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# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## ENERGY & ENVIRONMENT DIVISION

THE EFFECT OF ZINC CHLORIDE ON ORGANIC SOLVENTS  
AND COMPOUNDS MODELING CERTAIN BONDS IN COAL

Jon L. Maienschein\* and Edward A. Grens II

September 1980

\*Filed as a Ph.D. thesis

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THE EFFECT OF ZINC CHLORIDE ON ORGANIC  
SOLVENTS AND COMPOUNDS MODELING  
CERTAIN BONDS IN COAL

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## ABSTRACT

The action of treatment with organic solvent/zinc chloride mixtures on compounds modeling certain ether and aliphatic structures present in coal was examined at temperatures from 175 to 280°C. In coal liquefaction, ether and aliphatic linkages between aromatic units are among the most important bonds to be broken. Treatment of diaryl ethers and alkyl-aryl ethers with a 600-fold molar excess of zinc chloride resulted in cleavage of most ethers. Cleavage of ether carbon-oxygen bonds was not achieved only for those bonds in which the oxygen atom was attached directly to an aromatic ring; thus, diphenyl ether was not cleaved. For all other diaryl ethers, cleavage was rapid, with most cleavage products alkylating aromatic centers present in the treatment system; alkyl-aryl ethers were cleaved more slowly, yielding dealkylated phenols or naphthols. With treatment of diaryl alkanes under similar conditions, only diaryl methanes were cleaved, with fragments again alkylating aromatic species present. The reaction products for the ethers and diaryl alkanes confirmed previously proposed carbonium ion mechanisms. For both ether and aliphatic compounds, substituents on the aromatic rings accelerated the rate of the cleavage reaction.

In related studies of behavior of solvents with zinc chloride, hydroaromatic solvents were found not significantly soluble in zinc chloride at temperatures up to 300°C, but were degraded by zinc chloride-catalyzed cracking and polymerization reactions. Dodecane was non-reactive and insoluble.

## I. INTRODUCTION

In the coal liquefaction processes currently receiving the most attention, such as the Exxon Donor Solvent and SRC-II processes, temperatures well above pyrolysis are used to break up the coal structure. Recently, there have been exploratory studies of liquefaction at temperatures below pyrolysis as a means of selectively attacking certain bonds in coal, yielding a liquid product with minimum hydrogen consumption. To achieve liquefaction at low temperatures, a catalyst is necessary to promote bond cleavage. Homogeneous catalysts are required, since solid heterogeneous catalysts are unable to act upon the solid coal structure.

Molten zinc chloride is known to be an effective coal liquefaction catalyst at temperatures above and below pyrolysis (1,2,3). Here, at the Lawrence Berkeley Laboratory, a research program has been directed to the use of the massive amounts of zinc chloride in conjunction with organic solvents, at temperatures below that for coal pyrolysis, as a method to liquefy coal. In the course of the program, the desire to explain observed reactions in terms of fundamental chemistry led to the studies that comprise this work: the investigation of the chemistry of organic solvent/molten zinc chloride systems and of the reactions of coal model compounds in such systems.

### Zinc Chloride and Coal

Zinc chloride has long been recognized as an effective coal hydrogenation catalyst (1,4). Workers at the University of Utah have utilized

this activity by impregnating coal with zinc chloride in solution (2,5,6). Using a 5% catalyst loading, and heating the zinc chloride-loaded coal to 500°C under 12.8 MPa hydrogen pressure in a coiled tube reactor with residence times of 1 to 6 seconds, they obtained yields of up to 50% liquids and 20% gas (6). Recovery of zinc chloride from unreacted char, a crucial question for process economics, was better than 99% with a nitric acid wash (7).

Conoco Coal Development Company has investigated the use of massive amounts of zinc chloride to convert coal to gasoline-range materials. They built and operated a pilot plant for liquefaction of bituminous coal (8,9), and have also liquefied subbituminous coal (10,11). In contrast to the Utah work, Conoco used zinc chloride: coal ratios of approximately 1:1. Temperatures of 350-440°C and hydrogen pressures of 10-24 MPa were used, with residence times of one-half to three hours. Typical yields were 80-90%, with 50% being a gasoline-range product (10). Their pilot plant operations identified catalyst regeneration and corrosion as major problem areas (9,10).

Several other investigators have also used zinc chloride to liquefy coal but only at high temperatures (400-500°C) and high hydrogen pressures (14-28 MPa) (12-14). The application of zinc chloride to coal liquefaction at lower temperatures and pressures has received far less attention.

Here, at the Lawrence Berkeley Laboratory, zinc chloride is being explored as a coal liquefaction catalyst at temperatures below that for coal pyrolysis (15). Low temperatures (250-325°C) lead to the

attack of certain linkages in coal, while leaving much of the hydroaromatic structure intact. With zinc chloride in conjunction with organic solvents, conversion yields have been as high as 90% after two hours, with 60% being soluble in cyclohexane, and the remainder being pyridine soluble material (16).

Shinn suggested broad mechanisms for coal decomposition in the zinc chloride/solvent system (17). In these, zinc chloride, as a moderately active Lewis-acid catalyst, cleaves heteroatomic and aliphatic linkages between hydroaromatic clusters, the clusters being fairly non-reactive to zinc chloride. Broken bonds are terminated with hydrogen or by alkylation reactions with the solvent, and the fragments dissolve in the solvent. If the solvent is immiscible with the catalyst melt, this removes the fragments from contact with zinc chloride and terminates reaction.

The solvents used in this approach to coal conversion may be either immiscible with the zinc chloride melt, as with tetralin, or miscible with it, as with methanol. The solvents can serve as hydrogen donors and as alkylating agents. Of the immiscible solvents, tetralin has been of primary interest to date (3,15,16).

The zinc chloride/organic solvent treatments of coal carried out by Shinn and by Hershkowitz used similar reaction conditions (16,17). For experiments with an immiscible solvent, the zinc chloride was mixed with 10% water, to liquefy the salt and reduce viscosity; with miscible solvents, no water was added. For both cases, the zinc chloride:coal weight ratio was 6:1, and the solvent:coal weight ratio about

1:1. Temperatures between 225 and 325°C were investigated, with hydrogen pressures up to 5.5 MPa. Reaction times ranged from 10 minutes to two hours.

The degree of coal conversion was measured in terms of the fraction of the carbon content of the zinc chloride-treated coal soluble in cyclohexane, toluene, and pyridine. The pyridine solubility defined the total coal conversion, while cyclohexane solubility gave the "oil" yield.

Shinn studied a variety of solvents, both miscible and immiscible, with zinc chloride melts (17). He found that, for immiscible solvents, dihydroanthracene, mesitol, and a methylnaphthalene/tetralin mixture increased coal conversion when used with zinc chloride and water at 250°C, while piperidine and p-xylene decreased conversion. Of the miscible solvents, methanol, ethanol, isopropanol, and acetone increased conversion while acetic acid, N-N-dimethyl formamide, and t-butanol decreased it. Shinn selected methanol as a good solvent for use with zinc chloride. He observed overall coal conversion of 67% with zinc chloride/methanol at 250°C and 3.4 MPa for 1 hour, and almost complete solubility in pyridine after treatment for 1 hour at 275°C and 5.5 MPa.

Hershkowitz focused on the tetralin/zinc chloride treatment system at temperatures between 250 and 300°C (16). Typical yields were 80% pyridine solubility and 50% cyclohexane solubility from treatment at 300°C with 1.6 MPa hydrogen (3.4 MPa total pressure) for 1 hour.

Shinn and Hershkowitz both found that solvent was incorporated into the treated coal, with amounts of incorporation depending on solvent used and the temperature (16,17). At 250°C, the incorporation of both methanol and tetralin was approximately 20% by weight, while at 300°C tetralin incorporation was only 7% (16,17). Incorporation of other solvents ranged up to 200% for dihydroanthracene at 250°C (17). Shinn suggested that the methanol was incorporated by alkylating aromatic fragments in coal (17), while Hershkowitz has proposed that the alkylation of tetralin by reactive fragments is the incorporation mechanism with tetralin (16).

Hershkowitz observed no significant change in the atomic hydrogen/carbon ratio after treatment (16), while Shinn actually saw a decrease when using methanol with zinc chloride (17). Hershkowitz found that up to 50% of nitrogen in the raw coal was removed by treatment with zinc chloride and tetralin (16), while Shinn reported only 10-20% of the nitrogen was removed (17). Oxygen removal was found to correlate with total conversion to pyridine solubles both by Shinn (17) and by Hershkowitz (16). Shinn observed oxygen removal of up to 80% with zinc chloride and methanol at 275°C (with high solubility of the treated coal) (17), while Hershkowitz reported oxygen removals of 60% at 250°C with tetralin, and up to 90% removal at 300°C (with pyridine solubility of about 90%) (16).

### Zinc Chloride/Solvent Behavior

Available information concerning zinc chloride behavior with organic solvents of interest in this work is sparse, and is limited to reports of reactions catalyzed by the salt.

Morita and Hirosawa in 1975 found that tetralin, when treated with zinc chloride at 425°C under 21 MPa hydrogen for one hour, cracked with a conversion of 26% (18). The major product observed was 1-methylindan (10%), with alkylbenzenes accounting for most of the rest (5.8% butylbenzenes, 2.9% ethylbenzene, 1.1% toluene, 3.6% benzene). In studies from 1930 to 1950, several workers had reported that aluminum chloride (a much stronger Lewis acid than zinc chloride) dimerized tetralin to a  $C_{20}H_{20}$  molecule at temperatures from 30-80°C (19-21), though only isomerization products were observed at higher temperatures (22-24).

Morita and Hirosawa also treated decalin with zinc chloride at 425°C under 21 MPa hydrogen for one hour, and found a cracking yield of 35% (18). They found tetralin and methylindan to be the major products (21% combined) with alkylbenzenes also present (1.8% butylbenzenes, 6.1% ethylbenzene, 1.4% toluene, 0.7% benzene). They also observed significant amounts of methylcyclopentane (1.3%), methylcyclohexane (1.2%), and dimethylcyclopentane (0.9%). The reaction of decalin with aluminum chloride had been studied previously (25-27). In each study, it was observed that aluminum chloride, between room temperature and 100°C, converted the cis isomer of decalin to trans-decalin.



### Model Compound Reactions with Zinc Chloride

Because of the difficulty in identification of reactants and products, let alone reaction mechanisms, for a substance as complex as coal, simple chemical compounds containing linkages or other structural features of interest in coal are often studied to elucidate coal reactions. Here, the action of zinc chloride/organic solvent treatments on such model compounds is of interest.

The selection of model compounds is based upon certain significant features of the structure of coal. Coal appears to be composed of polynuclear aromatic clusters (containing 2-4 rings), which are connected by various chemical linkages (28). The aromatic clusters contain some sulfur, nitrogen, and oxygen, and are extensively substituted (28-30). The nature of the linkages between aromatic clusters is important in consideration of liquefaction below pyrolysis temperatures, as it is this type of bond that must be broken. The linkages taken primarily two forms: aliphatic, and heteroatomic.

Aliphatic linkages have been extensively investigated by depolymerization of coal with phenol-boron trifluoride mixtures. Heredy and coworkers developed this technique in the early 1960s. Using model compounds, they demonstrated that boron trifluoride catalysed rupture of methylene bridges (diaryl  $-CH_2-$  linkages), with the resulting fragments reacting with phenol to form 1,2-diarylmethanes (31). Thus, the identification of 1,2-diarylmethanes provided evidence that methylene bridges do exist in coal. In a series of papers, they presented data showing that methylene bridges between aromatic groups exist in

coals of all ranks, with generally more methylene bridges for coals of lower rank (32,33). They concluded that methylene bridge cleavage is a major step in coal liquefaction (34).

Brown, in a study of infrared spectra of several coals, reported in 1955 that methylene bridges are far more plentiful than methyl groups (35), though his later nuclear magnetic resonance (NMR) studies showed no methylene bridges (36). (In preparing his coal for NMR analysis, via vacuum carbonization, he may have destroyed methylene bridges, or the compounds containing methylene bridges may have been insoluble in his solvents.) In 1961, Oth and Tschamler found methylene bridges in a bituminous coal using NMR (37). In more recent studies, Imuta and Ouchi in 1973 and Niemann and Hombach in 1979, using procedures similar to those of Heredy, also found methylene bridges in coal (38,39).

None of the above studies indicated the presence of aliphatic bridges containing more than one carbon atom. Recent work by Whitehurst (40) (using a technique which degrades aromatic units while preserving aliphatic links), as interpreted by Shinn (17), indicated that linkages containing two carbon atoms (e.g., diaryl  $-\text{CH}_2-\text{CH}_2-$  bridges) are present in Wyodak subbituminous coal. Aliphatic side chains up to four carbon atoms in length have been identified by Whitehurst (40) and by Heredy (41).

Estimates of the number of aliphatic linkages have been made by Heredy (32,33) and by Shinn (17). The fraction of hydrogen located in aliphatic linkages between aromatic clusters was estimated to be between 2-5% in several coals; for subbituminous coal, around 2% of the hydrogen was taken to be in aliphatic linkages. Shinn estimated that another 17% of the hydrogen is on aliphatic side chains (17).

The major heteroatoms in coal are oxygen, nitrogen, and sulfur. Most nitrogen atoms and a large fraction of sulfur atoms are located in cyclic compounds within the coal (42,43). Also, in the subbituminous coal of primary interest in this work, nitrogen and sulfur are not plentiful (less than 1% of moisture free coal), while oxygen is the second most abundant element on a weight basis (17% of moisture free coal). For these reasons, nitrogen and sulfur linkages are not of interest here, while oxygen linkages are of great importance.

After an extensive study of oxygen functionalities in several coals, Blom reported in 1957 that hydroxyl, carbonyl, carboxyl, and methoxy groups were present, with no peroxides (44). He assumed that the oxygen unaccounted for (about 30%) was in ether links. Hydroxyl oxygen was the major form in all coals, carbonyl oxygen was present in small amounts (<10%), and carboxyl and methoxy oxygen appeared only in low rank coals. Of the two main oxygen groups in coal as found by Blom, hydroxyl and ether, only ether oxygen acts as a link between

hydroaromatic clusters. Ether linkages in coal were previously mentioned in other studies; in 1936, Biggs studied benzene extracts of coal and concluded that ether oxygen was present (45).

The presence of ether oxygen in coal has been demonstrated more recently by a reductive alkylation technique with a naphthalene anion in tetrahydrofuran. Sternberg and coworkers, in the early 1970s, found ether oxygen in bituminous and subbituminous coals, and estimated that two-thirds of the oxygen in the subbituminous coal was in ether form (46,47). Ignasiak and Gawlak used a similar method in 1977 to conclude that vitrinite from a bituminous coal was basically composed of small clusters (600-700 molecular weight) primarily linked by ether bonds (48). Also in 1977, Wachowska and Pawlak used the same technique to show that ether oxygen varied with coal rank, and that liquefaction of coal was strongly affected by rupture of ether bonds (49). Using a different approach, Ruberto and coworkers, in 1977, depolymerized coal in hydrophenanthrene solvents, concluding from the products that their subbituminous coal consisted of two and three ring structures linked mainly by oxygen (50).

A correlation between oxygen removal and coal conversion was observed in liquefaction with hydrogen donor solvents above 325°C by Szladow and Given (51) and by Cronauer and Ruberto (52). In the studies just completed, Shinn (17) and Hershkowitz (16) found similar correlations between oxygen removal and coal conversion in liquefaction with zinc chloride/organic solvent systems at temperatures below

325°C. Hershkowitz analyzed his zinc chloride/tetralin-treated coal for oxygen functional groups. He found that the oxygen that disappeared in conversion to pyridine solubles appeared to be predominately ether oxygen, indicating that ether link cleavage is occurring during liquefaction (16).

From the preceding discussion, it is evident that understanding the behavior of aliphatic and ether linkages is crucial to the study of coal liquefaction chemistry. Therefore, many model compound studies have focused on aromatic rings linked by aliphatic chains containing one to three carbons, and on diaryl and alkyl-aryl ethers. Studies on reactions of model compounds containing aliphatic linkages with zinc chloride and aluminum chloride, both Lewis-acid catalysts, have been made by many workers; many of these studies are summarized in Table I-1. Yur'ev and Levina reported in 1934 that aluminum chloride cracked biphenyl at 250-300°C (53). In 1978, Taylor found that biphenyl reacted in contact with aluminum chloride at 225°C, if sufficient catalyst was present (54). On the other hand, when zinc chloride was used to treat biphenyl at 425°C, Morita and Hirosawa saw only trace reaction products (18).

Diphenylmethane was found to be cleaved by aluminum chloride at 300-450°C by Tsuge and coworkers (55), and at 225°C by Taylor (54). However, Taylor observed no reaction of diphenylmethane in the presence of zinc chloride at 325°C (54).

Table I-1

Products Reported From Treatment of  
Diaryl-alkanes with Zinc Chloride or Aluminum Chloride

<u>Compound</u>	<u>Catalyst (cat:react. mole ratio)</u>	<u>Conditions</u>	<u>Principal Products</u>	<u>Ref.</u>
Biphenyl	AlCl <sub>3</sub>	250-300°C	benzene, cyclohexane, methylcyclopentane	53
Biphenyl	AlCl <sub>3</sub> (1:15)	225°C 6.9 MPa H <sub>2</sub> at 225°C 90 min. benzene solv.	no reaction (at 1:7 cat. ratio there was 80% conversion to many prod.)	54
Biphenyl	ZnCl <sub>2</sub> (1:1)	425°C 24 MPa H <sub>2</sub> 1 hour no solvent	trace products only	18
Diphenylmethane	AlCl <sub>3</sub>	300-450°C H <sub>2</sub> atmosphere	benzene, methyl-diphenyl- methane, phenylmethyl- diphenylmethane, dimethyl- diphenylmethane, anthracene	55
Diphenylmethane	AlCl <sub>3</sub> (1:15)	225°C 6.9 MPa H <sub>2</sub> at 225°C 90 min. benzene solv.	47% conversion; major products toluene and bibenzyl	54
Diphenylmethane	ZnCl <sub>2</sub> (1:0.71)	325°C 6.9 MPa H <sub>2</sub> at 325°C 90 min. cyclohexane solv.	no reaction	54
1,2-Diphenylethane	AlCl <sub>3</sub>	300-450°C H <sub>2</sub> atmosphere	benzene, phenylmethyl- 1,2-diphenylethane, methyl-1,2-diphenylethane, ethylbenzene	55
1,2-Diphenylethane	AlCl <sub>3</sub>	230-250°C	benzene and linear condensed polymer	56
1,2-Diphenylethane	AlCl <sub>3</sub>	100, 140°C heated in CO <sub>2</sub> until benzene evolution stops	benzene and polymer	57 58
1,2-Diphenylethane	AlCl <sub>3</sub> (1:15)	225°C 6.9 MPa H <sub>2</sub> at 225°C 90 min. benzene solv.	27% conversion; major products toluene and ethylbenzene	54
1,2-Diphenylethane	AlCl <sub>3</sub> (1:2) (by weight)	325°C 12.4 MPa H <sub>2</sub> (cold) 90 min. benzene solv.	100% conversion; major products cyclohexane, benzene, toluene, ethyl- benzene, propylbenzene, tar residue	59
1,2-Diphenylethane	ZnCl <sub>2</sub> (1:2) (by weight)	325°C 12.4 MPa H <sub>2</sub> (cold) 90 min. benzene solv.	no reaction	59

Table I-1  
(continued)

<u>Compound</u>	<u>Catalyst (cat:react. mole ratio)</u>	<u>Conditions</u>	<u>Principal Products</u>	<u>Ref.</u>
1,3-Diphenylpropane	AlCl <sub>3</sub>	140°C heated in CO <sub>2</sub> until benzene evolution stops	benzene and polymer	53
1,3-Diphenylpropane	AlCl <sub>3</sub> (1:15)	225°C 6.9 MPa H <sub>2</sub> at 225°C 90 min. benzene solv.	67% conversion; major product indan	54
1,3-Diphenylpropane	ZnCl <sub>2</sub> (1:0.71)	325°C 6.9 MPa H <sub>2</sub> at 325°C 90 min. cyclohexane solv.	no reaction	54
1,4-Diphenylbutane	AlCl <sub>3</sub>	140°C heated in CO <sub>2</sub> until benzene evolution stops	benzene and polymer	58

Several workers have studied the reactions of 1,2-diphenylethane catalyzed by aluminum chloride. With no solvent present, at temperatures between 100 and 250°C, benzene and a polymer were observed as products (56-58). Tsuge and coworkers reported in 1962 that treatment of 1,2-diphenylethane with aluminum chloride under hydrogen between 300-450°C gave benzene, ethylbenzene, and substituted diphenylethanes (55). Conklin in 1975 and Taylor in 1978 reported that in the presence of benzene, aluminum chloride catalyzed the reaction of 1,2-diphenylethane between 225 and 325°C under hydrogen pressure, giving extensive conversion to light cracking products (54,59). On the other hand, Conklin observed no reaction of 1,2-diphenylethane in the presence of zinc chloride at 325°C (59).

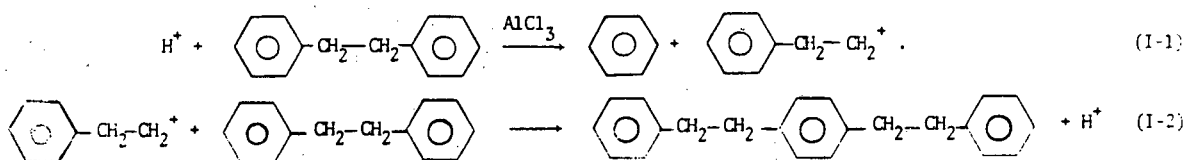
In 1951, Korshak and Kolesnikov reported that 1,3-diphenylpropane, when contacted with aluminum chloride at 140°C, gave benzene and a polymer (58). In 1978, Taylor added benzene and found extensive reaction at 225°C, with indan the main product (54). 1,3-diphenylpropane was non-reactive in the presence of zinc chloride at 325°C, according to Taylor (54). 1,4-diphenylbutane, when mixed with aluminum chloride at 140°C, yielded benzene and polymer in a manner similar to 1,2-diphenylethane and 1,3-diphenylpropane, according to Korshak and Kolesnikov (58).

From the observed reactions of aliphatic linkages, it can be seen that aluminum chloride is a much more active catalyst than zinc chloride, since reactions catalyzed by aluminum chloride at temperatures as low as 140°C are not observed with zinc chloride at 325°C. The



reaction products, as listed in Table I-1, are mostly aromatic, indicating that the aliphatic link rupture is accompanied by virtually no hydrogenation or cracking of aromatics.

Dobryanskii and Kornilova, in 1953, observed only asymmetric cleavage of the carbon-carbon bond adjacent to a ring in their work with 1,2-diphenylethane, 1,3-diphenylpropane, and 1,4-diphenylbutane catalyzed by aluminum chloride at 140°C (56). Their only products were benzene and a polymer. The polymer could be formed if the following reaction sequence occurred:



This carbonium ion mechanism was proposed by Taylor in 1978 for aliphatic link cleavage by aluminum chloride (54). It is consistent with the observation that, where hydrogen or a solvent is present to react with the carbonium ion before it can polymerize, little or no polymer formation is found (54,55,59,60). Also in agreement with this mechanism is the observation of Tsuge and Tashiro that methyl or hydroxyl substituents on an aromatic ring make the aliphatic link easier to cleave (60), since rings with these substituents form carbonium ions more readily than unsubstituted rings. These investigators also observed that substituents on a ring direct alkyl-aryl bond cleavage to the bond on the substituted aromatic ring (60).

From Taylor's work with biphenyl, diphenylmethane, 1,2-diphenylethane, and 1,3-diphenylpropane, biphenyl is obviously more stable than the others, since it alone was non-reactive at 225°C with aluminum chloride in a 15:1 reactant:catalyst ratio. This is consistent with the carbonium ion mechanism; the difficulty of forming the phenyl cation prevents the phenyl-phenyl cleavage.

Many studies have also been made of cleavage of diaryl and alkylaryl ethers with zinc chloride and aluminum chloride catalysts, with temperatures ranging from 50 to 425°C. These are summarized in Table I-2. Diphenyl ether has been found to be unreactive in the presence of boron trifluoride at 23°C (61), aluminum bromide at 220°C (62), and zinc chloride at 327°C (63,64), with only a small extent of reaction catalyzed by zinc chloride at 425°C (18).

In 1929, Short and Stewart found that aluminum chloride at 160°C catalyzed complete cracking of phenylbenzyl ether in one hour (65). Palmer and McVie observed similar behavior at 5-10°C in 1968 (66). In 1979, Mobley found that zinc chloride at 226°C also gave complete conversion of phenylbenzyl ether in one hour (63,64). From the products obtained in these three studies, it was concluded that the carbon-oxygen bond is broken only where the oxygen is not directly attached to the aromatic ring (63,64). This is consistent with the stability of diphenyl ether, since both oxygen bonds are to aromatic rings.

Table I-2

Products Reported From Treatment of  
Diaryl Ethers and Alkyl-aryl Ethers  
With Zinc Chloride or Aluminum Chloride

<u>Compound</u>	<u>Catalyst (cat:react. mole ratio)</u>	<u>Conditions</u>	<u>Principal Products</u>	<u>Ref.</u>
Diphenyl ether	BI <sub>3</sub> (1:1)	23°C atmos. pres. 2 hours	no reaction	61
Diphenyl ether	PCl <sub>5</sub> :pyridine or AlBr <sub>3</sub> :pyridine <sub>2</sub> or ZnCl <sub>2</sub> :pyridine <sub>2</sub>	220°C atmos. pres. 5-6 hours no solvent	no reaction	62
Diphenyl ether	ZnCl <sub>2</sub> (1:1)	425°C 24 MPa H <sub>2</sub> 1 hour no solvent	5% conversion; 2% phenol, 1.3% cyclo- hexanol, 0.5% benzene, 0.4% methylcyclopentane, 0.8% hexanes and pentanes	18
Diphenyl ether	ZnCl <sub>2</sub> (2.47:1)	327°C 13.6 MPa H <sub>2</sub> 1 hour benzene solv.	no reaction	63 64
Phenylbenzyl ether	AlCl <sub>3</sub>	5-10°C benzene solv.	phenol and diphenylmethane in equimolar amounts, and 2-benzylphenol	66
Phenylbenzyl ether	ZnCl <sub>2</sub> (0.4:1)	160°C atmos. pres. 1 hour no solvent	100% conversion; 23.8% phenol, 9.0% 2-hydroxy- diphenylmethane, 19.4% 4-hydroxydiphenylmethane, 40.4% 2,4-dibenzyl phenol, 7.4% resin	65
Phenylbenzyl ether	ZnCl <sub>2</sub> (3:1)	226°C 3.9 MPa H <sub>2</sub> 1 hour benzene solv.	100% conversion; phenol and diphenylmethane in equimolar amounts, and 2-hydroxydiphenylmethane	63 64
Dibenzyl ether	BF <sub>3</sub>	atmos. pres. benzene solv.	diphenylmethane, dibenzyl- benzene, polybenzylbenzene	67
Dibenzyl ether	AlCl <sub>3</sub> (1:1)	50°C atmos. pres. 5 hours	polymerized	68
Dibenzyl ether	ZnCl <sub>2</sub> (2.9:1)	232°C 4.8 MPa H <sub>2</sub> 1 hour benzene solv.	100% conversion to diphenylmethane	63 64

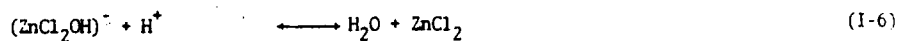
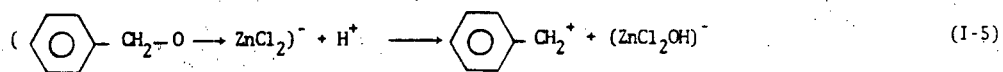
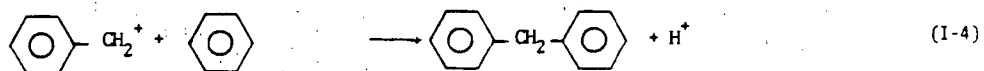
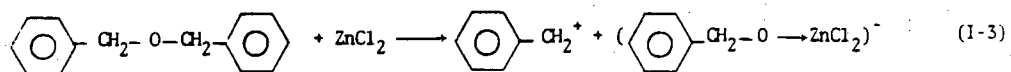
Table I-2  
(continued)

<u>Compound</u>	<u>Catalyst (cat:react. mole ratio)</u>	<u>Conditions</u>	<u>Principal Products</u>	<u>Ref.</u>
Phenyl-2-naphthyl ether	AlBr <sub>3</sub> (1.75:1) (by weight)	80°C atmos. pres. 4.5 hours benzene solv.	no reaction	69
Benzyl-1-naphthyl ether	ZnCl <sub>2</sub> (2.8:1)	226°C 5.0 MPa H <sub>2</sub> 1 hour benzene solv.	100% conversion; 1-naphthol, two isomers of benzyl-1-naphthol, diphenylmethane	63 64
Benzyl-n-propyl ether	BF <sub>3</sub>	50-100°C benzene solv.	diphenylmethane	70
Methoxybenzene	AlCl <sub>3</sub>	100°C atmos. pres. 2 hours	100% conversion to phenol	71
Methoxybenzene	AlCl <sub>3</sub> (1:1) (by weight)	125°C atmos. pres. 5 hours no solvent	trace of phenol	68
Methoxybenzene	ZnCl <sub>2</sub> :pyridine	200°C 2 hours	20% fission of ether	72
Triphenyl-methyl- p-tolyl ether	ZnCl <sub>2</sub> ( $\frac{1}{2}$ :1)	180°C atmos. pres. 30 min. no solvent.	66% triphenylmethanol 7.5% triphenylmethane	77

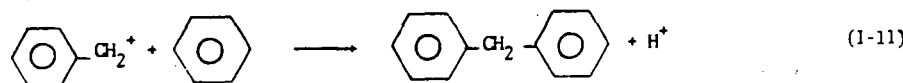
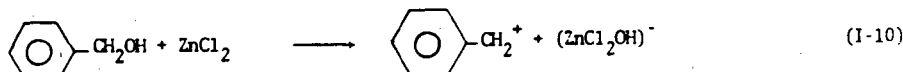
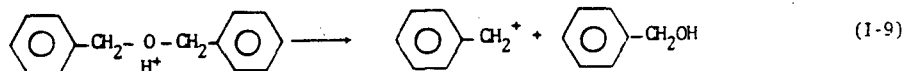
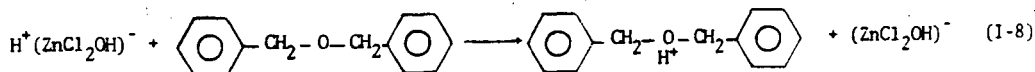
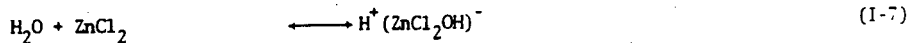
Mobley observed cleavage of both carbon-oxygen bonds in dibenzyl ether by zinc chloride in benzene at 232°C (63,64). The resulting benzyl fragments reacted with the benzene solvent, yielding diphenylmethane (63,64). In 1938, O'Connor and Sowa had seen the same behavior, with diphenylmethane production in the presence of benzene and boron trifluoride (67). Yamashita and Shimamura contacted dibenzyl ether with aluminum chloride at 50°C for five hours; they reported in 1958 that a polymer was the product (68).

Earlier, in 1937, Pfeiffer and Lowe had found that phenyl-β-naphthyl ether was non-reactive when exposed to aluminum bromide at 80°C (69). This is consistent with the stability of diphenyl ether, since the bond between the aromatic ring and oxygen is not cleaved by zinc chloride or aluminum chloride catalysts. Mobley has observed cleavage of benzylnaphthyl ether by zinc chloride at 226°C; here, the carbon-oxygen bond not involving aromatic carbon is being cleaved (63,64).

Mobley and Bell suggested a carbonium ion mechanism for diaryl ether reactions (63,64); for dibenzyl ether in the presence of benzene, they proposed two alternatives:



or



Carbonium ions are formed in Reactions (I-3), (I-5), (I-9), and (I-10), and react with benzene (the solvent) to form diphenylmethane in Reactions (I-4) and (I-11). These mechanisms, which are analogous to that suggested for aliphatic bridges, are in accord with experimental observations. The stability of the aromatic-oxygen bond is due to the difficulty of forming a phenyl carbonium ion. In the first mechanism, zinc chloride functions as a Lewis acid, while in the second, it combines with water to form a Brönsted acid.

Monacelli and Hennion had observed in 1941 that benzyl-*n*-propyl ether reacted when mixed with boron trifluoride at 50-100°C in benzene to give diphenylmethane (70). This indicates that the benzyl/oxygen bond was cleaved for this alkyl-aryl ether, and the reactive fragment then combined with benzene. In three studies, from 1942 to 1959, of

methoxybenzene treated with zinc chloride or aluminum chloride at temperatures of 100-200°C, phenol was the observed product, again indicating the stability of the aromatic ring/oxygen bond (68,71,72). This is in line with the results of several reports which indicate that acid catalysts promote dealkylation of alkyl-aryl ethers (73-76).

#### Scope of Work and Nature of Results

The present work has been concerned with the interactions of organic solvents with zinc chloride at temperatures up to 300°C, and with reaction of model compounds in zinc chloride/organic solvent systems. The model compound studies encompassed the investigation of products and mechanisms for the zinc chloride-catalyzed cleavage of diarylalkanes and diaryl and alkyl-aryl ethers in inert solvents, and in the presence of benzene, in the temperature range of 175-275°C.

The examination of interactions of zinc chloride with solvents established the types of interactions occurring between solvents and aqueous zinc chloride solutions around ambient temperatures, and determined the mutual solubilities of a few aromatic and aliphatic hydrocarbon solvents with zinc chloride, as well as reactions of these compounds when contacted with zinc chloride at elevated temperatures. When model compounds were treated with zinc chloride melts, the concentration of reactants and products was measured for reaction times

of 5 to 60 minutes, to allow calculation of rate constants and activation energies. Identification of some reaction products was made to verify postulated mechanisms.



## II. LOW TEMPERATURE SOLVENT INTERACTIONS WITH ZINC CHLORIDE

Solvents to be used in combination with zinc chloride catalysts in coal processing should, of course, not be rapidly degraded by the catalyst. For this reason, investigations of solvent/zinc chloride interactions under treatment conditions are appropriate. However, investigations at these relatively high temperature conditions are complex and time consuming, so that only a few solvents can be tested. To eliminate solvents not appropriate for high temperature investigations, a large number were tested at low temperature and atmospheric pressure. The primary interest was the reactions of the solvents with zinc chloride and their miscibility with aqueous zinc chloride solutions. Simple qualitative observations of phase behavior comprised most of the results.

### Equipment and Procedure

Glass sample bottles with 30 ml capacity were used to mix 10 ml of a zinc chloride/water solution and 10 ml of the appropriate solvent, at room temperature; mixing was accomplished by vigorous shaking by hand for a few minutes. The zinc chloride solution was composed of 200 g of zinc chloride (Matheson Coleman & Bell, reagent grade) with 130 ml distilled water. Solvents were all reagent grade, used as received, from many suppliers. Visual determination of miscibility was possible in all cases. For immiscible systems, the phase interface was clearly visible, while for miscible systems one continuous phase formed with no interface. A few solvents were partly soluble in the

aqueous zinc chloride solution; this was detected because the volume of one phase was obviously larger after mixing than before, and the volume of the other phase clearly smaller. A few solvents that were solid at room temperature were mixed with the zinc chloride solution at their melting points, an oil bath being used to heat the sample bottles.

### Results and Discussion

Sixty-nine solvents were contacted with aqueous zinc chloride at near ambient conditions. The solvents included aromatic hydrocarbons (with and without hydroxyl substituents), cyclic and non-cyclic ethers, ketones, alcohols, amines, and heterocyclic nitrogen compounds. The results are summarized in Table II-1.

Aromatic hydrocarbons are immiscible in zinc chloride, with hydroxyl substituents having no effect on miscibility. The diaryl and alkyl-aryl ethers are also immiscible.

The miscibility of cyclic ethers depends on their electron structure. In furan, one of the unshared electron pairs of oxygen is bound in the aromatic sextet of the molecule, and is not available for complexing with zinc chloride. Therefore, furan and zinc chloride are immiscible. Hydrogenation of the ring destroys the aromatic structure, freeing both electron pairs of oxygen and allowing zinc chloride to complex with dihydro- or tetrahydrofuran. The immiscibility of dihydropyran is possibly due to the presence of five carbon atoms in the

Table II-1

Low Temperature Interactions of  
Organic Solvents and Aqueous Zinc Chloride Solutions  
(equal volumes of solvent and  $\text{ZnCl}_2 + 40\%$  water)
















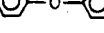
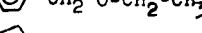






<u>Solvent</u>	<u>Structure</u>	<u>Behavior with Aqueous Zinc Chloride Solutions</u>	<u>Temperature</u>
Benzene		immiscible	room
Toluene		immiscible	room
o-Xylene		immiscible	room
p-Xylene		immiscible	room
Naphthalene		immiscible	80°C
Tetralin		immiscible	room
Phenanthrene		immiscible	101°C
Dihydroanthracene		immiscible	108°C
Phenol		immiscible	room, 120°C
o-Cresol		immiscible	room
m-Cresol		immiscible	room
p-Cresol		immiscible	room
1-Naphthol		immiscible	93°C
2-Naphthol		immiscible	122°C
Methoxybenzene		immiscible	room
Diphenyl ether		immiscible	room
Benzylethyl ether		immiscible	room
Furan		immiscible	room
Dihydrofuran		immiscible	room
Tetrahydrofuran		miscible	room
Dihydropyran		immiscible	room
Dioxane		miscible	room
Acetone	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	miscible	room
Acetophenone		immiscible	room

Table II-1  
(Continued)




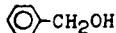
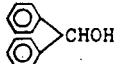
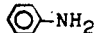
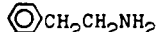

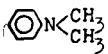
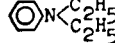
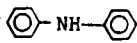








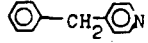









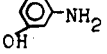
<u>Solvent</u>	<u>Structure</u>	<u>Behavior with Aqueous Zinc Chloride Solutions</u>	<u>Temperature</u>
iso-Propanol	$\text{CH}_3\overset{\text{OH}}{\text{CH}}\text{CH}_3$	miscible	room
iso-Butanol	$\text{CH}_3\overset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{OH}$	partial miscibility miscible	room 45°C
sec-Butanol	$\text{CH}_3\text{CH}_2\overset{\text{OH}}{\text{CH}}\text{CH}_3$	miscible	room
tert-Butanol	$\text{CH}_3\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{OH}$	miscible	room
iso-Pentanol	$\text{CH}_3\overset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{CH}_2\text{OH}$	immiscible	room 98°C
tert-Pentanol	$\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{OH}$	miscible	room
2-Ethyl-1-butanol	$\text{CH}_3\text{CH}_2\overset{\text{CH}_2\text{CH}_2\text{OH}}{\underset{\text{C}_2\text{H}_5}{\text{C}}}$	immiscible	room, 98°C
Hexanol	$\text{CH}_3(\text{CH}_2)_5\text{OH}$	immiscible	room, 98°C
1-Octanol	$\text{CH}_3(\text{CH}_2)_7\text{OH}$	immiscible	room, 98°C
1-Undecanol	$\text{CH}_3(\text{CH}_2)_{10}\text{OH}$	immiscible	room, 98°C
Tetradecanol	$\text{CH}_3(\text{CH}_2)_{13}\text{OH}$	immiscible	room, 98°C
Cyclohexanol		partial miscibility	room, 98°C
m-Methylcyclohexanol		immiscible	room, 98°C
2-sec-Butylcyclohexanol		immiscible	room
Benzyl alcohol		immiscible	room
Benzhydrol		immiscible	67°C
Anisyl alcohol	$\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{OH}$	immiscible	room
Dimethylamine	$\text{CH}_3\text{NHCH}_3$	white solid complex	room
Triethylamine	$(\text{C}_2\text{H}_5)_3\text{N}$	white solid complex	room
Aniline		solid complex	room
Phenethylamine		white solid complex	room
N-Methylaniline		brown solid complex	room
N,N-Dimethylaniline		white solid complex	room
N,N-Diethylaniline		white solid complex	room

Table II-1  
(continued)

<u>Solvent</u>	<u>Structure</u>	<u>Behavior with Aqueous Zinc Chloride Solutions</u>	<u>Temperature</u>
Diphenylamine		immiscible	53°C
Triphenylamine		immiscible	126°C
Ethylenediamine	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	white solid complex	room
Pyrrole		immiscible	room
Pyrrolidine		solid complex	room
Indole		immiscible	53°C
Pyridine		solid complex	room
Piperidine		solid complex	room
3,5-Dimethylpyridine		solid complex	room
2,4,6-Trimethylpyridine		solid complex	room
4-Benzylpyridine		solid complex	130°C
2,2'-Bipyridine		solid complex	room
2,6-Dimethylpiperidine		solid complex	room
Quinoline		solid complex	room
Isoquinoline		solid complex	room
Acridine		solid complex	111°C
Pyrazine		solid complex	53°C
Imidazole		miscible	90°C
8-Hydroxyquinoline		pasty complex	76°C
2-Hydroxypyridine		miscible	107°C
m-Aminophenol		miscible	123°C

ring, making it more like a hydrocarbon, while the two oxygen atoms in dioxane complex with zinc chloride to form a miscible solution.

Acetone is miscible with the zinc chloride/water solution because of its polarity. This is consistent with a published solubility value of 30.3% by weight zinc chloride in acetone at 18°C (78). Evidently the phenyl group of acetophenone is sufficient hindrance to prevent acetophenone/zinc chloride miscibility.

The polarity of small alcohols allows them to dissolve in the zinc chloride/water solution. Alcohols containing four or five carbon atoms are borderline, and larger alcohols do not dissolve. Similar behavior has been observed with alcohols and water (79, p. 497).

Most amines, as strong bases, complex with or react with zinc chloride, giving solid compounds when mixed with the zinc chloride/water solution. A visible reaction, with some foaming and gas evolution that appeared mildly exothermic, accompanied mixing. The failure of diphenylamine and triphenylamine to complex is probably due to the increasing aromatic character caused by additional phenyl groups.

Cyclic nitrogen compounds behaved similarly to cyclic ethers. Saturated cyclic compounds such as pyrrolidine or piperidine are strong bases ( $K_b \approx 10^{-3}$ ) (79, p. 1010, 1018), and therefore, react strongly with zinc chloride. Pyridine and its derivatives are much weaker bases ( $K_b \approx 10^{-9}$ , (79, p. 1018), but react with zinc chloride because of the aromatic electron structure. Pyridine has vacant  $\pi$ -orbitals in addition to lone pairs of electrons on the nitrogen atom that

take part in the usual acid/base interactions. These vacant  $\pi$ -orbitals accept electron density from filled orbitals in the zinc atom, thereby forming a type of  $\pi$ -bond between pyridine and zinc (80, p. 682). The complex formed, with both  $\pi$ -bonds and electron pair  $\sigma$ -bonds, is very stable.

When pyridine was mixed with aqueous zinc chloride, an exothermic reaction took place and a vapor (which appeared to be water) was evolved. Because water and zinc chloride complex only with electron pair  $\sigma$ -bonds, when pyridine was added the extra stability of the pyridine/zinc chloride complex resulted in displacement of water (which boiled off) and the formation of a complex containing one zinc chloride molecule and two pyridine molecules. (This composition for the complex was reported by Mason and Mathews (81), and by Kovaleva and coworkers (82), and verified by the University of California Micro-Analytical Laboratory). The reaction of piperidine with zinc chloride was much milder, presumably because the complex formed with piperidine is not stabilized by  $\pi$ -bonds.

Pyrrole and indole behaved quite differently from pyridine and the other cyclic nitrogen bases, because in their aromatic structures the electron  $\pi$ -clouds contain the very stable aromatic sextet, or six electrons, and the electrons on nitrogen are bound in the aromatic electron cloud (79, p. 1005). Donation of electrons requires sacrifice of aromatic character, which is very unfavorable; therefore, pyrrole and indole are weak bases ( $K_b \approx 10^{-14}$ ) (79, p. 1010) and do not complex with zinc chloride. The remaining cyclic nitrogen compounds

complex with zinc chloride. Addition of a hydroxyl group to pyridine, quinoline, and aniline evidently hinders complex formation, since the hydroxylated compounds were dissolved without much heat release, and in some cases without precipitation.

A qualitative assessment of stability of complexes of zinc chloride with pyridine, substituted pyridines, quinolines, and piperidine was made by measurement of approximate melting point; data are presented in Table II-2. Addition of hydrocarbon substituents destabilized the complex, as can be seen from the pyridine/zinc chloride complex compared to the dimethylpyridine or 4-benzylpyridine complexes. The dimethylpiperidine complex is not as stable as the dimethylpyridine complex; this is because of the extra stability of the  $\pi$ -bonded pyridine complex.

The isoquinoline complex melted at a temperature close to that of the pyridine complex, while the quinoline complex melted 100°C higher. The cause of this behavior is unknown.



Table II-2

Melting Points of Complexes of  
Zinc Chloride with Cyclic Nitrogen Bases  
(molar ratio of nitrogen base:ZnCl<sub>2</sub>=2:1)

<u>Solvent in Complex</u>	<u>Melting Range</u>
Dimethylpiperidine	105-115°C
4-Benzylpyridine	110-120°C
Dimethylpyridine	130-140°C
Pyridine	170-180°C
Isoquinoline	165-175°C
Quinoline	275-285°C

### III. HIGH TEMPERATURE INVESTIGATION OF ORGANIC SOLVENT/ZINC CHLORIDE SYSTEMS

High temperature studies of solvent/zinc chloride systems were undertaken to identify solvent degradation reactions catalyzed by the zinc chloride, and to observe the phase behavior of the system. To accomplish this, it was necessary to mix the solvent and salt melt together at temperatures of interest in coal liquefaction studies (between 150 and 300°C), and then to allow settling and phase separation. Samples of the resulting organic and inorganic phases could then be analyzed for mutual solubility and solvent reaction products.

Tetralin was extensively studied, since it has received major attention at Lawrence Berkeley Laboratory as a coal liquefaction agent in conjunction with zinc chloride (16). As a comparison, decalin was briefly studied. Mesitylene and dodecane were also tested with zinc chloride to find a solvent with a low vapor pressure that was non-reactive toward zinc chloride, for use in model compounds studies.

#### Equipment

In order to examine high temperature interactions of organic solvents with zinc chloride, an apparatus was constructed to mix solvent with zinc chloride at elevated temperatures, and then let the hot mixture separate before sampling. The apparatus allowed operation at temperatures between ambient and 350°C with pressures up to 3.4 MPa, and provided for preheating the organic and salt phases separately to

the final temperature before mixing. The equipment consisted of a main reactor with 500 ml capacity, in which mixing took place, associated sample, inlet, and vent lines, and a preheat vessel. An electrode sensor in the main reactor was included to detect the boundary between the solvent and salt phases, and a proportional temperature controller was used to maintain constant temperature during experiments. A schematic diagram of the apparatus is shown in Figure III-1.

The main reactor was fabricated from type 316 stainless steel (316SS) tube, with a 2-1/2 inch internal diameter and 1/4 inch wall thickness; it had an internal volume of 500 ml. This reactor was sealed to a top flange, also 316SS, with a replaceable copper gasket. The top flange was machined to accept six Cajon VCR fittings for tubing connections and one commercial stirring seal assembly manufactured by the Parr Instrument Company. The stirring seal, in turn, supported a stirring shaft and three stirring propellers (two were used for early experiments).

Tubes welded to the Cajon VCR fittings and extending into the reactor vessel were used for sample, inlet, and vent lines, as well as for a thermocouple well and an electrode housing. The VCR fittings were sealed to the flange with nickel gaskets. Initially these tubes had been welded directly onto the flange, but repeated failure of the welds (probably resulting from chloride ion corrosion and thermal stresses) led to the use of the Cajon fittings.

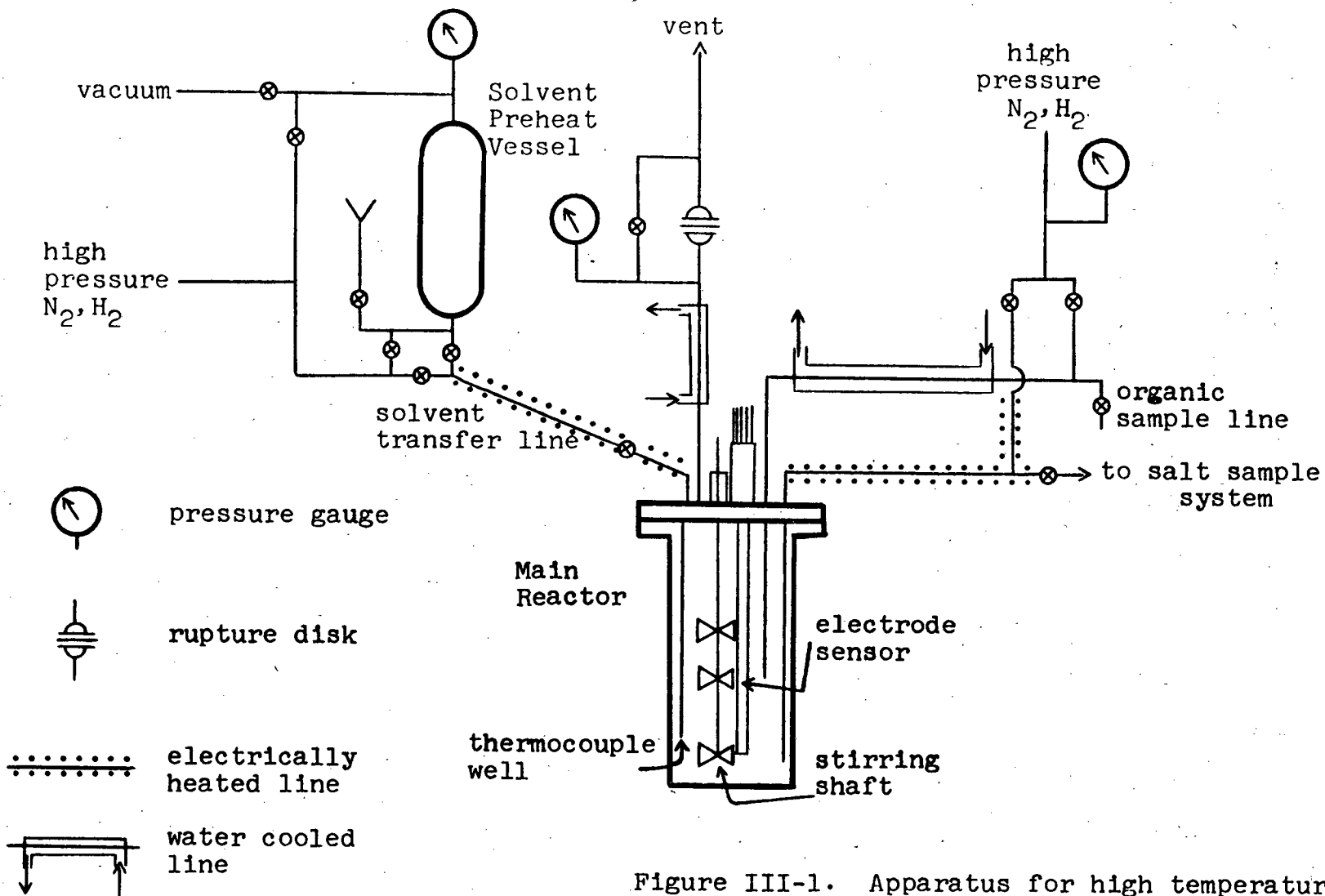


Figure III-1. Apparatus for high temperature organic solvent/zinc chloride contacting

For a few of the later experiments, the vent line was equipped with a water cooling jacket. There was a continual stream of gas out the vent (because of sample line backflushing), and the cooling jacket was added to provide reflux condensation to prevent depletion of organic solvent or water as a run progressed.

The solvent preheat vessel was a 300 ml 316SS sample cylinder, with a funnel attached to allow filling. The solvent preheat vessel and tubing connecting it to the main reactor were wrapped with high temperature heating tapes (576 and 144 watts respectively) and insulation.

The organic phase sample line, made of 1/8 inch outside diameter (OD) 316SS tubing, was equipped with a water jacket to cool samples; this prevented flashing as the samples flowed into sample bottles at atmospheric pressure. This line was also equipped for continuous metered backflush with gas during an experiment.

The zinc chloride-phase sample line was made of 1/4 inch OD 316SS tubing, and was wrapped with a 576 watt high temperature heating tape and insulation to insure against salt solidifying while being sampled. This line was also equipped for continuous metered backflush with gas during an experiment (except while sampling). During sampling, the molten salt passed into the salt sampling system shown in Figure III-2. The salt was collected in the salt sample bottle (2 dram capacity), while condensable vapors resulting from sample depressurization were collected in a hexane vapor trap. This trap consisted of a 1-1/4 inch ID copper tube packed with glass helices between

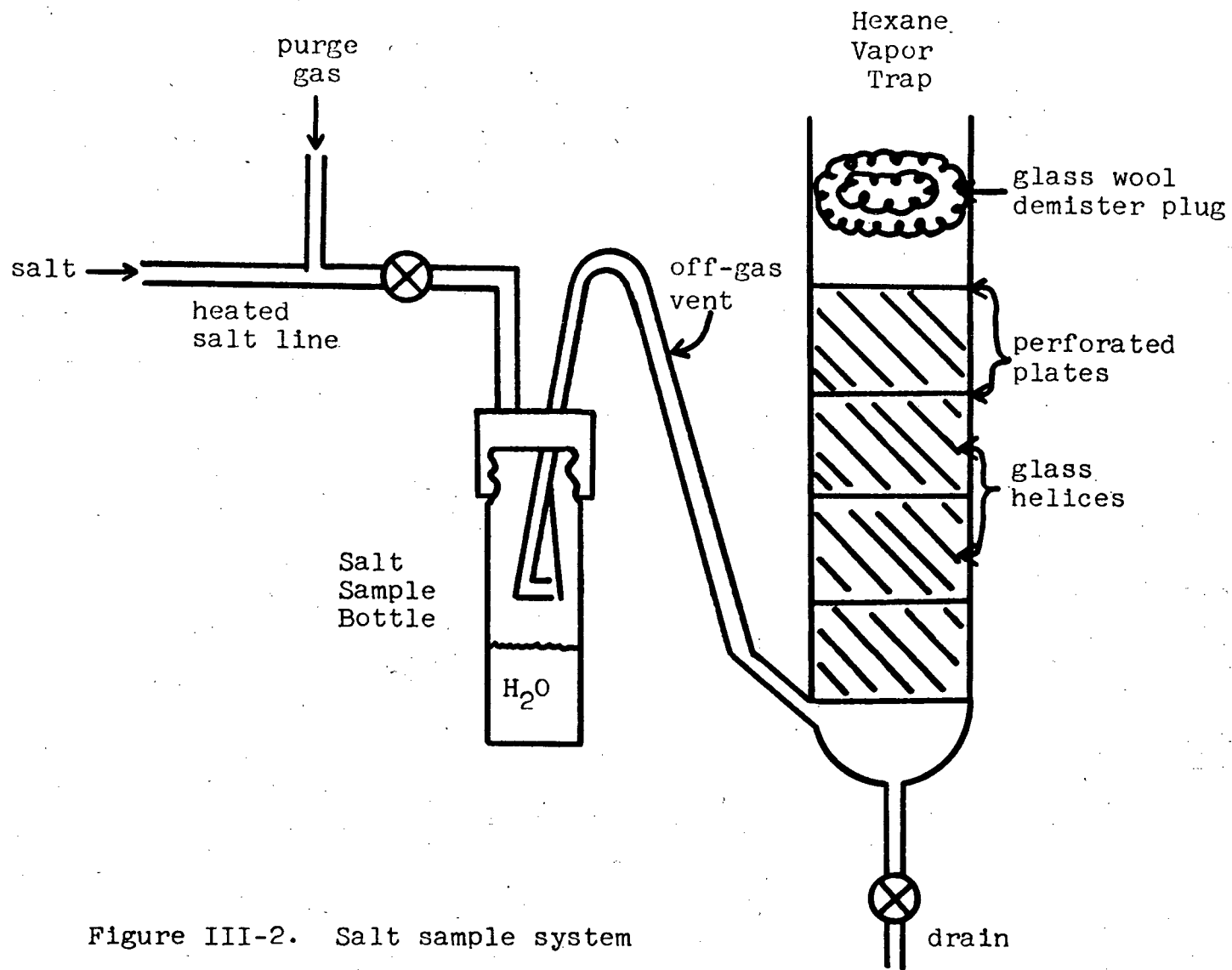


Figure III-2. Salt sample system

perforated plates, with a total packing height of about five inches; the entire trap was immersed in an ice bath. Hexane in the trap dissolved condensable vapors as they volatilized from the salt.

The electrode sensor was designed to indicate phase behavior, with the high electrical conductivity of molten zinc chloride and low electrical conductivity of organic solvents providing the means of detection. The electrode design, shown in Figure III-3, consisted of 15 platinum wires, each 1/4 inch longer than the next, with all but the final 1/4 inch covered by a Pyrex glass sheath. The 15 sheathed wires were held together by fiberglass sleeving, and were positioned so that they extended into the reactor within an inch of the bottom. The wires entered the reactor through a 15-hole Teflon seal, which was mounted on top of a 3 inch section of 3/4 inch OD 316SS tubing extending above the flange (this helped keep the seal cool). Each electrode wire was connected to the indicator circuit, where it lead to a 30 volt AC power supply through an incandescent light bulb; the other side of the power supply was grounded, as was the reactor. This circuit is shown in Figure III-3. For a wire immersed in the salt phase, the salt completed the electric circuit, causing the corresponding bulb to light; bulbs attached to wires immersed in organic remained unlighted. Thus, from the light panel, the location of the interface between phases could be determined, and observations on mixing efficiency and on the rate of phase separation could be made. A 60 Hz AC voltage was used to avoid water electrolysis.

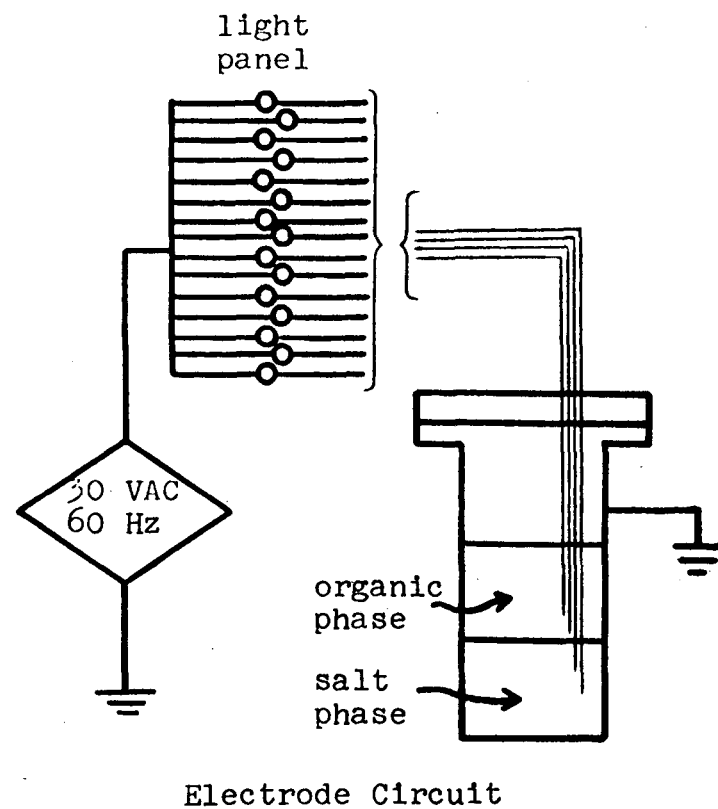
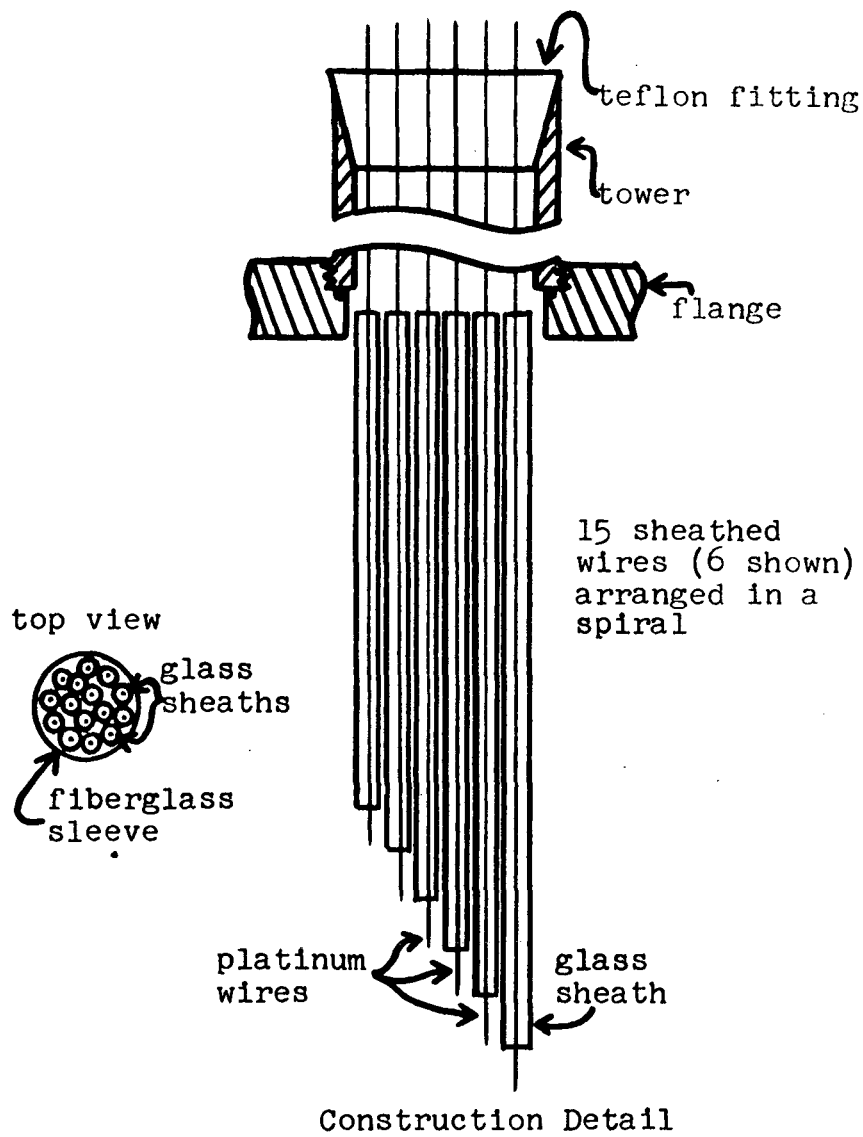


Figure III-3. Electrode sensor design



Reactor pressure, solvent preheat pressure, and the sample line backflush manifold pressure were measured by 316SS pressure gauges. An iron-constantan thermocouple inserted into the well in the main reactor interior was used to measure reactor temperature, and was used with an Omega Model 49 proportioning temperature controller to control the 600 watt reactor heater. Thermocouples were also used with an Omega Model 175 digital readout meter to monitor solvent preheat vessel, solvent transfer line, salt sample line, reactor top flange, stirring seal, and vent line temperatures. In addition, the main reactor and solvent preheat vessel temperatures were recorded on a Hewlett-Packard Model 7100B strip chart recorder.

Zinc chloride used was reagent grade from Matheson Coleman & Bell, with a minimum  $ZnCl_2$  content of 97.0%. Tetralin, decalin, mesitylene, and dodecane were all reagent grade from Aldrich Chemical Company. Hexane used in the hexane vapor trap was Distilled-In-Glass Non-Spectro grade from Burdick and Jackson Laboratories. All materials were used as received with no further purification.

#### Procedure

The procedure to conduct a solvent/zinc chloride contacting experiment had four basic activities: preheat of the solvent and zinc chloride separately to the desired temperature; stirred contact of the two phases together for a specific time; separation of the mixture (by gravity settling) into organic and salt phases; and sampling of both phases.

To start an experimental run, 160 ml of solvent was placed into the solvent preheat vessel, which was then purged with nitrogen to remove air and pressurized to about 340 kPa; heating of the vessel was then started. The zinc chloride and water were mixed in the main reactor vessel. Typically, 375 g of zinc chloride was used, with 38 ml water for a run with 10% water; this gave approximately equal volumes of the salt and solvent. The reactor vessel was closed and purged with nitrogen. Backflush of the sample lines with nitrogen was then started and continued throughout the experiment. After the purge, the reactor was pressurized to 690 kPa with nitrogen, the stirring commenced at a few hundred rpm, and heating of the reactor initiated.

When the solvent preheat vessel and main reactor both reached the desired temperatures, stirring was stopped and the solvent pressured into the reactor. To obtain a desired final temperature of the mixture, the reactor had to be heated about 25 to 35°C higher, since the solvent cooled somewhat during transfer. Stirring was then resumed at 1100-1200 rpm.

For the duration of contacting, usually 60 minutes, the reactor was held at constant temperature and pressure. The effectiveness of mixing was indicated by the electrode display. At the end of contacting, stirring was terminated and a settling time of 15 minutes allowed so that the phases could separate. Observation of the electrode display provided an indication of how rapidly the phases separated. After 15 minutes, sampling of the phases was started.

The organic phase was sampled after the backflush gas in the organic sample line was shut off and the cooling water flow to the jacket surrounding the line was started. The liquid was then allowed to flow smoothly into a sample bottle, with two or three 6 ml samples being taken.

Before molten salt samples were taken, the vapor trap was filled with 20 ml hexane, and the glass wool demister plug saturated with 10 ml hexane. Also, 3 ml water was placed in a 2 dram sample bottle, and the bottle attached to the sample line. With the backflush gas shut off, salt (and gas from the line) was allowed to flow into the bottle through the sample valve. After a few grams of salt had passed into the bottle, the backflush gas was again turned on; this forced the salt remaining downstream in the sample line into the sample bottle, and flushed the rest back into the reactor. The 2 dram vial with the aqueous salt sample was removed, and the hexane was drained from the vapor trap for analysis.

Although this procedure was followed in the majority of experiments, there were several variations. For the first six experiments, there was no solvent preheat, so the solvent was added to the zinc chloride/water mixture before heating. In several cases, the amount of zinc chloride used was as low as 300 g or as high as 438 g. For most of the experiments involving tetralin, nitrogen gas was used to pressurize the reactor; for the remaining experiments, hydrogen was used.

### Analysis

Organic phase samples were analyzed, primarily by gas chromatography (GC), to allow detection and identification of solvent degradation products. A Chromalytics Model MP-3 Thermal Chromatograph equipped with a Dexsil 300 column (8% loading on Chromosorb GHP, 6 feet long) and flame ionization (FID) and thermal conductivity detectors was used initially. A Hewlett-Packard Model 5840A Gas Chromatograph equipped with two Dexsil 300 columns (3% loading on Chromosorb WHP, 6 feet long) and dual flame ionization detectors was used for the remaining analyses. OV-225 columns (3% loading on Chromosorb WHP, 6 feet long) were used to achieve better separation with some samples. For all GC work, helium was used as the carrier gas, flowing at 20 cc/min through each 1/8 inch OD column. Temperature programming was employed to improve component separation; in the usual program, the column temperature rose from the initial 60°C at 10°C/min for 7 minutes, and 20°C/min thereafter, to the final temperature (320°C for Dexsil columns, 250°C for OV-225 columns) and was held there for 2 to 8 minutes. Peak identifications were made by comparison of retention times to those of known pure compounds.

For all experiments, the product analysis by GC was calculated on the basis of fraction of total peak area by FID. To be truly quantitative, response factors for all compounds should be measured for the particular detector in use; this was not done, since some peaks were not identified and some identified compounds were not readily available.

for calibration. Therefore, the calculated degradation yields are only semi-quantitative. However, the FID basically counts carbon atoms by ionizing molecules as they enter the detector; because the degradation products were chemically similar to the initial solvent (aromatic hydrocarbons in most cases), the products and solvent should ionize in a similar manner in the FID, and the FID response should be approximately equal for all these compounds.

Organic samples from a few experiments were analyzed by gas chromatography coupled with mass spectrometry (GCMS). This was done by Dr. A. Newton of Lawrence Berkeley Laboratory, using a Finnigan Model 4023 GCMS unit. Comparison of the mass spectrum of an unknown peak to a library of mass spectra (83) allowed identification of many unknown compounds. The zinc content of a few organic samples was measured with X-ray fluorescence by R. Giaque of Lawrence Berkeley Laboratory.

The molten salt samples were analyzed to determine solubility of organic materials in the molten salt; this required analysis of the aqueous salt sample and the hexane vapor trap liquid. The hexane from the vapor trap was analyzed by GC to detect any organic compounds that flashed off the salt sample. The aqueous salt sample was extracted with hexane at its boiling point in a Kontes Bantamware Ether Extraction unit to remove remaining organics; the hexane was analyzed by GC. From GC data for both hexane solutions and from sample weights, the amount of organic material dissolved in the salt was calculated.

To determine the extraction duration required for nearly complete removal of organic species from the aqueous phase, solutions of measured amounts of acetophenone in aqueous zinc chloride were extracted for times ranging from 30 minutes to 6 hours. An extraction time of one hour resulted in 90 to 95% recovery of the acetophenone; therefore, one hour extraction times were used for all analyses.

### Results and Discussion

The interactions of tetralin with zinc chloride were studied at 250 and 300°C, with several different concentrations of water in the salt melt. The effect of the presence of zinc oxide was tested at 250°C. Most experiments were performed with a nitrogen atmosphere, but one at 300°C was with hydrogen. The behavior, with a zinc chloride melt containing 10% water, of decalin, mesitylene, and dodecane was examined at 300°C under hydrogen.

For all experiments, the amounts of solvent and zinc chloride were chosen such that the volume ratios were approximately 1:1; this resulted in a zinc chloride:solvent molar ratio of about 2:1, and a weight ratio of about 2.6:1. In previous studies, much smaller ratios of zinc chloride to reactant had been used (54,63,64). The use of massive amounts was chosen to more closely reproduce the conditions used for treatment of coal in zinc chloride/organic solvent systems.

### Tetralin/Zinc Chloride

A number of different conditions were used in exploration of tetralin/zinc chloride interactions; conditions and products for the experiments are listed in Tables III-1 and III-2.

Zinc chloride containing 2-4% water is very viscous at 250°C, though increased water contents of 5-10% reduce viscosity considerably.\* For experiments with 2-4% water, mixing of the phases was poor; during stirring, the salt phase (as observed by the electrode display) extended no further than it did when quiescent. For experiments with higher water contents, mixing was generally better; in a majority of cases, the zinc chloride phase extended through most of the liquid in the reactor, as indicated by the steady lighting of most electrode display bulbs.†

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\*This observation was made by simple stirring of melts made with several water contents, in an exploratory part of this study. Molten zinc chloride has an unusually high viscosity when compared to other fused salts, apparently as a result of complex ions formed in the molten state (84). Drastic reductions in melt viscosity have been reported by the addition of sodium chloride (97) and by the addition of methanol (98) to the melt (perhaps resulting in destruction of the complexes), with the viscosity decreasing from 75 poise at 300°C for pure zinc chloride (84) to an estimated 0.6 centipoise at 275°C for zinc chloride containing 17% methanol (89). No measurements of viscosity were made here for melts with different water contents, but the effect of water should be similar to that of methanol.

†Because the bulbs were steadily lit, it appeared that the zinc chloride phase was continuous, with tetralin suspended in it; with a continuous tetralin phase, the zinc chloride-electrode contact would have been intermittent, with a corresponding flickering of the lights.

Table III-1

Conditions for tetralin/zinc chloride contacting

Exp. Run no.		Temp °C	%H <sub>2</sub> O	Time min.	P,MPa N <sub>2</sub>	P,MPa total	Mixing <sup>+</sup>	Heatup time,min.
22	*	250	--	60	1.55	1.79	--	--
23	*	300	--	60	1.16	1.72	--	--
1		200	7	60	1.22	1.37	G	30
6	**	250	3	40	1.01	1.37	P	40
9	**	250	3	40	1.01	1.37	P	--
7	**	250	4	30	1.15	1.55	P	--
8	**	250	4	30	0.43	0.82	P	--
2		250	5	46	0.96	1.37	F	30
4		250	5	30	0.96	1.72	G	20
10		250	5	30	0.96	1.37	F	--
3		250	6	30	0.60	1.03	G	30
5		250	6	48	1.11	1.55	G	22
11		250	6	30	0.94	1.37	F	--
13		250	10	60	0.79	1.37	G	--
16		250	10	60	1.06	1.65	F	--
21		250	10	60	1.20	1.79	F	--
17		300	10	60	0.16	1.68	G	--
18		300	10	60	0.16	1.68	F	--
19		300	10	60	0.23	1.75	G	--
24		300	10	60	0.27	1.79	VG	--
23	***	300	10	60	0 <sup>++</sup>	1.37	VG	--

\* thermal stability test - no ZnCl<sub>2</sub> used.

\*\* 3% ZnO added to melt.

\*\*\* hydrogen used instead of nitrogen.

+ Mixing definitions:

P - salt phase unexpanded during mixing

F - salt phase expanded slightly during mixing

G - salt phase expanded through most of liquid during mixing

VG - salt phase expanded throughout liquid during mixing

++ see text for explanation



Table III-2

Products from tetralin/zinc chloride contacting.

Products are percent by weight of treated organic phase.

Exp. Run no.	light products	butyl-benzene	methyl-indan	tetralin	naphthalene	methyl-tetralin	dimethyl-indan	dimer A*	dimer B**	total dimer	total yield
22	---	---	---	99	.1	---	.05	.06	---	.1	0.1
23	---	---	---	99	.1	---	.04	.06	---	.06	0.1
1	---	---	.1	94	++	.3	.3	3.0	.1	3.9	4.6
6	---	---	1.1	92	++	.7	tr	1.5	.9	2.5	4.3
9	---	---	.9	98	++	---	.03	.2	.2	.4	1.3
7	---	---	.1	96	++	.1	.1	.7	.3	1.2	1.5
8	---	---	.1	96	++	.03	.1	.9	.3	1.4	1.6
2	---	---	.1	93	++	3.0	.2	.6	.2	1.0	4.3
4	---	---	.1	95	++	.7	---	2.0	.4	2.5	3.3
10	---	---	.6	97	++	---	.05	1.0	.3	1.4	2.0
3	---	---	.1	94	++	.7	.1	2.0	1.0	3.2	4.1
5	---	---	.6	88	++	.9	.04	3.0	3.9	7.1	8.6
11	---	---	.1	98	++	tr	.07	.9	.3	1.3	1.5
13	---	---	---	99	tr	---	.05	.5	.3	.8	0.9
16	---	---	.2	98	.1	---	.1	.6	.1	.7	1.0
21	---	---	---	97	.2	---	.03	.3	.2	.5	0.5
17	.2	.8	1.3	96	.4	---	tr	.1	tr	.1	2.4
18	.2	.6	1.0	95	.5	.08	.17	1.3	.3	1.6	3.7
19	.2	.6	1.1	96	.5	---	.02	.3	.1	.4	2.3
24	.05	.6	2.8	94	.2	.14	---	.9	.8	1.7	5.3
23	.2	1.5	4.5	89	.8	.4	---	1.7	1.0	2.7	9.3

\* dimer A: 1,1',2,2',3,3',4,4'-octahydro-2,2'-binaphthyl

\*\* dimer B: 1,1',2,2',3,3',4,4'-octahydro-2,5'-binaphthyl

++ naphthalene not separated from tetralin in GC

In all cases, the tetralin/zinc chloride mixture rapidly separated into two phases when stirring was terminated, with typical separation times of 20 to 30 seconds (in the worst case, separation was complete after three minutes). The tetralin was found to contain 15 to 30 parts per million (ppm) zinc by weight after contacting at 250 and 300°C. However, when the organic sample was filtered through a 0.5 micron Teflon filter at room temperature, zinc was no longer detected in the filtrate. Therefore, zinc chloride was apparently insoluble in tetralin at room temperature, but was either slightly soluble or present in suspension at 250 to 300°C.

The tetralin solubility measured in zinc chloride with 10% water was small, ranging from a trace to 2 parts per thousand (ppt) for contacting at 300°C and from 2 to 8 ppt at 250°C. The solubility was so low that there was quite a bit of variance in measured values, as shown in Table III-3. Despite this variance, it appeared, in most cases, that the measured tetralin solubility decreased with increasing settling time, indicating that the tetralin was not in solution, but in a gradually separating suspension. In one experiment with 2% water, a large tetralin solubility was found (about 2% tetralin in the melt), which probably was the result of tetralin suspension in the very viscous melt.

Tetralin degradation products and yields, shown in Table III-2, have significant variation for similar experimental runs. For low water content runs, the poor mixing probably caused at least some of the variance. In addition, the first six experiments (Runs 1-6), were

Table III-3

Tetralin solubility measured in zinc chloride after contacting at 250°C and 300°C. Equal volumes of tetralin and zinc chloride + 10% water, contacted for 60 minutes at 1.37-1.78 MPa total pressure.

<u>Experimental Run no.</u>	<u>Temp. °C</u>	<u>Settling Time, min.</u>	<u>Tetralin Conc. ppt (molar)</u>	<u>Comments</u>
13	250	27	4.2	$\frac{1}{2}$ inch vapor trap (early design)
16	250	29 39	8.3 4.2	
21	250	20 28	2.7 2.4	
17	300	27 47	0.19 0.25	low level of tetralin in reactor
19	300	20 27 32	0.09 0.12 0.16	no demister plug
24	300	25 38 50	2.4 1.0 0.2	
26	300	23 49	0.04 trace	

performed without solvent preheat; the tetralin and zinc chloride/water solution were mixed cold and then heated, significantly increasing the contacting time of the two phases. These six experiments all showed much higher degradation of the tetralin than corresponding experiments with solvent preheat.

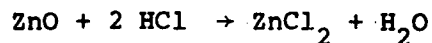
To determine if degradation products seen were the result of catalysis by zinc chloride, tetralin was held at 250°C and 300°C for one hour in the absence of zinc chloride (Runs 22,23). Total yield of degradation products was low in both cases, indicating that tetralin was thermally stable to 300°C. This is in agreement with stabilities reported by other workers (85,86).

When tetralin was contacted with zinc chloride at 250°C, the total degradation product yield ranged from 0.5 to 2% by weight (Runs 7-11, 13,16,21). A small amount (0.1-0.9%) of the tetralin was rearranged to methylindan (identification of the particular isomers of methylindan was not possible), and a larger fraction (0.4-1.4%) was dimerized. The dimer compounds shown in Table III-2 were tentatively identified by GCMS. In some cases, other dimer peaks with similar GC retention times were present, and were included in the total amount of dimer in Table III-2. In addition, small amounts of dimethylindan were found in most experiments.

The effect of the water content of the zinc chloride melt on tetralin degradation was examined in Runs 10,11,13,16, and 21 (all with solvent preheat and good mixing). At 5% water content, the total degradation product yield was 2% by weight, and at 6% water content the

yield was 1.5%, both after 30 minute contacting at 250°C; with 10% water content, the yield was from 0.5 to 1% after 60 minute contacting at 250°C. Although the variances in conversion data preclude confirmation of the effect, these data indicate a probable correlation between increasing water content of the melt and decreasing tetralin degradation.

Zinc oxide was added to the melt in a few experiments in an attempt to reduce corrosion, by removing HCl from the vapor via the reaction:



The effect of zinc oxide on degradation of tetralin appeared minimal, with slightly decreased total conversion, as seen from a comparison of the yields of Runs 7,8 and 9 with those of Runs 2,4 and 10. However, all of the experiments with zinc oxide also had low water content in the melt, causing poor mixing and adding uncertainty to the results.

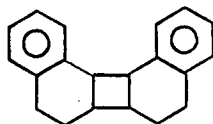
One contacting of tetralin with zinc chloride was made at 200°C (Run 1). The degradation products were similar to those found at 250°C. Comparison of conversions was not practical, since the experiment at 200°C was made without solvent preheat, and therefore had a large uncertainty in contacting time.

At 300°C under nitrogen, with 10% water in the melt, degradation products similar to those found at 250°C were seen, with additional cracking products also present (Runs 17,18,19,24). Methylindan yields at 300°C ranged from 1 to 3% by weight, significantly higher than yields at 250°C with 10% water. Dimer yields were also higher at 300°C than 250°C, with yields from 0.1 to 1.7%. In addition, significant amounts of butylbenzenes (0.6 to 0.8%) and lighter cracking products (0.05 to 0.2%) were present at 300°C, which were absent at 250°C. Since the formation of methylindan indicates cracking of the saturated ring of tetralin with recyclization of the fragment to form a five-membered ring, cracking occurs at 250°C as well as 300°C. However, at 250°C the only reaction of the fragment apparently forms the cyclic methylindan, while at 300°C, an additional capping of the fragments may take place to preserve butylbenzenes and other cracking products.

Hydrogen was used in one experiment at 300°C (Run 26). In this experiment, more rearrangement, dimerization, and cracking were observed, with a total degradation product yield of 9.3% by weight. Thus, it appears that molecular hydrogen plays a significant role when

present. Curiously, the amount of naphthalene formed also increased when hydrogen was used.\*

The degradation products that were observed here are consistent with those previously reported for treatment of tetralin with zinc chloride and aluminum chloride. Morita and Hirose treated tetralin with zinc chloride at 425°C under hydrogen and observed 1-methylindan as the major product, with butylbenzenes and other alkylbenzenes and aliphatic hydroaromatics also present (18). Orlow and Lichatschew also found methylindan from tetralin contacted with aluminum chloride at 460-470°C under hydrogen (22). The dimerization of tetralin by aluminum chloride has been reported by several investigators at temperatures of 30-80°C (19,20,21), although Turova-Poljak found no dimer at higher temperatures of 170-270°C (23,24). Dansi and Ferri suggested a molecular formula of  $C_{20}H_{20}$  for the dimer, with the structure (19):

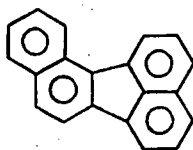


while Nenitzescu and Avram identified it as 10,11-benzofluoranthrene,

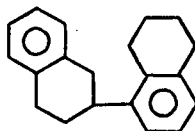
$C_{20}H_{12}$  (20):

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\*Although hydrogen was bubbling through the liquid as a result of backflushing sample lines, the total pressure in the reactor was less than the estimated vapor pressure of tetralin plus that of zinc chloride with 10% water. Presumably enough water boiled off the zinc chloride to reduce its vapor pressure - this would have given a water content of the melt of about 9%. The vapor above the liquid was probably mostly tetralin and water vapor.



Neitzescu proposed a mechanism having as intermediates both 1,1',2,2',3,3',4,4'-octahydro-(2,5')-binaphthyl:



and a  $C_{20}H_{20}$  structure similar to that suggested by Dansi. Thus, it is possible that the 1,1',2,2',3,3',4,4'-octahydro-(x,y)-binaphthyls identified by GCMS in degradation products from all experiments involving treatment of tetralin with zinc chloride indicate that zinc chloride had catalyzed the same reaction that was proposed by Neitzescu, but was not a sufficiently strong catalyst at 300°C to promote further condensation and dehydrogenation to a  $C_{20}H_{12}$  product.

#### Decalin/Zinc Chloride

Decalin was contacted with a zinc chloride melt containing 10% water at 300°C under a hydrogen partial pressure of 330 kPa for 60 minutes. The mixing was very good (the salt phase appeared continuous throughout the reactor) but almost five minutes was required for the phases to separate. This was much slower than the settling time of



about 30 seconds for tetralin. The phases separated completely, however, as the zinc chloride melt contained only about 5 ppm decalin.

Decalin has two isomers, cis and trans, which were present in roughly equal amounts in the untreated solvent. Decalin did not degrade when heated to 300°C in the absence of zinc chloride (Run 30, Table III-4); however, when it was contacted with zinc chloride at 300°C, about half of the cis isomer cracked while the trans isomer was essentially unchanged (Run 29, Table III-3). The major products were identified by GCMS as 12% by weight  $C_{10}H_{18}$  isomers (possibly butylcyclohexenes), 5% cyclohexane, 4.5% alkylcyclohexanes, and 0.5% methylindan (dozens of other cracking products were also present in trace quantities). There were also many heavy products, none more than about 0.2%, but together totaling about 2.5%. Total degradation was about 25%.

Morita and Hirosawa contacted decalin with zinc chloride at 425°C and also found extensive cracking (18). The attack of zinc chloride exclusively on cis-decalin is due to the strained configuration of the cis isomer compared to the trans-isomer. In cis-decalin, axial carbon-carbon bonds result in crowding of the adjacent rings, whereas in trans-decalin all carbon-carbon bonds are equatorial, and steric strain is much reduced (79, p. 974). Therefore, cis-decalin is much less stable than trans-decalin. Several investigators have shown that treatment of cis-decalin with aluminum chloride between 20 and 100°C yields trans-decalin (25,26,27).

Table III-4

Conditions and products for zinc chloride contacting with decalin, mesitylene, and dodecane.

<u>Experimental Run no.</u>	<u>Solvent</u>	<u>Temp. °C</u>	<u>%H<sub>2</sub>O</u>	<u>Time min.</u>	<u>P,MPa H<sub>2</sub></u>	<u>P,MPa total</u>	<u>Degradation Products percent by weight</u>
30	Decalin *	300	--	60	.33	1.10	no degradation (feed was 43% trans-decalin, 57% cis-decalin)
29	Decalin	300	10	60	.33	2.06	49% trans-decalin 25% cis-decalin 12% C <sub>10</sub> H <sub>18</sub> isomers 5% cyclohexane 4.5% C <sub>7</sub> -C <sub>9</sub> compounds 2.5% heavier than decalin 0.5% methylindan
32	Mesitylene *	300	--	60	.48	1.79	no degradation
33	Mesitylene	300	10	60	.34	2.61	78% mesitylene 20% other trimethylbenzenes 1% xylenes 1% tetramethylbenzenes
31	Dodecane	300	10	60	.34	1.82	no degradation

\* thermal stability test - no ZnCl<sub>2</sub> used.

note: in Runs 29, 31, and 33, mixing was very good, with fully expanded ZnCl<sub>2</sub> phase.

### Mesitylene/Zinc Chloride

Mesitylene (1,3,5-trimethylbenzene) was contacted with a zinc chloride melt containing 10% water at 300°C under a hydrogen partial pressure of 343 kPa for 60 minutes. The mixing was very good, as with decalin, and the phases separated in less than 45 seconds. No measurement was made of the mutual solubilities of the two phases.

Mesitylene was found to be thermally stable at 300°C (Run 32, Table III-4); however, treatment with zinc chloride at this temperature resulted in production of virtually all isomers of trimethylbenzene, and some xylene and tetramethylbenzene isomers as well (Run 33, Table III-3). Total conversion after one hour was about 22%. Evidently the methyl groups on the benzene ring are mobilized by zinc chloride, allowing them to shift position on the ring, and in some cases to transfer from molecule to molecule.

### Dodecane/Zinc Chloride

Zinc chloride with 10% water was used to treat dodecane at 300°C for 60 minutes, with 343 kPa hydrogen partial pressure. Again, mixing was very good, and phase separation was nearly complete one minute after stirring was stopped. Dodecane solubility in the zinc chloride melt was 40 ppm at most, with one sample showing zero solubility. No reactions were catalyzed in the dodecane by the zinc chloride melt (Run 31, Table III-4) - the dodecane was stable thermally and with respect to zinc chloride catalysis.

For model compound studies in an organic solvent/zinc chloride system, the organic solvent should not be subject to degradation by zinc chloride, since degradation products would obscure the analysis of model compound reaction products. Of the solvents studied here, only dodecane was not degraded by zinc chloride, and was suitable for model compound investigations.

#### IV. REACTIONS OF COAL MODEL COMPOUNDS CATALYZED BY ZINC CHLORIDE

Investigation of the reactions of coal model compounds in organic solvent/zinc chloride systems was undertaken to increase understanding of the chemistry of coal liquefaction in such systems. An organic solvent containing a small fraction of a model compound was contacted with a zinc chloride melt containing about 10% water at the appropriate temperature (175-275°C) and pressure (up to 2.8 MPa total pressure). After separation of the phases, the organic phase was analyzed to determine what reactions, if any, occurred involving the model compound. By measurement of model compound concentrations for several contacting times, disappearance rates were calculated.

The organic solvent used could not be reactive in zinc chloride up to 275°C; otherwise, products from zinc chloride-catalyzed solvent degradation would have masked model compound products in analysis. Of the solvents studied with zinc chloride at elevated temperature in this work, only dodecane was sufficiently stable, as has just been explained; therefore this was the solvent used for all model compound studies. Such solvents as benzene or toluene are also stable in zinc chloride, but their vapor pressures are excessive at the required temperatures, and their presence could have masked cleavage products from some of the model compounds during analysis.

Reaction of most model compounds with zinc chloride was expected to proceed via a carbonium-ion mechanism such as is shown in Reactions (I-1), (I-3), (I-5); the resulting ions tend to alkylate onto aromatic

centers, as shown in Reactions (I-2) and (I-4). In the absence of other aromatic compounds, the carbonium ion would alkylate the aromatic portion of the model compound, perhaps yielding a polymer or tar; this behavior has been reported in many investigations, as summarized in Tables I-1 and I-2. To avoid this polymer formation, a substrate was provided in the reaction mixture for alkylation by the carbonium ion. Thus, benzene or ethylbenzene was added to the model compound dodecane solution, in excess of the amount needed for complete reaction with the model compounds.

Model compounds were examined in the organic solvent at small concentrations, primarily to avoid reaction of model compound fragments, as they were formed, either with other fragments, the reactant, or products. The low concentrations ensured that fragments were surrounded by the non-reactive solvent containing benzene or ethylbenzene, thereby leading to fragment reaction with the benzene or ethylbenzene.

#### Equipment

The requirements for the investigation of model compound reactions catalyzed by zinc chloride melts at elevated temperatures were similar to those for study of high temperature solvent/zinc chloride interactions; accordingly, the same apparatus as described in Chapter III was used for this part of the investigation.

For the series of experiments with model compounds, the main reactor was replaced by a 600 ml high pressure (13.7 MPa) stirred auto-

clave, manufactured by Parr Instrument Company. This monel reactor was selected to avoid corrosion by zinc chloride melts. It was not possible to fit the electrode sensor into this autoclave; however, since the phase behavior of the dodecane/zinc chloride system had already been studied, and since the model compounds were present in such low concentrations as not to affect phase behavior, the electrode was not needed for these studies. Unlike the original reactor, the Parr autoclave was equipped with a glass liner that contained the liquid contents, so that the monel reactor was not contacted directly by the liquid.

Zinc chloride was reagent grade from Matheson Coleman & Bell, with a minimum  $ZnCl_2$  content of 97.0%. Dodecane was 99% purity from Aldrich Chemical Company. Benzene was analytical reagent grade from Mallinckrodt, while ethylbenzene (used in place of benzene for a few experiments) was from Matheson Coleman & Bell. A list of model compounds and sources is given in Table IV-1. All materials were used as received with no further purification.

#### Procedure

The reactions of model compounds in contact with a zinc chloride melt were examined for specific contacting temperatures and durations. Each experimental run consisted of preheat of the solvent containing benzene (or ethylbenzene) and the model compound simultaneous with separate preheat of the zinc chloride/water solution, followed by

Table IV-1

## Sources of chemicals used as model compounds

<u>Compound</u>	<u>Source</u>	<u>Purity</u>
Biphenyl	Aldrich Chemical Co.	unspec.
Diphenylmethane	Aldrich Chemical Co.	99%
1,2-Diphenylethane	Aldrich Chemical Co.	unspec.
1,3-Diphenylpropane	Pfaltz & Bauer	unspec.
2-Phenylnaphthalene	Pfaltz & Bauer	unspec.
4-Hydroxydiphenylmethane	Aldrich Chemical Co.	95%
Diphenyl ether	Chem Service, Inc.	99%
Phenylbenzyl ether	Pfaltz & Bauer	unspec.
Dibenzyl ether	Chem Service, Inc.	99%
Bis( $\alpha$ -methylbenzyl) ether	Chem Service, Inc.	95%
p-Hydroxyphenylbenzyl ether	Pfaltz & Bauer	unspec.
Methoxybenzene	Pfaltz & Bauer	unspec.
2-Methoxynaphthalene	Chem Service, Inc.	99%
1-Ethoxynaphthalene	Aldrich Chemical Co.	99%
2-Ethoxynaphthalene	Chem Service, Inc.	99%
2-Methoxydiphenyl	Givaudan Corp.	unspec.



stirred contact of the two phases, with periodic halting of stirring to allow phase separation (by gravity settling) and sampling.

In preparation of the organic phase, 2 ml of benzene (or ethylbenzene) was added to 160 ml dodecane, and then about 0.75 g of the model compound was dissolved in the mixture; this gave a molar ratio of benzene (or ethylbenzene) to model compound of 3.5-5:1. The organic mixture was then put into the solvent preheat vessel, and the procedure for the preheat and mixing of the organic and salt phases followed as described in Chapter III.

Periodically during mixing, stirring was stopped to allow sampling of the organic phase. Experiments with only dodecane and zinc chloride present had shown separation of the two to be complete in a minute or less; therefore, the unstirred mixture was allowed to settle for 4 to 5 minutes before sampling. After sampling the organic phase, stirring recommenced. The duration of contacting of the two phases was measured as only the total stirring time up to the point in question, because the salt and organic phases separated quickly when not stirred and were therefore in limited contact. The duration of contacting defined the time scale for reaction rate determinations.

Because the solubility of dodecane in the zinc chloride melt had been previously found to be low, salt samples were not deemed necessary for most experiments. Even if significant fractions of model compounds had dissolved in the zinc chloride, the analytical method was likely not sufficiently sensitive to detect them.

### Analysis

Organic samples were analyzed by gas chromatography (GC), using a Hewlett-Packard Model 5840A Gas Chromatograph equipped with dual OV-225 columns (3% loading on Chromosorb WHP, 6 feet long, 1/8 inch OD) and dual flame ionization detectors (FID). Helium was used as the carrier gas, flowing at 20 cc/min through each column. Temperature programming was used to improve component separation; for most analyses, the column temperature rose from an initial temperature of 60°C at 10°C/min for 7 minutes and 20°C/min thereafter, to a final temperature of 225°C, where it was held for 8 minutes. Comparison of retention times to those of known compounds allowed identification of peaks.

Because it was desired to follow reactant and product concentrations as time progressed, a quantitative GC technique utilizing an internal standard was employed. A known amount of an internal standard component (usually phenol or diphenyl) was added to each organic sample, so that each sample could be put on a common basis of equal peak areas of the internal standard. With this basis, peak areas were proportional to concentration for each component, enabling model compound disappearance and product buildup to be monitored as the reaction progressed. Reproducibility and accuracy of the internal standard were generally good, with deviations of 1 to 5% being typical for evaluation of known solutions.

For reactants, and for those products that could be obtained in a pure form, the GC was calibrated directly with a solution containing a known amount of the component, to determine FID response factors for these compounds. For products not available in pure form, response factors were estimated from response factors of similar compounds. For example, the FID response factors for benzene, ethylbenzene, and diphenylmethane were nearly equal when expressed as weight of compound per peak unit area. Therefore, the response factor for ethyldiphenylmethane was estimated as the average of the three known response factors.

Identification of a few products was made with GCMS, as described in Chapter III. The few salt samples that were taken were also analyzed as described in Chapter III.

### Results and Discussion

Two types of model compounds were studied with zinc chloride: those containing diaryl aliphatic linkages, and those containing diaryl or alkyl-aryl ether linkages. Most experiments were conducted at 250°C, with hydrogen pressure of 1.4 MPa. The water content of the zinc chloride melt was 10%.

The catalyst:reactant ratio was about 400:1 by weight, or about 600:1 on a molar basis, while in most earlier studies, ratios of approximately unity had been used (60,63,64,87). High catalyst ratios were selected here to eliminate effects of catalyst loading on reaction

mechanisms and rates; this conforms to current investigations of coal treatment with organic solvents and massive amounts of zinc chloride (16).

Prior to conduction of experiments with zinc chloride, the model compounds were tested for thermal stability by being held at 250°C, dissolved in dodecane, for one hour, with analysis of the solution by GC. The diaryl aliphatic compounds and alkyl-aryl ethers were stable at 250°C, since no degradation products were observed. Of the diaryl ethers, diphenyl ether was stable at 250°C, and dibenzyl ether, bis ( $\alpha$ -methylbenzyl) ether, and p-hydroxyphenylbenzyl ether were only slightly degraded, with less than 5% conversion in one hour. Only phenylbenzyl ether was significantly degraded, with 50% conversion in one hour. The major products were 2- and 4-hydroxydiphenylmethane (30%), phenol (14%) and toluene (8%), indicating thermal cleavage of the benzyl carbon-oxygen bond.

#### Diaryl Aliphatic Compounds

Biphenyl, diphenylmethane, 1,2-diphenylethane (bibenzyl), 1,3-diphenylpropane, 2-phenylnaphthalene, and 4-hydroxydiphenylmethane were treated with zinc chloride at 250°C for one hour. Of these, only diphenylmethane and 4-hydroxydiphenylmethane reacted significantly, as shown in Table IV-2. Phenylnaphthalene underwent a slow degradation.

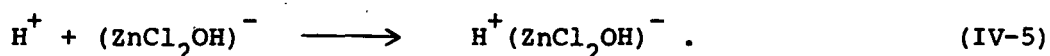
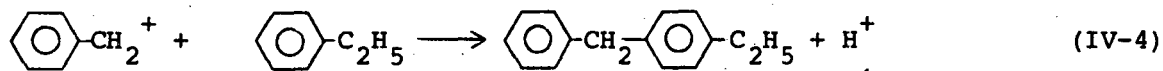
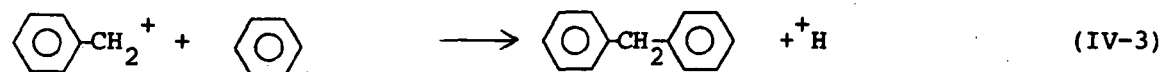
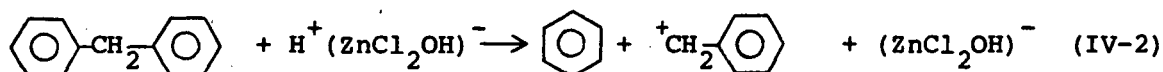
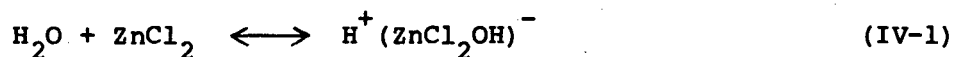
Diphenylmethane, when treated with zinc chloride and ethylbenzene in dodecane, gave benzene and ethyldiphenylmethane as products (Runs

Table IV-2

Results of diaryl aliphatic compound treatment with zinc chloride. In dodecane solvent, with equal volumes of dodecane and zinc chloride (containing 10% water). Zinc chloride:model compound molar ratio = 600:1. Treatment under 1.4 MPa hydrogen for 60 minutes.

<u>Compound</u>	<u>Aromatic Center</u>	<u>Temp. °C</u>	<u>Principal Products</u>	<u>Reaction Rate<sub>-1</sub> Constant, min<sup>-1</sup></u>	<u>Conversion at 60 min.</u>	<u>Exp. Run no.</u>
Biphenyl	Benzene	250	none	0	0	71
Biphenyl	Ethylbenzene	250	none	0	0	105
Diphenylmethane	Benzene	250	unidentified	.0038	20%	69
Diphenylmethane	Ethylbenzene	220	{ Benzene Ethyldiphenylmethane Diethyldiphenylmethane	.00634	32%	94
Diphenylmethane	Ethylbenzene	250		.0204	71%	88
Diphenylmethane	Ethylbenzene	280		.0544	95%	93
1,2-Diphenylethane	Benzene	250	none	0	0	86
1,2-Diphenylethane	Ethylbenzene	250	none	0	0	89
1,3-Diphenylpropane	Ethylbenzene	250	none	0	0	92
2-Phenyl-naphthalene	Ethylbenzene	250	unidentified	.0038	20%	98
4-Hydroxydiphenylmethane	Ethylbenzene	225	{ Benzene, Phenol Ethyldiphenylmethane	> .5	100%	107
4-Hydroxydiphenylmethane	Ethylbenzene	250		> .6	100%	108

88,93 and 94); however, use of benzene instead of ethylbenzene resulted in no apparent reaction (Run 69). This is consistent with the mechanism proposed by Taylor and by Mobley, in which protonation of the aromatic carbon attached to the aliphatic link leads to cleavage with carbonium ion formation (54,63,64):

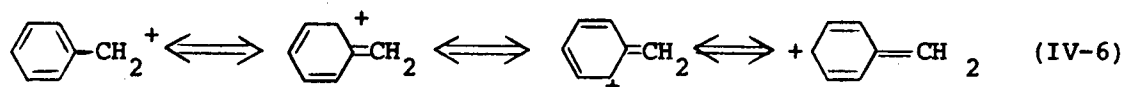


With benzene, Reactions (IV-2) and (IV-3) give products identical to reactants, so any reaction is not observable. With ethylbenzene, the products are ethyldiphenylmethane (ortho and para isomers) and benzene (Reactions (IV-2), (IV-4)), which were observed.

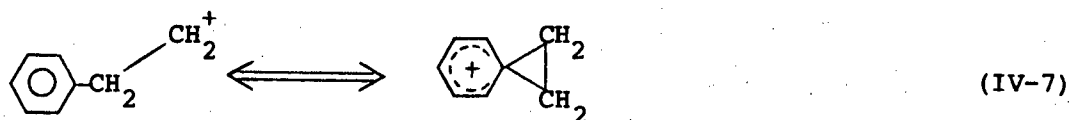
Taylor had found diphenylmethane to be nonreactive with zinc chloride (54). However, he used cyclohexane as the solvent, with the reactant being the only aromatic compound present. Apparently, when the carbonium ions formed, they either reacted with the benzene formed (by

the same reaction) to again yield the reactant, or they alkylated the diphenylmethane to give a polymeric tar.

The nonreactivity of biphenyl, 1,2-diphenylethane, 1,3-diphenylpropane, and phenylnaphthalene is attributable to the resulting carbonium ions being less stable (and hence more difficult to form) than the benzyl cation, and zinc chloride not being sufficiently active at 250°C to form them. The phenyl cation is very unstable, and has been formed only in superacid solutions (88,89); therefore, biphenyl is not cleaved under the conditions of these experiments. The cleavage reaction for aliphatic linkages is initiated by protonation of a carbon-carbon bond at one of the aromatic rings with subsequent formation of a carbonium ion. Therefore, for aliphatic linkages, cations must be formed that have the positive charge at the end of an aliphatic chain. The benzyl cation is stabilized by resonance with the aromatic ring (90):



and is easily formed; therefore, diphenylmethane was reactive. The phenethyl cation can also be stabilized by resonance (91,92,93,94):



However, this stabilization is weaker than that for the benzyl cation, so that 1,2-diphenylethane is not readily cleaved. The cation from

1,3-diphenylpropane is very unstable, since the positive charge is isolated at the end of the aliphatic chain where no resonance stabilization is possible; therefore, 1,3-diphenylpropane does not undergo degradation under treatment conditions. Phenyl-naphthalene was also fairly non-reactive, since formation of the phenyl or naphthyl cation would be required.

Aluminum chloride is a much stronger Lewis acid than zinc chloride, which can explain why reactions of 1,2-diphenylethane, 1,3-diphenylpropane, and 1,4-diphenylbutane were observed in contact with it, as mentioned in Chapter I.

The rate limiting step in carbonium ion reactions is generally the formation of the cation, since that is the only step involving carbon-carbon bond breaking. The resulting reaction is first order in the reactant (79 p. 466). Therefore, the rate expression for the reaction of diphenylmethane was expected to be:

$$\frac{d C_{\text{DPM}}}{dt} = - k C_{\text{DPM}} \quad (\text{IV-8})$$

which yields, when integrated:

$$\ln \frac{C_{\text{DPM}}}{C_{\text{DPM},0}} = - kt \quad (\text{IV-9})$$

where  $C_{\text{DPM}}$  is the concentration of diphenylmethane at time  $t$  and



$C_{\text{DPM},0}$  is the initial concentration. Concentration data as a function of time are shown in Figure IV-1 for temperatures of 220, 250, and 280°C. The values at 45 and 60 minutes for the experiment at 280°C were somewhat uncertain, because an impurity in the diphenylmethane interfered with the analysis. Therefore, the last point was ignored in calculation of the rate constant for 280°C; the rate constants were calculated by a linear regression of  $\ln (C_{\text{DPM}}/C_{\text{DPM},0})$  on  $t$ . The data fit the first order expression fairly well; there was some deviation for the 250°C and 280°C experiments, which indicated a reaction rate with order perhaps greater than unity. By use of an Arrhenius form for the rate constant as a function of temperature, the activation energy was estimated, by a regression analysis, to be 20.8 kcal/mole; the data are shown in Figure IV-2.

The product concentrations for the diphenylmethane reactions were measured in each sample in order to examine a mass balance for the system. In each case, only about 30 to 60% as much ethyldiphenylmethane was found as was expected on the basis of diphenylmethane disappearance, and about 75% as much benzene as expected. The benzene may have been diminished by being stripped out of the liquid, as it was formed, by the sample line purge gas. The ethyldiphenylmethane yield was probably low as a result of the diphenylmethane competing with ethylbenzene for the carbonium ion, despite the excess amount of ethylbenzene present. If, instead of reacting with ethylbenzene, the cation reacted with diphenylmethane, a polymeric product would result,

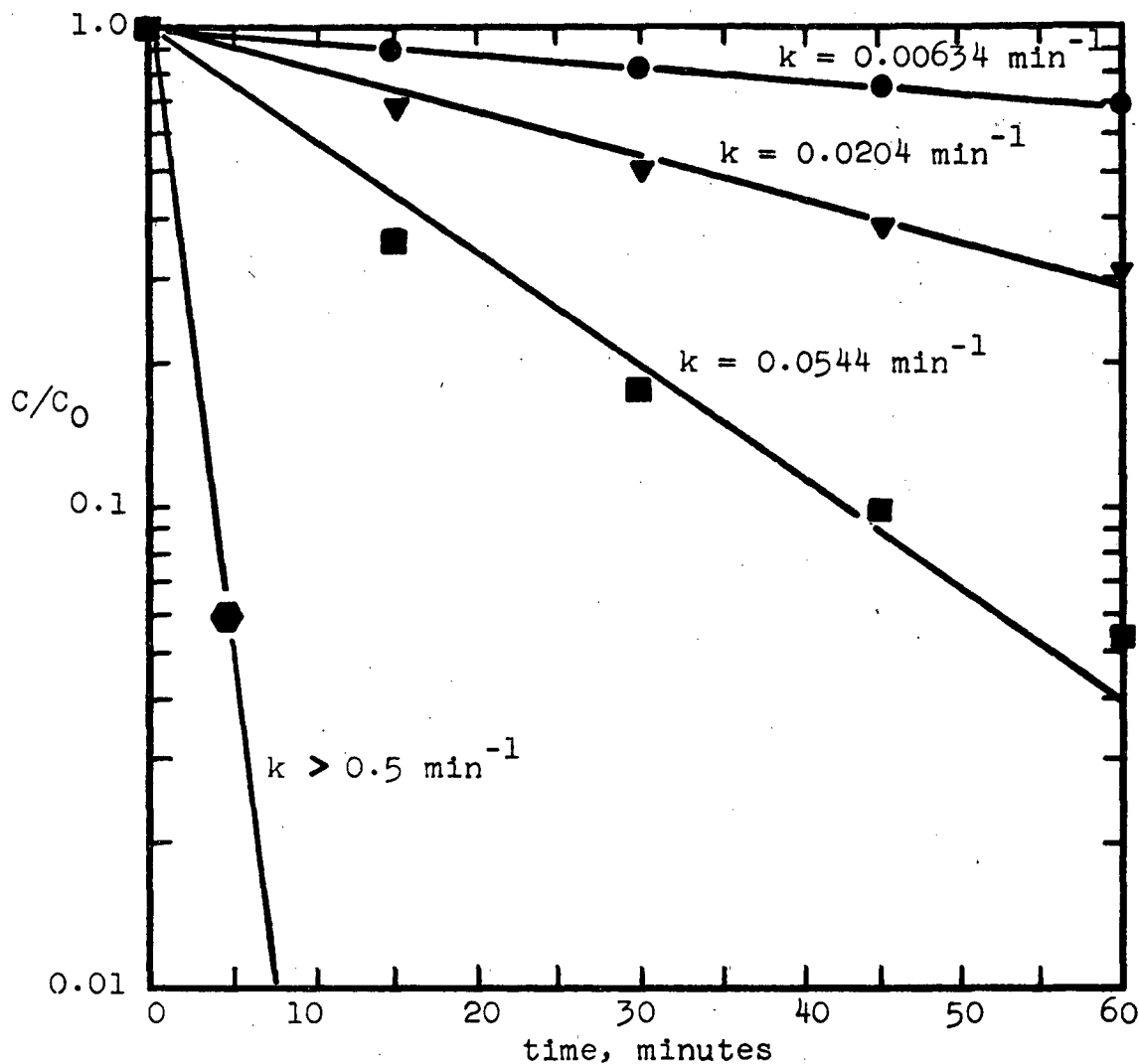


Figure IV-1

Concentration vs time for diphenylmethane ( and 4-hydroxy-diphenylmethane) treatment with zinc chloride. In dodecane with equal volumes of dodecane and zinc chloride (containing 10% water). Zinc chloride:model compound molar ratio = 600:1. Treatment under 1.4 MPa hydrogen for 60 minutes. Benzene present in all experiments (1-2%). ● 220°C (Run 94); ▼ 250°C (Run 88); ■ 280°C (Run 93); ● 4-hydroxy-diphenylmethane, 225°C (Run 107).

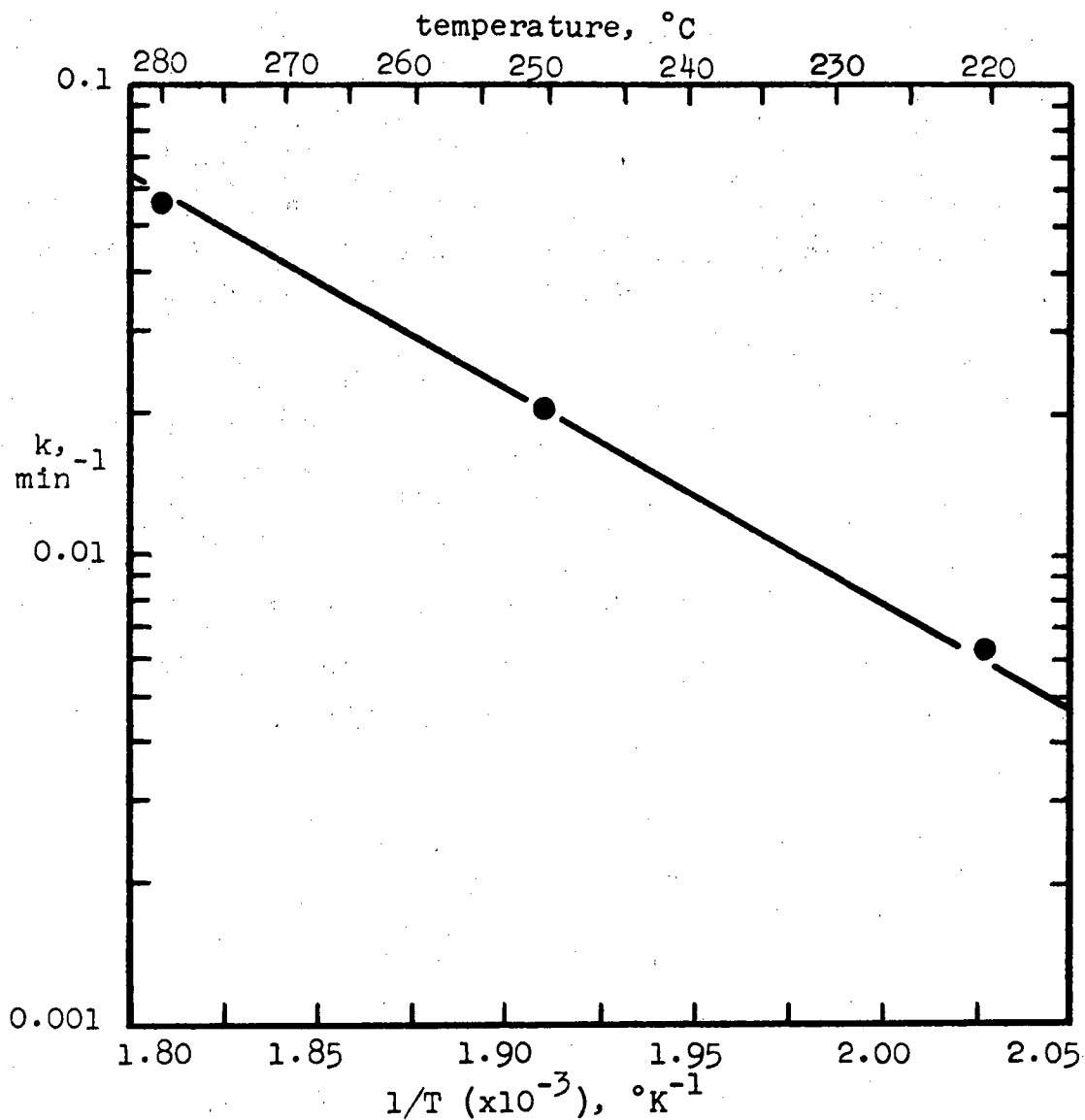


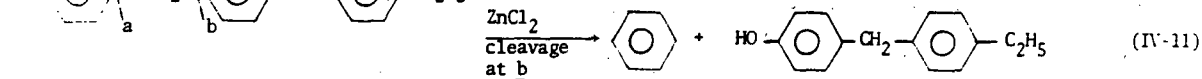
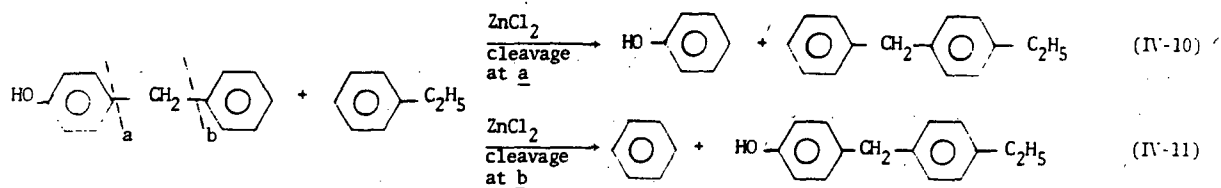
Figure IV-2

Determination of activation energy for diphenylmethane cleavage catalyzed by zinc chloride. Determined in dodecane, with equal volumes of dodecane and zinc chloride (containing 10% water). Zinc chloride:diphenylmethane molar ratio = 600:1. Treatment under 1.4 MPa hydrogen for 60 minutes. Ethylbenzene present in all experiments (1-2%).  $k$  = first order rate constant for disappearance of diphenylmethane. Slope of line = 10,470 °K.  $\Delta E_{\text{act}} = 20.8 \text{ kcal/mole}$ .

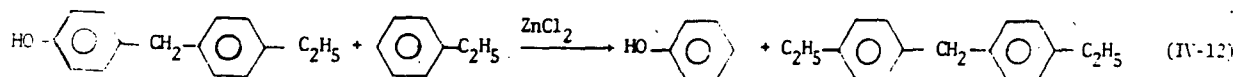
which probably would not be eluted from the GC. Any material consumed in this fashion would not appear in the products, thus giving rise to errors in the mass balance.

To examine the effect of aromatic ring substituents on reaction rates and mechanisms, 4-hydroxydiphenylmethane was treated at 225°C and 250°C. The reaction was very fast, with nearly complete conversion after 5 minutes, as shown in Table IV-2 and Figure IV-1. The rate constant of about  $0.6 \text{ min}^{-1}$  at 225°C was estimated from only the five minute data point, and is therefore very approximate. Nonetheless, this rate is some 100 times the rate for diphenylmethane at 220°C.

The cleavage of 4-hydroxydiphenylmethane can occur via two paths:



The product of Reaction (IV-11) can react further to give phenol:



Examination of product yields, shown in Table IV-3, offers insight on the relative rates of each pathway. At both 225°C and 250°C, more benzene was formed than phenol. This indicates that more cleavage occurred at position b on 4-hydroxydiphenylmethane, giving a hydroxybenzyl cation, than at position a, giving a benzyl cation. The hydroxyl substituent participates in the aromatic resonance of the benzyl cation, thereby stabilizing it (79, p. 363); the extra stability of the hydroxybenzyl cation therefore accelerates cleavage at b relative to cleavage at a. The ratio of cleavage at b to cleavage at a, given by the ratio of benzene to phenol in the products, was 1.68 at 225°C and 1.79 at 250°C (included in the benzene product was the diphenylmethane in the product, since it was presumably formed by alkylation of previously formed benzene by the benzyl cation).

From Reaction (IV-10), the amounts of phenol and ethyldiphenylmethane were expected to be equal; however, phenol was observed in much larger amounts. Two factors could have contributed to this result: first, the ethyldiphenylmethane could have been reacted further to form heavier compounds, and second, some excess phenol could have been formed from reaction of ethylhydroxydiphenylmethane, the product of Reaction (IV-11). This second possibility, in which the amount of phenol was increased by a secondary reaction, also suggests that the rate of cleavage at b may be even faster relative to that at a than cited above, since the benzene to phenol ratio was used to indicate relative rates.

Table IV-3

Reaction products from treatment of 4-hydroxydiphenylmethane with zinc chloride. In dodecane solvent, with equal volumes of dodecane and zinc chloride (containing 10% water). Zinc chloride:model compound molar ratio = 600:1. Treatment under 1.4 MPa hydrogen for 60 minutes.

<u>Feed</u>	<u>225°C-Run 107</u>		<u>250°C-Run 108</u>	
	<u>Moles</u>	<u>Yield</u>	<u>Moles</u>	<u>Yield</u>
Ethylbenzene	.0164	-	.0163	-
4-Hydroxydiphenyl- methane	.00436	-	.00436	-
<u>Products</u>				
Benzene	.00163	37.4%	.00191	43.8%
Toluene	.00007	1.6%	.00010	2.3%
Ethylbenzene	.0138	-	.0127	-
Phenol	.00111	25.5%	.00115	26.4%
Cresols	.00016	3.7%	.00029	6.7%
Diphenylmethane	.00023	5.3%	.00015	3.4%
Ethyldiphenylmethane	.00052	11.9%	.00037	8.5%
4-Hydroxydiphenyl- methane	.00023	-	.00003	-
Fraction of reactant recovered in products	73%		74%	

Toluene and cresols, which were observed in small amounts, were probably formed by hydrogen capping of the benzyl and hydroxybenzyl cations. The ethylhydroxydiphenylmethane formed in Reaction (IV-11), which was not observed, either did not elute from the GC or was reacted further as it was formed.

As with diphenylmethane, only about 75% of the 4-hydroxydiphenylmethane was accounted for in the products. Presumably the remainder was converted to heavier products by further reaction of the initially formed compounds or by alkylation of the reactant by the cations.

As with all the experiments in this work, the catalyst/reactant ratio was 600:1 on a molar basis. In other studies of 4-hydroxydiphenylmethane, Tsuge and Tashiro used aluminum chloride at 100°C with a catalyst/reactant molar ratio of 1:1 (60), and Frederick used zinc chloride at 325°C with a catalyst/reactant ratio of 1:4 (87). In both studies, the cleavage at the a position, (Reaction (IV-10)), was enhanced relative to cleavage at the b position, in contrast to the findings of this work. The much smaller catalyst to reactant ratios used by Tsuge and Tashiro and by Frederick could lead to catalyst loading effects, favoring cleavage at the a position, not evident with the large excess of catalyst used here. In addition, Frederick used benzene instead of dodecane as the main solvent, Tsuge and Tashiro used no solvent, and both studies were conducted at temperatures different from those used here.

When treated with zinc chloride at 250°C for one hour,  $\alpha$ -phenylnaphthalene slowly disappeared from solution with no observable products. A similar behavior was observed with diphenylmethane when reacted in the presence of benzene; there, the major reaction merely resulted in reformation of the reactant, but a secondary reaction gradually consumed the diphenylmethane. These secondary reactions were quite slow, with rate constants some 10 to 100 times lower than the cracking reaction, as shown in Table IV-2, and probably represented some sort of polymerization to heavy products that would not elute from the GC. Biphenyl was not subject to this slow degradation - evidently phenylnaphthalene is more reactive than biphenyl. This observation is consistent with Taylor's results, which showed phenylnaphthalene to be much more reactive than biphenyl when treated with aluminum chloride at 325°C (54).

#### Diaryl and Alkyl-aryl Ethers

Diaryl ethers studied here included diphenyl ether, phenylbenzyl ether, dibenzyl ether, bis( $\alpha$ -methylbenzyl) ether, and p-hydroxyphenylbenzyl ether. Methoxybenzene (anisole), 2-methoxynaphthalene, 1- and 2-ethoxynaphthalenes, and 2-methoxydiphenyl were the alkyl-aryl ethers examined in this work.

Except for diphenyl ether, the diaryl ethers were cleaved very rapidly by the zinc chloride melt at both 200 and 250°C, as shown in Table IV-4; cleavage was at least 97% complete after five minutes.

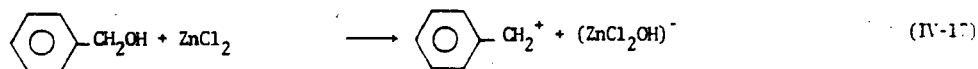
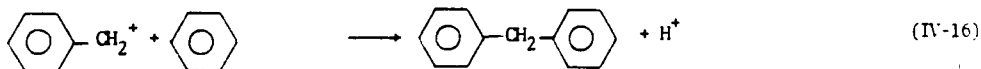
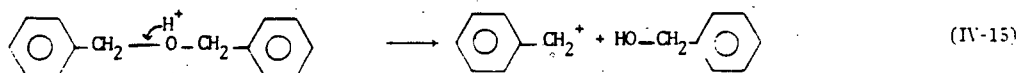
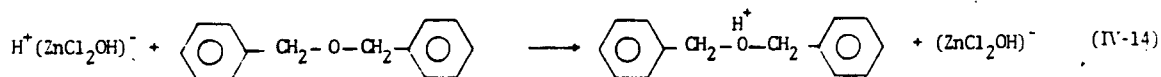


Table IV-4

Results of diaryl ether compound treatment with zinc chloride. In dodecane solvent, with equal volumes of dodecane and zinc chloride (containing 10% water). Zinc chloride:model compound molar ratio = 600:1. Treatment under 1.4 MPa hydrogen for 60 minutes. Benzene present (about 1% in dodecane) in all experiments except Run 59.

<u>Compound</u>	<u>Temp. °C</u>	<u>Principal Products</u>	<u>Reaction Rate<sup>-1</sup> Constant, min</u>	<u>Exp. Run no.</u>
Diphenyl ether	250	none	0	59
Phenylbenzyl ether	200	Phenol, Diphenylmethane, 2- and 4-Hydroxydiphenylmethane	> 1	90
Phenylbenzyl ether	250	Phenol, Diphenylmethane	-	65
Phenylbenzyl ether	250	Phenol, Diphenylmethane	> 0.8	84
Dibenzyl ether	200	Diphenylmethane	> 1	83
Dibenzyl ether	250	Diphenylmethane	-	64
Dibenzyl ether	250	Diphenylmethane	> 0.7	82
Bis( $\alpha$ -methylbenzyl) ether	250	1,1-Diphenylethane 2,3-Diphenyl-2-butene	-	67
Bis( $\alpha$ -methylbenzyl) ether	250		> 0.8	85
p-Hydroxyphenylbenzyl ether	250	Toluene, Diphenylmethane	> 1	104

The rate constants shown for diaryl ethers in Table IV-4 are order of magnitude estimates, since only one data point was used to calculate each (there was no detectable ether left in the 10 minute samples). The cleavage of dibenzyl ether to diphenylmethane in the presence of benzene is consistent with the mechanism proposed by Mobley for the zinc chloride catalyzed reaction; this involves protonation of the ether bond, with subsequent cleavage and formation of a carbonium ion (63,64):



The protonated ether is capable of cleavage only for nonaryl carbon-oxygen bonds. The stability of diphenyl ether, observed in this work and by Mobley (63,64), is due to the oxygen being attached directly to both aromatic rings.

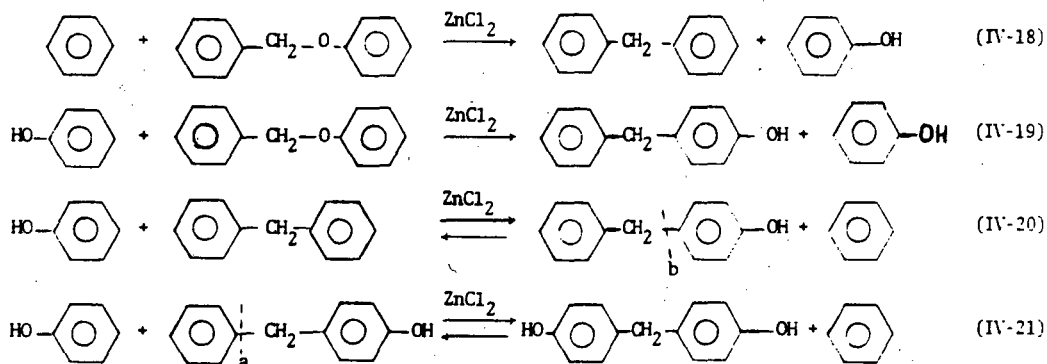
With dibenzyl ether, the only product observed was diphenylmethane, as formed by Reaction (IV-16). In all experiments, the diphenylmethane

formed represented only about 25% of the reacted dibenzyl ether. The rest of the dibenzyl ether that was cleaved probably alkylated the already formed diphenylmethane (or the feed ether), to give a polymeric substance that did not elute from the GC. Mobley also reported a low yield of diphenylmethane (63).

Phenylbenzyl ether reacted very quickly, when treated with zinc chloride, to give phenol, diphenylmethane, and 2- and 4-hydroxydiphenylmethane.\* The final two products were formed when the benzyl cation alkylated the phenol formed by earlier cleavage. At 200°C and 250°C, the products accounted for 50 to 60% of the original phenylbenzyl ether; however, the product distribution shifted greatly between these two temperatures. At 250°C, phenol and diphenylmethane were formed with a 40% yield, and the hydroxydiphenylmethanes were present in an 8% yield, while at 200°C, the phenol and diphenylmethane yield was 16%, and the hydroxydiphenylmethane yield was 45%. This behavior can be explained by the following reaction sequence:

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\*Phenylbenzyl ether cracked thermally at 250°C, but with only a 50% conversion after 60 minutes. Therefore, thermal cracking was an insignificant part of this observed, much faster reaction.



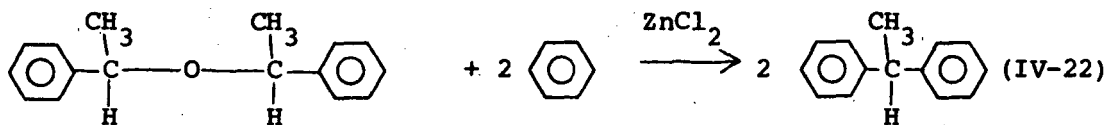
The first reaction represents the initial cleavage of phenylbenzyl ether, with formation of phenol and diphenylmethane. The second reaction involves alkylation of phenol instead of benzene to yield hydroxydiphenylmethanes (both 2- and 4- isomers would form, though for simplicity only the 4- isomer is shown). The final two reactions are phenol interchanges with diphenylmethane, hydroxydiphenylmethane, and dihydroxydiphenylmethane, catalyzed by zinc chloride, as observed in the investigation in this work of diaryl aliphatic compounds. From the results discussed earlier, it has been established that hydroxydiphenylmethane is much more reactive than diphenylmethane, presumably because of the stabilizing effect of the hydroxyl substituent on the carbonium ion formed. It should therefore be reasonable to assume that dihydroxydiphenylmethane would be even more reactive than hydroxydiphenylmethane. It was also seen that diphenylmethane reacted slowly at 250°C (with 10% conversion after 5 minutes), while hydroxydiphenyl-

methane had completely reacted after 5 minutes at 225°C. Based on this information, an explanation of the product distribution changes between 200°C and 250°C is possible. At 200°C, both Reactions (IV-18) and (IV-19) occur, yielding phenol, diphenylmethane, and hydroxydiphenylmethane. Reactions (IV-20) and (IV-21) are slow at 200°C (both forward and reverse), so the product ratio of 45% hydroxydiphenylmethane to 16% diphenylmethane represents approximately the relative rates of Reactions (IV-18) and (IV-19). Phenol is evidently much more reactive than benzene, since benzene was present in considerable excess; this behavior has been observed by Mobley (63,64). At 250°C, Reaction (IV-20) is still slow in the forward direction, but the reverse reaction, consuming hydroxydiphenylmethane, is fast. Similarly, Reaction (IV-21) presumably favors the formation of hydroxydiphenylmethane, which then reacts via the reverse of Reaction (IV-20) to form diphenylmethane. Thus, at 250°C, the fraction of hydroxydiphenylmethane formed initially may have been high, as at 200°C, but as it formed it was rapidly cleaved to diphenylmethane and phenol.

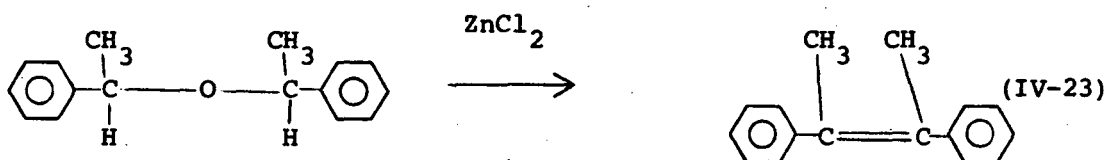
For phenylbenzyl ether, as for dibenzyl ether, 40 to 50% of the feed was not accounted for in the products, probably because of formation of heavy components by alkylation of diphenylmethane or hydroxydiphenylmethane by the benzyl carbonium ions.

The reaction of bis ( $\alpha$ -methylbenzyl) ether in zinc chloride was rapid at 235°C, being at least 98% complete after 5 minutes. However, in addition to the expected product of 1,1-diphenylethane, large

amounts of 2,3-diphenyl-2-butene were observed, with concentration of the latter being some 15 times the former. Evidently, two competing reactions are occurring:



and



with cis and trans isomers of 2,3-diphenyl-2-butene being formed.

Since one mole of the feed gives two moles of 1,1-diphenylethane, the rate of Reaction (IV-23) was evidently some 30 times faster than the rate of (IV-22).

Reaction (IV-23) represents a dehydration of the ether to form an olefin. The carbon-oxygen bond in ethers is similar chemically to that in alcohols (95), and alcohol dehydration occurs, in a manner like that observed for the ether, via a carbonium ion mechanism (79). In addition, elimination reactions have been noted for ethers in the presence of strong acids when secondary or tertiary carbonium ions are formed (96). Therefore, the dehydration behavior of the bis( $\alpha$ -methylbenzyl) ether is probably a result of the intermediate carbonium ion being secondary, while for all other ether model compounds examined here a primary cation is formed. As the carbonium ion is formed, it

can either react with benzene to give 1,1-diphenylethane, as a small fraction did, or it can react with the remaining fragment to give the diphenylbutene, as did the majority.

Of the bis( $\alpha$ -methylbenzyl) ether reacted, 86% was accounted for in the products, significantly higher than for other ethers. This is probably because discrepancies in mass balances arose largely from cation alkylation of the feed, with resulting polymer production. With the secondary cation reacting mainly in a dehydration reaction, relatively little was available for polymer formation, and most of the feed was converted to the observed olefin.

The behavior of *p*-hydroxyphenylbenzyl ether was studied to determine the effect, if any, of the hydroxyl substituent. With cleavage of the benzyl carbon-oxygen bond, diphenylmethane and hydroquinone would result, while activation of the phenyl carbon-oxygen bond would give phenol. Diphenylmethane was the only major product observed, indicating that only cleavage of the benzyl carbon oxygen bond occurs. No hydroquinone was observed, but any that was formed was probably dissolved in the zinc chloride melt, since it is polar. The reaction was very fast, and was complete in 5 minutes.

The alkyl-aryl ethers all reacted rapidly when treated with zinc chloride, with 95% converted in 5 to 10 minutes. In all such ethers examined, the oxygen was bonded directly to the aromatic ring; as with the diaryl ethers, this bond could not be broken. The effect of treatment with zinc chloride was dealkylation of the ether, resulting in phenol or naphthol, as shown in Table IV-5.

Table IV-5

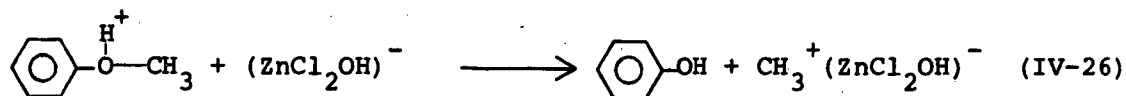
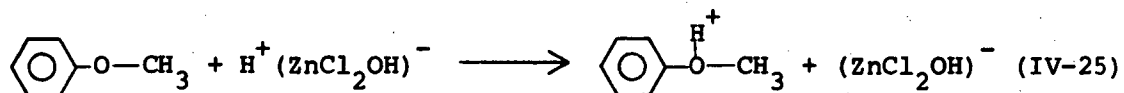
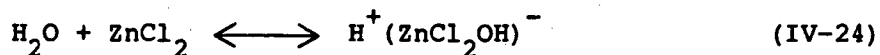
Results of alkyl-aryl ether compound treatment with zinc chloride. In dodecane solvent, with equal volumes of dodecane and zinc chloride (containing 10% water). Zinc chloride:model compound molar ratio = 600:1. Treatment under 1.4 MPa hydrogen for 60 minutes. Benzene present (about 1% in dodecane) in most experiments; ethylbenzene used instead in Runs 95,96,97.

<u>Compound</u>	<u>Temp. °C</u>	<u>Principal Products</u>	<u>Reaction Rate Constant, min<sup>-1</sup></u>	<u>Exp. Run no.</u>
Methoxybenzene	220	Phenol	>0.5	96
Methoxybenzene	250	Phenol	-	91
Methoxybenzene	250	Phenol	-	95
2-Methoxynaphthalene	175	2-Naphthol, Dimethyl-2-Naphthol	.0254	103
2-Methoxynaphthalene	200	2-Naphthol, Dimethyl-2-Naphthol	.110	100
2-Methoxynaphthalene	225	2-Naphthol, Dimethyl-2-Naphthol	.296 *	99,101,102
2-Methoxynaphthalene	250	2-Naphthol, Dimethyl-2-Naphthol	.370	81
1-Ethoxynaphthalene	250	Ethylbenzene, 1-Naphthol, Dimethyl-1-naphthol	.28	68
2-Ethoxynaphthalene	250	Ethylbenzene, 2-Naphthol, Dimethyl-2-naphthol	.33	80
2-Methoxydiphenyl	250	two unidentified compounds	.16	97

\* Standard deviation of three runs  $\pm$  1%. Doubling hydrogen pressure raised rate constant from 0.296 min<sup>-1</sup> to 0.305 min<sup>-1</sup>.



The cleavage of alkyl-aryl ethers probably involves protonation of the oxygen atom and subsequent displacement of the weakly basic phenol or naphthol (79). A possible mechanism for cleavage in the presence of zinc chloride and water is (79):



yielding, for the cleavage of methoxybenzene, phenol and methanol. Methanol and ethanol are very soluble in zinc chloride, so any formed from dealkylation of the ether would dissolve in the zinc chloride melt.\* Instead of forming methanol, the alkyl fragment could also alkylate the benzene (or ethylbenzene), the reactant, or the phenol or naphthol product. This behavior was not observed with methoxybenzene, but for 2-methoxynaphthalene dimethylnaphthols were present in the

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\*There was no analysis of the zinc chloride melt for methanol or ethanol, inasmuch as the alcohol would have been very dilute, and the high affinity of zinc chloride for it would have made removal difficult.

product (Runs 81,99-103), indicating methylation of the product naphthols (only trace amounts of toluene were detected). Products from ethoxynaphthalenes (Runs 68 and 80) included ethylbenzene as well as dimethylnaphthols; evidently ethylation of the benzene occurred along with alkylation of naphthol. For 2-methoxynaphthalene and 1- and 2-ethoxynaphthalene at 250°C, alkylation of the naphthol appears favorable, since more dimethylnaphthol was formed than naphthol (4 times as much for methoxynaphthalene, about 1 1/2 times as much for ethoxynaphthalenes). At lower temperatures, naphthol alkylation apparently becomes less favored, since dimethylnaphthol formation from methoxynaphthalene decreased with decreasing temperature until very little was observed at 175°C.

The rate of ether dealkylation was faster than the rate of aliphatic link cleavage, but slower than the cleavage of most diaryl ethers. At 250°C, methoxybenzene was cleaved at the highest rate, though there was so little remaining after 5 minutes that the rate constant shown in Table IV-5 is only an order of magnitude estimate. Cleavage of 2-methoxynaphthalene was slower, with 1- and 2-ethoxynaphthalene being cleaved slightly slower still. The cleavage of 2-methoxydiphenyl was quite slow at 250°C; possibly the presence of the second phenyl group adjacent to the methoxy group provides steric hindrance preventing the  $H^+(ZnCl_2OH)^-$  complex from approaching the oxygen atom.

Because the reaction rate was sufficiently slow to be accurately determined, 2-methoxynaphthalene was selected for extensive kinetic study, with reaction rates being determined at 175°C, 200°C, 225°C, and 250°C. A rate expression first order in the ether fit the data quite well, giving the same formula for the time dependence of concentration as that for diphenylmethane:

$$\ln \frac{C_{MN}}{C_{MN,0}} = -kt \quad (\text{IV-28})$$

Concentration data for 2-methoxynaphthalene are shown in Figure IV-3, and the rate constants calculated, from a linear regression analysis, are shown in Table IV-5. The rate constant at 225°C was calculated for three replicate experiments at that temperature, to check reproducibility of results. The standard deviation of the rate constant for the three runs was  $\pm 0.003$ , or about  $\pm 1\%$ .

To calculate an activation energy for the cleavage of methoxynaphthalene, a semilog plot of  $k$  vs inverse temperature was used, as shown in Figure IV-4. The rate constant at 250°C did not fit the trend exhibited by the rate constants at lower temperatures. The reaction at 250°C was so rapid that measurement of reactant concentrations after 5 minutes was probably affected by non-reactive impurities present initially in the model compound, with overestimation of unreacted methoxynaphthalene being the result. Alternatively, the higher temperature could have caused competing side reactions to become important. Using only the rate constants for 175, 200, and 225°C, the activation energy

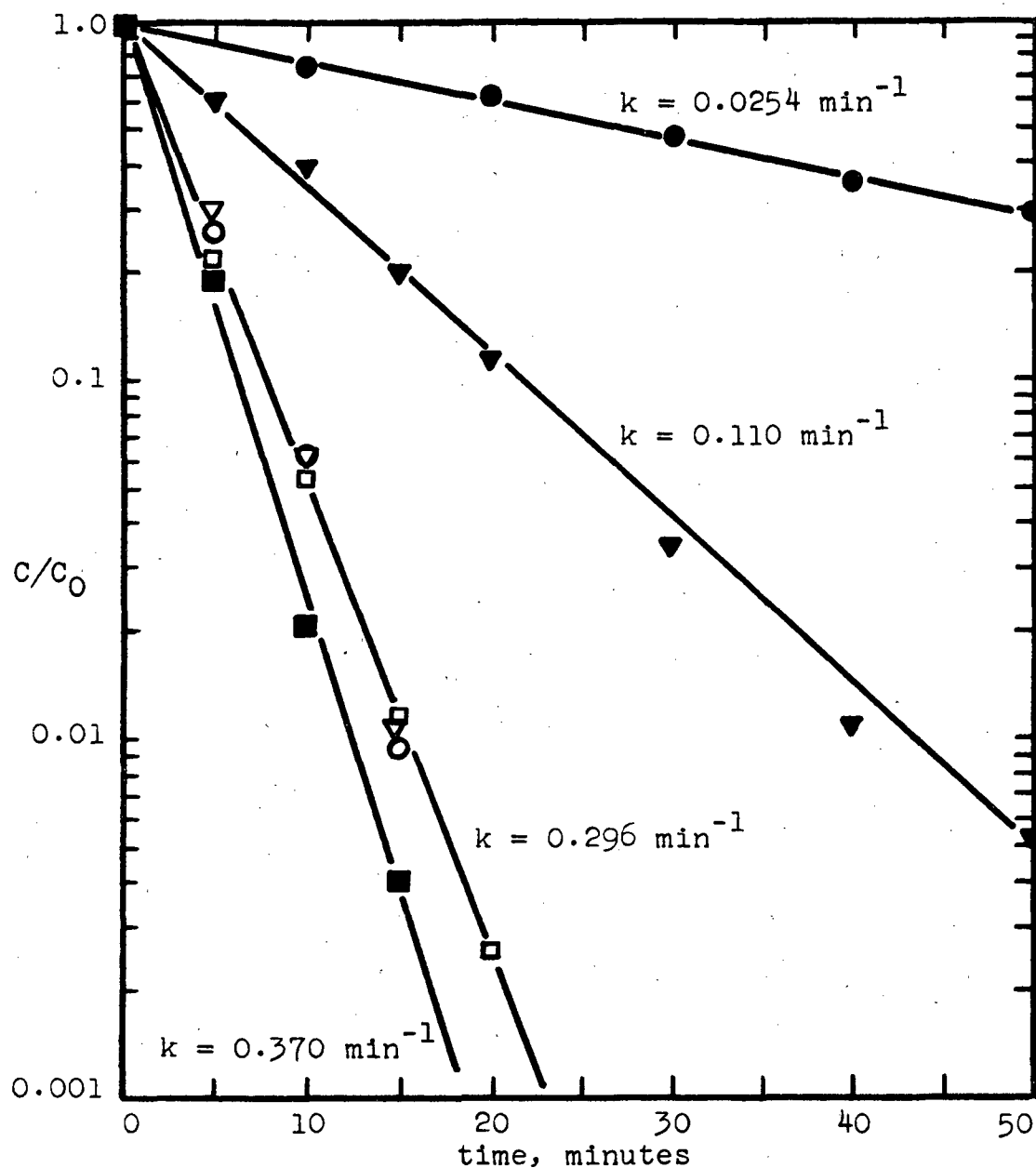


Figure IV-3

Concentration vs time for 2-methoxynaphthalene treatment with zinc chloride. In dodecane, with equal volumes of dodecane and zinc chloride (containing 10% water). Zinc chloride: 2-methoxynaphthalene molar ratio = 600:1. Treatment under 1.4 MPa hydrogen for 60 minutes. Benzene present in all experiments (1-2%). ● 175°C (Run 103); ▼ 200°C (Run 100); ▽ 225°C (Run 99); ◻ 225°C (Run 101); ○ 225°C (Run 102); 250°C (Run 81).

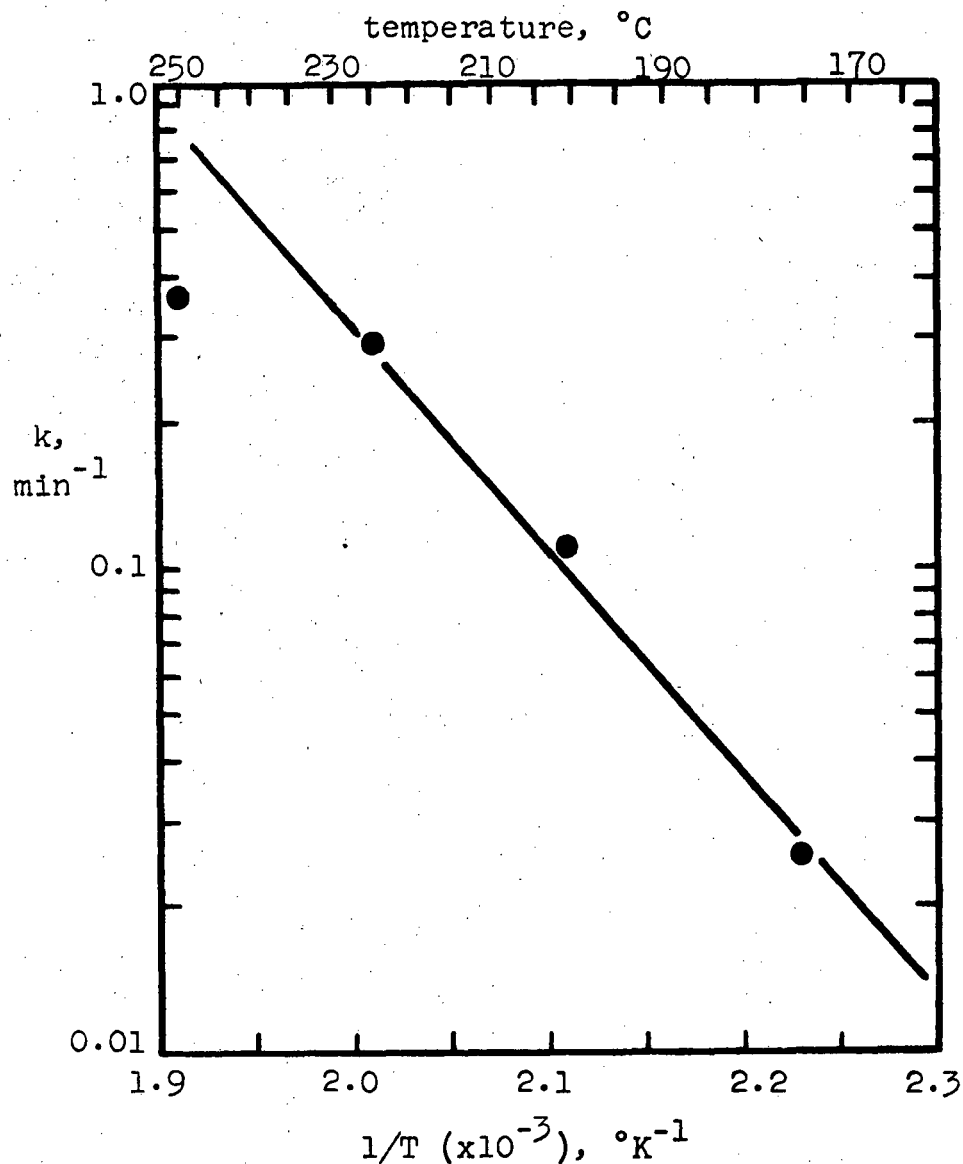


Figure IV-4

Determination of activation energy for 2-methoxynaphthalene cleavage catalyzed by zinc chloride. Determined in dodecane, with equal volumes of dodecane and zinc chloride (containing 10% water). Zinc chloride:2-methoxynaphthalene molar ratio = 600:1. Treatment under 1.4 MPa hydrogen for 60 minutes. Benzene present in all experiments (1-2%).  $k$  = first order rate constant for disappearance of 2-methoxynaphthalene. Slope of line = 11,000 °K.  $\Delta E_{\text{act}} = 21.9 \text{ kcal/mole}$ .

was found to be 21.9 kcal/mole, which is almost equal to the activation energy for diphenylmethane cleavage of 20.8 kcal/mole. Since both cleavage reactions involve protonation of the links and subsequent separation of the protonated species, it is reasonable that the activation energies be similar.

One experiment was conducted with 2-methoxynaphthalene at 225°C with 2.7 MPa hydrogen pressure, twice the usual pressure. The rate constant was only slightly increased, from  $0.296 \text{ min}^{-1}$  to  $0.305 \text{ min}^{-1}$ , indicating that gaseous hydrogen does not participate significantly in the rate-controlling reaction step (or any part of the reaction according to the postulated mechanism).

For experiments involving methoxybenzene, about 50% of the reacted methoxybenzene appeared as identifiable products (the remaining phenol may have been dissolved in the zinc chloride melt). For methoxynaphthalene and ethoxynaphthalene, the products accounted for nearly 100% of the reactant after extended periods (20 to 60 minutes).\*

#### Implications for Coal Liquefaction

From the reactions observed with model compounds, it is expected that during treatment of coal with zinc chloride at temperatures above

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\*At short times (5 to 10 minutes) the product concentration was much lower than expected from reactant disappearance. Since any conceivable reaction intermediate would have been detected in the analysis, a problem with short-time sampling for these runs might be indicated.

200°C, diaryl ether linkages should be rapidly broken.<sup>†</sup> Primary benzylic ethers should be cleaved with the oxygen removed as water, while the fragments alkylate whatever aromatic compounds are present. If sufficient solvent capable of being alkylated is not present, the fragments could alkylate onto the coal or coal products, yielding a char. Secondary benzylic ethers may, instead of being cleaved, be dehydrated to form olefin linkages in place of the ether linkages; this would remove oxygen from the coal, but would not break up the macromolecular structure.

Alkyl-aryl structures in coal will be dealkylated at a slower rate; from structures containing phenyl carbon-oxygen bonds, phenolic compounds will result, with no oxygen removal from the coal. Benzyl carbon-oxygen bonds will probably be broken for alkyl-aryl ethers as for diaryl ethers.

Aliphatic linkages with one carbon atom will be broken slowly, with one fragment alkylating either solvent or coal (or coal products). Longer aliphatic chains might break in a similar manner. In coal, aromatic structures linked by aliphatic bridges are certain to be extensively substituted in a manner that cannot be replicated by model compounds. Since substituents like those found in coal (i.e. hydroxyl and alkyl groups) have been shown to increase the rate of aliphatic link cleavage in simple model compounds, here and in other

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<sup>†</sup>Compounds analogous to diphenyl ether are not expected in the complicated coal structure.

studies (60,87), the presence of aromatic substituents may allow the cleavage of aliphatic linkages in coal which contain more than one carbon atom, despite the non-reactive nature of model compounds containing these bridges.

In all observed reactions, the hydrogen added to the model compounds was supplied by the alkylatable solvent, and gas phase hydrogen apparently did not participate. The presence of a hydrogen donor or hydrogen transfer agent, such as tetralin, could have caused hydrogenation of some fragments instead of alkylation; hydrogenation of such fragments formed from coal during treatment with zinc chloride and tetralin between 250 and 325°C has been inferred in current studies (16). However, tetralin could not be used as a hydrogen donor in this work, since degradation of the tetralin as a result of zinc chloride contact would have interfered with the analysis of model compound products. The effect of hydrogen transfer on model compound reactions was thus not investigated.



## V. CONCLUSIONS AND RECOMMENDATIONS

The results of the high temperature organic solvent/zinc chloride investigation indicate that hydroaromatic solvents used with zinc chloride for coal liquefaction will be subject to some catalytic degradation, with formation of light products from cracking and heavy products from dimerization, and possible further polymerization to tars. All solvents examined separated from zinc chloride quite readily by gravity settling; therefore, physical removal by settling of zinc chloride from organic phases containing coal liquefaction products may be feasible.

Studies of model compound reactions catalyzed by zinc chloride confirm that cleavage of aliphatic and ether bridges in model compounds, and presumably in coal, can occur via a carbonium ion mechanism, as proposed in earlier investigations. Cleavage of the diaryl aliphatic bridge containing one carbon atom leads to formation of one stable aryl group and one unstable fragment which alkylates aromatic compounds in the solution; thus, given sufficient light aromatics, cleavage of such bridges can result in fragmentation of the coal macromolecular structure, aiding liquefaction. If the only aromatic compounds present are those in coal and coal products, the alkylation of these aromatics by the ruptured bridge fragments can lead to char or tar formation as large fragments recombine. Cleavage of aliphatic bridges containing two or more carbon atoms was not observed here; however, the activating effect of substituents on aromatics as found in coal, may be strong enough that these links can also be cleaved.

Most diaryl ethers are cleaved quickly by zinc chloride, as long as there is one carbon atom between oxygen and the aromatic ring; bonds directly between oxygen and the aromatic ring are not broken. From formation of primary carbonium ions by ether cleavage, alkylation of aromatics in solution results, leading to coal dissolution or char formation, just as with aliphatic bridges. If secondary carbonium ions are formed, olefin formation, resulting in no significant reduction of the coal structure, competes with alkylation.

Alkyl-aryl ethers undergo dealkylation by zinc chloride. For compounds in which oxygen is bonded directly to the aromatic ring, no oxygen removal is observed, and phenolics result. The alkyl group may realkylate the phenol, resulting again in no reduction of the coal molecule.

A useful extension of this work would involve testing model compounds containing structures unexplored here. The behavior of linkages containing two or three carbon atoms between substituted aromatic rings would be of interest, to see if such links could be broken. An experiment with a compound such as phenethylphenyl ether would help check the stability of the phenethyl cation (not observed in this work from 1,2-diphenylethane). The products of diaryl ether cleavage in which secondary and tertiary carbonium ions are formed would help distinguish their behavior from that of primary cations; the cleavage of unsymmetric ethers would also be of interest. Treatment of a benzylic alkyl-aryl ether would show whether dealkylation is accompanied by oxygen removal. In all these studies, addition of a hydrogen donor

solvent would allow exploration of the possible participation of donated hydrogen in the cleavage reactions. Use of a solvent like tetralin for such investigations should be feasible with rapidly reacting model compounds, so that solvent degradation products would not build up during the reaction and obscure product analysis. The action of zinc chloride on these model compounds and in the presence of a hydrogen donor solvent would help in understanding the action of zinc chloride on coal.

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