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THE CHEMISTRY OF COAL MODEL COMPOUNDS - CLEAVAGE OF ALIPHATIC BRIDGES BETWEEN AROMATIC NUCLEI CATALYZED BY LEWIS ACIDS

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ABSTRACT

The condensed polynuclear aromatic clusters of coal are believed to be linked principally by straight-chain aliphatic bridges varying from 0-4 carbon atoms in length and the cleavage of these linkages is expected to be an important step in the coal liquefaction process. This study will focus on the means by which Lewis acid catalysts, specifically $AlCl_3$ and $ZnCl_2$, promote the cleavage of these linkages. To facilitate product identification and interpretation of reaction mechanisms, organic compounds which model the aliphatic bridges were used on substrates.

All experiments were performed in a magnetically stirred autoclave under either a H_2 or N_2 atmosphere at elevated pressure to determine the role of H_2. Reaction temperatures ranging from 200-350°C were used to avoid the complication of pyrolysis reactions. Reaction products were identified with the aid of gas chromatography/mass spectrometry, and quantitative product yields were determined by gas chromatography.

Experiments with $AlCl_3$ and the substrates containing two phenyl rings linked by 0-4 carbons atoms showed that $AlCl_3$ catalyzed cleavage of all the aliphatic bridges. The number of carbon atoms in the linkage was found to have an effect on substrate conversion, with aryl-aryl bonds being the most difficult to cleave. $ZnCl_2$ was totally inactive in cleaving the alkyl bridges in these compounds. Substitutents of a phenyl group by a phdroxyphenyl or a naphthyl group in the model compounds promoted the cleavage of aliphatic linkages in the presence of $AlCl_3$. In contrast to reactions with the diphenylalkanes, $ZnCl_2$ was also found to catalyze the cleavage of these compounds.

Several approaches for promoting the activity of the Lewis acid catalyst were investigated. Small amounts of water was found to reduce substrate conversion, whereas of tertiary hydride donors effected substantial increases in substrate conversion. The promotion of $AlCl_3$ and $ZnCl_2$ with HCl produced ambiguous results, increasing conversion in some cases yet reducing catalyst activity in others.

Plausible reaction mechanisms are proposed which explain the experimental results in this study. The role of gaseous H_2 in these mechanisms was also investigated.

I. INTRODUCTION

I. Coal Liquefaction

Lewis acids represented by metal halides have shown promise as coal liquefaction catalysts. Of the several metal halides found to promote liquefaction, greatest attention has been given to $ZnCl_2$ (1-6, 1-58, 1-59). This catalyst is known to catalytically effect the converson of coal to liquid products at temperatures below pyrolysis conditions, and can promote the transfer of hydrogen from hydrogen donor solvents (1-60, 3-44). In addition, $ZnCl_2$ appears to require less hydrogen to obtain liquid products than do solid catalysts. Furthermore, large bench-scale experiments (1-61) have demonstrated that a $ZnCl_2$ recovery of 99+ % is possible.

At present relatively little is known concerning the manner in which $ZnCl_2$ and other Lewis acid catalysts promote the depolymerization and hydrogenation of coal. To come to an understanding of their function it is important to establish how these catalysts interact with the organic structure of coal and what chemical transformations they are capable of effecting. With such knowledge it should be possible to develop more selective catalysts and to anticipate the types of liquid products that might be obtained from coal.

It is the aim of this work to look at one aspect of the general problem, namely the effect of Lewis acids on cleavage of aliphatic linkages, a reaction believed to be important in the liquefaction of coal. The balance of this chapter will review what is known about coal structure and the role of aliphatic linkages in this structure, as well as present a review of Lewis acid catalysts and a more complete discussion of scope and objectives of this work.

II. Coal Structure

Most of the information concerning the structure of coal and coal-derived liquids has come from the following sources:

a) Chemical analysis of functional groups present in coal;

b) Elemental analysis;

c) Molecular weight determinations;

d) ^{1}H-NMR and ^{13}C-NMR; and

e) Polarography.

Based on these and other experimental techniques, bituminous coal is believed to be a highly-crosslinked hydrocarbon polymer (1-8). Wiser (1-8) has proposed tht 60-75% of the carbon is contained in aromatic structures. A substantial fraction of the hydrocarbon network is saturated with respect to hydrogen, and about 15-25% of the carbon is thought to exist in hydroaromatic structures.

Recent work at Mobil Research and Development Corporation (1-9) has substantiated this representation of coal. By means of a chromatographic separation technique, compounds containing different functionalities were separated from coal-derived liquids into chemical classes. Following the characterization of several SRC's it was concluded that SRC and hence the parent coal contain a large number of compounds with similar hydrocarbon skeletons differing only by the nature and concentration of functional groups. The structures of the hydrocarbon skeletons were found to be consistent with Wiser's model of coal. Six-membered rings appear to predominate although significant quantities of five-membered rings may also exist. Most ring positions are occupied by carbon atoms, but many rings contain a sulfur, oxygen, or nitrogen atom. The Mobil group also performed high-resolution mass spectroscopic analyses of the volatile components (<300 M.W.) of SRC. The results obtained by this technique were also found to be consistent with the above structure of coal.

The basic structural units of coal appear to be single rings, condensed double rings, and larger polycondensed ring systems (1-8). X-ray as well as diamagnetic susceptibility data suggest that the average size of a ring cluster is about three condensed rings. More recent polarography results (1-9), however, indicate that coal contains only insignificant numbers of large polycondensed ring systems. The results suggest tht mono-aromatic, benzofurun, and naphthalene-like units are the principal types of aromatic rings present in short-contact time coal-derived liquids, which the authors propose to be representative of the parent coal. Short aliphatic side chains appear on some of the rings.

The aromatic and hydroaromatic structural units are linked together by various types of bridges to yield the hydrocarbon skeleton of coal. A wealth of research has been directed toward identifying the types of linkages which link together the aromatic and hydroaromatic units in coal. The basic conclusions (1-8) are that four principal types of linkages occur in coal: 1) Short aliphatic chains, probably not longer than four carbon atoms; 2) Ether linkages; 3) Sulfide and disulfide bridges; and 4) Direct aryl-aryl (biphenyl-type) bonds. Since aliphatic and ether linkages are believed to be the principal bridges in coal, the literature pertaining to these structures will be reviewed in some detail below.

Some of the earliest evidence for the presence of aliphatic linkages was presented by Heredy and Neuworth (1-19). Working initially with model compounds, they established that BF_3 could be used to catalyze the cleavage of aliphatic bridges between aromatic centers. One of the cleaved fragments was then terminated via reaction with phenol solvent. Using this technique (1-20) Neuworth and Heredy were able to demonstrate the presence of methylene linkages in coal between aromatic clusters, structures such as ($Ar-CH_2-Ar$). The extent of depolymerization was proportional to the number of $--CH_2--$ bridges found in the benzene-soluble fractions. It was found that cleavage of the methylene bridges could not account for the total depolymerization which had occurred. They concluded that methylene groups can account for only a small fraction of the aliphatic bridges in coal. This conclusion was based on a calculation of the number of linkages cleaved to produce soluble coal fragments with the average molecular weight observed. They gave no discussion, however, concerning the length of the majority aliphatic bridges believed to be present. Nevertheless, their results were consistent with the structural model of coal in which aromatic clusters are crosslinked with a relatively large number of bridges (mainly aliphatic) to form a rigid polymer.

Shortly after the work of Heredy and Neuworth, Lawson and Purdie (1-21) ozonized humic acid (obtained from a Warwickshire coal) in an aqueous medium and resolved the ether-soluble products by ion-exchange chromatography. They concluded that the basic structure of humic acid, and hence of the parent coal, consists of aromatic units joined by short, mainly unbranched aliphatic chains. Single methylene bridges were believed to form a particularly significant part of the structure. Using similar techniques, Montgomery et. al. (1-22) studied a mixture of acids obtained by the alkali-oxygen oxidation of bituminous coal follwed by decarboxylation. The most important innovation in this work was the use of mass spectrometry to identify the decarboxylation products. The presence of benzene, naphthalene, biphenyl, indan, and phenanthrene in the products proved the existence of these condensed ring systems in the coal itself. In addition to these parent compounds, many alkyl-substituted aromatic compounds were identified. The authors concluded that these alkyl groups come from aliphatic linkages between aromatic clusters as well as alkyl substituents on aromatic rings.

Recently new and highly-sophisticated NMR techniques such as ^{13}C-NMR and solid-state NMR have been applied to the study of coal structure. There is now abundant evidence for the presence of aliphatic linkages in coal extracts and a variety of coal-derived soluble materials, even though the data is conflicting. Heredy and co-workers (1-23) have obtained ^{1}H-NMR spectra of the depolymerization products from coals having 76.7-90.7% carbon, and found that 2.4-2.5% of the total hydrogen content exists in $--CH_2--$ bridge structures. Franz et. al. (1-24) have recently studied the products of the acid-catalyzed depolymerization of lignite by a combination of ^{1}H-NMR, ^{13}C-NMR, and GC/MS. The results confirm the presence of aliphatic bridge structures in coal, although no quantitative estimates were given. Their experiments proved, however, that depolymerization products possessing alkyl bridges are in fact derived from similar structures in coal, and not, for example, from aldehydes or analogous precursors. Larsen (1-18) cites other NMR evidence which indicates the presence of methylene groups in coal-derived materials. His evidence suggests, however, that methylene linkages between two aromatic centers ($Ar-CH_2-Ar$) are present in very limited quantities, probably no greater than 5% of the total methylene groups in coal.

The limited role of methylene bridges in coal is supported by the very recent work of Deno (1-25). He has developed an inverse oxidation technique using 30% aqueous H_2O_2 in trifluoroacetic acid (TFA) which oxidizes the aromatic structures in bituminous coal allowing the aliphatic structures to be isolated as carboxylic acids. The technique is termed "inverse oxidation" because the aliphatic component of the structure is preserved in contrast to the behavior of oxidizing agents such as HNO_3, O_2, Mn(VII), and Cr(VI), which selectively attack the benzylic hydrogen and form benzoic acid. When this technique is applied to Pittsburgh Seam or Illinois No. 6 coals, acetic acid is obtained as the principal product, indicating the preponderance of methyl groups in such structures as $Ar-CH_3$. The absence of mulonic acid ($HOOC-CH_2-COOH$) suggests that methylene linkages between aromatic centers occur infrequently. Of even greater importance, however, was the isolation of succinic acid ($HOOC-CH_2CH_2-COOH$) and glutaric acid ($HOOC-CH_2CH_2CH_2-COOH$) from the inverse oxidation of these coals. This suggests the presence of a significant number of two- and three-carbon aliphatic linkages between aromatic clusters. Previously these longer aliphatic linkages were assigned only a very limited or even non-existent role in bridging condensed polynuclear ring structures. Certainly

Deno's oxidation scheme opens a new vista for the determination of aliphatic structures in coal.

Another recently developed technique which adds further evidence for the role of aliphatic linkages was developed by Huston _et_. _al_. (1-26). The reaction of elemental fluorine with bituminous coal at ambient temperatures can be controlled to cause expulsion of hydrogen, oxygen, sulfur, and nitrogen as simple gaseous compounds, leaving a solid fluorinated coal behind. From the gravimetric stoichiometry of this reaction, a chemical method of measuring the aromaticity of the coal can be derived; and from mass spectrometery of the fluorinated coal, the fraction of cyclic carbon (aromatic plus alicyclic) can be esimated. The fluorinated coal, like the original coal, is a large polymer, but when pyrolyzed _in vacuo_ undergoes complete distillation without formation of char. The gravimetric and mass spectral analyses of the pyrolyzed, fluorinated coal showed that about 70% of the carbon in coal is aromatic. This and other results are consistent with a model which represents bituminous coal as a macromolecule containing condensed polynuclear aromatic clusters linked by carbon bridges. The authors conclude that 20% of carbon in coal is involved in aliphatic bridges between ring clusters.

The same authors (1-27) have applied numerous techniques to break up the macromolecular coal structure into smaller identifiable pieces with a minimum of chemical change so that the products can still be interpreted in terms of the original coal structure. Over 250 compounds have been identified as degradation products, using thermal cracking, catalytic cracking, hydrocatalytic cracking, hydrogenation, and selective oxidation with $Na_2Cr_2O_7$. All the results are consistent with the idea that bituminous coal consists largely of aromatic units extensively cross-linked with aliphatic and/or alicyclic bridges.

Ether oxygen atoms have also been found to participate in the linkages between aromatic clusters. Sternberg (1-11) suggests that one of the main functions of his reductive alkylation scheme is to cleave ether linkages in coal. The increase in pyridine solubility of reductively alkylated coal is thought to be due to depolymerization and an increase in phenolic hydroxyl groups resulting from ether cleavage. Takegami (1-24) concluded from a study of mild hydrogenation of bituminous coal that the formation of asphaltenes might be ascribed to cleavage of ether linkages. Ignasiak and Gawlak (1-13) have used a number of techniques well known to organic chemists which attack primarily carbon-oxygen bonds while leaving carbon-carbon bonds essentially intact (1-14, 1-15). They determined that the cleavage of ether linkages contributes substantially to the lowering of the number average molecular weight, and that the number of hydroxyl groups in the depolymerized coal correlates well with degree of molecular weight reduction. From this they concluded that the macromolecular weight of vitrinite of their high-rank Cretaceous coal is composed of relatively small groups (No. Ave. MW $\approx$ 670) almost exclusively interconnected by ether linkages. Ruberto (1-16) deduced from solvation studies of coal using a cobalt-molybdate catalyst and various solvent that half of the oxygen in a sub-bituminous coal is involved in ether structures, and proposed that the remaining half occurs chiefly as phenolic oxygen.

Furthermore, Wachowsk and Pawlak (1-17) have recently studied the action of potassium in THF on coals of different ranks as a means of determining the extent of ether linkages in coal. They found that the extent of ether linkages varies widely with coals from different ranks, but nevertheless concluded that the aromatic clusters in the studied coals are connected mainly by ether linkages.

Much evidence has been cited to substantiate the existence of carbon and oxygen linkages between condensed ring structures. The relative proportions of the various linkages in coal are not well known. Some authors (1-18, 1-21) suggest that aliphatic bridges predominate while others (1-13, 1-16, 1-17) propose that ether linkages predominate. Even though this topic is still a matter of debate, all the research to date seems to indicate that aliphatic and ether bridges are the most important structures in linking condensed ring systems.

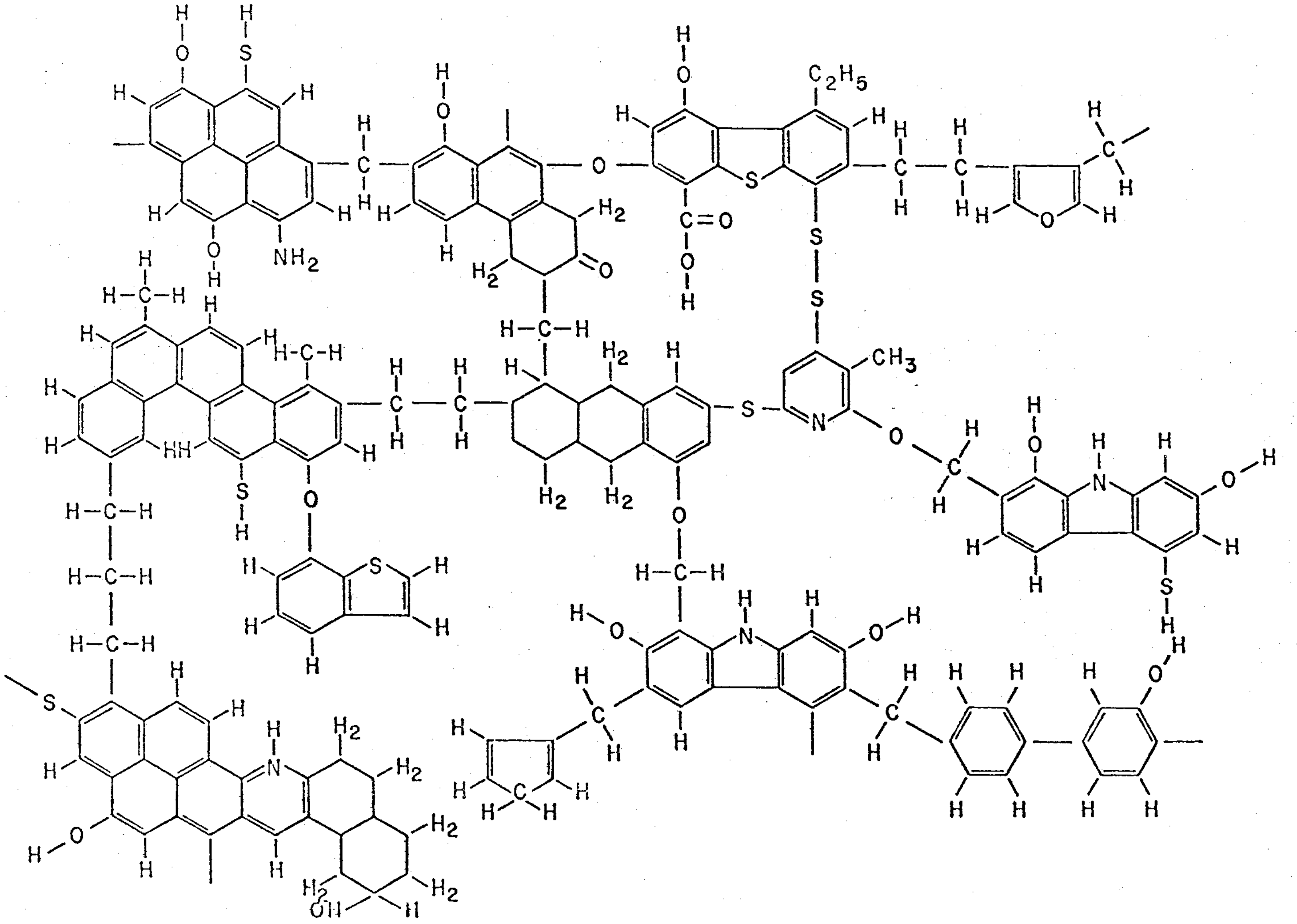
A related question about which more information is available is the frequency of crosslinks. This characteristic can be determined by measuring M_c, the average number molecular weight per crosslink. M_c can be determined from either solvent swelling or stress-strain characteristics. Although both types of measurements have been performed, the available data does not agree since solvent swelling was performed on <u>extracted</u> coal (1-28), whereas stress-strain characteristics have been measured for <u>raw</u> coal (1-29). M_c estimated from solvent swelling for bituminous coal is 1500-1800, but Larsen (1-18) considers this value low by a factor of 2. This data leads one to ask about the number of ring clusters per crosslink and the bridges between clusters. The BF_3/Phenol depolymerization technique (1-19) gives fragments whose number molecular weight lies between 350-575 (1-30). Van Krevelen's (1-31) work on the macromolecular gel structures of bituminous coals supports values of ~450 for ring cluster size.

Numerous workers have used evidence such as discussed above to compose a representative structure of the coal "molecule". One such model is that attributed to Wiser (1-32) and is shown in Fig. 1-1. This model and others should not be taken as definitive structures of coal, but rather as attempts to provide a representation of what is currently known about coal structure.

III. Lewis Acid Catalysts

Lewis acids in the form of metal halides (e.g. $ZnCl_2$ and $AlCl_3$) are known to promote a variety of reactions which contribute to the liquefaction of coal. Included among these reactons are the processes of depolymerization, alkylation, acylation, and hydrocracking reactions. A brief survey of these processes will be presented here. Since $AlCl_3$ and $ZnCl_2$ are the two major catalysts used in this study and because these two catalysts have been examined extensively in previous research, particular attention will be given to work which involves these materials.

Depolymerization of coal using Friedel-Crafts (i.e., Lewis Acid) catalysts was first reported in 1962 by Heredy and Neuworth (1-37). They discovered that the solubility of coal in a variety of organic solvents was considerably increased by treatment with boron trifluoride (BF_3) in phenol. The mechanism of this reaction presumably involved cleavage of methylene-aromatic bonds in the coal structure and subsequent alkylation of the methylene fragments onto the phenol solvent molecules.



XBL 7511-9365

Fig. 1-1. Wiser Model of Coal Structure.

The net effect of this process was the production of smaller and more readily extractable coal fragments.

A variety of Brönsted and Lewis acid catalysts have since been investigated for coal depolymerization. Darlage and Bailey (1-42) showed that depolymerization of coal works well for most phenolic solvents when catalyzed by BF_3 or H_2SO_4. Later studies (1-40, 1-41) have shown that coal rank is also an important factor, lower rank coals yielding higher solubilities.

The Friedel-Crafts alkylation of coal has also been investigated as a means of increasing the extractability of bituminous coal. Alkylation using $AlCl_3$ and alkyl chlorides has been studied by Kröger (1-43, 1-44). This treatment of coal results in a clear decrease in volatiles and increases in weight and extraction yields. Anywhere from 5 to 10 alkyl groups per 100 carbon atoms were introduced into the coal. The increased coal solubility was rationalized by the cleavage of methylene bridges between aromatic units in the coal, together with alkylation. Korshak and Kolesnikov (1-45) reported that polyxlylene, a polymer consisting of benzene rings linked by ethylene bridges, could be depolymerized to bibenzyl by the $AlCl_3$-catalyzed reaction with benzene.

Kölling (1-46) has used $AlCl_3$ as a Friedel-Crafts catalyst to acylate four bituminous coals of different rank with aliphatic acyl chlorides. Compared with the initial coal, the acylated coals were distinguished by considerably higher solubility in pyridine and other solvents. The extractability of the coals was found to depend on the chain length of the inserted aryl groups. It was concluded that the good extractability of acylated coals was mainly due to depolymerization of the coal structure during acylation, disappearance of hydrogen bridges by esterification of the phenolic hydroxyl groups, and neutralization of intermolecular forces between aromatic clusters by insertion of long-chain substituents.

Most applications of $AlCl_3$ to coal conversion, as evidenced by the above references, have been to use it as an alkylation or similar catalyst, but not to take advantage of its cracking abilities. This certainly may be due to the fact that some workers (1-46) have found low-rank coals to be less soluble in pyridine when treated with $AlCl_3$. In this case condensation reactions are assumed to predominate over cracking reactions. On the other hand, the same authors found a remarkable increase in the extraction yield of a dry steam coal treated with $AlCl_3$. In this case dissociation reactions were found to be dominant.

More recently Ross et. al. (1-47) have undertaken a systematic study of the use of $AlCl_3$ and other Lewis and Brönsted acids in converting coal to liquid products through cracking reactions at relatively low temperatures. In an initial set of experiments run to determine the role of $AlCl_3$, HCl, and H_2 in coal hydrocracking, no increase in THF or pyridine solubilities of the treated coal was found when one or more of these three components was absent. In a run with all three components present, however, substantial increases in solubilities were observed. This indicated that HCl is an effectve promoter for $AlCl_3$.

The above work with $AlCl_3/HCl$ resulted in a set of relatively mild experimental conditions. Next a series of Lewis acid catalysts were screened using a constant catalyst/coal weight ratio. All catalysts studied, except $AlCl_3$ and $AlBr_3$, were ineffective, reducing THF and pyridine solubilities because of internal alkylation of the coal. The ranking of all catalysts was thus established according to its effectiveness in increasing product solubilities:

$$AlCl_3 > AlBr_3 \gg SbCl_3 \approx SbF_3 \approx ZnCl_2 \approx TaF_3 \approx NiSO_4 \approx CoSO_4.$$

An ordering on a weight basis is deceptive because of the large differences in catalyst molecular weights. The next set of experiments was run at a constant catalyst/coal molar ratio. Here the ranking of the catalysts changed significantly:

$$SbBr_3 \approx SbCl_3 > AlBr_3 > AlCl_3 > Ni(AA)_2 > TaF_3 \gg SbF_3 \approx MoCl_3 \approx WCl_3$$

(AA = acetylacetonate)

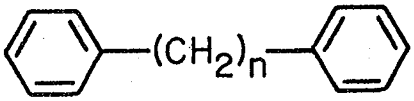
These experiments showed the interesting result that the popular coal conversion catalyst $ZnCl_2$ was not effective under these conditions. This may be attributed to the fact that $ZnCl_2$ was not molten in these experiments.

$ZnCl_2$ is currently being investigated for possible use in several commercial coal conversion processes. It has distinct advantages over $AlCl_3$ in that it is not hydrolyzed by water and other catalyst poisons and is much more amenable to recovery. The Consolidation Coal Company process (1-2) uses a $ZnCl_2$ catalyst for a direct hydrogenation process where coal is dissolved in a hydrogen donor solvent. Another process under development at the University of Utah (1-6, 1-7) involves direct catalytic hydrogenation of raw coal, where coal is crushed and impregnated with $ZnCl_2$ dissolved in water.

IV. Scope and Objectives

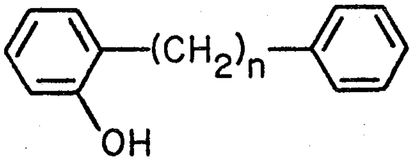
As noted in the introduction to this chapter and in the previous section, Lewis acids constitute a promising class of potential coal liquefaction catalysts. As we have seen, however, relatively little is known concerning the chemistry involved in their operation. The primary objective of this work is to identify the role of Lewis acids in the cleavage of aliphatic bridges between aromatic centers, since such reactions constitute an important step in the liquefaction process. Model compounds were used rather than coal in order to facilitate product identification and interpretation of reaction sequences.

Three types of model compounds were selected. The first consisted of biphenyl and diphenylalkanes as models of direct aryl-aryl bonds and aliphatic linkages in coal:

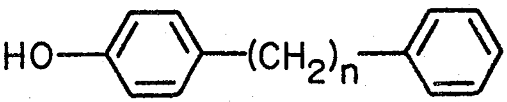


n = 0 Biphenyl
n = 1 Diphenylmethane
n = 2 Bibenzyl
n = 3 1,3-Diphenylpropane
n = 4 1,4-Diphenylbutane

The second type consisted of the hydroxylated analogs of biphenyl and diphenylmethane.

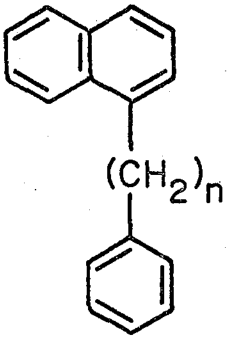


$n = 0$ 2-Phenylphenol
$n = 1$ 2-Hydroxydiphenylmethane



$n = 0$ 4-Phenylphenol
$n = 1$ 4-Hydroxydiphenylmethane

These compounds were selected because it is known that many of the aromatic groups in coal contain hydroxyl substituents. Finally, the third type of model was represented by 1-phenyl- and 1-benzylnaphthalene.



n = 0 1-Phenylnaphthalene
n = 1 1-Benzylnaphthalene

The specific goals of the work were:

1) To determine the influence of organic structures on the cleavge of aliphatic bridges between aromatic centers;

2) To establish the relationship between acid strength and catalytic activity of Lewis acids used to cleave aliphatic linkages;

3) To identify the role of molecular hydrogen in the cleavage process; and

4) To establish the influence of promoters on the activity of Lewis acid catalysts.

In addition to the major investigations noted above, a limited amount of work was done to establish the effectiveness of other approaches to the cleavage of aliphatic linkages. Particular attention was given to the application of organic bases, mild oxidation by sodium hypochlorite (NaOCl), hydrogenolysis by solid-supported mixed metal oxide catalysts, and the use of alkoxide salts as novel hydride donors.

Chromatography/Mass Spectrometry

D. Qualitative Analysis by Mass Spectrometry

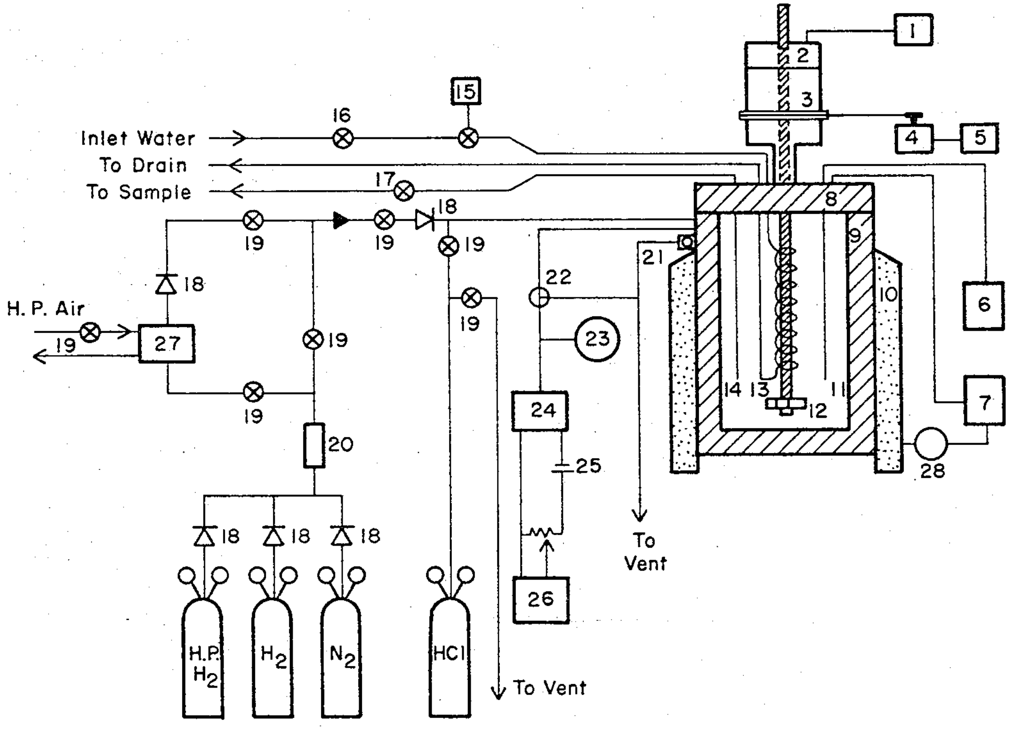
II - EXPERIMENTAL APPARATUS AND PROCEDURES

I. Autoclave System

The major experimental apparatus used in this investigation is a 300 cm^3 magnetically-driven stirred autoclave (Autoclave Engineers, Model APB-300). For safe operation the autoclave assembly is bolted to the concrete floor inside an explosion-proof bay constructed of 1/2 in. steel plate and equipped with a blow-out sky light. The steel plate door of the bay is closed during autoclave operation, thus totally isolating the autoclave from the operator and surrounding laboratory. All necessary operating controls and recording devices are located in a rack outside of the bay. The gas cylinders and associated valves used to fill the autoclave with the desired gas are also located outside the bay with the sole exception of the vent valve. A high-speed fan located in the roof of the operating bay ensures removal of all fumes from either reactants or products during assembly or disassembly of the autoclave. Figure 2-1 illustrates the autoclave with its accompanying stirring assembly, heating system, gas feed system, and necessary instrumentation. The important features of each of these systems are presented below.

A. The Autoclave

The autoclave is constructed of 316 stainless steel and has a maximum operating pressure of 5000 psig at 343°C. The internal operating volume is 300 cm^3 but is reduced to 260 cm^3 by the introduction of a glass liner, used to facilitate handling of reactants and products.



1. Tachometer
2. Tachometer Pickup Coil
3. Stirring Assembly
4. Variable Speed Motor
5. Motor Controls
6. Temperature Recorder
7. Temperature Controller
8. Autoclave Cover
9. Autoclave Body
10. Jacket-type Heater/Cooling H_2O Bath
11. Thermowell
12. Agitator Shaft and Impeller
13. Cooling Coil
14. Sampling Tube
15. Solenoid Valve
16. Gate Valve
17. Sampling Valve
18. Check Valve
19. Shutoff Valve
20. Line Filter
21. Safety Head with Rupture Disc
22. Three-way Valve
23. Pressure Gauge
24. Pressure Transducer
25. Power Supply
26. Pressure (MV) Recorder
27. Pneumatically Driven Diaphram Booster Pump
28. Voltage Control

Fig. 2-1. Experimental Apparatus

XBL 7712-11268

[a] Table 2-1

Catalysts and Substrates

I. Catalysts

Catalyst	Source	Physical State	Purity or Grade	F.W.	M.P. (°C)	B.P. (°C)
$AlCl_3$ (Anhydrous)	Mallinckrodt, Inc.	Powder	Reagent	133.34	193/2.5 atm.	subl. 180
$ZnCl_2$	Mallinckrodt, Inc.	Lumps	Reagent	136.28	283	732
5% NiO-20% WO_3-Al_2O_3	Nalco Chemical Co.	Powder	--	--	--	--

II. Substrates

Substrate	Source	Physical State	Purity or Grade	M.W.	M.P. (°C)	B.P. (°C)
Biphenyl	Aldrich Chemical Co.	Solid	Reagent	154.21	69-72	255
Diphenylmethane	Aldrich Chemical Co.	Liquid	99%	168.24	22-24	264
Bibenzyl(1,2-Diphenylethane)	Aldrich Chemical Co.	Solid	Reagent	182.27	50-53	284
1,3-Diphenylpropane	Frinton Laboratories	Liquid	Reagent	196.30	6	295
1,4-Diphenylbutane	Frinton Laboratories	Solid	Reagent	210.32	50-52	317
1-Phenylnaphthalene	Aldrich Chemical Co.	Liquid	98%	204.27	45	324-325
1-Benzylnaphthalene	K & K Labs Division, ICN Pharmaceuticals	Solid	Reagent	218.30	58.5	350
2-Phenylphenol	Aldrich Chemical Co.	Solid	99+%	170.21	56.5-57.5	282
4-Phenylphenol	Aldrich Chemical Co.	Solid	97%	170.21	165-167	321
2-Hydroxydiphenylmethane	Aldrich Chemical Co.	Solid	99%	184.24	53-54.5	312
4-Hydroxydiphenylmethane	Aldrich Chemical Co.	Solid	Reagent	184.24	83-85	200/10mm

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[a] Data for this table obtained from following sources: 1) Manufacturer's information; 2) Handbook of Chemistry and Physics, 51st ed., ed. by R. C. Weast, The Chemical Rubber Company, Cleveland, Ohio (1970); 3) Dictionary of Organic Compounds, 4th ed., Oxford University Press, New York (1965); 4) Encyclopedia of Chemical Technology, ed. by R. E. Kirk and D. F. Othmer, Interscience Encylopedia, Inc., New York (1960).

[a] Table 2-2

Solvents, Organic Additives, and Other Reagents

I. Solvents

Compound	Source	Purity or Grade	M.W.	B.P. (°C)	Critical Temp. (°C)
Benzene	Mallinckrodt, Inc.	Reagent	78.12	80.2	289
Cyclohexane	Aldrich Chemical Co.	Reagent	84.16	80.7	280

II. Organic Additives

Compound	Source	Purity or Grade	M. W.	B.P. (°C)
2,3-Dimethylbutane	Aldrich Chemical Co.	97%	86.18	58
Isopentane	Aldrich Chemical Co.	99+%	72.15	30
Isopropanol	Mallinckrodt, Inc.	Spectrophotometric	60.10	82.3

III. Other Reagents

Compound	Source	Grade or Purity	F. W.
Potassium t-Butoxide	Alfa Div., Ventron Corp.	95-99%	112.22
Potassium Methoxide	Alfa Div., Ventron Corp.	95-99%	70.14
Sodium Hypochlorite	Georgia Pacific Corp.	5.25 wt.% aqueous soln.	74.44

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[a] Data for this table obtained from references 1-3 of Table 2-1 and 4) R. C. Reid, *et al.*, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York (1977).

The autoclave body contains three ports for introduction and removal of gases. The first is used to introduce gas into the autoclave. The second is connected to a three-way valve with two ports on pressure. The open ports connect the autoclave volume with a pressure gauge and pressure transducer. The other port is opened to vent the autoclave and closed during pressurization. The third port in the autoclave body contains a safety assembly connected to the vent line. This assembly consists of a Teflon-coated Inconel rupture disc with experimental bursting pressures of 5394 psig at 22°C and 5016 psig at 204°C.

The cover of the autoclave is a circular flange which contains several access ports. The stirring assembly screws into an opening in the middle of the cover and forms a leak-tight seal with a thin 316 s.s. gasket. Through a smaller hole, a 1/8 in. thermowell tube is attached to the bottom side of the cover, permitting the tube to be submerged in the reaction mixture during operation. Another small opening permits attachment of a 1/8 in. sampling tube so that the contents of the autoclave can be removed during reaction by operation of a sampling valve. This port was not used, however, for the present experiments and was therefore plugged. A cooling coil is attached to two ports in the bottom side of the cover. Water inlet and outlet connections to the cooling coil are located on the side of the cover.

B. Stirring Assembly

Agitation of the autoclave contents is achieved by an impeller magnetically coupled to external rotating magnets. The external magnets are rotated by a DC motor (1/4 h.p., 2500 RPM maximum) equipped with a variable speed control and powered by an AC/DC converter. Thus agitation speed can be varied continuously up to a maximum of 1800 RPM. To obtain a reading of the stirring speed, a stator coil is placed over the top cylindrical portion of the Magnedrive assembly. The signal picked up on this coil is read out directly on a tachometer.

C. Heating and Cooling Systems

The autoclave is equipped with a heating and temperature control system designed to enable rapid heat-up and ensure temperature control within narrow limits. A jacket-type 1200 W furnace (Autoclave Engineers Series VF-8500) provides heat to the autoclave body and is mounted with brackets so that it may be easily slid on and off of the autoclave body.

To provide temperature control at a given set point, power to the heater is controlled by a time-proportioning temperature controller (Honeywell Pyr-o-vane Model 105C204). Acting in response to an iron-constantan thermocouple located in the thermowell, the controller is able to maintain a temperature to within ±2°C. Maximum temperature fluctuations after achieving temperature stabilization are in no case greater than ±5°C. To further facilitate temperature stability a Variac was installed between the furnace and temperature controller to permit the voltage applied to the heater to be varied from 0-120 V. The full 120 V is applied to the furnace during heat-up, but typically only 90 V is required at reaction temperature to permit control within the stated precision.

The temperature of the reaction mixture vs. time is continuously displayed on a temperature recorder (Leeds and Northrup Speedomax Type G). The recorder acts in response to a copper-constantan thermocouple located in the thermowell alongside the temperature controller thermocouple. Use of two separate thermocouples allows the temperature controlling and recording systems to be totally independent of each other. In theory this permits a double check on the reaction temperature. In practice it was found that the controller temperature reading is not very accurate and that it is difficult to calibrate. The Speedomax recorder was thus calibrated to read temperatures from ambient to 350°C. Accuracy with this method of calibration is ±1°C or better. This accuracy was confirmed up to 350°C by comparing the thermocouple reading with that of a mercury thermometer while both were immersed in a heated $NaNO_3$-KNO_3 bath.

Quenching a reaction and cooling the autoclave is achieved by running water through the 1/8 in. s.s. cooling coil which is immersed in the reaction mixture and simultaneously flowing water through a stainless steel cooling jacket raised up around the autoclave body. After power to the heater is shut off at the end of a run, the inlet and outlet water hoses are attached to the appropriate connections on the autoclave cover. The furnace is next lowered on a ring stand from around the autoclave body and the cooling jacket is raised and secured in its place. The cooling system is actuated by the operation of a solenoid valve from a switch in the instrument rack, allowing water to flow simultaneously through the cooling coil and jacket. Quenching of a reaction from 325°C to 50°C requires just over a minute, and cooling the autoclave to room temperature is accomplished in 10 minutes.

D. Gas Feed and Pressure Recording Systems

The gas manifold system shown in Fig. 2-1 was constructed to allow the autoclave to be pressurized with hydrogen, nitrogen, or hydrogen chloride (HCl), either separately or in any combination. Check valves were placed in appropriate locations to prevent accidental backfilling of a gas cylinder and to isolate the autoclave from the manifold system. The gas line through which all gases (except HCl) are introduced into the autoclave is equipped with a dual-disc (5/10 micrometer) line filter to trap out any particulate matter coming from the gas cylinders. The HCl line is separately connected to the gas inlet line just outside the autoclave without filters or check valves to minimize corrosion of the stainless steel manifold system.

The autoclave can either be pressurized directly from the gas cylinders or can be filled to yet higher pressures by directing the gas through a pneumatically-driven diaphragm booster pump. This pump (American Instrument Company, Model 46-14025) allows the autoclave to be pressurized up to 5000 psig. Its main function is to allow reactions to be run at pressures above tank pressure. The booster pump also proved to be invaluable in leak testing the entire autoclave system.

Autoclave pressure as explained previously can be continuously monitored on both a pressure gauge and a Leeds and Northrup Speedomax recorder whether the vent valve is opened or closed. The gauge is a standard 3-1/2 in. dial gauge with a 403 s.s. Bourdon tube and is located on the autoclave housing. The pressure vs. time can also be constantly monitored from the control panel by displaying the signal from a pressure transducer (Honeywell Model PP/I) on the aforementioned Speedomax recorder. The recorder is calibrated in psig by comparing its reading to that of the Bourdon tube gauge.

II. Experimental Procedures

A. Catalyst and Substrate Preparation

All catalysts and substrates used in this investigation are listed in Table 2-1 with their sources and pertinent physical data. All solvents, organic additives, and other reagents are listed in Table 2-2. A brief discussion of each of these classes of reagents will be given to explain special preparation techniques.

1. Catalysts

Anhydrous aluminum tri-chloride ($AlCl_3$) was the principal catalyst used in this investigation. Because this substance is extremely hygroscopic it requires special handling procedures. To avoid contact with the atmosphere, $AlCl_3$ was stored in a dry box under nitrogen. The dry box was equipped with a vacuum antechamber, a continuous nitrogen purge, and a phosphorus pentoxide (P_2O_5) dessicant. The $AlCl_3$ was used as received in its powdered form.

Zinc chloride ($ZnCl_2$) is also hygroscopic but is not hydrolyzed by water as is $AlCl_3$. All $ZnCl_2$ used was dried 24 hours in a vacuum oven at 110°C before introduction into the autoclave. Weight loss upon drying was typically 2-5%. After drying all subsequent handling was conducted in the dry box.

The $NiO\text{-}WO_3$ solid catalyst was obtained as 1/8-1/16 in. extruded pellets and was hand ground to less than 150 Tyler mesh. The powdered catalyst was dried for 24 hours in a vacuum oven at 110°C to remove all traces of water which might occupy acidic sites on the catalyst surface. Typical weight loss on drying was 1-2%. Again all subsequent handling and weighing was done in a dry box.

2. Substrates

All substrates, with the exception of the hydroxylated compounds, were used as received without further treatment or purification. Each substrate was analyzed by gas chromatography (GC) to check its purity. Only very minor impurities were found in the worst case, and observed purities were typically better than stated. For those substrates with Reagent Grade designations all purities were determined to be 99+%.

Since phenolic compounds are generally known to be hygroscopic, it was deemed necessary to dry all hydroxyl compounds to prevent hydrolysis of the $AlCl_3$ catalyst. With the exception of 4-phenylphenol the hydroxylated compounds were dried with anhydrous magnesium sulfate ($MgSO_4$) for 24 hours. Each compound was heated above its melting point on a heated magnetic stirrer in a stoppered glass flask with $MgSO_4$ which had previously been dried in a vacuum oven at 110°C. The liquid mixture was constantly stirred for 24 hours. The $MgSO_4$ was separated from the liquid substrate by vacuum filtering the hot mixture with a heated, coarse glass frit. All hydroxylated compounds were subsequently stored and handled in a dry box under nitrogen. 4-Phenylphenol was not dried because of its relatively high melting point (169°C), but did not have the appearance of being hygroscopic.

B. Preparation of Solvents and Other Reagents

1. Solvents

The benzene and cyclohexane solvents used in this study are both Reagent Grade and were analyzed by gas chromatography to check their purity. Because both solvents typically contain 0.02-0.05% water which could hydrolyze a substantial fraction of the $AlCl_3$ catalyst, it was imperative to dry them as much as possible. Both solvents were refluxed in a glass solvent still under a nitrogen atmosphere with a mixture of sodium metal and benzophenone. Refluxing was continued approximately 24 hours, or at least until the characteristically deep blue color of the Ketyl was observed, indicating that the solvent was water and oxygen free. The solvent was collected in a previously dried glass bottle and stored in a dry box under nitrogen until used. All handling and weighing of solvent was performed in the dry box.

2. Organic Additives

The organic additives listed in Table 2-2 are all Reagent Grade or better and were GC analyzed as a check on purity. No further purification was deemed necessary.

3. Other Reagents

Potassium methoxide and potassium t-butoxide were used as received without further purification or analysis. Both reagents were stored and handled in a dry box under nitrogen.

The sodium hypochlorite solution was also used as received. In the run using this reagent, the organic and aqueous phases were separated using a separatory funnel. The organic phase was subsequently dried with anhydrous $MgSO_4$ and analyzed, but the aqueous phase was discarded.

Potassium isopropoxide was used as a tertiary hydride donor in several runs but is not listed in Table 2-2 since it was prepared *in situ*. In a dry box under nitrogen, sufficient potassium metal was added to isopropanol to yield the desired amount of potassium isopropoxide.

C. Description of Reaction Procedure

1. Reactant Preparation

A run was begun by thoroughly cleaning and flame drying a glass liner. The liner was introduced while still warm into the dry box through the vacuum antechamber. The catalyst was weighed on a scale inside the dry box and transferred to the liner. The solvent was then similarly weighed and transferred to the liner, as were any organic additives. If the substrate was hygroscopic it also was weighed inside the dry box. Most substrates, however, were weighed outside the dry box due to space limitations in the box. In any event, a final weight of liner plus all reactants was recorded before introduction into the autoclave.

2. Autoclave Operation

The liner was next removed from the dry box and placed into the autoclave body. Four to six thin strips of 316 s.s. sheet were wedged in between the glass liner and autoclave walls to prevent the liner from spinning and perhaps breaking during agitation. The autoclave cover was then bolted to the autoclave body. Air trapped inside was flushed out by alternately pressurizing and venting the autoclave several times with the gas to be used during reaction. The autoclave was next filled with the appropriate gas to a pressure calculated from the ideal gas law to give the desired gas partial pressure at reaction temperature. For the HCl runs, the autoclave was first flushed with hydrogen, filled with HCl gas, and finally pressurized with hydrogen to prevent HCl from remaining in the gas lines.

Following gas pressurization, the voltage to the furnace was adjusted to 120 V (heater maximum) and the temperature controller turned on. The DC motor was simultaneously activated and stirring speed set at 1250 RPM. From experiments performed outside the autoclave with the stirring assembly and a glass liner, this speed was shown to be optimum in giving maximum agitation without throwing reactants out of the glass liner. With 120 V applied to the heater the temperature rose at a nearly linear rate of approximately 18°C/min. About 19 minutes were required to reach 225°C from room temperatures, and 22 minutes to reach 325°C.

Each reaction was allowed to run 90 minutes from the time at which reaction temperature was achieved. Once the temperature had stabilized about the set point, fluctuations were in no case greater than ±5°C and were typically ±2°C. For the few runs where the pressure dropped noticeably due to hydrogen consumption or leakage, the gas pressure was maintained by opening a hydrogen cylinder.

At the end of the run the reaction was quenched by shutting off power to the heater, quickly lowering the furnace and replacing it with the cooling jacket, and turning on the cooling water. With both modes of cooling in operation, quenching of the reaction from 325°C to 50°C required less than 2 minutes. Room temperature was achieved in 8-10 minutes. At this point the autoclave was vented and purged with nitrogen to remove the remaining hydrogen and product gases. The autoclave cover was then unbolted and the glass liner removed. The liner was immediately sealed with Parafilm to prevent product evaporation.

3. Autoclave Cleaning

To prevent contamination between runs the autoclave was scrupulously cleaned after each reaction. The inside of the autoclave and the stirring assembly were scraped clean of tar and subsequently scrubbed with acetone, water, pyridine, and acetone, in that order. The water served to dissolve any traces of $AlCl_3$ or other aluminum compounds, while the acetone and pyridine removed all organic material. The top cover of the stirring assembly was occasionally removed and the assembly flushed with pyridine and acetone. The autoclave was next filled with acetone, the cover bolted in place, and the autoclave heated to $200^{\circ}C$ under a nitrogen atmosphere for 1/2 hour. This hot acetone bath served to clean the autoclave and associated valves and tubing of all organic material which were not amenable to physical cleaning. The autoclave was thoroughly dried before the next run and the stirring assembly internals dried with an air stream. In no case were acetone or pyridine detected in the reaction products.

III. Reaction Product Analysis

A. Product Work-Up

After removal from the autoclave the glass liner and its contents were immediately weighed. Weight loss during reaction was consistently 2-3 gm., even for the blank runs involving only catalyst and solvent. This loss is attributed to solvent evaporation before and after reaction and during autoclave flushing, to a small unrecoverable amount of liquid in the concave bottom of the autoclave, and especially to entrainment of liquid in the stirring assembly internals. Gasification of reactants was also shown to play a role in several reactions.

The reaction products were next vacuum filtered with a medium fritted-glass Büchner funnel (pore size 10-15 microns) to remove all traces of tar, $AlCl_3$, and other insolubles. A bare minimum of vacuum was applied to minimize solvent evaporation, thereby preserving the original product distribution of the reaction. The weight and volume of liquid reaction products were then recorded for later use in product analysis. The liquid products were finally stored in a tightly-sealed glass bottle to await analysis.

No attempt was made to determine the absolute amount of tar formed or to analyze its composition. The tar recovered during filtering was only a small fraction of the total tar produced, as most of it was stuck to the walls of the glass liner and to the stirring assembly. A relative indication of tar formation is given in the data tables as "% Reactants Recovered as Liquid Products". The only material not recovered as liquid products is tar, gasified reactants, and other losses as outlined above. Since losses other than tar formation were rather constant from run to run, changes in the "% Reactants Recovered" data indicate relative changes in the amount of tar formation. Also, no attempt was made to collect or analyze gaseous products formed during reaction.

B. Qualitative Analysis by Gas Chromatography

1. The Gas Chromatograph

The major analytical tool used for qualitative product identification and quantitative analysis was gas chromatography (GC). The gas chromatograph used in this investigation is a dual column unit (Varian Associates, Model 1420-10) equipped with linear temperature programming capabilities and a thermal conductivity (TC) detector. Both sample and reference columns are 1/8 in. in diameter by 10 ft. in length and were packed with 5% OV-225 on a Chromosorb P support. The OV-225 liquid phase is a Cyanopropyl-methyl Phenyl-methyl silicone polymer of intermediate polarity, chosen to separate compounds both on the basis of boiling point and polarity. The maximum operating temperature for OV-225 is 275°C, and at this temperature compounds with boiling points up to 325°C could be eluted.

Ultra-High Purity helium (99.998 + %) was used as the carrier gas with a typical column flow rate of 30 ml/min. Other standard GC operating conditions were: 1) TC detector filament current 150 mA; 2) Injector temperature 250°C; 3) Detector Oven temperature 280°C; and 4) 80 psig helium tank pressure. For most analyses the GC was programmed from 80-275°C at 20°C/min., these conditions providing adequate peak resolution with little peak broadening and minimum analysis time. For reactions where low molecular weight organic additives (e.g., isopentane) yielded a number of light aliphatic products, the initial programming temperature of 20°C was achieved by cooling the GC oven with dry ice. In all cases the maximum column temperature was maintained for at least 10 minutes at the end of the program to ensure that all high molecular weight compounds had been eluted. With these operating conditions the TC detector could produce an integratable peak with as little as 0.05 micrograms material.

Gas chromatography was chosen as the most efficient method to separate the liquid reaction products. The major problems were then to positively identify the numerous peaks emerging from the GC column and to relate the peak areas to the amount of each component present. These problems form the bases of qualitative and quantitative GC analysis, respectively, and will both be considered in more detail.

2. Qualitative GC Methods

The chromatographic method used to identify GC peaks is that of peak coincidence or standard additions. A small aliquot of the reaction products is doped or spiked with a known compound suspected to be a reaction product and GC analyzed. The resulting chromatogram is compared to one of the reaction products alone. If one of the unknown peaks is shown to increase in size while retaining the characteristic shape of a well resolved peak, it is most probably the added known compound. Many of the reaction products were initially identified by this method, the majority of the necessary compounds being purchased from the suppliers listed in Tables 2-1 and 2-2.

Peak coincidence with a known compound is a necessary but not sufficient condition for positive identification of an unknown peak. Many compounds of interest have identical retention times on the GC column used in this study since separation is effected on the basis of both molecular weight and polarity. Isomers of the same compound most often exhibit this trait. It was therefore necessary to confirm these preliminary GC identifications by a non-chromatographic technique. Mass spectrometry (MS) and Gas Chromatography/Mass Spectrometry (GC/MS) were both used in this confirmatory role and also to identify peaks which could not be identified by the chromatographic technique. It should be noted that all major reaction products were identified at least once by both chromatographic and mass spectral techniques for a series of reactions where similar substrates and reaction conditions were used.

C. Qualitative Analysis by Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS is an analytical method in which a gas chromatograph (GC) and mass spectrometer (MS) are interfaced such that the spectrometer serves as a detector for the GC effluent. By scanning the entire mass range of the effluent gases every few (0.5-5) seconds, a complete mass spectrum of every peak eluted from the column is obtained. Because of the large amount of data thus acquired, the mass spectral information is best handled with a mini-computer and accompanying tape or disk storage system. The mass spectrum of each chromatographic peak can then be recalled and compared with mass spectra of known compounds in a mass spectral library. If the unknown mass spectrum matches closely a known spectrum, identification is highly probable. For absolute identification the pure compound must be obtained and its mass spectrum recorded on the same instrument. The mass spectra and GC retentions must be nearly identical to confirm identification.

1. The GC/MS System

The GC/MS system used in this study, located at the Lawrence Berkeley Laboratory of the University of California, is a Finnigan

Instruments Model 4023. This system is comprised of a Finnigan Model 9610 gas chromatograph, a Finnigan Model 4000 quadripole mass spectrometer, and a Model 2400 Finnigan/Incos data system.

The 9610 gas chromatograph is a microprocessor-controlled unit in which the column oven can operate from -100°C to +400°C in either isothermal or temperature programmed mode. Either packed or capillary columns can be used. The column used here is a glass column measuring 2 m.m. in diameter by 2 m. in length, and is packed with 3% OV-225 on Chromosorb W/HP. The GC effluent goes into a jet separator in which most of the helium carrier gas is pumped away while the rest of the effluent enters the ion source of the mass spectrometer. Before the jet separator a separate line to a valve and vacuum pump allows diversion of most of the solvent peak from the ion source. Because the exit port of the GC is under vacuum, GC operation under these conditions is somewhat different from normal atmospheric operation. At any given temperature elution times are faster and a column has somewhat increased resolution. Typical GC flow rate was 20 ml/min. The temperature program used for these analyses was 70-200°C at 10°C/min., the upper temperature being maintained until the last peak was obtained.

The quadrpole mass filter has a rated resolution of 400, and in practice is capable of unit mass resolution to 1000 a.m.u. The ionizer is an electron impact source with a rhenium filament producing an electron current up to 0.5 mA at energies from 10-150 eV. Usual scan conditions in this study were 0.25 mA at an ionization energy of 70 eV.

The quality of a mass spectrum during a GC/MS analysis is closely related to the scanning rate. A mass spectrum can be severely distorted due to changing sample concentration during the elution of the chromatographic peak (2-2). Since the capillary column used in this study gives rise to narrow peaks, the entire mass spectrum was scanned in 2 seconds to allow multiple scans over the same peak. The data system records all these spectra and averages them together to minimize distortions due to changing compound concentration during a scan. It is this average spectrum which is compared to the library spectra.

The data system is equipped with software to treat the data in several ways. The basic ones are the presentation of the total ion chromatogram (equivalent to the GC spectrum), the presentation of mass spectra for selected chromatographic peaks, and the identification of the compound by comparing the experimental mass spectrum to the mass spectra of known compounds in the library. The Finnigan data system possesses two mass spectral libraries, each containing approximately 25,000 compounds, which may be independently searched. The library from the National Bureau of Standards (NBS) contains no duplicates, whereas the National Institute of Health (NIH) library contains many duplicate entries from different sources. The NIH library is actually more useful in identifying unknown peaks since the mass spectrum of a compound can vary somewhat between different instruments and experimental conditions.

2. Qualitative GC/MS Methods

The GC/MS system was used for two purposes, to confirm peaks tentatively identified by GC analysis and to initially identify unknown peaks. The former purpose is straightforward, but the latter deserves more explanation. Once a peak was tentatively identified by the GC/MS data system, its plausibility from the chemistry of the reaction system was determined. If it appeared to be a likely reaction product, the quality of fit between the experimental and library spectra was examined. This is indicated by a dimensionless number ranging from 0-1000, 1000 being a perfect fit and 0 indicating none. In all cases compounds correctly identified by GC/MS have fits of 700 or greater, and in most cases are 800 or better.

If a tentative identification met both of these criteria the pure compound was obtained. It was first GC analysed to see if its peak coincided with the identified peak in the reaction mixture. Its mass spectrum was then obtained on the same Finnigan mass spectrometer and compared by the data system to the spectrum of the suspected peak. If the GC analysis was positive and the mass spectra had a fit of 800 or greater, positive identification was concluded. In only one or two cases was the identified pure compound not readily available, but in these analyses the quality of the mass spectral fit and the plausibility of the identified reaction product from the known chemistry of the reaction left little reason to doubt the identification.

D. Qualitative Analysis by Mass Spectrometry

Before the GC/MS system was available the aforementioned methods of mass spectral identification and confirmation were performed by manually collecting the GC peak of interest and submitting this sample for mass spectral analysis. The peak was collected on the Varian analytical GC by simply placing a disposable pipet over the sample column exit port as the peak of interest was eluted while simultaneously surrounding the pipet with dry ice to ensure condensation of the sample. Multiple injections of the reaction product mixture were made and the peak of interest collected until a small visible drop of sample had been obtained. The 70 eV low resolution mass spectrum was then obtained on an AEI MS-12 single-focusing mass spectrometer equipped with the usual batch and direct probe inlet systems. Data were collected and tabulated in both tabular and graphical form with a Finnigan/Incos Model 2400 Data System. Unfortunately this system does not have the capabilities of comparing an experimental spectrum with library spectra.

The confirmatory and identifying roles of mass spectrometry by this method are essentially the same as the strategy described for the GC/MS system. Peaks tentatively identified by GC were confirmed by comparing the mass spectra of the GC collected peak and the pure compound. A peak unidentifiable by GC analysis was collected and its subsequent mass spectrum compared with libraries of printed spectra (2-3, 2-4, 2-5). Such a search usually turned up a number of similar spectra but only a few such spectra corresponded to compounds which were plausible reaction products. The pure compounds were then obtained and first GC analyzed. This procedure usually eliminated at least one or more possibilities. The mass spectra were next obtained and compared to the unknown spectrum. These two procedures usually led to positive identification. Because of the great deal of time and expense involved in identifying a peak by this method, it was only performed in a few cases before the GC/MS system became available.

E. Quantitative Analysis by Gas Chromatography

The second major application of gas chromatography in this work is that of quantitative analysis, correlating a peak area to a molar amount of material. Such determinations are important to determine relative reaction product distributions and especially to calculate substrate conversion.

In this study quantitative GC was used to determine both % molar composition of the liquid reaction products and % substrate conversion. Two different sets of TC correction factors were determined for all major identified GC peaks, relative molar correction factors for determining % molar composition and relative weight correction factors for calculating % substrate conversion. Different response factors were used for these difference functions to avoid pitfalls in quantitative GC which can lead to serious error, and each method will be considered in more detail.

1. Relative Molar Correction Factors

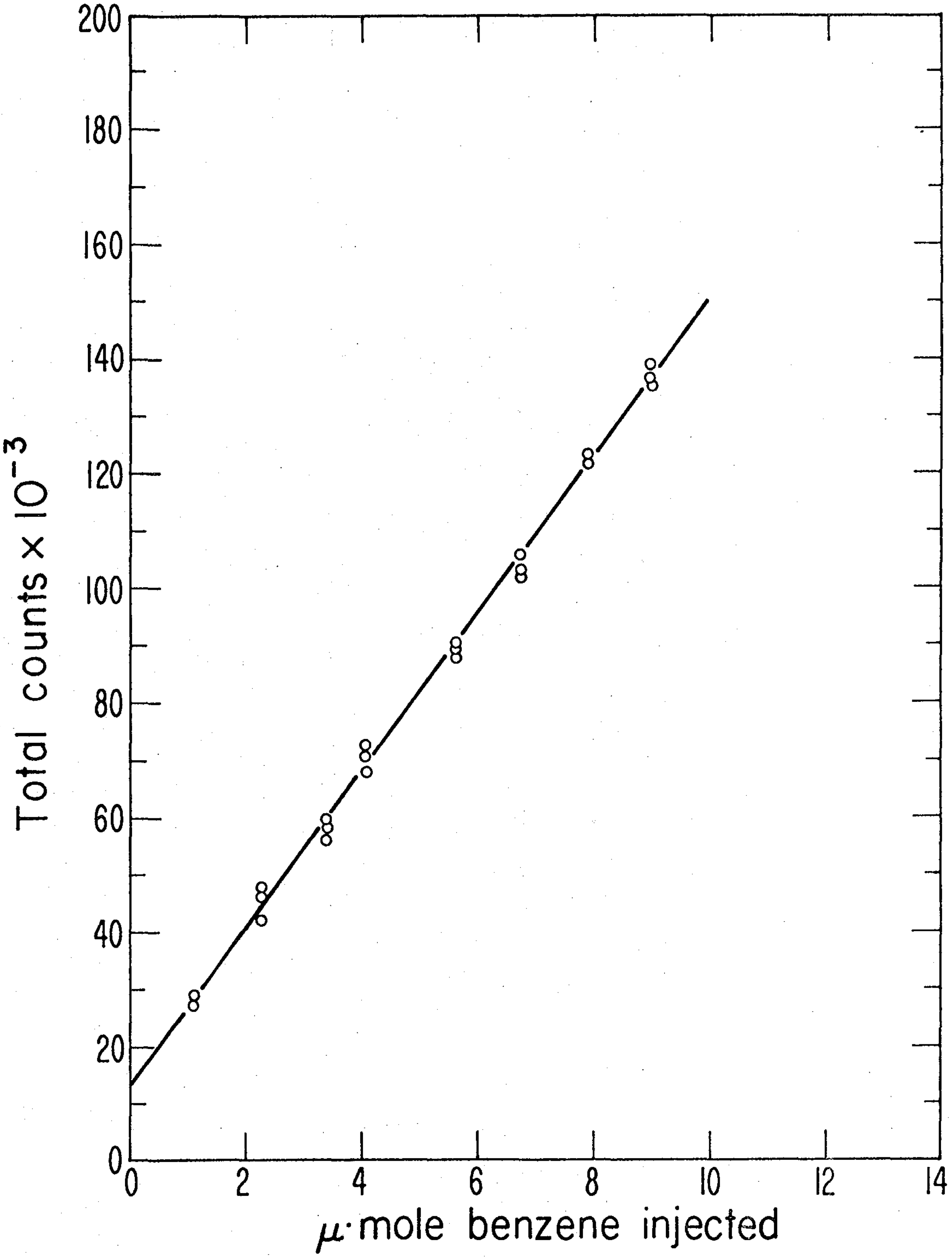
Since identical peak areas of different compounds can correspond to different molar amounts of material, correction factors must be determined which are used to adjust the peak areas such that all peaks have the same Area/Mole ratio. Percent molar composition is then easily determined for each compound by Eq. 2-1,

2-1)
$$\text{Mole \% A} = \frac{\text{Area A}}{\sum\limits_{\text{all peaks}} \text{Area}_i} \times 100$$

Since this method requires the selection of one reference Area/Mole (A/M) ratio to which all other ratios are corrected, it is common practice to set this ratio equal to one for an arbitrarily selected compound. All correction factors are then relative to the reference compound. Benzene was selected as the reference compound in this study because of its frequent use as a solvent and appearance as a reaction product.

The A/M ratio for benzene was accurately determined by making multiple injections with a 1.0 microliter (μl) syringe at several volumes ranging from 0-1.0 μl. This data was then plotted as in Fig. 2-2 as Total Integration Counts vs. μ mole of compound injected into the GC. Total integration counts, the product of integration counts read from the electronic integrator times recorder attenuation, is directly proportional to peak area. The line drawn through the data is a least squares determination. The desired A/M ratio is simply the slope of this line and is obtained by a linear regression method. The data were fitted to a straight line, $y = mx + b$. The determined coefficients are m = 13,703 Total Counts/μ·mole and b = 13,495 Total Counts. The coefficient of determination r^2 was found to be 0.9955, and indicates how closely the equation fits the experimental data. The closer r^2 is to 1, the better the fit.

The reasons for determining the Area/Mole ratio by making multiple injections at varying volumes are apparent from Fig. 2-2. First of all, the fact that the response line does not intersect the origin suggests that the volume read on the syringe body is not the true volume injected. It appears that the syringe still contains liquid



XBL 784-2471

Fig. 2-2. Molar Thermal Conductivity Response Factor for Benzene when the plunger reads zero and hence contains more liquid than is indicated. For the response factors determined in this study this syringe error typically ranges from 0-15% of total syringe volume. Second, the vertical scatter in data for multiple injections at one volume indicates that identical injections are not very reproducible. The scatter is often much worse, esecially for heavier liquids and solids that must be dissolved in a solvent. Typical precision for multiple injections has a standard deviation of 2-10% of the resultant average peak area.

This method of determining Area/Mole ratios thus circumvents the aformentioned sample injection problems. The A/M ratio determined from the slope is not dependent on vertical position of the line and hence on syringe volume errors. Making multiple injections at each volume and putting a least squares line through the data corrects for nonreproducibility of sample injections.

The Area/Mole ratio for each substrate and all major reaction products was determined by this method. Solid compounds were first dissolved in a suitable solvent. Fig. 2-3 shows the TC response factor for bibenzyl which was dissolved in benzene. The data were again fitted to a straight line, $y = mx + b$. The coefficients were determined to be $m = 29{,}036$ Total Counts/μ·mole Bibenzyl, $b = 1{,}044$ Total Counts, and $r^2 = 0.9880$. By calibrating the chart recorder it is possible to determine an absolute TC response factor for each compound in units of m·mol/mV·sec. These response factors are listed in Table 2-3 as Absolute Molar Response Factors R_i, where i is an index representing the compound in question. The GC parameters under

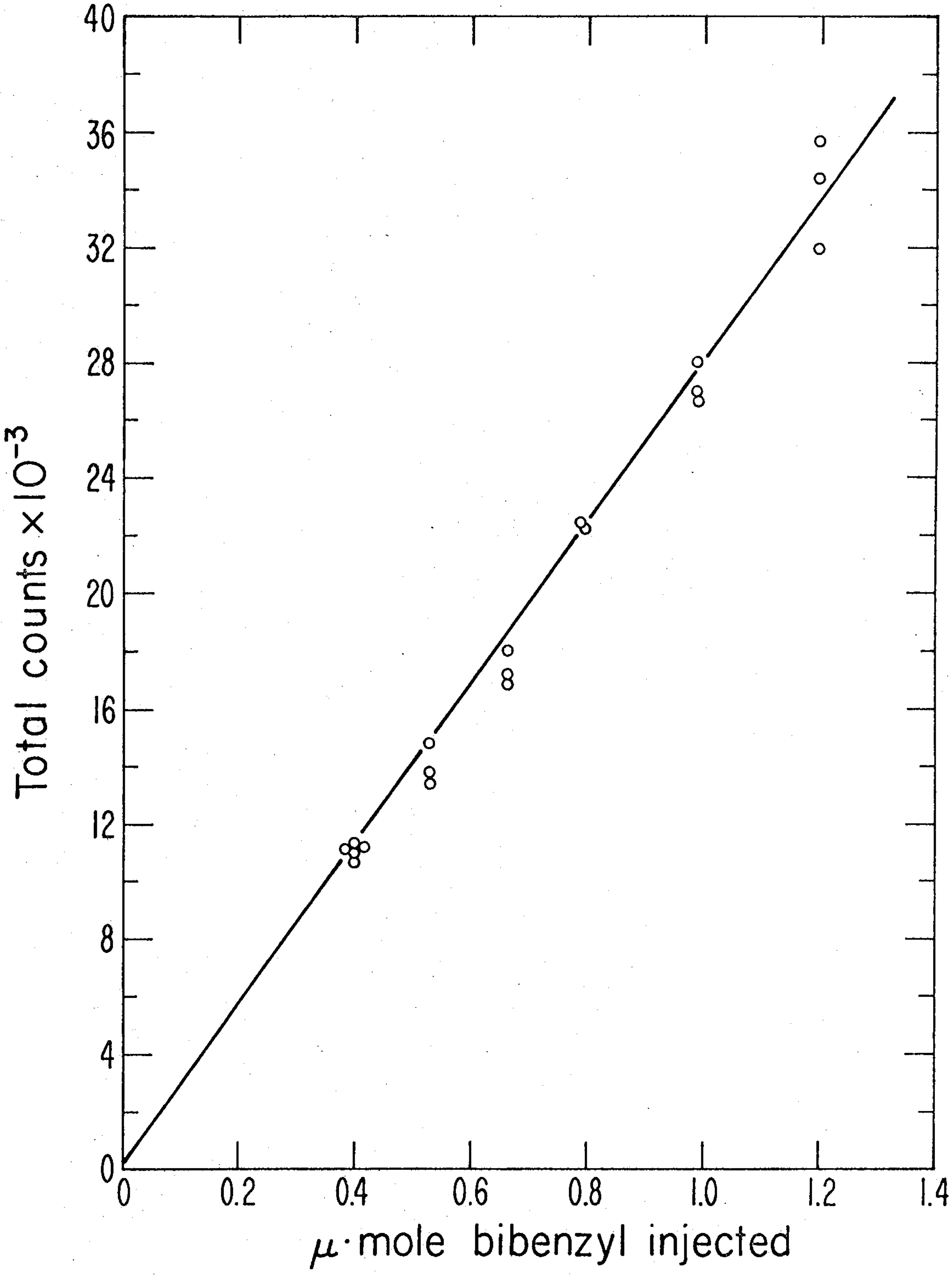


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Fig. 2-3. Molar Thermal Conductivity Response Factor for Bibenzyl

Table 2-3

Thermal Conductivity Response and Correction Factors

Compound	Absolute Molar Response Factor R_i (m·mol/mV·sec)	Relative Molar Correction Factor M_i	Relative Weight Correction Factor W_i
Benzene	14.30	1.000	1.000
1-Benzylnaphthalene	4.015	3.533	1.293
Bibenzyl	6.750	2.119	1.383
n-Butylbenzene	9.011	1.587	1.070
t-Butylbenzene	---	---	1.175
o-Cresol	---	---	1.148
Cyclohexane	13.26	1.079	1.011
Cyclohexylbenzene	7.216	1.982	1.265
Cyclopentane	14.80	0.967	0.964
Dicyclohexyl	7.359	1.944	1.288
2,3-Dimethylbutane	12.74	1.123	0.964
Biphenyl	9.608	1.489	1.231
1,4-Diphenylbutane	6.477	2.208	1.326
Diphenylmethane	6.920	2.067	1.251
1,3-Diphenylpropane	6.251	2.288	1.431
Ethylbenzene	9.709	1.473	1.051
2-Hydroxydiphenylmethane	8.294	1.725	1.403
4-Hydroxydiphenylmethane	12.73	1.124	2.583
Indan	11.25	1.271	1.225
Isopentane	17.46	0.819	0.913
Isopropanol	18.40	0.777	0.941
Methylcyclopentane	12.69	1.127	0.977
Naphthalene	10.18	1.405	1.127
Phenol	14.03	1.020	1.142
1-Phenylnaphthalene	6.349	2.253	1.339
1-Phenylphenol	8.784	1.628	1.371
i-Propylbenzene	10.41	1.374	1.064
n-Propylbenzene	9.377	1.525	1.058
Tetralin	10.62	1.347	1.245
Toluene	13.31	1.075	1.019

GC Conditions

Carrier Gas - High Purity Helium (99.998+%)
Flow Rate - 30 ml/min.
He Tank Pressure - 80 psig
Filament Current - 150 mA
Detector Temp. - 280°C
Injector Temp. - 240°C

Recorder Conditions

Scale - 1 mV
Integration - 12,000 counts/min.
Chart Speed - 1 in./min.

which these factors are valid are also listed in Table 2-3. The relative Molar Correction Factor M_i is obtained by dividing the response factor of each compound by the benzene response factor. These values are also tabulated in Table 2-3.

The correction factor M_i is used to correct all peak areas so that the same Area/Mole ratio is obtained for each peak. This is done by dividing a peak area by its appropriate correction factor M_i. These corrected peaks areas are then normalized by Eq. 2-1 to yield mole % of each compound in the liquid reaction products. All molar concentration data presented hereafter were determined by this method.

The important feature of determining product composition by this method is that it does not necessitate knowing the absolute amount of liquid injected into the GC since only relative peak areas are needed to calculate product composition. For very minor reaction products or identified compounds that are not readily available, a correction factor for an isomer or similar compound was used. For unidentified peaks a correction factor of a neighboring known peak was used. In all cases the concentration of such compounds was very small (<0.1 mole %) so that any error induced by usage of an approximate or assumed correction factor is negligible.

2. Relative Weight Correction Factors

This type of correction factor was determined to permit calculation of the absolute amount of substrate and all reaction products recovered and thereby ascertain the amount of substrate coverted to other products, and to permit mass balance calculations. Percent substrate conversion is calculated by Eq. 2-2,

2-2) $$\%\ \text{Substrate Conversion} = \frac{\text{Wt. Substrate Charged} - \text{Wt. Substrate Recovered}}{\text{Wt. Substrate Charged}} \times 100.$$

Thus substrate conversion figures are only an indication of the disappearance of substrate, and give no information regarding the fate of the converted substrate, i.e., whether it appears as liquid products, tar, or gases. This question is addressed, however, by using the GC-determined weights of all reaction products to make a mass balance. The method, assumptions, and results of these mass balances will be discussed in the next chapter.

To determine a relative weight TC factor W_i, a standard solution of compound i and a reference compound is prepared. Benzene was again chosen for the reference compound for the same reasons listed above. The solution is GC analyzed and the relative weight correction factor W_i calculated from Eq. 2-3,

2-3) $$W_i = \frac{X_i/A_i}{X_B/A_B} = \frac{X_i}{X_B} \cdot \frac{A_B}{A_i} .$$

X_i = weight fraction of component i in standard solution
X_B = weight fraction of benzene in standard solution
A_i = GC peak area of component i

For each compound this procedure was repeated three times to permit determination of an average W_i and the resultant precision of these correction factors. As before the precision of W_i is better for lighter compounds than heavier compounds, but an average precision for all

W_i's is $\pm 3\%$ (one standard deviation). The average W_i's are listed in Table 2-3.

As seen from Eq. 2-3 a compound with a W_i greater than 1.0 produces a smaller GC peak than does benzene for an equivalent weight of material. This is consistent with the experimental values listed in Table 2-3, since all compounds with W's greater than 1.0 have higher molecular weights than benzene, and hence an equiweight injection will contain fewer moles of any given compound.

Once these correction factors are known, the weight composition of any reaction product mixture may be determined. Eq. 2-3 is first solved for the ratio of weight fractions as in Eq. 2-4,

2-4) $$\frac{X_i}{X_B} = W_i \cdot \frac{A_i}{A_B} \; .$$

Thus this ratio may be obtained for each peak in the chromatogram by simply calculating the ratio of peak areas A_i/A_B. The weight fraction of each compound is obtained by using the boundary condition that weight fractions add to 1.0,

2-5) $$\sum_i X_i = 1.0 \quad .$$

Pulling the weight fraction of benzene X_B out of the summation sign and dividing by X_B yields Eq. 2-6,

2-6)
$$1 + \sum_{i \neq B} \frac{X_i}{X_B} = \frac{1}{X_B} \quad .$$

Since $\sum_{i \neq B} \frac{X_i}{X_B}$ is known by adding all the ratios obtained from Eq. 2-4, X_B for the reaction mixture is obtained from Eq. 2-6. The weight fraction of each compound is then easily calculated from the known ratio X_i/X_B. Now since the weight of the liquid reaction products is known, these weight fractions permit determination of the absolute amount of each compound recovered from the reaction. Mass balance information and % substrate conversion figures are derived from these weights.

This technique of using relative weight correction factors to calculate substrate conversion and mass balance information was chosen so that all this data could be obtained from only ratios of GC peaks and the total weight of liquid products. If an absolute molar response factor R_i were used to determine the weight of substrate recovered, then the absolute volume of liquid injected into the GC must be known accurately. Hence the use of weight correction factors avoids the errors inherent in syringe sampling. As before, a response factor of an isomer or similar compound was used for very minor reaction products (<0.1 mole %) or minor identified products whose pure compounds are not readily available. For minor unidentified products, the response factor of a known neighboring compound was used.

3. Accuracy of Correction Factors

In the preceding sections a range was given for the precision of the experimentally-determined TC correction factors, thus indicating how this type of error influences the accuracy of quantitative GC data. But many other factors influence the accuracy of this data, all of which must be considered for one to determine the absolute accuracy of quantitative GC data, i.e., how close these data are to the theoretically correct values. Sampling technique, consistency of detector, recorder, and electronic integrator performance, and accuracy of TC correction factors all influence quantitative GC determinations. It is impossible to separate the effects of these factors and determine, for example, the absolute accuracy of the TC correction factors, but it is imperative to know their combined effects on the accuracy of the data.

Several standard solutions were carefully prepared with benzene solvent and representative reaction products and substrates from Table 2-3 so that weight % and mole % figures were accurately known. Each solution was GC analyzed three times and the resultant mole % and weight % calculations performed using the appropriate correction factors from Table 2-3. These figures were compared with the true concentration values of the standard solutions. Accuracy of larger peaks is much better than accuracy of smaller peaks, and experimental data for lighter compounds are better than for heavier compounds. There is in general a good deal of scatter in the data so that the only approximate statements of accuracy may be made. For molar concentration data, accuracy for peaks greater than 5 mole % ranges from ±(0-5) %. For smaller peaks the accuracy ranges from ±(2-10) %. For weight concentration data accuracy is generally always within ±(0-5) % for all peak sizes, except for heavy compounds such as the substrates where accuracy ranges from ±(0-10) %. As an approximate generalization all molar concentration and substrate conversion data are accurate to ±5%.

III. RESULTS AND DISCUSSION

I. Preliminary Experiments

A. Effect of Temperature on Reaction of Benzene

All substrates were initially dissolved in a solvent prior to reaction with a catalyst at elevated temperatures. The use of a solvent ensured intimate contact between substrate and catalyst, and also facilitated product analysis by keeping liquid and solid substrates and reaction products in one phase. For the present studies benzene was used as the primary solvent since it was found to dissolve all of the reactants and products. For reasons to be presented later, cyclohexane was also used as a solvent in some reactions, but exhibited a lesser ability to dissolve all substrates.

To determine whether benzene reacts with $AlCl_3$ sufficiently to mask the products derived from the substrate itself, a series of runs was performed with benzene and $AlCl_3$ alone, at temperatures ranging from 200-350°C and at a catalyst loading equivalent to that used for a run with substrate. As with all runs in this study, the reaction was conducted for 90 minutes at reaction temperature under 1000 psig H_2.

The results of these experiments are presented in Table 3-1. The convention used to present the results in this Table is identical to that in all other tables and hence will be outlined here. Reaction products are listed in order of their relative elution from the gas chromatograph. Light, non-polar aliphatics thus appear first, while heavy, polar aromatic compounds appear last. Each compound is listed with its molar concentration in the liquid reaction products. Concentrations less than 0.01 mole % are listed as "Trace" since the corres-

Table 3-1

Effect of Temperature on Reaction of Benzene

Reaction Conditions

P = 1000 psig H_2 @ reaction temp.
t = 90 min. @ reaction temp.
ω = 1250 RPM

Reactants

Benzene - 61.5 gm. (0.787 mole)
$AlCl_3$ - 0.70 gm. (0.0053 mole)

Run No.	[a] B-1	[a] B-2	B-3	B-4
Temp. (°C)	200	250	300	350
Product	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**
Cyclopentane	Trace	Trace	Trace	Trace
Methylcyclopentane	Trace	Trace	Trace	Trace
Cyclohexane	Trace	Trace	Trace	Trace
Benzene	99.61	99.31	99.79	99.44
Toluene	0.12	0.20	0.06	0.18
Ethylbenzene	0.25	0.45	0.15	0.31
Isopropylbenzene	Trace	Trace	Trace	0.01
n-Propylbenzene	Trace	0.02	Trace	0.02
Unknown	---	---	Trace	Trace
Unknown	---	---	Trace	Trace
Cyclohexylbenzene	Trace	Trace	Trace	Trace
Biphenyl	Trace	Trace	---	Trace
Diphenylmethane	0.02	0.02	0.01	0.04
Bibenzyl	Trace	Trace	---	Trace

---

[a] Benzene *not* distilled in Na-Benzophenone

ponding GC peak was not large enough to actuate the electronic integrator. Chromatographic peaks which could not be unambiguously identified are listed as "unknown," but in all cases they represent only very minor reaction products. "Heavy Unknown(s)" are defined as unidentfied peaks with GC retention times greater than that of the substrate used in the reaction.

The results of Table 3-1 show that in the presence of $AlCl_3$ benzene does not react extensively over a wide temperature range (200-350°C). In all cases the extent of benzene conversion is less than 1 mole %. It is interesting to note, however, that the benzene which does react produces a wide variety of products, the principle ones being toluene and ethylbenzene.

The effects of temperature and drying of the benzene are also presented in Table 3-1. The concentrations of toluene and ethylbenzene are seen to approximately double as temperture increases from 200°C to 250°C and from 300°C to 350°C, yet fall by a factor of three between the runs at 200°C and 250°C. The decrease in the concentration of reaction products is explained by noting that the benzene in Runs B-3 and B-4 (300°C, 350°C) was distilled in Na-benzophenone. One can thereby conclude that water acts as a promoter for $AlCl_3$. This observation not only suggests the addition of more water to serve as a promoter for $AlCl_3$, but also points out the necessity of drying the solvent so that observed catalytic effects are due to the Lewis acid alone.

B. Effect of Catalyst Loading on Substrate Conversion

An important consideration in reactions involving substrates was to first select an appropriate reaction tempertaure. The results shown in Table 3-1 with benzene and $AlCl_3$ alone showed that solvent reactions would be insignificant at that catalyst loading anywhere in the temperature range of interest (200-350°C). Since it was desired to study the catalytic reactions without the influence of pyrolytic reactions, tempertures below 350°C were used most frequently, 225°C and 325°C being the major temperatures chosen.

The first objective in runs with substrate was to study the effects of catalyst concentration on substrate conversion and to determine an optimum catalyst loading. This condition is important since the major objective is to maximize substrate conversion to liquid products. Excessive $AlCl_3$ catalyst effects unwanted gasification and tar formation reactions, and too little catalyst may be ineffective due to complexation with benzene or the substrate itself. Results of $AlCl_3$ catalyst loading experiments with biphenyl, diphenylmethane, and bibenzyl are shown in Tables 3-2, 3-3, and 3-4, respectively. Several items on these tables deserve explanation before discussing the results.

Each run with substrate is listed with its corresponding amount of $AlCl_3$ reacted alone. This gives an indication of the extent of benzene reaction caused by the higher catalyst loadings. All such blank runs are numbered with the prefix "B". Next, substrate conversion is calculated on the basis of disappearance of substrate charged to the autoclave, ascertained from the unreacted substrate recovered

Table 3-2

Effect of $AlCl_3$ Loading on Diphenyl Conversion

Reaction Conditions

T = 225°C
P = 1000 psig H_2 @ 225°C.
t = 90 min. @ 225°C.
ω = 1250 RPM

Reactants

Biphenyl - 11.84 gm. (0.0768 mole)
Benzene - 61.5 gm. (0.787 mole)

Run No.	5	B-7	7	B-8	8	B-9
$AlCl_3$ (gm.)	0.70	0.70	1.40	1.40	2.87	2.84
Biphenyl/$AlCl_3$ Mole Ratio	14.7	0.0	7.1	0.0	3.6	0.0
Product	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**
Cyclopentane	---	---	Trace	---	Trace	---
Methylcyclopentane	---	Trace	0.06	Trace	0.23	Trace
Cyclohexane	Trace	---	0.01	---	0.06	Trace
Methylcyclohexane	---	---	Trace	---	0.05	---
Benzene	89.04	99.68	87.88	98.34	85.46	96.54
Toluene	---	0.12	0.53	0.62	1.59	1.34
Ethylbenzene	---	0.15	0.88	0.83	2.06	1.67
Isopropylbenzene	Trace	---	0.04	0.05	0.35	0.08
n-Propylbenzene	---	---	0.06	0.08	0.31	0.14
t-Butylbenzene	0.08	---	---	---	Trace	---
n-Butylbenzene	---	---	Trace	---	0.07	---
Unknowns	---	---	0.03	---	0.26	---
Dicyclohexylmethane	---	---	Trace	---	0.05	Trace
Unknown	---	---	Trace	---	Trace	---
Cyclohexylbenzene	---	---	Trace	---	0.05	Trace
Biphenyl	10.88	---	9.94	0.02	8.29	0.08
Diphenylmethane	---	0.04	---	0.02	Trace	0.05
Unknowns	---	---	0.23	0.01	0.35	Trace
Bibenzyl	---	0.01	0.04	0.04	0.17	0.10
Heavy Unknowns	Trace	---	0.30	Trace	0.68	Trace
Biphenyl Conversion (%)	0	---	8	---	29	---
Reactants Recovered as Liquid Products (%)	96	---	90	---	83	---

Table 3-3

Effect of $AlCl_3$ Loading on Diphenylmethane Conversion

Reaction Conditions

T = 225°C.
P = 1000 psig H_2 @ 225°C.
t = 90 min. @ 225°C.
ω = 1250 RPM

Reactants

Diphenylmethane - 12.92 gm (0.0768 mole)
Benzene - 61.5 gm. (0.787 mole)

Run No.	4	B-7	6	B-8
$AlCl_3$ (gm.)	0.70	0.70	1.40	1.40
Diphenylmethane/$AlCl_3$ Mole Ratio	14.7	0.0	7.1	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Methylcyclopentane	---	Trace	Trace	Trace
Cyclohexane	Trace	---	Trace	---
Benzene	94.51	99.68	93.35	98.34
Toluene	1.09	0.12	1.97	0.62
Ethylbenzene	0.06	0.15	0.17	0.83
Isopropylbenzene	0.07	---	0.39	0.05
n-Propylbenzene	---	---	Trace	0.08
n-Butylbenzene	0.02	---	Trace	---
Unknown	---	---	0.14	---
Dicyclohexyl	0.04	---	Trace	---
Unknown	0.06	---	Trace	---
Dicyclohexylmethane	---	---	0.01	---
Unknown	---	---	Trace	---
Cyclohexylbenzene	0.02	---	0.03	---
Phenylcyclohexylmethane	---	---	Trace	---
Unknown	---	---	Trace	---
Biphenyl	---	---	Trace	0.02
Diphenylmethane	4.03	0.04	3.83	0.02
Bibenzyl	0.10	0.01	0.11	0.04
Diphenylmethane Conversion (%)	47	---	53	---
Reactants Recovered as Liquid Products (%)	93	---	88	---

Table 3-4

Effect of $AlCl_3$ Loading on Bibenzyl Conversion

Reaction Conditions

T = 225°C.
P = 1000 psig H_2 @ 225°C.
t = 90 min. @ 225°C.
ω = 1250 RPM

Reactants

Bibenzyl - 14.00 gm. (0.0768 mole)
Benzene - 61.5 gm. (0.787 mole)

Run No.	1	B-7	2	B-5	3	B-6
$AlCl_3$ (gm.)	0.70	0.70	1.67	1.67	3.86	3.86
Bibenzyl/$AlCl_3$ Mole Ratio	14.7	0.0	6.3	0.0	2.6	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Methylcyclopentane	0.02	Trace	0.06	---	0.07	Trace
Cyclohexane	---	---	Trace	---	Trace	---
Methylcyclohexane	Trace	---	Trace	---	Trace	---
Benzene	90.75	99.68	91.15	97.87	90.29	93.19
Toluene	0.92	0.12	1.19	0.91	1.62	2.88
Ethylbenzene	1.75	0.15	2.03	1.13	2.29	2.89
Isopropylbenzene	0.18	---	0.07	0.02	0.18	0.22
n-Propylbenzene	0.07	---	0.07	0.06	0.10	0.35
n-Butylbenzene	0.03	---	0.03	---	0.02	Trace
Unknown	0.09	---	0.07	---	0.02	---
Unknown	0.19	---	0.25	---	0.21	---
Dicyclohexylmethane	Trace	---	Trace	---	Trace	---
Cyclohexylbenzene	0.02	---	Trace	Trace	Trace	Trace
Biphenyl	0.06	---	0.20	Trace	0.16	0.19
Diphenylmethane	0.11	0.04	0.13	0.01	0.07	0.13
Bibenzyl	5.46	0.01	4.20	Trace	4.56	0.14
Heavy Unknowns	0.38	---	0.57	---	0.41	0.02
Bibenzyl Conversion (%)	27	---	44	---	48	---
Reactants Recovered as Liquid Products (%)	91	---	94	---	81	---

as determined by quantitative gas chromatography. Thus this data gives no information concerning the fate of the reacted substrate. Finally, the data listed as "% Reactants Recovered as Liquid Products" was determined from the known weights of organic reactants (substrate plus solvent) charged to the autoclave and the weight after filtering of liquid products recovered from the reaction. This data is thus calculated on a catalyst-free basis. The failure to achieve 100% liquid product recovery can be attributed to solvent evaporation during filtering and tar formation during reaction. Since losses due to solvent evaporation were approximately constant in all runs, variations in "% Reactants Recovered" figures give an indication of the relative amounts of tar formation between various reactions.

The results for biphenyl shown in Table 3-2 include three runs where the weight of $AlCl_3$ has been doubled from the preceding reaction. The lowest catalyst loading of 0.70 gm $AlCl_3$/70ml benzene in Run 5 is the same as that for the reactions of benzene and $AlCl_3$ alone shown in Table 3-1. A lower catalyst loading was not used due to the very small amount of catalyst involved, making accurate weighing difficult and increasing the probability of losing a substantial fraction of the catalyst to hydrolysis by trace amounts of water.

Several important trends become apparent from Table 3-2. First of all, substrate conversion is seen to increase steadily as catalyst loading increases. Also very noticeable is the great increase in the number of minor reactions produced with increasing catalyst loading. Unfortunately, however, these changes are accompanied by a dramatic increase in tar production.

The results of catalyst loading effects on the cleavage of diphenylmethane are shown in Table 3-3, where again the catalyst loading has been doubled between runs. The increase in catalyst loading is seen to have only a very minor effect on substrate conversion, which is accompanied by a similar small decrease in diphenylmethane concentration. Again the higher catalyst loading yields a wide variety of minor reaction products. The major reaction product is toluene, and its concentration approximately doubles as catalyst loading doubles. A good portion of this increase, however, may be due to the increased reactivity of benzene at the higher loading. In contrast to biphenyl, the lower catalyst loading with diphenylmethane produces a significant amount of tar, indicating that diphenylmethane is more reactive than biphenyl and also plays an important role in tar production. As before, the higher catalyst loading yields more extensive tar formation.

Table 3-4 shows similar results of catalyst loading effects on bibenzyl conversion. The increased catalyst loading in Run 2 significantly increases substrate conversion, yet a further increase in Run 3 does not. As before, increased catalyst loading produces an almost linear increase in tar production. (The low value of "Reactants Recovered" in Run #1 is due to experimental difficulties in filtration.) The major reaction product is ethylbenzene closely followed by toluene. This data indicates that cleavage of bibenzyl is predominately asymmetric, with cleavage occurring at a phenyl ring. Such information is useful in proposing plausible mechanisms. It is of special interest to note that the concentrations of toluene and ethylbenzene are <u>higher</u> in Blank Run B-6 than in Run 3 with substrate. This suggests that the presence of bibenzyl suppresses the production of ethylbenzene and toluene from benzene at this higher catalyst loading.

The results of these experiments with various catalyst loadings have suggested a substrate/catalyst mole ratio of ~14.7 for further experiments. Use of significantly larger catalyst loadings has little effect on substrate conversion, while masking the main reactions through production of numerous minor products and large amounts of tar.

II. Reactions of Aliphatic Bridges between Phenyl Rings

A. Effect of Chain Length

The first objective after having determined optimum operating conditions was to study the effect of chain length on aliphatic bridge cleavage. In conjunction with this goal it was also desired to study the effects of temperature and solvent medium on these reactions. Tables 3-5, 3-6, 3-9, and 3-12 show the results of reaction of alkyl-bridged phenyl rings with bridge length varying form 0-4 carbons, with the indicated combination of temperatures and solvents.

Table 3-5 shows the results of previous Runs 1, 4, and 5, whereas Run 9 with 1,3-diphenylpropane is new. The interesting feature of this latter run is that indan is the major reaction product. This fact is an important clue in elucidating a plausible reaction mechanism, and will be discussed when appropriate mechanisms are presented after Table 3-7. The most important trend to be gained from this table, however, is the zig-zag pattern of substrate conversion. Substrates with an even number (0,2) of carbon atoms in the aliphatic bridge exhibit significantly lower conversion in benzene solvent than do

Table 3-5

[a] Cleavage of Aliphatic Bridges between Phenyl Rings

Reaction Conditions

T = 225°C
P = 1000 psig H_2 @ 225°C.
t = 90 min. @ 225°C.
ω = 1250 RPM

Reactants

substrate - 0.0768 mole
Benzene - 61.5 gm. (0.787 mole)
$AlCl_3$ - 0.70 gm. (0.0052 mole)

Run No.	5	4	1	9	B-7
Substrate	Biphenyl	Diphenylmethane	Bibenzyl	1,3-Diphenylpropane	No Substrate
Substrate/$AlCl_3$ Mole Ratio	14.7	14.7	14.7	14.7	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Benzene	89.04	94.51	90.75	91.89	99.68
Toluene	---	1.09	0.92	0.16	0.12
Ethylbenzene	---	0.06	1.75	0.36	0.15
Isopropylbenzene	Trace	0.07	0.18	0.08	---
n-Propylbenzene	---	---	0.07	0.07	---
t-Butylbenzene	0.08	0.02	---	---	---
n-Butylbenzene	---	---	0.01	---	---
Indan	---	---	---	4.79	---
Cyclohexylbenzene	---	0.02	0.02	Trace	---
Biphenyl	10.88	---	0.06	---	---
Diphenylmethane	---	4.03	0.11	0.03	0.04
Bibenzyl	---	0.10	5.46	0.12	0.01
1,3-Diphenylpropane	---	---	---	2.25	---
Heavy Unknowns	Trace	Trace	0.38	0.12	---
Substrate Conversion (%)	0	47	27	67	---
Reactants Recovered as Liquid Products (%)	96	93	97	96	---

[a] 1. Several minor peaks have been dropped for ease of comparison. Mole % figures may therefore not add to 100%.

Table 3-6

Cleavage of Aliphatic Bridges between Phenyl Rings

Reaction Conditions

T = 325°C
P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

Substrate - 0.0768 mole (Runs 34, 31, 27, 35)
- 0.00951 mole (Run 42)
Benzene - 61.5 gm. (0.787 mole)
$AlCl_3$ - 0.70 gm. (Runs 34, 31, 27, 35, B-20)
- 0.09 gm. (Run 42)

Run No.	34	31	27	35	42	B-20
Substrate	Biphenyl	Diphenylmethane	Bibenzyl	1,3-Diphenylpropane	1,4-Diphenylbutane	No Substrate
Substrate/$AlCl_3$ Mole Ratio	13.7	13.7	14.5	14.7	14.7	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole%)
Methylcyclopentane	---	Trace	0.08	Trace	---	Trace
Cyclohexane	Trace	Trace	0.27	---	0.04	Trace
Benzene	90.25	95.84	92.56	91.99	98.90	99.41
Toluene	---	2.14	0.86	0.31	---	0.19
Ethylbenzene	0.05	0.12	2.72	0.55	---	0.23
Isopropylbenzene	0.13	0.03	0.10	0.26	---	0.08
n-Propylbenzene	0.05	Trace	0.07	0.20	---	0.10
n-Butylbenzene	0.04	Trace	0.01	---	---	---
Indan	---	---	---	4.62	---	---
Tetralin	---	---	---	---	0.10	---
Dicyclohexyl	---	Trace	0.05	0.06	---	---
Cyclohexylbenzene	---	Trace	0.01	---	---	---
Biphenyl	9.48	---	Trace	---	---	Trace
Diphenylmethane	---	1.85	0.08	0.08	---	---
Bibenzyl	---	---	3.02	0.07	---	Trace
1,3-Diphenylpropane	---	---	---	1.81	---	---
1,4-Diphenylbutane	---	---	---	---	0.97	---
Heavy Unknowns	---	0.02	0.17	0.06	---	---
Substrate Conversion (%)	4	74	58	73	17	---
Reactants Recovered as Liquid Products (%)	96	93	94	94	94	---

those substrates with an odd number (1,3) of carbon atoms in the alkyl bridge.

Table 3-6 shows results of reaction of the same series of substrates, except in this table results for 1,4-diphenylbutane have been added. The important difference here is that the temperature has been increased to 325°C. This temperature was carefully chosen to be below the region where pyrolysis of coal begins, generally 350°C and greater. Several runs were made with substrate and solvent at 325°C in the absence of catalyst. All substrates were found to be stable at 325°C and no thermal decomposition products were observed.

When compared to runs at 225°C (Table 3-5), the reactions in Table 3-6 show that the reaction products and relative product distributions are essentially the same at 325°C. The major difference is that substrate conversion is substantially higher at 325°C for all substrates, increasing by as much as a factor of two in one case. The zig-zag pattern of substrate conversion is still evident at 325°C, with substrates containing an even number (0,2,4) of carbon atoms in the aliphatic bridge exhibiting significantly lower conversion than those containing an odd number (1,3) of carbons in the alkyl linkage. The extremely low conversion (17%) for 1,4-diphenylbutane in Run 42, however, could be misleading. A much smaller amount of substrate was used because of its high cost, and in order to maintain a catalyst/substrate ratio identical to that for other substrates, the catalyst concentration was also reduced. This small amount of catalyst (0.18 gm.) may have been mostly complexed with benzene, limiting its interaction with the substrate. Benzene is known (3-4) to form both chemical and physical complexes with $AlCl_3$. (This explanation was shown to be correct when 1,4-diphenylbutane was run in cyclohexane solvent, a reaction to be presented later). Even though substrate conversion was low in this run, it is interesting to note that the major product tetralin is not a simple cleavage product. Such information will prove valuable in elucidating mechanisms for these reactions.

A clearer picture of substrate reaction products may be gained by considering a mass balance of the substrate charged to each reaction. This type of calculation subtracts out the solvent and solvent reaction products, allowing one to see clearly the fate of reacted substrate. The absolute weight of each reaction product recovered was determined using the weight GC correction factors as outlined in Chapter I. Unless otherwise noted, the following assumptions were made in making all mass balances in this study: 1) All material lost during the course of reaction is solvent; 2) All material lost from evaporation during filtering is solvent; 3) All tar production is derived from substrate; and 4) All major and minor reaction products are derived from the substrate, except in those cases where they obviously come from the solvent (e.g., methylcyclopentane was shown in blank runs to be an isomerization product of cyclohexane solvent). These assumptions are certainly only approximations and not strictly valid, yet their application leads to substrate mass balances which are within ±5% in almost all cases. They are furthermore based on experimental observations. Tar production, for example was always substantially greater in runs with substrate.

As an example of this type of calculation, the mass balance of 1,3-diphenylpropane in Run 35 is presented in Table 3-7. A balance is first performed on the benzene solvent, from which it becomes evident that significant amounts of benzene are being produced from substrate cleavage. In the 1,3-diphenylpropane balance, the weights of recovered compounds are those determined by quantitative gas chromatography. Each "% Yield (wt.)" figure is that weight percentage of the charged substrate which is converted to the listed compound. For the substrate itself, however, this figure indicates the percentage of original substrate which is recovered unreacted. The sum of these figures then yields the percentage of beginning substrate which is accounted for by the listed compounds. This sum has been rounded to the nearest 1% in all cases.

Table 3-7

1,3-Diphenylpropane Mass Balance for Run 35

1. Benzene Mass Balance

Wt. (gm).	Compound
63.93	Benzene recovered
+ 2.30	Benzene lost during reaction and filtering
-62.42	Benzene charged to reaction
3.81	Benzene produced during reaction

2. 1,3-Diphenylpropane Mass Balance

Compound	Wt. (gm.)	% Yield (wt.)
Indan	4.82	3.20
1,3-Diphenylpropane	4.12	27.3
Benzene	3.81	25.3
Minor Products	1.83	12.1
Tar	0.50	3.3
		100%

Even though a 100% balance is rather fortuitous, this mass balance indicates that the above assumptions are essentially correct and that the quantitative GC data are sufficiently accurate to permit reasonable mass balances on the substrate.

Table 3-8 presents mass balances for Runs 31, 27, and 42, the other runs in Table 3-6 where significant substrate conversion occurred. In these and subsequent tables the solvent mass balance is eliminated for sake of brevity, but unless other wise noted, the assumptions in making these balances remain the same as before.

Table 3-8

Substrate Mass Balances for Runs 31, 27, 42

1. Diphenylmethane Balance for Run 31

Compound	Wt. (gm.)	% Yield (wt.)
Benzene	4.95	40.7
Diphenylmethane	3.21	26.4
Tar	2.00	16.5
Toluene	1.57	12.9
Minor Products	0.19	1.6
		98%

2. Bibenzyl Balance for Run 27

Compound	Wt. (gm.)	% Yield (wt.)
Bibenzyl	5.88	42.0
Ethylbenzene	2.80	20.0
Benzene	2.25	16.1
Tar	1.78	12.7
Minor Products	0.72	5.1
Toluene	0.63	4.5
		100%

3. 1,4-Diphenylbutane Balance for Run 42

Compound	Wt. (gm.)	% Yield (wt.)
1,4-Diphenylbutane	1.67	83.5
Benzene	0.23	11.5
Tetralin	0.09	4.5
		100%

Table 3-9 shows results at the lower temperature (225°C) for the first experiments performed in cyclohexane solvent, where the reactions of bibenzyl in benzene and cyclohexane are compared. The change in solvents is seen to yield dramatic changes when compared to Run 1, a previous run in benzene. Substrate conversion is almost a factor of three higher in cyclohexane, with a corresponding drop in bibenzyl concentration. Most dramatic, however, is the observation tht benzene is by far the major reaction product. Ethylbenzene concentration is half of that in the benzene run. If bibenzyl were to cleave to yield ethylbenzene and benzene, then the benzene/ethylbenzene mole ratio would be 1.0. Yet in Run 23 this ratio is 9.0, indicating that either benzene is reacting to form other products such as tar, or that ethylbenzene is being dealkylated to form benzene. This questioned is partially answered by considering the results of Run 58 presented in Table 3-10, where ethylbenzene was run as a substrate in cyclohexane with $AlCl_3$ catalyst. These results prove that ethylbenzene is indeed partially dealkylated to benzene or converted to other products under these conditions.

This question is further answered by considering a mass balance of bibenzyl in Run 23, shown in Table 3-11.

Table 3-9

Effects of Solvent on Cleavage of Bibenzyl

Reaction Conditions

$T = 225^{\circ}C.$
$P = 1000$ psig H_2 @ $225^{\circ}C.$
$t = 90$ min. @ $225^{\circ}C.$
$\omega = 1250$ RPM

Reactants

Bibenzyl - 14.0 gm. (0.0768 mole)
Benzene - 61.5 gm. (Runs 1, B-7)
Cyclohexane - 54.5 gm. (Runs 23, B-16)
$AlCl_3$ - 0.70 gm. (0.0052 mole)

Run No.	1	B-7	23	B-16
Solvent	Benzene	Benzene	Cyclohexane	Cyclohexane
Bibenzyl/$AlCl_3$ Mole Ratio	14.7	0.0	14.7	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	---	---	---	2.42
Methylcyclopentane	0.02	Trace	8.11	52.26
Cyclohexane	---	---	81.33	41.89
Methylcyclohexane	Trace	---	---	0.77
Benzene	90.75	99.68	6.90	0.26
Ethylcyclohexane	---	---	---	0.13
Toluene	0.92	0.12	0.30	---
Ethylbenzene	1.75	0.15	0.77	---
Isopropylbenzene	0.18	---	---	---
n-Propylbenzene	0.07	---	---	---
n-Butylbenzene	0.03	---	---	0.70
Dicyclohexyl	0.19	---	0.03	0.67
Cyclohexylbenzene	0.02	---	0.03	---
Biphenyl	0.06	---	---	---
Diphenylmethane	0.11	0.04	---	---
Bibenzyl	5.46	0.01	2.37	---
Heavy Unknowns	0.38	---	0.15	---

Substrate Conversion (%)	27	---	72	---
Reactants Recovered as Liquid Products (%)	97	---	94	---

Table 3-10

Reaction of Primary Products Obtained from the Cleavage of Model Compounds

Reaction Conditions	Reactants
T = 325^{o}C.	substrate - 0.0768 mole
P = 1000 psig H_2 @ 325^{o}C.	Cyclohexane - 66.2 gm. (0.787 mole)
t = 90 min. @ 325^{o}C.	$AlCl_3$ - 0.70 gm. (0.0052 mole)
ω = 1250 RPM	

Run No.	57	58	[a]62	B-19
Substrate	Toluene	Ethylbenzene	Phenol	None
Substrate/$AlCl_3$ Mole Ratio	13.7	13.2	7.2	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	6.55	3.58	0.12	3.60
Methylcyclopentane	36.78	40.10	0.10	34.62
Cyclohexane	44.45	45.65	91.53	58.98
Methylcyclohexane	1.54	0.97	---	0.99
Unknown	1.35	0.37	---	---
Benzene	0.52	3.45	---	0.29
Ethylcyclohexane	0.16	0.11	---	---
Toluene	7.24	0.11	---	---
Ethylbenzene	0.75	3.86	---	---
Isopropylbenzene	0.10	---	---	---
n-Propylbenzene	0.28	0.21	---	---
n-Butylbenzene	0.30	1.59	---	---
Phenol	---	---	7.51	---
Heavy Unknowns	---	---	0.75	---
Substrate Conversion (%)	29	54	26	---
Reactants Recovered as Liquid Products (%)	94	95	91	---

[a] $AlCl_3$ loading doubled due to water present in phenol.

Table 3-11

Bibenzyl Mass Balance for Run 23

Compound	Wt. (gm.)	% Yield (wt.)
Cyclohexane	3.92	27.9
Bibenzyl	3.89	27.6
Benzene	3.87	27.5
Tar	1.60	11.4
Ethylbenzene	0.67	4.8
Minor Products	0.34	2.4
Toluene	0.18	1.3
		103%

The basic picture that emerges for this reaction is that bibenzyl is cleaved to yield ethylbenzene and benzene. The ethylbenzene is partially dealkylated to benzene, while a substantial fraction of the benzene appears to be hydrogented to cyclohexane. This is indeed a surprising result, since Run B-20 of Table 3-6 shows that only a trace of cyclohexane is produced on reaction of benzene and $AlCl_3$ alone. This topic will be further discussed later in this Chapter. The fact that the mass balance is greater than 100% suggests an error in the assumptions. The participation of solvent in tar production, for example, would yield mass balances greater than 100% since we have assumed all tar comes from substrate.

The same series of substrates in Table 3-6 was next run in cyclohexane solvent at 325°C with identical reactant loadings. Table 3-12 shows the results of these experiments. Compared to the analogous runs in benzene (Table 3-6), substrate conversion is higher in cyclohexane in all cases, and the zig-zag pattern is still evident, even though the differences between conversion figures are much less in cyclohexane. Conversions for biphenyl and diphenylmethane are substantially higher, whereas conversions of the other three substrates are only increased

Table 3-12

Cleavage of Aliphatic Bridges between Phenyl Rings

Reaction Conditions

T = 325°C.
P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

Substrate - 0.0768 mole (Runs 48, 49, 50, 51)
- 0.0095 mole (Run 41)
Cyclohexane - 61.5 gm. (0.787 mole)
$AlCl_3$ - 0.70 gm. (Runs 48, 49, 50, 51, B-19)
- 0.09 gm. (Run 41)

Run No.	48	49	50	51	41	B-19
Substrate	Biphenyl	Diphenylmethane	Bibenzyl	1,3-Diphenylpropane	1,4-Diphenylbutane	No Substrate
Substrate/$AlCl_3$ Mole Ratio	14.1	14.7	14.7	14.7	12.7	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole%)
Light Aliphatics	4.28	0.14	0.45	0.39	Trace	3.60
Methylcyclopentane	33.76	1.41	9.52	8.17	0.44	34.62
Cyclohexane	51.59	86.34	80.62	77.60	97.83	58.98
Methylcyclohexane	1.49	---	0.13	0.15	---	1.88
Benzene	0.86	8.33	5.74	7.31	0.66	0.29
Ethylcyclohexane	0.14	---	---	---	---	0.23
Toluene	0.17	1.75	0.25	0.14	---	---
Ethylbenzene	0.06	0.16	1.14	0.18	---	---
Isopropylbenzene	---	0.06	Trace	Trace	---	---
n-Propylbenzene	---	---	Trace	0.09	---	---
n-Butylbenzene	---	---	0.03	---	---	---
Indan	---	---	---	4.70	---	---
Tetralin	---	---	---	---	0.70	---
Dicyclohexyl	---	0.02	Trace	0.05	---	---
Dicyclohexylmethane	---	0.17	Trace	---	---	---
Cyclohexylbenzene	---	0.11	Trace	---	---	---
Biphenyl	6.89	---	---	---	---	---
Diphenylmethane	---	1.37	---	---	---	---
Bibenzyl	---	---	1.80	---	---	---
1,3-Diphenylpropane	---	---	---	1.14	---	---
1,4-Diphenylbutane	---	---	---	---	0.37	---
Heavy Unknowns	0.77	0.14	0.33	---	---	0.41

$\frac{\text{Methylcyclopentane}}{\text{Cyclohexane}}$ Mole Ratio	0.65	0.016	0.12	0.11	0.0045	0.59
Substrate Conversion (%)	32	82	76	83	68	---
Reactants Recovered as Liquid Products (%)	94	93	91	96	97	---

10-20%. Comparison of Tables 3-6 and 3-12 shows that major reaction products and relative product distributions are essentially the same in cyclohexane and benzene. The reactions in cyclohexane, however, reveal that benzene is the major product in each case, a fact obscured by the use of benzene as a solvent. The runs with diphenylmethane, bibenzyl, and 1,3-diphenylpropane all show that far more benzene (1.5-5.0 times) is produced than the accompanying cleavage product, toluene, ethylbenzene, and indan, respectively. Runs 57 and 58 from Table 3-10 discussed previously show that both toluene and ethylbenzene are indeed capable of dealkylation to benzene with $AlCl_3$ under these reaction conditions.

It is also interesting to note at the bottom of Table 3-12 that substrate conversion is roughly inversely proportional to the methylcyclopentane/cyclohexane mole ratio. When substrate conversion is high the catalyst is chiefly occupied in reactions with the substrate, permitting little isomerization of cyclohexane to methylcyclopentane. When substrate conversion is lower, it thus appears that more catalyst is available for cyclohexane isomerization.

Mass balances for Runs 48, 49, 50, and 51 are presented in Table 3-13. No balance was attempted for Run 41 because of the small amount of 1,4-diphenylbutane used, but it is evident that tetralin and benzene are the only products formed.

Table 3-13

Substrate Mass Balances for Runs 48, 49, 50, 51

1. Biphenyl Balance for Run 48

Compound	Wt. (gm.)	% Yield (wt.)
Biphenyl	8.07	68.0
Heavy Unknowns	1.55	13.1
Tar	1.52	12.8
Minor Products	0.66	5.6
Benzene	0.31	2.6
		102%

2. Diphenylmethane Balance for Run 49

Compound	Wt. (gm.)	% Yield (wt.)
Benzene	5.52	42.7
Diphenylmethane	2.36	18.3
Tar	2.00	15.5
Toluene	1.27	9.8
Minor Products	0.95	7.4
Cycloheane	0.80	6.2
		100%

3. Bibenzyl Balance for Run 50

Compound	Wt. (gm.)	% Yield (wt.)
Cyclohexane	3.83	27.4
Benzene	3.66	26.1
Bibenzyl	3.36	24.0
Tar	1.60	11.4
Ethylbenzene	1.12	8.0
Heavy Unknowns	0.62	4.4
Minor Products	0.20	1.4
		103%

4. 1,3-Diphenylpropane Balance for Run 51

Compound	Wt. (gm.)	% Yield (wt.)
Indan	5.04	33.2
Benzene	5.04	33.2
1,3-Diphenylpropane	2.52	16.6
Cyclohexane	1.25	8.2
Tar	0.75	4.9
Minor Products	0.64	4.2
		100%

It is now instructive to consider plausible mechanisms which might explain the observed experimental results. The first important question to address is the nature of the active catalytic species in reactions catalyzed by Lewis acids. In the past it was believed that the action of proton acids, such as H_2SO_4 or HF, differed in kind from that of Fridel-Crafts Lewis acids, such as $AlCl_3$ and BF_3. In more recent years (3-5) it has been concluded that the types of acid catalysts differ only in degree. In principal, therefore, there is no difference between the Lewis-acid catalyzed Friedel-Crafts reactions and similar reactions carried out under the catalytic effect of Bronsted acids. Ths conclusion leads one to suspect that the active catalytic species in both systems may be similar, and/or reaction mechanisms are the same.

It has been amply demonstrated (3-6) that a source of protons or other cations such as water or hydrogen halide must be present, even if in comparatively small amounts, for the acidic halides to show catalytic activity. It must therefore be realized that many Friedel-Crafts reactions catalyzed by Lewis acids are actually proton-catalyzed reactions. In fact, truly anhydrous, freshly sublimed, pure $AlCl_3$ fails to initiate many Friedel-Crafts reactions without the addition of H_2O or HCl as promoters (3-49).

The exact nature of the proton catalytic species is not definitively known and is a matter of debate. Several workers (3-7) have suggested that the co-catalyst of $AlCl_3$ is actually HCl formed by hydrolysis with H_2O. Others (3-7) have postulated the co-catalyst exists as the unstable conjugte acid $H^+AlCl_4^-$, yet other evidence (3-7) shows that the active species in some cases is the complex acid $H^+(HlCl_3OH^-)$. For sake of brevity the proton catalytic species will be designated as the generic form $H^+AlCl_4^-$.

From the evidence for the existence of the active catalytic species as a proton acid, it is therefore reasonable to postulate that the initiating step in these reactions is protonation of the substrate. Thus a mechanism for the cleavage of biphenyl would proceed as shown in Figure 3-1. The comparative unreactivity of biphenyl is most probably explained on the basis of the relativity instability of the phenyl cation. When formed in benzene solvent, it immediately substitutes onto benzene to form the original biphenyl substrate. In cyclohexane, however, the phenyl cation cannot react by this relatively fast route, and must seek stabilization by another pathway. Possibilities in this system include reduction by gaseous H_2 to form benzene, substitution onto benzene formed form cyclohexane solvent (see blank run B-19, Table 3-12), and reaction with the substrate itself to eventually yield polyphenyl polymers appearing either as "heavy uknowns" or tar. These ideas are supported by results of the mass balance for Run 48 shown in Table 3-13.

The type of reaction shown in Figure 3-1, similar to an electrophilic substitution reaction, is known to proceed via a S_N1 mechanism where formulation of species I in Figure 3-1 is the rate-determining step (3-50). The formation of the phenyl cation (II) is thus relatively fast, but nevertheless is an unfavorable reaction due to the large activation energy. The major reason for an abnormally high activation energy in this case is the relative instability of the phenyl cation (II).

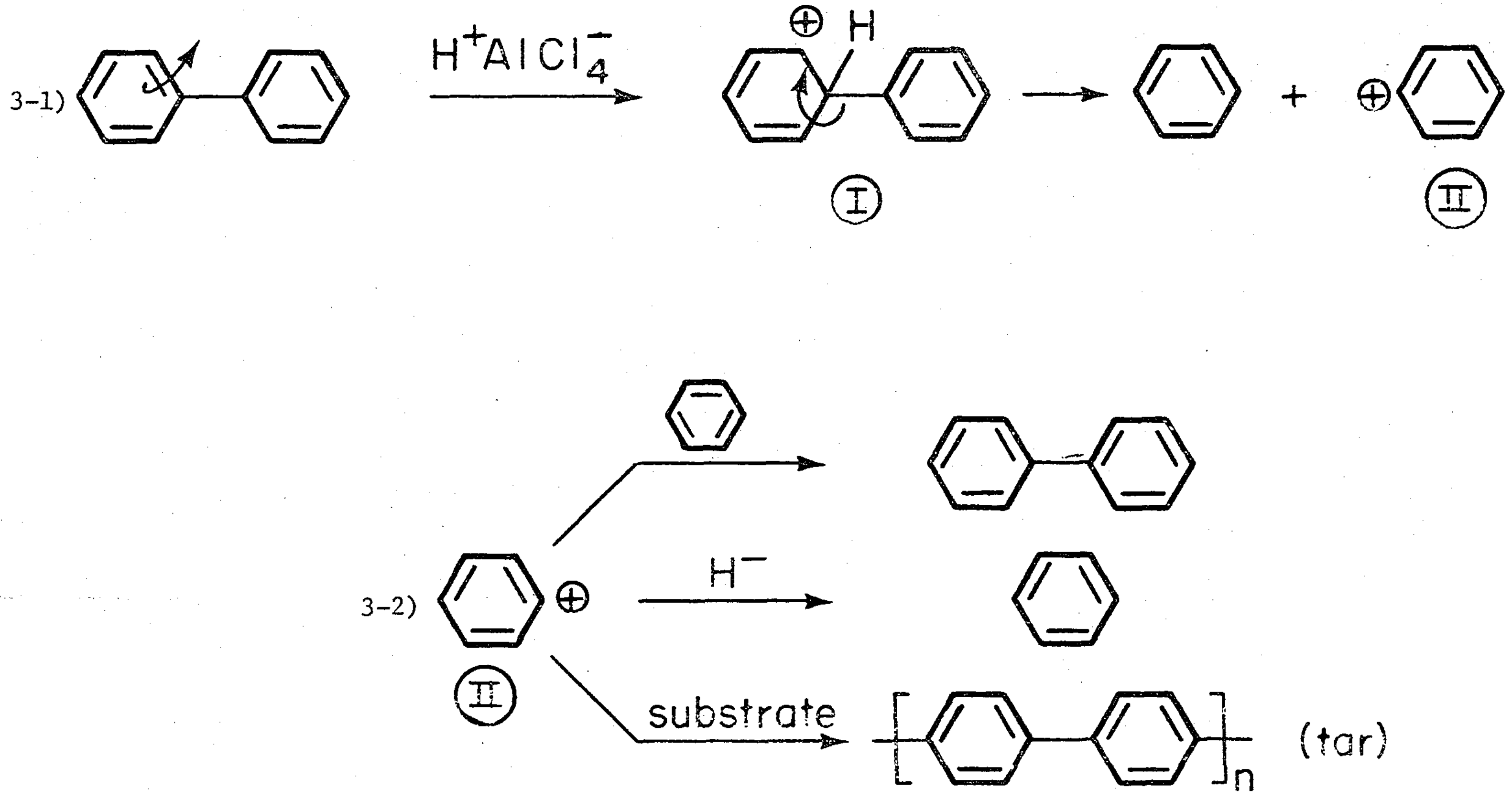

Fig. 3-1. Mechanism of Biphenyl Clevage

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This instability is related to the greater neighboring electron-withdrawing sp^2 carbon atoms and the inability to hyperconjugate. There is no opportunity for delocalization of the positive charge in the phenyl cation since the vacant orbital is perpendicular to and hence cannot overlap with the aromatic electron orbitals. Thus in benzene solvent (Run 34, Table 3-6) the phenyl cation immediately reacts with a benzene molecule to yield the original substrate, resulting in very low substrate conversion. In cyclohexane solvent, however, this reaction pathway is not possible, and the phenyl cation must find stabilization through another route, in this case mainly reaction with the substrate to eventually yield a polyphenyl polymer. Conklin (3-2) has shown detailed mechanisms by which tarry polymers are formed from both substrate and benzene under the influence of $AlCl_3$ in these systems. The relatively low substrate conversion in cyclohexane solvent (Run 48, Table 3-12) suggests that the activation energy for dissociation of the benezonium ion is large, thus indicating that the aryl-aryl bond in biphenyl is difficult to cleave.

The role of gas-phase H_2 in reducing carbonium ion intermediates (in this case the phenyl cation) in these reactions is uncertain. Later experiments (Tables 3-15, 3-18) with the other substrates seem to indicate that gaseous H_2 plays only a minor role, if any, in substrate conversion. Another possible source of hydrogen required to stabilize carbonium ions is that liberated in a Scholl-type condensation of benzene (3-9).

A mechanism for the cleavage of diphenylmethane is shown in Figure 3-2, and in the initial stages is entirely analogous to that shown

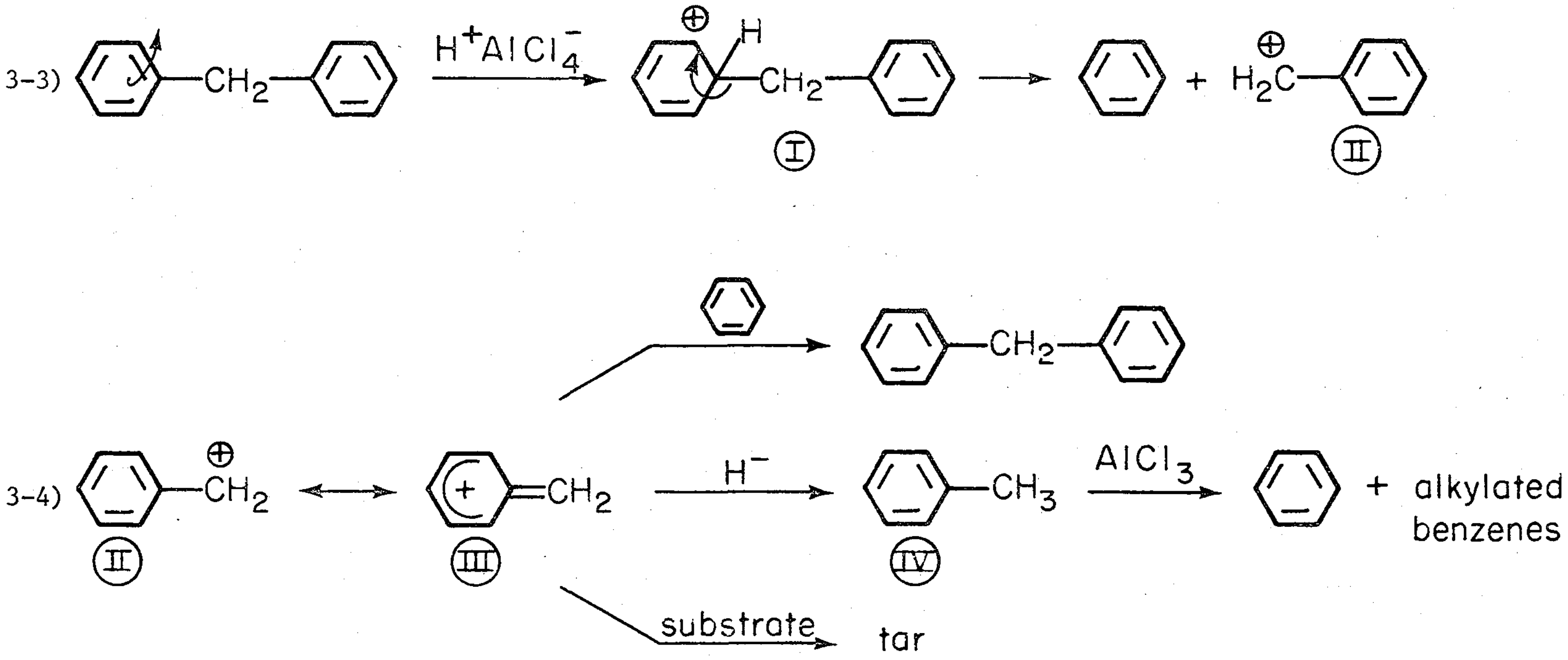

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Fig. 3-2. Mechanism of Diphenylmethane Cleavage for biphenyl. In this case, however, the intermediate benzyl cation is much more stable than the phenyl cation due to the resonance stabilization depicted in Figure 3-2 (species III). This stabilization greatly lowers the activation energy for cleavage of the benzenonium ion (I), and hence substrate conversion in both solvents is dramatically higher than for biphenyl. Furthermore, the benzyl cation is sufficiently stable to permit further reactions than just alkylation onto benzene. The observed 74% conversion of substrate in benzene solvent (Run 31, Table 3-6) suggests that the pathways to form toluene (IV) and tar are more important than that involving alkylation of benzene to yield the original substrate. (It should be emphasized that these reaction mechanisms depict major pathways only. Many more reaction pathways are operative which yield the host of minor products.) Inspection of the diphenylmethane mass balance of Run 49 (Table 3-13) shows that far more benzene is produced than toluene (benzene/toluene mole ratio = 5.2). This suggests that the toluene produced is dealkylated to yield benzene or other products. Run 57 of Table 3-12 shows that toluene is indeed capable of dealkylation or conversion to other alkylated benzenes under these conditions.

The mechanism for cleavage of bibenzyl is shown in Figure 3-3. Its basic aspects again are analogous to those mechanisms presented previously. The phenylethyl cation (II) is known (3-10) to be resonance stabilized by conversion to the non-classical cation shown as structure III. This cation follows essentially the same types of reaction pathways as does the benzyl cation. Inspection of the mass balance of bibenzyl in cyclohexane solvent (Run 50, Table 3-13) again suggests that the

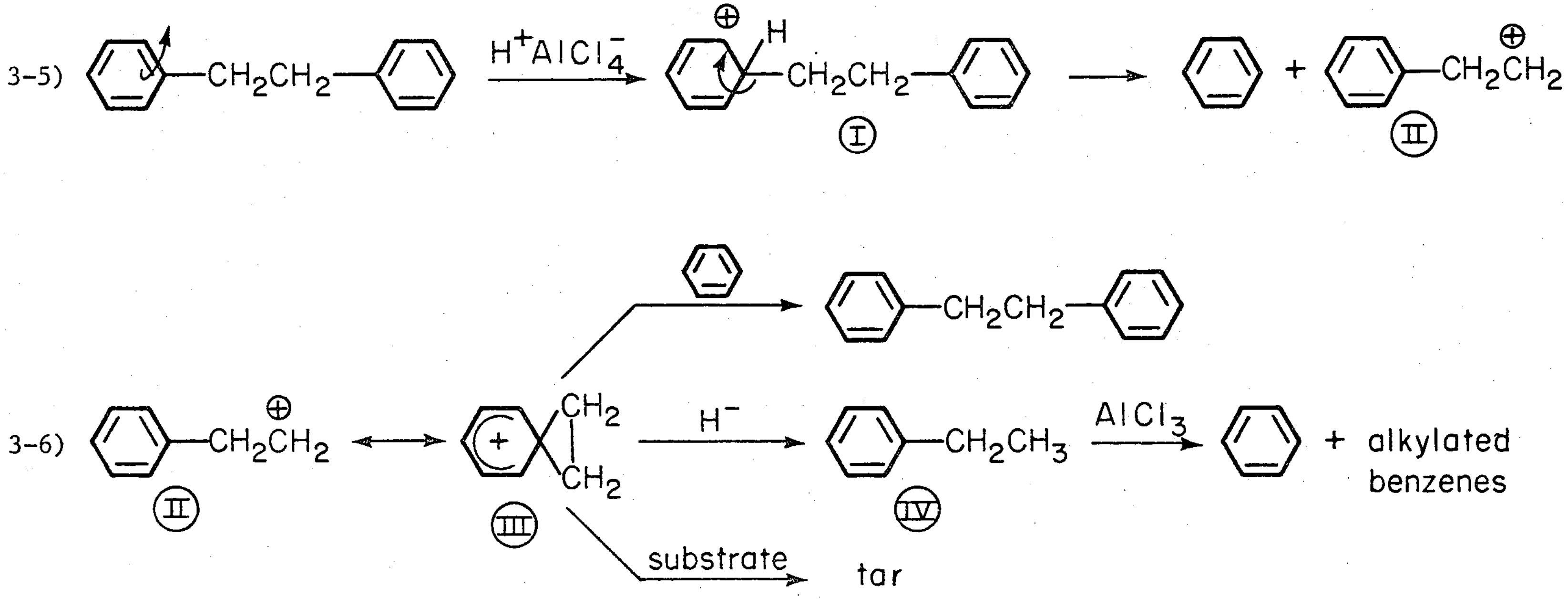

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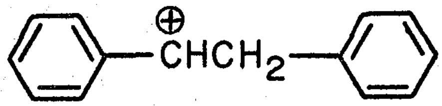
Fig. 3-3. Mechanism of Bibenzyl Cleavage ethylbenzene produced in reaction 3-6 is dealkylated to benzene or converted to other alkyl benzenes. Run 58 (Table 3-10) in which ethylbenzene is the substrate shows this to be the case. Over 50% of the ethylbenzene is converted to benzene and other alkyl benzenes. The conversion of ethylbenzene noted in Table 3-10 is almost twice that of toluene, and ethylbenzene is observed to produce much more benzene. This observation is in agreement with the known order of the rates of dealkylation of alkyl benzenes, t-alkyl > sec-alkyl > primary alkyl > methyl (3-11).

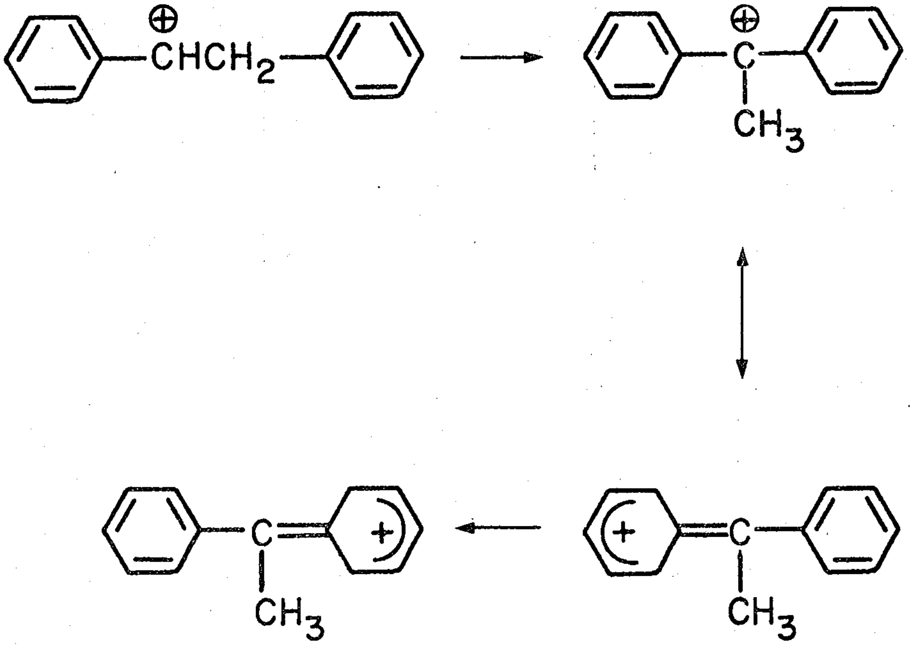
The hydride ions needed in reaction 3-6 to stabilize the phenylethyl cation (III) could be obtained by hydride abstraction from bibenzyl, yielding ethylbenzene and the following carbonium ion,



3-7)

This is a specially attractive route since this carbonium ion may be further resonance stabilized by a 1,2-phenyl shift as shown below.

3-8)



Conklin (3-12) has shown a mechanism by which the ion shown in line 3-7 can react further with bibenzyl to also yield ethylbenzene. In fact, hydride abstraction from the substrate by an intermediate carbonium ion could be a major pathway for ion stabilization for all substrates except biphenyl which has no aliphatic hydrogen. This may be another reason for the relatively low conversion of biphenyl.

The mechanism for cleavage of 1,3-diphenylpropane provides the first example in these reactions of substantial carbonium ion rearrangement. Run 51 in Table 3-12 and the corresponding mass balance (Table 3-13) both indicate that benzene and indan are by far the major reaction products. A mechanism which explains these products is presented in Figure 3-4. In this case the minor pathways to starting material,

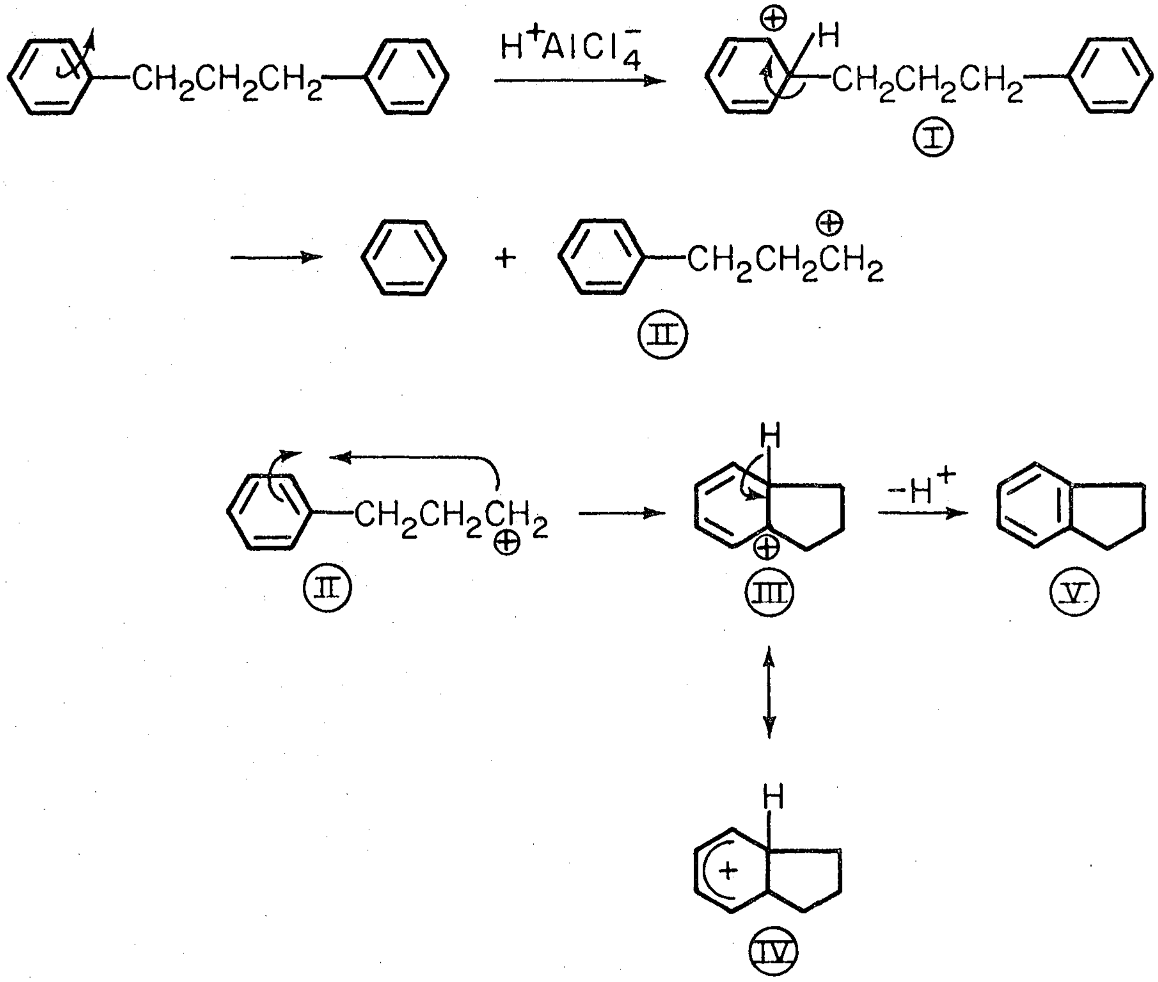


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Fig. 3-4: Mechanism of 1,3 Diphenylpropane Cleavage and p 84a.

tar, and minor products have been eliminated for the sake of clarity. The n-propylphenyl cation (II) is resonance stabilized following internal alkylation at the ortho position as shown, forming the protonated indan molecule (III) whose resonance structures are symbolized by IV. Upon loss of the proton indan (V) is formed. The fact that more benzene is produced than indan (benzene/indan mole ratio = 1.5. See Mass Balance for Run 51, Table 3-13.) again leads to the conclusion that either n-propylbenzene (from reduction of species II) or indan itself is being dealkylated to benzene or converted to other products. These reactions are indeed reversible, and it has been shown (3-13) that 5.9-8.4% yields of 1,3-diphenylpropane are obtained from reaction of indan with $AlCl_3$.

The mechanism for cleavage of 1,4-diphenylbutane is entirely analogous to that for 1,3-diphenylpropane, except that the additional carbon in the alkyl chain leads to the formation of tetralin. Run 41 of Table 3-12 shows that benzene and tetralin are the sole products of this reaction. The substantial conversion of 1,4-diphenylbutane in Run 41 confirms the previous suggestion that benzene complexed sufficiently with the small $AlCl_3$ loading in Run 42 to deactivate the catalyst toward the substrate. In Run 41 the cyclohexane is not capable of such aromatic complex formation, and hence is able to interact with the substrate. This fact may indeed be a partial reason for the overall higher coversion in <u>all</u> cyclohexane runs. The substrate conversion figure for this run, however, should be viewed with caution in considering it a part of the zig-zag pattern. Run 41 was performed with far less substrate and catalyst (even though their molar ratio was the same) than the other runs, resulting in much lower reactant concentrations which may have effected the reaction kinetics and increased the possibility of catalyt hydrolysis by trace amounts of water.

It is now of interest to consider the zig-zag pattern of substrate conversion noticed in Tables 3-6 and 3-12 in light of the relative stabilities of the respective reaction intermediate carbonium ions, the benzyl, phenylethyl, and phenylpropyl cations. The phenyl cation is not included because it is clearly far less stable than the above ions and since the kind of data discussed below which reflects relative stabilities of such carbonium ions is not available for phenyl derivatives.

Solvolysis, nucleophic substitution in which the solvent is the nucleophile, is the most common reaction for studying the nature of carbonium ions (3-51). Since there is no added strong nucleophile, solvolysis for most compounds proceeds via S_N1 mechanisms with the formation of intermediate carbonium ions. A commonly studied system is one in which the solvent is acetic acid (HOAc) and the substrates are alkyl esters of sulfonic acids: ROTs, alkyl tosylates (alkyl p-toluenesulfonates); and ROBs, alkyl brosylates (alkyl p-bromobenzenesulfonates) (3-52). Loss of the weakly basic sulfonte anion generates a cation which combines to yield the acetate,

3-9)

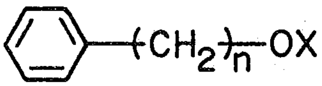
$$\text{R-OTs} \xrightarrow[\text{NaOAc}]{\text{HOAc}} \text{R-OAc}$$

Alkyl Tosylate   Alkyl Acetate

Since the rate-determining step in S_N1 reactions is generation of the carbonium ion, a comparison of the rates of solvolysis of a series of substrates will yield information about the relative stabilities of the intermediate carbonium ions.

Table 3-14 shows rate constants for solvolysis in acetic acid (HOAc) of the following series of arylalkyl tosylates or brosylates,

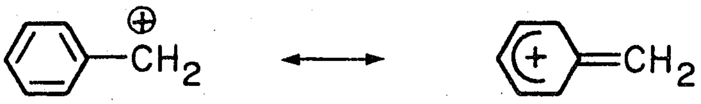
3-10)



X = Ts or Bs
n = 1-4

The carbonium ions formed in solvolysis of these compounds are the same as those formed in the above Friedel-Crafts mechanisms (Figures 3-2, 3-3, 3-4) where a phenyl ring is cleaved from the initial substrate. It is seen from this table that the rate constants follow the same zig-zag pattern (with the exception of V) as do substrate conversion figures in Tables 3-6 and 3-12. Even though solvolysis data is not available for phenyl tosylate, its rate constant would certainly be extremely small due to the instability of the resulting phenyl cation. Benzyl tosylate, on the other hand, is seen to have by far the largest rate constant, no doubt due to the resonance stabilization of the benzyl cation,

3-11)



The phenylethl cation produced on solvolysis of II or III (Table 3-14) is is known (3-10, 3-17, 3-31) to stabilize itself by formation of a bridged benzenonium ion,

Table 3-14

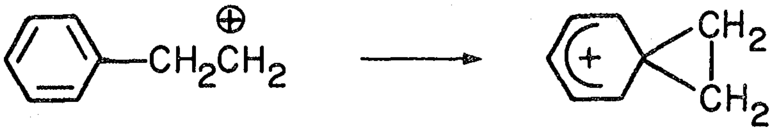
Rate Constants for Acetolysis of Arylalkyl Tosylates and Brosylates

	Compound Solvolyzed	Temp (°C)	Rate Constant k x10^6 (sec^{-1})	[2]Relative Rate	Reference
I.	CH_2OT_s	75	[1]231	359	3-14
II.	$CH_2CH_2OT_s$	75	0.644 (± 0.02)	1.0	3-15
III.	$CH_2CH_2OB_s$	75	0.85	---	3-16
IV.	$CH_2CH_2CH_2OB_s$	75	1.07 (± 0.00)	1.7	3-16
V.	$CH_2CH_2CH_2CH_2OB_s$	75	1.45 ± (0.03)	2.3	3-16

---

[1] Extrapolated from data at lower temperatures.

[2] All rate constants have been made relative to that of II for ease of comparison.

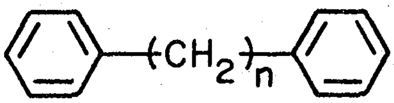


3-12)

The small rate relative to benzyl tolyslate is indicative of the large degree of ring strain in the bridged benzenonium ion. It is important to note that the solvolysis rates of β-phenylethyl tosylate (II) and β-phenylethyl brosylate (III) are roughly equivalent. This observation allows one to compare the solvolysis rates of the tosylates and brosylates listed in Table 3-14, since data is not available in this series of compounds involving only one ester type.

The carbonium ions resulting from the solvolysis of 1-phenyl-3-propylbrosylate (IV) and 1-phenyl-4-butylbrosylate (V) are believed (3-16) not to form such bridged benzenonium ions, but rather achieve stabilization through internal alkylation as shown in Figure 3-4 to yield the protonated indan and tetralin molecules, respectively, which are seen to be resonance stabilized. The fact that the solvolysis rates of these two esters are about twice that of phenylethyltosylate (II) indicates that there is much less ring strain in the protonated indan and tetralin ions than in the bridged phenylethyl cation, and entropy effects of internal alkylation can account for these two solvolysis rates being significantly less than that of benzyltosylate (I).

From the above discussions some important generalizations may be drawn concerning the cleavage of the alkyl bridge between phenyl rings in this series of model compounds,



3-13) n = 0-4

Initiation of the mechanism involves protonation of the substrate at the 1-position of a phenyl ring by the Lewis acid complex, followed by cleavage of the alkyl-aryl bond to yield benzene and an alkyl-aryl carbonium ion. Thus regardless of length, cleavage of an alkyl bridge between two aromatic centers will always occur at one of the aryl-alkyl bonds. The relative reactivity of these model compounds is seen to be governed by the relative stabilities of the carbonium ions resulting from cleavage, this being a *kinetically-controlled* process. Since the relative ratios of substrate conversion in Tables 3-6 and 3-12 are far from equal to the relative stabilities shown in Table 3-14 of the resultant carbonium ions, it may be concluded that the *thermodynamics* of reactants and products to a large degree governs the final product distributions.

B. Effect of Gas-Phase Composition

Results are shown in Table 3-15 for three substrates which were run under both H_2 and N_2 atmospheres in an attempt to ascertain the role of gaseous hydrogen in the above experiments and reaction mechanisms. It is seen that for diphenylmethane and 1,3-diphenylpropane conversion is about 25% *higher* with H_2, indicating that hydrogen from the gas phase is indeed participating in the reaction mechanisms. In order to determine the differences in reaction products it is most instructive

Table 3-15

Cleavage of Aliphatic Bridges Between Phenyl Rings Under N_2 Atmosphere

Reaction Conditions

T = 325°C.
P = 1000 psig H_2 or N_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

Substrate - 0.0768 mole
Benzene - 61.5 gm. (0.787 mole)
$AlCl_3$ - 0.70 gm. (0.0052 mole)

Run No.	54	31	55	30	56	35
Substrate	Diphenylmethane	Diphenylmethane	2-Hydroxy-diphenylmethane	2-Hydroxy-diphenylmethane	1,3-Diphenylpropane	1,3-Diphenylpropane
Atmosphere	Nitrogen	Hydrogen	Nitrogen	Hydrogen	Nitrogen	Hydrogen
Substrate/$AlCl_3$ Mole Ratio	14.3	13.7	14.5	14.7	14.7	14.7
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Cyclohexane	Trace	Trace	Trace	---	Trace	---
Benzene	94.86	95.84	93.63	94.30	92.11	91.99
Toluene	1.62	2.14	0.15	0.12	0.15	0.31
Ethylbenzene	0.08	0.12	---	---	0.29	0.55
Isopropylbenzene	0.20	0.03	---	---	0.13	0.26
n-Propylbenzene	---	Trace	---	---	0.12	0.20
Indan	---	---	---	---	3.98	4.62
Phenol	---	---	3.10	3.27	---	---
o-Cresol	---	---	0.34	0.23	---	---
p-Cresol	---	---	0.14	0.05	---	---
Diphenylmethane	3.22	1.85	0.48	0.73	0.05	0.08
Bibenzyl	0.02	---	---	0.02	0.04	0.07
1,3-Diphenylpropane	---	---	---	---	3.10	1.81
2-Hydroxydiphenylmethane	---	---	1.26	0.83	---	---
4-Hydroxydiphenylmethane	---	---	0.82	0.44	---	---
Heavy Unknowns	---	0.02	---	---	0.05	0.06
Substrate Conversion (%)	57	74	85	90	55	73
Reactants Recovered as Liquid Products (%)	93	93	97	97	95	96

to consider the mass balances for each substrate as shown in Table 3-16. As 2-hydroxydiphenylmethane was found to be soluble only in benzene, all substrates were run in benzene to avoid possible differences in solvent reactions.

Table 3-16

Mass Balances for Diphenylmethane and 1,3-Diphenylpropane

1. Diphenylmethane

	Wt. (gm.)		% Yield (wt.)	
Compound	Run 54(N_2)	Run 31(H_2)	N_2	H_2
Diphenylmethane	5.51	3.21	42.6	26.4
Benzene	4.44	4.95	34.8	40.7
Tar	1.57	2.00	12.2	16.5
Toluene	1.05	1.57	8.1	12.4
Minor Products	0.30	0.19	2.3	1.6
			100%	98%

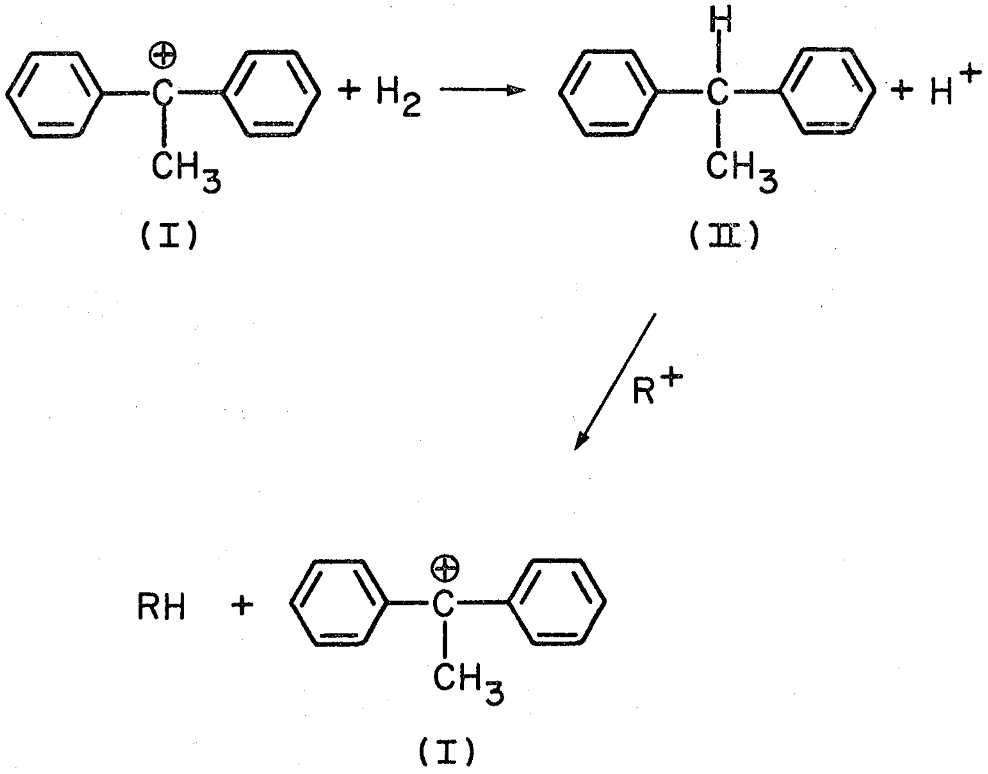
2. 1,3-Diphenylpropane

	Wt. (gm.)		% Yield (wt.)	
Compound	Run 56(N_2)	Run 35(H_2)	N_2	H_2
1,3-Diphenylpropane	6.78	4.12	44.9	27.3
Indan	4.14	4.82	27.4	32.0
Benzene	2.99	3.81	19.8	25.3
Minor Products	0.92	1.83	6.1	12.1
Tar	0.34	0.50	2.3	3.3
			100%	100%

Inspection of Table 3-16 reveals that for both substrates, weights of all reaction products are larger in the H_2 runs by about the same percentage. One can therefore conclude that gas-phase hydrogen is indeed participating in the reduction of carbonium ions to products, but these results give no indication of <u>how</u> this is occurring. It is possible that the hydrogen may be reacting directly with the liquid-phase carbonium ion, 3-14) $R^+ + H_2 \longrightarrow RH + H^+$,

where R^+ is a carbonium ion. Another possibility is that some species is acting as a hydrogen shuttle, accepting H^- from gaseous H_2 and donating it further to other ions. For example, such a species in reactions with bibenzyl may be the tertiary carbonium ion shown in reactions 3-8 and 3-15.

3-15)



1,1-Diphenylmethane (II) would be an excellent tertiary hydride donor due to the resonance stabilization afforded by the two neighboring phenyl groups. Siskin (3-18) and Wristers (3-20) have found that strong acid systems such as HF/TaF_5 and $HBr/AlBr_3$ can effectively catalyze conversion of benzene to hexanes under very mild conditions <u>without</u> using H_2-activation catalysts. They proposed that an essential component of the reaction scheme is a tertiary hydrocarbon. The carbonium ion thus produced is then reduced through reaction with H_2 back to the starting hydrocarbon. The mechanism may thus be envisioned as follows,

3-16)
$$\begin{gathered} \mathrm{Ar} + \mathrm{HA} \longrightarrow \mathrm{ArH}^+ + \mathrm{A}^- \\ \mathrm{ArH}^+ + \mathrm{RH} \longrightarrow \mathrm{ArH}_2 + \mathrm{R}^+ \\ \mathrm{A}^- + \mathrm{R}^+ + \mathrm{H}_2 \longrightarrow \mathrm{RH} + \mathrm{HA} \end{gathered}$$

The net reaction is thereby the acid- and hydrocarbon-catalyzed addition of hydrogen to the aromatic substrate,

3-17)
$$\mathrm{Ar} + \mathrm{H}_2 \longrightarrow \mathrm{ArH}_2 .$$

On the basis of this evidence it is therefore possible that a tertiary carbonium ion such as I is acting as a catalyst in shuttling hydrogen from the gas phase to solvated carbonium ions. This idea may be tested by adding a tertiary hydrocarbon to the reaction mixture and examining its effect on substrate conversion. Such experiments were indeed carried out in this study and will be presented later in this chapter.

Mass balances for the two runs with 2-hydroxydiphenylmethane (2-HDPM) are shown in Table 3-17. It is seen that substrate conversion is much more insensitive to gas-phase composition than for the two hydrocarbon substrates, with only slightly larger conversion under

H_2. It is, however, interesting to note that the amount of rearrangement product 4-hydroxydiphenylmethane (4-HDPM) formed in the N_2 run is much greater than in the H_2 run, indicating that rearrangement of the substrate is more favorable than conversion to other products when H_2 is absent. This again suggests that gas-phase H_2 is indeed participating in the reaction mechanism. This substrate will be discussed further when the effects of aromatic substituents on alkyl bridge cleavage are considered.

Table 3-17

Mass Balances for 2-Hydroxydiphenylmethane (2-HDPM)

Compound	Wt. (gm.) Run 55(N_2)	Wt. (gm.) Run 30(H_2)	% Yield (wt.) N_2	% Yield (wt.) H_2
Substrate (2-HDPM)	2.11	1.43	14.9	10.0
Benzene	6.36	7.11	45.0	50.0
Phenol	2.51	2.70	17.8	19.0
Diphenylmethane	0.87	1.34	6.2	19.4
4-HDPM	1.65	0.90	11.7	6.3
Minor Products	0.57	0.38	4.0	2.7
			100%	97%

To study solvent effects when a substrate is reacted under different atmospheres, diphenylmethane was run in cyclohexane and benzene under both H_2 and N_2. The results are presented in Table 3-18. It is seen from Runs 49 and 59 that in cyclohexane solvent H_2 and N_2 yield the same substrate conversion, and the mass balances in Table 3-19 show that reaction products are identical.

Table 3-18

Effects of Solvent and Gas Composition on the Cleavage of Diphenylmethane

Reaction Conditions

$T = 325^{o}C.$
$P = 1000$ psig H_2 @ $325^{o}C.$
$t = 90$ min. @ $325^{o}C.$
$\omega = 1250$ RPM

Reactants

Diphenylmethane - 12.92 gm. (0.0768 mole)
Solvent - 0.787 mole
$AlCl_3$ - 0.70 gm. (0.0052 mole)

Run No.	31	49	54	59
Atmosphere	Hydrogen	Hydrogen	Nitrogen	Nitrogen
Solvent	Benzene	Cyclohexane	Benzene	Cyclohexane
Substrate/$AlCl_3$ Mole Ratio	13.7	14.6	14.3	13.2
Product	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**
Light Aliphatics	---	0.14	---	0.15
Methylcyclopentane	---	1.41	---	1.09
Cyclohexane	Trace	86.34	Trace	87.51
Benzene	95.84	8.33	94.86	8.32
Toluene	2.14	1.75	1.62	1.31
Ethylbenzene	0.12	0.16	0.08	0.10
Isopropylbenzene	0.03	0.06	0.20	Trace
n-Propylbenzene	Trace	---	---	---
Dicyclohexyl	---	0.02	---	Trace
Unknown	---	0.28	---	0.06
Diphenylmethane	1.85	1.37	3.22	1.41
Bibenzyl	---	---	0.02	---
Heavy Unknown	0.02	0.14	---	0.07
Substrate Conversion (%)	74	82	57	82
Reactants Recovered as Liquid Products (%)	93	93	93	91

Table 3-19

Diphenylmethane Mass Balances - Effects of Solvent and Gas Composition

1. Cyclohexane Solvent

	Wt. (gm.)		% Yield (wt.)	
Compound	Run 49(H_2)	Run 59(N_2)	Run 49(H_2)	Run 59(N_2)
Benzene	5.52	5.36	42.7	41.4
Diphenylmethane	2.36	2.35	18.3	18.2
Tar	2.00	0.72	15.5	5.6
Toluene	1.27	0.93	9.8	7.2
Minor Products	0.95	0.21	7.4	1.6
Cyclohexane	0.80	3.65	6.2	28.2
			100%	102%

2. Benzene Solvent

	Wt. (gm.)		% Yield (wt.)	
Compound	Run 31(H_2)	Run 54(N_2)	Run 31(H_2)	Run 54(N_2)
Benzene	4.95	4.49	40.7	34.8
Diphenylmethane	3.21	5.51	26.4	42.6
Tar	2.00	1.57	16.5	12.2
Toluene	1.57	1.05	12.9	8.1
Minor Products	0.19	0.30	1.6	2.3
			98%	100%

Surprisingly enough, however, the N_2 run yields substantially more cyclohexane and less tar than the H_2 run. No reason for the substantial production of cyclohexane under a N_2 atmosphere is evident. An internal mass balance for the data in Table 3-19, however, also confirms the production of cyclohexane from the substrate. Assuming that diphenylmethane cleaves to yield benzene and other products, 46 wt.% (phenyl fragment) of converted substrate should appear as benzene and 54 wt.% (benzyl fragment) as other products. The weight ratio of other products (tar, toluene, minor products, cyclohexane) to benzene should therefore be 54/46 = 1.17. In Run 59 this ratio is (5.51 gm./5.36 gm.) = 1.03, which is in good agreement.

Comparison of Runs 31 and 54 in benzene, however, shows that substrate conversion is substantially higher under a H_2 atmosphere. The mass balances of Table 3-19 show that reaction products are the same and relative product distributions are very similar. This information again suggests that H_2 plays a role in substrate conversion. In cyclohexane the lack of sensitivity of substrate conversion to atmosphere suggests that sufficient hydrogen is available from the solvent. Yet in benzene aliphatic hydrogen is not available, and gas-phase H_2 is perhaps being used to stabilize reaction intermediates.

C. Cleavage of Aliphatic Bridges Catalyzed by $ZnCl_2$

As discussed in Chapter 1, $ZnCl_2$ is an attractive coal liquefaction catalyst yet very little is known about the mechanisms by which it operates and which organic structures in coal it attacks. To shed some light on this question $ZnCl_2$ was used as the catalyst in reactions with the model compounds discussed above. Before presenting these results, however, it is instructive to consider the differences in Lewis acidities between $ZnCl_2$ and $AlCl_3$.

The relative strengths of proton (Brönsted) acid and bases are relatively easy to determine and quantify because such properties are to a large extent independent of the solvent system. Yet no such simple relationships and quantitative determinations can be made for Lewis acids whose relative strengths depend very much on the base to which they are referred (3-20). The products of the reactions of Lewis acids with any given bases are different for each acid; each acid-base complex has its own characteristic properties which may have specific effects on the rates of any reactions that are catalyzed by Lewis acids (3-21).

It is therefore extremely difficult to compare quantitatively the Lewis acidities of $ZnCl_2$ and $AlCl_3$, yet at least some qualitative generalizations can be made. The active catalytic species of $ZnCl_2$ is not definitely known, but some workers (3-22) have proposed the structure $(H^+)_2(ZnCl_2OH_2)^{-2}$. In general the ability of a Lewis acid to accept an electron pair is greater, the greater the electronegativity of the central atom and the greater the number and electronegativities of the attached atoms. On this basis $AlCl_3$ would be expected to be the stronger Lewis acid, since Al is more electronegative and also is bonded to three Cl atoms vs. only two for Zn. Furthermore, for $AlCl_3$ a vacant 3p-orbital is available to accept an electron pair, whereas with $ZnCl_2$ two of the 4d orbitals appear to be available (3-23). Since a p-orbital has electron density closer to the nucleus than a d-orbital and hence less shielding from the positive charge of the nucleus, $AlCl_3$ would be expected to be a strong Lewis acid. It is therefore not surprising that experimental data (3-24, 3-25) support the conclusion that $AlCl_3$ is a substantially stronger Lewis acid than $ZnCl_2$.

Table 3-20 shows the results of reaction of $ZnCl_2$ with diphenylmethane, bibenzyl, and 1,3-diphenylpropane in cyclohexane solvent. These results may be quickly summarized by noting that $ZnCl_2$ does not catalyze cleavage of any of the hydrocarbon substrates under these conditions, even with the relatively small substrate/$ZnCl_2$ loadings noted in Table 3-20. These findings may be considered to be support

Table 3-20

Cleavage of Aliphatic Bridges Between Phenyl Rings

Reaction Conditions

$T = 325^{o}C.$
$P = 1000$ psig H_2 @ $325^{o}C.$
$t = 90$ min. @ $325^{o}C.$
$\omega = 1250$ RPM

Reactants

Substrate - 0.0275 mole
Cyclohexane - 54.5 gm. (0.633 mole)
$ZnCl_2$ - 5.14 gm. (0.0377 mole)

Run No.	45	26	47	B-21
Substrate	Diphenylmethane	Bibenzyl	1,3-Diphenylpropane	No Substrate
Substrate/$ZnCl_2$ Mole Ratio	0.71	0.73	0.72	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	0.15	Trace	---	0.76
Methylcyclopentane	0.08	0.18	Trace	0.53
Cyclohexane	95.65	95.85	96.71	98.71
Benzene	0.22	0.10	Trace	---
Toluene	Trace	---	---	---
Diphenylmethane	3.91	---	---	---
Bibenzyl	---	3.88	---	---
1,3-Diphenylpropane	---	---	3.29	---
Substrate Conversion (%)	0	0	*0	---
Reactants Recovered as Liquid Products (%)	97	96	96	---

for the hypothesis that the active catalytic species is a complex acid such as $H^+ ZnCl_2OH^-$ ($H_2O \cdot ZnCl_2$). In this case $ZnCl_2$ is not a sufficiently strong Lewis acid to polarize the HO·····H bond in the H_2O molecule enough to cause dissociation and subsequent protonation of the substrate. $AlCl_3$, on the other hand, would be capable of such dissociation of the acid complex. This negative result with $ZnCl_2$ leads one to question what kinds of transformations it *is* effecting with coal. This queston will be further addressed in the next section.

III. Effects of Aromatic Substituents on Cleavage of Aliphatic Bridges

As was discussed in Chapter I coal is believed to be composed of highly-substituted, polynuclear aromatic clusters linked by various types of bridges. It is therefore of importance to consider the effects of aromatic substituents and condensed aromatic systems on the cleavage of alkyl bridges. The hydroxyl group (-OH) was chosen as a model substituent because of its common occurrence in coal, and the naphthyl group was chosen as a prototype of condensed aromatic systems.

A. Cleavge of Hydroxylated Biphenyl and Diphenylmethane Compounds

The reaction products from 2-phenylphenol and 4-phenylphenol are shown in Table 3-21. The previous results for biphenyl are also listed for the sake of comparison. In Run 39 it is noted that 2-phenylphenol undergoes substantial conversion compared to biphenyl, yet it is intriguing to observe that the only product is a rearrangement product, *3*-phenylphenol. If this isomerization were to proceed via a carbonium ion mechanism analogous to those outlined above, the following pathway could be envisioned as shown in Fig. 3-5.

Table 3-21

Cleavage of Hydroxylated Biphenyl Compounds

Reaction Conditions

T = 325°C.
P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

substrate - 0.0768 mole
Benzene - 61.5 gm. (0.787 mole)
$AlCl_3$ - 0.70 gm. (0.0052 mole)

Run No.	34	39	44
Substrate	Biphenyl	2-Phenylphenol	4-Phenylphenol
Substrate/$AlCl_3$ Mole Ratio	13.7	14.7	14.7
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Cyclohexane	Trace	---	Reaction
Benzene	90.25	93.19	Products
Ethylbenzene	0.05	---	Not
Isopropylbenzene	0.13	---	Soluble
n-Propylbenzene	0.05	---	in Benzene
n-Butylbenzene	0.04	---	
Biphenyl	9.48	---	-See Text-
2-Phenylphenol	---	5.43	
3-Phenylphenol	---	1.39	
4-Phenylphenol	---	Trace	

Substrate Conversion (%)	4	38	---
Reactants Recovered as Liquid Products (%)	96	97	---

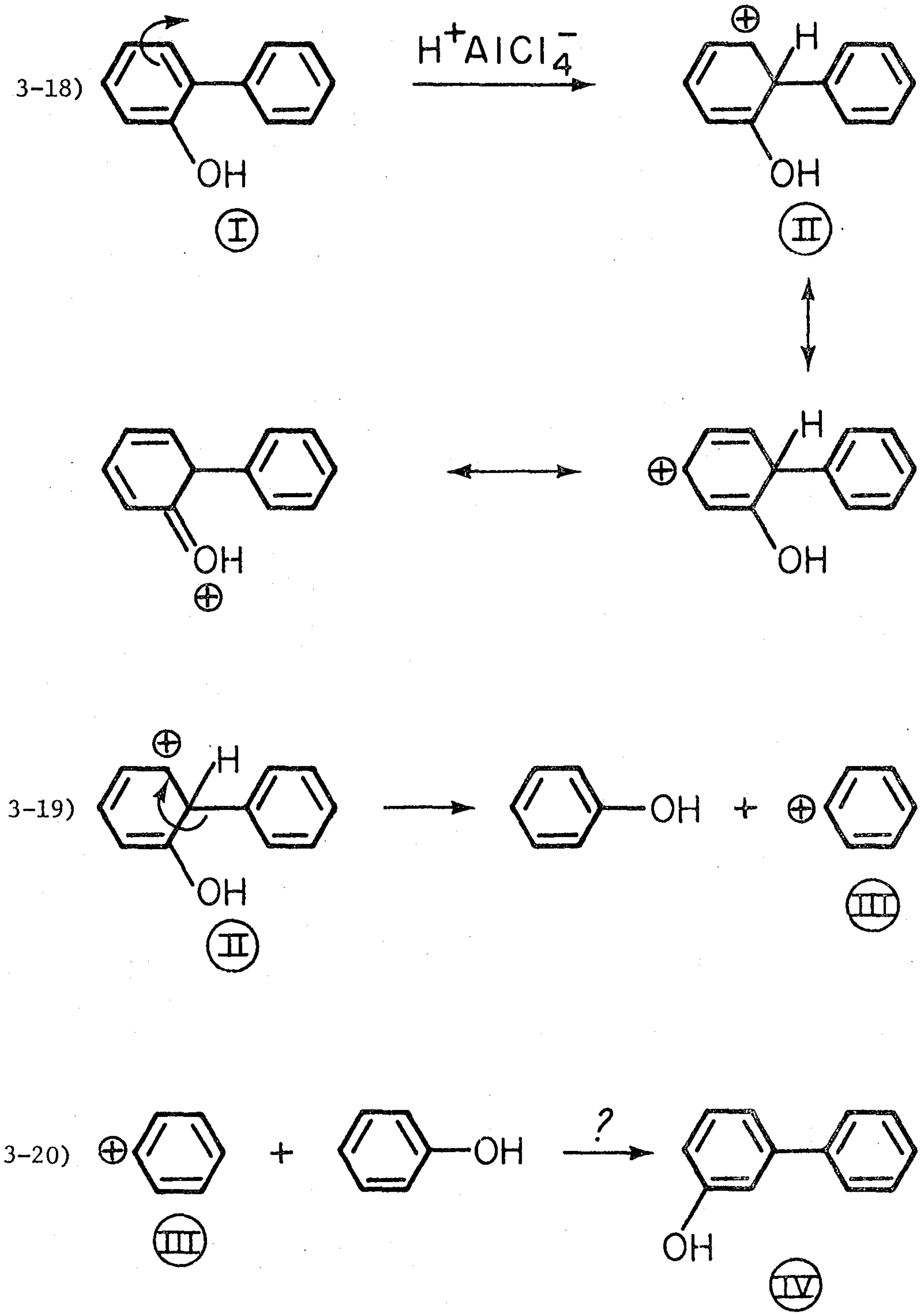


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Fig. 3-5. Possible Mechanism for Reaction of 2-Phenylphenol.

Protonation of the substrate is certain to occur on the ring containing the hydroxyl group because of the strong resonance stabilization afforded by the oxygen atom as shown in reaction 3-18. Cleavage of the benzenonium ion (II) would then yield phenol plus the unstable phenyl cation as shown in reaction 3-19. The observed 3-phenylphenol would be formed by substitution of the phenyl cation back onto phenol.

There are several experimental results of Run 39, however, which seem to indicate that such a carbonium ion mechanism is not operative in this case. Even though phenol is much more reactive toward the phenyl cation than is benzene because of the powerful activating effect of the hydroxyl group, the fact that absolutely no biphenyl is observed the when the reaction occurs in benzene solvent seems to cast doubt on the existence of a phenyl cation intermediate. Second of all, if the phenyl cation were to react with phenol as shown in reaction 3-20, the powerful directing effect of the hydroxyl group would yield exclusively a mixture of the ortho-para isomers (3-26). Such evidence seems to indicate that another mechanism is operative in this case.

Hay (3-27) has reported that on attempted Friedel-Crafts acylation of 2-phenylphenol using $AlCl_3$ catalyst, 3-phenylphenol was isolated as the major product. In similar work Olah (3-28) has studied the isomerization of o-, m-, and p-terphenyl with water-promoted $AlCl_3$. The equilibrium mixture obtained starting with any one of the isomers consisted of about 63% m- and 37% p-terphenyl with no ortho isomer present. Olah concluded that the isomerization of o-terphenyl occurs through migration of the phenyl group by an intramolecular 1,2-shift. Weingarten (3-29) has further reported the intramolecular phenyl migration in the $AlCl_3$-catalyzed rearrangement of mono- and dichlorobiphenyls.

One can conclude from the experimental observations and the evidence from the literature that the reaction observed in Run 39 with 2-phenylphenol occurs via intramolecular phenyl migration rather than through a carbonium ion mechanism. This is direct evidence that the aryl-aryl bond is not cleaved to any extent, again presumably due to the relative instability of the phenyl cation. This seems to suggest that aryl-aryl linkages in coal are especially difficult to cleave under the influence of Lewis acid catalysts, even when the aromatic rings have activating substituents.

4-phenylphenol was reacted in the presence of $AlCl_3$ in Run 44, but after reaction the autoclave was filled with a thick gelatin, the substrate being totally insoluble in benzene and having incorporated the solvent to form a gelatin. After evaporating the solvent in a vacuum oven at 110°C, 97.2% of the original substrate weight was recovered as a solid. This material was dissolved in pyridine and GC analyzed. This analysis showed the solid to consist solely of 4-phenylphenol plus a small amount of high molecular weight unknowns. Mass spectral analysis confirmed the presence of high molecular weight (200-250) compounds, but no identification was possible. Since phenol and biphenyl were found to be very soluble in pyridine, the absence of these peaks in the GC analysis indicated the absence of any cleavage products in the reaction mixture. It is interesting to note further that no 3-phenylphenol was found. This is entirely in agreement with Hay (3-27) who found that 4-phenylphenol does not isomerize under the influence of $AlCl_3$, even when reacted for extended periods of time.

Table 3-22

Cleavage of Hydroxylated Diphenylmethane Compounds

Reaction Conditions

T = 325°C.
P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

substrate - 0.0768 mole
Benzene - 61.5 gm. (0.787 mole)
$AlCl_3$ - 0.70 gm. (0.0052 mole)

Run No.	31	30	40	B-20
Substrate	Diphenylmethane	2-Hydroxy-diphenylmethane	4-Hydroxy-diphenylmethane	No Substrate
Substrate/$AlCl_3$ Mole Ratio	13.7	14.7	14.5	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Benzene	95.84	94.30	93.35	99.41
Toluene	2.14	0.12	0.16	0.19
Ethylbenzene	0.12	---	---	0.23
Isopropylbenzene	0.03	---	---	0.08
Phenol	---	3.27	3.07	---
o-Cresol	---	0.23	Trace	---
p-Cresol	---	0.05	0.10	---
Diphenylmethane	1.85	0.73	0.58	---
Bibenzyl	---	0.02	---	Trace
2-Hydroxydiphenylmethane	---	0.83	0.81	---
4-Hydroxydiphenylmethane	---	0.44	1.93	---
Heavy Unknowns	0.02	---	---	---

Phenol/Toluene Mole Ratio	---	27	19	---
Substrate Conversion (%)	74	90	74	---
Reactants Recovered as Liquid Products (%)	93	97	95	---

One can thereby conclude that the conversion of 4-phenylphenol in Run 44 is essentially zero, again showing the difficulty of cleaving the aryl-aryl bond.

Table 3-22 shows the results of reactions of 2- and 4-hydroxydiphenylmethane with $AlCl_3$. A previous reaction of diphenylmethane is included for sake of comparison. The mass balances for Runs 30 and 40 are shown in Table 3-23.

Table 3-23

Mass Balances for 2- and 4-Hydroxydiphenylmethane (HDPM)

	Wt. (gm.)		% Yield (wt.)	
Compound	Run 30(2-HDPM)	Run 40(4-HDPM)	2-HDPM	4-HDPM
Benzene	7.11	4.45	50.0	31.4
Phenol	2.70	2.41	19.0	17.0
2-HDPM	1.43	1.32	10.0	9.3
Diphenylmethane	1.34	1.02	9.4	7.2
4-HDPM	0.90	3.77	6.3	26.6
Minor Products	0.38	0.20	2.7	1.4
Tar	----	1.02	----	7.22
			97%	100%

These results show the interesting fact that conversion of 4-hydroxydiphenylmethane (4-HDPM) and diphenylmethane are the same, yet the conversion of 2-hydroxydiphenylmethane (2-HDPM) is substantially higher. The mass balance information in Table 3-23 shows that for the most part, the same relative product distribution is present in both runs, although a much higher percentage of benzene is formed in Run 30. (It was not possible to run these substrates in cyclohexane since both are insoluble.) In both cases approximately the same weight percentage of the original substrate is converted to the other isomer. Thus it is evident in at least one that case the a hydroxyl substituent does promote cleavage of the methylene linkage, and that the location of the hydroxyl group appears to have an effect on this promoting ability, although the nature of this effect is not readily apparent. But the general result is in agreement with the work of Tsuge and Tashiro (3-30) who studied cleavage of a series of alkyl-substituted diphenyl methanes under the influence of $AlCl_3$. They found that substrate conversion was increased by adding alkyl substituents to one of the phenyl rings; the higher the relative basicity of the alkyl group the more readily the substrate is cleaved. These results combined with the experimental findings of this study allow one to postulate reasonable a mechanism for these results.

A mechanism showing conversion of 2-HDPM to the major products benzene and phenol is presented in Figure 3-6. A mechanism for 4-HDPM would be entirely analogous.

The preponderance of phenol and benzene as major reaction products indicates that protonation occurs on the phenyl ring containing the hydroxyl group. Furthermore, protonation preceding cleavage must occur at the 1-position, since the resulting benzenonium ion (II) is the only one which can react by cleavage of the alkyl-aryl bond. Protonation occurs on this particular phenyl group because of the powerful resonance stabilization afforded the benzenonium ion (II) by the hydroxy oxygen as shown in reaction 3-21. The benzenonium ion then dissociates as in reaction 3-23 to form phenol and the relatively stable benzyl cation. It is this stability which affords the

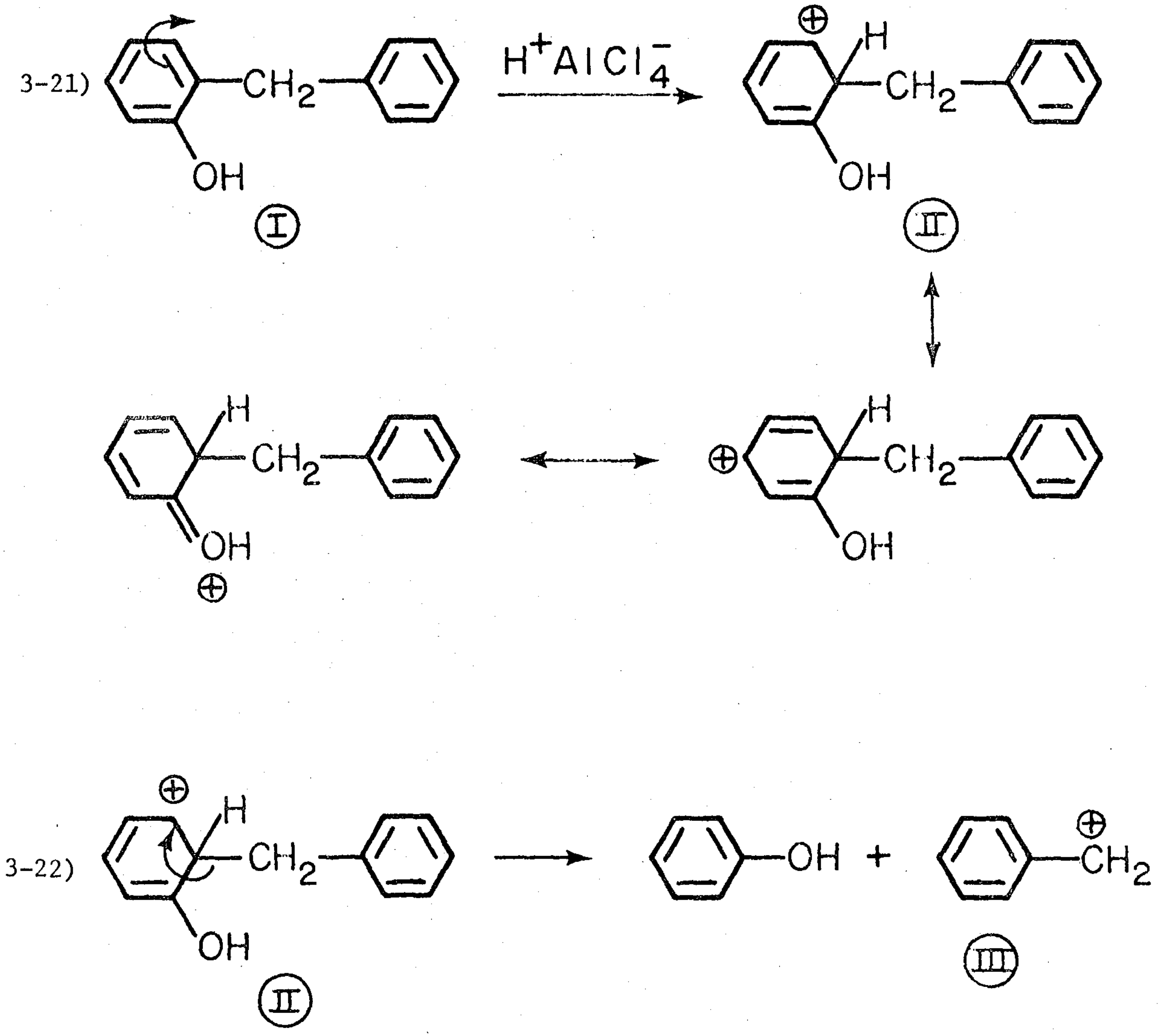

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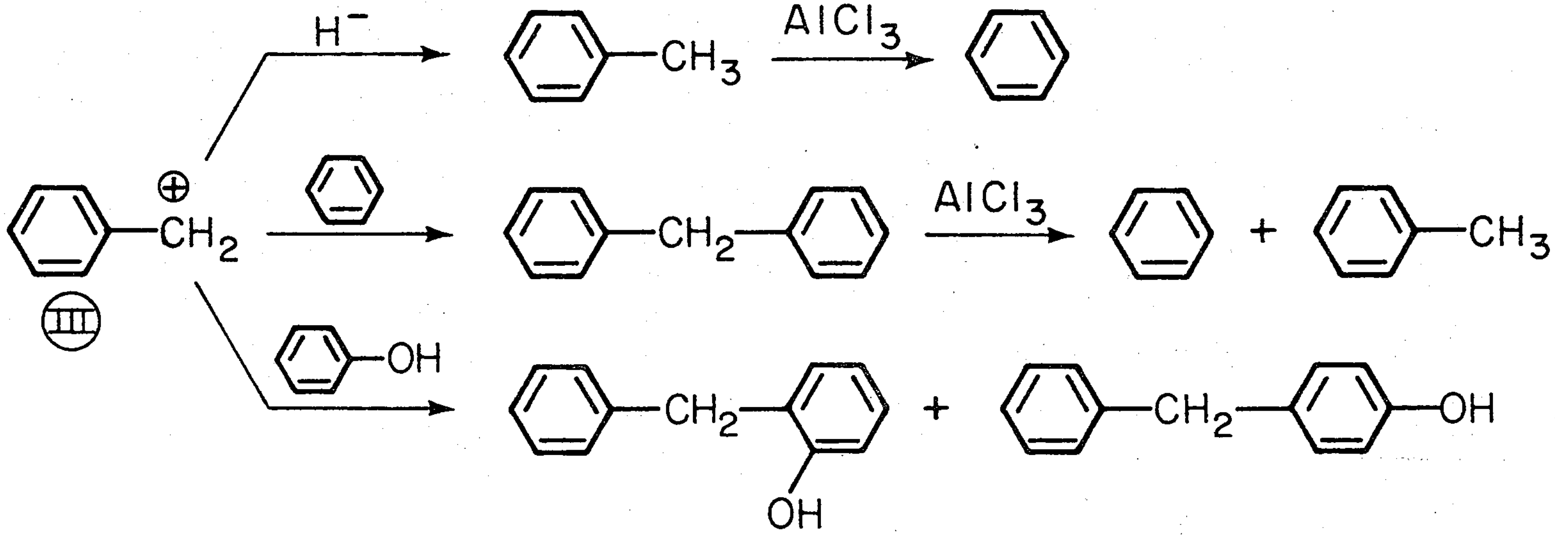
Fig. 3-6. Mechanism of 2-Hydroxydiphenylmethane Cleavage

3-23)



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benzyl cation the opportunity to follow the various reaction pathways shown in reaction 3-23. The fact that benzene is again the major product suggests that toluene is being partially dealkylated to benzene and that diphenylmethane is being cleaved to yield benzene and more toluene.

The observation in Table 3-22 that o- and p-cresol are produced as minor products demonstrates the fact that protonation and cleavage can also occur at the phenyl ring not containing the hydroxyl group, as shown in the following mechanism in Fig. 3-7. Occurrence of the cresols in such small amounts indicates that this process is either higher kinetically or thermodynamically (2-3 kcal/mole) in energy relative to the mechanism which yields the major products, mainly due to the fact that the benzenonium ion (II) shown in Fig. 3-7 is not resonance stabilized by phenolic oxygen.

Table 3-24 presents results for the reaction of the same hydroxylated substrates using $ZnCl_2$ as the catalyst. Run 45 with diphenylmethane is shown for sake of comparison to ascertain the effect of the hydroxyl group. This table shows the startling result that whereas $ZnCl_2$ does not catalyze cleavage of the hydrocarbon substrates (see Table 3-20) such as diphenylmethane at all, it does effect substantial conversion of their hydroxylated analogs. The GC data of Table 3-24 and the mass balances shown in Table 3-25 indicate that the major reaction products and relative product distributions are essentially the same as for the $AlCl_3$-catalyzed reactions, suggesting that the reaction mechanisms and active catalytic species for both catalysts are entirely analogous.

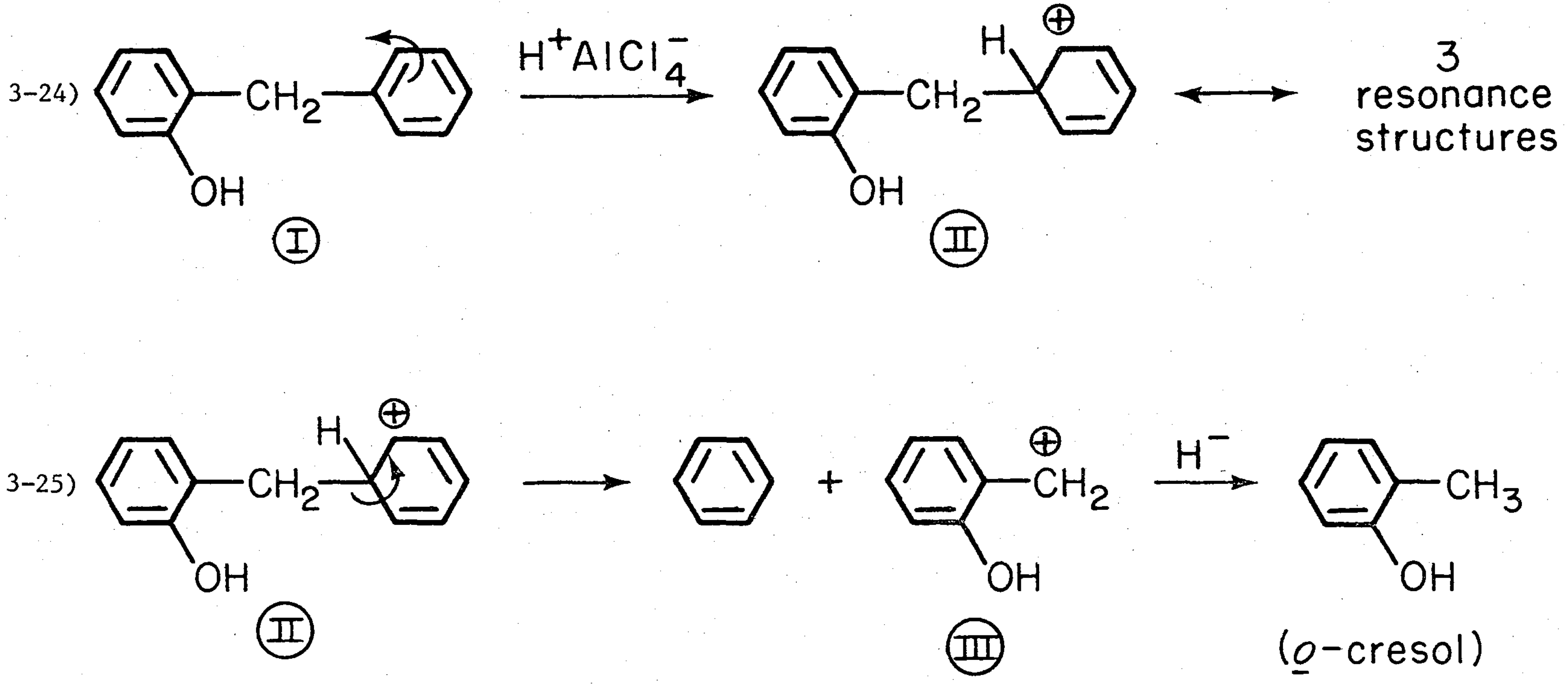

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Fig. 3-7. Mechanism of Cleavage of 2-Hydroxydiphenylmethane to Yield Minor Products.

Table 3-24

Cleavage of Hydroxylated Diphenylmethane Compounds

Reaction Conditions	Reactants
T = 325°C.	substrate - 0.0275 mole
P = 1000 psig H_2 @ 325°C.	Benzene - 61.5 gm. (0.787 mole), Runs 46, 53, B-22
t = 90 min. @ 325°C.	Cyclohexane - 54.5 gm. (0.648 mole), Run 45
ω = 1250 RPM	$ZnCl_2$ - 5.14 gm. (0.0377 mole)

Run No.	45	46	53	B-22
Substrate	Diphenylmethane	2-Hydroxy-diphenylmethane	4-Hydroxy-diphenylmethane	No Substrate
Solvent	Cyclohexane	Benzene	Benzene	Benzene
Substrate/$ZnCl_2$ Mole Ratio	0.71	0.75	0.75	0.0
Product	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**
Light Aliphatics	0.15	---	---	---
Methylcyclopentane	0.08	---	---	---
Cyclohexane	95.65	Trace	Trace	0.01
Benzene	0.22	97.72	96.55	99.99
Toluene	Trace	0.11	0.11	---
Ethylbenzene	---	0.03	---	---
Isopropylbenzene	---	---	0.52	---
n-Propylbenzene	---	---	0.04	---
Phenol	---	0.69	1.35	---
p-Cresol	---	---	0.05	---
Diphenylmethane	3.91	0.22	0.70	---
2-Hydroxydiphenylmethane	---	1.23	0.29	---
4-Hydroxydiphenylmethane	---	---	0.39	---
Phenol/Toluene Mole Ratio	---	6.3	12	---
Substrate Conversion (%)	0	63	86	---
Reactants Recovered as Liquid Products (%)	97	99	98	---

Table 3-25

Mass Balances for 2- and 4-Hydroxydiphenylmethane (HDPM)

Compound	Wt. (gm.) Run 46(2-HDPM)	Wt. (gm.) Run 53(4-HDPM)	% Yield (wt.) 2-HDPM	% Yield (wt.) 4-HDPM
Benzene	2.76	1.88	53.6	34.9
2-HDPM	1.91	0.45	37.1	8.4
4-HDPM	----	0.73	----	13.6
Phenol	0.52	1.01	10.1	18.8
Diphenylmethane	0.36	1.16	7.0	21.6
Minor Products	0.11	0.64	2.1	11.9
			110%	109%

The dramatic effect of the hydroxyl group on the conversion of these substrates may be rationalized on the basis of the proposed complex acid ($H^+ZnCl_2OH^-$) as the active catalytic species. The hydroxyl group greatly increases the basicity of the phenyl ring through resonance donation of an unshared electron pair of oxygen. Thus the hydroxylated phenyl ring is a sufficiently strong Lewis base to abstract a proton from the $ZnCl_2$ acid complex, whereas an unsubstituted phenyl ring is not. This fact is further evidence for the stronger Lewis acidity of $AlCl_3$, since it is capable of catalyzing cleavage of both hydroxylated and unsubstituted substrates as shown above. The hydroxyl group also lowers the activation energy for formation of the protonated benzenonium ion by resonant charge delocalization (3-53), thus allowing this reaction to proceed at a faster rate than that of the analogous unsubstituted substrate. These two factors thus account for the ability of $ZnCl_2$ to catalyze the cleavage of the hydroxylated substrates whereas it is totally inactive toward the unsubstituted substrates.

An important insight into the chemistry of $ZnCl_2$-catalyzed reactions may be gained by observing in Tables 3-24 and 3-25 that the reaction of 4-HDPM yields 2-HDPM, yet the converse does not occur. Vollhardt (3-31) has suggested that with 2-HDPM, $ZnCl_2$ may be forming a complex simultaneously with the oxygen of the hydroxyl group and the -electron system of the other phenyl ring. Construction of molecular models shows the geometry to be possible, with Zn supplying two empty 4p orbitals for overlap with the -electron cloud and an unshared electron pair of oxygen. Even though formation of such a complex would not necessarily prevent cleavage of the methylene linkage, it may be sufficiently strong to hold the phenol molecule and benzyl cation together long enough after cleavage for the benzyl cation to be stabilized by further reaction. This loose complex would thus prevent attack of the benzyl ion at the para-position of phenol to form 4-HDPM. This type of complex formation may also explain the lower conversion of 2-HDPM shown in Table 3-24.

The $ZnCl_2$ experiments have some important ramifications for coal conversion processes using $ZnCl_2$ as a catalyst. First, a clearer picture now emerges showing what chemical transformations $ZnCl_2$ is effecting on coal. It has great difficulty cleaving aliphatic bridges between single, unsubstituted phenyl rings and in cleaving aryl-aryl bonds, yet readily facilitates cleavage of linkages connecting aromatic nuclei with ring-activating substituents. Since coal is known to be highly substituted with oxygen, nitrogen, and alkyl substituents, $ZnCl_2$ is likely able to catalyze cleavage of the large majority of alkyl linkages in coal. Furthermore, coal is known to be an organic polymer with many polynuclear condensed ring systems, so alkyl bridges between isolated phenyl rings are no doubt rather unimportant. The effect of replacing a phenyl ring with larger aromatic systems will be examined in the next section.

A further benefit of using $ZnCl_2$ may be gleaned from the mass balances of Table 3-25. Here it is seen that there is absolutely no tar formation, with all substrates being converted to liquid products. Thus there is a distinct selectivity advantage over the more drastic action of $AlCl_3$ which produces moderate amounts of tarry polymer and gases with these same substrates.

B. Cleavage of Bridges between Naphthyl-Phenyl Ring Systems

Since coal contains many polynuclear condensed aromatic ring systems, it is desirable to study the effects of these ring systems on the cleavage of alkyl bridges between aromatic nuclei. To this end 1-phenylnaphthalene (1-PN) and 1-benzylnaphthalene (1-BN) were reacted in the presence of both $AlCl_3$ and $ZnCl_2$. These substrates are analogous to biphenyl and diphenylmethane, respectively, where one phenyl ring has been replaced by a naphthyl group.

The results for the $AlCl_3$ runs are shown in Table 3-26. It should be noted that far less substrate was used in these runs in comparison to the corresponding biphenyl and diphenylmethane runs due to the high cost of these materials. Run 43 shows the remarkable result that over 90% of 1-phenylnaphthalene is converted to other products, in contrast to only 32% for biphenyl. Only very small amounts of cleavage products (benzene, naphthalene) are present, however, with the isomer 2-phenylnaphthalene (2-PN) being the major reaction product.

Table 3-26

[a] Cleavage of Aliphatic Bridges between Naphthyl-Phenyl Nuclei

Reaction Conditions

T = 325°C

P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

substrate - 0.0768 mole (Runs 48, 49)
- 0.0149 mole (Runs 43, 52)
Cyclohexane - 66.2 gm. (0.787 mole)
$AlCl_3$ - 0.15 gm. (Runs 43, 52)
- 0.73 gm. (Runs 48, 49, B-19)

Run No.	48	43	49	52	B-19
Substrate (gm.)	Biphenyl (11.86)	1-Phenylnaphthalene (3.02)	Diphenylmethane (12.92)	1-Benzylnaphthalene (3.24)	No Substrate (-)
Substrate/$AlCl_3$ Mole Ratio	14.1	12.7	14.7	12.7	0.0
Product	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**
Light Aliphatics	4.28	Trace	0.14	0.04	3.60
Methylcyclopentane	33.76	0.80	1.41	0.19	34.62
Cyclohexane	51.59	98.14	86.34	97.97	58.98
Methylcyclohexane	0.89	---	---	---	0.99
Benzene	0.86	0.07	8.33	0.55	0.29
Toluene	0.17	---	1.75	0.09	---
Ethylbenzene	0.06	---	0.16	---	---
Isopropylbenzene	---	---	0.06	---	---
Tetralin	---	0.03	---	---	---
Naphthalene	---	0.01	---	0.82	---
2-Methylnaphthalene	---	---	---	0.07	---
1-Methylnapthalene	---	---	---	0.01	---
Diphenyl	6.89	---	---	---	---
Diphenylmethane	---	---	1.37	0.12	---
1-Phenylnaphthalene	---	0.10	---	---	---
Unknown	---	0.03	---	---	---
2-Phenylnaphthalene	---	0.83	---	---	---
1-Benzylnaphthalene	---	---	---	0.01	---
2-Benzylnaphthalene	---	---	---	0.13	---
Heavy Unknowns	0.77	---	0.14	---	---

Substrate Conversion (%)	32	94	82	99	---
Reactants Recovered as Liquid Products (%)	94	94	93	98	---

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[a] Since smaller molar quantities of substrate were used in Run 43 and 52, conc. figures are not directly comparable with the other runs.

Table 3-27

Mass Balances for 1-Phenylnaphthalene and 1-Benzylnaphthalene in $AlCl_3$-Catalyzed Reactions

1. 1-Phenylnaphthalene (Run 43)

Compound	Wt. (gm.)	% Yield (wt.)
2-Phenylnaphthalene	1.45	48.0
Cyclohexane	1.28	42.4
1-Phenylnaphthalene	0.17	5.6
Benzene	0.04	1.3
Unknown	0.04	1.3
Tetralin	0.03	1.0
Naphthalene	0.01	0.3
		100%

2. 1-Benzylnaphthalene (Run 52)

Compound	Wt. (gm.)	% Yield (wt.)
Cyclohexane	1.59	49.1
Naphthalene	0.77	23.8
2-Benzylnaphthalene	0.34	10.5
Benzene	0.33	10.2
Minor Products	0.14	4.3
Diphenylmethane	0.11	3.4
1-Benzylnaphthalene	0.03	0.9
		102%

The mass balances in Table 3-27 confirm this conclusion, and also show the surprising result that a great deal of cyclohexane appears to be produced. This indeed is a troublesome conclusion, since no reaction pathway is readily apparent. If benzene produced from cleavage of substrate were being reduced to cyclohexhane, then one would expect to see a corresponding amount of naphthalene, which is not the case. Another possibility is the extensive cracking and reduction of naphthalene to cyclohexane, which is an unlikely reaction in the presence of $AlCl_3$. Yet another explanation is that apparent cyclohexane production is an artifact of GC analysis and the subsequent mass balances. For example, if a high molecular weight compound were dissolved in the liquid products yet not eluted from the GC column during analysis, this would force the calculated weight fractions of the identified liquid product constituents to be artificially high. Such an error would have the greatest impact on the calculated weight of solvent recovered from the reaction, since its weight fraction, being by far the largest, would be increased by the largest amount. In the solvent mass balance this error would cause the calculated weight to be greater than the actual weight of solvent recovered, forcing one to conclude that cyclohexane had been produced in the reaction. In the substrate mass balance, then, the absence of the uneluted compound could easily be compensated for by the apparent production of cyclohexane.

Even though this type of error would explain the apparent cyclohexane production, it would also raise the question of how the high molecular weight compound is being produced. About the only possibility in this system would be cleavage of 1-PN to yield naphthalene and a phenyl cation, which could react with the substrate to yield a diphenylnaphthalene. In the presence of $AlCl_3$, however, 1-PN is known (3-32, 3-33, 3-36) to isomerize by an intramolecular phenyl shift, and no evidence has been found for cleavage reactions proceeding via a carbonium ion mechanism. Also, it is questionable whether polycyclic compounds such as di- and higher-substituted phenylnaphthalenes would be soluble in cyclohexane at room temperature.

Even though the production of cyclohexane in these reactions is questionable, it should be emphasized that the resolution of this question has no material effect on the basic conclusions of these experiments. The calculated weights recovered of identified compounds and substrate conversion figures would not be substantially altered in either case.

The apparent lack of any substantial amounts of cleavage products and the appearance of the 2-phenylnaphthalene isomer as the major product suggests that the aryl-aryl bond is not cleaved to a significant extent, but rather that the isomerization product is formed by an intramolecular 1,2-phenyl shift. This observation is entirely consistent with the reported work of others. Nefedov and Shih (3-32) have reported 70% conversion of 1-phenylnaphthalene isomerized to 2-phenylnaphthalene in the presence of $AlCl_3$. Olah (3-28) has shown strong evidence that the $AlCl_3$-catalyzed isomerization of o-terphenyl to p-terphenyl occurs solely by intramolecular 1,2-phenyl shift. More recent work by Olah (3-33) on the $AlCl_3$-catalyzed isomerization of alkyl naphthalenes has shown that naphthalene derivatives with larger substituents such as t-butyl and phenyl tend to isomerize primarily by intramolecular migrations occurring in the protonated naphthalenium ion intermediate (σ-complex).

The isomerization of 1-phenylnaphthalene (1-PN) to 2-phenylnaphthalene (2-PN) is essentially thermodynamically controlled (3-33). Weingarten (3-36) has found that both 1-PN and 2-PN yield an equilibrium mixture of 3% 1-PN and 97% 2-PN upon $AlCl_3$-catalyzed isomerization. Construction of molecular models shows that there is significant steric interaction between the α-phenyl and 5-naphthyl hydrogens in 1-PN, forcing the phenyl group to be rotated slightly out of the plane of the naphthyl group. Experimental evidence (3-37) has shown the interplane angle for 1-PN in CCl_4 solvent to be 66°. On the other hand, the naphthyl and phenyl groups of 2-PN can be completely coplanar without significant steric interaction between naphthyl-phenyl hydrogens. 2-PN is therefore the more thermodynamically stable isomer, even though 1-PN is the kinetically favored product. The naphthalenium ion intermediate formed by protonation of 1-PN at the α-position is more stable than the corresponding ion of 2-PN because the former has more resonance structures in which the aromatic sextet of the neighboring benzene ring is preserved (3-34). Thus one would expect on a kinetic basis to see mainly 1-PN because its intermediate naphthalenium ion is formed faster than the corresponding ion of 2-PN. The appearance of 2-PN as the major product suggests that at 325°C all reactions are fast enough to reach thermodynamic equilibrium. These observed results are entirely consistent with those (3-25) of another sterically-hindered naphthalene derivative, 1-naphthalene-sulfonic acid (1-NSA). Desulfonation occurs more readily at the α-position, 2-NSA tending to resist desulfonation. At low temperatures desulfonation is slow and the product that is formed faster, 1-NSA, is isolated. At higher temperatures, thermodynamic equilibrium is more readily established, and the more stable 2-NSA acid is isolated as the major product.

The fact that the major reaction of 1-PN with $AlCl_3$ appears to be an intramolecular isomerization again suggests the relative instability of the phenyl carbonium ion and the difficulty in cleaving aryl-aryl bonds. Protonation of 1-PN would occur primarily on the naphthyl group because of the greater number of resonance structures possible than with protonation on the phenyl ring. Cleavage of the resulting phenyl-naphthalenium ion would yield naphthalene and the phenyl cation. The fact that we observe mainly isomerization products and little evidence of cleavage suggests that the activation energy for cleavage is significantly higher than that of isomerization, primarily because of the instability of the resulting phenyl cation.

In contrast, Run 52 with 1-benzylnaphthalene (1-BN) shows that cleavage of the methylene linkage is a significant reaction in this case. Fully 99% of the substrate is converted to other products, and the mass balance of Table 3-27 shows that the amounts of cleavage products are substantial. The increased conversion over diphenylmethane shows the activating effect toward cleavage of the naphthyl group, which can be explained on the basis of the mechanism postulated in Fig. 3-8. Protonation of the substrate is kinetically favored on the naphthyl group because of the increased resonance stabilization of the resulting ion over protonation on the phenyl ring. Furthermore, protonation at the <u>1</u>-position of the naphthyl group is favored because the change in hybridization of this carbon atom from $sp^2 \rightarrow sp^3$ relieves the steric interaction between the naphthyl and phenyl hydrogens. Cleavage of the resulting phenyl naphthalenium ion (I) results in naphthalene and the benzyl cation (II), which can follow the reaction pathways shown in reaction 3-28.

In contrast to the intramolecular isomerization of 1-phenylnaphthalene, the acid-catalyzed isomerization of the two isomers of benzylnaphthalene is known to be a reversible process (3-38) which procees via a carbonium ion mechanism (3-39). Substitution of the benzyl cation

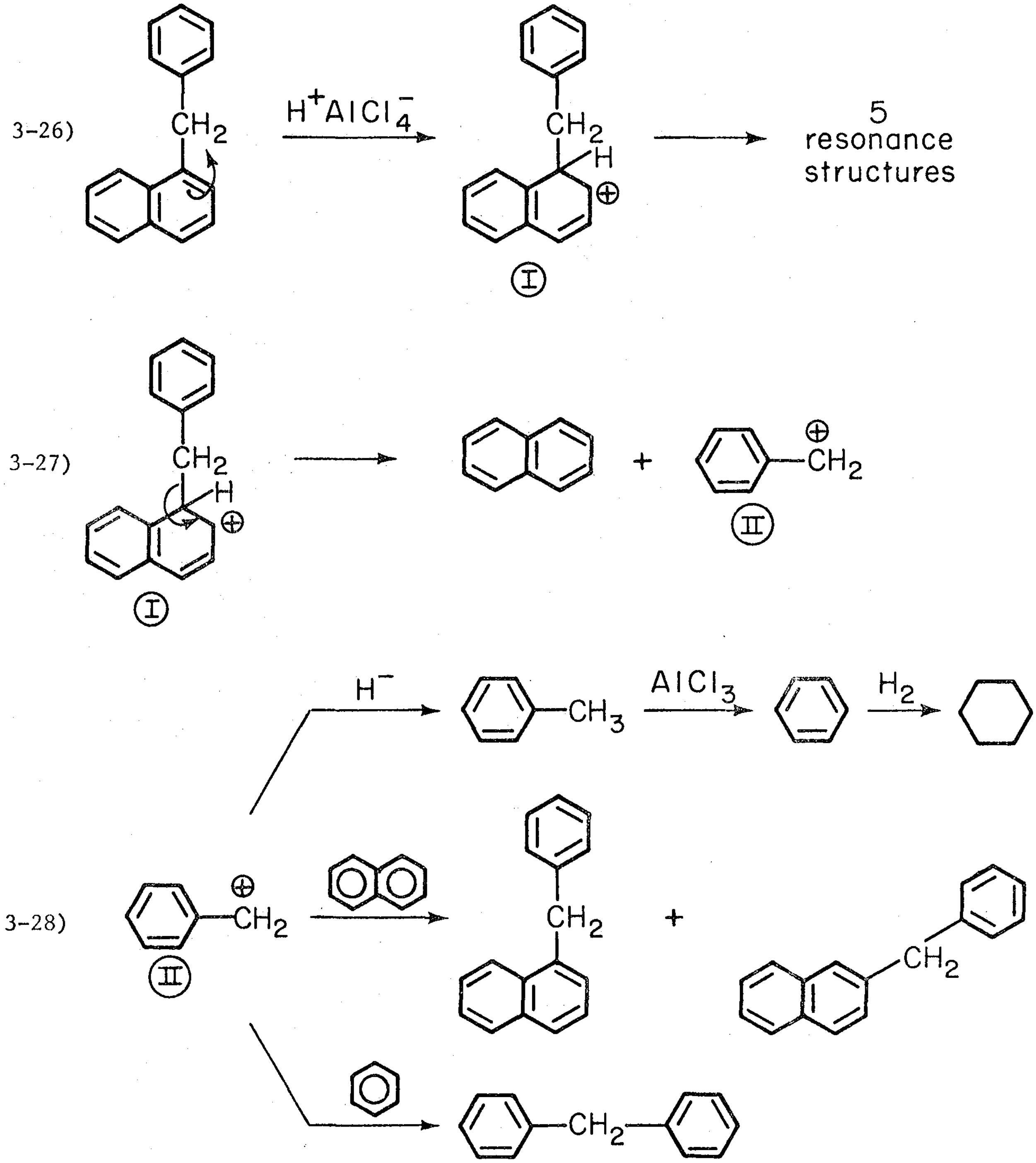

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Fig. 3-8. Mechanism of -1Benzylnaphthalene Cleavage.

at the α-position of naphthalene is the kinetically favored route because of resonance stabilization effects, yet β-attack yields the more thermodynamically stable isomer (3-38) because of less steric interaction between the naphthyl-phenyl hydrogens. Thus at sufficientl high temperatures it is possible to achieve an equilibrium mixture of isomers. The mole ratio of 2-BN/1-BN calculated from Table 3-26 is similar to reported results for $AlCl_3$-catalyzed isomerization of both benzylnaphthalene isomers (3-40).

The production of benzene, 1- and 2-methylnaphthalene in Run 52 indicates that protonation of 1-BN may also occur on the phenyl ring, the resulting benzyl naphthalenium ion cleaving to initially yield benzene and a 1-methylnaphthyl carbonium ion. The fact that these products appear in minor amounts indicates that this reaction pathway is a higher energy process relative to the mechanism yielding the major products. This observation can be explained on the basis of the kinetic arguments outlined above.

The mass balance for 1-BN in Table 3-27 again shows cyclohexane to be a major reaction product. Similar comments about this question apply here as were discussed for 1-PN. If 1-BN were to be cleaved to yield naphthalene and a benzyl cation, then the molar amounts of naphthalene and products derived from the benzyl cation should be the same. In the 1-BN mass balance for Run 52 in Table 3-27, however, the molar quantity of products assumed to be derived from the benzyl cation (cyclohexane, toluene, benzene, diphenylmethane) are over four times the molar quantity of naphthalene. Thus one can conclude that either cyclohexane is being produced from naphthalene or that a similar

GC analysis problem exists here as was suggested for 1-PN. In this case a high molecular weight compound not eluted from the GC might be produced by alkylation of the benzyl cation onto substrate. It is again doubtful, however, if such a polycyclic compound would be soluble in cyclohexane.

Table 3-28 compares the results of $ZnCl_2$- and $AlCl_3$-catalyzed reaction of 1-phenylnaphthalene and 1-benzylnaphthalene. These runs show the surprising result that $ZnCl_2$ effects moderate conversion of both substrates, whereas the same catalyst loading of $ZnCl_2$ did not catalyst any conversion whatsoever of their phenyl analogs (see Table 3-20). It should be noted, however, that the molar catalyst loading in the $ZnCl_2$ runs is substantially higher than in the $AlCl_3$ runs. Table 3-28 and the mass balances in Table 3-29 show that the reaction products and their relative distributions are essentially the same as in the $AlCl_3$ runs. This lends further credence to the argument that the active species for both catalysts are similar (i.e., a complex proton acid), and that the reaction mechanisms are identical. The $ZnCl_2$ results further suggest that replacement of a phenyl ring by a naphthyl group sufficiently increases the Lewis bascitity of these model compounds so that the naphthyl substrates are capable of abstracting a proton from the complex Lewis acid to initiate reaction.

Table 3-28

Cleavage of Aliphatic Bridges Between Naphthyl-Phenyl Nuclei - Comparison of Catalysts

Reaction Conditions

T = 325^{o}C
P = 1000 psig H_2 @ 325^{o}C.
t = 90 min. @ 325^{o}C.
= 1250 RPM

Reactants

Substrate - 0.0149 mole (Runs 43, 52)
- 0.0201 mole (Run 60)
- 0.0276 mole (Run 61)
Cyclohexane - 0.787 mole (Runs 43, 52)
- 0.470 mole (Run 60)
- 0.648 mole (Run 61)
$AlCl_3$ - 0.0011 mole (Runs 43, 52)
$ZnCl_2$ - 0.028 mole (Runs 60, 61)
- 0.041 mole (Run 61)

Run No.	43	61	52	60
Substrate	1-Phenylnaphthalene	1-Phenylnapthalene	1-Benzylnapthalene	1-Benzylnaphthalene
Catalyst	$AlCl_3$	$ZnCl_2$	$AlCl_3$	$ZnCl_3$
Substrate/Catalyst Mole Ratio	12.7	0.73	12.7	0.73
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	Trace	0.10	0.04	0.20
Methylcyclopentane	0.80	0.18	0.19	0.41
Cyclohexane	98.14	96.15	97.97	96.80
Benzene	0.07	---	0.55	0.15
Toluene	---	---	0.09	0.11
Naphthalene	0.01	---	0.82	0.38
2-Methylnapthalene	---	---	0.07	Trace
1-Methylnapthalene	---	---	0.01	Trace
Diphenylmethane	---	---	0.12	Trace
1-Phenylnaphthalene	0.10	3.06	---	---
Unknown	0.03	0.04	---	---
2-Phenylnaphthalene	0.83	0.48	---	---
1-Benzylnaphthalene	---	---	0.01	1.63
2-Benzylnapthalene	---	---	0.13	0.32
Heavy Unknowns	---	---	---	---
Substrate Conversion (%)	94	20	99	41
Reactants Recovered as Liquid Products (%)	94	95	98	95

Table 3-29

Mass Balances for 1-Phenylnaphthalene and 1-Benzylnaphthalene in $ZnCl_2$-Catalyzed Reactions

1. 1-Phenylnaphthalene (Run 61)

Compound	Wt. (gm.)	% Yield (wt.)
1-Phenylnaphthalene	4.64	82.4
2-Phenylnaphthalene	0.72	12.8
Minor Products	0.06	1.1
		96%

2. 1-Benzylnaphthalene (Run 60)

Compound	Wt. (gm.)	% Yield (wt.)
1-Benzylnaphthalene	2.60	59.2
Cyclohexane	0.92	21.0
2-Benzylnaphthalene	0.50	11.4
Naphthalene	0.21	4.8
Benzene	0.50	11.4
Toluene	0.04	0.9
		98%

These results have great significance in understanding the chemistry of $ZnCl_2$-catalyzed coal conversion. Since condensed polynuclear aromatic structures of 2-3 rings are the principal building blocks of the coal structure and are linked principally by aliphatic and ether linkages, it would thus appear than $ZnCl_2$ is capable of catalyzing cleavage of a substantial fraction of these alkyl linkages.

IV. Effects of Promoters on Lewis Acid Catalysts

A. Promotion of $AlCl_3$ with H_2O

Friedel-Crafts reactions are nearly always carried out in the presence of a co-catalyst or promoter, a substance present in very small amounts which activates the Lewis acid by proton or other cation formation. Evidence cited earlier suggests that trace amounts of a promoter such as H_2O are necessary for $AlCl_3$ to even exhibit any catalytic activity in many systems. It is therefore of interest to investigate the further addition of appropriate promoters to the Lewis-acid catalyzed reactions of this study.

Table 3-30 shows results of the reactions of bibenzyl in the presence of $AlCl_3$ where small amounts of H_2O were added to the reaction mixture as a co-catalyst. After the glass liner had been placed in the autoclave, the water was injected onto the side of the liner just before bolting the cover in place. In most instances the water therefore did not contact the organic reactants until stirring had begun. The low solubility of $AlCl_3$ in benzene at 25°C (0.1 gm. $AlCl_3$/100 gm. benzene, ref. 3-41) ensured that most of the $AlCl_3$ was sitting in the bottom of the liner. Even if the water did contact the benzene, it would have to fall through the solvent (about 13 cm.) before contacting the catalyst. The assumption therefore made was that the water did not react with the $AlCl_3$ until <u>after</u> the autoclave had been sealed, ensuring any HCl produced would remain in the reaction vessel.

The results of Table 3-30 show that the addition of water is essentially ineffective in promoting $AlCl_3$-catalyzed cleavage of bibenzyl. Even though the relative product distributions for the $AlCl_3/H_2O$

Table 3-30

Cleavage of Aliphatic Bridges Between Phenyl Rings

Reaction Conditions

T = 325°C.
P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

substrate - 0.0275 mole
Cyclohexane - 54.5 gm. (0.633 mole)
$ZnCl_2$ - 5.14 gm. (0.0377 mole)

Run No.	45	26	47	B-21
Substrate	Diphenylmethane	Bibenzyl	1,3-Diphenylpropane	No Substrate
Substrate/$ZnCl_2$ Mole Ratio	0.71	0.73	0.72	0.0
Product	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**
Light Aliphatics	0.15	Trace	---	0.76
Methylcyclopentane	0.08	0.18	Trace	0.53
Cyclohexane	95.65	95.85	96.71	98.71
Benzene	0.22	0.10	Trace	---
Toluene	Trace	---	---	---
Diphenylmethane	3.91	---	---	---
Bibenzyl	---	3.88	---	---
1,3-Diphenylpropane	---	---	3.29	---

Substrate Conversion (%)	0	0	0	---
Reactants Recovered as Liquid Products (%)	97	96	96	---

are the same as in the run without H_2O, substrate conversions are lower for each run where water was added. When the water loading reaches a large fraction of the catalyst loading as in Run 13, the low substrate conversion figure indicates the majority of the catalyst has been destroyed. These experiments seem to suggest, therefore, that if H_2O is indeed a co-catalyst for $AlCl_3$, then only trace amounts are required, much less than the minimum 9.5 μ·l added in Run 10. Such minute quantities of water would certainly be found on the walls of the autoclave body, on the stirring assembly, and inside the stirring assembly internals, even though great care was taken to eliminate all traces of water from the organic reactants. These results indicate that larger amounts of water only serve to deactivate the catalyst through hydrolysis or some other poisoning mechanism. It has been shown in similar systems (3-48) that the trace amounts of water required to activate the Lewis acid catalyst lie far below those concentrations normally reached by severe drying methods.

B. Promotion of $AlCl_3$ with Tertiary Hydride Donors

As discussed previously it has been proposed (3-18, 3-20) that a tertiary hydrocarbon could act as a catalytic hydrogen donor in the strong-acid catalyzed hydrogenolysis of benzene to hexanes. It is therefore of interest to determine whether the addition of a tertiary (3^o) hydrocarbon would enhance the $AlCl_3$-catalyzed cleavage of the aliphatic bridges in the model compounds studied here. Table 3-31 shows the effects of adding several tertiary hydride donors on the cleavage of bibenzyl. The addition of isopropanol presumably totally deactivated the catalyst either through complexation or through hydro-

Table 3-31

Cleavage of Bibenzyl with $AlCl_3$ and Tertiary Hydride Donors

Reaction Conditions

T = 225°C
P = 1000 psig H_2 @ 225°C.
t = 90 min. @ 225°C.
ω = 1250 RPM

Reactants

Bibenzyl - 14.0 gm. (0.0768 mole) - Runs 1, 14, 15, 20
Benzene - 17.6 gm. (0.225 mole) - Runs 14, 15, 20
- 61.5 gm. (0.787 mole) - Runs 1, B-7
3° Hydride Donor - 50 ml. (Runs 14, 15, 20)
$AlCl_3$ - 0.70 gm. (0.0052 mole)

Run No.	1	14	15	20	B-7
3° Hydride Donor	None	Isopentane	Isopropanol	2,3-Dimethylbutane	None
Donor/Bibenzyl Mole Ratio	0.0	5.62	8.25	5.04	0.0
Bibenzyl/$AlCl_3$ Mole Ratio	14.7	14.3	14.3	14.1	0.0
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	0.02	---	1.07	0.60	---
Isopentane	---	55.67	---	---	---
2,3-Dimethylbutane	---	---	---	55.90	---
Methylcyclopentane	0.02	---	1.83	---	Trace
Isopropanol	---	---	64.24	---	---
Benzene	90.75	35.77	24.80	36.71	99.68
Toluene	0.92	0.60	---	0.35	0.12
Ethylbenzene	1.75	1.75	---	1.42	0.15
Isopropylbenzene	0.18	0.33	---	0.09	---
n-Propylbenzene	0.07	0.19	---	Trace	---
n-Butylbenzene	0.01	0.26	---	Trace	---
Dicyclohexyl	0.19	0.21	---	0.05	---
Cyclohexylbenzene	0.02	---	---	Trace	---
Biphenyl	0.06	---	---	---	---
Diphenylmethane	0.11	---	---	Trace	0.04
Bibenzyl	5.46	4.22	7.97	4.48	0.01
Heavy Unknowns	0.38	0.45	---	0.28	---
Substrate Conversion (%)	27	48	0	48	---
Reactants Recovered as Liquid Products (%)	97	91	95	96	---

lysis by the water (0.2 wt. %) present in isopropanol. Substrate conversion figures in Table 3-31 show that isopentane and 2,3-dimethylbutane (DMB) both substantially increase conversion of bibenzyl over the run without hydride donor. Mass balances in Table 3-32 more accurately show the fate of the converted bibenzyl. Here it is seen that cleavage products (toluene, ethylbenzene) and tar formation are less with a 3^o hydride donor, yet the production of benzene increases from zero to a substantial fraction of the substrate. This indicates that the 3^o hydride donors have a dramatic effect on the cleavage reaction mechanisms. The lack of significant amounts of alkylated benzenes further suggests that the hydride donor is indeed acting as a catalyst rather than a reactant. The experimental results are consistent with the mechanism shown in Figure 3-3 for the cleavage of bibenzyl. It appears that the hydride donor is indeed reducing the phenylethyl cation shown in reaction 3-6, the resulting ethylbenzene being dealkylated to form benzene. The disappearance of diphenylmethane and the decrease in tar production in the hydride donor runs further suggest that the other reaction pathways for the phenylethyl cation (II, III) are much less favorable than reduction by the hydride donor. It is of further interest to note that conversion of substrate to benzene seems to be proportional to hydride donating ability of the hydrocarbon. DMB is a better hydride donor than isopentane because it has an additional methyl group to inductively stabilize the resulting 3^o carbonium ion. We indeed notice that an additional 8% of the original bibenzyl is converted to benzene using DMB, even though overall substrate conversion is the same for both isopentane and DMB.

Table 3-32

Bibenzyl Mass Balances - Tertiary Hydride Donor Reactions

Run No.	1	14	20
Hydride Donor	None	Isopentane	2,3-Dimethylbutane
Product (gm.)			
Bibenzyl	10.28	7.34	7.27
Toluene	0.65	0.39	0.21
Ethylbenzene	1.74	1.61	1.21
Tar	1.81	1.50	0.46
Benzene	0.0	3.51	4.64
Total Product Weight (gm.)	14.48	14.35	13.79
Bibenzyl Charged (gm.)	14.00	14.02	14.00
% Mass Balance	103%	102%	99%
Wt. % Bibenzyl Converted to Benzene	0.0%	25%	33%

Assumptions

1. All toluene and ethylbenzene come from substrate
2. All minor reaction products come from benzene and hydride donor.
3. All tar comes from substrate.

The use of low molecular weight, aliphatic hydride donors does have its problems both in these model compound studies and in coal conversion processes. In Run 14 with isopentane almost 4 gm. of the hydride donor was lost, presumably due to evaporation before and after reaction and during product work-up. The pressure after reaction for both hydride donor runs was 250 psig (25°C) greater than starting pressure, whereas Run 1 with no hydride donor exhibited no such pressure increase. This suggests that both hydride donors are cracking to yield gaseous products. Calculations based on the ideal gas law show that if isopentane

Table 3-33

Cleavage of Biphenyl with $AlCl_3$ and Tertiary Hydride Donor

Reaction Conditions

T = 325°C.
P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

Biphenyl - 11.84 gm. (0.0768 mole)
Cyclohexane - 66.2 gm. (0.787 mole)
[1]DMB - 6.62 gm. (0.0768 mole), Run 64
$AlCl_3$ - 0.70 gm. (0.0052 mole)

Run No.	48	64
[1]DMB/Biphenyl Mole Ratio	0.0	1.0
Diphenyl/$AlCl_3$ Mole Ratio	14.1	14.1
Product	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	4.28	3.78
2,3-Dimethylbutane	---	10.40
Methylcyclopentane	33.76	38.14
Cyclohexane	51.59	36.75
Methylcyclohexane	1.49	1.35
Unknown	---	0.90
Benzene	0.86	1.11
Ethylcyclohexane	0.14	0.17
Toluene	0.17	0.28
Ethylbenzene	0.06	0.14
Biphenyl	6.89	5.52
Heavy Unknowns	0.77	1.49
Substrate Conversion (%)	32	40
Reactants Recovered as Liquid Products (%)	94	95

[1] DMB = 2,3-Dimethylbutane

were cracked into two gaseous products (e.g., ethane and propane), the pressure increase approximately accounts for the missing 4 gm. of isopentane. Similar calculations hold true for Run 20 with DMB. For this run, however, only half as much hydride donor was lost, suggesting the lower vapor presure of DMB. Furthermore, Ross (1-47) has shown that in several cases the addition of a 3° hydride donor actually <u>decreases</u> coal conversion to soluble products in a $HCl/AlCl_3/H_2$ environment. He suggested that a sizeable fraction of the H_2 was being consumed in cracking of the hydride donor (DMB).

Table 3-33 shows results of the effect of DMB on conversion of biphenyl, the most difficult substrate to cleave. The concentration figures are not directly comparable due to the addition of DMB in Run 64. In addition, it should be noted that a tertiary hydride donor, methylcyclopentane, is already present in <u>both</u> runs due to isomerization of cyclohexane solvent. Substrate conversion figures in Table 3-33 and mass balances in Table 3-34 show that the addition of DMB does indeed catalyze additional conversion of substrate, with the production of benzene having doubled in Run 64.

Table 3-34

Biphenyl Mass Balances - Addition of Tertiary Hydride Donor

Compound	Wt. (gm.) Run 48	Wt. (gm.) [1]Run 64	% Yield (wt.) Run 48	% Yield (wt.) [1]Run 64
Biphenyl	8.07	7.15	68.0	60.2
Heavy Unknowns	1.55	1.93	13.1	16.3
Tar	1.52	1.60	12.8	13.5
Minor Products	0.66	0.37	5.6	3.1
Benzene	0.31	0.78	2.6	6.6
			102%	100%

[1] DMB added as 3° hydride donor.

C. Promotion of $AlCl_3$ and $ZnCl_2$ with HCl

Since the active catalytic species for $AlCl_3$ and $ZnCl_2$ is generally believed to be a complex proton acid such as $H^+AlCl_4^-$, it is therefore of interest to see if the concentration of such a species could be increased by the addition of a Brönsted acid such as gaseous, anhydrous HCl to the reaction system. In this sense HCl is acting as a promoter for the Lewis acid catalyst. If protonation to form a carbonium ion is indeed the initial step in Lewis-acid catalyzed cleavage reactions, then an increase in the Brönsted aciditiy should increase the reaction rate and overall substrate conversion.

Table 3-35 compares results for runs of bibenzyl and biphenyl with $AlCl_3$, both with and without addition of HCl. Substrate conversion figures show the disappointing result that HCl substantially decreases substrate conversion in both cases. The mass balances in Table 3-36, however, reveal some interesting differences in the HCl runs. HCl seems to suppress tar formation in both cases yet enhance the production of cyclohexane. The reduction of benzene to cyclohexane in the presence of a strong acid system such as $AlCl_3$/HCl is in agreement with the results of Siskin (3-18) and Wristers (3-19) who studied this reaction with a variety of similar acid systems.

Table 3-35

Cleavage of Aliphatic Bridges Between Phenyl Rings with $AlCl_3$/HCl

Reaction Conditions

T = 325°C.
P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C
ω = 1250 RPM

Reactants

substrate - 0.0768 mole
Cyclohexane - 66.2 gm. (0.787 mole)
$AlCl_3$ - 0.70 gm. (0.0052 gm.)

Run No.	48	63	50	65
Substrate	Diphenyl	Diphenyl	Bibenzyl	Bibenzyl
HCl (psig @ 25°)	0.0	500	0.0	400
HCl/$AlCl_3$ Mole Ratio	0.0	51.4	0.0	41.9
Substrate/$AlCl_3$ Mole Ratio	14.1	13.9	14.7	14.2
Product	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**	**Conc. (Mole %)**
Light Aliphatics	4.28	0.96	0.45	0.62
Methylcyclopentane	33.76	23.71	9.52	4.49
Cyclohexane	51.59	66.92	80.62	86.17
Methylcyclohexane	1.49	---	0.13	---
Benzene	0.86	Trace	5.74	3.60
Ethylcyclohexane	0.14	---	---	---
Toluene	0.17	---	0.25	0.14
Ethylbenzene	0.06	---	1.14	0.67
Isopropylbenzene	---	---	Trace	Trace
n-Propylbenzene	---	---	Trace	Trace
n-Butylbenzene	---	---	0.03	Trace
Biphenyl	6.89	8.26	---	---
Bibenzyl	---	---	1.80	3.97
Heavy Unknowns	0.77	0.15	0.33	0.35

Substrate Conversion (%)	32	20	76	48
Reactants Recovered as Liquid Products (%)	94	92	91	91

Table 3-36

Mass Balances for Biphenyl and Bibenzyl - $AlCl_3$/HCl Runs

1. Biphenyl (Runs 48, 63)

Compound	Wt. (gm.) Run 48	Wt. (gm.) Run 63(HCl)	% Yield (wt.) Run 48	% Yield (wt.) Run 63(HCl)
Biphenyl	8.07	9.50	68.0	79.9
Heavy Unknowns	1.55	0.17	13.1	1.4
Tar	1.52	----	12.8	0.0
Minor Products	0.66	----	5.6	0.0
Benzene	0.31	----	2.6	0.0
Cyclohexane	----	2.66	0.0	22.4
			102%	104%

2. Bibenzyl (Runs 50, 65)

Compound	Wt. (gm.) Run 50	Wt. (gm.) Run 65(HCl)	% Yield (wt.) Run 50	% Yield (wt.) Run 65(HCl)
Cyclohexane	3.83	3.39	27.4	24.2
Benzene	3.66	2.25	26.1	16.1
Bibenzyl	3.36	7.26	24.0	51.9
Tar	1.60	----	11.4	----
Ethylbenzene	1.12	0.65	8.0	4.6
Heavy Unknowns	0.62	0.63	4.4	4.5
Minor Products	0.20	0.04	1.4	0.6
			103%	102%

Table 3-37 contains results of the effect of HCl on $ZnCl_2$-catalyzed cleavage of 2-hydroxydiphenylmethane (2-HDPM). Comparison of Runs 46 and 66 shows that $ZnCl_2$/HCl is capable of complete conversion of 2-HDPM, whereas $ZnCl_2$ alone catalyzes conversion of only 63% of the substrate. Comparison of Runs 66 and 67 shows, however, that the role of HCl as a promoter is unclear, since HCl alone also catalyzes 100% conversion of 2-HDPM. The mass balances in Table 3-38 show the interestng result that the relative product distributions are different for the $ZnCl_2$/HCl run (66) and the HCl run (67). The benzyl cation produced in the HCl-catalyzed cleavage of 2-HDPM (Run 67) appears

Table 3-37

Cleavage of 2-Hydroxydiphenylmethane with $HCl/ZnCl_2$

Reaction Conditions

T = 325°C.
P = 1000 psig H_2 @ 325°C.
t = 90 min. @ 325°C.
ω = 1250 RPM

Reactants

Substrate - 0.0275 mole
Benzene - 61.5 gm. (0.787 mole)
$ZnCl_2$ - 5.14 gm. (0.0377 mole)
(Runs 46, 66)

Run No.	46	66	67
$ZnCl_2$/Substrate Mole Ratio	1.33	1.37	0.0
HCl (psig @ 25°C)	0.0	400	400
$HCl/ZnCl_2$ Mole Ratio	0.0	5.57	---
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	Trace	0.30	0.15
Benzene	97.72	92.10	93.36
Toluene	0.11	2.08	1.26
Ethylbenzene	0.03	1.01	0.06
Isopropylbenzene	---	0.30	0.28
n-Propylbenzene	---	0.10	---
t-Butylbenzene	---	0.11	0.25
Phenol	0.69	1.67	3.08
o-Cresol	---	0.10	Trace
p-Cresol	---	0.16	0.13
Diphenylmethane	0.22	2.06	1.44
2-Hydroxydiphenylmethane	1.23	---	Trace
Phenol/Toluene Mole Ratio	6.3	0.80	2.4
Substrate Conversion (%)	63	100	100
Reactants Recovered as Liquid Products (%)	99	88	---

to follow pathways producing mainly diphenylmethane and tar. Yet in Run 66 with $ZnCl_2$/HCl the benzyl cation yields mainly diphenylmethane and toluene with no tar formation at all.

Table 3-38

2-Hydroxydiphenylmethane Mass Balances: $ZnCl_2$/HCl Runs

Compound	Wt. (gm.) Run 66 ($ZnCl_2$/HCl)	Wt. (gm.) Run 67 (HCl)	% Yield (wt.) Run 66 ($ZnCl_2$/HCl)	% Yield (wt.) Run 67 (HCl)
Diphenylmethane (54%)	1.63	1.08	30.6	19.9
Toluene	1.29	0.74	24.2	13.7
Phenol	1.10	1.93	20.7	35.6
Ethylbenzene	0.89	0.05	16.7	0.9
Propylbenzenes	0.34	0.22	6.4	4.1
Cresols	0.17	0.08	3.2	1.5
Butylbenzenes	0.10	0.22	1.9	4.1
Tar	----	1.01	----	18.6
			104%	98%

It should be noted that a minor modification was made in the assumptions used to make the mass balances in Table 3-38. In the production of diphenylmethane in this system it is obvious that the benzyl fraction (54 wt. % of diphenylmethane) comes from the substrate and the phenyl fraction (46 wt. % of diphenylmethane) from the benzene solvent. Since diphenylmethane is by far the major product (3.02 gm.) in Run 66 and the second most abundant (2.00 gm.) product in Run 67, it was necessary to correct for that fraction of diphenylmethane which comes from the solvent. For this reason only 54% of the diphenylmethane produced in each reaction is attributed to the substrate. As seen in Table 3-38 this modification again produces mass balances on the substrate within ±5%.

Since complete conversion of 2-HDPM could be effected by both $ZnCl_2$/HCl <u>and</u> HCl alone, it was desired to study the promotional effect of HCl on $ZnCl_2$ for a substrate which $ZnCl_2$ alone could not cleave. Table 3-39 shows the results of bibenzyl conversion catalyzed by $ZnCl_2$/HCl. $ZnCl_2$ alone has no effect on bibenzyl, yet $ZnCl_2$/HCl is seen to catalyze 39% conversion of this substrate. The mass balance for Run 68 in Table 3-40 shows that the reaction products are similar to those obtained with $AlCl_3$-catalyzed conversion of bibenzyl, with ethylbenzene and benzene seen to be the major products. This again suggests that the $ZnCl_2$/HCl-catalyzed reactions proceed by mechanisms similar to the $AlCl_3$ reactions. Compared to the mass balance for the $AlCl_3$/HCl run (Run 65, Table 3-40), $ZnCl_2$/HCl is seen to produce no cyclohexane from benzene formed on conversion of substrate, indicating that $ZnCl_2$/HCl is a milder catalyst system than $AlCl_3$/HCl and possesses no hydrogenation capabilities. It should also be noted that HCl appears to inhibit tar production when used in conjunction with a Lewis acid, yet yields substantial amounts of tar when used alone as a catalyst (Table 3-38).

Table 3-39

Cleavage of Bibenzyl with HCl/$ZnCl_2$

Reaction Conditions	Reactants
T = 325°C.	Bibenzyl - 0.0277 mole
P = 1000 psig H_2 @ 325°C.	Cyclohexane - 54.5 gm. (0.633 mole)
t = 90 min @ 325°C.	$ZnCl_2$ - 5.14 gm. (0.0377 mole)
ω = 1250 RPM.	

Run No.	26	68
HCl (psig @ 25°C)	0.0	400
HCl/$ZnCl_2$ Mole Ratio	0.0	5.8
Substrate/$ZnCl_2$ Mole Ratio	0.73	0.69
Product	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	Trace	10.53
Methylcyclopentane	0.18	6.77
Cyclohexane	95.85	76.20
Methylcyclohexane	-----	0.63
Unknown	-----	0.52
Benzene	0.10	1.14
Ethylcyclohexane	-----	0.08
Toluene	-----	0.55
Ethylbenzene	-----	0.97
Isopropylbenzene	-----	0.05
n-Propylbenzene	-----	0.15
t-Butylbenzene	-----	0.14
n-Butylbenzene	-----	0.05
Bibenzyl	3.88	2.25
Substrate Conversion (%)	0.0	39

Table 3-40

Bibenzyl Mass Balances for HCl-Promoted Runs

Compound	[1]Wt. (gm.)		% Yield (wt.)	
	Run 68($ZnCl_2$)	Run 65($AlCl_3$)	Run 68($ZnCl_2$)	Run 65($AlCl_3$)
Cyclohexane	-----	3.39	-----	24.2
Bibenzyl	3.11	7.26	61.2	51.9
Ethylbenzene	0.71	0.65	14.0	4.6
Benzene	0.53	2.25	10.4	16.1
Heavy Unknowns	-----	0.63	-----	4.5
Minor Products	0.30	-----	5.9	-----
Toluene	0.28	0.09	5.5	0.6
			97%	102%

[1] Different weights of substrate were used in these reactions. Weight figures are therefore not directly comparable. See Tables 3-35 and 3-39.

The results of Table 3-39 unfortunately are not unequivocal concerning the promotional effect of HCl on $ZnCl_2$. Equipment difficulties prevented running the control reaction of bibenzyl catalyzed by HCl alone. Thus it is not certain whether HCl is truly promoting the activity of $ZnCl_2$ or whether HCl alone is capable of catalyzing 39% conversion of bibenzyl (See Run 68, Table 3-39).

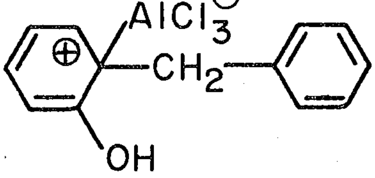
The reason for apparent deactivation of $AlCl_3$ by HCl is not readily apparent and the results using HCl as a promoter in Lewis-acid catalyzed coal conversion research are conflicting. Zielke (3-43) has reported that the addition of HCl to a $ZnCl_2$ melt inhibits coal conversion by slowing down the reaction and forming more char. Larsen (3-44) proposes that inhibition of liquefaction by HCl is caused by competition between $ZnCl_2$ and HCl for the organic oxygen and nitrogen bases in coal. He postulates that $ZnCl_2$ does not catalyze coal conversion by carbonium ion mechanisms as proposed in this study, but rather that $ZnCl_2$ forms complexes with the nitrogen and oxygen bases in coal. These complexes are thought to be hydrogen transfer agents which bring about the rapid hydrogenation and hydrogenolysis of coal. This type of reaction, however, could not be operative with biphenyl and bibenzyl substrates since they contain no oxygen or nitrogen. Larsen (3-44) admits that other mechanisms must be operative with $ZnCl_2$, since pyrene, a four-ring condensed aromatic hydrocarbon, is known (3-45) to be hydrocracked by $ZnCl_2$. Zelke (3-45) also found that the addition of HCl <u>inhibited</u> $ZnCl_2$-catalyzed conversion of pyrene by favoring coke production. No explanation for this observation was given, even though the author proposed that the active catalytic species is a complex proton acid such as $H^+ ZnCl_2OH^-$ and that hydrocracking proceeds via carbonium ion mechanisms similar to those proposed here. It is possible that HCl is indeed enhancing the cracking ability of $ZnCl_2$ but that carbonium ions are being formed so rapidly from bond scission that they polymerize with the substrate before being reduced by a hydrogen source. Such an explanation, however, is not applicable to these runs with biphenyl and bibenzyl since the mass balances in Table 3-36 show that the use of HCl greatly <u>reduces</u> tar formation.

Ross (3-46) has studied the effect of HCl on $AlCl_3$-catalyzed conversion of coal to pyridine- and THF-soluble extracts. He found that at 190° no additional HCl was necessary for coal hydrocracking, but that added HCl did not inhibit reaction or decrease conversion. Apparently the presence in coal of proton sources such as phenolic groups and trace amounts of water could hydrolyze some of the $AlCl_3$

to produce sufficient HCl. On the other hand, experiments at 210°C clearly showed that added HCl substantially increased conversion, suggesting that the active catalytic species contains elements of $AlCl_3$ and HCl.

Inspection of Table 3-35 shows that $AlCl_3/HCl$ gives the same reaction products with biphenyl and bibenzyl as does $AlCl_3$ alone. Comparison of Tables 3-39 and 3-12 reveals that $AlCl_3$ and $ZnCl_2/HCl$ also yield the same reaction products on conversion of bibenzyl. Inspection of Table 3-37 shows that $ZnCl_2$, $ZnCl_2/HCl$, and HCl all give the same products when used as catalysts for cleavage of 2-HDPM. These results offer very strong evidence that the Lewis-acid catalyzed reactions discussed in this investigation do indeed proceed via carbonium ion mechanisms initiated by protonation of the substrate. A Brönsted (proton) acid such as HCl can exhibit no Lewis acid characteristics and can initiate reaction only by protonation. The fact that $AlCl_3$ and $ZnCl_2$ both give the same products as does HCl on reaction of 2-HDPM is a necessary but not sufficient condition that the Lewis-acid catalyzed reactions are proceeding via the same mechanistic pathways as are the Brönsted (HCl) reactions. It is possible that a Lewis acid could attack an aromatic ring of a substrate directly to form the complex shown below,

3-29)



This species would then react similarly to the mechanisms shown above but its formation involves no complex proton acid ($H^+AlCl_4^-$, $H^+AlCl_3OH^-$, etc.). If the $AlCl_3$ complex were formed faster than the corresponding protonated benzenonium ion, and both reacted to give the same products, then the addition of HCl would force the reaction to proceed via the slower protonation mechanism. This would account for the reduction in substrate conversion, assuming reaction had not had time to reach thermodynamic equilibrium.

The overwhelming majority of the organic chemistry literature (3-47) on this topic, however, supports the idea that the active catalytic species in Lewis acid systems is indeed a complex proton acid. It is nevertheless clear from both this work and the cited literature that the results of HCl-promoted, Lewis-acid catalyzed coal conversion work are contradictory, and that the promotional effect of Bronsted acids such as HCl on Lewis acid catalysts is uncertain. This would be a fruitful area for further investigation, not only as an attempt to find a co-catalyst for a successful coal conversion catalyst such as $ZnCl_2$, but also in order to achieve a better understanding of the active catalytic species and mechanisms operative in these systems. The results of the HCl experiments cannot be readily explained on the basis of the mechanisms proposed in this study, and suggest that the Lewis acid catalyst systems are more complex than presently thought.

V. Other Methods of Cleaving Aliphatic Bridges

A. Cleavage of Bibenzyl with Organic Bases

It has been proposed (3-54) that organic bases may effect dissolution of coal in processes similar to those in which hydrogen donor solvents such as tetralin are used. Catalytica Associates (1-33) in their study of new catalytic materials for coal liquefaction also surveyed the use of organic and inorganic bases. In this study potassium t-butoxide and potassium methoxide were chosen as representative common organic bases to see if such materials could cleave aliphatic bridges. It should be emphasized, however, that this reaction was not intended to be catalytic in nature. In this case the base is actually acting as a reagent.

Table 3-41 shows results for the reaction of bibenzyl with the aforementioned bases. When used at a molar loading equivalent to that of $AlCl_3$ in previous runs, potassium t-butoxide is seen in Run 36 to be ineffective for the conversion of bibenzyl. In Run 37 where the bibenzyl/base mole ratio has been decreased to 1.0, however, 20% of the substrate is seen to be converted to other products. Run B-18 is a blank run carried out in the absence of bibenzyl. Comparison of these last two runs seems to suggest that toluene and biphenyl are the main reaction products. Experimental difficulties in recovering reaction products, however, prevented the determination of an accurate mass balance, so it is impossible to positively account for the converted bibenzyl.

Table 3-41

Cleavage of Bibenzyl with Organic Bases

Reaction Conditions	Reactants
T = 325°C.	Bibenzyl - 14.00 gm. (0.0768 mole)
P = 1000 psig H_2 @ 325°C.	Benzene - 61.5 gm. (0.787 mole)
t = 90 min. @ 325°C.	Base - Variable Loadings
ω = 1250 RPM	

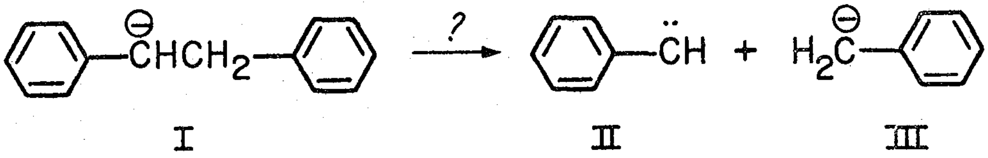
Run No.	36	[a] 37	[a] B-18	[a] 38
Base	Potassium t-Butoxide	Potassium t-Butoxide	Potassium t-Butoxide	Potassium Methoxide
Bibenzyl/Base Mole Ratio	14.7	1.00	0.0	0.99
Product	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)	Conc. (Mole %)
Light Aliphatics	0.13	0.50	---	---
Cyclohexane	---	---	0.04	Trace
Benzene	91.13	87.84	99.65	91.42
Toluene	---	3.91	---	0.04
Ethylbenzene	---	0.22	---	---
n-Propylbenzene	---	0.03	---	---
Biphenyl	---	1.45	0.19	---
Bibenzyl	8.74	6.05	0.12	8.55
Substrate Conversion (%)	0	20	---	0
Reactants Recovered as Liquid Products (%)	97	91	---	90

[a] Substantial gas formation in these reactions. Initial cold pressure 500 psig; final cold pressure 600 psig. See text for explanation.

The effect of base strength on bibenzyl conversion was investigated in Run 38 using potassium methoxide as an analogous but weaker base (3-55). This run shows that a weaker base is incapable of promoting reactions of bibenzyl.

The reaction of organic bases with bibenzyl would involve an entirely different type of mechanism than Lewis-acid catalyzed cleavage reactions. Whereas a Lewis acid would initiate reaction by protonation of an aromatic ring at the 1-position, an alkoxide ion would abstract a benzylic proton to yield t-butanol and the following carbanion,

3-30)



This type of reaction would thus be governed by the nature of nucleophilic carbon rather than that of electrophilic carbon characteristic of carbonium ion mechanisms. If species I were to cleavage as indicated to yield II and III , these two species could then conceivably be reduced by hydrogen to toluene, which is noted to be the major product in Run 37. Vollhardt (3-31) has suggested, however, that such a mechanism is unlikely in this system because of the high instability (i.e., high activation energy of formation) of the resultant carbene (II). He further suggests that the observed toluene is produced through a series of reactions between the t-butoxide anion and the benzene solvent. Nevertheless, the disappearance of 20% of the substrate indicates that t-butoxide is indeed effecting some sort of bibenzyl conversion.

It is of further interest to note that no t-butanol whatsoever was found in the product mixture. The alcohol would be formed from t-butoxide by the proposed proton abstraction from bibenzyl. This fact and the large amounts of gas production noted in Table 3-41 suggests that any t-butanol formed is dehydrated to isobutylene (B.P. - 7°C).

B. Oxidation with NaOCl

Chakrabartty *et. al.* (3-56, 3-57, 3-58, 3-59) have published a series of papers describing of aqueous sodium hypochlorite (NaOCl) oxidation of coal structure. Their scheme is supposed to discriminate between aliphatic (sp^3) and aromatic (sp^2) carbon, the former being oxidized to give aliphatic acids and the latter being impervious to NaOCl oxidation. By analyzing the products of coal oxidation by NaOCl one can thereby deduce the relative abundance of aromatic and hydroaromatic structures in coal.

To briefly examine this scheme in our work, bibenzyl dissolved in benzene was reacted in the presence of aqueous NaOCl at 325°C for 90 minutes under a H_2 atmosphere (Run 33). The NaOCl solution was the same as that used by Chakrabartty, a 5.25 wt. % aqueous solution sold as household bleach. As predicted, the bibenzyl was recovered totally unreacted, lending credence to Chakrabartty's hypothesis. Mayo (3-60) has criticized the assumptions of this method, however, pointing out the fact that success of NaOCl oxidations is highly sensitive to NaOCl/substrate mole ratio and to reaction medium pH, acidic solutions being found to cause rapid destruction of NaOCl by disproportionation. He concluded that the selectivity and utility of this reagent is still uncertain, and that Chakrabartty's conclusions are not necessarily correct.

C. Hydrogenolysis of Model Compounds by Solid Acid Catalysts

Solid-supported mixed metal oxides have long been used in petroleum refining as cracking and hydrogenation catalysts. Typically one metal oxide serves as the cracking catalyst, while the other possesses hydrogenation capabilities. It is of interest to question whether such catalysts might be applicable to coal liquefaction processes. Tanner (1-34) has surveyed the use of such catalysts in catalytic conversion of solvent refined coal (SRC) to liquid products. It was desired in this study to briefly examine the utility of such catalysts in cleaving the aliphatic bridges of these model compounds.

The two catalysts chosen for investigation in this study were $NiO-WO_3$ supported on Al_2O_3 and $NiO-MoO_3$ similarly supported. (See Table 2-1 for compositions and sources.) Tanner (3-61) found these two catalysts to be most effective among those surveyed in increasing solubility of SRC. Five grams of each catalyst were reacted with 5 gm. of bibenzyl under 1000 psig H_2 for 90 minutes, in runs at both 225°C and 325°C. (Runs 24, 25, and 22 - the $NiO-MoO_3$ catalyst was run at 325°C only.) In all runs the mixed metal catalysts were found to be totally ineffective in promoting any reaction of bibenzyl whatsoever. This is in agreement with Tanner (3-62) who found that the mixed metal oxides are all relatively inactive for promoting the hydrogenation and solubilization of SRC. Both Tanner's and the present results may well stem from the fact that these catalysts are most often used in industrial processes at temperatures in excess of 400°C and in the sulfided form, neither of which conditions were met in these experiments.

D. Potassium Isopropoxide as Hydride Donor

The use of tetralin and similar hydrogen-donor solvents in coal conversion schemes is well known (3-63). Ross (3-54) has found that isopropanol and the isopropoxide anion in isopropanol can also act as hydrogen donors, yielding products similar to those generated in tetralin-based systems. The following type of mechanism is envisioned:

3-31) $^{-}OCH(CH_3)_2 + \text{Coal} \qquad O{=}C(CH_3)_2 + \text{Coal H}^{-}$

3-32) $\text{Coal H}^{-} + HOCH(CH_3)_2 \qquad \text{Coal H}_2 + {}^{-}OCH(CH_3)_2.$

This mechanism is analogous to the known Meerwein - Pondorff (3-64) reduction of carbonyl gropus with isopropoxide salts in isopropanol. Ross (3-54) has demonstrated that treatment of coal with aluminum and potassium isopropoxide salts in isopropanol markedly increases pyridine extractibility and increases the H/C ratio and suggests that isopropoxide is acting as a hydride donor.

Potassium isopropoxide in isopropanol was used in several runs to investigate its ability to promote cleavage of bibenzyl by hydride donation. The desired amount isopropoxide salt was prepared _in situ_ by reacting potassium metal with reagent grade isopropanol. After evolution of H_2 gas had ceased the other reagents were added. In all such runs the reagents consisted of 14 gm. bibenzyl, 20 ml. benzene, 50 ml. isopropanol, and 2.80 gm. potassium isopropoxide, the bibenzyl/alkoxide weight ratio being equivalent to that used by Ross. The benzene was added to ensure solubility of all organic reaction products. Other reaction conditions were $225^{\circ}C$, 90 minutes, and 1000 psig H_2.

Run 19 with isoproxide in isopropanol and bibenzyl showed no conversion of substrate at all. The addition of 0.70 gm. $AlCl_3$ in Run 18 yielded the same results. Run 29 repeated the conditions of Run 19, except the temperature was increased to $325^{\circ}C$. Again no reaction of bibenzyl was observed. It was concluded that hydride donation by isopropoxide was ineffective in this system, suggesting that Ross' scheme must be attacking structure in coal other than aliphatic bridges between aromatic ring systems.

CHAPTER IV - CONCLUSIONS

This work has shown that $AlCl_3$ is an effective catalyst for promoting cleavage of aliphatic linkages between aromatic nuclei. The cleavage of such bridges is a function of the strength of the Lewis acid catalyst, since $AlCl_3$ was found to effect cleavage of all the diphenylalkane substrates, whereas $ZnCl_2$ was totally inactive with compounds. The results were explained on the basis of carbonium ion mechanisms where the initial step involves protonation of the substrate complex Bronsted acid such as $H^+AlCl_4^-$, $H^+AlCl_3OH^-$, etc. The number of carbon atoms in the aliphatc bridge was also shown to affect substrate conversion, with substrates containing an odd (1,3) number of carbons exhibiting greater conversion than those with an even (0,2,4) number. Direct aryl-aryl bonds such as present in biphenyl were found to be the most difficult to cleave. These results were explained on the basis of the relative stbilities of carbonium ion reaction stabilities of carbonium ion reaction intermediates, indicating that the reaction are kinetically controlled.

Aromatic hydroxyl substituents and naphthyl end groups were both found to enhance substrate conversion with $AlCl_3$ catalyst. Whereas $ZnCl_2$ was totally inactive in catalyzing cleavage of the diphenylalkanes, it was found to effect moderate conversion of the hydroxyl and naphthyl analogs. These results suggest that the hydroxyl and naphthyl groups can stabilize reaction intermediates through increased resonant charge delocalization not possible in their diphenylalkane analogs. The $ZnCl_2$ experiments indicate that these groups sufficiently increase the basicity of the substrate to permit it to abstruct a proton from the complex Bronsted acid.

The role of the gaseous H_2 in the reaction mechanisms was investigated by running identically reactions under both H_2 and N_2 atmospheres. The results showed that gas-phase H_2 does play a role in reducing reaction intermediates, since substrate conversion was higher under a H_2 atmosphere for several substrates. The results were ambiguous, however, since some substrates exhibited identical conversion under both H_2 and N_2 atmospheres. The fact that substantial conversion occurs for all substrtes under N_2 indicates that most of the hydrogen needed to stabilize reaction intermediates comes from the reaction medium itself. Possible hydrogen sources include disproportionation of the substrate and Scholl-type condensation reactions of aromatics.

The choice of solvent was also found to have an effect on substrate conversion, with all conversions being higher in cyclohexane. This fact was rationalized on the basis of two obsevations. First, $AlCl_3$ is known to complex with benzene and thus reduce its activity toward the substrate. An aliphatic solvent such as cyclohexane cannot form such aromatic complexes. Second, carbonium ion intermediates can react with benzene solvent to form the initial substrate, whereas reaction intermediates in cyclohexane cannot participate in electrophilic substitution reaction with the solvent to regenerate the original substrate.

Several approaches were studied for promoting the activity of the Lewis acid catalyst through addition or in situ formation of a co-catalyst. The addition of small amounts of water was found to be totally ineffective, reducing substrate conversion in all cases.

Saturated hydrocarbons serving as tertiary hydride donors were found to be moderately effective in increasing substrate conversion, and were especially effective in reducing cleavage products to benzene. This scheme appears to be a possible method of activating gas-phase H_2 in coal liquefaction processes, although their use was found to have several drawbacks. A substantial fraction of the added hydrocarbon was lost to a combination of hydrocracking during reaction and evaporation during product work-up.

The addition of anhydrous HCl as a co-catalyst to $AlCl_3$ and $ZnCl_2$ systems was found to be of questionable utility. Substrate conversion in $AlCl_3$/HCl runs was lower in all cases compared to the corresponding $AlCl_3$ run. No satisfactory explanation was found although several possibilities are presented. $ZnCl_2$/HCl was found to effect complete conversion of several substrates, but the promotional effect of HCl on $ZnCl_2$ is uncertain since HCl alone was seen to produce the same results.

Several other schemes for effecting cleavage of aliphatic bridges were investigated but yielded negative results. Attempted cleavage of substrates by treatment with organic bases was unsuccessful and yielded only solvent reaction products. Mild oxidation of substrates using NaOCl, although not a catalytic process, was also found to be totally ineffective. Several solid-supported, mixed metal-oxide catalysts were similarly determined to be ineffective in promoting substrate cleavage, probably because temperatures used in this study are at least 100°C below those at which these catalysts become effective.

This work allows one to gain a better understanding of the effects of $ZnCl_2$ on the depolymerization and liquefaction of coal. $ZnCl_2$ appears to be incapable of catalyzing cleavage of a substantial fraction of the aliphatic bridges in coal.

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