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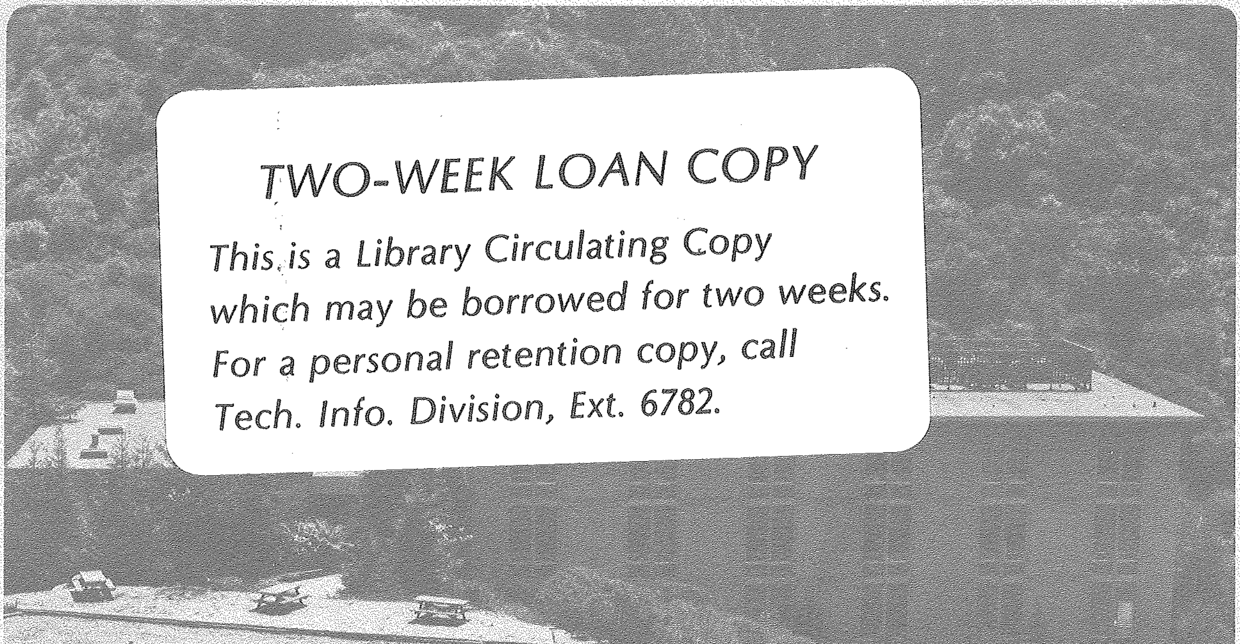

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David Paul Mobley

Abstract

Ether structures are believed to play a key role in linking the macromolecular units present in coal. A number of compounds which model the ether structures found in coal were subjected to reaction in the presence of zinc chloride. Reactions were carried out in a batch autoclave at temperatures between 136°C and 327°C and under hydrogen or nitrogen pressure up to 16.8 MPa.

Both cyclic and non-cyclic ethers reacted, provided that at least one methylene group was adjacent to the ether oxygen atom. Complete elimination of oxygen to form water was achieved with dibenzyl and cycloaliphatic ethers, but oxygen bonded directly to a phenyl or naphthyl group was converted to an unreactive phenolic hydroxyl group. The reaction products observed can be explained in terms of carbonium ion mechanisms similar to those used to explain Friedel-Crafts chemistry. In these mechanisms, the $ZnCl_2$ may be active in either a Lewis acid or a Bronsted acid form.

Further studies were conducted on the reactions of dibenzyl ether using zinc chloride together with either nickel, zinc, or magnesium. These reactions were conducted in cyclohexane solution at 225°C under hydrogen

pressure. The presence of the metallic component, in particular Raney nickel, enhanced the hydrogenolysis of dibenzyl ether while reducing the formation of insoluble resins observed when zinc chloride was used alone. It is proposed that the metal activates molecular H_2 and promotes its reaction with benzylic carbonium ions formed through the action of zinc chloride on dibenzyl ether.

The catalytic activities of nickel, iron, molybdenum, and zinc sulfides for the hydrogenolysis of dibenzyl ether were studied, using the conditions cited for the zinc chloride-metal systems. Nickel sulfide showed very high activity, while the remaining three sulfides were inactive. The addition of $ZnCl_2$ to NiS reduced the activity of the NiS. The presence of H_2 was essential for the progress of the reaction.

Compounds containing sulfur structures similar to those present in coal were reacted in the presence of zinc chloride, under conditions similar to those employed with the ether compounds. Zinc chloride was found to promote removal of sulfur from sulfides and disulfides in which sulfur is bonded to a methylene group, but had no effect on diaryl sulfides, diaryl disulfides, or thiophenic structures. In those cases where sulfur was removed, a significant portion was found to be retained in the $ZnCl_2$ phase. The products obtained from the action of $ZnCl_2$ on the sulfur compounds was consistent with the carbonium ion mechanisms used to interpret the action of $ZnCl_2$ on ether structures.

Alexis T. Bell

Dedication

To Deb
and
to Dad and Mom

Acknowledgments

No wonder of it: sheer plod makes plough down sillion
Shine, and blue-bleak embers, ah my dear,
Fall, gall themselves, and gash gold-vermilion.

from The Windhover
Gerard Manley Hopkins

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CONTENTS

LIST OF TABLES

In the following text, sections II through V are manuscripts which have either already been published in technical journals or have been submitted for publication. Each of these sections is self-contained and can be read independently.

I. Introduction

The United States is currently faced with a shortage of domestically produced liquid fuels while possessing relatively abundant coal reserves. This situation has brought about a renewed interest in conversion of coal to liquid fuels. In order to produce a clean-burning liquid fuel from coal, the organic structure of the coal must undergo chemical bond cleavage (or cracking), hydrogenation, and removal of the heteroatomic elements (that is, oxygen, sulfur, and nitrogen). Experience has shown that in order to perform these chemical processes selectively and at economical process conditions, catalysts are necessary.

One catalyst that has been shown to produce clean liquid fuels from coal with only moderate hydrogen consumption is zinc chloride. However, there is a lack of information about the specific chemical processes which $ZnCl_2$ catalyzes in coal. A thorough understanding of $ZnCl_2$/coal chemistry could enable one to make optimum use of $ZnCl_2$ as a catalyst or to develop improved catalyst systems.

In the present study the effects of $ZnCl_2$ on the oxygen and sulfur structures present in coal have been investigated, using model compounds to represent these structures. These results were then used to develop and test some novel catalyst systems.

As an introduction to the specific investigations that were performed, a survey will be presented of the information available concerning the forms and abundance of organic oxygen and sulfur in coal. The known effects of Lewis acids on oxygen- and sulfur-containing coal model compounds will then be discussed, and a brief look will be taken at some applications of $ZnCl_2$ to coal. Finally, the scope and objectives of the present investigation will be outlined.

Organic Oxygen in Coal

After carbon and hydrogen, oxygen is the third most abundant element in the organic matter of coal on a molar basis. For example, in a representative group of coals used in a study of oxygen type, the weight percent oxygen in the organic portion ranged from 2.0 in a hard coal to 22.6 in a lignite and 27.8 in a brown coal[1]. The quantity of oxygen is usually determined by subtracting the other determined quantities (carbon, hydrogen, sulfur, and nitrogen) from 100 percent. This method naturally concentrates the analytical errors in the oxygen value. However, direct chemical or nuclear activation methods exist for oxygen determination[2].

The oxygen functional groups which appear in coal are phenolic hydroxyls, ethers, carbonyls, and carboxyls. The presence of phenolic hydroxyls can be detected by IR spectrometry, and some investigators have assigned bands in the IR spectra of coal to ethers, but this assignment is ambiguous[3].

A number of chemical methods are available for the quantitative analysis of oxygen functional groups in coal.

In one of the most thorough studies of its kind, Blom et al. were able to identify hydroxyl, carbonyl, carboxyl, and methoxyl groups in vitrains of coals of various rank[1]. The test for peroxides was negative and the approximately 30% of the oxygen unaccounted for by the analyses was assumed to be primarily etheric. Blom et al. correlated the percent of each oxygen type with the percent carbon in the coals, showing that hydroxyl is the predominant functional group, carbonyl exists in small quantity (less than 10%), and methoxyl and carbonyl groups occur only in coals of lower rank. A later study by Sarkar[4], using whole coals, confirmed the conclusions of Blom et al. Again, hydroxyl oxygen was predominant, accounting for 27 to 49% of the total organic oxygen. A direct method for ether oxygen determination was employed by Bhaumik et al.[5]. They concluded that approximately 60% of the oxygen that was unreactive in tests for hydroxyl, carboxyl, and carbonyl was in fact etheric.

In a recent study, Ruberto and Cronauer tested the chemical methods for oxygen group analysis by using them on a mixture of oxygen-containing model compounds[2]. While the methods failed to make proper identifications in some cases, they were in general found to be adequate.

In an effort to further refine the classification of organic oxygen in coal, Yokoyama et al. studied pyridine extracts of coals[6]. From the lack of the appropriate signal for alkyl ethers in the ^{1}H-NMR spectrum of the extracts, it was concluded that the oxygen not identifiable as hydroxyl, carbonyl, or carboxyl must exist either in heterocyclic structures or diaryl ethers. This conclusion, however, may be valid for the extract but not for the coal itself.

While hydroxyls, in particular phenolic hydroxyls, are usually the most abundant oxygen functionality in coal, there is evidence to show that ethers are the most important functionality in a structural sense. Takegami et al. concluded from nitric acid hydrogenolysis of a bituminous coal that the formation of benzene-soluble products could be attributed to the cleavage of ether bonds in the coal.[7] In a more recent study, Ignasiak and Gawlak subjected a high rank vitrinite to reductive alkylation under conditions which would cleave C-O bonds while leaving C-C bonds intact[8]. They concluded that the macromolecular network of the vitrinite was composed of units of number average molecular weight of 600 to 700 primarily linked by ether oxygen. This result is supported by reductive alkylation studies on coals of various rank performed by Wachowska and Pawlak[9]. Their results show that while the number of ether groups varies with coal rank, these groups play a key role in linking the aromatic structures in coal. Finally, Ruberto et al. have concluded from solvation studies that a subbituminous coal consisted primarily of two- and three-condensed-ring structures linked mainly by oxygen[10]. A significant portion of the oxygen in the coal occurred in ethers α or β to aromatic moieties or as furans.

Data given by Ruberto and Cronauer[2] for a bituminous coal can be used to calculate a ratio of carbon atoms to ether linkages of 34. Thus, ether oxygen is relatively abundant and structurally significant. The cleavage of ether bonds is therefore believed to be an important process in coal liquefaction.

Organic Sulfur in Coal

Sulfur occurs in coal in both organic and inorganic forms. The total sulfur content of coals ranges from 0.2 to 10 weight percent with most coals containing between 1.0 and 4.0 weight percent sulfur[11]. The ratio of inorganic to organic sulfur varies, but is usually around 2:1[11].

The functional types of organic sulfur in coal have usually been determined indirectly by identification of compounds in coal extracts rather than coal itself. Roy[12] and, more recently, Ozdemir[13] have identified compounds in coal extracts that can be classified as thiols, disulfides, sulfides, and thiophenes. Similarly, Minra et al. found thiols, disulfides, alkyl and aryl sulfides, saturated heterocyclic sulfur compounds, and dibenzothiophenes in coal extracts, accounting for up to 80% of the organic sulfur in the coals tested[14].

The relative quantity of heterocyclic or thiophenic sulfur has usually been taken to be that amount that is refractory under severe conditions. For example, Thiessen observed that 45% of the organic sulfur in a coal remained in the products after coking and concluded that at least that much of the original sulfur in the coal was heterocyclic[15]. Kavcic[16], using methyl iodide, and Roy[12], using

$KMnO_4$, similarly concluded that the 70% of the sulfur that was unreactive consisted of heterocyclic or ring structures.

In direct chemical determinations using methyl iodide, Pritezhaeva et al. reported 5 to 20% of the organic sulfur occurred in sulfides[17]. Rodionova and Barauskii, using chemical degradation techniques on a variety of coals, observed that the variation in the total organic sulfur content could be attributed to the variation in thiophenic sulfur content[18]. They also noted that no thiols were detected. This final result is consistent with the view of Attar and Corcoran, who suggest that thiols and disulfides are too weak to have survived the coalification process[11]. They reason that thiols and disulfides could appear in coal products as a result of reactions between inorganic sulfur and the organic matrix of coal.

While there is a shortage of definitive analyses on sulfur functionalities in coal, the available evidence indicates that a majority of the organic sulfur exists in thiophenic structures. This is an important result because sulfur must be removed from coal to produce a clean-burning fuel and because thiophenic structures are very stable. Aitken et al. have shown, for example, that dibenzothiophene is thermally stable to 950°C[19]. Thus a catalyst or reagent is necessary to affect complete sulfur removal from coal.

Effects of Lewis Acids on Oxygen- and Sulfur-Containing Coal Model Compounds

Table I-1 is a list of reactions of oxygen- and sulfur-containing coal model compounds which are promoted by Lewis acids, and in particular, metal halide catalysts. A class of reaction between ethers and strong Lewis acids can be shown, using aluminum chloride as an example, as

$$R_2O + AlCl_3 \rightarrow R_2O{:}AlCl_3 \rightarrow ROAlCl_2 + RCl$$

In this reaction, quite high temperatures are often required for the decomposition of the complex. Further references to this reaction can be found elsewhere[20,21], but have not been included in the table because the Lewis acid is not acting catalytically in this case. Similar reactions between Lewis acids and sulfides are also known[22].

From the table one can see that benzyl ethers are susceptible to reaction in the presence of Lewis acids. The products seem to result from a combination of intramolecular and intermolecular reactions in which the bond between the ether oxygen and the benzyl portion is cleaved[26,27,29]. In contrast, phenyl ethers are at best only slightly reactive, even under rather severe conditions.

Phenolic hydroxyl compounds are hydrogenated in the presence of $ZnCl_2$ at elevated temperatures and hydrogen pressures. In some cases, such as β-naphthol, dehydroxylation also occurs.

Sulfides appear to behave similarly to their analogous ethers. Alkyl or benzyl sulfides are cleaved by the action of Lewis acids.

TABLE I-1. Reactions of Oxygen- and Sulfur-Containing Coal Model Compounds in the Presence of Lewis Acid Catalysts

Substrate	Catalyst	T(°C)	P(MPa)	Time	Solvent	Products and/or Reactions	Ref.
Diphenyl ether	BI_3 cat./subs.= 1.0	23	--	2 hr	--	No reaction	23
Diphenyl ether	PCl_5:pyridine or $AlBr_3$:(pyridine)$_2$ or $ZnCl_2$: (pyridine)$_2$	220	atmos.	5-6 hr	None	No ether cleavage	24
Diphenyl ether	$ZnCl_2$ cat./subs.= 1.0 (wt)	425	23.5-24.5 H_2	1 hr	None	Conversions (mol %) 2.0 phenol 0.5 benzene 1.3 cyclohexanol 0.4 methylcyclopentane 0.8 hexanes and pentane	25
Phenyl benzyl ether	$ZnCl_2$ cat./subs.= 0.4 (wt)	160	atmos.	1 hr	None	Yields (wt% of feed): 23.8 phenol 9.0 2-hydroxydiphenylmethane 19.4 4-hydroxydiphenylmethane 40.4 2,4-dibenzylphenol 7.4 resin	26
Dibenzyl ether	BF_3	--	atmos.	--	Benzene	Diphenylmethane, dibenzylbenzene, and polybenzylbenzenes	27
β-Naphthyl phenyl ether	$AlBr_3$ cat./subs.= 1.75 (wt)	80	atmos.	4.5 hr	Benzene	No reaction	28
Triphenylmethyl p-tolyl ether	$ZnCl_2$ cat./subs.= 0.5 (wt)	180	atmos.	30 min	None	Yields (wt% of feed): 66 triphenylmethanol 7.5 triphenylmethane	29

TABLE I-1. (continued)

Substrate	Catalyst	T(°C)	P(MPa)	Time	Solvent	Products and/or Reactions	Ref.
Phenol	2:3 $ZnCl_2$/ H_2O $ZnCl_2$/subs.= 0.5 (mol)	120	--	1.5 hr	Diisopropyl ether	Isopropyl phenyl ether (If ethanol is used as solvent, product is phenetole; if methanol is used as solvent, product is anisole)	30
Phenols	$ZnCl_2$ or $Al(OH)_3$ or $Cr(OH)_3$ or $Co(OH)_2$	460-480	23.5 H_2	--	--	Reduction and hydrogenation	31
Cresol	$ZnCl_2$ or $Ni(OH)_2$ or $Al(OH)_3$ or $Cr(OH)_3$ or $Co(OH)_2$	465	21.6 H_2	1 hr	--	Hydrogenation products -- liquid hydrocarbons	32
m-Cresol	$ZnCl_2$ cat./subs.= 1.0 (wt)	425	23.5-24.5 H_2	1 hr	None	Conversions (mol %): 32.0 toluene 15.3 3-methylcyclohexanol 42.6 aliphatic hydrocarbons	25
ß-Naphthol	ZnCl cat./subs.= 1.0 (wt)	425	23.5-24.5 H_2	1 hr	None	Conversions (mol %): 43.3 tetralin 20.6 naphthalene 8.6 1-methylindan 21.6 benzene and alkylbenzenes 4.9 aliphatic hydrocarbons	25

TABLE I-1. (continued)

Substrate	Catalyst	T(°C)	P(MPa)	Time	Solvent	Products and/or Reactions	Ref.
t-Butyl o-tolyl sulfide	$ZnCl_2$ cat./subs.= 0.1 (wt)	166-180	--	105 min.	--	o-Thiocresol (85% theoretical yield)	33
Benzyl phenyl sulfide	$AlCl_3$	50	--	24 hr	None	21.3% thiophenol	34
Benzyl phenyl sulfide	$AlCl_3$	50	--	11 hr	Benzoyl chloride	3.8% thiophenol 23.0% phenyl thiolbenzoate	34
Benzyl phenyl sulfide	$SnCl_4$	50	--	11 hr	None	5.6% thiophenol	34
Benzyl phenyl sulfide	$ZnCl_2$	50	--	11 hr	Benzoyl chloride	0.8% thiophenol 26.7% phenyl thiolbenzoate	34

Zinc Chloride Applied to Coal

As early as the 1920's, it was observed that $ZnCl_2$ possessed activity for hydrogenation and liquefaction of coal[35-40]. An extensive bibliography of this and other early work on the liquefaction of coal has been published by the U.S. Bureau of Mines[41]. A large number of metal halides have been tested for catalytic activity in coal liquefaction in studies by the Bureau of Mines[42] and, more recently, by the Shell Oil Company[43,44]. These screening studies showed that there are some metal halides more active than $ZnCl_2$. However, $ZnCl_2$ has been selected for further study in a number of recent investigations because it is relatively inexpensive compared to the more active metal halides and because it showed good selectivity for producing liquid products.

The most well-developed coal liquefaction process based on $ZnCl_2$ catalysis is that of the Conoco Coal Development Company (formerly Consolidation Coal Company)[45-50]. This process is based on using approximately equal weights of $ZnCl_2$ and coal at about 400°C and 3000 psi hydrogen for 1 hour to give high yields of gasoline in a single step. Presently, a 100 lb/hr pilot plant with facilities for regeneration of spent $ZnCl_2$ catalyst has been built and tested.

Another approach, using low concentrations (about 5 weight percent) of $ZnCl_2$ impregnated on finely-ground coal has been studied at the University of Utah[51-54]. Typical operating conditions in this scheme are 500°C, 2000 psi hydrogen, with a coal particle residence time of 2 to 6 seconds. While the low residence time and catalyst loading are attractive, the higher temperature results in a lower selectivity for liquid products than the Conoco Coal process. The University of Utah approach has been used to develop a 50 lb/hr bench-scale reactor.

Recent studies at the University of California have been directed toward utilizing $ZnCl_2$ for coal liquefaction at relatively mild processing conditions[55-57]. This is accomplished by using massive amounts of $ZnCl_2$ together with solvents. While the direct production of gasoline-type fuels has not been achieved, essentially complete conversion of sub-bituminous coal to pyridine soluble material has been obtained using a 5:1 $ZnCl_2$ to coal ratio at 275°C, 200 psi hydrogen in the presence of methanol.

Goals and Scope of the Study

The primary objective of this study was to investigate the chemistry of $ZnCl_2$ with oxygen and sulfur structures present in coal. In order to facilitate the identification of reaction pathways, model compounds were used. In the course of pursuing the primary objective, it was found that $ZnCl_2$ had activity for cleaving certain of the structures studied, but did not activate hydrogen to terminate the cleavage products. Thus, a secondary objective was to find hydrogen-activating cocatalysts that worked effectively with $ZnCl_2$. Nickel was found to be a good cocatalyst, but it was recognized that sulfur in coal could convert nickel to nickel sulfide. Further studies were conducted to determine the activity of nickel sulfide or other metal sulfides for hydrogenolysis of ethers.

Experiments were conducted on the model compounds in solution under hydrogen or nitrogen pressure and at temperatures at or below 325°C. The results should be a satisfactory representation of a part of the chemistry of coal and the selected catalyst systems at sub-pyrolysis coal processing conditions.

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II. The Effects of Zinc Chloride on the Cleavage of Ether Structures Present in Coal

Introduction

Recent studies have suggested that ether oxygen plays an important role in linking the macromolecular units or clusters present in coal. Takegami et al.[1] concluded from a study of mild hydrogenation of bituminous coal that the formation of asphaltenes might be ascribed to the cleavage of ether linkages. More recently, Ignasiak and Gawlak[2] examined the molecular weights of products obtained from reductive alkylation of a high-rank vitrinite. They concluded that the macromolecular network of vitrinite is composed of relatively small units (number-average molecular weight 600-700) which are linked primarily by ether oxygen atoms. Ruberto et al.[3] deduced from solvation studies of coal that sub-bituminous coal appears to consist primarily of two- and three-ring condensed aromatic structures linked mainly by oxygen atoms. It was estimated that roughly half of the oxygen content of the coal is involved in such ether structures. Finally, Wachowska and Pawlak[4] noted that while the extent of ether linkages varies widely with coal rank, ether groups represent the main linkages between aromatic clusters.

The reactions which ether groups undergo during the conversion of coal to liquid products are not well understood. In studies of the solvent refining of coal, Whitehurst et al.[5] observed that the consumption of hydrogen required to achieve a given level of conversion correlates closely with the amount of oxygen removed as water. A similar correlation was noted earlier by Weller et al.[6] in their studies of coal liquefaction using a $SnCl_2$ catalyst. Both of these observations strongly suggest that the hydrogen consumed is required to remove oxygen atoms from ether linkages present between aromatic clusters. Such an interpretation is not unreasonable, since the cleavage of ether linkages is energetically favorable compared to, say, the cleavage of aliphatic linkages.

It is expected that the presence of a catalyst during coal liquefaction may accelerate the cleavage of ether linkages. A catalyst of particular interest in this regard is $ZnCl_2$. Extensive work[7-9] has shown that $ZnCl_2$ promotes the liquefaction of coal with only a moderate consumption of hydrogen. In recent studies it has also been demonstrated[10] that $ZnCl_2$ will promote the conversion of a subbituminous coal to pyridine soluble components at temperatures below which pyrolysis can occur (<350°C). Furthermore, initial evidence has been obtained[11] to suggest that the degree of conversion correlates with the removal of oxygen from the coal. These latter results suggest that $ZnCl_2$ may catalyze the cleavage of ether linkages and thereby promote a reduction in molecular weight.

The present studies were undertaken to determine the extent to which $ZnCl_2$ catalyzes the cleavage of ether linkages. To facilitate the identification of reaction pathways and products, our studies were conducted with model compounds chosen to reflect ether structures present in coal. Ethers containing phenyl, benzyl, and naphthyl groups were studied as well as cyclic ethers.

Experimental

Batch reactions of oxygen containing model compounds were carried out in a 300 cm^3 316 stainless steel, stirred autoclave (Autoclave Engineers, Inc. Model ABP-300). To minimize contact with the autoclave walls the reaction mixture was contained in a glass liner. In a typical experimental run, the reactant, solvent, and catalyst were weighed and introduced to the glass liner. A sample of the solution was taken for analysis before the catalyst was introduced to the mixture. The filled liner was then placed in the autoclave, and the autoclave was sealed and pressurized to obtain the desired cold starting pressure.

The reaction mixture was brought to reaction temperature and pressure by means of an electric heating mantle surrounding the autoclave. This phase took from 20 minutes (to reach a temperature of 225°C) to 30 minutes (to reach a temperature of 325°C). The reactor was maintained at the reaction temperature for 60 minutes, and was then rapidly quenched. Quenching was accomplished by both an internal cooling coil and an external cooling jacket. This method of cooling enabled the autoclave contents to be cooled to less than 100°C within 2 minutes of the start of quenching and to be brought to room temperature in 15 to 20 minutes.

Throughout the heat-up, reaction, and cool-down phases the autoclave contents were stirred at 600 RPM. Since the reaction was run as a closed system, no gas was fed to or bled from the autoclave during these periods. The final cold pressure was noted and compared with the starting cold pressure to determine whether gas had been consumed or generated in the course of the reaction.

After the autoclave contents had reached room temperature, they were removed from the autoclave, together with the glass liner. The recovered products were weighed and the solid and liquid products were separated by filtration. The liquid products were analyzed by gas chromatography on a 1/8" x 10' column packed with 5% OV-225 on Chromosorb P. A second column, packed with 3% Dexsil 300 on Chromosorb W/HP was used for analysis in the cases where products of reaction had higher boiling points than could be eluted from the OV-225 column. Product identification was made using a Finnigan 4023 GC-MS. In some instances products were identified from infrared and ^{1}H-NMR spectra of collected chromatographic fractions.

Experiments were run with each model compound and solvent without the $ZnCl_2$ present to insure that the observed reactions were indeed catalytic.

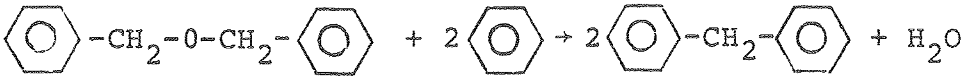
The following compounds were used as models of ether linkages: diphenyl ether (Eastman Organic Chemicals), dibenzyl ether (Eastman Organic Chemicals), benzyl phenyl ether (Frinton Laboratories), and benzyl α-naphthyl ether (Eastman Kodak Co.). Four cyclic ethers were also examined: furan (Aldrich), tetrahydrofuran (Mallinckrodt), 2,3-dihydrobenzofuran (Aldrich), and tetrahydropyran (Aldrich). Each of the model compounds was used as obtained. As solvents for the reactants and products we used: benzene (Mallinckrodt), cyclohexane (MCB), and tetralin (Eastman Organic Chemicals). $ZnCl_2$ (Mallinckrodt) was also used as received.

Results and Discussion

Non-cyclic Ethers

The products obtained upon reaction in the presence of $ZnCl_2$ of model compounds containing ether linkages are summarized in Table II-1. In this table, conversion refers to the amount of reactant which disappeared in the course of the reaction, while the percent theoretical yield of the individual products is calculated on the basis of the initial amount of reactant. Since the percent theoretical yield is also based on the amount of product actually recovered, some of the deviation from theoretical yields can be attributed to system losses, which averaged 7%.

The reaction pattern exhibited by dibenzyl ether is characteristic of other model compounds and hence will be discussed first. As seen from Table II-1., dibenzyl ether reacts in benzene to produce diphenylmethane in high yield via the following reaction.



(1)

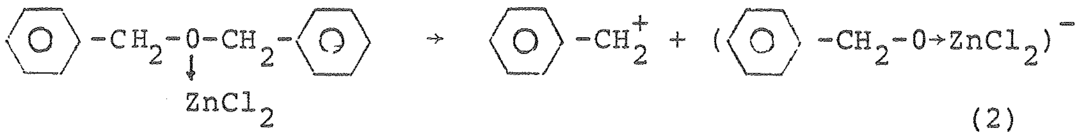
Table II-1. Reaction Products Obtained from Ethers in the Presence of Zinc Chloride

Reactants	Solvent	Moles Solvent / Mole Reactant	Moles $ZnCl_2$ / Mole Reactant	Gas	Reaction Temp (°C)	Reaction Press., MPa	Products	% Theoretical yield of product	% Conversion of reactant
Dibenzyl Ether	Benzene	21.6	2.93	H_2	232	4.83	Diphenylmethane	80	100
Dibenzyl Ether	Benzene	21.6	0.291	N_2	228	5.07	Diphenylmethane	88	100
Dibenzyl Ether	Tetralin	13.9	2.87	H_2	233	4.10	β-Benzyl tetralin	41	100
							α-Benzyl tetralin	25	
Dibenzyl Ether	Tetralin	14.2	2.94	N_2	227	4.38	β-Benzyl tetralin	38	100
							α-Benzyl tetralin	24	
Dibenzyl Ether	Cyclohexane	17.9	2.92	H_2	230	4.79	Tar	-	94
Diphenyl Ether	Benzene	18.3	2.47	H_2	327	13.62	No Reaction	-	0
Diphenyl Ether	Tetralin	12.0	2.49	H_2	230	9.69	No Reaction	-	6.5
Benzyl Phenyl Ether	Benzene	22.0	2.99	H_2	226	3.90	Phenol	61	100
							Diphenylmethane	59	
							2-Hydroxydiphenylmethane	14	
Benzyl Naphthyl Ether	Benzene	20.7	2.84	H_2	226	5.00	1-Naphthol	29	100
							2 isomers of benzyl-1-naphthol	20	
							Diphenylmethane	14	

Similarly, when tetralin is used as a solvent instead of benzene, the α and β isomers of benzyltetralin are obtained. However, when the solvent is cyclohexane, tars are formed and no lower molecular weight products are observed in significant yield.

The reaction products obtained from dibenzyl ether can be interpreted in terms of mechanisms used to describe Friedel-Crafts chemistry[12]. The essential feature of these mechanisms is the formation of a benzyl carbonium ion through the $ZnCl_2$-promoted cleavage of the dibenzyl ether. The carbonium ion thus formed then attacks an aromatic center, if one is available, to yield the benzylation product.

Formation of the benzyl carbonium ion may be envisioned to occur by pathways similar to those used to explain ether cleavage by other Lewis acids. For example, following the mechanism proposed by Monacelli and Hennion[13] for the cleavage of ethers by BF_3, a benzyl carbonium ion could be formed by decomposition of the addition product formed between $ZnCl_2$ and dibenzyl ether (reaction 2).



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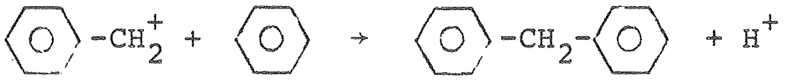

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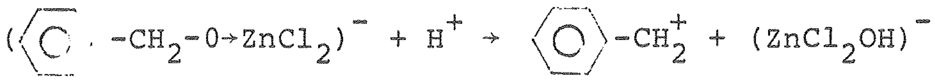


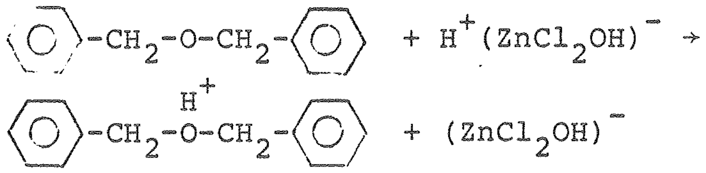
(4)

$$(ZnCl_2OH)^- + H^+ \rightarrow H_2O + ZnCl_2 \qquad (5)$$

The remaining fragment of the addition product proceeds to form a second carbonium ion (reaction 4). The carbonium ions thus formed react with benzene to yield diphenylmethane via reaction 3. Finally, the catalyst is regenerated in reaction 5.

Burwell et al.[14] observed that at least some ethers require the presence of strong Brönsted acids to undergo cleavage in the presence of BF_3. This suggests a second mechanism (reactions 6-9) in which the ether must first be protonated to form the oxonium ion before it decomposes to the carbonium ion.

$$ZnCL_2 + H_2O \rightarrow H^+(ZnCL_2OH)^- \qquad (6)$$



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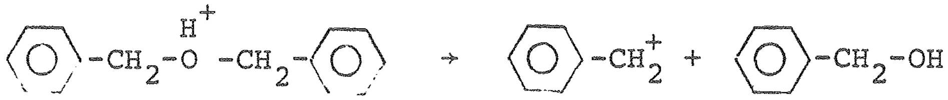

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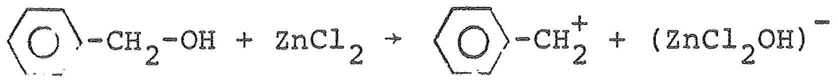
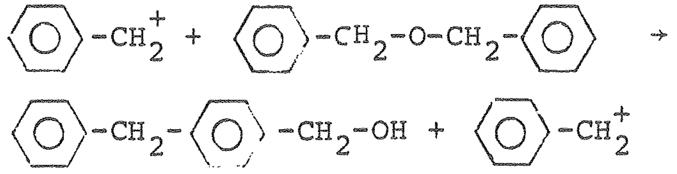


(9)

The active catalytic species in this instance is a Brönsted acid. If, as is usually the case, $ZnCl_2$ is not completely dry, sufficient water will be present to generate the protonic species $H^+(ZnCl_2OH)^-$ via reaction 6[15]. The alcohol generated by the oxonium ion decomposition forms a second carbonium ion as in reaction 9. The carbonium ions again form products by attack on an aromatic center as in reaction 3 above.

The present study contains no evidence to distinguish between these mechanisms. Indeed, it is plausible that both mechanisms could operate simultaneously. The second mechanism could be promoted by the formation of water as a product of the first mechanism, which does not require water as an initiator.

The carbonium ion mechanism can also explain the reactions of dibenzyl ether in cyclohexane. In this case, the only aromatic center available to the benzyl carbonium ions is dibenzyl ether itself. As a result, reaction of the carbonium ion leads to polymer and tar formation via condensation reactions. Reactions 10 and 11 exemplify the types of propagation reactions which might be involved in the condensation process.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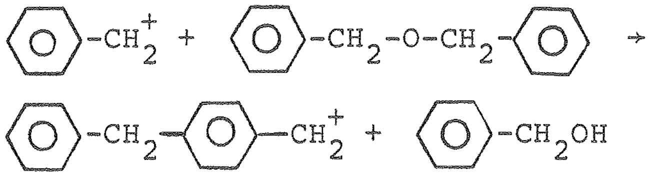


(11)

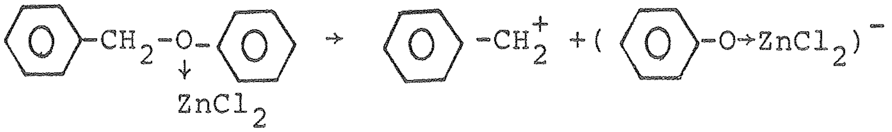
The role of gaseous hydrogen in the reactions of dibenzyl ether was also investigated. As seen in Table II-1, substitution of nitrogen for hydrogen had virtually no effect on the yield or distribution of products. These results and experiments in which the H_2 pressure was varied suggest that gaseous H_2 does not participate in the reaction mechanism.

Finally it should be noted that while the data presented in Table II-1 refer to 225 to 230°C, experiments were conducted with dibenzyl ether at temperatures between 136 and 305°C. No other products were observed in these experiments and only the yield declined with reduction in the temperature.

In contrast to dibenzyl ether, diphenyl ether does not react, either in the presence of benzene or tetralin. This result agrees with those of earlier investigators who found diaryl ethers to be unreactive under the same conditions at which other ethers could be cleaved by Lewis acids[16-18]. The stability of diphenyl ether is also consistent with the proposed mechanism of ether cleavage, which would require the formation of a highly unstable phenyl ion.

From the above results, one would expect an alkyl aryl ether to undergo an assymetric cleavage. This is indeed the case, as can be seen from the results of experiments using benzyl phenyl ether and benzyl naphthyl ether (Table II-1).

In the case of benzyl phenyl ether, the cleavage mechanism can be described as follows:



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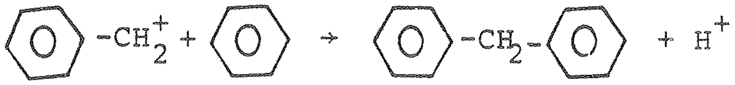

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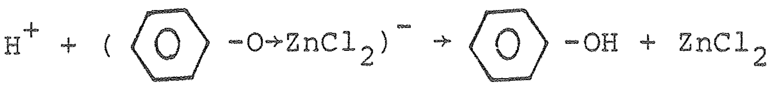


(14)

The expected phenol and diphenylmethane are seen in fairly high yields. In addition, however, 2-hydroxydiphenylmethane is observed, as a result of benzylation of the phenol. The appearance of 2-hydroxydiphenylmethane can probably be ascribed to the higher activity of phenol than benzene for electrophilic attack, a factor which compensates for the higher concentration of benzene than phenol. The effect of $ZnCl_2$ on pure benzyl phenyl ether has previously been reported by Short[19] with similar results.

In an attempt to see whether the nature of the aromatic group associated with the ether alters the rate of ether cleavage, reactions were conducted with benzyl naphthyl ether. The products obtained are analogous to those obtained in the reaction of benzyl phenyl ether, showing no differences in the type of reaction. However, the product yields were noticeably smaller than with benzyl phenyl ether.

Cyclic Ethers

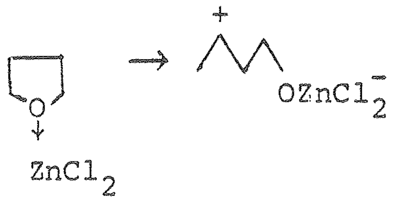
Table II-2 summarizes the products formed during the reactions of cyclic ethers in the presence of $ZnCl_2$. In

Table II-2. Reaction Products Obtained from Cyclic Ethers in the Presence of Zinc Chloride

Reactants	Solvent	Moles Solvent / Moles Reactant	Moles $ZnCl_2$ / Moles Reactant	Gas	Reaction Temp (°C)	Reaction Press., MPa	Products	% Theoretical yield of product	% Conversion of reactant
Tetrahydrofuran	Benzene	21.6	2.93	H_2	324	14.10	s-Butylbenzene	11.8	-
							Isopropylbenzene	4.75	
							n-Butylbenzene	4.51	
							1-Methylindan	3.74	
							Ethylbenzene	0.80	
							Tetralin	0.44	
							Toluene	0.29	
Tetrahydropyran	Benzene	20.7	2.83	H_2	324	13.96	s-Pentylbenzene	8.15	100
							1-Methyltetralin	5.17	
							Isopropylbenzene	4.52	
							t-Pentylbenzene	3.27	
							1,3-Dimethylindan	2.93	
							Ethylbenzene	1.62	
							1,1-Dimethyl-1-2-propenylbenzene	1.37	
							2-Methylnaphthalene	1.17	
							1,1-Dimethylindan	1.04	
							1-Methylnaphthalene	1.03	
							s-Butylbenzene	0.88	
							Toluene	0.60	
Furan	Benzene	21.4	2.95	H_2	325	14.17	No significant products	-	31.1
2,3-Dihydrobenzofuran	Benzene	21.5	2.91	H_2	325	15.27	Phenol	27.5	98.3
							Hydroxy-1,2-diphenylethane	10.8	
							Ethylbenzene	9.50	
							2-Ethylphenol	4.99	
							1,1-Diphenylethane	4.24	
							4-Ethylphenol	1.84	
							Diphenylmethane	1.43	
							Toluene	0.71	
							Bibenzyl	0.17	
2,3-Dihydrobenzofuran	Benzene	21.6	2.98	N_2	323	16.79	Phenol	30.4	98.6
							Ethylbenzene	9.67	
							Toluene	7.10	
							Hydroxy-1,2-diphenylethane	6.93	
							2-Ethylphenol	4.16	
							Diphenylmethane	3.78	
							1,1-Diphenylethane	2.14	
							Bibenzyl	1.19	

general, it is observed that the products obtained from these reactions are much more numerous and the yields of identifiable products are much lower than those obtained in the reaction of noncyclic ethers. A second general result is that α,β-saturated cyclic ethers (i.e. tetrahydrofuran, tetrahydropyran, and 2,3-dihydrobenzofuran) are reactive, while unsaturated cyclic ethers, such as furan, appear to be stable.

The predominant product obtained from the reaction of tetrahydrofuran in benzene is sec-butyl benzene. The higher abundance of this product with respect to n-butylbenzene is again consistent with a carbonium ion mechanism and reflects the greater stability of a secondary carbonium ion. The first steps of this mechanism are shown in reactions 15 and 16.



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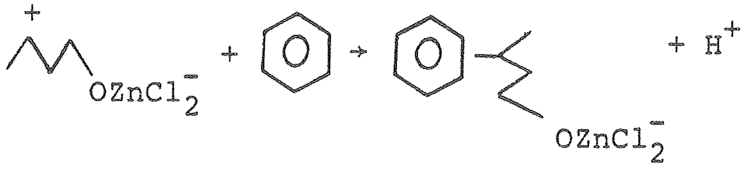
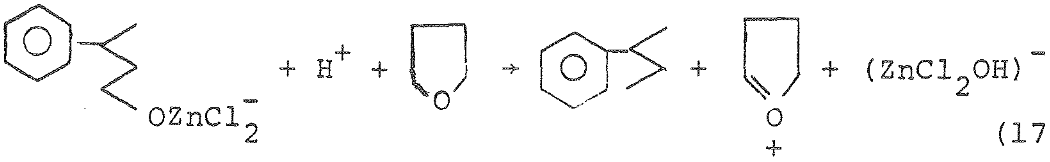
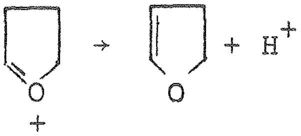


(16)

The presence of the n-butylbenzene among the products, however, suggests the possibility of a concerted-step mechanism. In either case the hydrogen necessary to complete the process probably comes from a portion of the tetrahydrofuran as shown below.



(17)



(18)

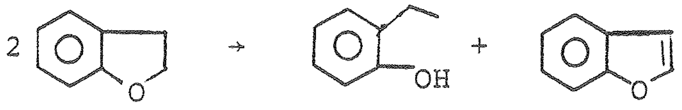
The presence of significant amounts of isopropylbenzene along with small amounts of ethylbenzene and toluene indicates that cracking of the carbon chain occurs. The closed-ring products (i.e. 1-methylindan and tetralin) could arise from a second attack on the benzene ring by the activated carbon chain, starting with the product of reaction 16, for example.

The products obtained from the reaction of tetrahydropyran in benzene are similar to those of tetrahydrofuran. However, there are apparent differences in product distributions. For example, while sec-pentylbenzene is the major product, no significant amount of the n-pentylbenzene isomer is seen. In addition, 1-methyltetralin (in analogy to 1-methylindan above) is present in high relative abundance. Small amounts of the isomers of methylnaphthalene are seen, indicating some dehydrogenation of the methyl tetralins as they are formed.

As was noted before, tetrahydrofuran and tetrahydropyran gave low product yields. This can be partially attributed to consumption of some of the reactants to provide hydrogen for the reactions. In addition, during the reaction some of the reactant is likely to associate with the $ZnCl_2$ and remain in the $ZnCl_2$ phase during product work-up, thus not being accounted for in the liquid product[20].

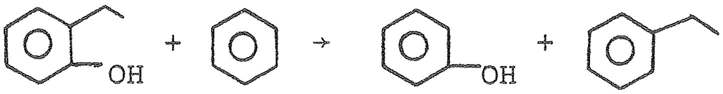
A saturated cyclic ether structure more representative of those found in coal is 2,3-dihydrobenzofuran. The reactions of this compound are somewhat different in nature to those of the cyclic ethers discussed above. Whereas no significant thermal reactions were noted with other model compounds, dihydrobenzofuran undergoes some cleavage to form 2-ethylphenol in the absence of a catalyst.

In the presence of $ZnCl_2$, the principle products are phenol, ethylbenzene and hydroxy-1,2-diphenylethane. It is proposed that the first steps result in a disproportionation of the 2,3-dihydrobenzofuran to yield 2-ethylphenol and benzofuran.



(19)

The benzofuran very likely contributes to tar formation, accounting for the observed low overall yields of other products. Ethylbenzene and phenol are possibly formed as a result of an exchange reaction between ethylphenol and benzene.



(20)

The hydroxy-1,2-diphenylethane is produced by a reaction analogous to those of the cyclic ethers discussed above. The bond between the oxygen and adjacent saturated carbon is cleaved, leaving an alkyl fragment which is activated to attack an aromatic center, namely benzene. The presence of other products, principally toluene, indicate fragmentation of the alkyl chain. Here again, we note that the reaction products are not greatly dependent on the gas used (H_2 or N_2), although the product distributions are somewhat different.

No cleavage products were observed when furan was heated up to 325°C in benzene containing $ZnCl_2$ but some of the furan was consumed. The absence of cleavage products can be attributed to the fact that a stable carbonium ion cannot be formed from cleavage of furan. The disappearance of a significant amount of furan can be ascribed to the formation of a stable complex with $ZnCl_2$ which remains in the $ZnCl_2$ phase, and to the formation of some tar. While the hydrogenation of furan to tetrahydrofuran would make further reaction possible, there was no evidence for tetrahydrofuran formation at a hydrogen pressure of 13.9 MPa.

Conclusions

The present study has shown that both cyclic and noncyclic ethers react readily in the presence of $ZnCl_2$ provided that the ether oxygen is adjacent to at least one methylene group. During the initial steps of cleavage both types of ether form fragments which rapidly alkylate aromatic centers. For dibenzyl and cyclo-aliphatic ethers the oxygen atom is removed completely to form water. However, if the oxygen is bonded to a phenyl or naphthyl group then a phenolic hydroxyl group is formed, which is stable to further reaction. The distribution of products obtained from different substrates and the effects of different solvents can be interpreted in terms of carbonium ion mechanisms similar to those used to explain Friedel-Crafts chemistry. Both the experimental results and the proposed reaction mechanisms suggest that gaseous hydrogen is not involved in forming the observed products.

Based upon the results reported here it is possible to predict the effects of $ZnCl_2$ on ether linkages present in coal. Linkages of the form $Ar-CH_2-O-CH_2-Ar$ should cleave with the elimination of oxygen as water. The remaining benzylic carbonium ions should then react with aromatic moieties present in the solvent. Structures of the type $AR-O-CH_2-Ar$ will also undergo cleavage. However, in this case the oxygen atom will be retained as a phenol. Cleavage of both types of linkage should result in a reduction in the molecular weight of the coal structure and an increase in the solubility of the fragments in aromatic and hydroaromatic solvents. By contrast, oxygen atoms present in diaryl ethers and in furan, benzofuran, and dibenzofuran-type structures are not expected to undergo reaction at temperatures below 350°C and in the presence of $ZnCl_2$. Likewise, phenolic hydroxyl groups will also be unaffected.

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III. Hydrogenolysis of Dibenzyl Ether Using Zinc Chloride-Metal Cocatalyst Systems

The cleavage of benzylic ether linkages is believed to be one of the processes which occurs during coal liquefaction in the presence of Lewis acids. We recently reported that $ZnCl_2$ will readily promote the cleavage of various ethers under conditions where thermolysis of the ethers does not occur[1]. The observed products indicated that $ZnCl_2$ promotes the formation of benzylic carbonium ions. These carbonium ion intermediates yielded benzylation products via electrophilic substitution in the presence of aromatic centers or insoluble resins via cationic condensation in the absence of aromatic centers other than the ether itself. The benzylic carbonium ions did not readily abstract hydride ions from molecular hydrogen. However, reports of reactions of carbonium ions in super acid systems[2,3] suggested that reaction of the benzylic carbonium ions with molecular hydrogen might be possible. In the present communication we wish to report that the use of $ZnCl_2$ together with a metal capable of activating molecular hydrogen facilitates the transfer of hydride ions to benzylic carbonium ions and inhibits the formation of condensation products.

The reactant used in these experiments was dibenzyl ether, which was dissolved in cyclohexane. Reactions were carried out in a 300 cm^3 stirred, stainless steel autoclave fitted with a glass liner. Products were identified with the aid of a gas chromatograph/mass spectrometer. Quantitative analyses were carried out by gas chromatography.

The results presented in Table III-1 show that the addition of nickel, zinc, or magnesium to $ZnCl_2$ causes a significant enhancement in the yield of toluene and a reduction in the yield of insoluble resin, relative to that observed using $ZnCl_2$ alone. The $Ni/ZnCl_2$ cocatalyst system was found to be the most active. The use of a high surface area Raney nickel in place of powdered nickel permitted a reduction in the catalyst concentration, hydrogen pressure, and reaction time required for a given yield of toluene.

It should be noted that nickel alone produced a significant conversion of the ether to toluene and benzyl alcohol. This is not surprising since the activity of nickel for the hydrogenolysis of benzyl ethers is well established[4].

Working with the $Ni/ZnCl_2$ system it was established that the hydrogenolysis of dibenzyl ether to toluene did not occur when the autoclave was pressurized with nitrogen instead of hydrogen. This result, together with the observed decrease in pressure during a run carried out with hydrogen, indicate that molecular hydrogen is the hydride source for hydrogenolysis of the ether. Use of methylcyclopentane, a potential tertiary hydride donor which could be formed by isomerization of cyclohexane, as the

Table III-1.

Products Obtained from the Hydrogenolysis of Dibenzyl Ether Using Zinc Chloride-Metal Catalysts(a)

Catalyst	Catalyst loading (mole)	Reaction time (min)	Reaction pressure (MPa)	Products	% yield	% Conversion(b) of ether
None	-	60	13.8	Toluene	1.4	3.8
				Bibenzyl + o,m, and p-benzyl toluenes	0.1	
$ZnCl_2$	5.0×10^{-3}	60	13.6	Toluene	3.9	100
				Bibenzyl + o,m, and p-benzyl toluenes	2.5	
				Insoluble resin(e)	97	
Ni(c)	2.0×10^{-1}	60	13.8	Toluene	19.5	38.2
				Benzyl alcohol	5.7	
				Bibenzyl + o, m, and p-benzyl toluenes	2.3	
				Insoluble resin(e)	2.5	
Ni(c) $ZnCl_2$	2.0×10^{-1} 5.0×10^{-3}	60	13.7	Toluene	39.6	100
				Bibenzyl + o,m, and p-benzyl toluenes	12.3	
				Insoluble resin (e)	35	
Ni(c) $ZnCl_2$	2.0×10^{-1} 1.0×10^{-3}	60	13.7	Methylcyclohexane	0.5	96.5
				Toluene	65.6	
				Bibenzyl + o, m, and p-benzyl toluenes	8.2	
				Insoluble resin(e)	6.0	
Raney Ni(d)	2.0×10^{-3}	30	3.14	Methylcyclohexane	2.3	23.7
				Toluene	21.2	
				Bibenzyl + o, m, and p-benzyl toluenes	2.4	

Table III-1. (continued)

Catalyst	Catalyst loading (mole)	Reaction time (min)	Reaction Pressure (MPa)	Products	% yield	% Conversion of ether(b)
Raney Ni(d)	2.0×10^{-3}	30	3.21	Toluene	60.2	97.4
$ZnCl_2$	1.0×10^{-3}			Diphenylmethane	0.2	
				Bibenzyl + o,m and p-benzyl toluenes	7.1	
				Insoluble resin(e)	22	
Zn(c)	2.0×10^{-1}	60	13.8	Toluene	0.5	2.1
				Bibenzyl + o,m and p-benzyl toluenes	0.5	
Zn(c)	2.0×10^{-1}	60	13.7	Toluene	7.4	28.8
$ZnCl_2$	5.0×10^{-3}			Bibenzyl + o,m and p-benzyl toluenes	1.8	
				Insoluble resin(e)	29	
Mg(c)	2.0×10^{-1}	60	14.0	Toluene	7.1	69.7
$ZnCl_2$	5.0×10^{-3}			Benzyl alcohol	0.7	
				Bibenzyl + o,m and p-benzyl toluenes	2.3	
				Insoluble resin(e)	56	

(a) Reactions at 225°C of 2.0×10^{-2} mole dibenzyl ether in 50 ml of cyclohexane under hydrogen pressure.

(b) In addition to experimental error, the total percent yield may be less than the percent conversion due to the presence of soluble, but undetected resins, or may be greater than the percent conversion due to incorporation of solvent into insoluble resins.

(c) Powdered metal; nickel: -200 mesh, zinc: dust, Mallinckrodt reagent, pretreated with dilute HCl wash to remove oxide, magnesium: 40 mesh.

(d) Prepared by the method of L. F. Fieser and M. Fieser, ["Reagents for Organic Syntheses", Vol. 1, p. 723, New York, Wiley (1967)], but stored under cyclohexane after ethanol wash.

(e) The result of cationic polymerization of dibenzyl ether.

solvent had no significant effect on the reaction products or yields obtained. This result confirms that it is the nickel which activates the hydrogen and promotes its subsequent reaction. The possibility that $NiCl_2$, formed through the interaction of Ni and $ZnCl_2$ might be an active component can be discounted since $NiCl_2$ was found to be inactive for hydrogenolysis of dibenzyl ether.

The present observations suggest that the enhanced yields of toluene and the reduced formation of insoluble resin obtained when a metal is used in conjunction with $ZnCl_2$, can be ascribed to the cooperative actions of the two catalyst functions. In our previous studies we suggested that $ZnCl_2$ is active as a Brönsted acid [e.g., $H^+(ZnCl_2OH)^-$] and that it is the interaction of this form of the catalyst with dibenzyl ether which leads to the formation of benzyl carbonium ions[1]. In view of the low dielectric coefficient of cyclohexane, these ions are likely to be present in the form of a soluble but undissociated salt [e.g., $(C_6H_5CH_2)^+ (ZnCl_2OH)^-$]. The reaction of such a salt with a pair of hydrogen atoms, formed on the surface of the metal, could lead to the formation of toluene and the regeneration of the Brönsted acid form of $ZnCl_2$.

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IV. Hydrogenolysis of Dibenzyl Ether Using Metal Sulfide Catalysts

The hydrogenolysis of ether linkages is believed to be an important process in the selective liquefaction of coal. In a recent communication we reported that $ZnCl_2$ in combination with Ni, Zn, or Mg metal promotes the hydrogenolysis of dibenzyl ether to form toluene, in the present of hydrogen at 225°C[1]. These results suggest that similar cocatalysts might be used to effect the hydrogenolysis of ether linkages in coal. It is recognized, however, that the sulfur present in coal might present a problem since it could react with the metallic component of the cocatalyst system to form sulfides. It is, therefore, of interest to establish whether metal sulfides are active for the hydrogenolysis of aromatic ethers. In this communication we wish to report that nickel sulfide catalyzes the hydrogenolysis of dibenzyl ether but that a number of other metal sulfides are inactive for this reaction.

The reactant used in these experiments was dibenzyl ether, with the exception of one experiment performed with diphenyl ether. Cyclohexane was used as a solvent in all cases. Reactions were carried out in a 300 cm^3 stirred, stainless steel autoclave fitted with a glass liner. Products were identified with the aid of a gas chromatograph/mass spectrometer, and quantitative analyses were carried out by gas chromatography.

The results presented in Table IV-1 show that powdered NiS catalyzes the hydrogenolysis of dibenzyl ether to toluene. Under similar conditions, however, FeS, MoS_2, and ZnS do not yield significantly more toluene than is produced in the absence of catalyst. Diphenyl ether was found to be unreactive under conditions at which dibenzyl ether did react, namely 4.0×10^{-3} mole NiS, 14.1 MPa H_2 pressure at 225°C for 1 hour.

Two samples of NiS were used for the present experiments, neither of which was characterized. The first sample of NiS catalyzed the complete conversion of the ether to toluene. The second sample of NiS was somewhat less active and its use resulted in only a partial conversion of the ether. In this case, significant quantities of benzyl alcohol and cyclohexylmethanol were observed in addition to toluene. The benzyl alcohol is probably an intermediate produced during the first stages of hydrogenolysis. During the latter stages of reaction, the benzyl alcohol is reduced to toluene. Hydrogenation of the benzene ring apparently occurs in parallel to produce cyclohexylmethanol.

The hydrogenolysis activity of NiS was not increased by the presence of $ZnCl_2$. In fact, at low concentrations of NiS, the system NiS/$ZnCl_2$ yielded high proportions of insoluble resin, a product which is characteristic of the reaction in the presence of $ZnCl_2$ alone. This result differs from that observed for the $ZnCl_2$/Ni cocatalyst system,

Table IV-1.

Products Obtained from the Hydrogenolysis of Dibenzyl Ether Using Metal Sulfide Catalysts(a)

Catalyst	Catalyst loading (moles)	Reaction Pressure (MPa)	Products	% Yield	% Conversion(b) of ether
None	-	13.8	Toluene	1.4(e)	3.8
			Bibenzyl + o,m and p-benzyl toluenes	0.1	
NiS(c)	6.10×10^{-2}	13.0	Toluene	92.1	100.0
			Bibenzyl + o,m and p-benzyl toluenes	0.5	
NiS(d)	2.01×10^{-2}	14.0	Toluene	20.2	44.5
			Benzyl alcohol	10.0	
			Cyclohexylmethanol	9.5	
			Bibenzyl + o,m and p-benzyl toluenes	0.5	
NiS(d)	4.0×10^{-3}	13.8	Benzyl alcohol	13.4	28.4
			Toluene	11.4	
			Cyclohexylmethanol	1.6	
			Bibenzyl + o,m and p-benzyl toluenes	0.4	
FeS	5.0×10^{-2}	14.2	Toluene	2.4	3.4
			Cyclohexylmethanol	0.6	
			Benzyl alcohol	0.5	
			Bibenzyl + o,m and p-benzyl toluenes	0.2	
MoS_2	4.0×10^{-3}	14.0	Toluene	2.8	5.8
			Cyclohexylmethanol	2.2	
			Benzyl alcohol	0.7	
			Bibenzyl + o,m and p-benzyl toluenes	0.5	
ZnS	5.00×10^{-2}	14.0	Toluene	2.7	10.7
			Benzyl alcohol	0.7	
			Bibenzyl + o,m and p-benzyl toluenes	0.4	

Table IV-1. (continued)

Catalyst	Catalyst loading (moles)	Reaction pressure (MPa)	Products	% Yield	% Conversion of ether[(b)]
NiS[(c)]	6.10×10^{-2} 1.0×10^{-3}	12.7	Toluene	89.3	100.0
			Bibenzyl + o,m and p-benzyl toluenes	1.1	
NiS[(d)]	4.0×10^{-2}	13.5	Toluene	13.2	87.0
			Bibenzyl + o,m and p-benzyl toluenes	6.5	
			Benzyl alcohol	1.3	
			Cyclohexylmethanol	0.9	
			Diphenylmethane	0.2	
			Insoluble resin	51.0	

(a) One hour reaction at 225°C of 2.0×10^{-2} mole dibenzyl ether in 50 ml of cyclohexane under hydrogen pressure.

(b) The total percent yield may be less than the percent conversion due to the presence of soluble, but undetected resins.

(c) First sample of NiS.

(d) Second sample of NiS.

(e) Yields of toluene are based on two moles toluene per mole dibenzyl ether.

which was found to be more active than nickel alone.

It must be concluded, therefore, that NiS does not promote the transfer of hydride ions to benzyl carbonium ions generated by the action of $ZnCl_2$ on the dibenzyl ether, as has been proposed for Ni[1].

The role of hydrogen was also examined. When the autoclave was pressurized with nitrogen instead of hydrogen, dibenzyl ether did not react in the presence of NiS. This result together with an observed decrease in hydrogen pressure when hydrogenolysis does occur, indicate that molecular hydrogen is an essential reactant. Upon opening the autoclave following a reaction conducted with hydrogen, the odor of H_2S was detected. While this indicates that some reduction of the sulfide occurs, it is unlikely that the NiS is converted extensively to nickel since the sulfide is thermodynamically favored over nickel at the temperature of the reaction[2].

References and Notes

1. D. P. Mobley and A. T. Bell, submitted to J.A.C.S.
2. The equilibrium constant for the reaction

$$NiS + H_2 \rightleftarrows Ni + H_2S$$

is calculated to be 1.4×10^{-4} at 225°C, using thermodynamic data of D. D. Wagman, et al. ["Selected Values of Chemical Thermodynamic Properties", U. S. Bureau of Standards, Washington, D.C. (1968)], and R. E. Balzhiser, et al. ["Chemical Engineering Thermodynamics", Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1972)].

V. The Effects of Zinc Chloride on Sulfur Removal from Coal-Related Structures

Introduction

Organic sulfur in coal occurs primarily in the form of thiophenes. Smaller amounts of sulfur are also present in the form of thiols, sulfides, and disulfides[1-3]. The removal of sulfur is an important step in coal liquefaction and usually requires a catalyst to achieve a high degree of desulfurization. The present study was undertaken to determine the ability of $ZnCl_2$ to catalyze the removal of sulfur from coal-related structures. This work was motivated by the recognition that while $ZnCl_2$ has shown considerable promise as a coal liquefaction catalyst[4-7], little is known concerning its desulfurization characteristics. To facilitate the identification of reaction products and pathways, the present studies were carried out using model compounds containing sulfur in structures resembling those found in coal.

Experimental

Experimental Apparatus and Procedure

Batch reactions of sulfur containing model compounds were carried out in a 300 cm^3, 316 stainless steel, stirred autoclave (Autoclave Engineers, Inc. Model ABP-300) fitted with a glass liner. In a typical experimental run, the reactant, solvent, and catalyst were weighed and introduced to the glass liner. A sample of the solution was taken for analysis before the catalyst was introduced to the mixture.

The filled liner was then placed in the autoclave and the autoclave was sealed and pressurized with hydrogen to obtain the desired cold starting pressure.

The reaction mixture was brought to reaction temperature and pressure by means of an electric heating mantle surrounding the autoclave. This phase took from 20 minutes (to reach a temperature of 225°C)to 30 minutes (to reach a temperature of 325°C). The reactor was maintained at the reaction temperature for 60 minutes, and was then rapidly quenched. Quenching was accomplished by both an internal cooling coil and an external cooling jacket. This method of cooling enabled the autoclave contents to be cooled to less than 100°C within 2 minutes of the start of quenching and to be brought to room temperature in 15 to 20 minutes.

After the autoclave contents had reached room temperature, they were removed from the autoclave, together with the glass liner. The recovered products were weighed and the solid and liquid components were separated by filtration. The liquid products were identified using a Finnigan 4023 gas chromatograph/mass spectrometer. Quantitative analysis of these products was made by gas chromatography on a 1/8" x 10' column packed with 5% OV-225 on Chromosorb P. In some instances, gas products collected from the head space of the autoclave were analyzed by gas chromatography on a 3/16" x 15' column packed with Poropak Q.

Materials

The following compounds were used as models of sulfide and disulfide structures in coal: diphenyl sulfide (Eastman Organic Chemicals), dibenzyl sulfide (Eastman Organic Chemicals), diphenyl disulfide (Eastman Organic Chemicals) and dibenzyl disulfide (Eastman Organic Chemicals). Thiophenic structures were modeled by: thiophene (Aldrich), tetrahydrothiophene (MCB), and dibenzothiophene (Eastman Organic Chemicals). Each of the model compounds was used as obtained. Benzene (Mallinckrodt) and cyclohexane (MCB) were used as solvents fro the reactants and products. Zinc chloride (Mallinckrodt) was used as received.

Results and Discussion

The products, yields and conversion levels obtained from the reaction of sulfur-containing model compounds are summarized in Table 1. The length of reaction at temperature was 60 minutes in all cases listed. In this table, conversion is defined as the fraction of reactant which disappeared in the course of reaction. The percent theoretical yield is based on that amount of the product that could theoretically be obtained from the initial reactant. The discrepancy for a given reactant between the sum of the theoretical yields of products and the conversion can be ascribed to two causes. About 7% is due to incomplete recovery of products. The remainder of the discrepancy is due to formation of tars or resins and in some cases to complexing of reactants or products with the $ZnCl_2$. The tars are usually soluble, but have sufficiently high molecular weights to escape detection by gas chromatography.

Table V-1. Reaction Products Obtained from Sulfur Model Compounds in the Presence of Zinc Chloride

Reactant	Solvent	Moles Solvent / Mole Reactant	Moles $ZnCl_2$ / Mole Reactant	Reaction Temperature (°C)	Reaction Pressure (MPa)	Products	% Theoretical yield of product	% Conversion of reactant
Dibenzyl sulfide	Benzene	23.4	3.18	325	13.6	Toluene Bibenzyl Stilbene Diphenylmethane	24.9 17.5 14.3 11.8	100
Dibenzyl sulfide	Benzene	23.7	0	325	14.1	Bibenzyl Toluene Stilbene	43.5 33.0 7.8	100
Dibenzyl sulfide	Benzene	17.8	2.42	225	13.8	Diphenylmethane	58.7	98.5
Dibenzyl disulfide	Benzene	27.1	3.67	320	14.2	Bibenzyl Toluene Stilbene Diphenylmethane	27.4 26.2 7.1 2.9	100
Dibenzyl disulfide	Benzene	27.3	0	321	13.7	Bibenzyl Toluene Stilbene	52.0 32.0 3.8	100
Diphenyl sulfide	Cyclo-hexane	16.8	0	324	14.4	Benzene Thiophenol	15.7(1) 11.0(2)	32.5
Diphenyl sulfide	Cyclo-hexane	16.7	2.80	323	12.1	Benzene	7.4(1)	6.0
Diphenyl sulfide	Benzene	19.8	2.67	325	13.8	No identifiable products	-	21.9
Diphenyl disulfide	Benzene	24.0	0	321	13.8	Thiophenol Diphenyl sulfide	54.5(1) 30.6(2)	100
Diphenyl disulfide	Benzene	24.0	3.28	323	13.1	Diphenyl sulfide Thiophenol	52.1(2) 21.2(1)	82.8

Table V-1 (continued)

Reactant	Solvent	Moles Solvent / Mole Reactant	Moles $ZnCl_2$ / Mole Reactant	Reaction Temperature (°C)	Reaction Pressure (MPa)	Products	% Theoretical yield of product	% Conversion of reactant
Thiophene	Benzene	21.3	2.95	325	14.8	No reaction	-	5.9
Dibenzothiophene	Benzene	20.2	2.79	325	13.7	No reaction	-	8.0
Tetrahydrothiophene	Benzene	21.7	2.93	226	13.6	Complex with $ZnCl_2$		91.7
Tetrahydrothiophene	Benzene	21.5	2.98	321	15.8	Butanes	15	91.2
						Propane	13	
						Hydrogen sulfide	6	
						Ethane	3(1)	
						Methane	2(3)	
						sec-Butylbenzene	2.4	
						Toluene	1.3(2)	
						Isopropylbenzene	0.9(2)	
						n-Butylbenzene	0.8	

(1) Based on 2 moles product per mole reactant

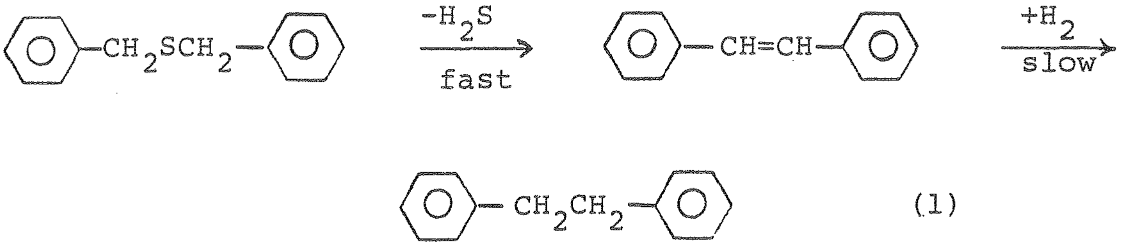
(2) Based on 1 mole product per mole reactant

(3) Based on 4 moles product per mole reactant

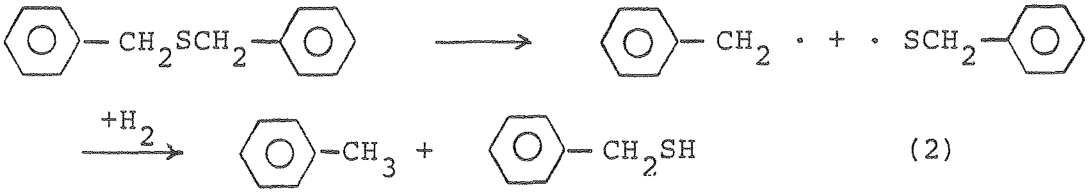
Dibenzyl Sulfide

Dibenzyl sulfide is representative of a class of sulfur compounds which are capable of undergoing both thermal and catalytic reactions. As shown in Table V-1, at 325°C in the presence of benzene and $ZnCl_2$, dibenzyl sulfide produces toluene, bibenzyl, stilbene and diphenylmethane. Under the same conditions but without $ZnCl_2$, toluene, bibenzyl and stilbene are again observed but not diphenylmethane, suggesting that the diphenylmethane arises from a reaction promoted by $ZnCl_2$. This conclusion is confirmed by the reactions of dibenzyl sulfide at 225°C. At this temperature, no reaction occurs in the absence of $ZnCl_2$. With $ZnCl_2$ present, the sole product found is diphenylmethane (Table V-1).

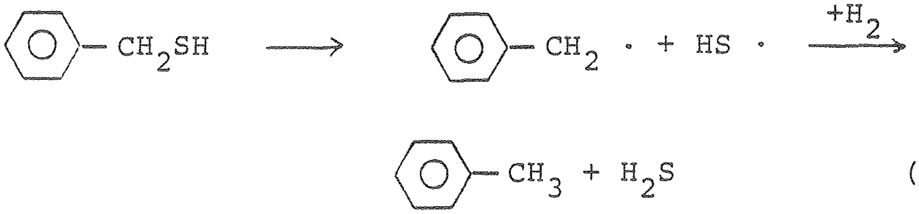
To gain some insight into the mechanism of the thermal reactions, a run was performed in which dibenzyl sulfide dissolved in benzene, was heated to 325°C, and then rapidly quenched. The products of this experiment showed an almost complete conversion of dibenzyl sulfide, a high ratio of stilbene to bibenzyl, and almost the same yield of toluene as that obtained following a one-hour run at 325°C. These results together with those presented in Table V-1 suggest that dibenzyl sulfide rapidly reacts to toluene and stilbene, and that the hydrogenation of stilbene to bibenzyl occurs more slowly. A possible mechanism for these reactions is suggested by reactions 1 through 3.



(1)



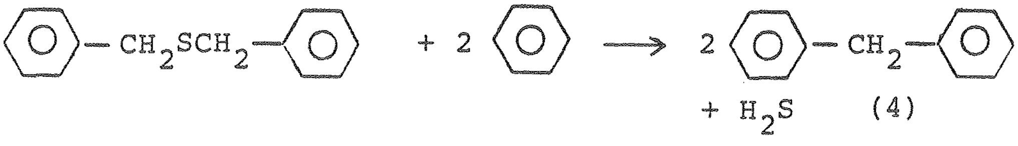
(2)



(3)

Since benzyl mercaptan is not seen as a product, for this mechanism to be plausible it must be assumed that any mercaptan formed is rapidly consumed.

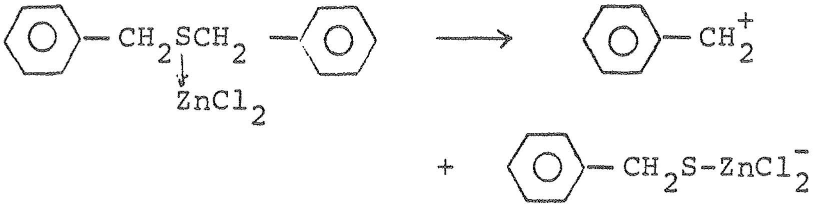
The reaction of dibenzyl sulfide under the influence of $ZnCl_2$ results in the formation of diphenylmethane via reaction 4.



(4)

This process can be explained by two possible mechanisms, both of which involve the formation of benzyl carbonium ions through the action of the catalyst on the reactant.

The first mechanism is represented by reactions 5 through 8. The reaction is initiated through the formation and subsequent decomposition of an adduct between $ZnCl_2$ and dibenzyl sulfide, in a manner similar to that observed for diisopropyl sulfide[8]. The benzyl carbonium ions produced in reactions 5 and 7 rapidly react with benzene to form diphenylmethane via reaction 6 and the catalyst is regenerated by reaction 8.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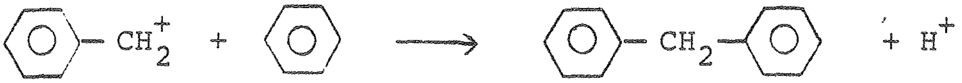
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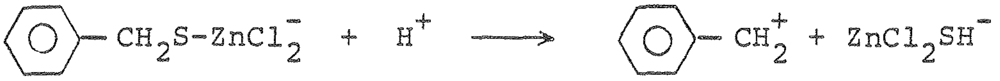
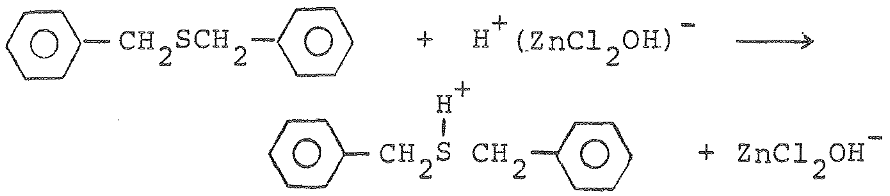

(7)

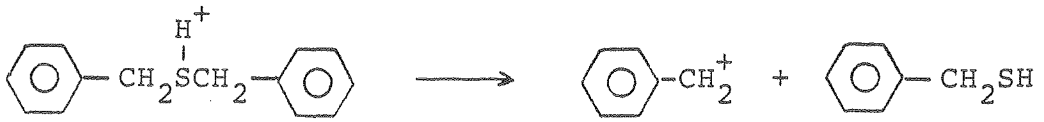
$$ZnCl_2SH^- + H^+ \longrightarrow H_2S + ZnCl_2 \qquad (8)$$

Reactions 9 through 12 comprise an alternative mechanism for generating benzyl carbonium ions. In this instance, $ZnCl_2$ reacts first with water, present as an impurity in the $ZnCl_2$ to form a Brönsted acid [i.e., $H^+(ZnCl_2OH)^-$]. This species then protonates the dibenzyl sulfide (reaction 10) thereby initiating its decomposition to a benzyl carbonium ion and a mercaptan (reaction 11) which in turn undergoes reaction to form a second benzyl carbonium ion (reactions 12 and 13).

$$ZnCl_2 + H_2O \rightleftharpoons H^+(ZnCl_2OH)^- \qquad (9)$$



(10)



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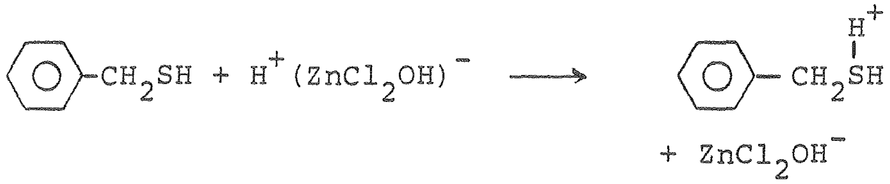

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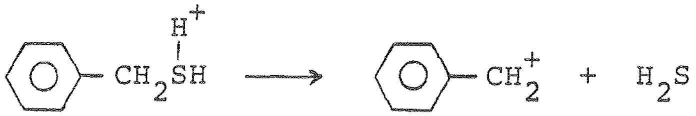


(13)

The two mechanisms suggested above are analogous to those proposed earlier for the reactions of dibenzyl ether catalyzed by $ZnCl_2$[9] and the reactions of other ethers catalyzed by BF_3[10,11].

Comparison of the product composition obtained with and without the addition of $ZnCl_2$ shows that in the presence of the catalyst the yield of identifiable products and the ratio of bibenzyl to stilbene are lower. The lower yield may be the result of polymerization side reactions promoted by $ZnCl_2$ or complexing of Lewis basic species with $ZnCl_2$. The lower ratio of bibenzyl to stilbene suggests that the hydrogenation of stilbene may somehow be inhibited by $ZnCl_2$.

Dibenzyl Disulfide

The behavior of dibenzyl disulfide is very similar to that of dibenzyl sulfide, as can be seen from Table V-1.

Toluene, bibenzyl and stilbene are produced either in the presence or absence of $ZnCl_2$ and diphenylmethane is produced only in the presence of $ZnCl_2$. Here again, the catalyst appears to suppress the yield of products and the ratio of bibenzyl to stilbene.

It seems reasonable that the types of mechanisms proposed for both the thermal and catalyzed reactions of dibenzyl sulfide should also be applicable to dibenzyl disulfide. However, a broader spectrum of detailed reaction paths might be expected for the disulfide since it can decompose with rupture of either the carbon-sulfur or sulfur-sulfur bond. While it is conceivable that dibenzyl sulfide might be produced from dibenzyl disulfide, the rapid reaction of the sulfide would make its presence in the products unlikely.

Diphenyl Sulfide

The thermal reaction of diphenyl sulfide was studied in cyclohexane, since benzene is a likely reaction product in this case. At 325°C diphenyl sulfide was partially converted to benzene and thiophenol. In the presence of $ZnCl_2$ the conversion was lowered and benzene was the only observed product. If the catalyzed reaction is carried out in benzene, some diphenyl sulfide is lost from solution but no identifiable products are produced.

These results indicate that diphenyl sulfide does not undergo a $ZnCl_2$ promoted cleavage reaction. This is consistent with the proposed carbonium ion chemistry since cleavage aided by $ZnCl_2$ would require the formation of a highly unstable phenyl carbonium ion. The apparent inhibition of the thermal reaction by $ZnCl_2$ may be due to an acid-base interaction between diphenyl sulfide and $ZnCl_2$. A similar interaction might explain the absence of thiophenol as a product when $ZnCl_2$ is present.

Diphenyl Disulfide

Diphenyl disulfide undergoes thermal decomposition much more readily than diphenyl sulfide at 325°C. Diphenyl sulfide and thiophenol were the only products observed, since the reaction was carried out in benzene solution. The presence of $ZnCl_2$ decreased the conversion and increased the ratio of diphenyl sulfide to thiophenol formed. These observations again suggest that thermal rather than catalytic reactions are dominant. Most likely, reaction begins with rupture of the sulfur-sulfur bond. The pair of free radicals thus produced may react with benzene to form diphenyl sulfide or with hydrogen to form thiophenol. The inhibition of the reaction by $ZnCl_2$ may in some way arise from association of the catalyst with the diphenyl disulfide or with the diphenyl sulfide, preventing its further reaction to thiophenol. Such an interpretation might also explain the predominance of diphenyl sulfide over thiophenol in the presence of $ZnCl_2$.

Thiophene and Dibenzothiophene

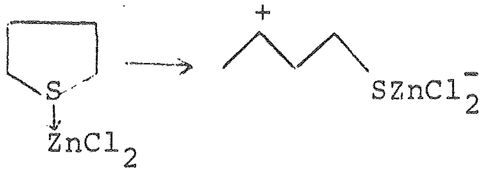
Neither thiophene nor dibenzothiophene underwent thermal reaction at 325°C. The addition of $ZnCl_2$ resulted in a slight loss of reactant, probably due to the formation of an adduct with the catalyst, but did not result in observable reaction products.

Tetrahydrothiophene

Tetrahydrothiophene was found to be thermally stable at 325°C. When heated with $ZnCl_2$ at 226°C for one hour, nearly all of the tetrahydrothiophene was consumed from the solution, but no soluble products were observed. Analysis of the gases in the autoclave head space also failed to reveal any reaction products. Thus, the only product appeared to be a complex of tetrahydrothiophene and $ZnCl_2$ which remained in the solid $ZnCl_2$ phase. This conclusion is supported by elemental analysis of the solids collected after reaction and previous reports that tetrahydrothiophene will form complexes with other Lewis acids[12,13].

When the reaction temperature is increased to 321°C, the complex of tetrahydrothiophene formed at lower temperature decomposes. The resulting products in the gas phase are saturated C_1 through C_4 hydrocarbons and H_2S. In the liquid phase, the primary product is sec-butylbenzene, along with some n-butylbenzene, isopropylbenzene, and toluene. These products are similar to those observed when tetrahydrofuran is reacted in the presence of $ZnCl_2$[9].

The production of sec-butylbenzene can be explained by a carbonium ion mechanisms as shown below.



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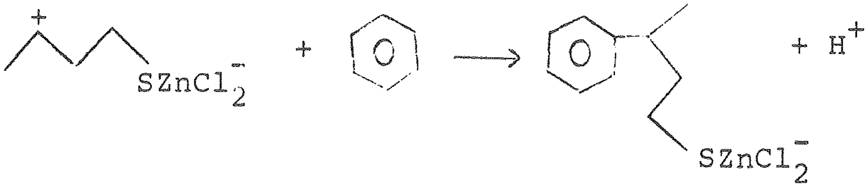

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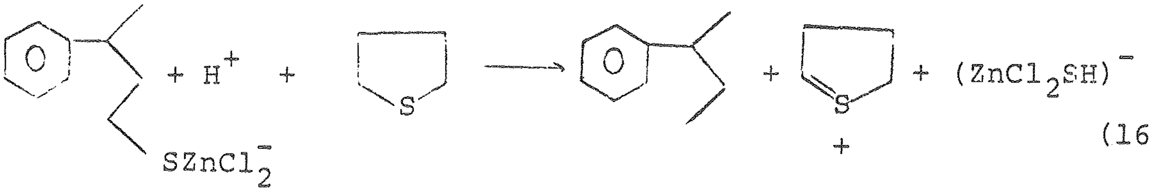

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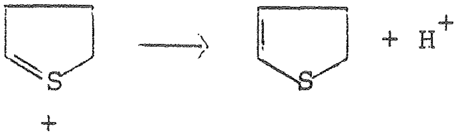

(17)

Reaction 14 produces a secondary carbonium ion, which then reacts with benzene via Reaction 15. Reaction 16 and 17 show a possible mechanism for abstracting hydrogen from tetrahydrothiophene to terminate the alkyl chain.

The presence of isopropylbenzene, toluene and C_1 through C_3 hydrocarbons in the products indicates that the four-membered carbon chain of tetrahydrothiophene is cracked. It is interesting to note that these gases are all saturated species. The source of hydrogen is unknown, though existence of a char in the solid phase suggests that a part of the reactant may have been condensed with a concurrent release of hydrogen.

It is also significant to note that while some H_2S is found in the gaseous products, the majority of the sulfur remains in the solid phase. Part of this may be due to an incomplete reaction of the adduct formed between tetrahydrothiophene and $ZnCl_2$. The balance may due to the reaction of H_2S with $ZnCl_2$ to form ZnS, a reaction which is thermodynamically favored[14]. While analyses for ZnS were not obtained it seems very likely that this product may be formed not only during the reactions of tetrahydrothiophene but also of other substrates from which sulfur is released.

Conclusions

The present investigation has shown that $ZnCl_2$ promotes the removal of sulfur from sulfides and disulfides in which the sulfur atom is bonded to a methylene group. Reaction is initiated either by proton transfer from the Brönsted acid form of the catalyst or by direct complexing of the reactant to $ZnCl_2$. During subsequent steps a carbonium ion is produced which can participate in electrophilic substitution with an aromatic center. It is observed that a significant portion of the sulfur removed is retained by the $ZnCl_2$ as a Lewis acid/base adduct or reacts with the $ZnCl_2$ to form ZnS. These studies have also demonstrated that $ZnCl_2$ does not promote the removal of sulfur from diphenyl sulfide, diphenyl disulfide, thiophene, or dibenzothiophene.

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Appendix - Quantitative Analysis Using Gas Chromatography

Gas chromatography was used for the quantitative analysis of the products of reaction of the model compounds. It was assumed that the weight ratio of a product compound to the solvent was equal to the ratio of areas under the corresponding peaks in the chromatogram, adjusted by a response factor for the particular product compound. The response factor was determined from the chromatograph of a solution of the product compound of known concentration.

If A designates the area under a peak in the chromatogram, w designates the weight fraction of a compound in solution, and subscripts 0 and 1 refer to the solvent and solute, respectively, then the response factor, R_1, of the solute is given by

$$R_1 = \left(\frac{A_o}{A_1}\right)\left(\frac{w_1}{w_o}\right) \qquad (1)$$

Thus a response factor can be obtained for any compound in the solvent of interest by analysis of a mixture of the compound and solvent of known composition.

To determine the composition of a binary mixture of the same components, one merely uses the previously calculated response factor and Equation (1) in the form

$$\frac{w_1}{w_o} = \left(\frac{A_1}{A_o}\right) R_1 \qquad (2)$$

To apply this method to a multi-component system, one can determine response factors for each solute separately as above, using Equation (1). For example, if there are n solutes, n response factors, R_1, R_2, R_3, ... R_n, are found. It can also be stated that

$$\sum_{i=0}^{n} w_i = 1 \tag{3}$$

From Equations (1) and (3) one can derive an expression for the weight fraction of any component, i, in the solution (Equation (4)).

$$w_i = \frac{\left(\frac{A_i}{A_o}\right) R_i}{1 + \sum_{j=1}^{n} \left(\frac{A_j}{A_o}\right) R_j} \tag{4}$$

Table A-1 and A-2 list response factors derived using Equation (1) for use in the present studies. These tables also list the time for elution of each component, measured from the time of injection of the sample to the time of maximum peak height.

It should be noted that there are potential sources of error in the method of analysis discussed above. The method requires that each peak in the chromatogram be identified and that a standard analysis be performed for each component. In a few instances, minor reaction products could not be identified. When this was the case, a response factor was estimated for the peak, using the fact that the response factors increase in a roughly linear fashion with elution time.

Another type of error would result if the solution being analyzed contained compounds which are of such high boiling point that they could not be eluted from the column, since such compounds would not be included in the sum of weight fractions. The size of this error would, of course, be unknown, since the heavy components would remain undetected. However, in the present study the total weight fraction of solutes was in the range of 10 to 15%. This means that the denominator of the right-hand side of Equation (4) cannot be much different from 1.0, and thus the maximum possible error of this type is not large.

Table A-1. Elution Times and Response Factors for Compounds Appearing in Liquid Reaction Products (Operating Mode 1)

Gas Chromatograph Data:

Column: 5% OV-225 on Chromosorb P, 1/8" X 10'

Detector type: Thermal conductivity

Helium flow rate: 20 ml/min

Temperature program: 160-240°C at 20°C/min, then hold at 240°C.

Compound	Elution Time (min)	Response factor
Solvent: Benzene		
Toluene	0.95	1.12
Thiophene	1.94	1.67
2,3-Dihydrobenzofuran	2.44	1.13
Phenol	3.18	2.07
Diphenyl ether	4.24	1.27
Diphenylmethane	4.36	1.22
Bibenzyl	4.89	1.20
Diphenyl sulfide	6.03	1.46
Stilbene	7.76	1.31
Dibenzyl sulfide	9.86	1.81
Diphenyl disulfide	9.94	2.01
Dibenzothiophene	10.24	1.69
Dibenzyl disulfide	19.53	2.66
Solvent: Tetralin		
Benzene	0.87	0.803
Diphenyl ether	4.18	0.980
Diphenyl sulfide	5.89	1.05
Dibenzyl ether	6.76	1.24
Phenanthrene	10.48	1.18
Solvent: Cyclohexane		
Diphenyl sulfide	5.95	1.39
Dibenzyl ether	6.67	1.24

Table A-2. Elution Times and Response Factors for Compounds Appearing in Liquid Reaction Products (Operating Mode 2)

Gas Chromatograph Data:

Column: 5% OV-225 on Chromosorb P, 1/8" X 10'

Detector Type: Thermal conductivity

Helium flow rate: 20 ml/min

Temperature program: 80-240°C at 20°C/min, then hold at 240°C

Compound	Elution Time (min)	Response factor
Solvent: Benzene		
Furan	1.04	1.17
Cyclohexane	1.13	1.09
Tetrahydropyran	1.88	0.974
Thiophene	1.97	1.11
Toluene	2.31	0.912
Tetrahydrothiophene	2.90	1.00
Ethylbenzene	2.95	0.941
Isopropylbenzene	3.37	0.999
sec-Butylbenzene	3.93	1.24
n-Butylbenzene	4.32	0.973
t-Pentylbenzene	4.43	1.22
Indan	4.54	1.32
sec-Pentylbenzene	4.60	0.973
Tetralin	5.68	1.10
2,3-Dihydrobenzofuran	5.83	1.08
Phenol	6.63	1.13
2-Ethylphenol	7.21	1.10
2-Methylnaphthalene	7.38	1.20
1-Methylnaphthalene	7.48	1.18
Diphenylmethane	8.15	1.18
Bibenzyl	8.58	1.07
Dibenzyl ether	10.35	1.31
Dibenzyl sulfide	13.43	2.06
2-Hydroxydiphenylmethane	14.34	1.96

Table A-2. (Cont.)

Compound	Elution time (min)	Response factor
Solvent: Cyclohexane		
Methylcyclopentane	0.98	(1.00)*
Methylcyclohexane	1.35	0.871
Ethylcyclohexane	1.86	1.00
Toluene	2.26	0.919
Cyclohexylmethanol	5.22	1.21
1,2-Dicyclohexylethane	6.61	1.28
Benzyl alcohol	6.77	1.17
Cyclohexylphenylmethane	6.97	1.22
Diphenyl ether	7.84	1.15
Diphenylmethane	8.09	(1.21)
Bibenzyl + o, m, and p-Benzyltoluenes	8.67	(1.22)
Dibenzyl ether	10.28	1.48
Solvent: Methylcyclopentane		
Toluene	2.26	0.964
Bibenzyl	8.60	1.17
Dibenzyl ether	10.16	1.48

* Values in parentheses are estimated.