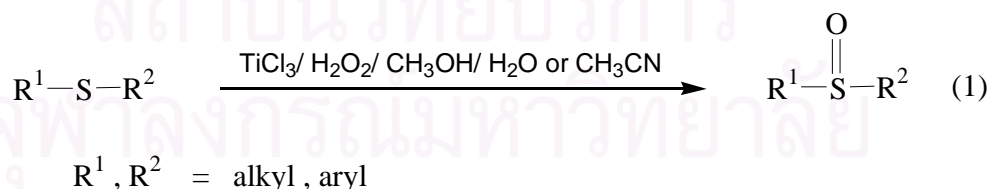
Homogeneous catalysts suffer from one key disadvantage when compared to their heterogeneous counterparts. They are often quite difficult to separate from reaction products.¹⁻⁴

2.2 Literature Reviews

2.2.1 Catalyst for oxidation of sulfur compounds

2.2.1.1 Titanium complexes

In 1981, Watanabe *et.al.*⁵ reported a mild and facile preparation of sulfoxides using the titanium(III) trichloride/hydrogen peroxide (Scheme 2.1). This procedure was found to satisfy the following requirements: (a) the oxidation is highly selective and mild, yielding only sulfoxides but no sulfones even in the oxidation of diphenyl sulfide; (b) the oxidation is complete within a few minutes; (c) the procedure is very simple and the isolation of sulfoxides can be carried out readily.



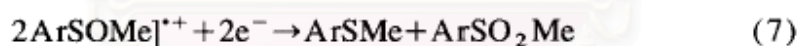
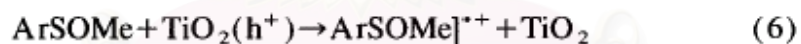
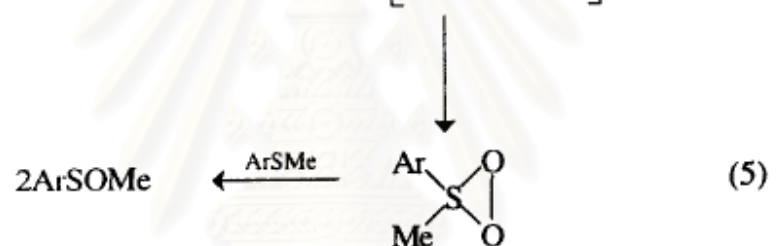
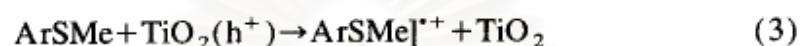
Scheme 2.1 Sulfide oxidation by TiCl₃/hydrogen peroxide.

In 1984, Pitchen *et.al.*⁶ reported that the Sharpless catalyst ($\text{Ti}(\text{OiPr})_4 + 1 \text{ mol eq. diethyl tartrate (DET) + 2 } t\text{-BuOOH}$) modified by the addition of one mol eq. H_2O gives a new homogeneous reagent which cleanly oxidize sulfides into sulfoxides in dichloromethane. The best results were obtained for the stoichiometry $\text{Ti/DET/H}_2\text{O}/t\text{-BuOOH} = 1:2:1:2$. The *e.e.* observed mainly ranges between 75 and 90% for alkyl aryl sulfoxides and 50-71% for dialkyl sulfoxides. A strong temperature dependence on *e.e.* was also observed in the asymmetric oxidation of methyl *p*-tolyl sulfoxide.

In 1993, Komatsu *et.al.*⁷ reported the asymmetric oxidation of sulfide to chiral sulfoxides in moderate yield with *tert*-butyl hydroperoxide (TBHP). The reaction was catalyzed by titanium complex produced *in situ* from a titanium alkoxide and a chiral binaphthol. Up to 96% *e.e.* were obtained with commercial aqueous 70% TBHP under atmospheric condition at 25°C with 2.5 mol % of the catalyst. The presence of more than 1 mol equiv of water relative to sulfide was essential for the oxidation, and it was found that water was necessary not only to produce an effective catalyst for the highly enantioselective oxidation but also to maintain the catalytic activity of the titanium-binaphthol complex for a longer time. The nature of the solvent had a remarkable effect upon the *e.e.* of the sulfoxide. Carbon tetrachloride was proven to be the solvent of choice; the use of other chlorinated solvent resulted in low enantioselectivity. From a mechanistic standpoint, it was revealed that the initial asymmetric oxidation to the chiral sulfoxide (~50% *e.e.*) was followed by the kinetic resolution of the sulfoxide; that is, the titanium-binaphthol complex catalyzed not only the asymmetric oxidation but also the subsequent kinetic resolution.

In 1998, Somasundaram and Srinivasan⁸ investigated the oxidation of aryl methyl sulfides results in the formation of sulfoxides as the major product with small amount of sulfone. Increases in the irradiation time lead to disproportionation reaction. However, TiO_2 acts as an effective photocatalyst for the oxidation of aryl methyl sulfoxides to give exclusively sulfones. They propose the mechanism in Equations (1-11) when the photogenerated hole (h^+) readily accepts an electron from the sulfide adsorbed on the

surface of the photocatalyst to give the sulfide radical cation $\text{ArSMe}^{\cdot+}$. There are instances of formation of such a radical cation. One important finding is that the irradiation time plays an important role in determining the products. Lower irradiation time invariably leads to the formation of sulfoxides as the major product.



C-S bond cleavage:



In 1998, Donnoli *et.al.*⁹ investigated a new catalytic procedure for the asymmetric oxidation of aryl alkyl and aryl benzyl sulfides to optically active sulfoxides by hydrogen peroxides. This oxidation of sulfides is mediated by a chiral Ti complex formed *in situ* by reacting $\text{Ti}(i\text{-PrO})_4$, (R,R)-diphenylethane-1,2-diol, and water. The condition of the reaction (stoichiometric composition of the catalyst, temperature, and the presence of additives and solvent) have been determined in order to reach the highest enantioselectivity. The oxidation protocol is quite versatile as the values of chemical yields (60-73%) and of enantioselectivity (*e.e.* 70-80%) achieved for aryl alkyl sulfides are almost independent of the nature of the aryl substituent and of the size of the alkyl group. Notably, aryl benzyl sulfides, which are poor substrates for the Ti/DET catalyzed oxidations, afforded very high *e.e.* (92-99%) with this oxidation system.

In 2001, Sala *et.al.*¹⁰ investigated the oxidation of sulfide to sulfoxide catalyzed by the commercial $\text{Cp}_2\text{Ti}(\text{X})_2$ (X = Cl, OTf)/*t*-butyl hydroperoxide (TBHP). The asymmetric version of prochiral sulfide oxidation was achieved using Cp_2TiCl_2 in the presence of (+)-(R)-BINOL, as chiral ligand and activated 4 °A molecular sieves. From these results it emerges that the role of molecular sieve is not limited to remove HX from the reaction mixture otherwise similar yields of sulfoxide should have been respectively observed. It is known that mineral acids can catalyze the oxidation of sulfides to sulfoxides.

In 2001, Hulea *et.al.*¹¹ investigated the sulfoxidation of aromatic sulfur compounds with hydrogen peroxide over Ti containing molecular sieve. It has been shown that the large-pore catalytic materials, such as Ti-beta and mesoporous Ti-HMS, are active for the selective oxidation of thiophene derivatives to the corresponding sulfone, whereas the medium-pore zeolite TS-1 is totally inactive in the oxidation of polyaromatic sulfur compounds with H_2O_2 . It has also been shown that thiophenes are less reactive than thioethers.

2.2.1.2 Iron complexes

In 2002, Sivasubramanian *et.al*¹² studied the oxidation of *para*-substituted phenyl methyl sulfides, carried out with several oxo(salen)iron (salen = *N,N*-bis(salicylidine)ethylenediaminato) complexes in acetonitrile. The oxo complex $[O = Fe^{IV}(\text{salen})]^{*+}$, generated from iron(III)-salen complex and iodosylbenzene, effectively oxidizes the organic sulfides to the corresponding sulfoxides. The formation of $[O = Fe^{IV}(\text{salen})]^{*+}$ as the active oxidant is supported by resonance Raman study. The kinetic data indicate that the reaction is first-order in the oxidant and fractional-order with respect to sulfide. The substituted effect, UV- vis absorption, and EPR spectral studies indicate oxygen atom transfer from the oxidant to the substrate in the rate-determining step.

In 2002, Hangun *et.al*¹³ developed a series of iron(III) complexes called TAML[®] (for Tetra Amino Macrocyclic Ligand) activators that enhance the oxidizing ability of hydrogen peroxide at low catalyst concentration and mild reaction conditions. The general structure of TAML[®] activators is shown in Figure 1. The R and X groups are used to control activator reactivity, selectivity and lifetime. They are non-toxic and are most effective at very low concentration (1-5 μM ; 0.5-2 ppm). They reported a practical system using Fe-TAML and H_2O_2 as catalyst and oxidant, respectively. Micromolar concentration of FeF_2B activates H_2O_2 to convert greater than 99% of millimolar solution (>7000:1 substrate:catalyst concentrations) of dibenzothiophene derivatives to the corresponding sulfones under mild conditions. The choice of dibenzothiophene derivatives was based on their relative abundance in petroleum.

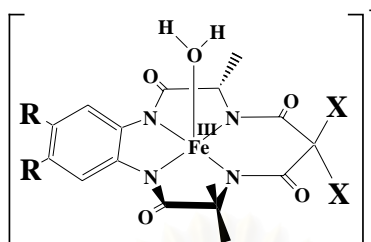


Figure 2.1. Structure of TAML activators.

2.2.1.3 Rhenium complexes

In 1996, Brown and Espenson¹⁴ reported the oxidation of organic sulfides to the sulfoxides by hydrogen peroxide. The oxidation was successfully catalyzed by CH_3ReO_3 , a water-soluble organometallic oxide. A kinetic study was carried out in 1:1 (v/v) acetonitrile-water at pH 1 and at 25°C. The kinetic can be resolved into two steps. First, H_2O_2 and CH_3ReO_3 react to form 1:1 to 2:1 rhenium peroxides, denoted as **A** and **B**, respectively. In the second step **A** and **B** react with the substrate forming the product. The rate constant for the various steps of these reactions were evaluated using steady-state techniques and are on the order of $10^3 \text{ Lmol}^{-1}\text{s}^{-1}$ for aryl methyl sulfides and $10^4 \text{ Lmol}^{-1}\text{s}^{-1}$ for dialkyl sulfides. **A** is more active than **B**. The kinetic results point to a mechanism that involves the nucleophilic attack of the sulfur atom on a peroxide oxygen of the rhenium peroxide. This formulation is consistent with the accelerating effects of electron-donating substituents.

In 2002, Wang *et.al*¹⁵ investigated the conversion of sulfides to sulfoxides using *tert*-butyl hydroperoxide (TBHP) and $\text{MeReO}(\text{mtp})\text{PPh}_3$ as catalyst. The rhenium-catalyzed reaction is rapid and yields clean sulfoxides; under minimally different conditions, sulfones are instead formed cleanly and quantitatively. (Equations 12-13) (TBA is *tert*-butyl alcohol).



The method offers the advantage that one product or the other can be obtained in high purity by a modest variation of conditions. The reactions occur smoothly at 25-50°C in chloroform. Other chelating dithiolate ligands can be used with comparable results. These oxidations were tested for dialkyl, alkyl-aryl, and diaryl sulfides; thiophene; and thianthrene. Even the “hard” sulfide, 4,6-dimethyldibenzothiophene (DMDBT) was quantitatively oxidized to the dioxide with TBHP:DMDBT 3.0 – 3.5 and 0.05 – 3.8% mol of MeReO(mtp)PPh₃.

2.2.1.4 Acid as catalyst

In 1954, Edwards and Stenlake¹⁶ studied oxidation of saturated alkyl sulfides with chromic acid in pyridine and manganese dioxide in light petroleum. The oxidation of di-*n*-butyl sulfide by chromic acid in pyridine at room temperature gave di-*n*-butyl sulfoxide in 49% yield without trace of the sulfone. Use of large excess of reagent both at room temperature and at 100°C also gave only the sulfoxide. Similar oxidation of dibenzyl sulfide gave dibenzyl sulfoxide in 70% yield after 5 days at room temperature. Oxidation of di-*n*-butyl sulfide with activated manganese dioxide in light petroleum gave the sulfoxide exclusively; reaction was slow at room temperature, but yield of 71% was obtained after 85 hr. Dibenzyl sulfoxide was obtained, similarly, in 75% yield after 72 hr at room temperature. The method is suitable for oxidation of diallyl sulfide which, after 76 hr, gave diallyl sulfoxide in 13% yield.

In 1995, Breton *et al*¹⁷ reported that silica gel and alumina, mediate the reactivity of (CH₃)₃COOH, providing a convenient method for oxidation of sulfides, sulfoxides, or alkenes. Treatment of dibutyl sulfide (1a) with 1 mol equiv of (CH₃)₃COOH, either anhydrous or 70% aqueous, in the presence of silica gel readily afforded sulfoxide 2a. Only very slow oxidation occurred in the absence of silica gel. Similar treatment of

sulfide **1a** with 2 mol equiv of $(\text{CH}_3)_3\text{COOH}$ afforded sulfone **3a** in high yield, which could also be obtained by oxidation of sulfoxide **2a**. Comparable results were obtained using silica gel that had been recycled twice, as well as with the phenyl benzyl analogs **1b** and **2b**. By contrast, acid-catalyzed oxidation of sulfide **1a** with an excess of $(\text{CH}_3)_3\text{COOH}$ afforded only sulfoxide **2a**. Basic alumina gave poor yield of sulfoxide **2a** but readily mediated the oxidation of sulfoxide **2a** to sulfone **3a**.

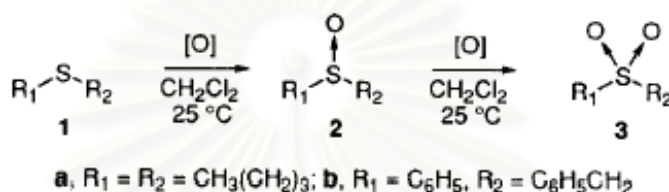


Figure 3 Sulfide oxidation by $(\text{CH}_3)_3\text{COOH}$.

In 1996, Bonadies *et.al*¹⁸ studied a convenient acid-catalyzed oxidation of sulfides to sulfoxides by *tert*-butyl hydroperoxide (TBHP). When starting material **1** reacted with a twofold excess of TBHP in the presence of catalytic amount (10%) of camphorsulfonic acid (CSA) in chloroform solution at room temperature, the selective oxidation of sulfides **1** takes place with very good yield (>80%).

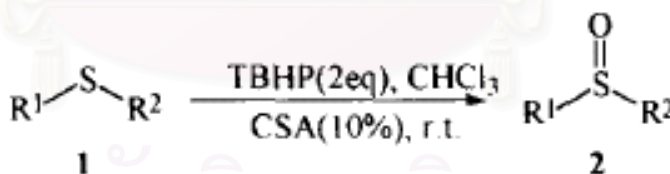


Figure 2 Sulfide oxidation by camphorsulfonic acid.

In 2000, Otsuki *et.al*¹⁹ investigated the oxidation of sulfur compounds (thiophene, benzothiophene and dibenzothiophene), and straight run-light gas oil (SR-LGO, S: 1.35 wt%), and vacuum gas oil (VGO, S: 2.17 wt%). They were conducted with a mixture of hydrogen peroxide and formic acid. The thiophene could not be oxidized at 50°C. Benzo[*b*]thiophene and dibenzothiophene with higher electron density can be oxidized. The sulfur compounds in SR-LGO and VGO appeared to be oxidized to a detectable

levels (*c.a.*, 0.01 wt% S) by GC-FPD analysis. The IR spectra of oxidized SR-LGO and VGO showed the formation of sulfones. The removal of sulfur compounds by extraction became more effective for the oxidized samples than for the original samples. The most effective solvent for removal of sulfur compounds was dimethylformamide (DMF). The recovery of oil was, however, lowest with DMF.

In 2001, Te *et.al*²⁰ investigated the oxidation reactivities of dibenzothiophenes using toluene solutions of the model compounds. A series of polyoxometalate/H₂O₂ system were evaluated for dibenzothiophene oxidation. The H₂O₂ solutions of phosphotungstic acid and its salt were very active catalyst systems for the model compound oxidation, while their molybdenum counterpart systems were much less active. The H₂O₂ solutions of silicotungstic and silicomolybdic compounds were the least active catalyst systems for the reaction. Oxidation reactivities decreased in the order of dibenzothiophene > 4-methyldibenzothiophene > 4,6-dimethyldibenzothiophene. However, the oxidation of the dibenzothiophene was achieved under mild reaction conditions and it was easy to increase reaction temperature or reaction time to achieve high oxidation conversions. Interestingly, in a formic acid/H₂O₂ system, the oxidation reactivity of the dibenzothiophene showed the reverse trend, suggesting that steric hindrance might play a role when bulky polyoxoperoxo species, which likely forms in a hydrogen peroxide solution, acts as catalyst.

2.2.1.5 Other catalysts

In 1981, Trost and Curran²¹ studied the chemoselective oxidation of sulfides such as thioanisole in the presence of other common functional groups to sulfones with potassium hydrogen persulfate in aqueous methanol. They found that KHSO₅ in aqueous methanol is a highly chemoselective oxidizing agent for the conversion of sulfides to sulfones.

In 1989, Ramsden *et.al*²² used sodium hypochlorite as an oxidizing agent for the oxidation of lipophilic organic sulfide employing phase-transfer catalysis (PTC). The PTC results in nearly complete oxidation of the substrate in 20 min, with high selectivity to the sulfoxide, compared to 5 h in its absence. Kinetic studies showed that the reaction occurs *via* transfer into the organic phase. Under certain conditions the transfer is rate limiting. The addition of a transition metal catalyst (TPPMnCl) further increased the rate and led to the complete conversion of the sulfide to the sulfone illustrating that NaOCl(aq) is a potent oxidizing agent in these biphasic systems.

In 2001, Bennett *et.al*²³ studied the mechanism for the oxidation of aryl sulfides by peroxydicarbonate ion in cosolvent/water media (Figure 2.2). The results are consistent with a charge-separated transition state relative to the reactant, with an increase of positive charge on the sulfur following nucleophilic attack of the sulfide at the electrophilic oxygen of peroxydicarbonate. Activation parameters for oxidations of ethyl phenyl sulfide in *tert*-butyl alcohol/water were reported.

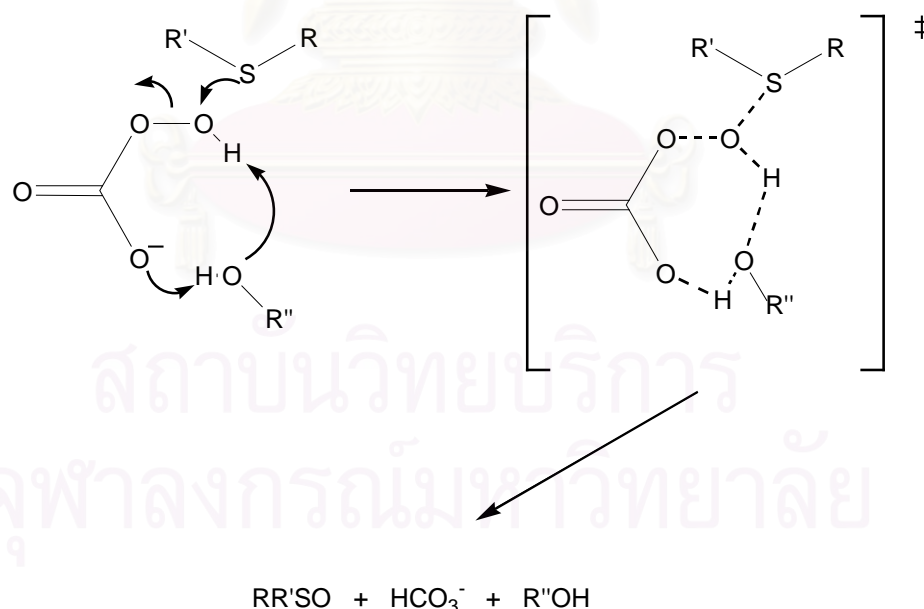


Figure 2.2 Mechanism of sulfide oxidations by peroxydicarbonate.

CHAPTER III

EXPERIMENTAL

In the present study of the oxidation of diethyl sulfide, thiophene and benzothiophene with titanocene catalysts, the experiment was divided into four steps.

1. Sulfur compounds oxidation using titanium complexes as catalyst.
2. Characterization of oxidation products.
3. Study of the optimum conditions for sulfur compounds oxidation by using titanocene catalyst.
4. Study of the kinetics of sulfur compounds oxidation reaction.

The details of the experiments were explained in the following.

3.1 Operation and Apparatus

Some reactions were done in an inert gas atmosphere (prepurified nitrogen) and used standard Schlenk technique. All equipments used in the oxidation of sulfur compounds are listed as follows :

3.1.1 Schlenk line

Schlenk line consists of nitrogen and vacuum line. The vacuum line was equipped with a solvent trap and a vacuum pump, respectively. The nitrogen line was connected to the moisture trap and the oil bubble that contained enough oil to provide a seal from the atmosphere. The Schlenk line is shown in Figure 3.1.

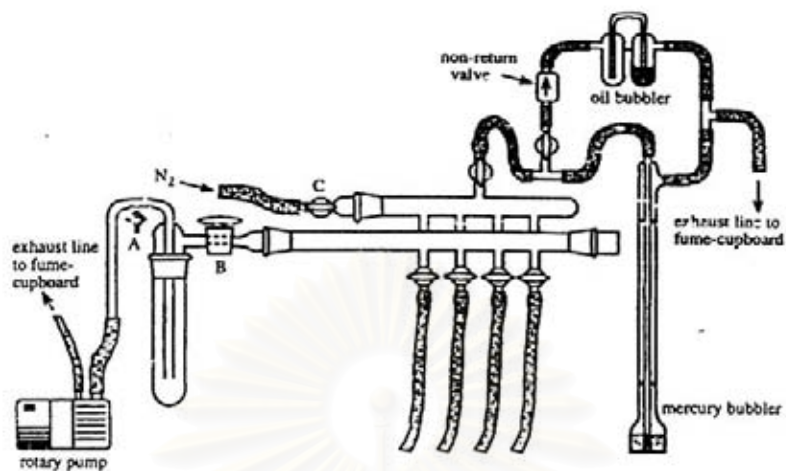


Figure 3.1 Schlenk line.

3.1.2 Schlenk flask

A Schlenk flask has a side-arm to connect to the Schlenk line. Some typical models are shown in Figure 3.2.

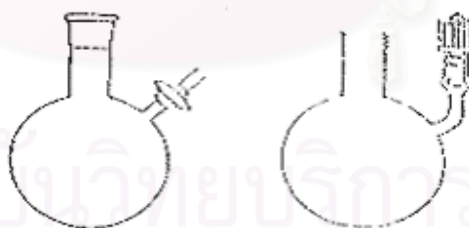


Figure 3.2 Schlenk flasks.

3.1.3 Vacuum pump

A pressure of $10^{-3} - 10^{-1}$ mm Hg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

3.1.4 Heating bath

The oil bath with thermometer was used for high temperature reaction.

3.1.5 Inert gas supply

Ultra high purity nitrogen gas was purified by passing through three columns packed with 4°A molecular sieve, NaOH and P₂O₅, respectively. The inert gas was used to feed into nitrogen line of Schlenk line.

3.1.6 Syringe and Needle

The syringes with volume of 50, 10, 5, 2, 1 and 0.5 ml and the needles No. 19, 20, and 22 were used.

3.2 Reagents and Solvents

The reagents and solvents used in this experiment were analytical grade.

Table 3.1 Chemical reagents and suppliers

Reagents and Solvents	Supplier
1. Ultra high purity nitrogen gas (99.999%)	Thai Industry Gas Co.,Ltd., Thailand
2. Toluene	Lab Scans Co., Ltd., Ireland
4. Dichloromethane	Merck, Germany
5. Benzothiophene	Fluka Chemie A.G., Switzerland
6. Dibenzothiophene	Fluka Chemie A.G., Switzerland
7. Diethyl sulfide	Fluka Chemie A.G., Switzerland
8. Thiophene	Fluka Chemie A.G., Switzerland
9. 80% <i>tert</i> -butyl hydroperoxide in di- <i>tert</i> -butylperoxide	Merck, Germany
10. Sodium sulfate anhydrous	Merck, Germany
11. Pyridine	Fluka Chemie A.G., Switzerland
12. Potassium carbonate anhydrous	Fluka Chemie A.G., Switzerland
13. 4°A Molecular sieve	Merck, Germany
14. Dicyclopentadienyltitanium dichloride	Merck, Germany

3.3 Analytical Measurements

3.3.1 Column chromatography

Column chromatography was used to separate the products of oxidation. The column was glass tube, 1 cm diameter and 25 cm length. Stationary phase was 70-230 mesh (60 G) of silica gel.

3.3.2 Gas chromatography - Mass spectrometry

Gas chromatography was carried out on Varian, Star 3400CX and mass spectrometry was carried out on Varian, Saturn 4D at Department of Chemistry, Chulalongkorn University.

Gas chromatography was carried out on Agilent, 6890N and mass spectrometry was carried out on Agilent, 5793N at Central Instrument Facility, Faculty of Science, Mahidol University.

3.3.3 Fourier Transform Infrared Spectrometer

Fourier transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University. The liquid samples were spread on NaCl cells. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 cm^{-1} to $4,000\text{ cm}^{-1}$ in transmittance mode.

3.3.4 Nuclear Magnetic Resonance Spectrometer

$^1\text{H-NMR}$ spectra were obtained on Bruker ACF 200 MHz at Department of Chemistry, Chulalongkorn University. The NMR spectra were measured in chloroform-d and deuterium oxide (D_2O) at room temperature. The center peak of chloroform-d and deuterium oxide (D_2O) were used as the internal reference ($^1\text{H-NMR}$ at 7.2 ppm and 4.6 ppm).

3.4 General Procedure for Oxidation of Sulfur Compounds

In a round bottom flask, catalyst Cp_2TiCl_2 (0.136 mmol), dichloromethane (5 ml) and 4 Å molecular sieve (500 mg), were added followed by sulfur compound substrate (1 mmol). Then *tert*-butylhydroperoxide (TBHP) (80% in organic solvent, 1.2 mmol) as an oxidant was added to the reaction mixture. After the reaction was complete, the mixture was centrifugated. The aqueous phase with molecular sieve was separated from the organic phase. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography using a mixture of hexane-ethyl acetate (1:1) as an eluent. The equivalent fractions monitored by TLC were combined and the solvents were completely evaporated.

3.5 Study on the Optimum Conditions for the Oxidation of Sulfur Compounds

3.5.1 Effect of temperature

The effect of temperature in oxidation of sulfur compounds was investigated.

3.5.2 Effect of time

The oxidation of sulfur compounds was studied by varying time.

3.5.3 Effect of solvent type

Types of solvents were varied: dichloromethane, chloroform and toluene.

3.5.4 Effect of additive

Different types of additives were used: molecular sieve, sodium sulfate anhydrous and potassium carbonate.

3.5.5 Effect of amounts of oxidant and catalyst

The effect of the amounts of oxidant and catalyst in oxidation of sulfur compounds were investigated.

3.6 Kinetic Study of Sulfur Compounds Oxidation

The kinetic study for sulfur compounds (diethyl sulfide, thiophene, benzothiophene and dibenzothiophene) oxidation was performed by using titanocene as catalyst under optimum conditions. The reaction was monitored by UV-visible spectrometer.



CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Study on the Optimum Conditions for the Oxidation of Sulfur Compounds

4.1.1 Oxidation of diethyl sulfide

Various factors are evaluated to find optimum conditions for the diethyl sulfide oxidation. The parameters studied in this reaction are temperature, reaction time, types of solvent, amounts of oxidant and catalyst and effect of additive. The results are collected in Table 4.1.

Table 4.1 Various conditions for diethyl sulfide oxidation reaction

Entry	Cp ₂ TiCl ₂ (mmol)	TBHP (mmol)	Solvent	Additive	Time (hr)	Temp (°C)	% Sulfoxide	% Sulfone
1	0.136	1	CH ₂ Cl ₂	m.s	4	-20	81	0
2	0.136	2	CH ₂ Cl ₂	m.s	4	-20	89	0
3	0.136	1	CH ₂ Cl ₂	Na ₂ SO ₄	4	-20	79	0
4	0.136	1	CH ₂ Cl ₂	m.s	4	30	12	44
5	0.27	1	CH ₂ Cl ₂	m.s	4	-20	30	35
6	0.136	1	toluene	m.s	4	-20	52	0
7	0.136	1	CH ₂ Cl ₂	m.s	2	-20	33	0
8	0.136	1	CH ₂ Cl ₂	K ₂ CO ₃ ^a	2	-20	39	20

Reaction conditions: diethyl sulfide 1 mmol (0.15 ml); additive 0.5 g and solvent 5 ml.

^a K₂CO₃ 0.25 g.

The results show that at -20° C with molecular sieve or Na₂SO₄ as additive, and dicholomethane or toluene as solvent, the selective product is diethyl sulfoxide (entry 2).

The result on the effect of temperature indicated that the % yield of diethyl sulfone is enhanced with increasing temperature (entries 1 and 4). This is in good agreement with that reported.¹⁶

The effect of time was observed in entries 1 and 7, at 2 and 4 hrs of the reaction give 33% and 81% yield of diethyl sulfoxide. From the results, it can be described that for a short time (2 hrs) the catalyst cannot react with oxidizing agent completely so % yield of diethyl sulfoxide is low (33%). For 4 hrs, the reaction is completed so yield of diethyl sulfoxide is increased to 81%.

When the amount of the oxidant was doubled, the yield of product was increased. It can be explained that in the oxidation of sulfur compounds, increasing amount of oxidant (TBHP) reacts with more substrate, as shown in the following reactions (TBA is *tert*-butyl alcohol).



The solvent effect on the oxidation was investigated (entries 1 and 6), it was found that CH_2Cl_2 gives better yield than toluene⁹⁻¹⁰ so CH_2Cl_2 is the solvent of choice for further reactions.

Effect of different additive can be seen from the experimental results. In entries 1 and 3, on the other hand, when using sodium sulphate, Na_2SO_4 or molecular sieve (m.s) % yields of sulfoxide were comparable. Molecular sieve was reported to trap mineral acid into its pore size and resulted in high yield of sulfoxide in the oxidation of sulfides to sulfoxides.¹⁰ In entries 7 and 8, the results showed that K_2CO_3 (base) reacts with acid (HX) which resulted from the reaction, so product initially formed, sulfoxide, was transformed into sulfone. The base removal of HX from the reaction mixture produced two effects, as follows.

1) The shift of the equilibrium towards the generation of the intermediate 1 with consequent enhancement of the reaction rate.

2) The suppression of the acid- catalyzed oxidative pathway.

The two effects operate in opposite directions, one favoring, the other reducing the conversion.



The effect of catalyst in the oxidation reaction of diethyl sulfide indicates that using 0.27 mmol catalyst in 4 hrs at -20°C gives 30% yield of sulfoxide and 35% of diethyl sulfone which is higher than using 0.136 mmol catalyst (81% of sulfoxide only). The increasing of catalyst amount gives more chance of reaction between oxidizing agent and catalyst, so % yield of product is increased.

4.1.2 Oxidation of thiophene

The parameters studied in this reaction are same as in section 4.1. The results are collected in Table 4.2. Effect of time is shown in Table 4.3.

Table 4.2 Various conditions for thiophene oxidation

Entry	Cp ₂ TiCl ₂ (mmol)	TBHP (mmol)	Additive	Temp (°C)	% Sulfoxide	% Sulfone
1	0.270	2	ms	30	52	11
2	0.270	1	ms	30	32	0
3	0.136	1	ms	30	21	0
4	0.136	2	ms	30	40	0
5	0.136	4	ms	30	0	100
6	0.136	2	ms	0	0	0
7	0.136	2	pyridine ^a	30	0	86

Reaction conditions: thiophene 1 mmol (0.15 ml); additive 0.5 g; dichloromethane 5 ml time 24 hrs.

^a Pyridine 0.25 g time 24 hrs.

The suitable condition of oxidation of thiophene is at room temperature for 24 hrs with 0.27 mmol of catalyst and 2 mmol of TBHP. Yields of thiophene sulfoxide and thiophene sulfone under this condition are 52 and 18 %, respectively.

The effects of amounts of catalyst and oxidizing agent on the oxidation reaction of thiophene are the same as in the oxidation of diethyl sulfide. Yields of products in 24 hrs are thiophene sulfoxide (52%) and thiophene sulfone (11%).

When using pyridine as additive, it can be seen from the result that the product can be converted from thiophene sulfoxide to thiophene sulfone.

Table 4.3 The effect of time for thiophene oxidation reaction

Entry	Time (hr)	% Sulfoxide	% Sulfone
1	24	40	0
2	48	28	34
3	72	0	78

Reaction conditions: thiophene 1 mmol (0.15 ml); Cp_2TiCl_2 0.136 mmol; TBHP 2 mmol; molecular sieve 0.5 g; dichloromethane 5 ml.

The result shows that as time continued, the second product, sulfone was resulted from the transformation of the initial product, sulfoxide. This will be further confirmed by the kinetic experiment below.

4.1.3 Oxidation of benzothiophene

To reach optimum conditions for the benzothiophene oxidation, the parameters studied in this reaction are same as in section 4.1.1. The results are collected in Tables 4.4 – 4.6.

Table 4.4 The effect of temperature for benzothiophene oxidation

Entry	Temperature (°C)	% Sulfoxide	% Sulfone
1	-20	0	0
2	0	0	0
3	30	13	0

Reaction conditions: benzothiophene 1 mmol (0.12 ml); Cp_2TiCl_2 0.136 mmol; TBHP 1 mmol; molecular sieve 0.5 g; dichloromethane 5 ml; time 24 hrs.

From the above experimental results, when temperature for benzothiophene oxidation was increased to 30°C, sulfoxide was produced. At low temperatures, no product was obtained, this might be due to the insufficient energy provided for the oxidation.

Table 4.5 The effect of oxidizing, catalyst and time for benzothiophene oxidation

Entry	Cp_2TiCl_2 (mmol)	TBHP (mmol)	% Sulfoxide			% Sulfone		
			24 hr	48 hr	72 hr	24 hr	48 hr	72 hr
1	0.136	1	13	42	25	0	3	52
2	0.136	2	28	60	26	0	20	72
3	0.27	1	18	44	21	0	16	63
4	0.27	2	32	71	12	0	20	81

Reaction conditions: benzothiophene 1 mmol (0.12 ml); dichloromethane 5 ml.

From experimental data, the optimum condition for benzothiophene oxidation using titanocene catalyst is 1 mmol of substrate, 2 mmol of oxidizing agent (TBHP), 0.27 mmol of catalyst and dichloromethane as solvent at 30°C. Two types of product, benzothiophene sulfoxide (benzothiophene 1-oxide) and benzothiophene sulfone (benzothiophene 1,1-dioxide) were produced. Again, it seems that the benzothiophene sulfoxide converted to benzothiophene sulfone as % yield of the former decreased with the increasing of the latter.

When amount of oxidizing agent was increased from 1 mmol to 2 mmol, the reaction can occur more rapidly (42% vs 60%). The effect of amount of catalyst gives the same result as that for thiophene oxidation.

Table 4.6 The effect of nitrogen gas in benzothiophene oxidation

Entry	Cp ₂ TiCl ₂ (mmol)	TBHP (mmol)	Solvent	Additive	Time (hr)	Temp (°C)	% Sulfoxide	% Sulfone
1	0.136	2	CH ₂ Cl ₂	ms	48	30	60	20
2*	0.136	2	CH ₂ Cl ₂	ms	48	30	52	16

* under N₂

The oxidation reaction under N₂ for 48 hrs with 0.136 mmol catalyst and 2 mmol oxidizing agent showed the lower yield (52 %) compared with the reaction performed in oxygen (60%), this might be explained by the participation of O₂ in the flask.

4.1.4 Oxidation of dibenzothiophene

The parameters studied in this reaction are same as in section 4.1. The results of oxidation of benzothiophene are collected in Table 4.7.

Table 4.7 The effect of time for dibenzothiophene oxidation reaction

Entry	Cp ₂ TiCl ₂ (mmol)	TBHP (mmol)	% Sulfoxide				% Sulfone			
			48 hr	72 hr	96 hr	120 hr	48 hr	72 hr	96 hr	120 hr
1	0.27	2	28	54	38	9	0	15	42	87
2	0.27	4	39	50	14	0	11	31	71	100

Reaction conditions: dibenzothiophene 1 mmol (0.184g); dichloromethane 5 ml.

From the results, the optimum condition for oxidation of dibenzothiophene to dibenzothiophene sulfoxide is 0.27 mmol of catalyst, 2 mmol of TBHP at room temperature for 72 hrs (50% sulfoxide). When increasing amount of oxidizing agent from 2 to 4 mmol more sulfone was produced.

4.2 Study on the Kinetics for the Oxidation of Sulfur Compounds

The kinetics of the reaction was studied for the progress of the reaction. The sulfur compounds oxidation catalyzed by titanocene using TBHP as an oxidizing agent in dichloromethane was examined. The sulfur compounds studied include diethyl sulfide, thiophene, benzothiophene and dibenzothiophene. The reaction was monitored by UV-visible spectrometry.

Conversion of substrate was calculated using their initial concentration at 0 min (C_0) and concentration after t min reaction (C_t). Conversion x is expressed as equation (4), assuming that the volume and mass of the reaction mixture were constant.

$$x = \frac{C_0 - C_t}{C_0} \quad (4)$$

Table 4.8 Wavelength at maximum absorption (λ_{\max}) of substrate

Substrate	λ_{\max} (nm)
diethyl sulfide	231
thiophene	231
benzothiophene	229
dibenzothiophene	237

4.2.1 Kinetics of diethyl sulfide oxidation

The general oxidation procedure of diethyl sulfide using titanocene as catalyst was carried out. At different reaction time proceeded, from the reaction mixture was sampling and find concentration of diethyl sulfide (substrate) by UV-visible spectrometry ($\lambda_{\text{max}} = 231$).

Table 4.9 The kinetic study of diethyl sulfide oxidation

Time (hrs)	Absorbance	diethyl sulfide (mmol)
0	0.274	1.06
0.5	0.239	0.93
1.0	0.227	0.88
1.5	0.193	0.75
2.0	0.161	0.63
2.5	0.124	0.48
3.0	0.089	0.36
3.5	0.062	0.25
4.0	0.046	0.19

Reaction conditions: diethyl sulfide 1 mmol; Cp_2TiCl_2 0.136 mmol; TBHP 2 mmol; molecular sieve 0.5 g at -20°C .

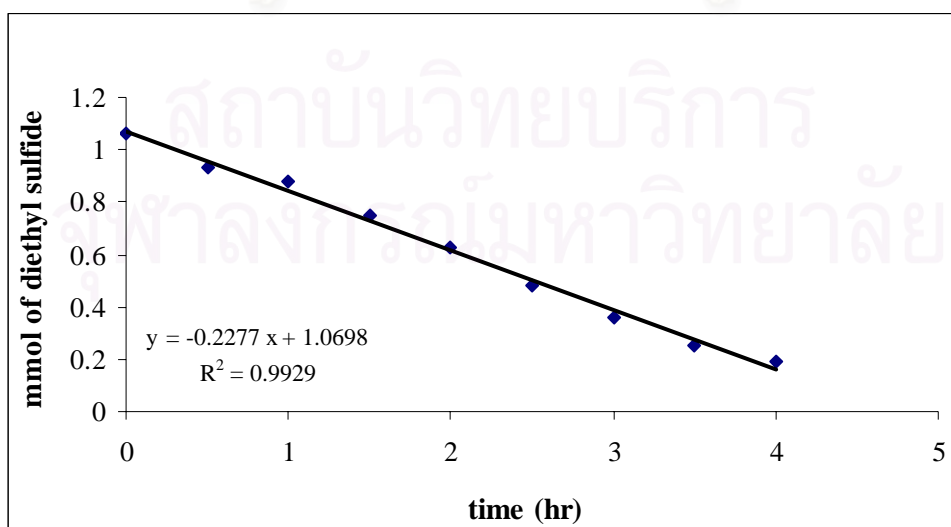


Figure 4.1 The kinetic study of diethyl sulfide oxidation.

From data in Table 4.7 and Figure 4.1 with variation of time, it was found that the time around 4 hours was adequate for the oxidation of diethyl at -20°C . In term of kinetic study, the results displayed that the rate of conversion of diethyl sulfide under this condition was $227.7 \mu\text{mol}$ per hour. For comparison, it should be noted that the rate of methyl p-totyl sulfide oxidation by using the same catalyst was reported to be $39.6 \mu\text{mol}$ per hour. (sulfide 1 mmol; Cp_2TiCl_2 0.14 mmol; TBHP 1.2 mmol; molecular sieve 0.5 g at -20°C)

4.2.2 Kinetics of thiophene oxidation

The same procedure as in section 4.2.1 was performed, except that diethyl sulfide was replaced with thiophene.

Table 4.10 The kinetic study of thiophene oxidation

Time (hrs)	Absorbance	thiophene (mmol)
0	1.907	1.07
4	1.848	1.03
8	1.607	0.89
12	1.351	0.74
18	1.163	0.62
24	0.981	0.52
28	0.717	0.36
32	0.573	0.28

Reaction conditions: thiophene 1 mmol; Cp_2TiCl_2 0.27 mmol; TBHP 2 mmol; molecular sieve 0.5 g; dichloromethane 5 ml at 30°C

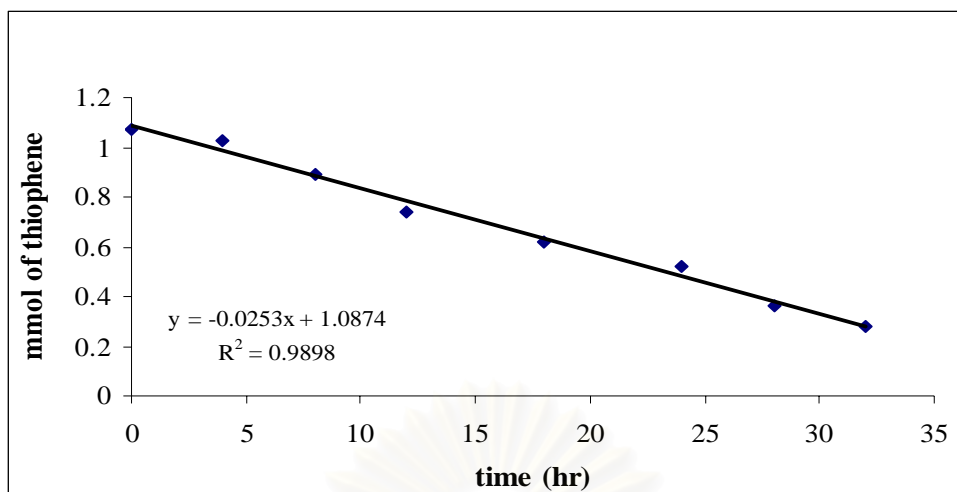


Figure 4.2 The kinetic study of thiophene oxidation.

At room temperature (30°C), the results displayed that the rate of conversion of thiophene under this condition was 25.3 μmol per hour.

4.2.3 Kinetics of benzothiophene oxidation

The same procedure as in section 4.2.1 was performed, except that diethyl sulfide was replaced with benzothiophene. Concentration of benzothiophene (substrate) was determined by UV-visible spectrometry ($\lambda_{\text{max}} = 229$).

Table 4.11 The kinetic study of benzothiophene oxidation

Time (hrs)	Absorbance	benzothiophene (mmol)
0	1.443	0.85
6	1.395	0.80
12	1.226	0.75
18	1.138	0.65
24	0.937	0.55
30	0.742	0.44
36	0.459	0.25
48	0.309	0.15
54	0.191	0.06

Reaction conditions: benzothiophene 1 mmol; Cp_2TiCl_2 0.27 mmol; TBHP 2 mmol; molecular sieve 0.5 g at 30°C.

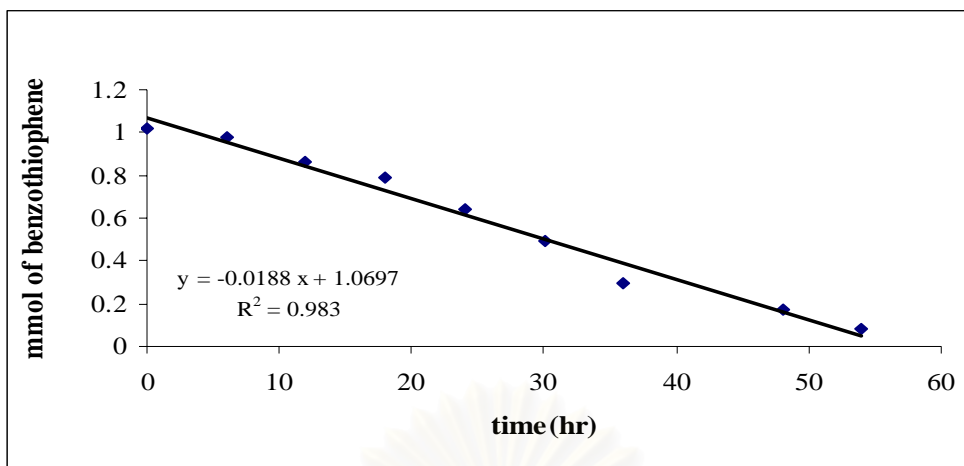


Figure 4.3 The kinetic study of benzothiophene oxidation

From data in Table 4.11 and Figure 4.3 with variation of time, it was found that the time around 48 hours was adequate for the oxidation of benzothiophene at room temperature (30°C). Rate of conversion of benzothiophene under this condition was 18.8 μmol per hour.

4.2.4 Kinetics of dibenzothiophene oxidation

The same procedure as in section 4.2.1 was followed, except that diethyl sulfide was replaced with dibenzothiophene. Dibenzothiophene substrate was monitored by UV-visible spectrometry at $\lambda_{\text{max}} = 237$.

Table 4.12 The kinetic study of dibenzothiophene oxidation

Time (hrs)	Absorbance	dibenzothiophene (mmol)
0	2.687	1.05
30	2.351	0.92
54	1.613	0.63
72	1.170	0.46
102	0.656	0.26
106	0.534	0.21
120	0.236	0.09

Reaction conditions: dibenzothiophene 1 mmol; Cp_2TiCl_2 0.27 mmol; TBHP 2 mmol; molecular sieve 0.5 g at 30°C.

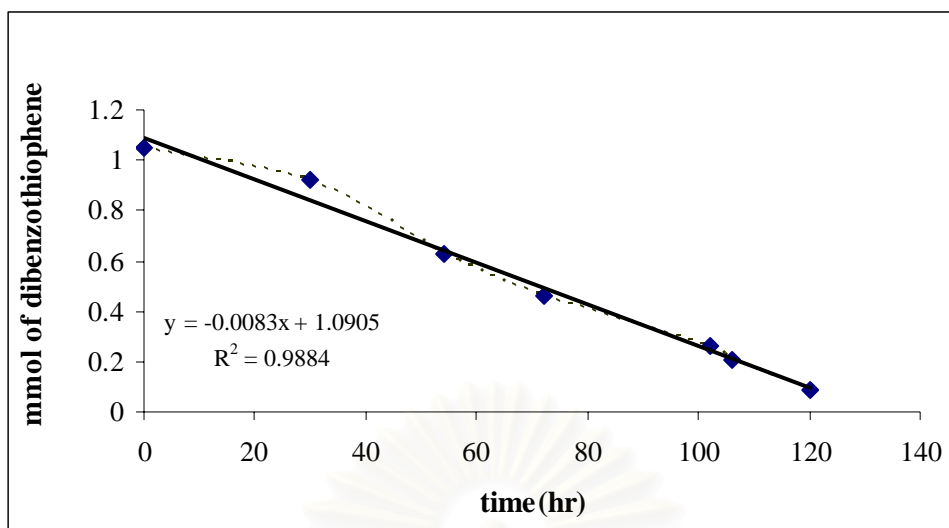


Figure 4.4 The kinetic study of dibenzothiophene oxidation.

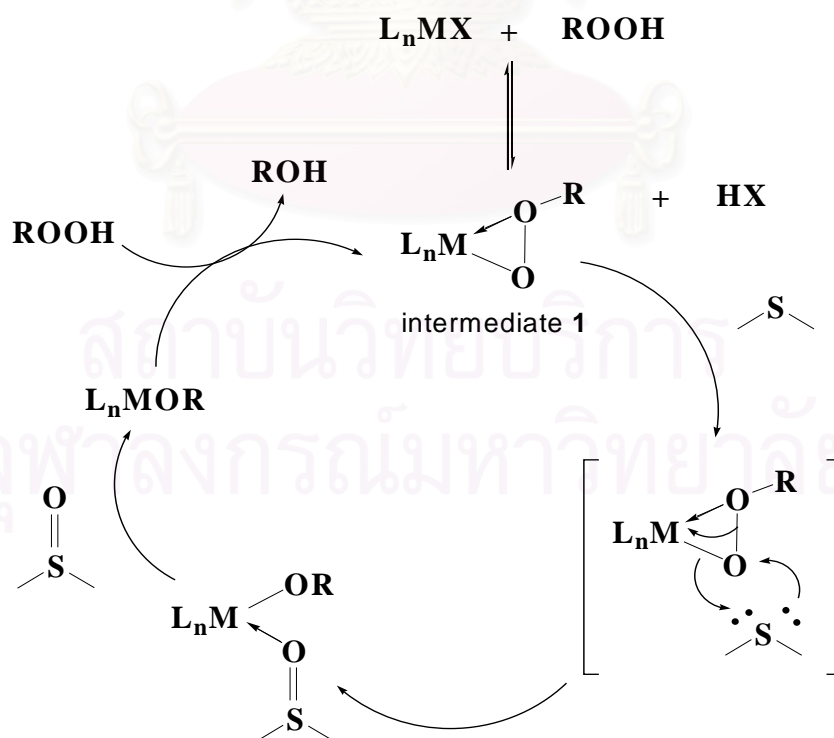
From data in Table 4.12 and Figure 4.4 with variation of time, it was found that conversion of dibenzothiophene increases with time. The reaction was initially slow (before 30 hrs). Rate of conversion of dibenzothiophene under this condition was $8.3 \mu\text{mol}$ per hour. The slow rate is caused by the steric effect of the catalyst. When using strong oxidizing power catalyst, e.g. $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{H}_2\text{O}_2$ system, the rate of dibenzothiophene oxidation was reported to be $5.26 \times 10^3 \mu\text{mol}$ per hour with only sulfone as product, while in this work, the $\text{Cp}_2\text{TiCl}_2/\text{TBHP}$ gave sulfoxide and sulfone as products.

Comparing rate of the oxidation for different sulfur compounds, the order is: diethyl sulfide > thiophene > benzothiophene > dibenzothiophene. Generally, trend for sulfur compounds oxidation reactivity is: methyl phenyl sulfide > diphenyl sulfide > 4-methyldibenzothiophene > dibenzothiophene > benzothiophene > thiophene. Interestingly, in titanocene system, the oxidation reactivity of the sulfur compounds showed the reverse trend, due to the steric hindrance of sulfur compounds and cyclopentadienyl groups in titanocene.

4.3 Proposed Mechanism for the Titanium-TBHP Catalyzed Oxidation of Sulfur Compounds

From the obtained results, they showed that sulfoxide is a major product from sulfur compounds oxidation and sulfone is the second product. When time was increased, % yield of sulfoxide was decreased while % yield of sulfone was increased. It is suggested that the oxidation reaction was continued. This conclusion was confirmed by the kinetic data obtained above which show that substrate (sulfur compounds) was changed to the first product (sulfoxide) and then it was converted further to the second product (sulfone).

In this work, mechanism of sulfur compounds oxidation was proposed as shown in Scheme 4.1. L_nMX (Cp_2TiCl_2) catalyst was reacted with oxidizing agent (TBHP) to give electrophilic intermediate **1** (peroxo-titanium complex), together with acid (HX). This reaction may be reversible. A chloride leaving group favors the formation of intermediate **1**, faster generation of this catalytic species, therefore, enhancing the reaction rate. The intermediate reacted further with sulfur compound to give sulfoxide and sulfone products.



Scheme 4.1 Mechanism for the titanium-TBHP catalyzed oxidation of sulfur compounds.

4.4 Characterization of Products from Oxidation Reaction

4.4.1 Fourier Transform Infrared Spectrometer (FT-IR)

The infrared spectroscopy is an effective method to identify sulfur compound. It is sufficient to characterize the functional groups of sulfoxide and sulfone in the wave number of 1070-1030 and 1160-1140, 1230-1150 cm^{-1} . The spectra of diethyl sulfide, diethyl sulfoxide and diethyl sulfone were in Figure 4.5 and Table 4.11. The spectra of thiophene, thiophene sulfoxide and thiophene sulfone were shown in Figure 4.6 and Table 4.12. Benzothiophene, benzothiophene sulfoxide and benzothiophene sulfone spectra were in Figure 4.7 and Table 4.13. Spectra of dibenzothiophene, dibenzothiophene sulfoxide and dibenzothiophene sulfone were in Figure 4.8 and Table 4.14.

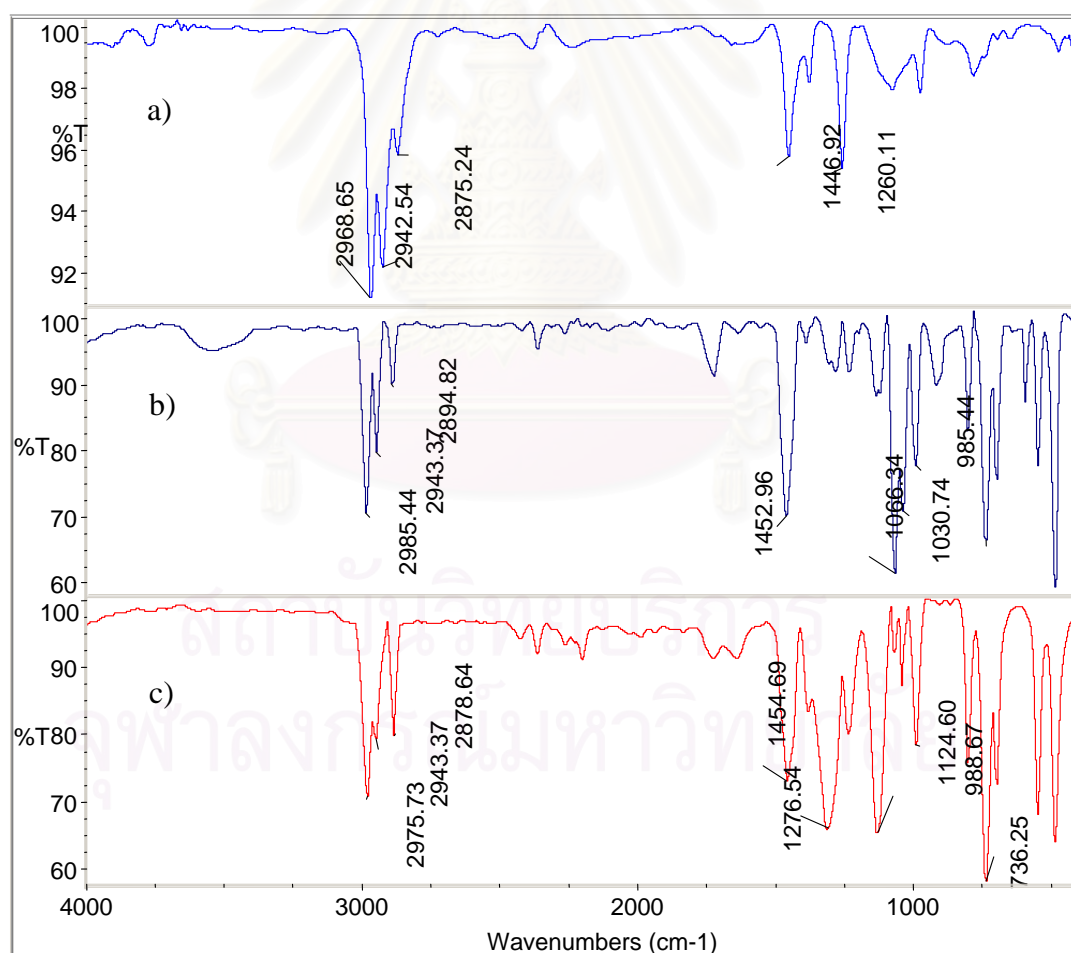


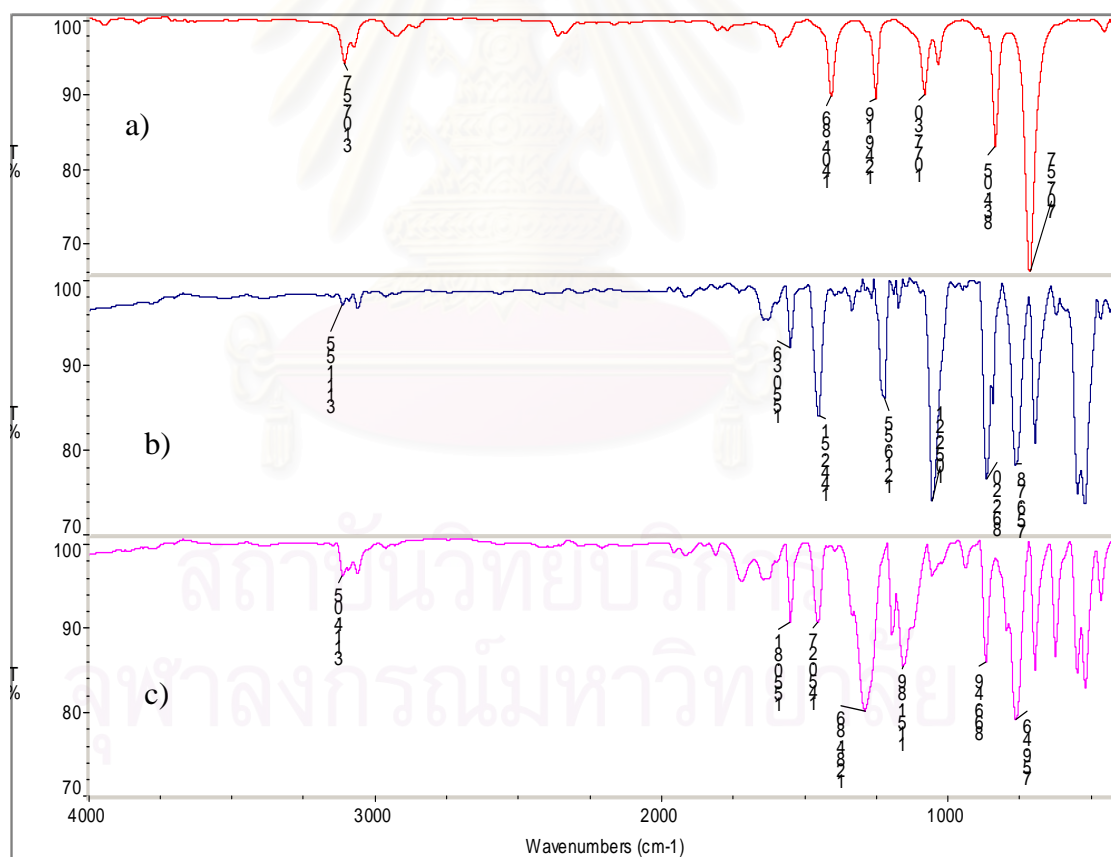
Figure 4.5 FT-IR spectra of the diethyl sulfide and products.

a) Diethyl sulfide b) Diethyl sulfoxide c) Diethyl sulfone.

Table 4.13 FT-IR data of the diethyl sulfide, diethyl sulfoxide and diethyl sulfone

Wave number (cm ⁻¹)	Assignment
700-600	C-S stretching
1030	S=O stretching of sulfoxide
1124, 1276	S=O stretching of sulfone
1475-1450	C-H bending in alkyl chain

From the IR spectrum of diethyl sulfoxide (Figure 4.5, b) and diethyl sulfone (Figure 4.5, c) as comparing with diethyl sulfide (Figure 4.5, a), it could be observed that the absorption band of S=O stretching of sulfoxide and S=O stretching of sulfone were clearly observed at 1030, 1124 and 1276 cm⁻¹ respectively.

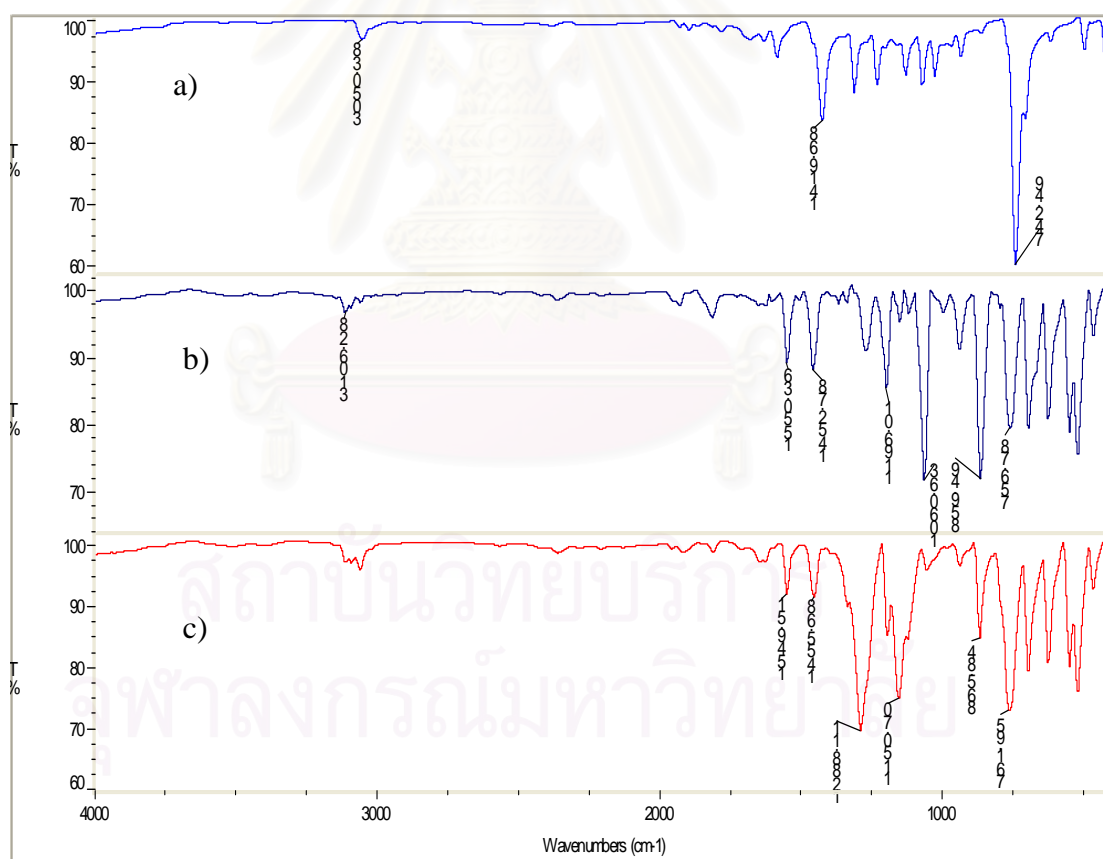
**Figure 4.6** FT-IR spectra of the thiophene and products.

a) Thiophene b) Thiophene sulfoxide c) Thiophene sulfone.

Table 4.14 FT-IR data of the thiophene, thiophene sulfoxide and thiophene sulfone

Wave number (cm^{-1})	Assignment
700-600	C-S stretching
1052	S=O stretching of sulfoxide
1151, 1284	S=O stretching of sulfones
1600-1500	C=C stretching (aromatic)

From the IR spectrum of thiophene sulfoxide (Figure 4.6, b) and thiophene sulfone (Figure 4.6, c) as comparing with thiophene (Figure 4.6, a), it could be observed that the absorption band of S=O stretching of sulfoxide and S=O stretching of sulfone were clearly observed at 1052, 1151, and 1284 cm^{-1} respectively

**Figure 4.7** FT-IR spectra of the benzothiophene and products.

a) Benzothiophene b) Benzothiophene sulfoxide c) benzothiophene sulfone

Table 4.15 FT-IR data of the benzothiophene, benzothiophene sulfoxide and benzothiophene sulfone

Wave number (cm^{-1})	Assignment
700-600	C-S stretching
1060	S=O stretching of sulfoxide
1150, 1288	S=O stretching of sulfone
1600-1500	C=C stretching (aromatic)

From the IR spectrum of benzothiophene sulfoxide (Figure 4.7, b) and benzothiophene sulfone (Figure 4.7, c) as comparing with benzothiophene (Figure 4.7, a), it could be observed that the absorption band of S=O stretching of sulfoxide and S=O stretching of sulfone were clearly observed at 1060, 1150, and 1288 cm^{-1} respectively

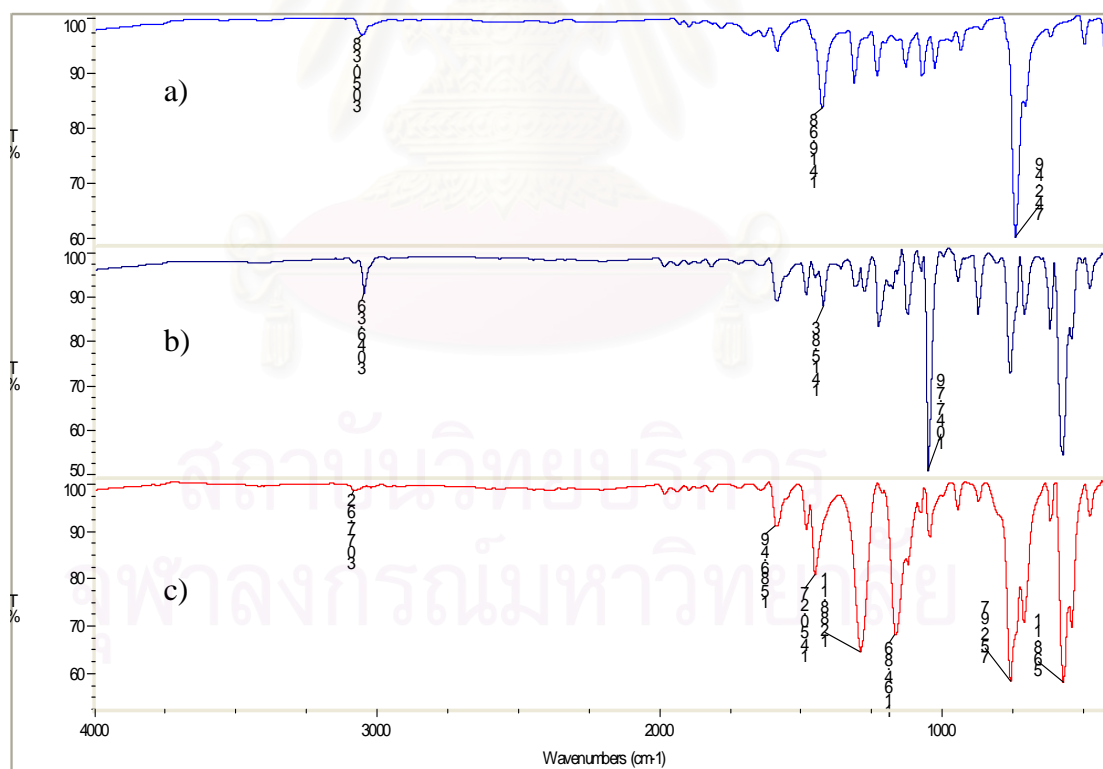


Figure 4.8 FT-IR spectra of the dibenzothiophene and products.

a) Dibenzothiophene b) Dibenzothiophene sulfoxide c) Dibenzothiophene sulfone.

Table 4.16 FT-IR data of the dibenzothiophene, dibenzothiophene sulfoxide and dibenzothiophene sulfone

Wave number (cm ⁻¹)	Assignment
700-600	C-S stretching
1047	S=O stretching of sulfoxide
1164, 1288	S=O stretching of sulfone
1600-1500	C=C stretching (aromatic)

From the IR spectrum of dibenzothiophene sulfoxide (Figure 4.8, b) and dibenzothiophene sulfone (Figure 4.8, c) as comparing with dibenzothiophene (Figure 4.8, a), it could be observed that the absorption band of S=O stretching of sulfoxide and S=O stretching of sulfone were clearly observed at 1047, 1164, and 1288 cm⁻¹ respectively

4.4.2 Gas chromatography-Mass spectrometry (GC-MS)

The GC-MS is an effective method to identify sulfur compounds. MS spectra of the diethyl sulfoxide and diethyl sulfone were shown in Figures 4.9 and 4.10. Thiophene sulfoxide and thiophene sulfone spectra were displayed Figures 4.11 and 4.12. Benzothiophene sulfoxide and benzothiophene sulfone spectra were in Figures 4.13 and 4.14. Dibenzothiophene sulfoxide and dibenzothiophene sulfone spectra were shown in Figures 4.15 and 4.16.

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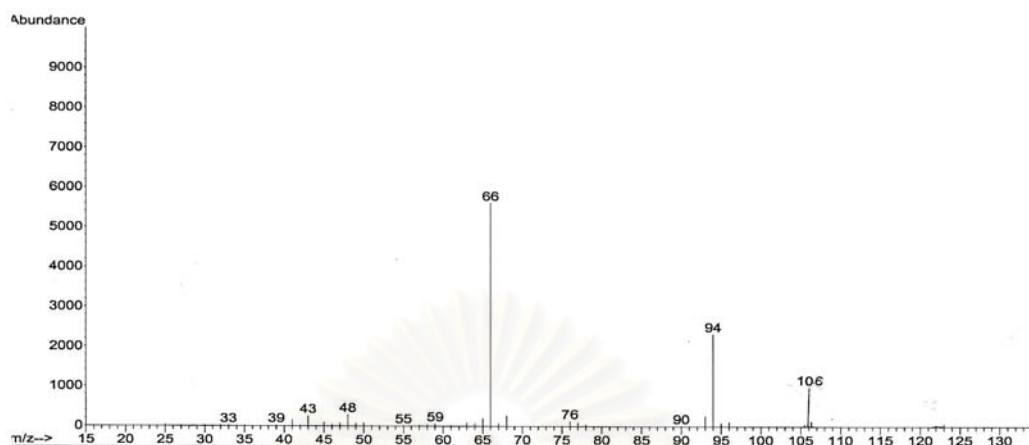


Figure 4.9 MS spectrum of diethyl sulfoxide.

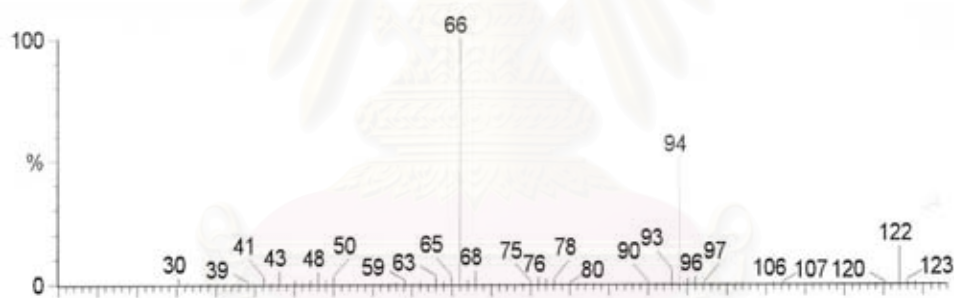


Figure 4.10 MS spectrum of diethyl sulfone.

Diethyl sulfoxide and diethyl sulfone are the products from the oxidation of diethyl sulfide catalyzed by Cp_2TiCl_2 . GC-MS spectra (Figures 4.9 and 4.10) showed $m/z = 106$ and 122 , which are the molecular mass of diethyl sulfoxide and diethyl sulfone respectively.

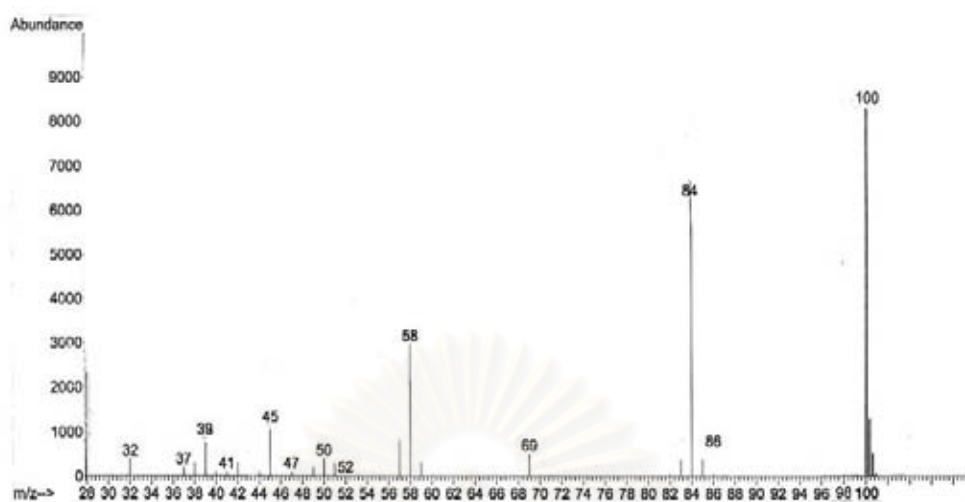


Figure 4.11 MS spectrum of thiophene sulfoxide.

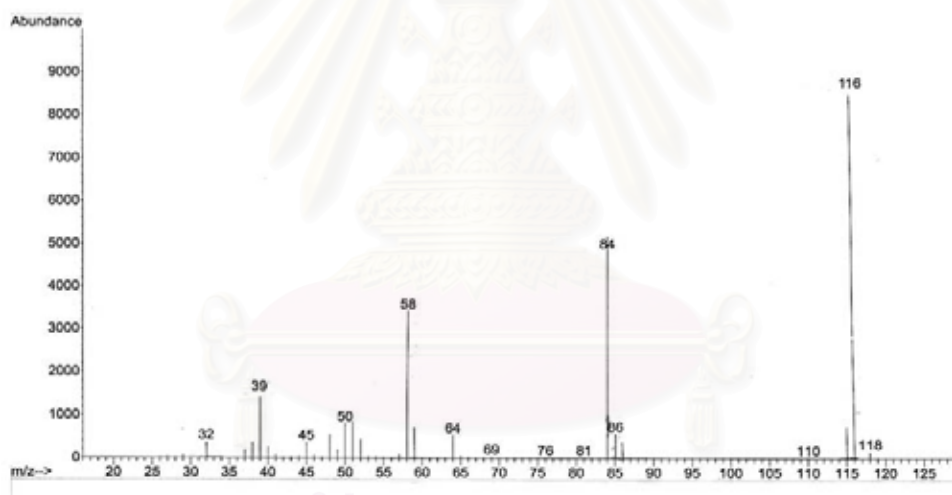


Figure 4.12 MS spectrum of thiophene sulfone.

GC-MS spectra in Figures 4.11 and 4.12 show molecular peak of thiophene sulfoxide and thiophene sulfone respectively. At $m/z = 100$ which is the molecular mass of thiophene sulfoxide and $m/z = 116$ which is the molecular mass of thiophene sulfone.

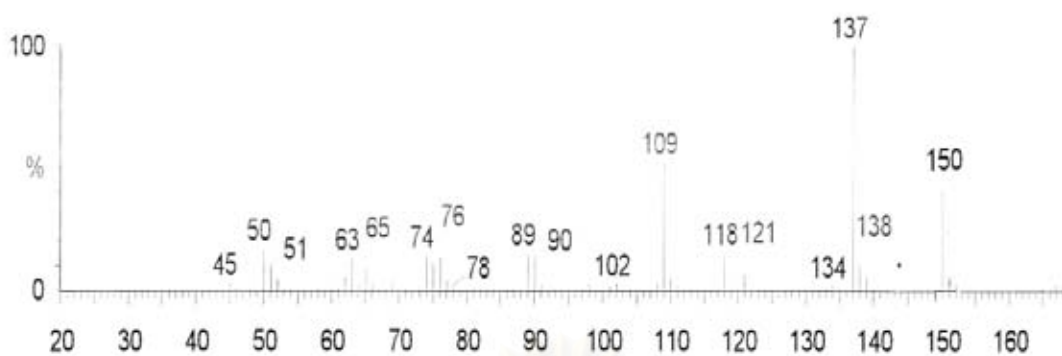


Figure 4.13 MS spectrum of benzothiophene sulfoxide.

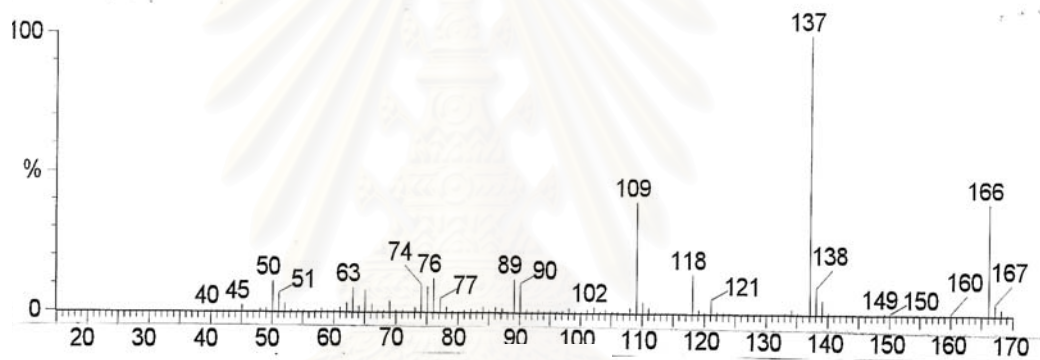


Figure 4.14 MS spectrum of benzothiophene sulfone.

GC-MS spectra in Figures 4.13 and 4.14 show molecular peak of benzothiophene sulfoxide and benzothiophene sulfone respectively. At $m/z = 150$ which is the molecular mass of benzothiophene sulfoxide and $m/z = 166$ which is the molecular mass of benzothiophene sulfone.

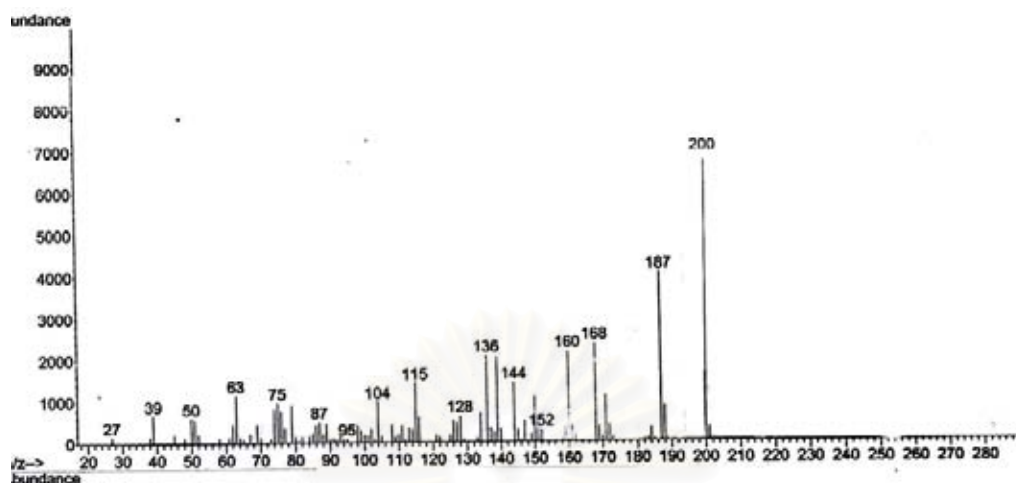


Figure 4.15 MS spectrum of dibenzothiophene sulfoxide.

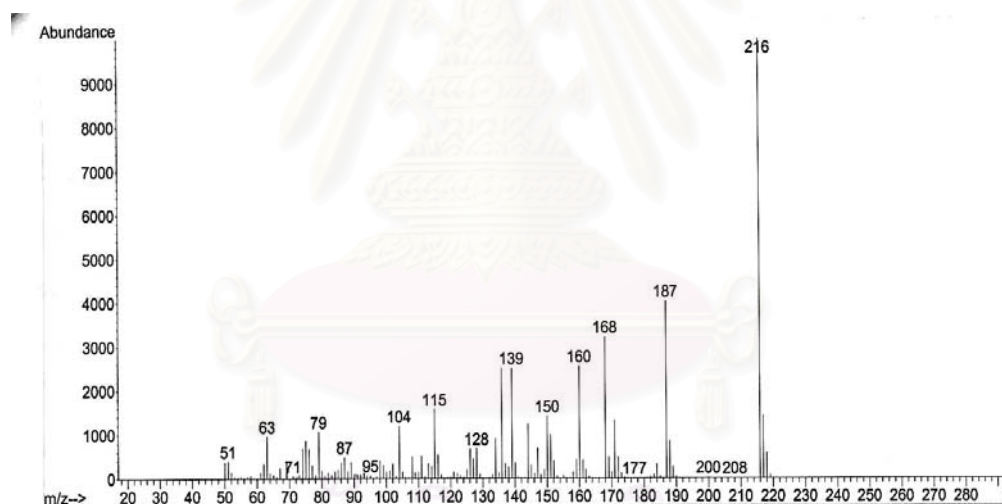


Figure 4.16 MS spectrum of dibenzothiophene sulfone.

GC-MS spectra in Figures 4.15 and 4.16 show molecular peak of dibenzothiophene sulfoxide and dibenzothiophene sulfone respectively. At $m/z = 200$ which is the molecular mass of dibenzothiophene sulfoxide and $m/z = 216$ which is the molecular mass of dibenzothiophene sulfone.

4.4.3 Nuclear Magnetic Resonance Spectrometer(NMR)

Proton nuclear magnetic resonance (^1H NMR) is a tool for molecular structure analysis. The chemical shift of the diethyl sulfide, diethyl sulfoxide and diethyl sulfone spectra were shown in Figures 4.16, 4.17 and 4.18. Figures 4.19, 4.20 and 4.21 are the spectrum of thiophene, thiophene sulfoxide and thiophene sulfone respectively. The spectra of benzothiophene and these products were presented in Figures 4.22-4.24. Figure 4.25-4.27 were indicated the chemical shift of dibenzothiophene, dibenzothiophene sulfoxide and dibenzothiophene sulfone.

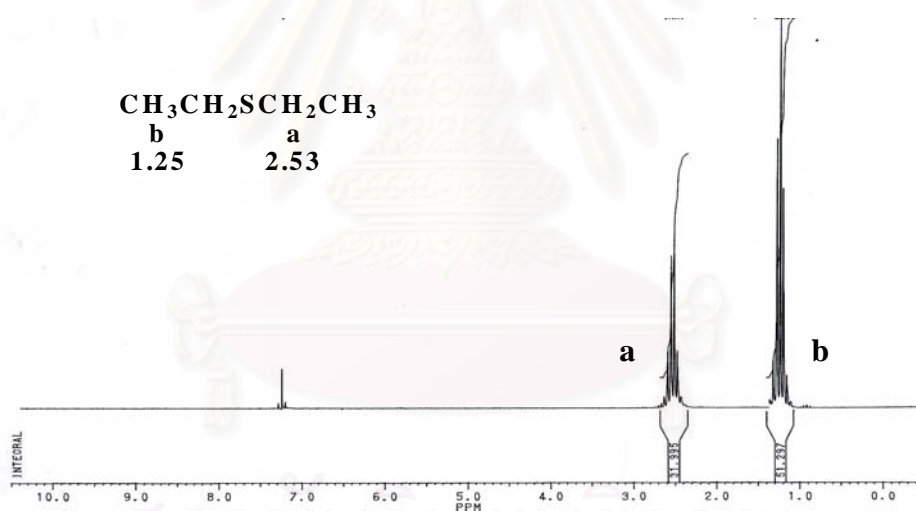


Figure 4.17 ^1H NMR spectrum of the diethyl sulfide (CDCl_3).

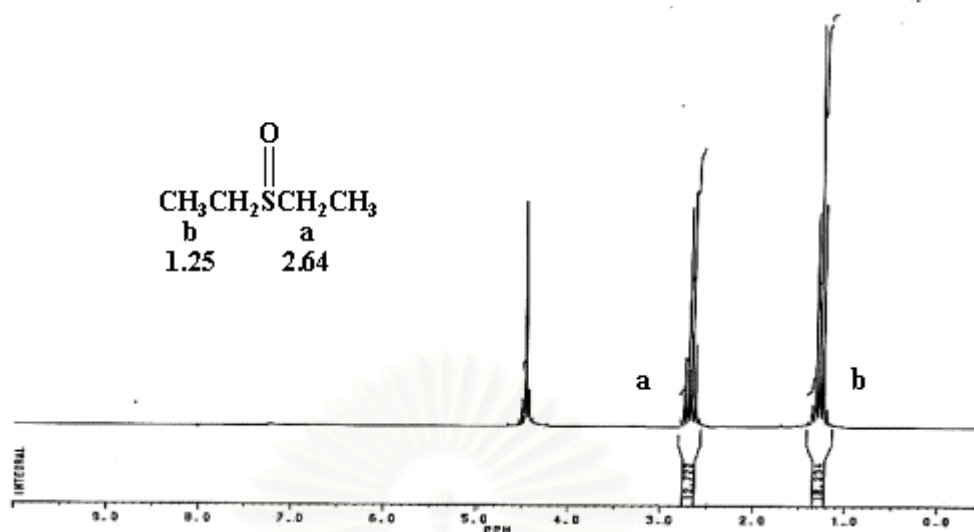


Figure 4.18 ^1H NMR spectrum of the diethyl sulfoxide (D_2O).

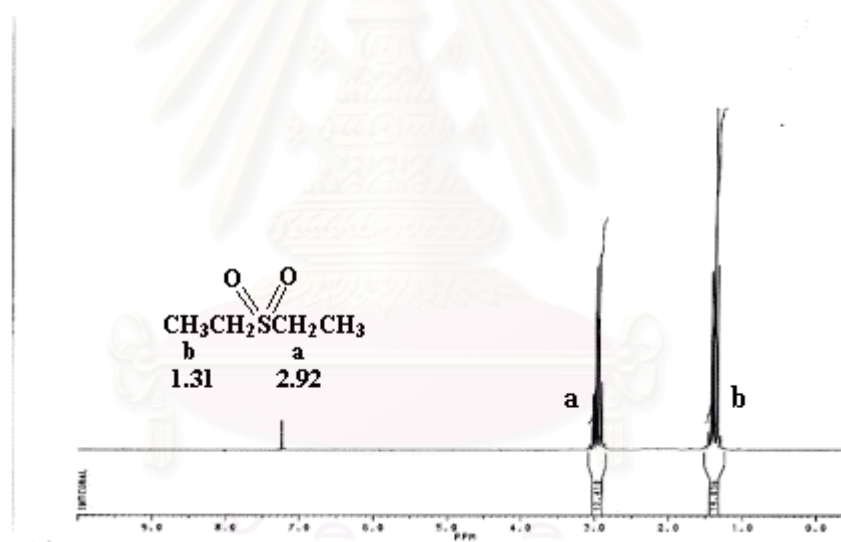


Figure 4.19 ^1H NMR spectrum of the diethyl sulfone (CDCl_3).

Figures 4.17-4.19 show the spectra of diethyl sulfide and products. The spectrum revealed that a proton near the $\text{S}=\text{O}$ in molecule, shifted to higher chemical shift from 2.53 to 2.64 ppm. This can be explained by the electron withdrawing effect from O atom which caused the deshielding. For diethyl sulfone of which SO_2 affected more to the proton nearby, the resonance shifted further downfield from diethyl sulfoxide (2.92 ppm).

The ^1H NMR spectra of thiophene, benzothiophene, dibenzothiophene and their oxidized products were presented in Figures 4.20-4.28.

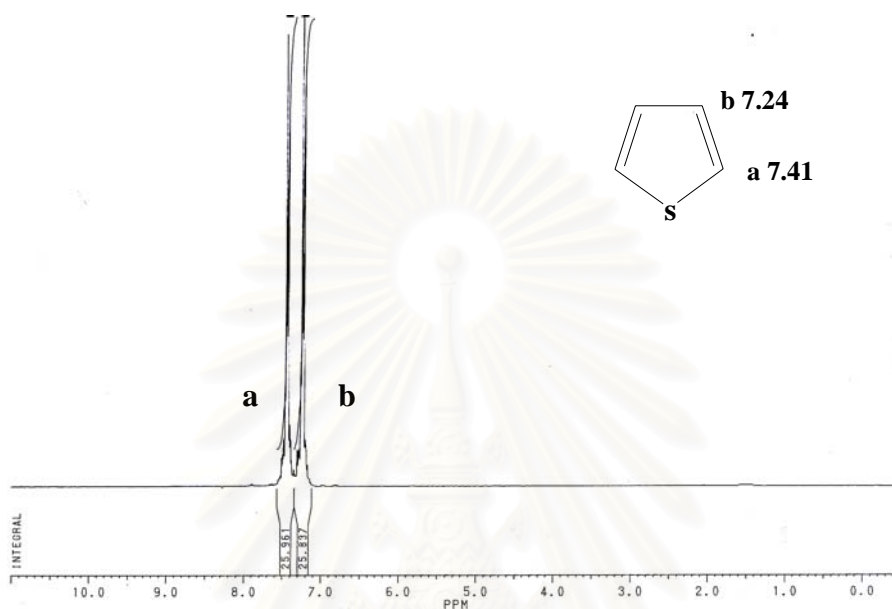


Figure 4.20 ^1H NMR spectrum of the thiophene (CDCl_3).

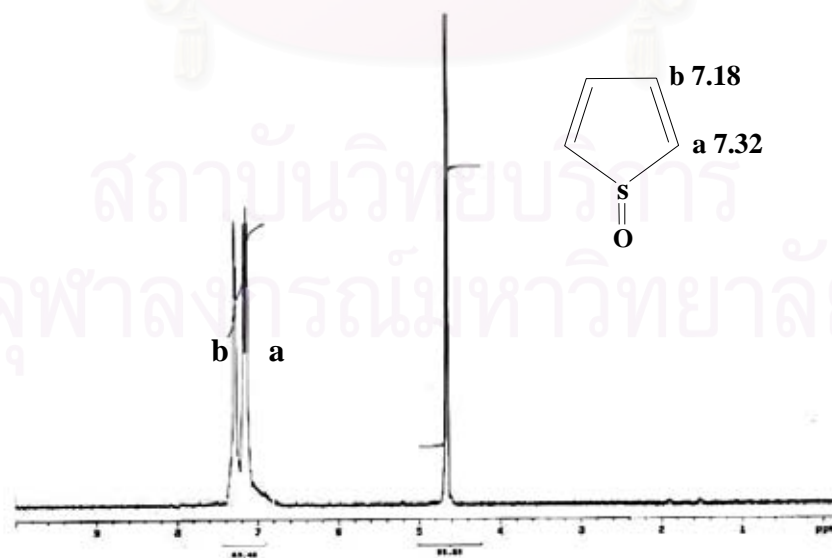


Figure 4.21 ^1H NMR spectrum of the thiophene sulfoxide (D_2O).

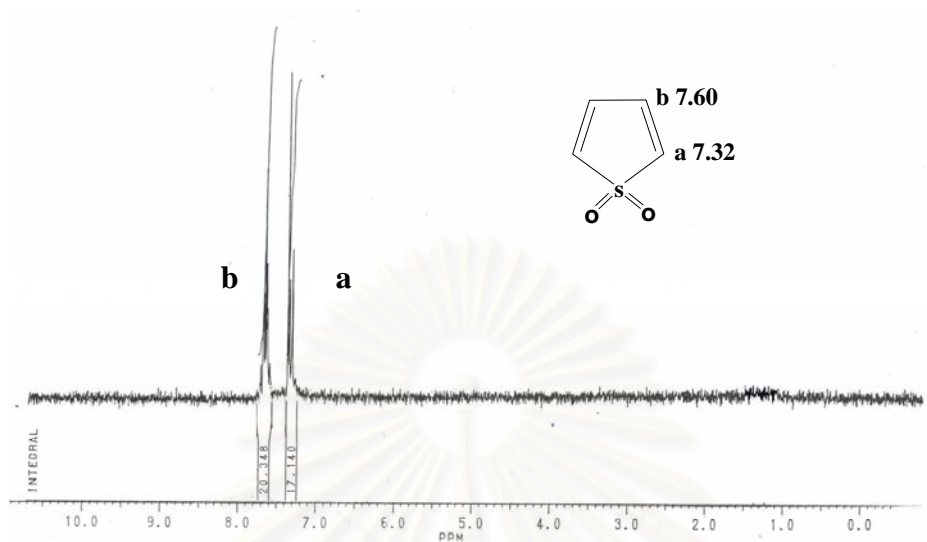


Figure 4.22 ^1H NMR spectrum of the thiophene sulfone (CDCl_3).

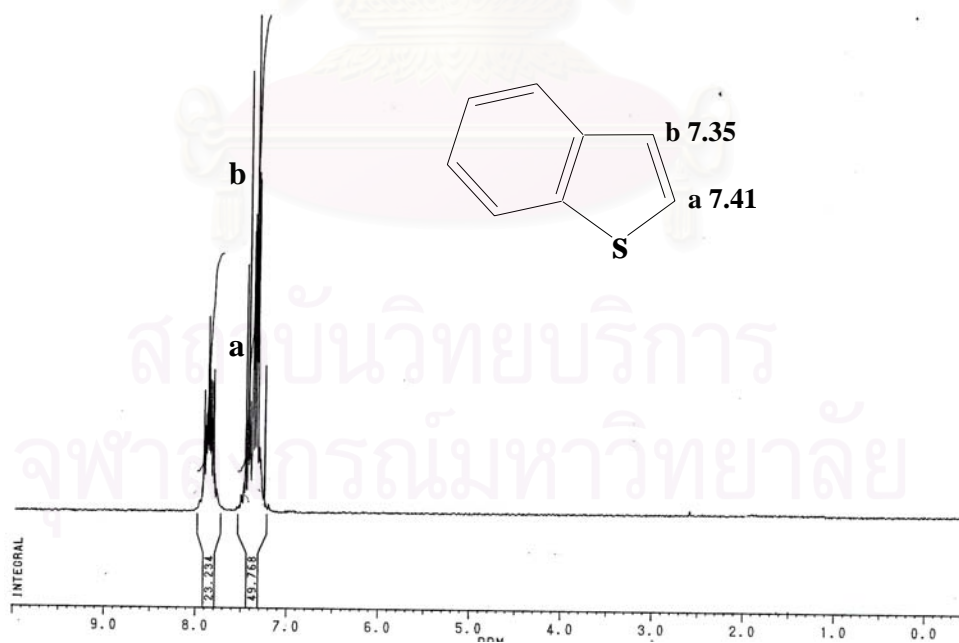


Figure 4.23 ^1H NMR spectrum of the benzothiophene (CDCl_3).

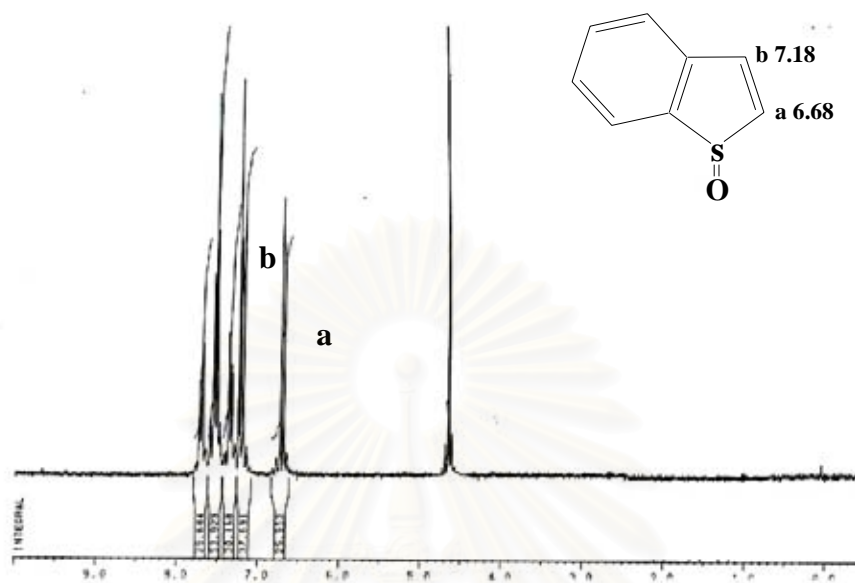


Figure 4.24 ^1H NMR spectrum of the benzothiophene sulfoxide (D_2O).

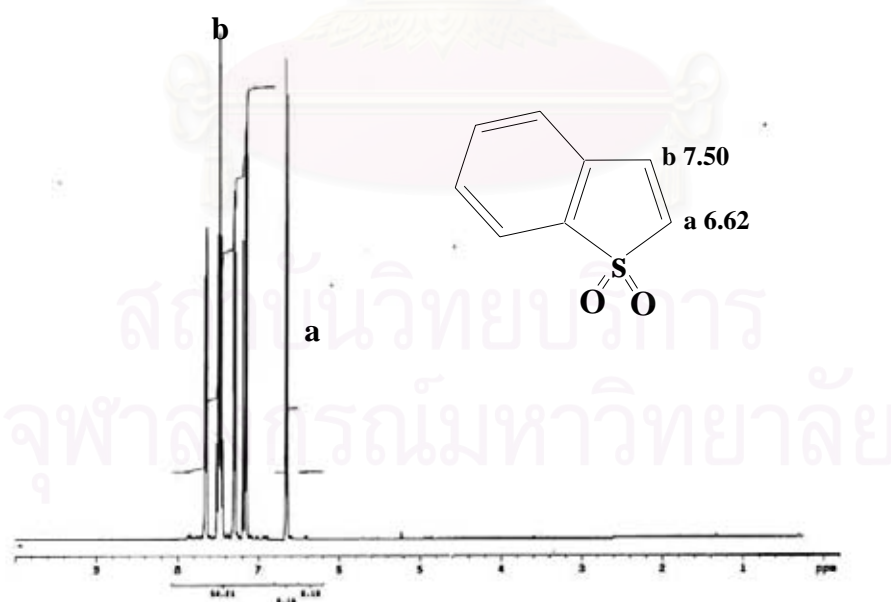


Figure 4.25 ^1H NMR spectrum of the benzothiophene sulfone (CDCl_3).

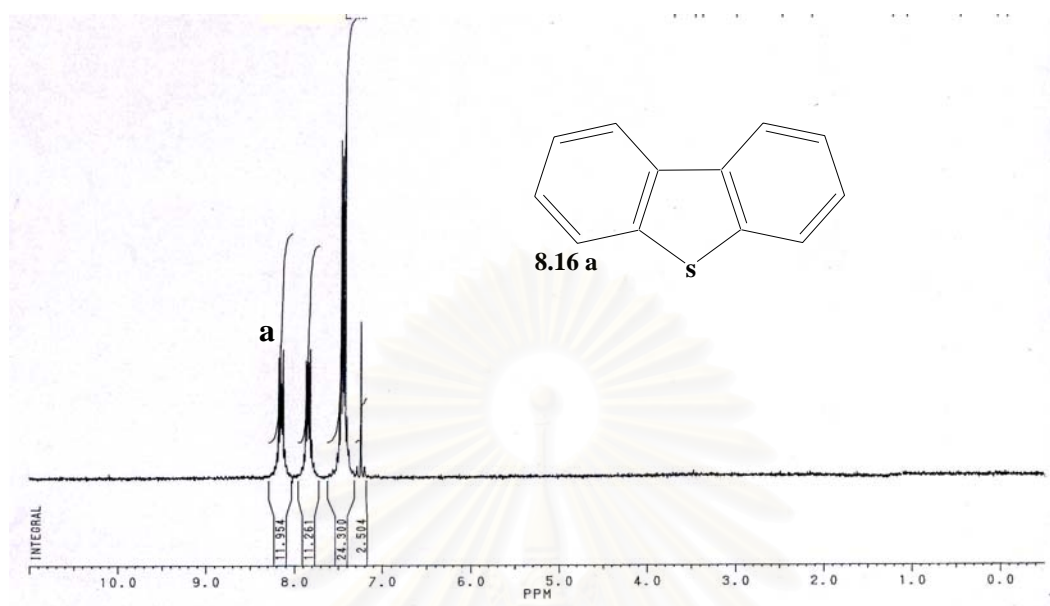


Figure 4.26 ^1H NMR spectrum of the dibenzothiophene (CDCl_3).

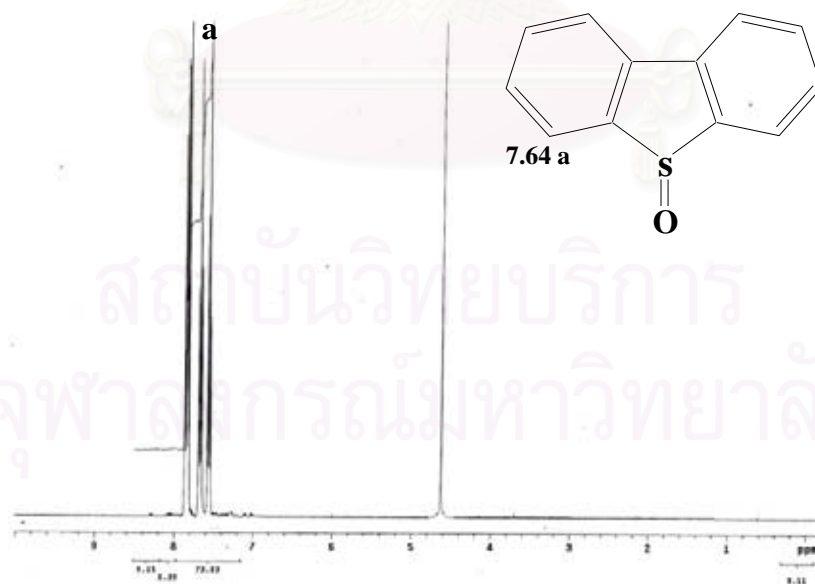


Figure 4.27 ^1H NMR spectrum of the dibenzothiophene sulfoxide (D_2O).

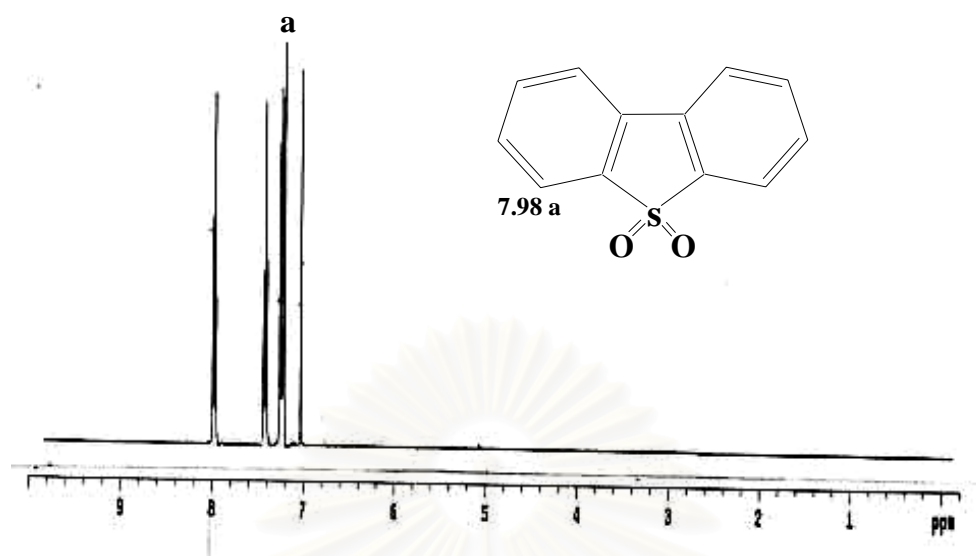
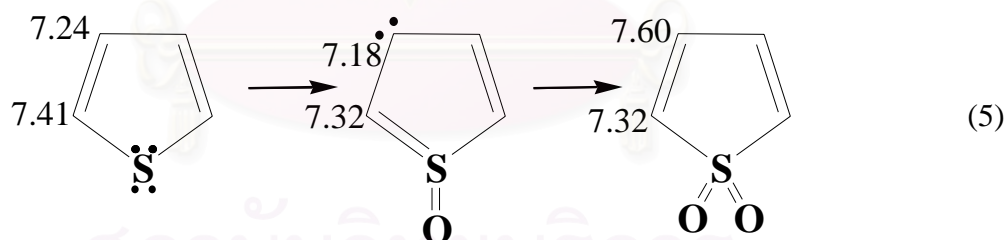


Figure 4.28 ^1H NMR spectrum of the dibenzothiophene sulfone (CDCl_3).

In all of these compounds it was found that the resonances of protons belonging to sulfoxide products and sulfone products were shifted upfield compared with those of the substrate, this is in contrast to the results obtained from the sulfide series. It can be explained by the equation below (thiophene).



For thiophene sulfoxide, the chemical shift of proton at the ortho position is shifted upfield (from 7.41 to 7.18 ppm) because a lone pair electron on the sulfur atom can delocalize in the ring. Meanwhile the downfield shift for the proton at the meta position resulted from the favor resonance as shown.

In thiophene sulfone, all lone pair electrons of sulfur atom were bonded to oxygen atoms, therefore, the chemical shifts of protons at ortho and meta positions were affected less (from 7.18 to 7.32, from 7.32 to 7.60 ppm).

CHAPTER V

CONCLUSION AND SUGGESTION

From the proceeding results and discussions, the main focus of this research is to search for the optimum conditions for the oxidation of sulfur compounds (diethyl sulfide, thiophene, benzothiophene and dibenzothiophene) catalyzed by titanocene.

In this study, it was found that the solvent system, oxidizing agent, temperature, time and additive affected the oxidation. The optimum condition for diethyl sulfide oxidation to achieve highest yield of diethyl sulfoxide was at -20°C , 4 hrs, titanocene 0.136 mmol, oxidizing 2 mmol, with molecular sieve as additive, and dichloromethane as solvent. The titanocene catalytic system shows high selectivity (mole ratio of sulfoxide/sulfone = 89).

For other substrates (thiophene, benzothiophene and dibenzothiophene) the optimum condition was titanocene 0.27 mmol, oxidizing 2 mmol, with molecular sieve as additive, and dichloromethane as solvent at room temperature (30°C). The optimum time for thiophene, benzothiophene and dibenzothiophene were 24, 48 and 72 hrs respectively. The sulfoxide and sulfone products were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance and gas chromatography - mass spectrometry. The titanocene catalytic system shows selectivity (mole ratio of sulfoxide/sulfone) of 5, 5 and 4 for thiophene, benzothiophene and dibenzothiophene respectively. This results from steric effect of titanocene catalyst.

The kinetic study was performed with initial rate method using UV-visible spectrometry. It can be found that the rate of diethyl sulfide was faster than other substrates. Order of the rate of reaction was: diethyl sulfide > thiophene > benzothiophene > dibenzothiophene, due to the steric hindrance of sulfur compounds and cyclopentadienyl groups in titanocene.

Suggestion for the future work

From all aforementioned results and discussion, the future work should be focused on the following:

1. The oxidation of other sulfur compounds using titanocene as catalyst should be attempted such as 4,6-dimethyl dibenzothiophene.
2. Study the detailed kinetics of the oxidation reaction in order to find rate law of the reaction.



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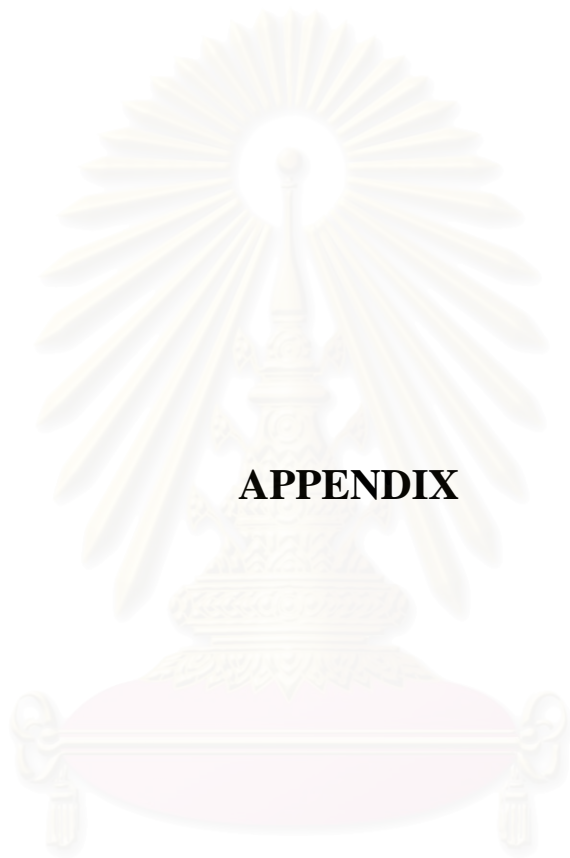
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APPENDIX

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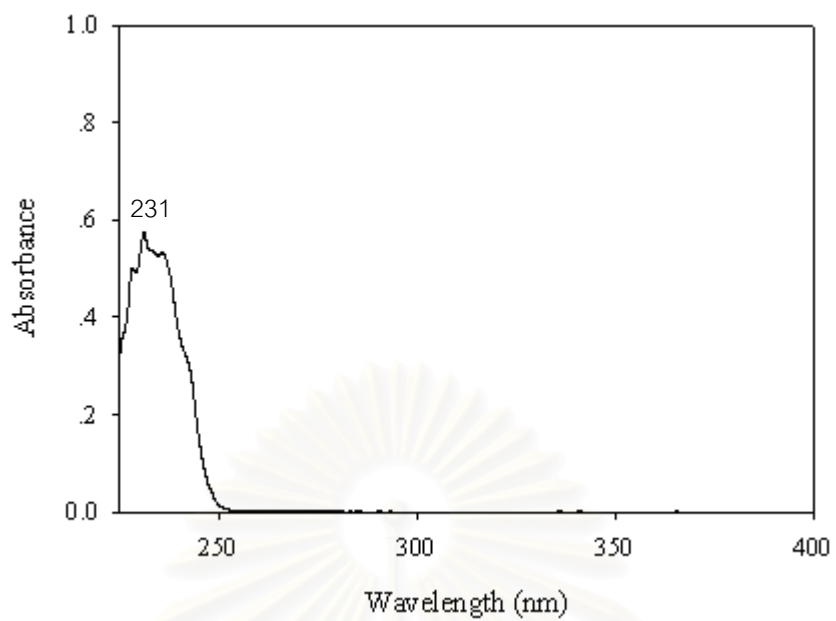


Figure A λ_{\max} of diethyl sulfide

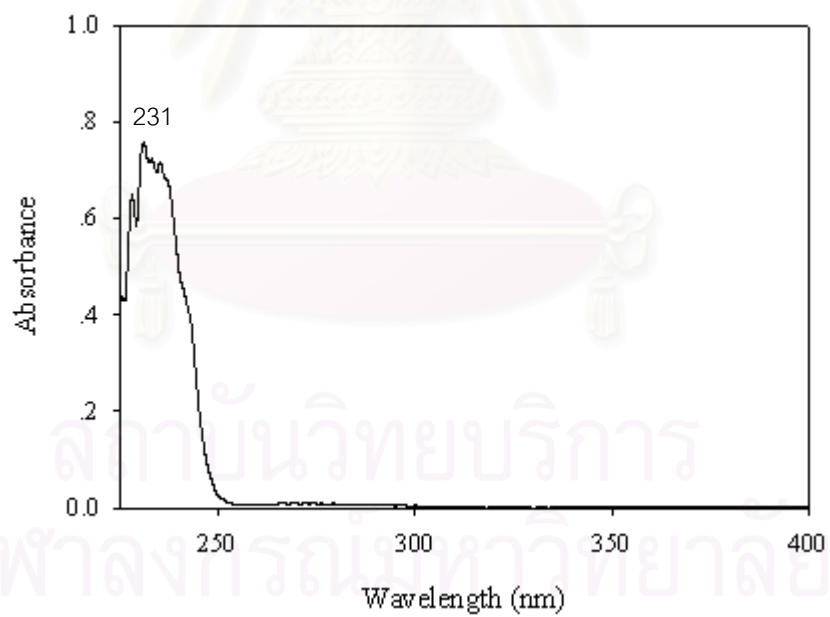


Figure B λ_{\max} of thiophene

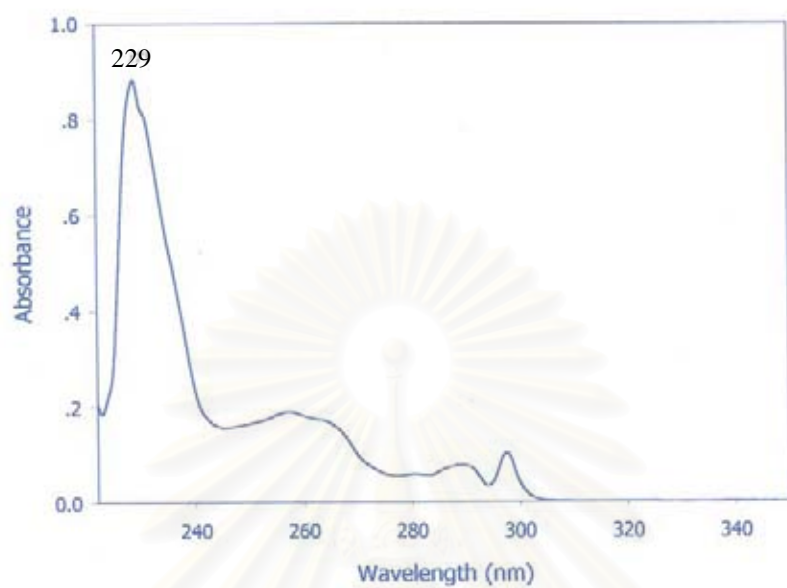


Figure C λ_{\max} of benzothiophene

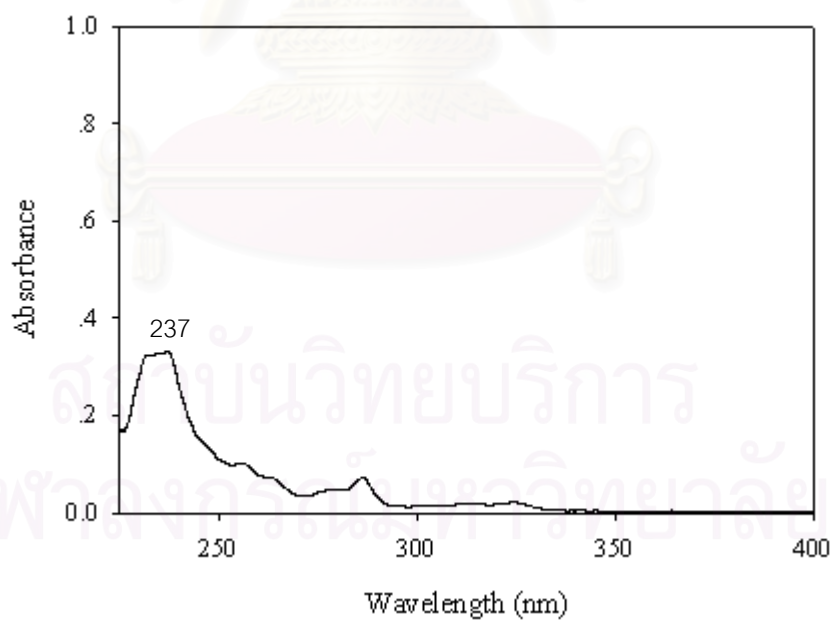


Figure D λ_{\max} of dibenzothiophene

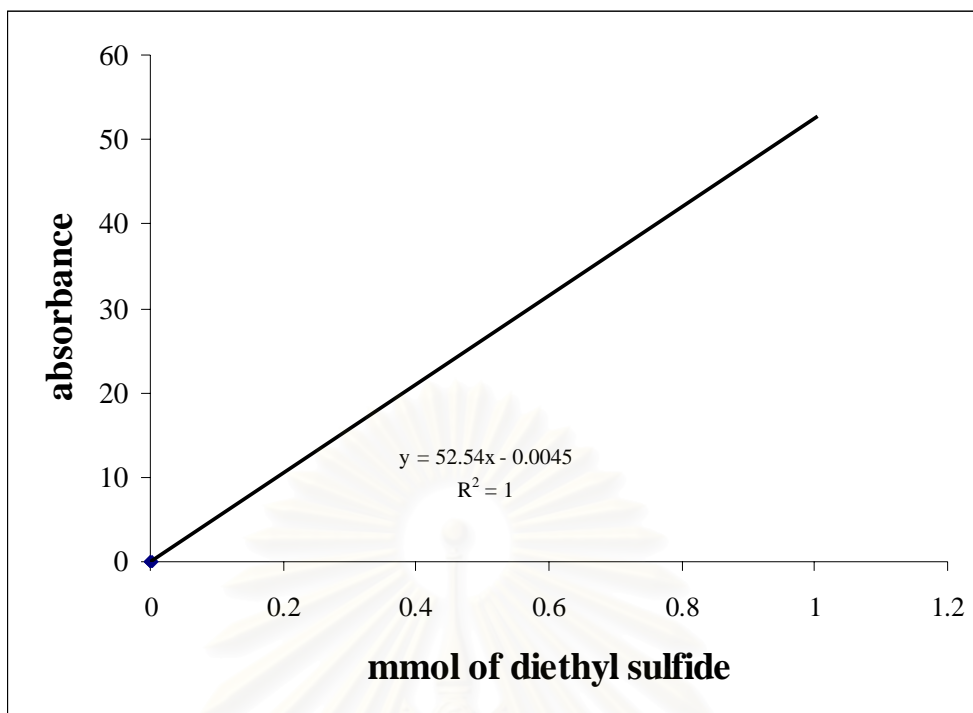


Figure E Standard curve of diethyl sulfide.

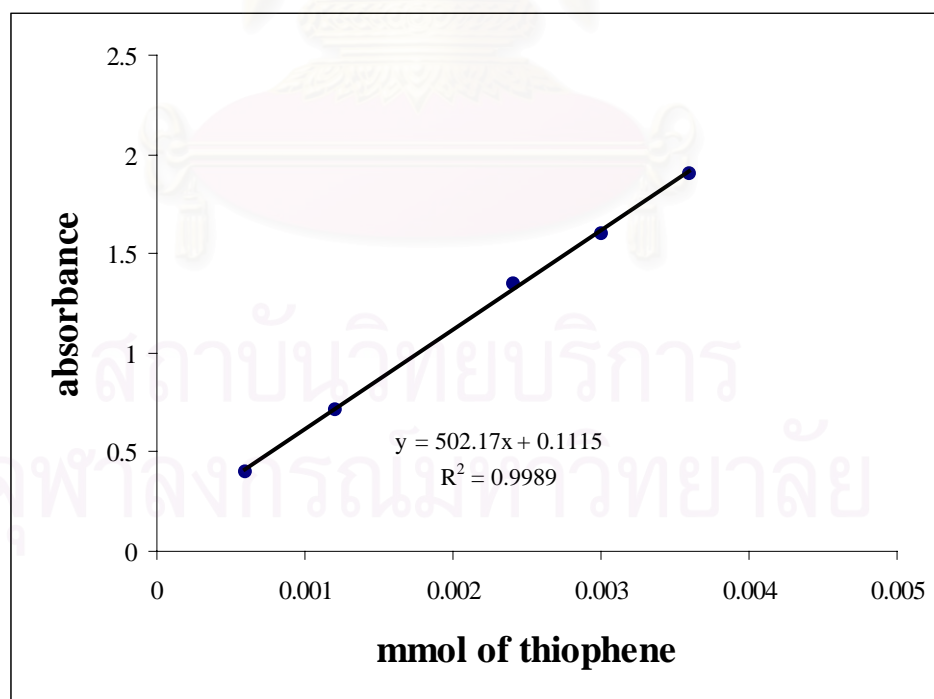


Figure F Standard curve of thiophene.

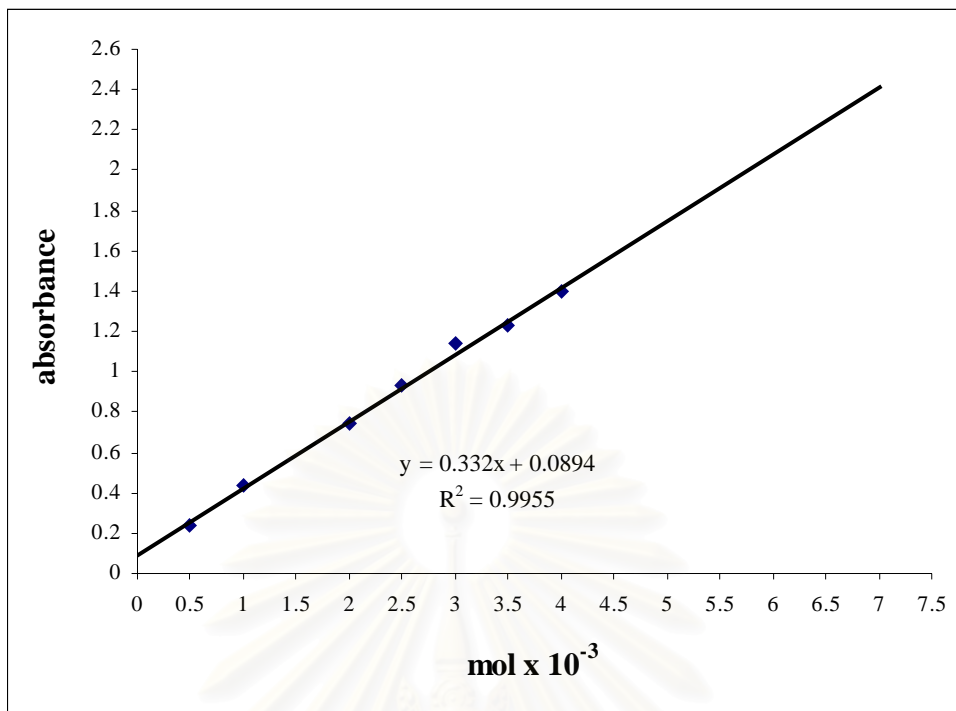


Figure G Standard curve of benzothiophene.

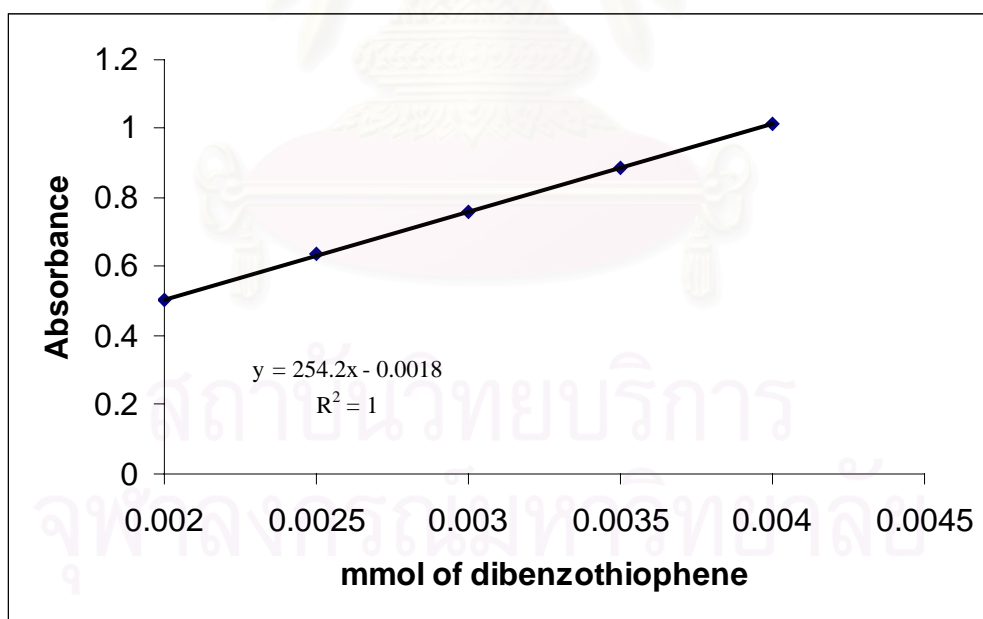
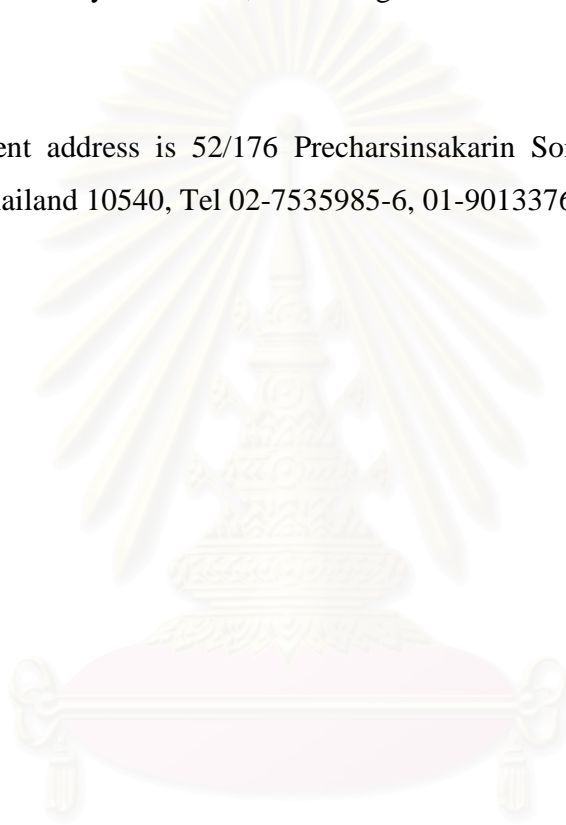


Figure H Standard curve of dibenzothiophene.

VITA

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