FE-2305-18
Distribution Category UC-90

INVESTIGATION OF MECHANISMS OF HYDROGEN TRANSFER IN COAL HYDROGENATION

Phase I Final Report
for July 1976 to December 1977

D. C. Cronauer
D. M. Jewell
Y. T. Shah
R. J. Modi

GULF RESEARCH & DEVELOPMENT COMPANY
P. O. Drawer 2038
Pittsburgh, Pennsylvania 15230

GR&DC Contract No. 621CE014
File FT07

Date Published February 1978

MASTER

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

Under Contract No. E(4918)2305

INVESTIGATION OF MECHANISMS OF HYDROGEN TRANSFER IN COAL HYDROGENATION: E(49-18)-2305

Phase I Final Report
for July, 1976 to December, 1977

Report Outline

Illustrations

Illustrations (cont'd) Page

Illustrations (cont'd) Page

Illustrations (cont'd) Page

Tables

PHASE I FINAL REPORT FOR THE PERIOD OF
JULY 1976 TO DECEMBER 1977

ABSTRACT

The objective of this study is to develop an understanding of the mechanism of hydrogen transfer to coal and intermediates during liquefaction. This report is issued to describe experimentation and results of the first phase of the study. Emphasis was placed upon hydrogen-transfer reactions of model compounds representative of structural moieties present in or produced from coal at conditions comparable to those used in coal liquefaction.

Screening experiments were first undertaken to determine the relative ease of fragmenting C-C, C-N, C-O, and C-S bonds in the presence of a hydrogen-donor solvent. Condensed aromatics, such as benzofuran, were stable at temperatures up to 475°C. Non-condensed aromatics, such as dibenzyl, fractured in the range of 400-475°C. Dibenzyl ether, aromatic sulfides, and compounds having carbonyl and alcohol groups reacted readily at temperatures below 425°C.

Detailed experimentation using various donors with dibenzyl indicates that the thermal reaction of dibenzyl forming benzyl radicals is rate controlling. The reaction rate is independent of the donor solvent (tetralin, decalin, mesitylene), but the product distribution is dependent upon the type of solvent. Hydroaromatics donor solvents such as tetralin rearranged to form methyl indane-type compounds thereby resulting in a solvent of reduced hydrogen donor capacity.

Experiments with hetero compounds indicated that the relative order of reactivity is the following: furans < phenols < ketones < aldehydes < chain benzyl ethers < thioethers. Before a multiple bonded oxygen or sulfur atom can be removed as a gas (H_2O or H_2S), it must be reduced to a C-O or C-S form. This reduction is usually fast at temperatures of 300-375°C. To cleave the C-O or C-S bond for removal, higher temperatures are necessary.

The study of hydrogen transfer using either a deuterium atmosphere or deuterium-tagged donor was not successful at temperatures above 400°C due to scrambling. Experimentation at lower temperatures with heteroatom containing compounds was successful. It was shown that essentially all of the hydrogen added to the cleaved acceptor comes from the donor solvent or via intramolecular rearrangement and not from dissolved hydrogen. Dissolved hydrogen does serve the role of re-hydrogenating the hydrogen depleted donor solvent.

OBJECTIVE AND SCOPE OF WORK

The overall objective of this study is to develop an understanding of the mechanism of hydrogen transfer to coal during coal liquefaction. This is being done using both tagged and untagged compounds as donors and acceptors. The tagged compounds include those containing stable (^{13}C and deuterium) or radioactive (^{14}C and tritium) isotopes. In addition, it includes those compounds having functionality that allows for isolation by extraction, for example, tetrahydroquinoline. Experimentation is being done at conditions consistent with processes currently being developed to liquefy coal.

The project is divided into two 18-month phases, the first covering the study of model compounds and the second consisting of the application of these results to the study of coal and coal-derived liquids. The first stage (six months) of Phase I consisted of preparatory work and experimentation relevant to the testing of analytical techniques and determining the scope of reaction conditions for subsequent experimentation.

Two research areas are being covered concurrently in Stage 2. The primary area consists of in-depth experimentation of selected acceptors with a series of donors (with and without tags). Sufficient experimentations are being carried out with each acceptor to develop a kinetic model of the transfer reaction. The second area consists of investigating background or scrambling reactions which may interfere with the above results.

The following is a summary of the tasks included in Stages 1 and 2 of Phase I:

A. Phase I - Model Compound Investigation (18 months)
Stage 1 - Preparative Work (6 months)

(a) Establish an inventory of model compounds including donors and acceptors such as tetralin, phenanthrene, octahydrophenanthrene, and coal-derived aromatics containing heteroatoms. Compounds containing the above-mentioned tags will also be purchased or synthesized.

(b) Select appropriate methods for the analysis of feed and product streams.

(c) Conduct preliminary experimentation and establish optimum plans for the continuing program. These experiments will be made to test analytical procedures, confirm tracer and material balances, and determine the extent of reactions between various donors and acceptors.

(d) Submit a report on the above and set up a plan for subsequent experimentation.

B. Stage 2 - Model Compound Experimentation (12 months)

Some changes of the original plan have been included as a result of observations from the preliminary experiments of Stage 1.

(a) Perform experiments for selected hydrogen transfer reactions using both tagged and untagged model compounds having similar characteristics to those present in coal liquefaction. Emphasis will be placed upon experimentation at conditions typical for coal liquefaction. Runs will be made with nitrogen or hydrogen (selected runs with deuterium) to identify the role of dissolved hydrogen. Catalytic runs will also be made using finely divided catalyst and a high degree of agitation.

(b) Perform necessary analytical work.

(c) Reduce the data and interpret the results to explain hydrogen transfer kinetics and mechanisms.

(d) Submit a comprehensive report of the Phase I program.

SUMMARY OF PROGRESS TO DATE

The project is continuing essentially on schedule. Experimentation with model compounds has been completed; however, additional spot runs with selected compounds may be done to test theories being developed during the study of hydrogen-transfer experiments with coal and coal-derived liquids. The screening experiments of Stage 1 were completed and reported in the Semi Annual Report (January, 1977). With respect to Stage 2, hydrogen transfer experiments were done with various donors and the acceptors: 1) dibenzyl and its analogs such as diphenyl butane, 2) stilbene, 3) oxygen-containing compounds such as ethers and alcohols, and 4) sulfur-containing compounds. Kinetic expressions have been formulated for the reactions. Interesting side reactions included the formation of stable donor/acceptor adducts and the high level of rearrangement (isomerization) of hydroaromatic donor solvents. Both of the latter reactions resulted in loss of solvent donor capacity.

Experimentation with deuterium gas and deuterium-tagged tetralin indicated that excessive H-D scrambling occurred above 400°C for effective study of reactions. At reduced temperatures, the transfer reactions were effectively studied with oxygen-containing compounds. The role of the donor solvent (as opposed to dissolved gas) was shown to be of major importance.

The ^{13}C tagged donor solvents were used primarily to follow the rearrangement and adduct formation reactions. Procedures have also been established for their use in Phase II.

A copy of the program schedule is included in Figure 1.

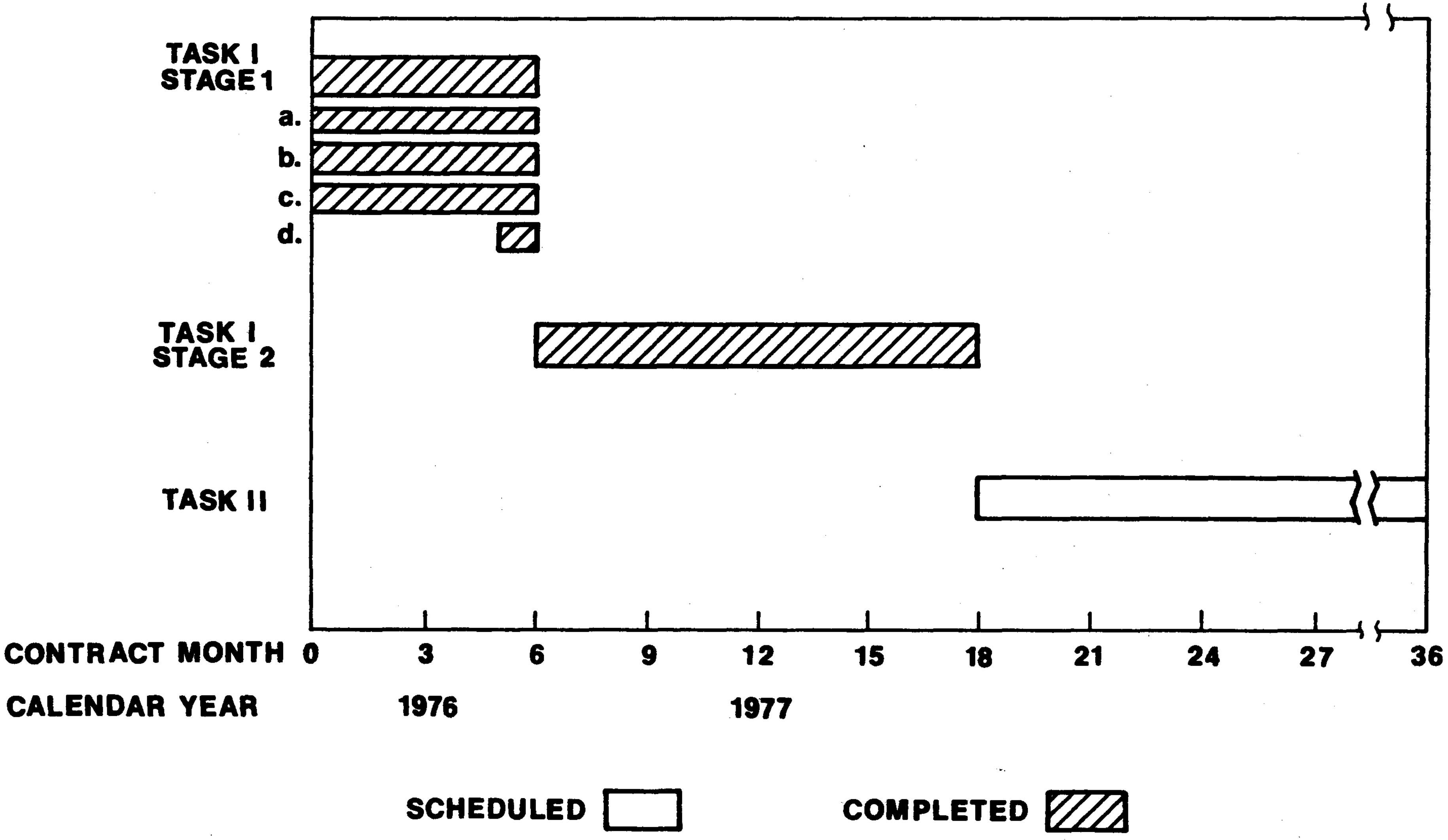


Figure 1: Program schedule for the investigation of mechanisms of hydrogen transfer

CONCLUSIONS: IMPLICATION OF RESULTS TO COAL LIQUEFACTION

The following is a summary of the results of this phase (I) of the study of hydrogen transfer in model compounds at conditions consistent with coal liquefaction. Subsequently, the implication of these results toward coal liquefaction is discussed.

- Condensed aromatics, such as dibenzofuran, dibenzothiphene, carbazole, and phenanthrene are stable in hydrogen transfer solvents at temperatures up to 475°C.

- The rate controlling step in the cleavage of dibenzyl-type linkages is the formation of the benzyl-free radical. The reaction rate is first order and independent of the donor solvent.

- Linkages longer than two carbons cleave predominantly beta to the aromatic ring to generate benzyl radicals which then react as above. However, the rate constants appear to be less than those of dibenzyl cracking. Diphenyl methane (and ether) are relatively stable at liquefaction conditions.

- Benzyl radicals can abstract hydrogen from any available source such as hydroaromatics (tetralin), naphthenes (decalin), alkyl aromatics (mesitylene), and dissolved hydrogen.

- It is emphasized that "classical" hydroaromatics are not necessary for the liquid to function as a donor solvent. It was observed that alkyl groups can also donate hydrogen.

- The presence of sulfur or oxygen heteroatoms in a linkage increases the rate of cleavage over C-C bonds.

- Of the compounds studied in a good donor solvent, the relative order of group reactivity is furans < phenols < ketones < aldehydes < chain ethers < thioethers.

- Hydrogen transfer cracking of dibenzyl ether occurs primarily through an intra-molecular reaction which appears to be first order and forms benzaldehyde and toluene with low levels of benzyl alcohol.

- The reaction of benzaldehyde (at a low concentration level) appears to be first order with respect to both aldehyde and donor solvent concentration. Toluene and water are the primary products.

- In the reaction of benzyl alcohol with an effective donor solvent, benzaldehyde and toluene appear to be produced concurrently, with the aldehyde undergoing further reduction to toluene.

- Tetralones can be reduced by either intra- or inter-molecular reaction.

- Acetophenones reduce stepwise through the alcohol to ethyl benzene products.

- Phenols and α-naphthol are quite stable at even 450°C (842°F). Naphthols react slowly with hydroaromatic solvents.

- Dibenzyl sulfide reacts rapidly in either good or poor donor solvents to yield predominantly toluene and smaller amounts of stilbene and dibenzyl.

- Stilbene will reduce with only a good donor solvent to form dibenzyl in the 350-400°C temperature range.

- Hydroaromatics rearrange to form methyl indane-type compounds, thereby resulting in a solvent of reduced hydrogen donor capacity. The major rearrangement reaction is that of isomerization of six- to five-membered rings rather than simple ring opening.

- The presence of free radicals enhances solvent degradation by greatly promoting both the above rearrangement reaction and subsequent dealkylation.

- Good donor solvents can form adducts (such as benzyl tetralin) with coal free radicals (i.e., benzyl) at moderate temperatures (< 425°C). These become increasingly stable due to ring rearrangement at high temperatures (>425°C).

- Poor donor solvents can form stable adducts with coal free radicals at any temperature due to the formation of diaryl-, diaryl methane, and similar structures.

- Due to H/D interchange and scrambling reactions on carbon, the study of hydrogen transfer using deuterium-tagged donors was not successful at temperatures above 400°C.

- At temperatures below 400°C, dissolved deuterium gas does not effectively compete with tetralin as a donor to model acceptor compounds.

- Deuterium from the gas phase was incorporated into tetralin as the hydrogen transfer reactions proceeded, thereby indicating that the solvent functions as a "transfer agent."

Table I is given in this section to provide a direct comparison between the rate constants measured for the various hydrogen transfer reactions. For reference, the half-lives of these reactions at 450°C are also given. It is noted that all of the reactions are reduced to pseudo first order with the condition that the donor solvent is at high concentration. The relative levels of reactivity are summarized in Table I and are described in depth in the report.

A. Implication to Liquefaction

Many of the current liquefaction processes are based on the principle that coal in an organic solvent is thermally cracked into smaller units which are ultimately stabilized by hydrogen supplied from a gas or liquid phase or both. The term "hydrogen transfer" is commonly used to describe the stabilization step.

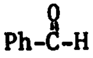
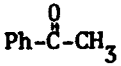
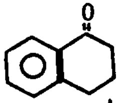
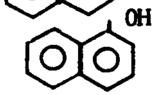
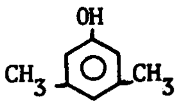
The objective of this project is to learn specific aspects of the chemistry involved in coal thermolysis, solvent interaction, selectivity of coal structures for abstracting hydrogen from various types of solvent molecules, the competition of molecular and combined hydrogen during the transfer step, and relative kinetics of all key reactions that can be identified.

In this phase, the assumption is made that coals can be viewed as consisting of large molecules with individual structures that react in a manner similar to the selected model compounds.

Based on the model acceptors studied, coal will begin to crack in the 250-300°C (482-572°F) range with the cleavage of S-S and C-S bonds. This can be expected with coals containing high levels of organic sulfur. Low rank coals such as peat, brown, lignite, and subbituminous coals will crack reasonably well at 300-400°C (572-752°F), due to the cleavage of ether bonds. If hydrogen bonds between alcohols, carbonyls, and nitrogen functions are a significant feature of the natural coal structure, they will be drastically reduced due to dehydroxylation

TABLE I

Summary of Reaction Kinetics
(Reactions in Excess of Tetralin)

Acceptor	Formula	Rate Constant K (min^{-1}) 400°C	450°C	Half Life $t_{1/2}$ (min) (450°C)	Activation Energy (cal/g mole)
Dibenzyl	$Ph-CH_2-CH_2-Ph$	$1.1x10^{-3}$	$1.3x10^{-2}$	55.0	48 100
Diphenyl Methane[1]	$Ph-CH_2-Ph$	-	$3x10^{-4}$ (max)	40+ hours	-
Diphenyl Butane	$Ph-(CH_2)_4-Ph$	-	$1.1x10^{-2}$	64.8	-
Phenyl Hexane	$Ph-(CH_2)_5-CH_3$	-	$6.3x10^{-3}$	110	-
Stilbene	$Ph-CH=CH-Ph$	$1.3x10^{-2}$	$6x10^{-2}$	11.6	28 400
Diphenyl Ether	$Ph-O-Ph$	-	-	40+ hours	-
Dibenzylether	$Ph-CH_2-O-CH_2-Ph$	$4.8x10^{-2}$	$2.5x10^{-1}$	2.8	36 000
Benzaldehyde	 $Ph-\overset{O}{\overset{\parallel}{C}}-H$	$2.5x10^{-2}$	$1.2x10^{-1}$	5.8	32 000
Acetophenone	 $Ph-\overset{O}{\overset{\parallel}{C}}-CH_3$	$7.5x10^{-4}$	$4.3x10^{-3}$	161.2	33 500
Tetralone		$1.9x10^{-3}$	$6.8x10^{-3}$	101.9	24 750
Naphthol		$4x10^{-4}$	$2.3x10^{-3}$	301.4	34 000
Benzyl Alcohol	$Ph-CH_2OH$	$2x10^{-2}$	$4x10^{-2}$	17.3	26 200
Xylenol[1]		-	$3x10^{-4}$ (max)	40+ hours	-

Note (1) Reactivity extremely low; maximum given.

reactions. The organic oxygen content of coals should be significantly reduced by hydrogen transfer cracking in the 300 to 400°C region. Coals can form unsaturated products, such as olefins, if reaction temperatures do not exceed 400°C.

Carbon-carbon bonds are essentially not broken in coals until the reaction temperature exceeds 400°C.(752°F). Above this temperature, olefins can be chemically reduced if hydroaromatic or molecular hydrogen is available. Much of the organic oxygen and sulfur should be removed from coals with liquefaction times of one hour or more, unless they are present in an aromatic system such as phenols, furans, or thiophenes. Most heterocyclic nitrogen compounds are quite stable to hydrogen transfer cracking reactions. They will distribute among the liquid products as a function of structure.and molecular weight.

Most organic structures can actually serve as a "hydrogen source" for coal radicals. It is quite difficult to find a truly inert solvent; cycloparaffins, alcohols, aromatic and hydroaromatic hydrocarbons, and heterocyclic compounds can all "donate" hydrogen to reactive-free radicals. It has been demonstrated that even strict aromatic solvents (mesitylene) can compete fairly well with "ideal hydroaromatic" solvents (tetralin) as donors. For free radical stabilization, hydroaromatic hydrogens are preferred, but not necessary.

The form of combined hydrogen in a solvent can strongly affect the types of products resulting from thermally cracked coal. If sufficient (or excess) hydroaromatic hydrogen is available to stabilize all acceptor radicals, a maximum amount of solvation and distillates will be formed. In addition, a minimum amount of repolymerization of coal will occur. All solvents are capable of irreversibly reacting with coal radicals to consume solvent with the formation of adducts. This is a potentially serious problem since it is directly related to the need to produce and maintain a balance of recycle solvent in many liquefaction processes.

This study indicated that the structure of the donor solvent is very significant. In particular, hydroaromatics, which readily transfer hydrogen, rearrange to isomeric forms of enhanced stability. These isomers are less likely to transfer hydrogen. The ideal structure for donor solvents is the six-membered hydroaromatic ring (i.e., cyclohexene, tetralin, tetrahydroquinoline, etc.). Under thermal conditions needed to crack coal and initiate the hydrogen transfer process, the hydroaromatic portion of solvent molecules contract to five-membered rings. A portion of these rings then dealkylate. For practical purposes, the isomerization process is irreversible. This may be of particular importance in processes which depend upon the use of recycle solvents.

The amount of isomerization is dependent upon temperature, reactor residence time, and, in particular, the level of acceptor radicals. Coals with high levels of reactive oxygen and/or organic sulfur would be expected to increase the problem of solvent adduction due to the high concentration of intermediate radicals.

The solvent isomerization creates an additional basic problem in following the progress of liquefaction, namely measuring the amount of transferred hydrogen. It is possible to measure the level of "transferable hydrogen" (hydroaromatic hydrogen) in the feed and product liquids through the use of ^{13}C-NMR, which takes into account five-membered rings. However, due to the confounding of hydrogen transfer with solvent adduction and isomerization, it is not possible to isolate the portion due to hydrogen transfer alone. It is questionable to calculate "transferred hydrogen" by simply using relative ratios of liquid components (for example, tetralin/naphthalene, etc.).

Studies in this phase of the project have indicated that acceptor radicals show a distinct preference for combined hydrogen over molecular hydrogen under conditions of coal liquefaction. This preference is enhanced if the concentration of hydroaromatics is high. Molecular hydrogen appears to primarily play the role of "re-hydrogenating" the donor solvent. On a somewhat negative side, molecular hydrogen also enhances dealkylation reactions resulting in high gas yields and hydrogen consumption.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Experimental and Analytical Procedures

Preliminary experiments were made using both a micro-unit and a stirred batch autoclave. At the completion of the initial screening experiments, the decision was made to proceed in the study of model compounds using only the batch autoclave system. The micro-unit has been described in both the Semi Annual and Annual Reports and will not be described herein.

The kinetic experiments were performed in a 300 cc batch stirred autoclave. The unit also had a 300 cc heated feed tank to permit the injection of reactants at elevated temperatures under pressure. A schematic of the experimental setup is shown in Figure 2. In most of the runs, a sample (typically 75 grams) of donor was charged to the reactor and heated to the desired temperature. The typical heat-up time was 60-80 minutes. At this temperature, an additional charge (usually 75 grams) of donor and acceptor was injected using nitrogen at 10.3 MPa (1500 psig). The injected liquid was typically preheated to 275-300°C. At the time of injection, the reactor temperature dropped 5-10°C, but it recovered within three minutes. Provisions were made to take 5-10 cc samples from the reactor during the run with the sample line cooled with dry ice to minimize losses.

The donor/acceptor reaction products were analyzed on a high-resolution capillary GLC with a 100-foot SCOT column. Selected samples were also analyzed using a medium-resolution GLC interfaced to a duPont 21-491 mass spectrometer. Specific samples were analyzed by conventional and high-pressure liquid chromatography. Further analysis of isolated products were carried out using a CEC-103 low-voltage mass spectrometer and a CFT-20/FT NMR instrument with both hydrogen and carbon-13 probes.

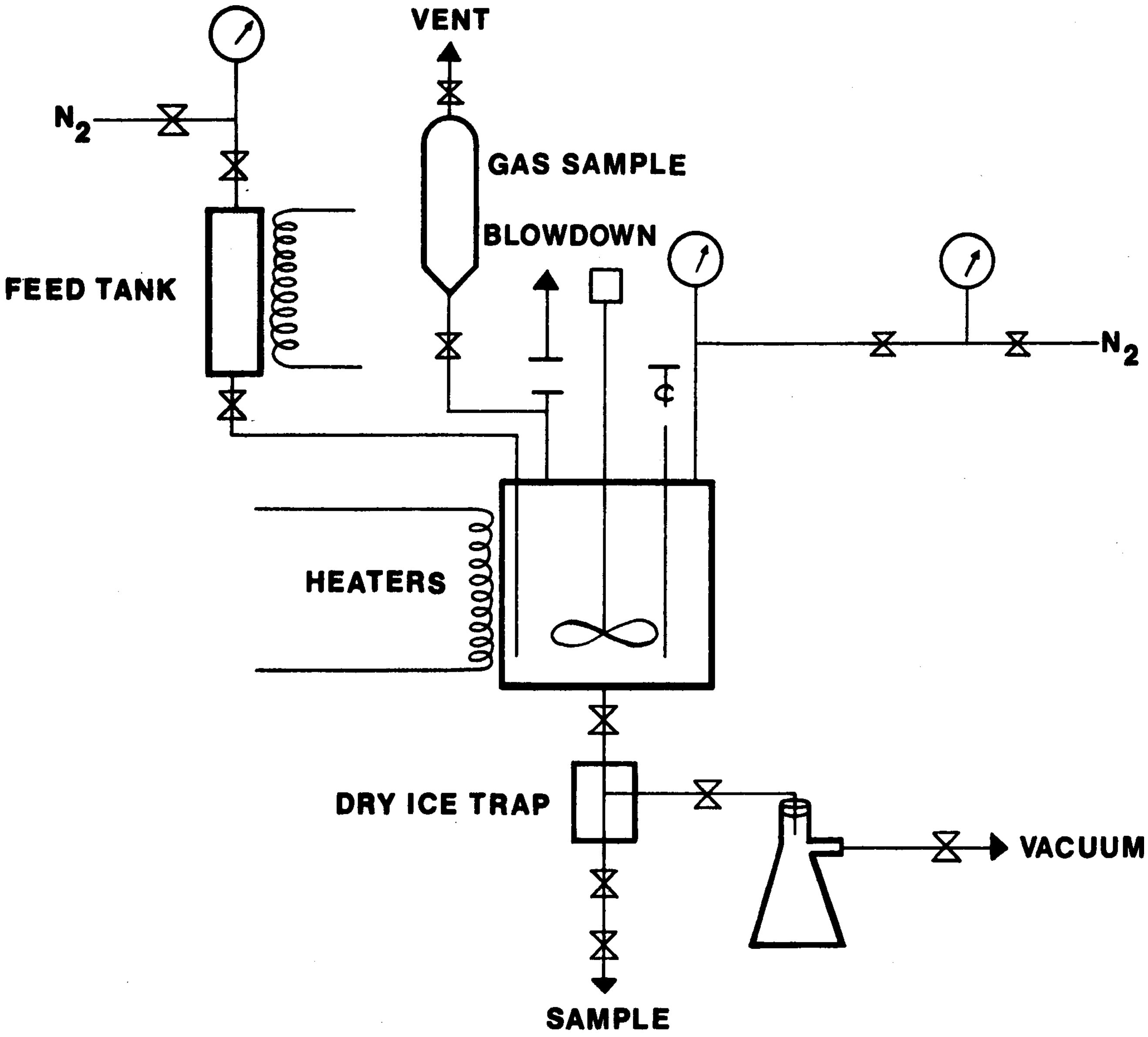


Figure 2: Schematic of experimental unit

B. Screening of Donors and Acceptors

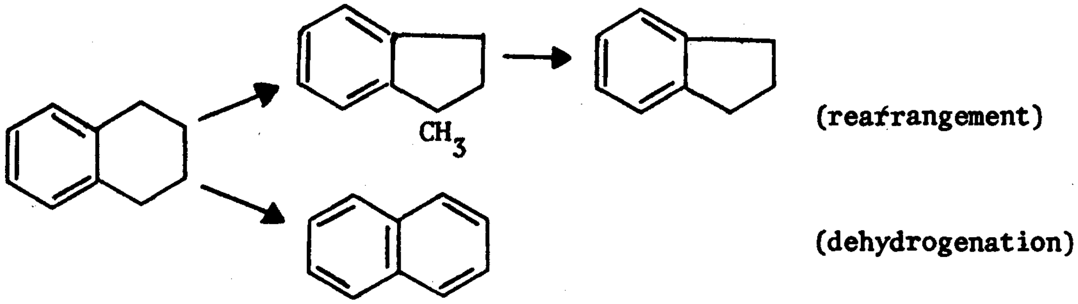
During the first six months (Stage 1) of experimentation, screening experiments were made to choose model donor and acceptor compounds that would be subsequently studied in depth during Stage 2. The results of these preliminary experiments were given in both the Semiannual and Annual Reports; therefore, only a summary will be given herein.

1. Donors

The primary characteristics considered in the choice of donors were the following: 1) the known ability to donate hydrogen, 2) their existence in typical coal liquids, 3) availability and cost, and 4) simplicity for structural analysis. At this time, the choice was limited to hydroaromatics.

a. Tetralin - This compound has long been recognized as an excellent donor solvent for coal liquefaction, and it is readily available. Due to the recognized ability of tetralin to donate hydrogen, only the disadvantages of using the solvent will be discussed herein. The primary disadvantages of using tetralin arise from its low molecular weight with resulting low boiling point and its tendency to undergo thermal rearrangement to 1-methyl indane at temperatures above 425°C. Methyl indane and its derivatives are not hydrogen donors, thus inhibiting the desired reaction.

The rearrangement reaction shown below is much faster than thermal dehydrogenation to naphthalene at temperatures above 425°C.



In batch autoclave experiments at temperatures to 475°C and residence times to three hours, a sizable conversion of tetralin to methyl indane and indane occurs. Furthermore, tetralin rearrangement is promoted by the presence of a compound with the potential ability to serve as an acceptor taking on hydrogen and subsequently releasing it. At the above conditions, a 10% conversion of tetralin was observed. This rearrangement appears to occur even if essentially no detectable change of the acceptor is observed. Specific reference is made to runs with condensed aromatics (phenanthrene). The effect of temperature and acceptor concentration was shown in Figures 5 and 6 of the Annual Report; however, the study was enlarged upon and is discussed in a latter section of this report.

b. Octahydrophenanthrene - This compound has been shown(1) to be an effective hydrogen donor in coal liquefaction. Donor/acceptor experiments were not made, but the thermal stability of both the symmetric and asymmetric isomers was checked in autoclave runs of 60-minute duration at 427°C (800°F). The symmetric isomer was shown to be stable with greater than 95% recovery of unchanged solvent. (The symmetric isomer is less stable than tetralin.) The asymmetric isomer was found to be unstable as demonstrated by a rapid pressure rise. Analysis of the liquid product indicated that essentially all of the starting compound was lost and about 50% cracked to compounds having less than 12 carbons. The remaining component was the symmetric isomer.

When each of the above isomers was used as solvent for the liquefaction of Big Horn, WY, subbituminous coal, greater than 90% MAF solvation (based on pyridine extraction) was observed. (Run conditions were: 427°C, 60 minutes, 3.4 MPa [500 psig] initial pressure, and a solvent to coal ratio of 3 to 1.) Surprisingly, the asymmetric isomers did not undergo extensive decomposition to low molecular weight species. This implies that the hydrogen transfer to the dissolving coal proceeded faster than the thermal cracking of the solvent.

2. Acceptors

A series of experiments were made in both the micro- and autoclave units with tetralin and various acceptors. In summary, the relative order of acceptors for hydrogen transfer was concluded to be the following:

> condensed aromatics << non-condensed aromatics such as dibenzyl, < aromatic compounds having attached hetero-functionality < aromatic ethers < aromatic sulfides

The following is a discussion of the results leading to the above conclusions. Reference should be made to the Semiannual and Annual Reports for further details.

a. Condensed Aromatics - Phenanthrene, dibenzofuran, dibenzothiophene, and N-ethylcarbazole are condensed aromatics known to be present in coal or coal-derived liquids. In the screening runs with tetralin, they all appeared to be extremely stable at temperatures up to 475°C. Conversion levels of less than 10 wt.% were observed at residence times up to three hours.

b. Non-condensed Aromatics - A significant level of dibenzyl reaction was recorded at a reaction temperature of 475°C. Therefore, experiments were carried out in both the micro-unit and autoclave. The results of batch autoclave experiments confirmed that little dibenzyl reaction occurred in tetralin at 400°C and hold-times to 180 minutes. Essentially total conversion of dibenzyl to toluene was observed at 475°C and the same hold-time.

With the substitution of a heteroatom in the diaryl chain link (dibenzylether), high conversion levels were observed at temperatures over 400°C. The primary reaction products from the ether reaction were toluene and benzaldehyde.

c. Aliphatic Ethers - These ethers readily cracked at low temperatures. The cracking appeared to begin at the heteroatom, expelling carbon monoxide. With the absence of detectable, high molecular weight fragments, it appeared that tetralin was not capable of stabilizing the cracking process.

d. α-Tetralone - This compound was chosen as an example of a carbonyl group which is probably present in coals. A wide range of conversions were observed at reaction temperatures of 400° and 475°C. Therefore, it was decided to study this compound further in Stage 2.

e. 8-Hydroxy-quinoline - As an extension of the tetralone series, we chose an acceptor containing both a hydroxyl function and a basic aromatic nitrogen ring. The choice was also based upon its availability, solubility in tetralin, its assumed presence in coal structures, and its potential to abstract hydrogen via its heterocyclic ring.

At moderate temperatures (300°-425°C), dehydroxylation occurred with a loss of water. At higher temperatures, fracturing was observed and insufficient hydrogen was available from the tetralin so that tarry, pentane-insoluble products were formed. This inability to stabilize the intermediates is noteworthy, and this may be part of the reason why there appears to be a concentrating of the nitrogen functionality in asphaltene fractions.

C. Kinetics of Hydrogen-Transfer Cracking of Dibenzyl

Detailed hydrogen transfer experimentation was undertaken using dibenzyl with various solvents for the following reasons:

1) Dibenzyl represents C-C bonds attached to two rings; similar carbon linkages are believed to exist in coal.

2) The dibenzyl C-C bond fractures at coal liquefaction conditions (400-450°C).

3) The products are readily analyzed.

Most of the reactions were performed in tetralin. A limited number of reactions were done in 2,6-dimethyl tetralin, decalin, and sym-octahydrophenanthrene to determine the effect of donor structural changes. 1,3,5-Trimethylbenzene (mesitylene) was used as an inert solvent in which to test the thermal stability of dibenzyl at 450°C. Although mesitylene (MST) is thermally stable at this temperature, it reacts with benzyl-free radicals.

A list of experimental conditions examined in this study is shown in Table II. These experiments were performed for contact times ranging from 0 to 180 minutes and for temperatures between 400° and 475°C.

To verify that the wall of the reactor did not catalyze the reaction, a run was made with 10% dibenzyl and 90% tetralin under a nitrogen atmosphere at 450°C with mesh screens of the same material as the reactor wall added to the reactor. As shown in Figures 3 and 4, the conversions of both dibenzyl and tetralin were not changed by the increased metal surface area. The study reported here is, therefore, believed to represent purely thermal hydrogen transfer reactions.

1. Primary Reaction

The primary reaction in this study involves the thermal cracking of dibenzyl followed by stabilization of the free radicals by reaction with a donor solvent. This reaction can be characterized by:

Table II

LIST OF EXPERIMENTS FOR THE DIBENZYL STUDY

	Acceptor Solvent	Donor Solvent	Temperature (°C)
HT77-6-17	Dibenzyl (10%)	Tetralin (90%) in N_2	400, 425, 437, 450, 463, 475
HT77-40	Dibenzyl (10%)	Tetralin (90%) in H_2	450
HT77-58-60	Dibenzyl (10%)	Mesitylene (90%) in N_2	425, 437, 450
HT77-37-39	Dibenzyl (10%)	Mesitylene (90%) in H_2	425, 450, 475
HT77-28	Dibenzyl (10%)	Dimethyl Tetralin (40%) + Mesitylene (50%) in N_2	450
HT77-29	Dibenzyl (10%)	H_8P (40%) + Mesitylene (50%) in N_2	450
HT77-72	Dibenzyl (10%)	H_8P (7%) + Tetralin (33%) + MST (50%) in N_2	450
HT77-19	Dibenzyl (20%)	Decalin (80%) in N_2	450
HT77-21	Dibenzyl (10%)	Tetralin (40%) + Decalin (50%) in N_2	450
HT77-22	Dibenzyl (25%)	Tetralin (75%) in N_2	450
HT77-23	Dibenzyl (33%)	Tetralin (67%) in N_2	450
HT77-77	Dibenzyl (50%)	Tetralin (50%) in N_2	450
HT77-61	Dibenzyl (40%)	Tetralin (10%) + Mesitylene (50%) in N_2	450
HT77-78	Dibenzyl (10%)	Tetralin (90%) + Wire Screen in N_2	450
HT77-42-44	Dibenzyl (22%)	D_4 Tetralin (29%) + MST (49%) in N_2	400, 425, 450
HT77-151-152	Dibenzyl (10%)	Tetralin (85%) + Nalcomo Cat. (5%) in N_2	400, 425
HT77-153	Dibenzyl (10%)	Tetralin (85%) + Kaolin (5%) in N_2	425
HT77-154	Dibenzyl (10%)	Tetralin (85%) + Ni4303 Cat. (5%) in N_2	425
HT77-155	Dibenzyl (10%)	Tetralin (85%) + Charcoal (5%) in N_2	425
HT78-4	Dibenzyl (10%)	Tetralin (85%) + Nalcomo (5%) in H_2	425
HT78-5	Dibenzyl (10%)	Tetralin (85%) + Kaolin (5%) in H_2	425

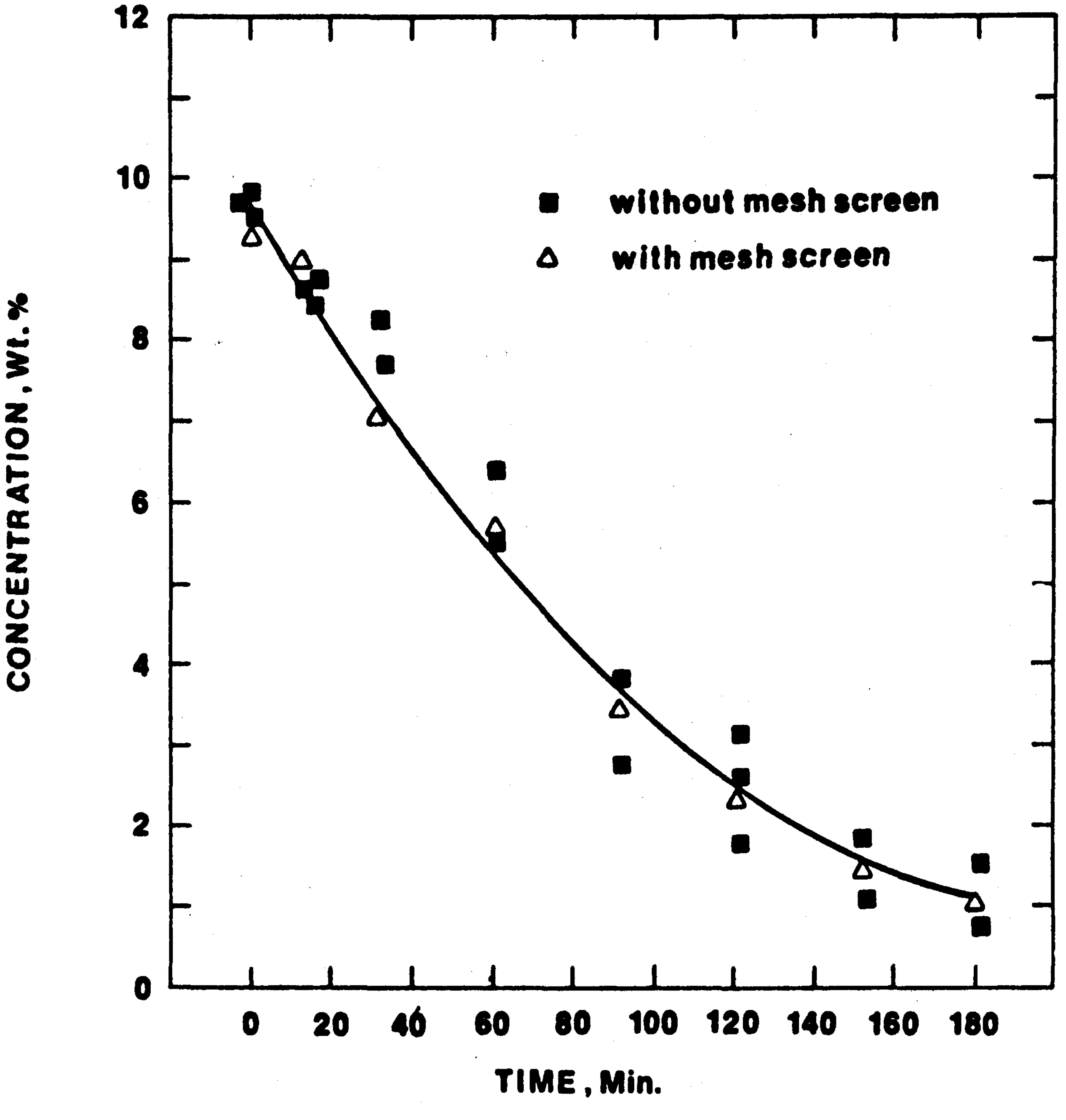


Figure 3: Dibenzyl concentration versus time for a feed of 10% dibenzyl with 90% tetralin in a nitrogen atmosphere at 450°C

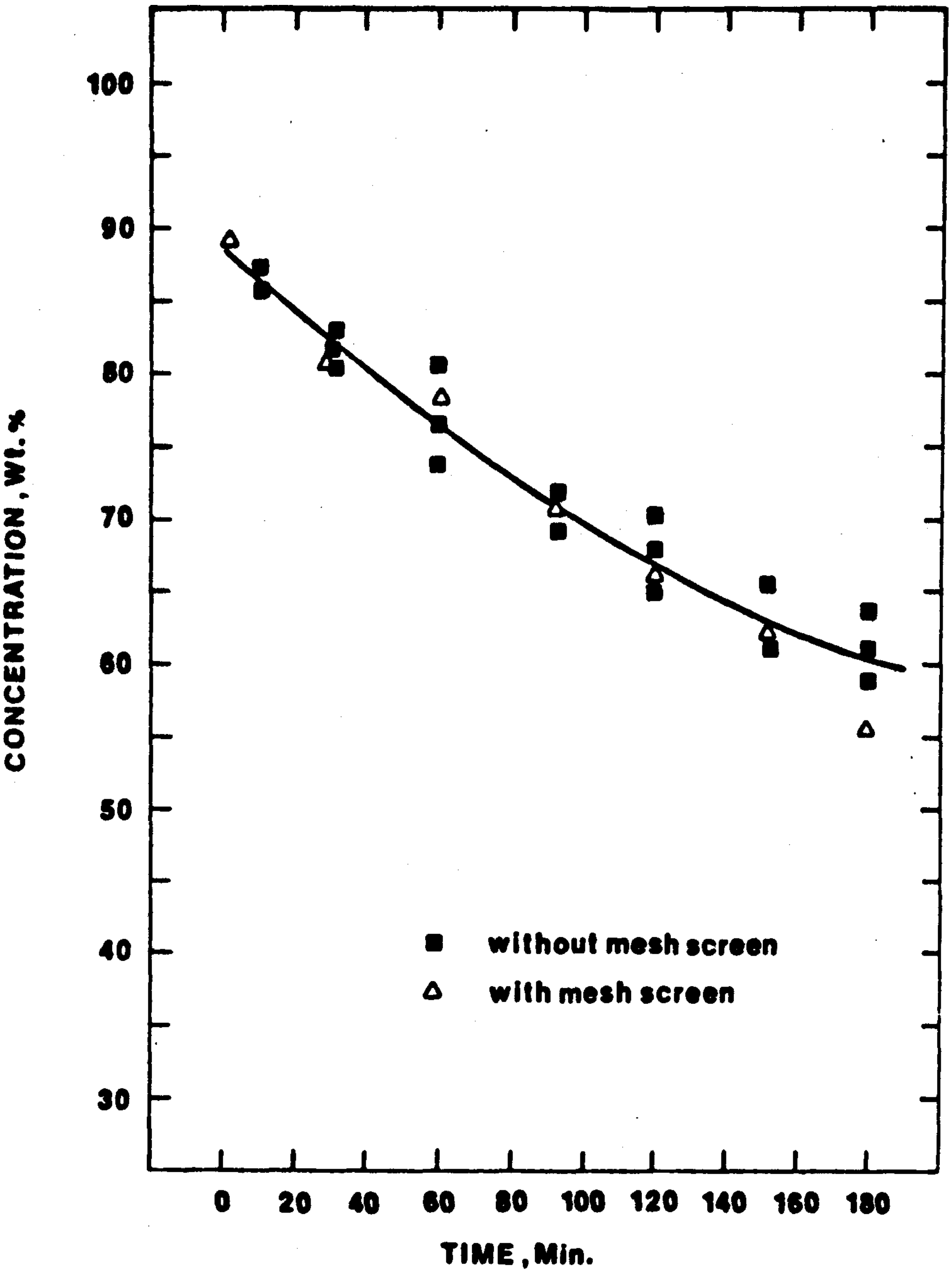


Figure 4: Tetralin concentration versus time for a feed of 10% dibenzyl with 90% tetralin in a nitrogen atmosphere at 450°C

$$\text{Dibenzyl} \xrightarrow[\Delta]{k_1} 2\ (\text{Benzyl}) \qquad (1)$$

$$(\text{Benzyl}) + \text{Donor Solvent} \longrightarrow \text{Products} \qquad (2)$$

where (Benzyl) represents the active benzyl free radical. With each donor solvent, a number of secondary reactions also occur producing a variety of products. The mechanisms for these secondary reactions are complex and differ with each solvent. They may involve the formation of more free radicals and a series of chain transfer reactions. The effect of the donor solvent on dibenzyl conversion depends on the relative rates of reactions (1) and (2). If the rate of reaction (1) is comparable to or greater than that of reaction (2), the nature of the donor solvent will affect the rate of dibenzyl conversion to toluene. However, if the first reaction is slower, the rate of the formation of products from the overall reaction, namely

$$\text{Dibenzyl} + \text{Donor Solvent} \longrightarrow \text{Products (primarily toluene)} \qquad (3)$$

will not be significantly dependent upon the nature of the donor solvent. The formation of the benzyl free radical [reaction (1)] in this case is largely a thermal process, independent of solvent. Once the free radical is formed, it reacts with any donor solvent to form products.

The hydrogenolysis of dibenzyl to form toluene has been discussed in the literature (Tsuge et al., 1962; Horrex and Miles, 1951; Yusa and Oda, 1941; Fortina et al., 1971; Brower, 1977). However, a detailed discussion of the kinetics of the primary and secondary reactions taking place in the presence of a donor solvent does not appear to have been published.

Analysis of experimental data indicates that reaction (1) is the limiting reaction for dibenzyl conversion to the benzyl radical. Thus, for all donor solvents examined in this study, the rate of disappearance of dibenzyl can be expressed as:

$$\frac{dC_B}{dt} = -k_1C_B \qquad (4)$$

where C_B is the concentration (weight percent) of dibenzyl.

The values of k_1 for all the systems examined in this study are illustrated in the form of an Arrhenius plot in Figure 5. The activation energy for k_1 was found to be approximately 48 100 cal/g mole. This activation energy is consistant with that of Horrex and Miles,(1) who reported a value of 48 000 cal/g mole for the primary cracking reaction. This latter work was done in the vapor phase while that of the present study is in the liquid phase.

The fact that Equation (4) correlated the experimental data for all systems implies that the benzyl free radical is very active and readily reacts with or extracts hydrogen from any available solvent. Furthermore, recombination of benzyl free radicals does not occur at a significant rate. Combination of the benzyl radical with mesitylene radicals to form adducts can be a significant reaction in the absence of sufficient hydroaromatics. Combination of benzyl radicals with good donor solvent molecules, such as tetralin and octahydrophenanthrene, was not observed.

To determine if an external catalyst would affect the benzyl/tetralin reaction, a series of runs were made at 425°C using the following catalysts or supports:

1) Nalcomo 477 (CoMo on Al_2O_3):Nalco Chemical Co.

2) Ni 4303 (NiW on Al_2O_3):Harshaw Chemical Co.

3) Colloidal kaolin:Fisher Scientific Co.

4) Nuchar activated carbon:Westvaco Chemical Div.

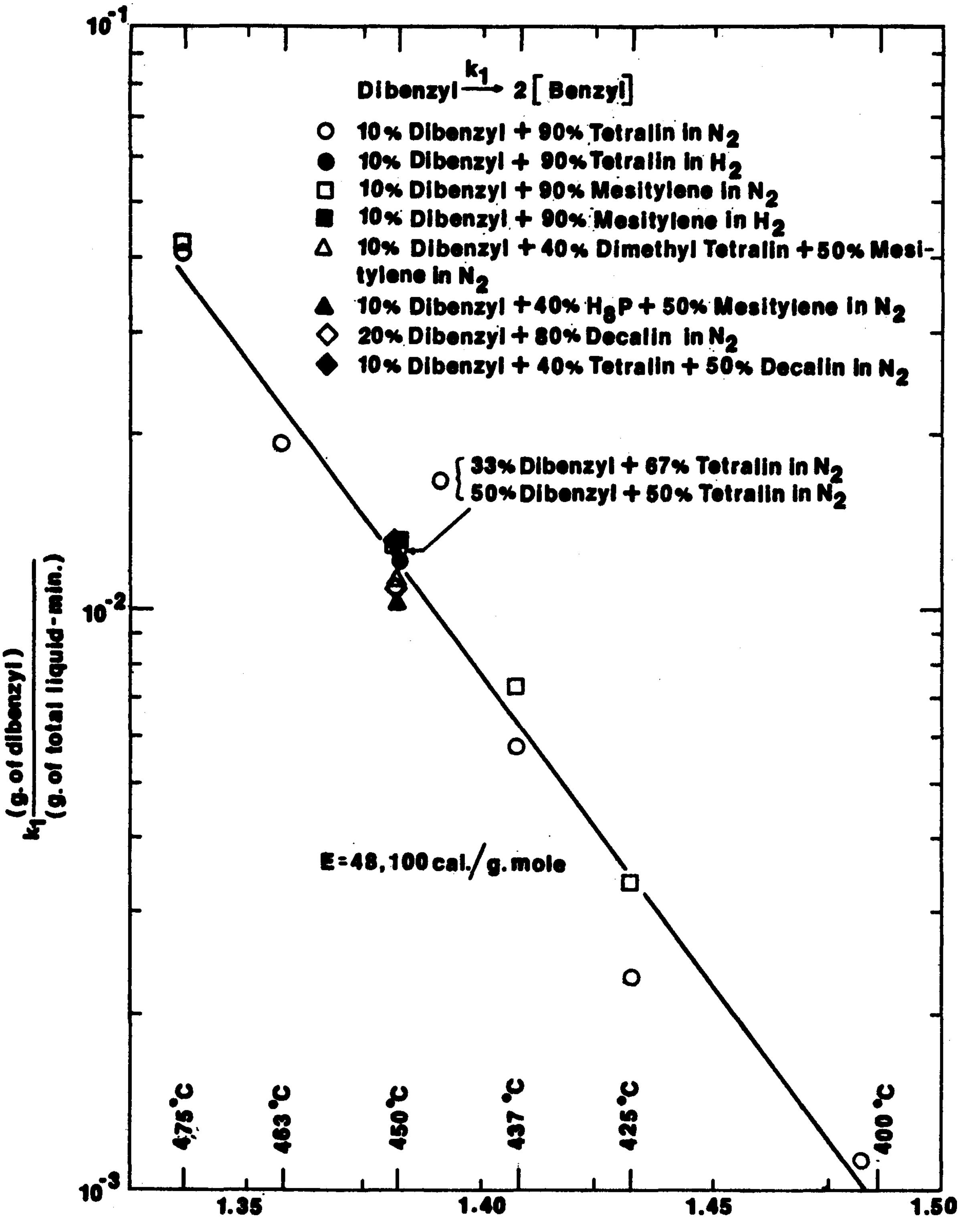


Figure 5: Arrhenius plot for the primary dibenzyl reaction

The runs were made with a charge level of 5 wt.% of solids to the reactor. As shown in Figure 6, there was no major enhancement of the dibenzyl cracking reaction with the introduction of these solids when the runs were made in a nitrogen atmosphere. In addition, runs were made with Nalcomo and kaolin in a hydrogen atmosphere (1500 psig total pressure). Again, no reaction enhancement was observed. This provides further confirmation that the primary reaction is the thermal cracking of dibenzyl. Obviously, this lack of catalytic effect cannot be extrapolated to the liquefaction of coal where many different types of bonds are breaking. In addition, the catalyst presumably also functions to regenerate the donor solvent.

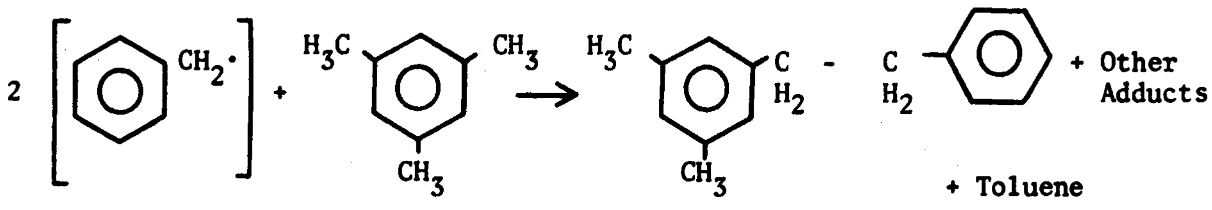
2. Secondary Reactions

Unlike the primary reaction, secondary reactions are strongly dependent upon the structure of the solvent. The product distribution is, therefore, a function of the donor solvent.

a. Reactions with mesitylene in nitrogen - When mesitylene (MST) is used with dibenzyl under a nitrogen atmosphere, the major secondary reaction is given by:

$$2\ \text{(Benzyl)} + 2\ \text{Mesitylene} \xrightarrow{N_2} 2\ \text{Toluene} + \text{Dimer} \qquad (5)$$

The dimer is considered to be di-mesitylene; however, the products from this reaction may vary. Mesitylene can also react with benzyl radicals to form other polymer products:



(Benzyl) Mesitylene MST/Benzyl Adduct (6)

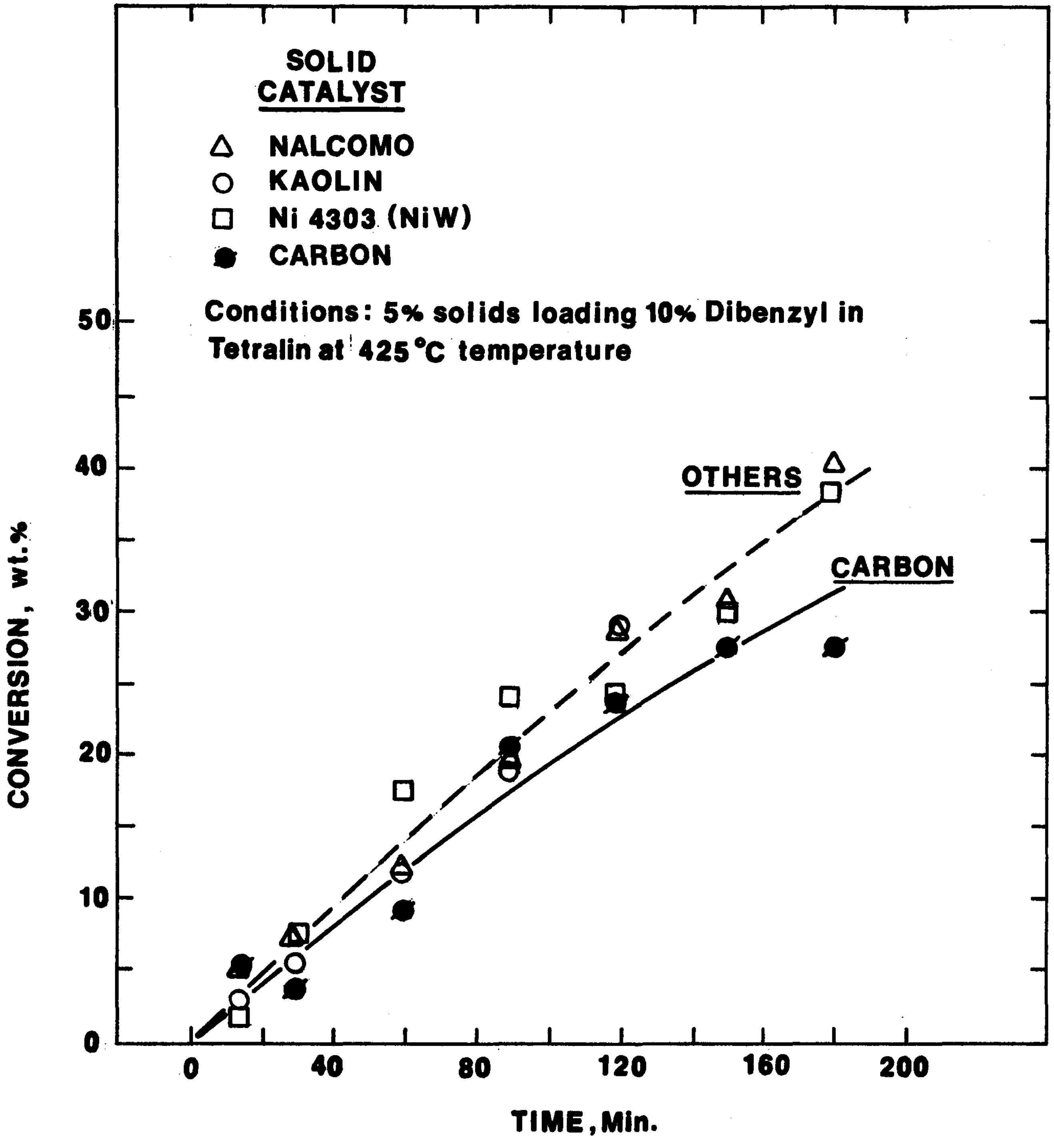


Figure 6: Dibenzyl cracking in tetralin and in the presence of catalytic solids at 425° C.

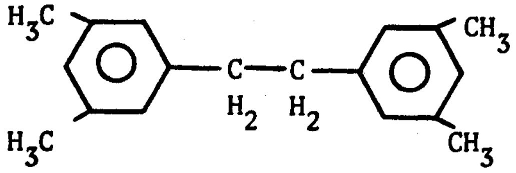
Experimental data indicate that the rate of adduct formation may not be first order with respect to mesitylene concentration.

GC-MS studies were performed to identify major products. Some typical toluene and adduct concentrations obtained in these studies are shown in Figures 7 and 8. These studies identify toluene as the predominant product.

b. Reactions with mesitylene in hydrogen - The major secondary reaction is identical to that when the mesitylene/dibenzyl system is used under a nitrogen atmosphere (see reaction [5]). The other secondary reaction (6) also occurs. Unlike the previous case, the presence of hydrogen promotes cracking of mesitylene to form xylenes. Typical concentrations of cracked products in this system are illustrated in Figure 9.

By-products from the reaction of dibenzyl with mesitylene in either H_2 or N_2 results in a family of adducts. Nearly all the adducts incorporate mesitylene or mesitylene fragments (xylene). The distribution of adducts is dependent upon the reaction time, atmosphere (N_2 or H_2), concentration of acceptor radicals, and concentration of other solvent molecules. One dimer preferentially formed results from abstraction of H from the $-CH_3$ group.

The above dependence was determined by observing several GLC curves. Figure 10 shows the typical product distribution for the dibenzyl/mesitylene system with a nitrogen atmosphere. Again, toluene and adducts are the primary products. It is noted that, in this case, one particular adduct is preferentially formed. It has been identified as 3,3',5,5'-tetramethyl dibenzyl, which is the primary mesitylene dimer.



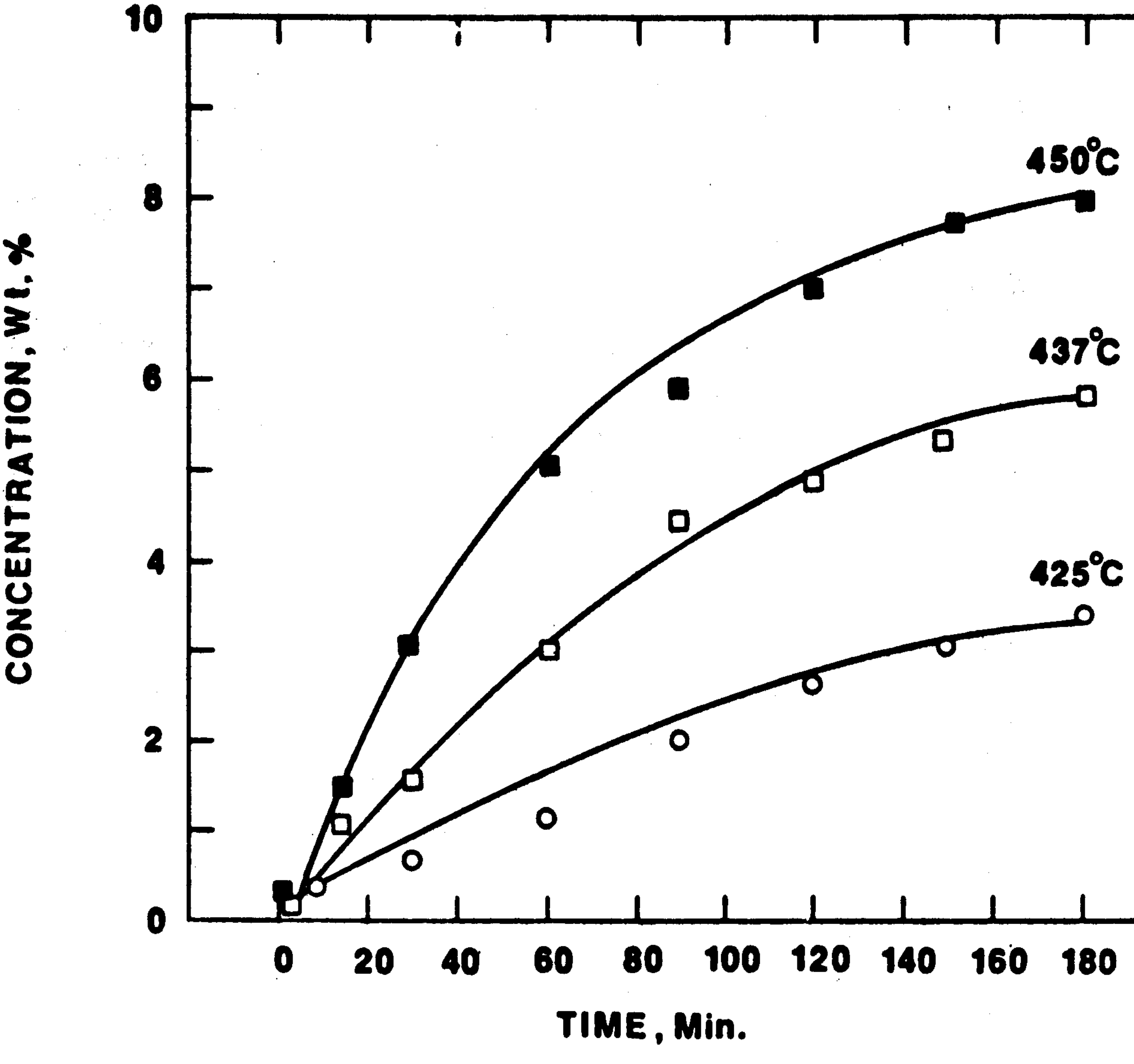


Figure 7: Toluene concentration versus time for a feed of 10% dibenzyl with 90% mesitylene in a nitrogen atmosphere

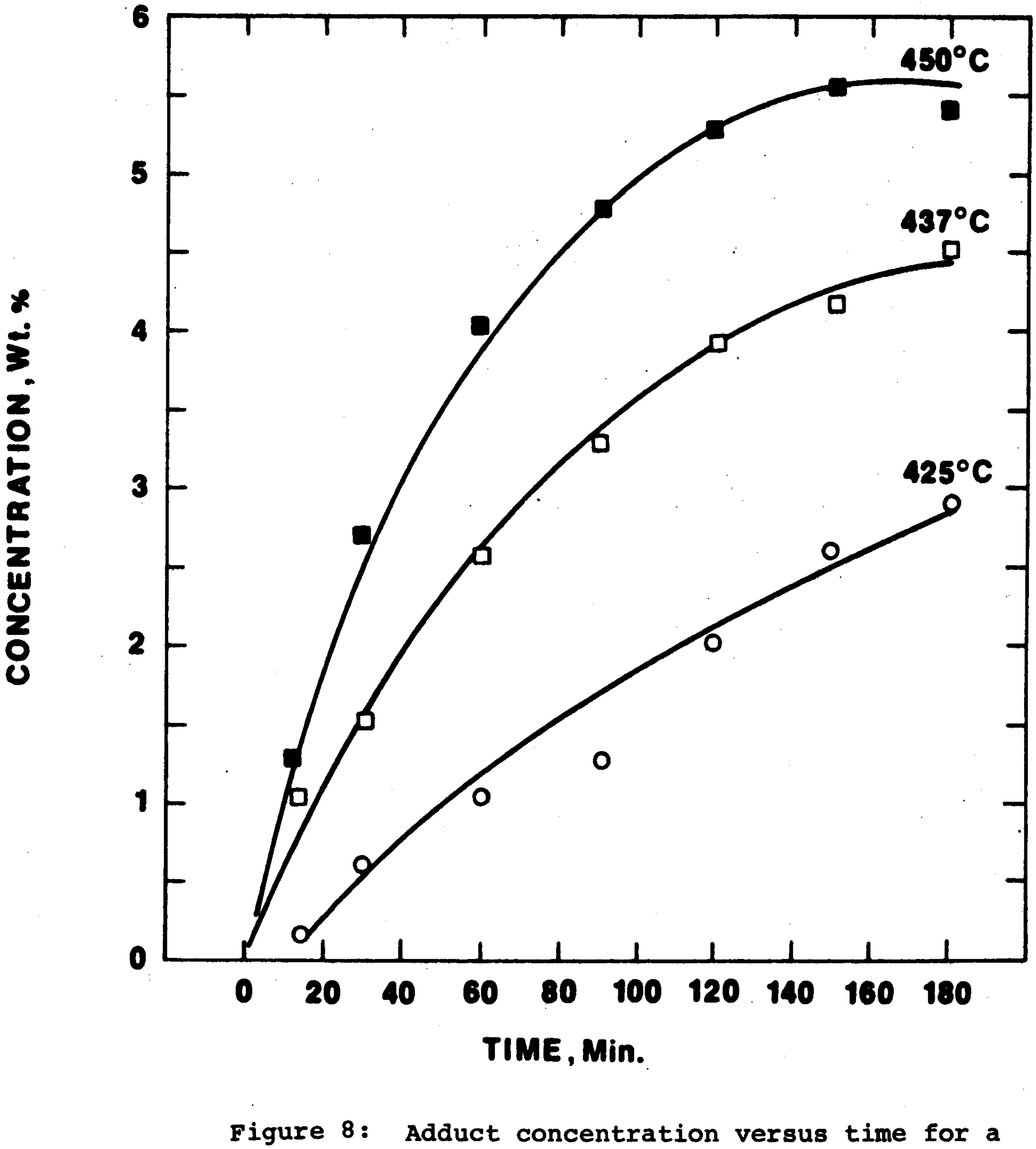


Figure 8: Adduct concentration versus time for a feed of 10% dibenzyl with 90% mesitylene in a nitrogen atmosphere

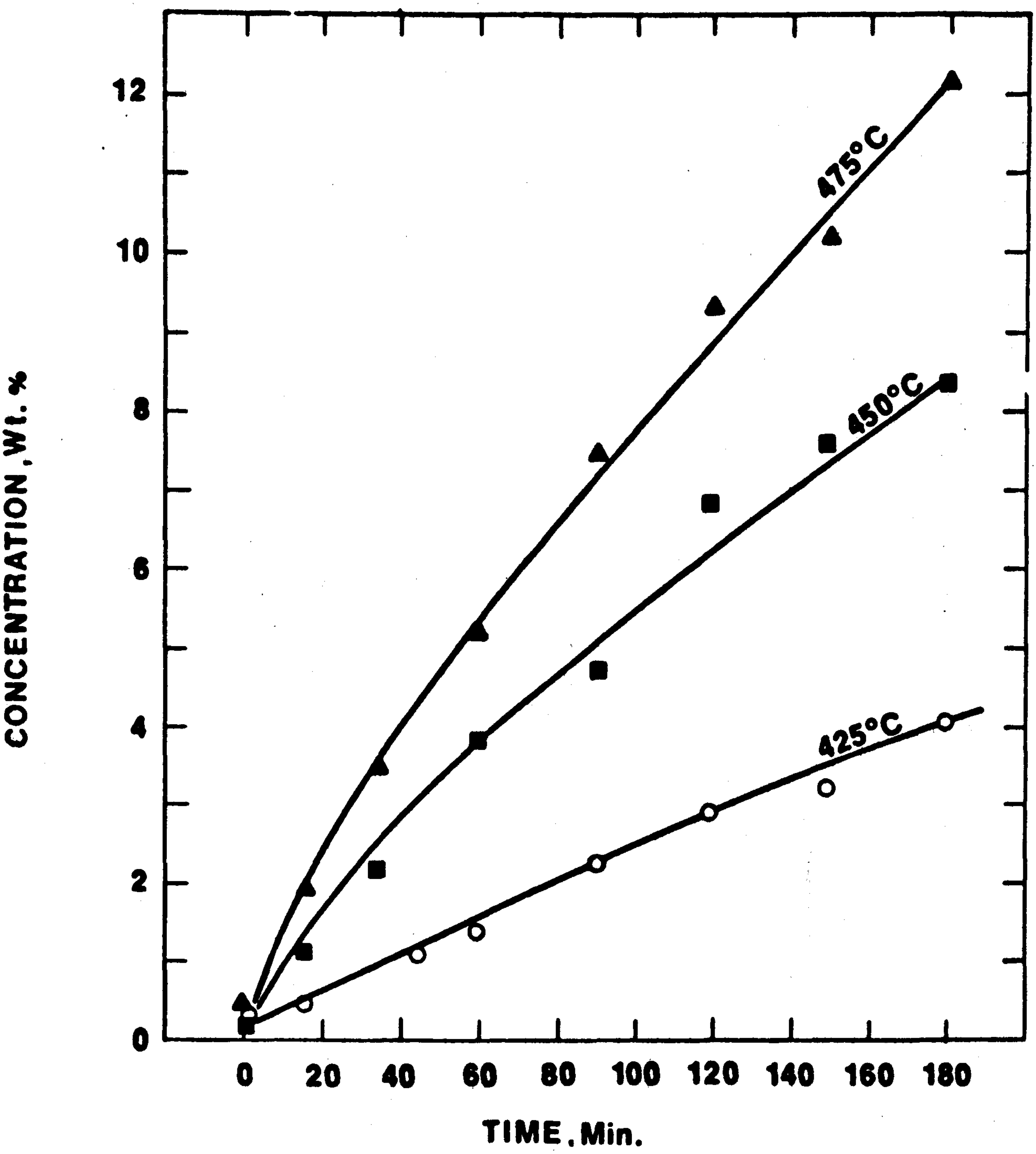


Figure 9: Cracked products concentration versus time for a feed of 10% dibenzyl with 90% mesitylene in a hydrogen atmosphere

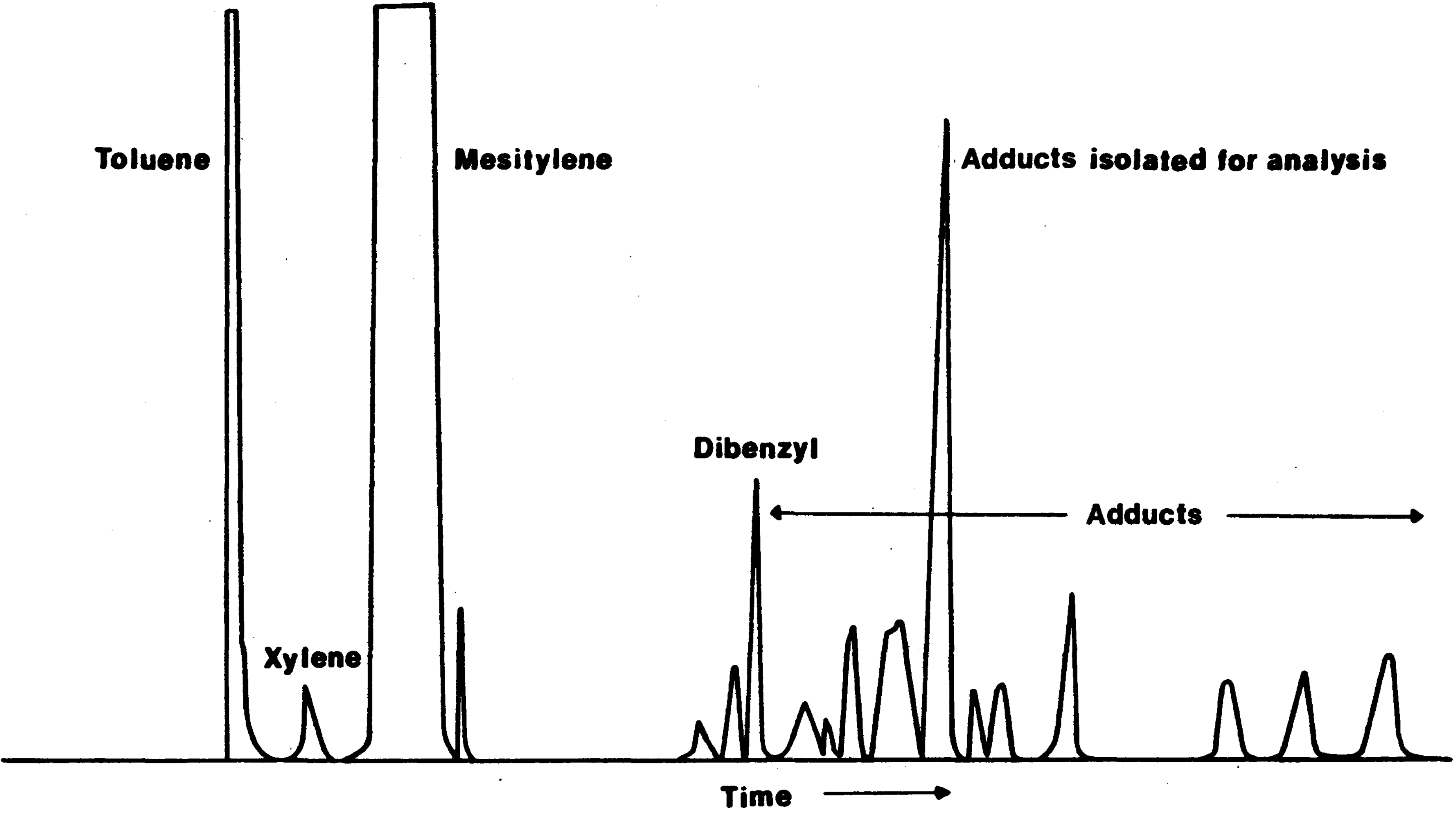
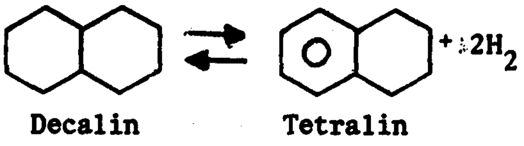
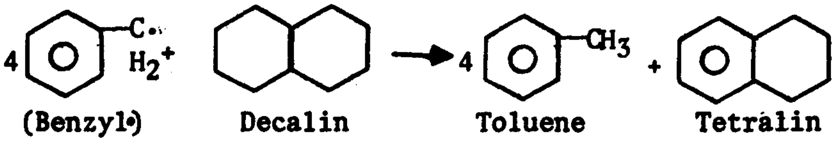


Figure 10: GLC curve of the dibenzyl/mesitylene system in a nitrogen atmosphere after a 3-hour reaction period

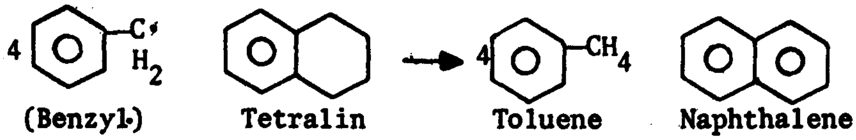
c. Reactions with decalin in nitrogen - It is thermodynamically likely that decalin will dehydrogenate to form tetralin. Therefore, the following reactions are possible when using decalin:



(7)



(8)



(9)

Decalin can react with dibenzyl by reaction (8) or by a series of reactions (7 and then 9). The series of reactions will produce a significantly greater amount of naphthalene than will reaction (8).

Results from experiments at 450°C and three hours with 20% dibenzyl and 80% decalin showed a low production of naphthalene (1.4 wt.%), while an 8% naphthalene yield is observed when tetralin is used as the solvent (see Figure 11). These results imply that reaction (8) is considerably faster than reaction (7).

Experiments were made using a solvent mixture of 40% tetralin and 50% decalin with 10% dibenzyl. Naphthalene production in this case was close to that when using tetralin alone (see Figure 11). This implies

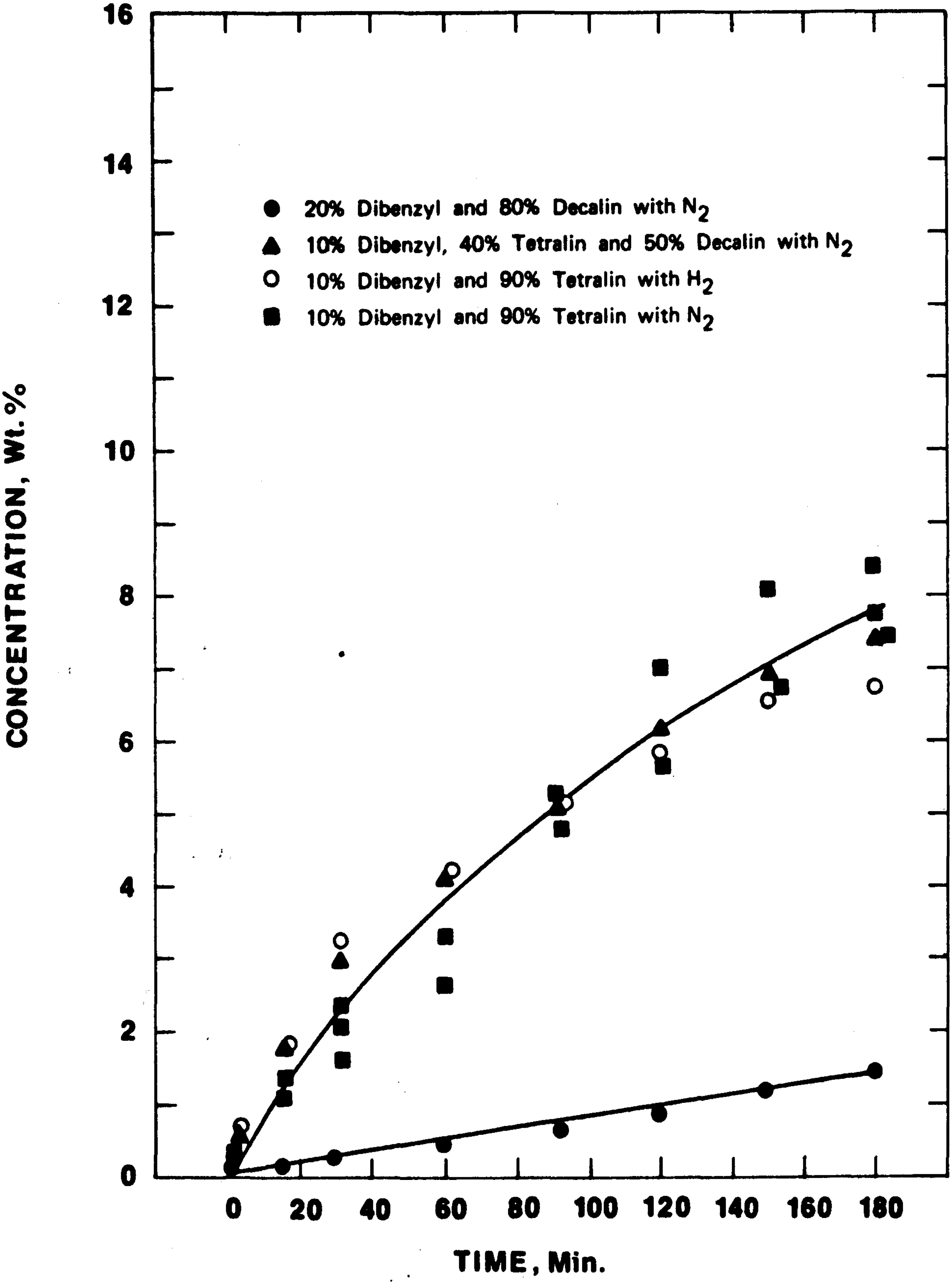


Figure 11: Naphthalene concentration versus time for different feeds at 450°C

that reaction (9) is more favorable than reaction (8), and tetralin is a better hydrogen source than decalin for the benzyl free radicals. This is further substantiated by examining the production of toluene illustrated in Figure 12. As shown in this figure, for a temperature of 450°C, the toluene production for the dibenzyl/tetralin system is very similar to that for the dibenzyl/tetralin/decalin system. However, both are considerably different from that observed in the dibenzyl/decalin system.

The dibenzyl/decalin system produces more cracked products than the dibenzyl/tetralin system. This is illustrated in Figure 13 for a temperature of 450°C. The figure also shows that, as one would expect, the cracking of solvent is also enhanced by the presence of a hydrogen atmosphere.

D. Hydrogen-Transfer of Non-Condensed Analogs of Dibenzyl

To evaluate the effect of chain length between non-condensed aromatic hydrocarbons, three additional hydrocarbons were reacted with tetralin at 450°C. These were diphenylmethane, 1,4-diphenylbutane, and 1-phenylhexane.

The conversion profiles of these reactions and that of dibenzyl are shown in Figure 14. Each compound was more stable than dibenzyl. Diphenyl methane was essentially unreactive. 1-Phenylhexane converted to a lower rate than either dibenzyl or diphenylbutane. This lower rate is attributed to the presence of only one activating (phenyl) group.

Ethylbenzene and toluene were the sole liquid products from the hydrogen transfer cracking of the non-condensed aromatics. The yields of these latter compounds are shown as a function of time in Figures 15 and 16. No evidence was found for propyl- or butylbenzene in the liquid phases of the runs with 1-4,diphenylbutane and 1-phenylhexane. The

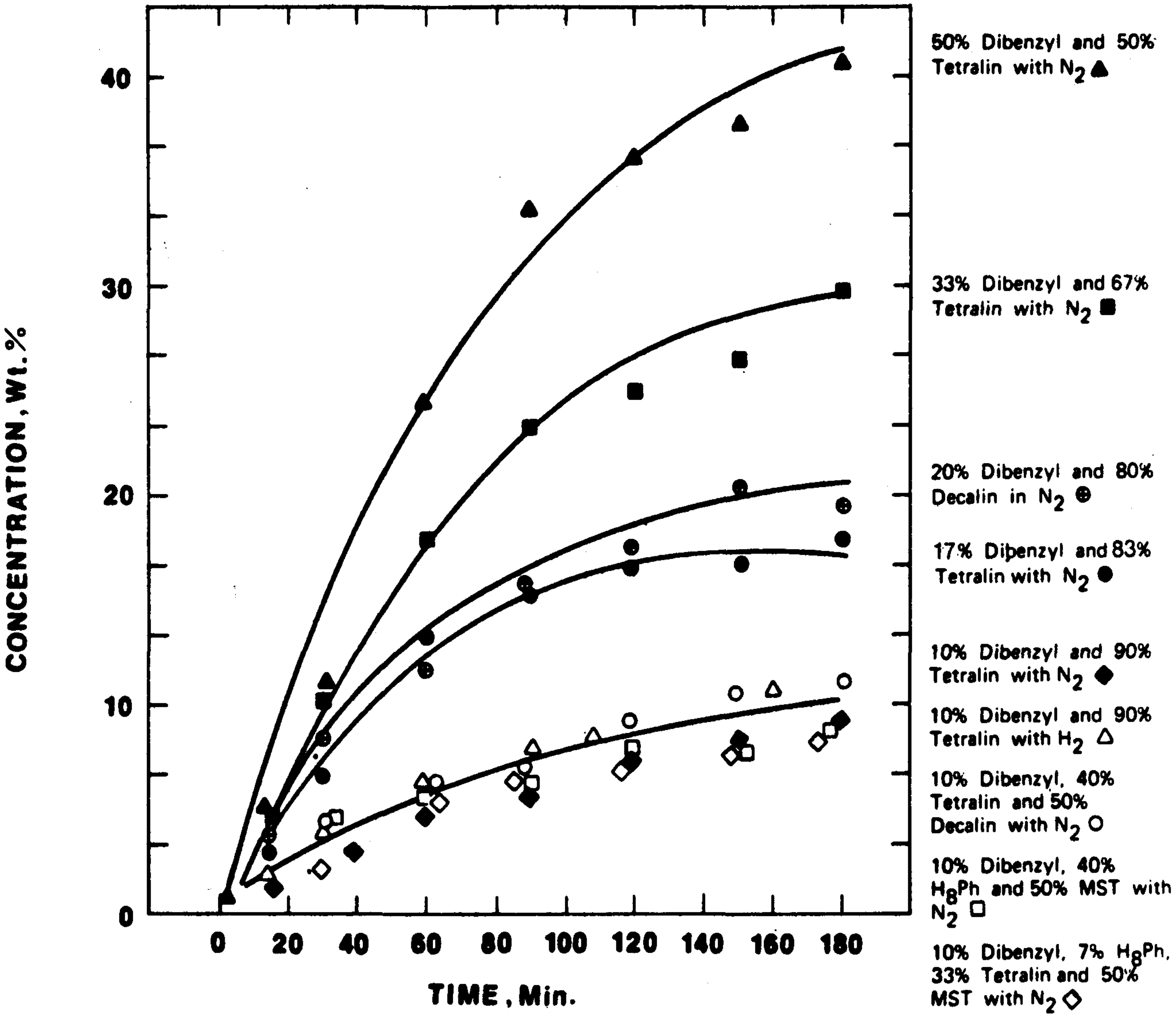


Figure 12: Toluene concentration versus time for different feeds at 450°C

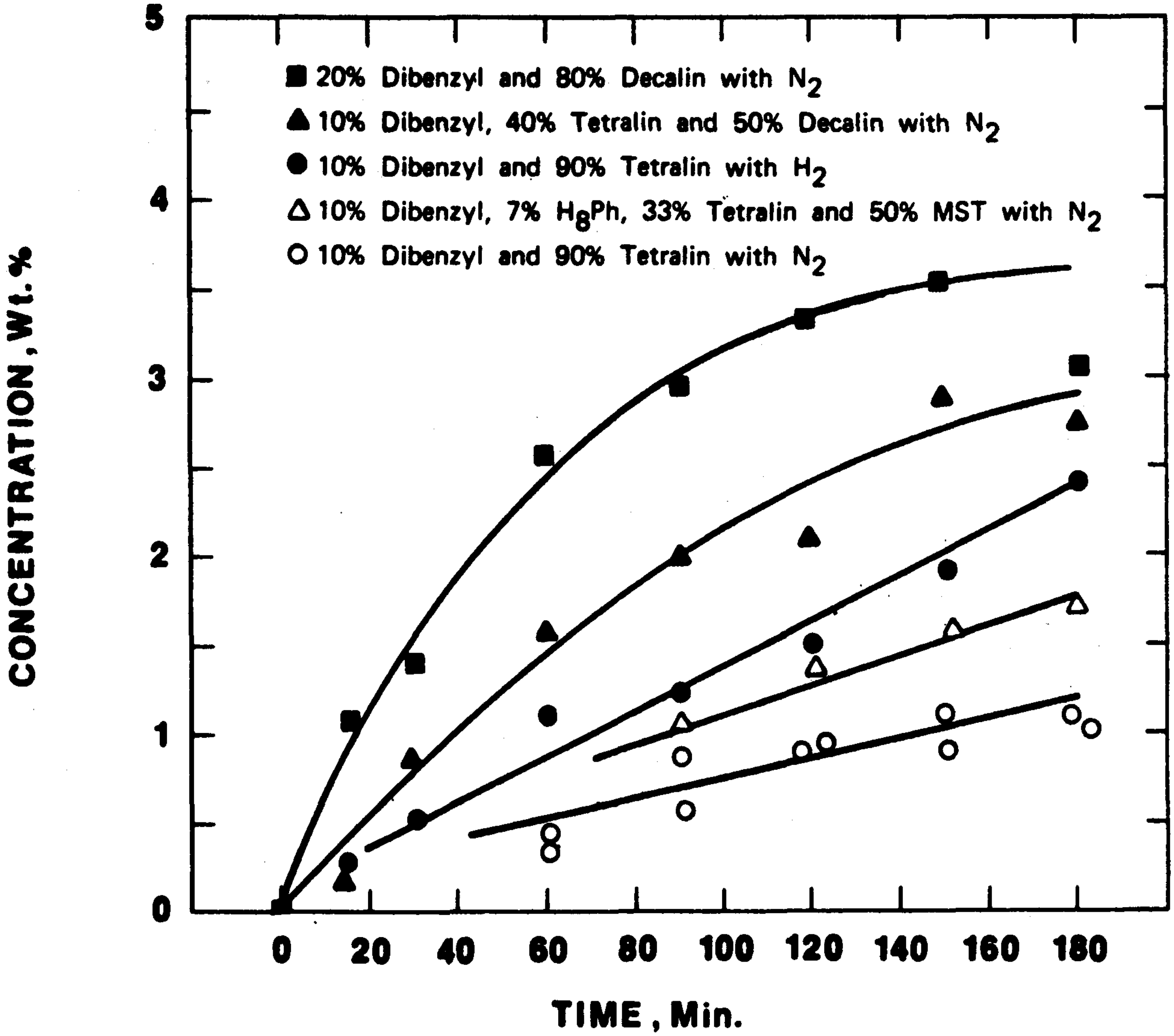


Figure 13: Cracked products* concentration versus time for different feeds at 450° C.

*Benzene plus light unknowns as determined by GLC

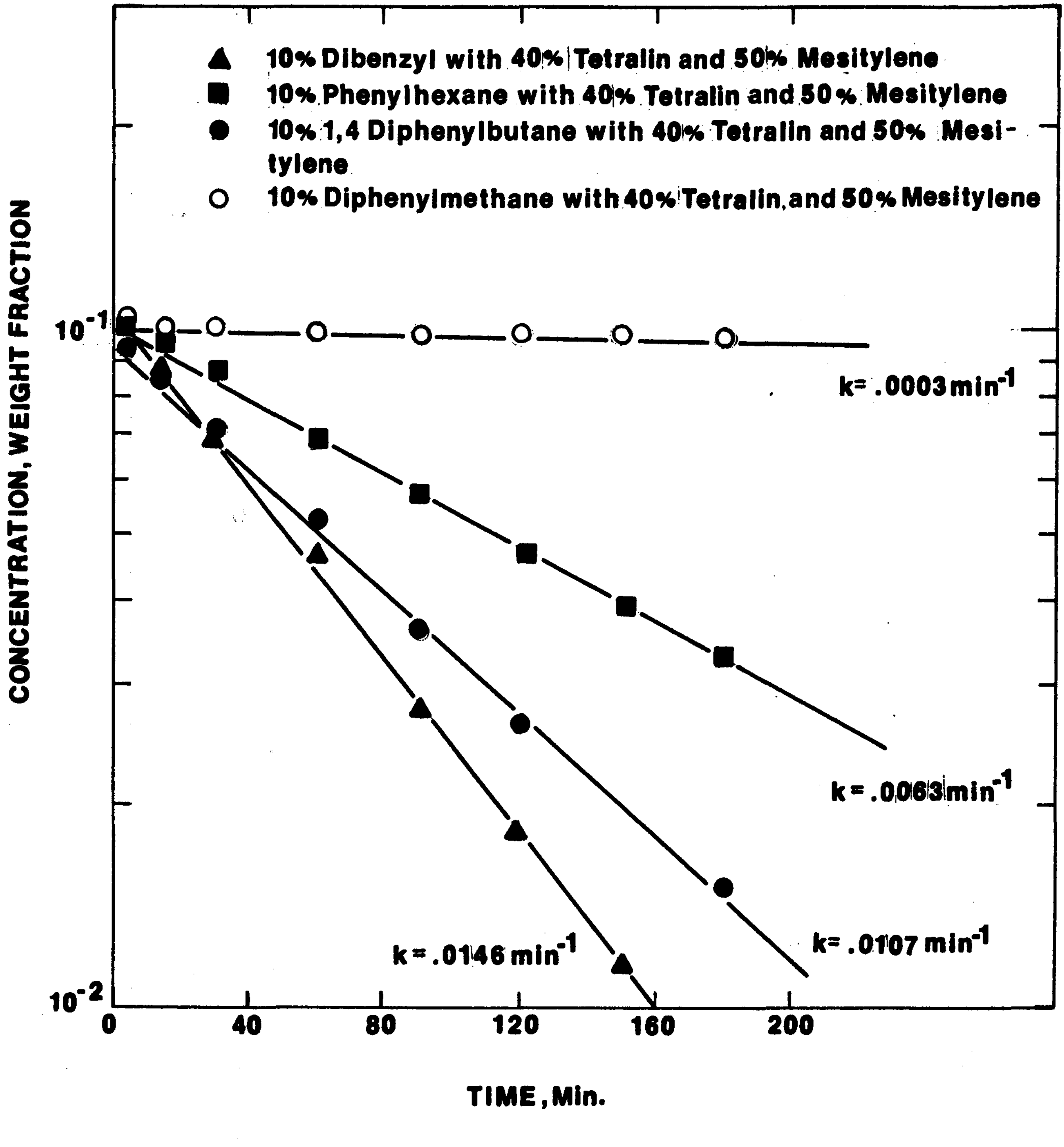


Figure 14: Conversion of dibenzyl analogs (phenyl alkanes) at 450° C.

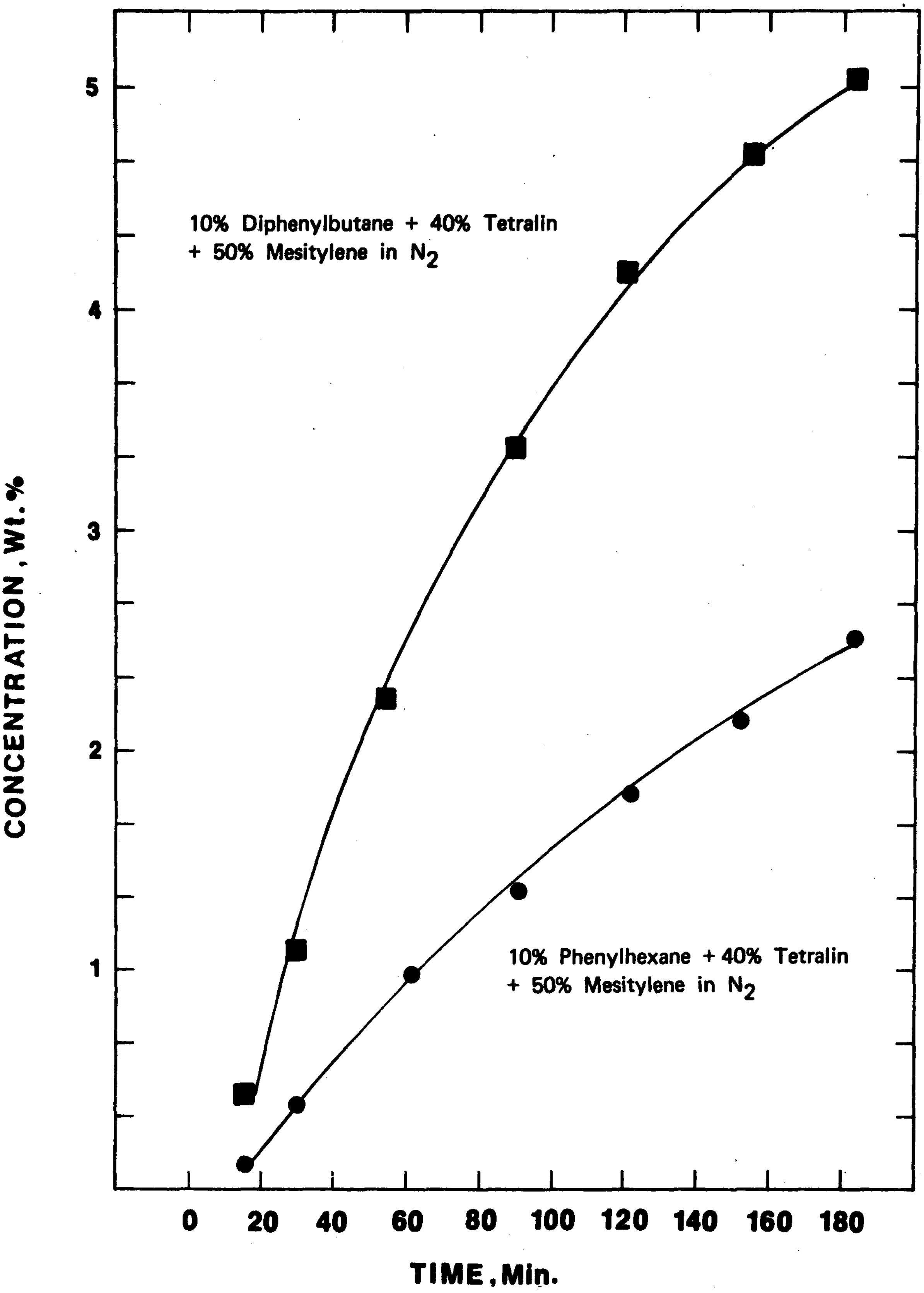


Figure 15: Formation of ethyl benzene versus time for the acceptors diphenylbutane and phenylhexane at 450°C

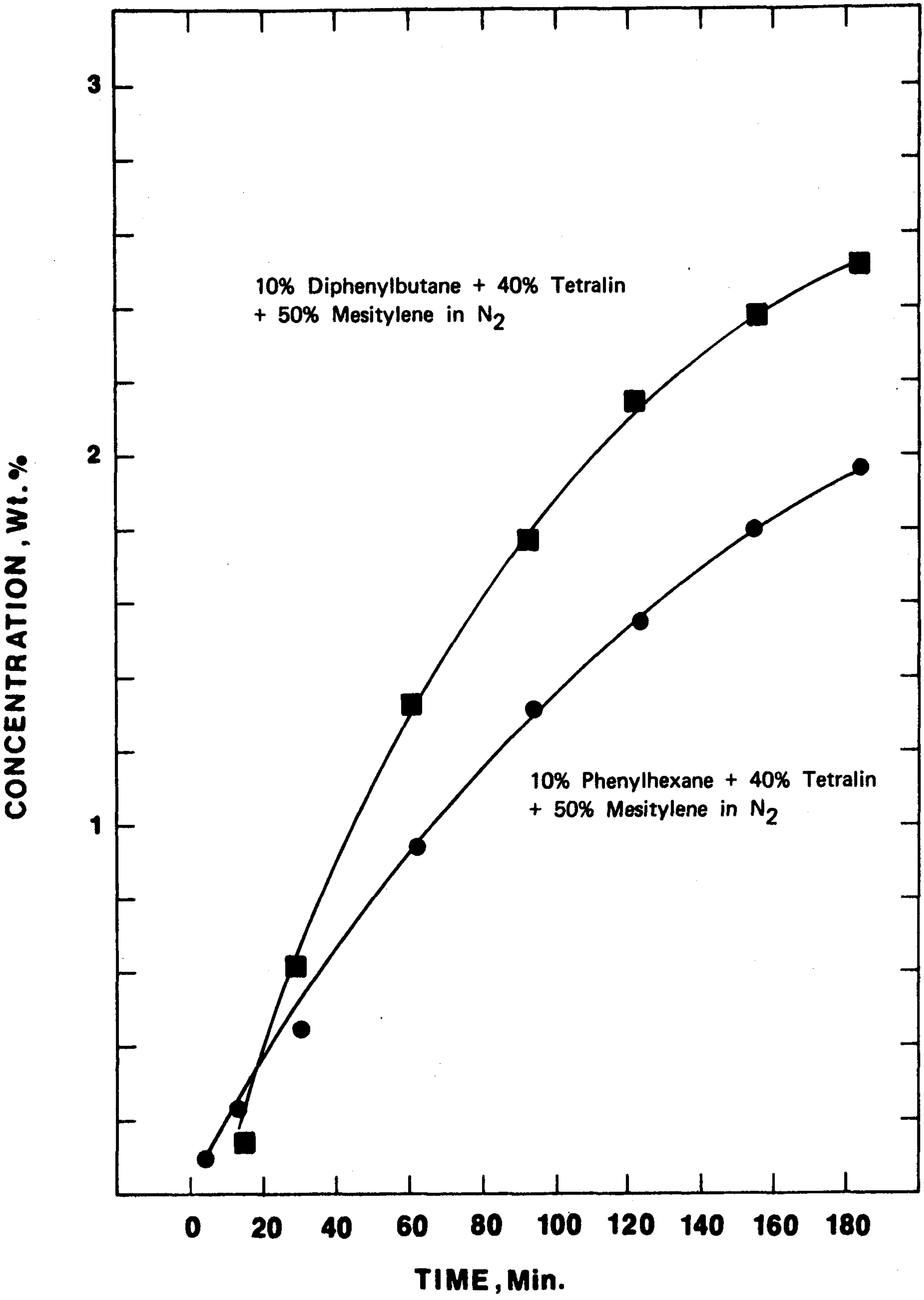
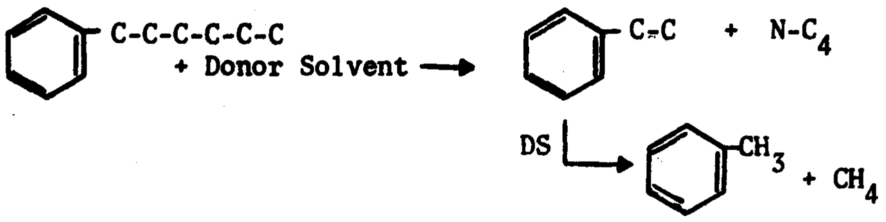


Figure 16: Formation of toluene versus time for the acceptors diphenylbutane and phenylhexane at 450°C

major gaseous products were n-butane and methane in the latter run. This is consistent with a step-wise reaction as follows:



(10)

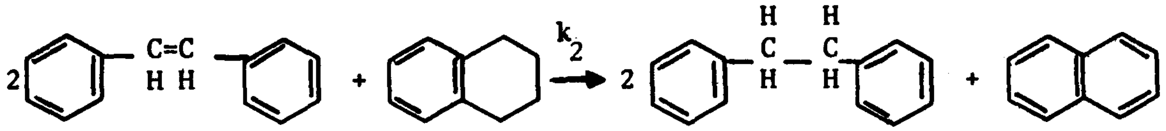
(11)

The experiments with both phenylhexane and diphenylbutane indicate that aromatic resonance stabilization of free radicals may not be significant beyond the β-position of chain substituents.

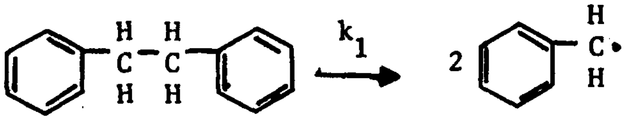
E. Experimentation with Stilbene

Two hydrogen transfer runs were made using stilbene (due to its structural similarity to dibenzyl) to study the role of olefins, as intermediates in cracking. The stilbene/tetralin runs were made at 400°C and 450°C. The plots of the concentrations of stilbene, dibenzyl, and toluene are given in Figures 17 and 18, respectively.

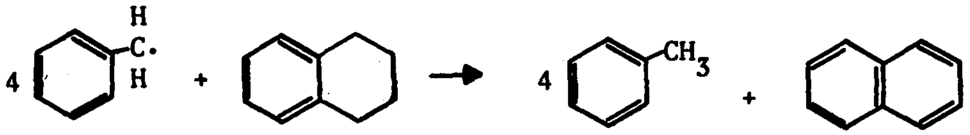
The following reaction sequence was assumed:



(12)



(13)



(14)

The rate of disappearance of stilbene was found to best fit the expression:

$$\frac{d\,C_s}{dt} = -k_2 C_s C_t \tag{15}$$

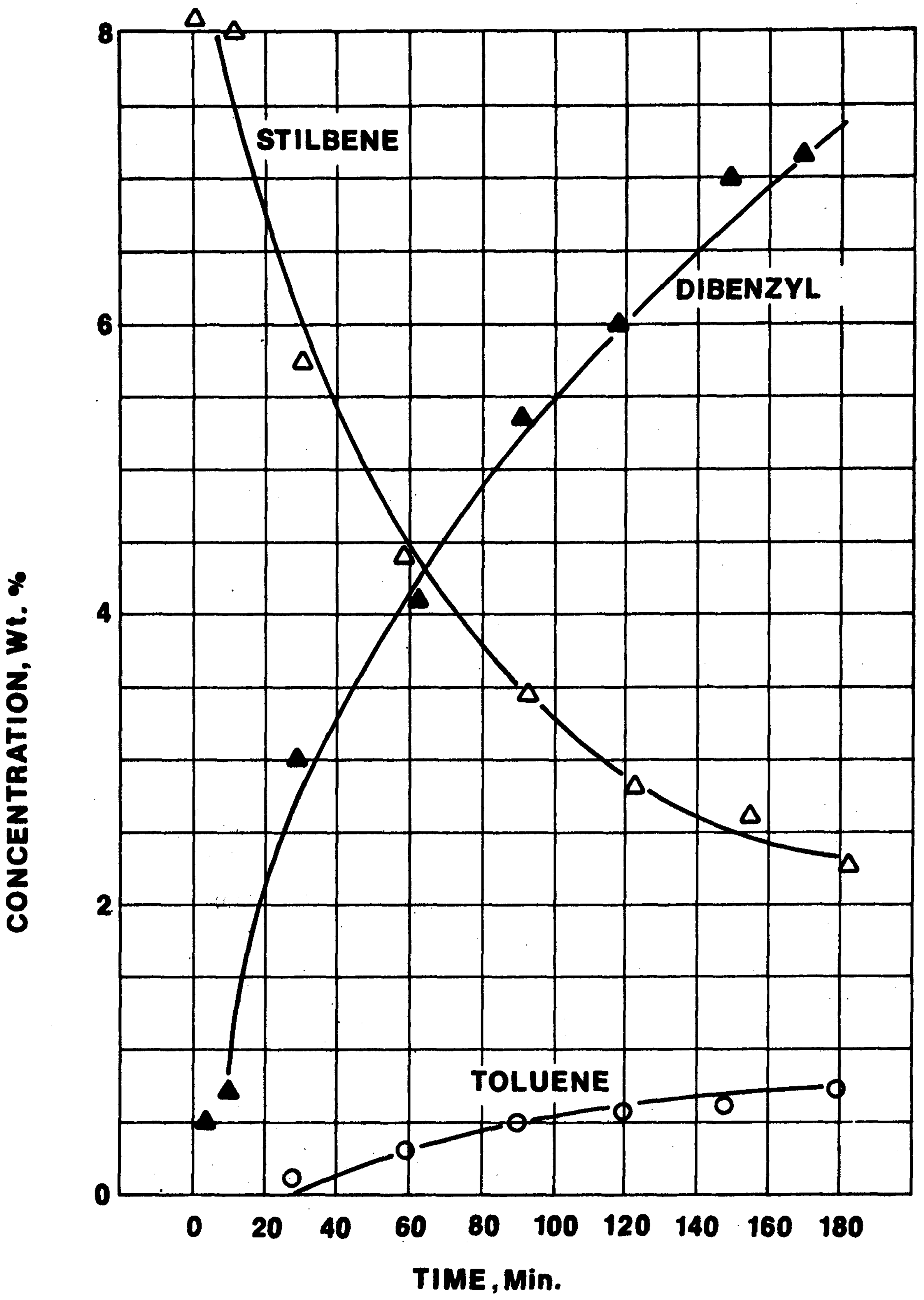


Figure 17: Concentration curves for the conversion of stilbene to dibenzyl and toluene at 400°C

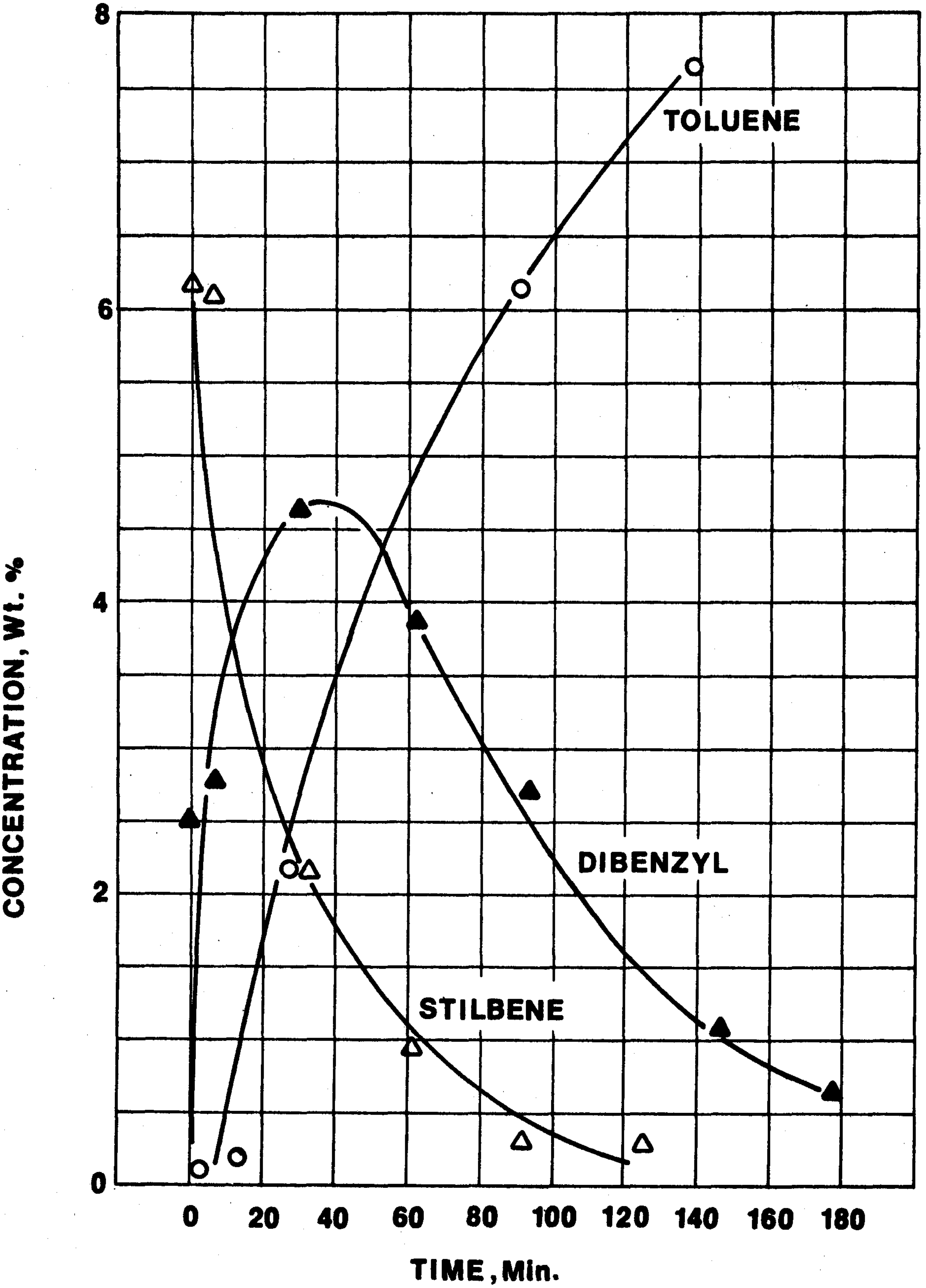


Figure 18: Concentration curves for the conversion of stilbene to dibenzyl and toluene at 450°C

where C_s and C_t are stilbene and tetralin concentrations in weight percent. The Arrhenius plot, Figure 19, indicates an activation energy of 28 400 calories/gram mole.

On a very speculative basis, the dependence of the reaction rate upon tetralin concentration is an indication that the transfer may occur via a concerted four-centered reaction and a free radical intermediate may not be necessary. This may be particularly true at low temperatures where hydrogenation proceeds smoothly but cracking does not occur. Further experimentation would be necessary to test that hypothesis.

F. Rearrangement (Isomerization) Reactions of Donors

During the study of the model compounds, numerous observations were made indicating that donor solvents readily rearrange over the temperature range of 300° to 475°C. Rearrangements are not solely due to thermal effects but appear to be initiated by free radicals, even at mild conditions. Rearrangements not only lead to a drastic decrease in the hydrogen-transfer capability of donor solvents, but also appear to be related to the equally important problem of solvent incorporation (adduction) with acceptor molecules or fragments of the latter.

Tetralin - Since most of the studies used tetralin as solvent, we were not totally surprised to find rearrangements. Curran et al.(2) observed that tetralin decomposed to "C_4 benzenes and indane" and seemed to be promoted by coal extracts; they speculated on several structures for the C_4 benzenes without firm structural evidence. Recent studies by Whitehurst et al.(3) indicated that tetralin rearranged to 1-methyl indane and that this rearrangement was solely temperature dependent. These rearrangements, in either case, were considered minor side-reactions. Both considered these rearrangements to proceed through free radical processes.

The first series of screening reactions made at 400° to 475°C immediately demonstrated the following:

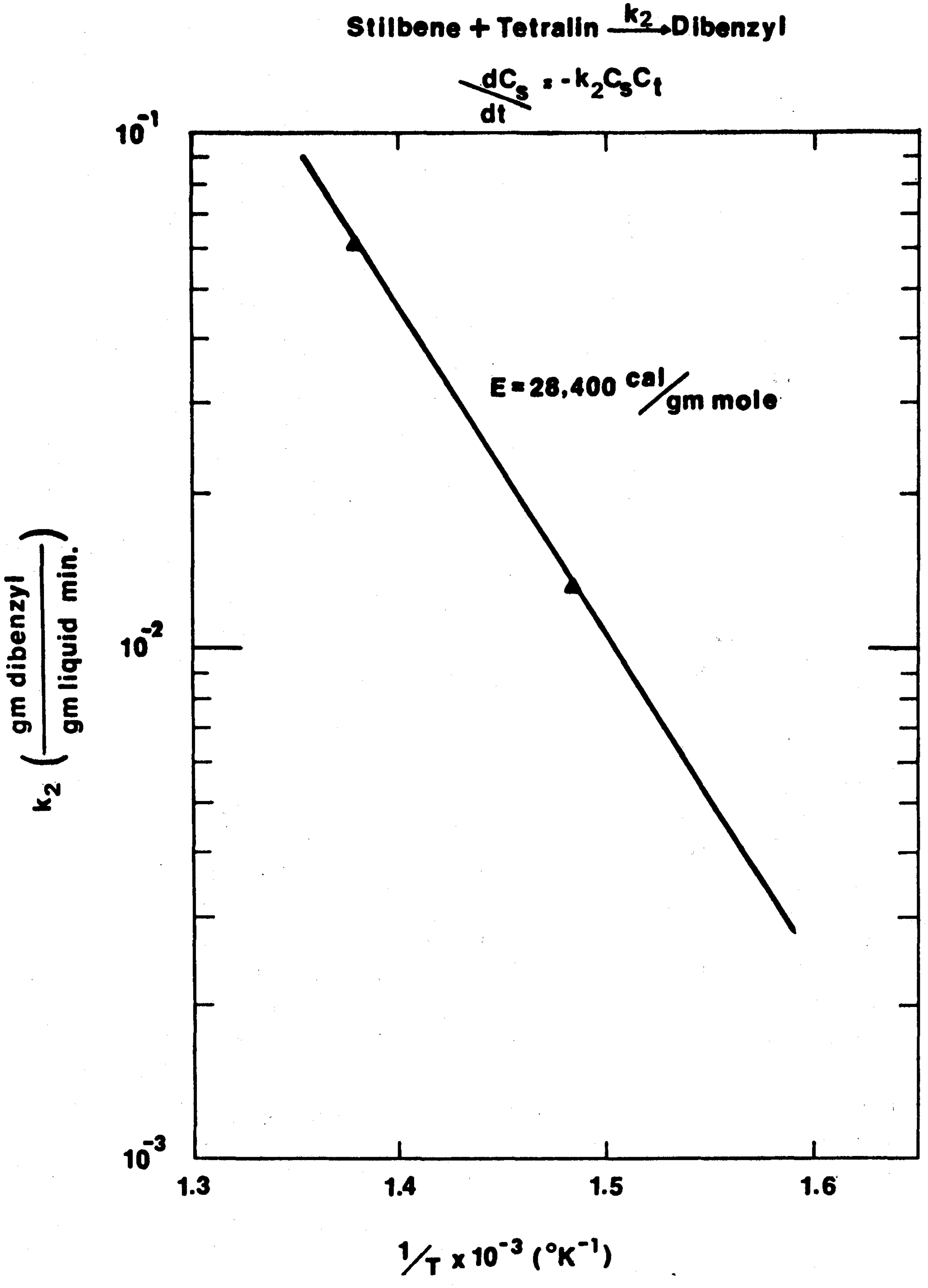
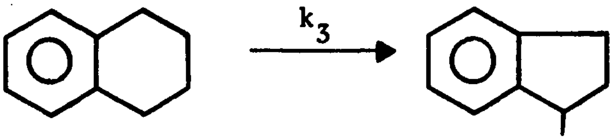


Figure 19: Arrhenius plot for the stilbene to dibenzyl reaction

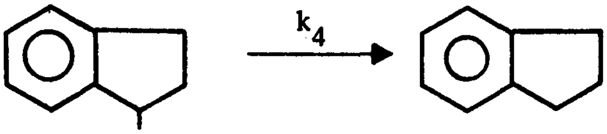
1) tetralin rearranged readily to a methyl indane,
2) the rate of rearrangement was dependent on both temperature and time,
3) the rearrangement was promoted by both good and poor hydrogen acceptors, and
4) tetralin converted further to indane by dealkylation of the methyl indane.

When studying in detail the tetralin/dibenzyl system, we were able to better delineate the primary rearrangement reaction:



(13)

The rearranged product, methyl indane can, in turn, crack to indane:



(14)

In the absence of any previously published data, reaction (13) was assumed to be first order with respect to tetralin concentration. This model fits the experimental data very well. Figure 20 shows Arrhenius plots of k_3 for the following systems: 10% dibenzyl with 90% tetralin in a nitrogen atmosphere, 50% tetralin with 50% mesitylene in nitrogen, 40% tetralin with 50% mesitylene and 10% phenanthrene in nitrogen, and 10% dibenzyl + 50% mesitylene + 35% tetralin + 5% octahydrophenanthrene in nitrogen. The graph shows that while the presence of phenanthrene slightly alters the value of the reaction rate constant, the presence of dibenzyl increases the rate constant by an order of magnitude. Therefore, the rearrangement to methyl indane is significantly promoted by benzyl free radicals. It is further noted that there is a difference in activation energy in the absence or presence of dibenzyl. This is indicative of a change of reaction mechanisms depending upon the presence or absence of free radicals.

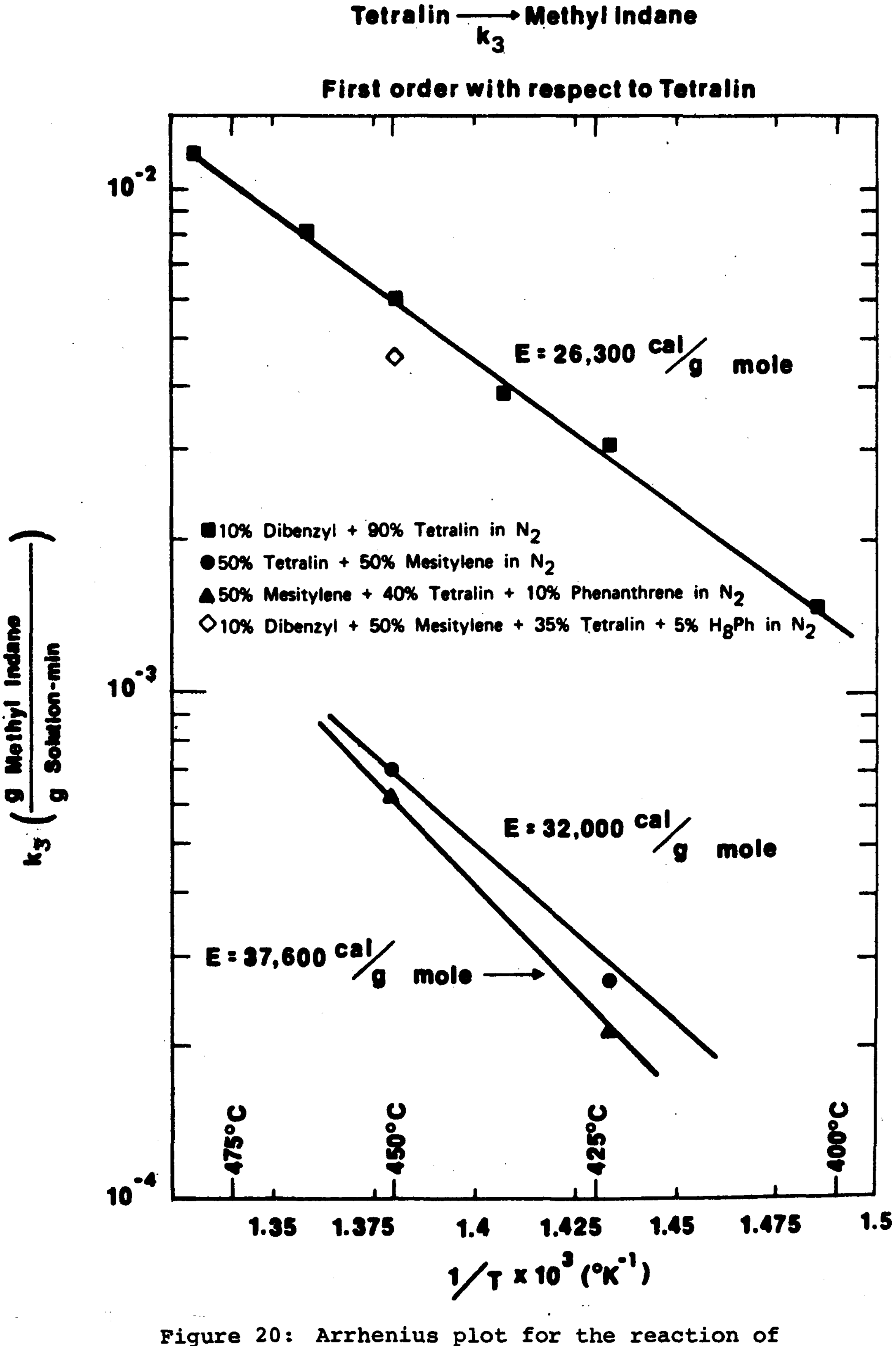
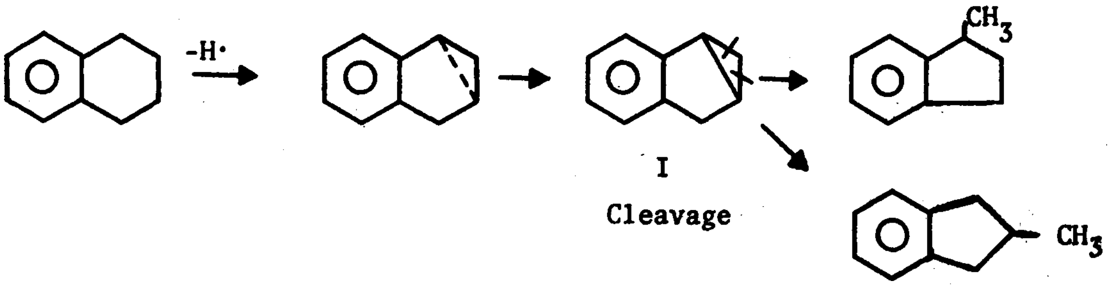


Figure 20: Arrhenius plot for the reaction of tetralin forming methyl indane

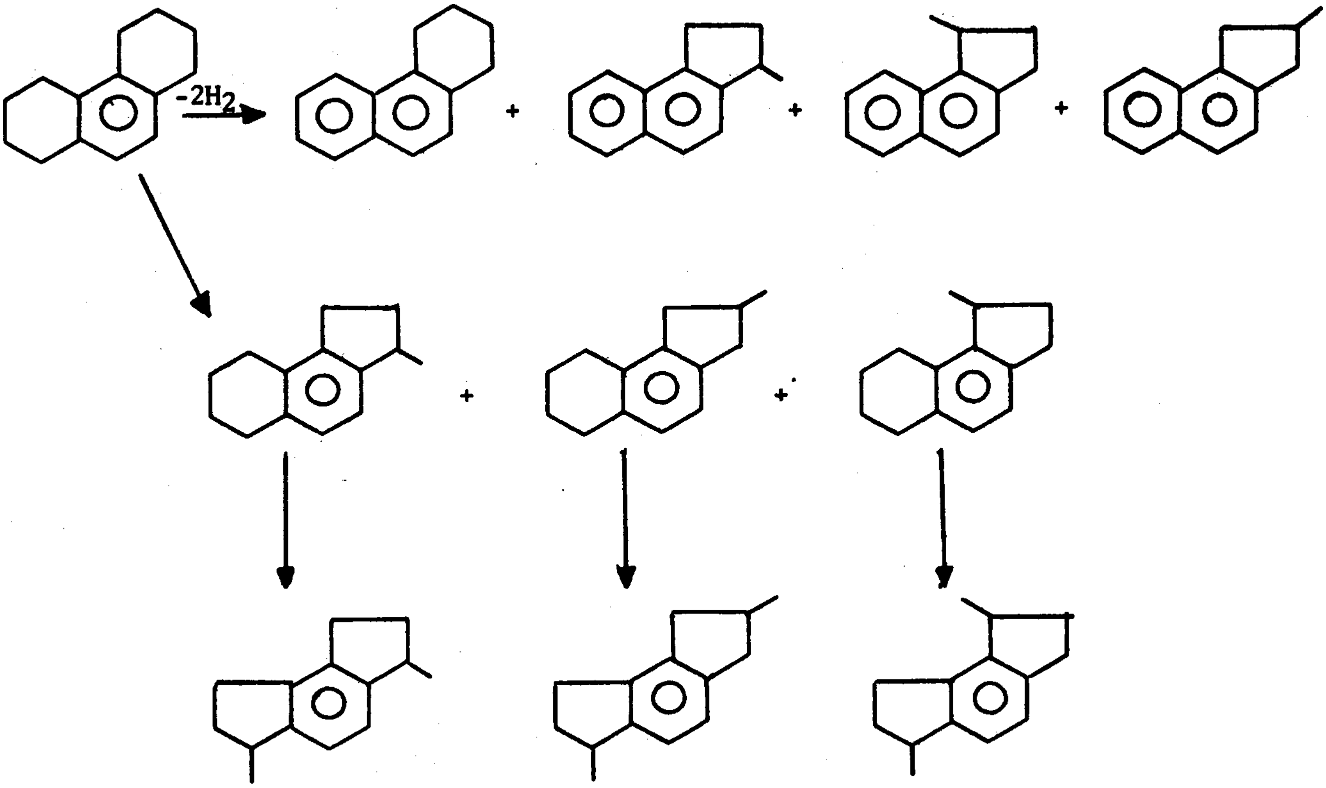
We wish to propose a possible mechanism for the formation of methyl indane through a free radical route. It is noted that insufficient data are available for confirmation, but this is given for future thought. It is first noted that, if hydrogen is abstracted from tetralin at the 1,2 or 1,4 sites, the formation of 1,2 or 2,3 dihydronaphthalene is likely. If abstraction occurs at the 1,3 sites, the subsequent formation of a new three-membered ring intermediate could occur. This ring could then cleave to yield two possible methyl indane structures, as shown below:



It is noted that intermediate-I is a known compound(4) and that 2-methyl indane may be present but not distinguished from its isomer by current GLC-MS techniques (reference is made to a latter section dealing with the rearrangement of ^{13}C-tagged octahydrophenanthrene).

Due to the importance of this rearrangement to donor solvent chemistry, these reactions are being studied with a substituted tetralin (2,6-dimethyl tetralin) and octahydrophenanthrene, which were synthesized as shown in the Appendix. With alkylated tetralins, rearrangment can still occur with the formation of di- and tri-alkyl indanes. These reactions have been carried out and a number of products observed. Isolation and identification by liquid chromatography and ^{13}C-NMR techniques have not been completed. The complexity of products indicates that many alkyl indane isomers are formed. Since a ^{13}C label has been placed on C-4 of 2,6-dimethyl indane, the assignment of all carbons in the NMR spectra should be simplified.

Hydrogenated Phenanthrenes - sym-Octahydrophenanthrene, hereafter designated as H_8Ph, would be expected to follow the same rearrangement as tetralin except with more isomer possibilities. Since dehydrogenation always accompanies rearrangement, isomers of tetrahydrophenanthrene can also be expected. These reactions have also been performed, and structural studies carried out. The following structures are possible products for the pure solvent:



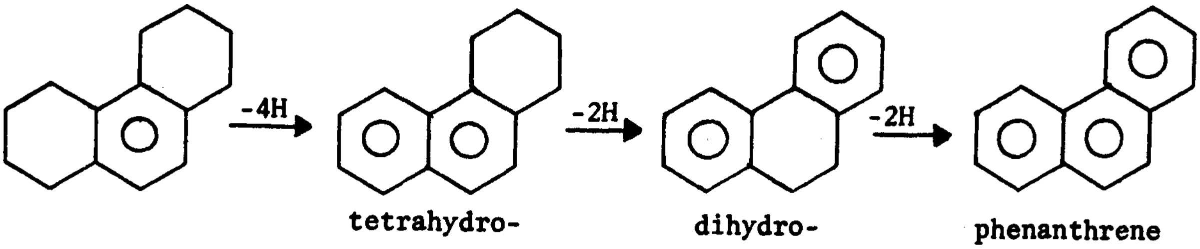
The above structures indicate that, unlike tetralin which yields one isomer, hydrophenanthrenes have multiple structures which each, in turn, forms various isomers. Furthermore, the amounts of these isomers are dependent upon the type of hydrogen-transfer reactions and the environment of the system. Therefore, modeling of the reactions has not been undertaken.

We have attempted to determine the structures of the major products by applying chromatographic and spectroscopic techniques to selected systems. In particular, we have studied products from purely thermal experiments using both ^{13}C labeled and unlabeled H_8Ph. It was observed that the presence of free radicals only changed the relative amounts of the products but not their structures.

The fact that sym-H_8Ph is indeed unstable at 450°C is illustrated by Figure 21 which shows that after three hours, 60% has isomerized. Since the methyl and dimethyl isomers, as a group, were resolved by packed-bed GLC and identified by mass spectrometry, their concentrations are also plotted. Smaller amounts of tetrahydrophenanthrene isomers are present but not shown on this figure. In the study of the rearrangement of octahydrophenanthrene a ^{13}C labeled sample was also used to learn more about the rearrangement process.

From the initial GLC studies to observe H_8Ph stability presented in Figure 21, we were able to qualitatively detect the formation of numerous isomers (by GLC/MS). The GLC curves of several of these isomers are given in Figure 22. These data indicated that the phenanthrene system was indeed complex.

Thermal treatment or any hydrogen transfer reaction would yield three stable dehydrogenation products as follows:



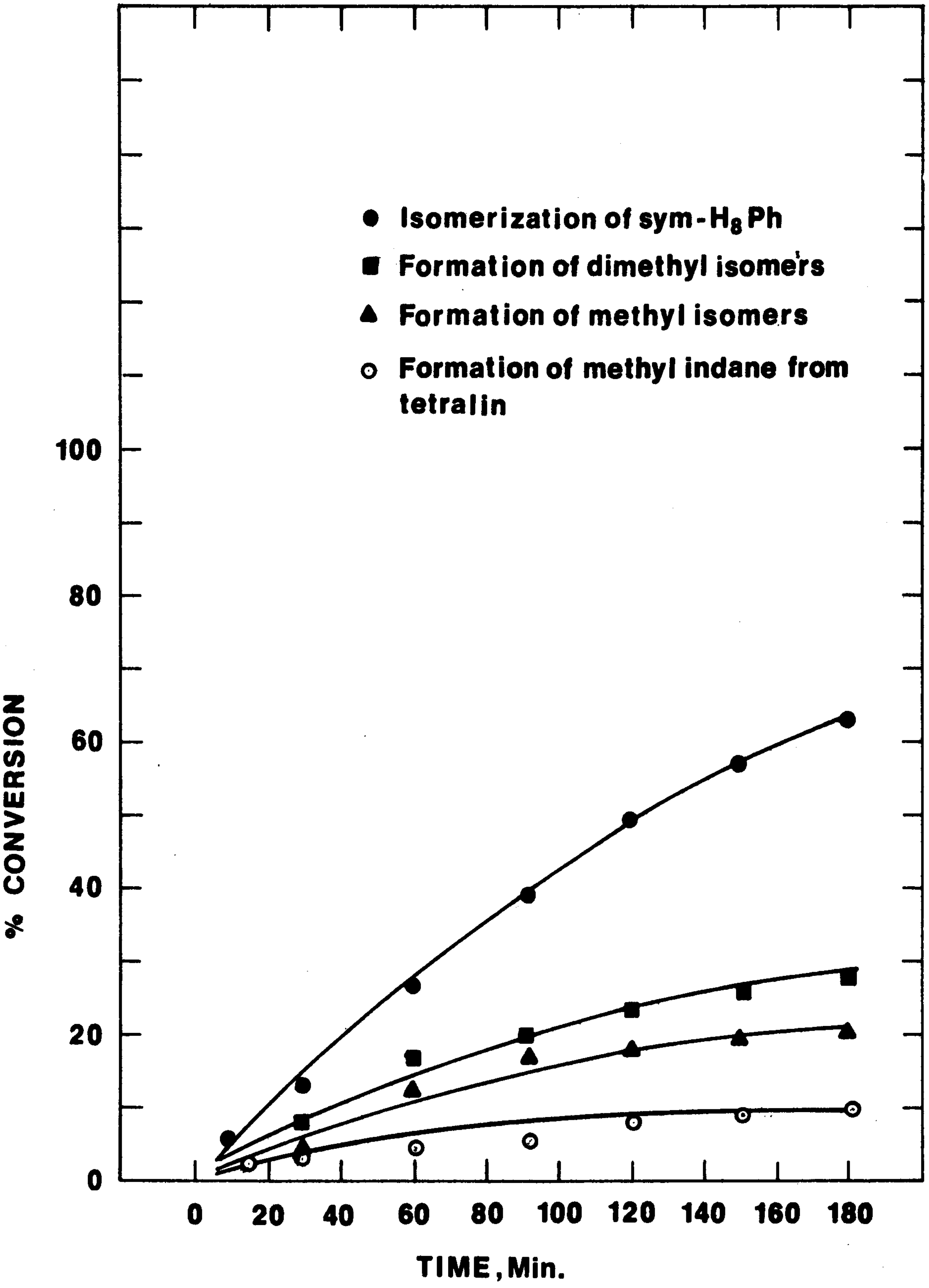


Figure 21: Stability of octahydrophenanthrene at 450°C

An additional intermediate, hexahydrophenanthrene, can also be formed. Numerous isomeric structures are possible for this intermediate and its existence is strongly indicated (as shown later) by mass spectrometry. Since two possible tetrahydro-derivatives exist (hydroaromatic ring being either A or C with ^{13}C label, using steroid nomenclature), each of these can be viewed as a "tetralin derivative." Methyl-indane-type isomers of these tetrahydrophenanthrenes are, therefore, expected.

Considering the complexity of the total reaction mixtures, we decided to separate the mixtures according to number of aromatic rings prior to applying HPLC to each sub-fraction. The technique of aromatic separation had previously been developed and described in the literature.(6) The HPLC technique was developed by J. C. Suatoni of Gulf Research & Development; this technique used a 10 mm x 50 cm column packed with 10μ Lichrosorb (silica), n-hexane as solvent, refractive index detector, and a flow rate of 9.0 ml/min.

The first sample studied in depth was that of the 180-minute period of Run HT77-46 in which H_8Ph stability was studied at 450°C (see Figure 21). This sample contained the following approximate distribution:

Unconverted H_8Ph	38%
Mono-methyl isomers	28%
Di-methyl isomers	21%
Dehydrogenation products	13%

Figure 22 shows the GLC trace of two different monoaromatic concentrates--one is predominantly a monomethyl isomer and the second, dimethyl, in which both rings are contracted. Contrary to the tetralin system, strong ^{13}C-NMR evidence for methyl groups on the β positions of the five-membered rings was obtained.

The ^{13}C-NMR spectra of pure H_8Ph and of the two monoaromatic concentrates shown in Figure 22, are shown in Figures 23, 24, and 25. The appearance of new signals at 19-21.3 ppm is indicative of methyl

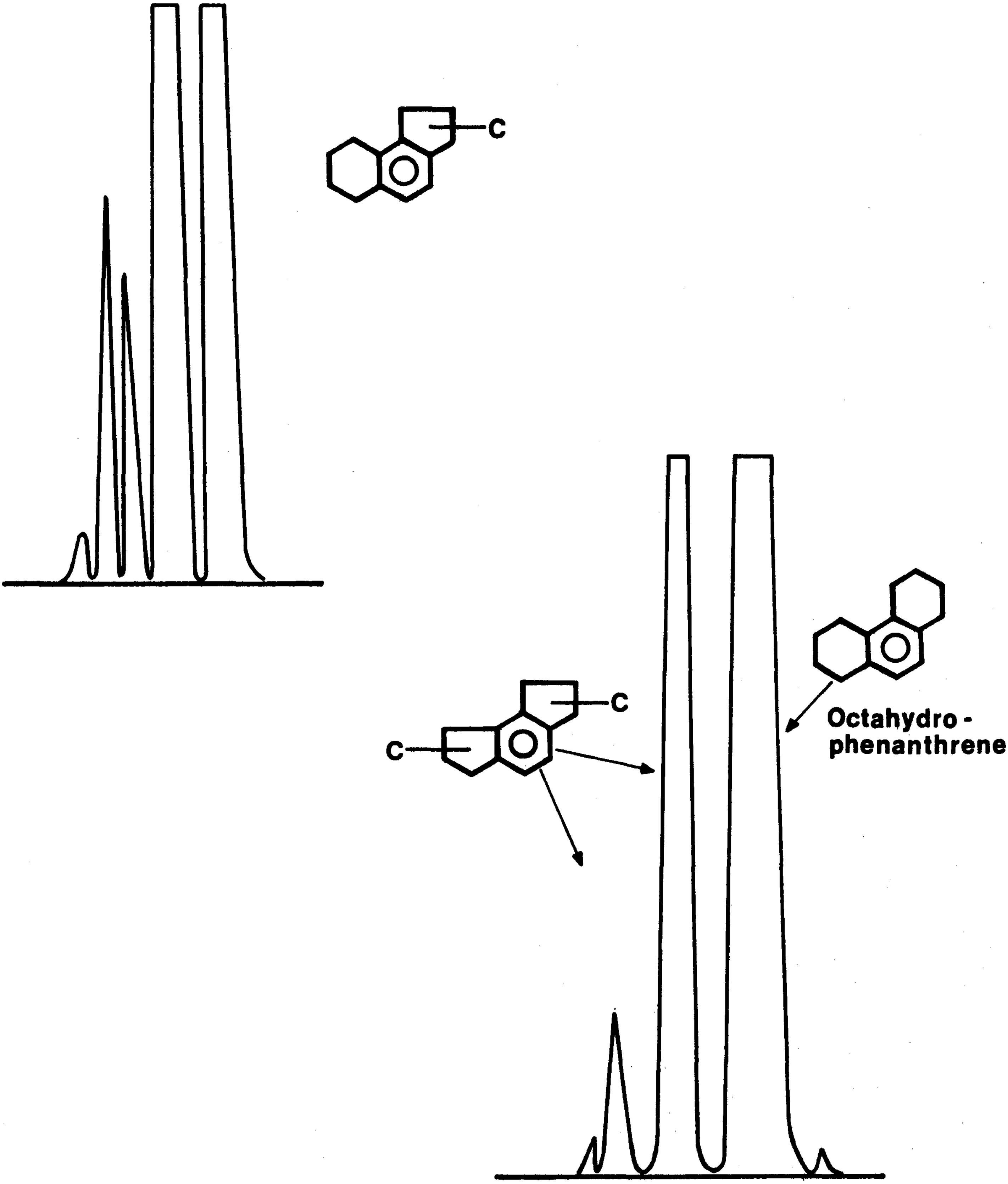


Figure 22: Isomers of Octahydrophenanthrene separated by liquid chromatography and gas-liquid chromatography

groups in a variety of positions on saturated rings; the new signals between 30-35 ppm are indicative of five-membered rings being formed at the expense of the eight hydroaromatic carbons which have signals at 22.9, 23.5, 26.3, and 30.1 ppm.

The absence of a sharp line at ∿14 ppm indicates that ring opening to a n-butyl substituent did not occur. The rearranged isomers also have the same precise mass as sym-octahydrophenanthrene which is further evidence that ring opening did not occur.as inplied by the work of Curran et al.(2) in which experimentation was done with tetralin.

The question of rearrangement of octahydrophenanthrenes was further studied by performing both thermal and 10% dibenzyl reactions at 450°C on both unlabeled and ^{13}C-labeled solvents. All products were separated by preparative liquid chromatography and preparative HPLC. All major fractions (>20 mg) were then analyzed by ^{13}C-NMR, mass spectrometry (70 ev), and ultraviolet absorption spectroscopy. The "best fit" structure(s) was then deduced based on published data of related compounds. Minor components have not been studied.

The major usefulness of the ^{13}C label is to distinguish the two hydroaromatic rings in the tetra- and octahydro products. The presence of benzyl free radicals had no effect on the structure of any given fraction. However, larger quantities of ^{13}C-phenanthrene and ^{13}C-tetrahydrophenanthrenes were formed when the reaction took place in the presence of free radicals. This effect of having acceptor free radicals present is shown in Table III. These results demonstrate that hydrogen is abstracted from H_8Ph when dibenzyl cracking occurs. In addition, a significant level of isomerization of the hydrophenanthrenes occurs.

Based upon the above data, we do not feel that absolute values of transferred hydrogen can be calculated from routine product analysis. Specifically, isomerization is difficult to measure and it plays a significant role in setting the amount of hydrogen apparently being transferred.

Figure 23: ^{13}C NMR Spectrum of Sym-Octahydrophenanthrene (Saturate Region)

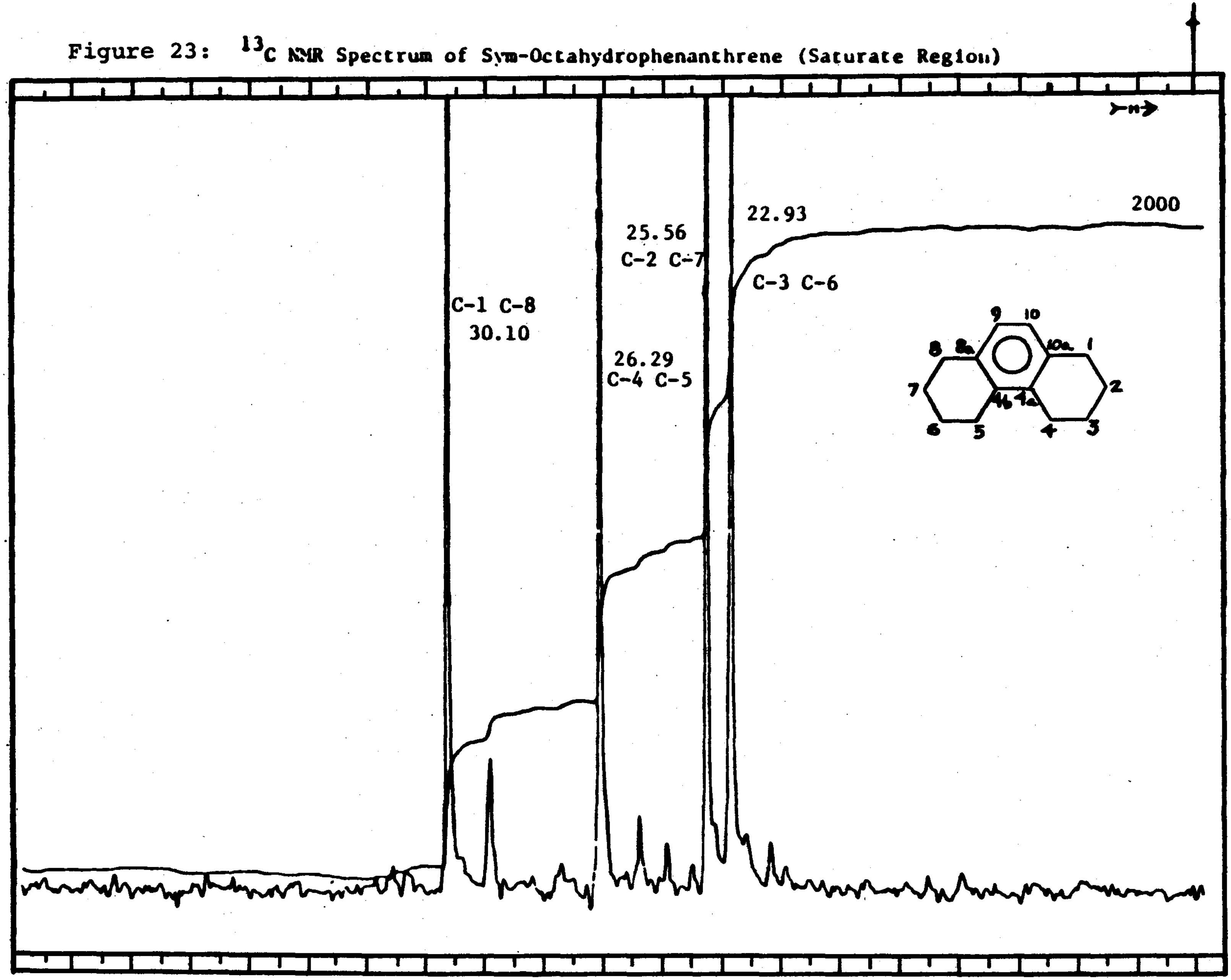


Figure 24: ^{13}C-NMR spectrum of monomethyl isomers of rearranged octahydrophenanthrene

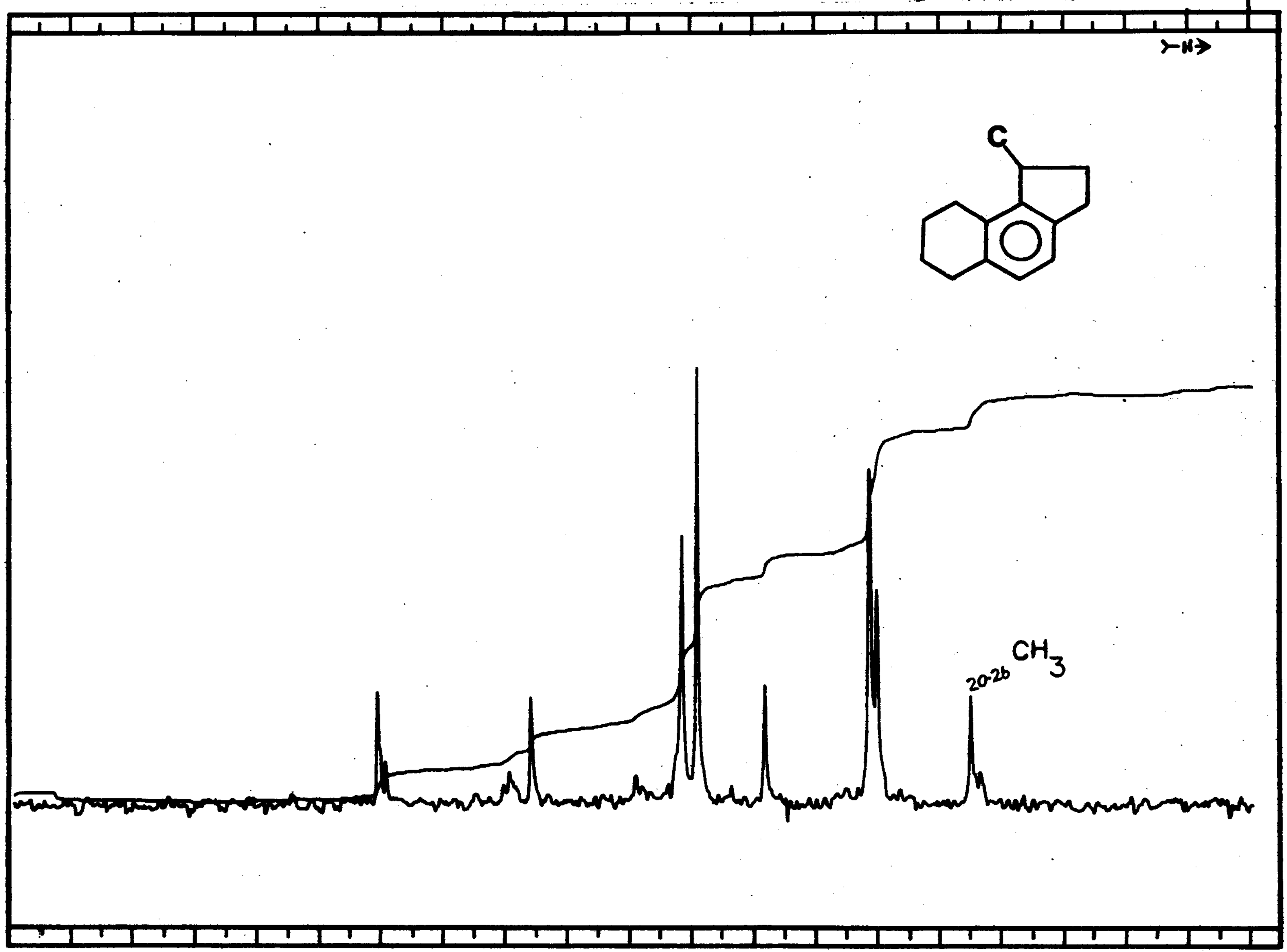
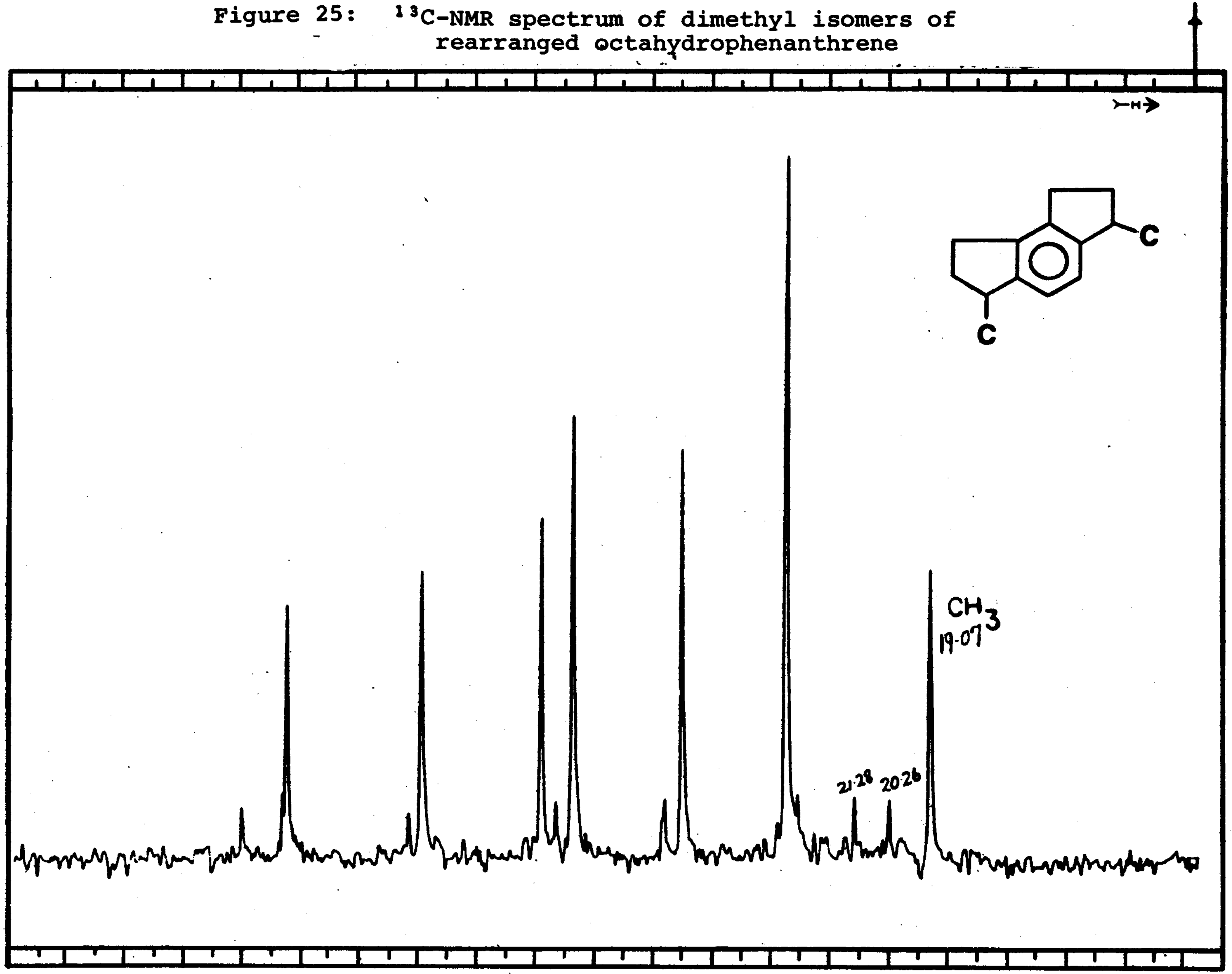


Figure 25: ^{13}C-NMR spectrum of dimethyl isomers of rearranged octahydrophenanthrene



Octahydrophenanthrene is known to be an excellent donor solvent for coals.(5) Due to its higher boiling point and greater number of transferable hydrogens than tetralin, one might speculate that H_8Ph would be the better donor solvent. From the results of the cracking experiments with model acceptors, the kinetics of any particular cleavage are the same in either tetralin or octahydrophenanthrene, provided that a minimum amount of hydrogen is available. The observation that both tetralin and octahydrophenanthrene rearrange over a wide temperature range and each is promoted by free radicals indicates that the volatility of solvent is not important, at least in these batch autoclave experiments.

A discussion of the means and results of identifying the major structural patterns of isolated fractions is given in the Appendix.

Conclusions - The rearrangement (isomerization) of hydroaromatic donor solvents has the potential to play a significant role in coal liquefaction. Specifically, high levels of effective hydrogen donors rearrange to isomers having poor donor quality. The rearrangement reactions of the tetralin and octahydrophenanthrene systems have been studied with the following conclusions being drawn:

- The isomerization of hydroaromatic donor solvents is a general phenomenon which occurs in two- and three-ring systems. Presumably, this can be extrapolated to multiple-ring systems.

- The rate of rearrangement appears to be first order with respect to donor solvent concentration. The activation energy of the reaction (in the case of tetralin) is in the range of 26 to 32 kcal/g mole, depending upon whether a free radical precursor, such as dibenzyl, is present or not, respectively.

Table III

DEHYDROGENATION AND REARRANGEMENT OF OCTAHYDROPHENANTHRENE: THERMAL AND DIBENZYL CRACKING REACTIONS

(180 minute samples of runs at 450°C)

Run No. (HT 77-)	29		46	
Donor Solvent Analysis				
Octahydrophenanthrenes				
sym - H_8Ph (unconverted feed)	16.8%		38.0%	
iso - H_8Ph	30.9		49.0	
Total		47.7%		87.0%
Tetrahydrophenanthrenes				
sym - H_4Ph	22.3		--	
iso - H_4Ph	12.1		--	
Total		34.4		13.0
Miscellaneous Hydrophenanthrenes (Including di-)		7.2		0.0
Phenanthrene		10.7		0.0
		100.0%		100.0%
Feed Composition, Wt.%				
Tri-methyl benzene	60%		60%	
H_8Ph (unlabelled)	30		40	
Dibenzyl	10		—	
		100.0%		100.0%

DCC:smm
CR&CD
GR&DC
3/16/78

- At similar conditions, the extent of isomerization of three-ring hydroaromatics, H_8Ph, is greater than that having two rings, tetralin.

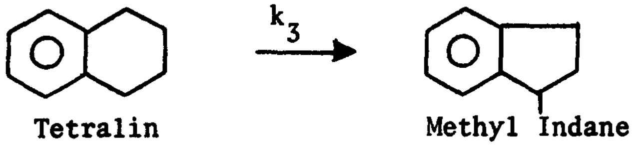
- The rate of rearrangement is strongly affected by the presence or absence of free radicals (acceptors). Namely, tetralin isomerization to methyl indane is increased by an order of magnitude when benzyl radicals are present.

- A wide range of isomers have been isolated for the two-and three-ring systems. Both 1- and 2-methyl-indane-type systems have been found from experiments using ^{13}C tagged feed. The distribution of isomeric structures does not appear to be affected by the presence of free radicals.

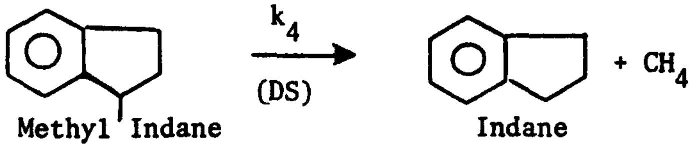
In summary, isomerization of donor solvents will play a major role in liquefaction processes, particularly those using recycled solvents. Techniques will have to be developed for the routine analysis of solvent streams to differentiate between compounds having "donatable" hydrogen and those having hydrogen tied up in more stable isomers.

G. Thermal Stability of Donor Solvents

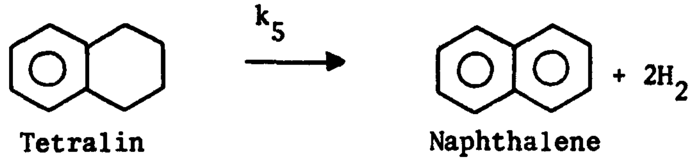
The following reactions can occur because of the instability of tetralin above 400°C.



(13)



(14)



(15)

Reaction (13) has been discussed in the previous section. The latter two reactions will be discussed herein. It is noted that correlations derived for the dealkylation and dehydrogenation of tetralin should, in general, be applicable to H_8Ph. Experimentation with H_8Ph has not been undertaken due to the complexity of analysis.

The data indicate (see Figure 26) that for the system of 50% mesitylene with 50% tetralin in nitrogen, methyl indane dealkylation, reaction (14), occurs slowly. For low levels of production of indane, it can be characterized by a zero order mechanism. Thus,

$$\frac{dC_I}{dt} = k_4 \tag{16}$$

The above equation also correlates the data with systems of 10% dibenzyl and 90% tetralin in nitrogen; 50% mesitylene, 40% tetralin, and 10% phenanthrene in nitrogen; and 50% mesitylene, 35% tetralin, 5% H_8Ph, and 10% dibenzyl in nitrogen. The Arrhenius plots for k_4 obtained for these systems are described in Figure 27. As shown, the presence of dibenzyl significantly increases the rate of reaction (14). Phenanthrene appears to somewhat hinder the reaction rate.

Preliminary analyses of data at 450°C with 10% dibenzyl and 90% tetralin in hydrogen and dibenzyl with tetralin in nitrogen at high dibenzyl concentrations (>25%) indicate that for these systems, reaction (14) is no longer zero order (see Figure 28). In these cases, reaction (14) is most likely first order with respect to methyl indane concentration. Also, the rate of indane production with a feed of 90% tetralin plus 10% dibenzyl in a hydrogen atmosphere is double that with the same feed in a nitrogen atmosphere.

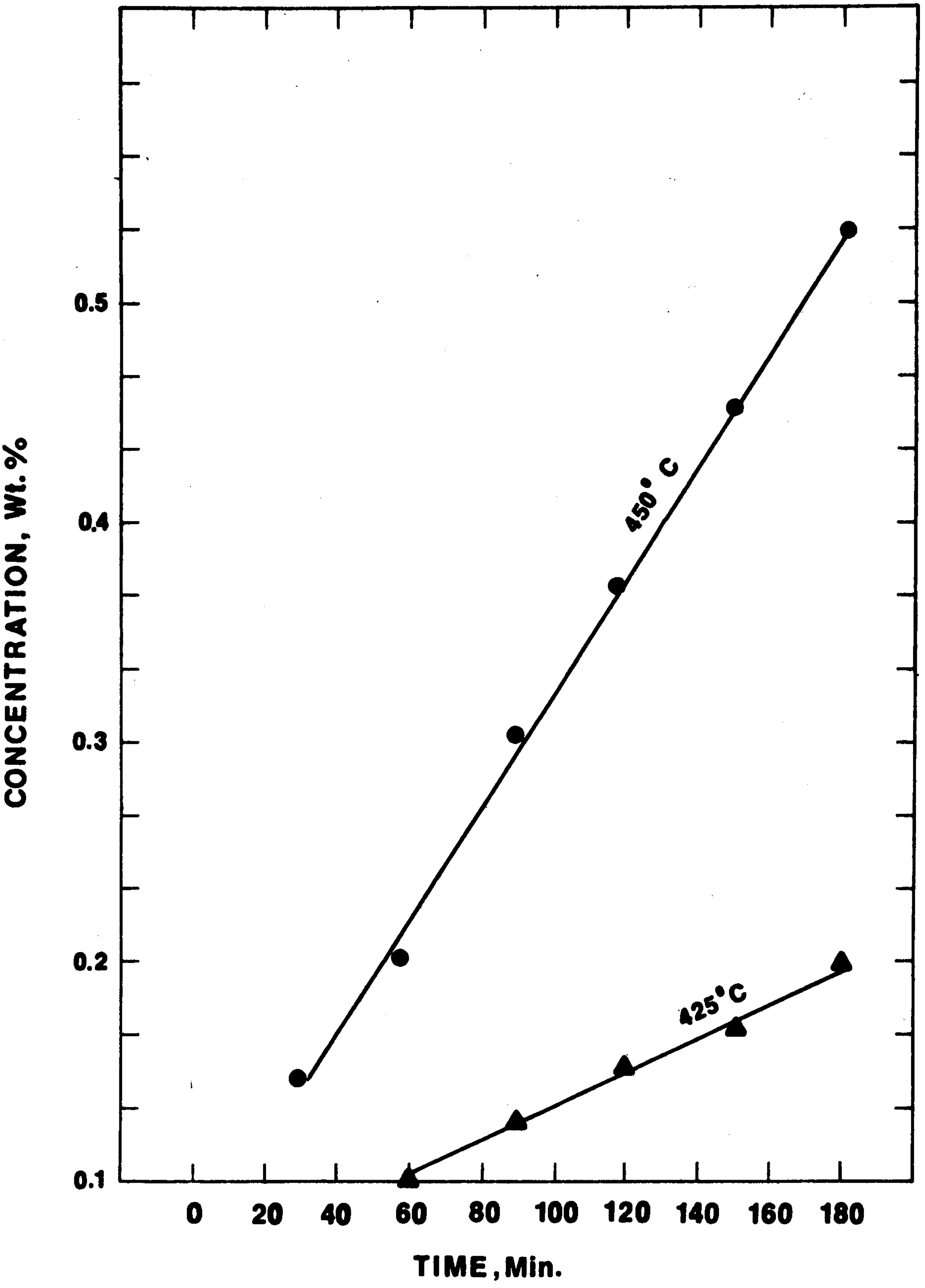


Figure 26: Indane concentration versus time for a feed of 50% mesitylene and 50% tetralin in nitrogen

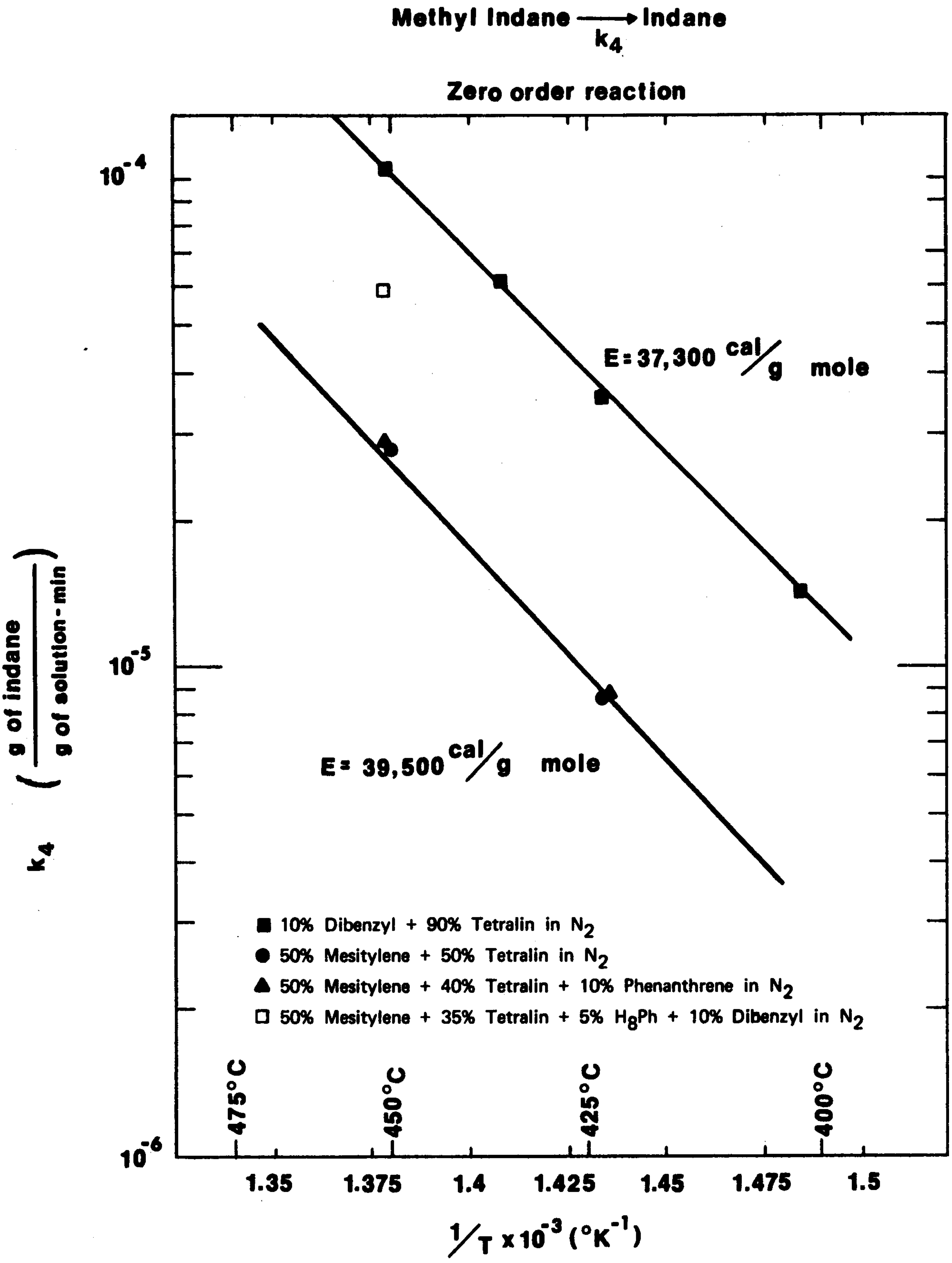


Figure 27: Arrhenius plot for the cracking of methyl indane to form indane

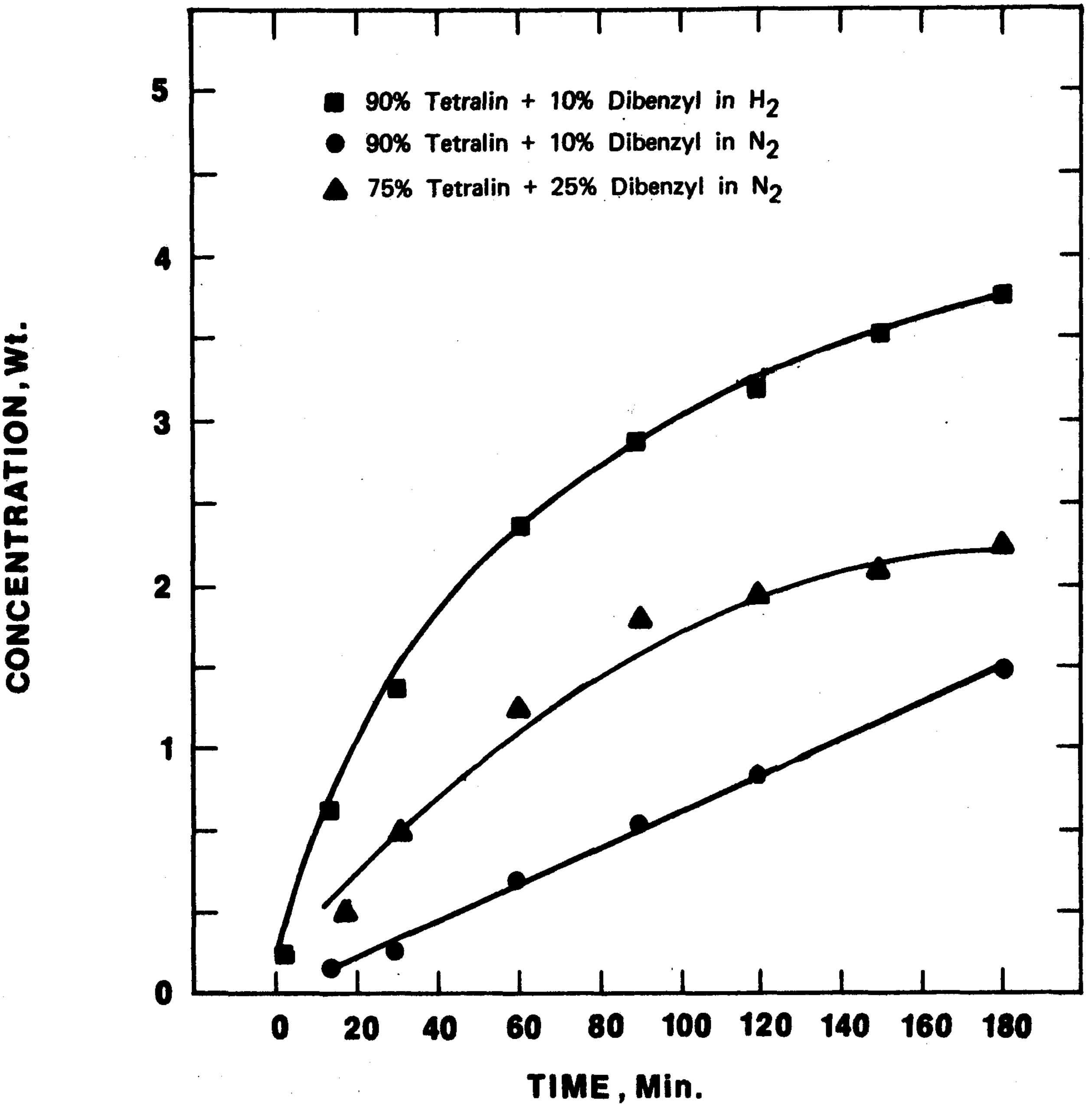


Figure 28: Indane concentration versus time for different feeds at 450°C

The naphthalene formation by reaction (15) can be obtained by subtracting the naphthalene production from reaction (9) from total naphthalene production. This net production is believed to occur by reaction (15). For the tetralin systems: 90% tetralin with 10% dibenzyl in nitrogen, 50% tetralin with 50% mesitylene in nitrogen, and 40% tetralin with 50% mesitylene and 10% phenanthrene in nitrogen, the net production rate of naphthalene follows the rate expression:

$$\frac{d\bar{C}_N}{dt} = k_5 \tag{17}$$

where k_5 is the zero order rate constant and $d\bar{C}_N/dt$ is the net production rate of naphthalene by reaction (15). The Arrhenius plots for k_5 are shown in Figure 29. The rate constant, k_5, is only mildly increased by the presence of an acceptor (dibenzyl). Phenanthrene appears to somewhat hinder reaction (15).

H. Hydrogen Transfer to Oxygenated Compounds

After studying the behavior of various hydrocarbons as acceptors in hydrogen transfer reactions, it was decided to evaluate the effect of hydrogen transfer solvents upon heterocompounds. Particular emphasis was placed upon the study of oxygen-containing compounds due to their reasonable reactivity and high concentration in coals of low rank. Functional groups were chosen that would provide a reasonable comparison with hydrocarbons previously studied. In addition, these groups would be likely constitutents of coals.

The screening experiments had indicated that a heteroatom in an aromatic ring did not substantially increase the molecular activity with respect to hydrogen transfer. For example, dibenzofuran, dibenzothiophene, and carbazoles are essentially inert to tetralin at temperatures up to 475°C. They did show that if a sulfur or oxygen were not part of the aromatic system, they would generally enhance reactivity. Based on this work, experimentation with dibenzyl ether and various carbonyls and hydroxyls was undertaken. The following is a discussion of the results.

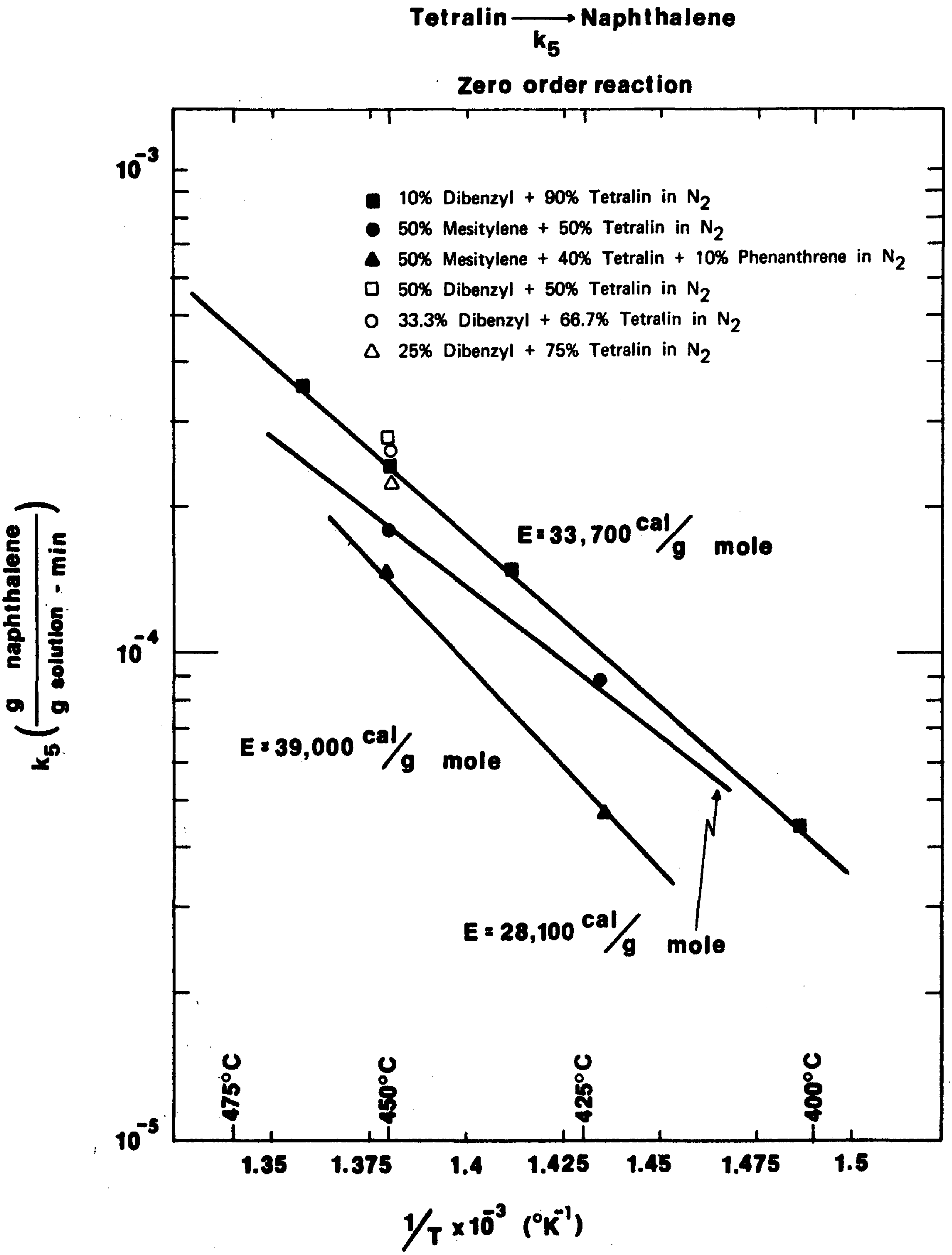


Figure 29: Arrhenius plot for tetralin dehydrogenation to naphthalene

1. Dibenzyl Ether

The study of the hydrogen transfer cracking of dibenzyl ether is an obvious extension of the experimentation with dibenzyl due to the relative ease of breaking the C-O bond, the means available for product analysis, and the known presence of ethers in coals, particularly those of low rank. Since preliminary screening experiments showed a rapid conversion of ethers above 400°C, a temperature range of 300-400°C was chosen for the kinetic study. This study was made using tetralin and mesitylene as solvents. Since tetralin was essentially stable to rearrangement below 400°C, this provided a system to evaluate hydrogen transfer with a minimum of ring contraction to methyl indane.

Assuming that dibenzyl ether will thermally cleave at the β-position, similar to dibenzyl, the initial intermediates are expected to be $Ph\text{-}CH_2\cdot$ and $Ph\text{-}CH_2O\cdot$ radicals. If hydrogen is abstracted from a good donor solvent, toluene and benzyl alcohol would be the stable end products. These sole products had been observed in the literature(7,8) for the solvent tetrahydroquinoline.

However, our analyses (GLC, MS, IR) have shown that benzaldehyde was formed in place of benzyl alcohol. Figure 30 is an example of the GLC separation indicating benzaldehyde (mass spectrometer detector); this was confirmed by co-injection techniques and infrared spectra, as shown in Figure 31.

Calculation of the major component concentrations from these experiments confirmed that benzaldehyde was a reaction intermediate (see Figures 32 through 37). In particular, Figure 33 demonstrates that, at higher temperatures, the benzaldehyde was reacting with tetralin and, as confirmed by subsequent experiments with pure benzaldehyde, was converted primarily to toluene with only little conversion to the alcohol. Figure 35 indicates that, within analytical experimental error, little net change in tetralin concentration occurred in the 300-365°C range. Figure 36, however, shows that a limited amount of naphthalene was being formed by direct hydrogen transfer.

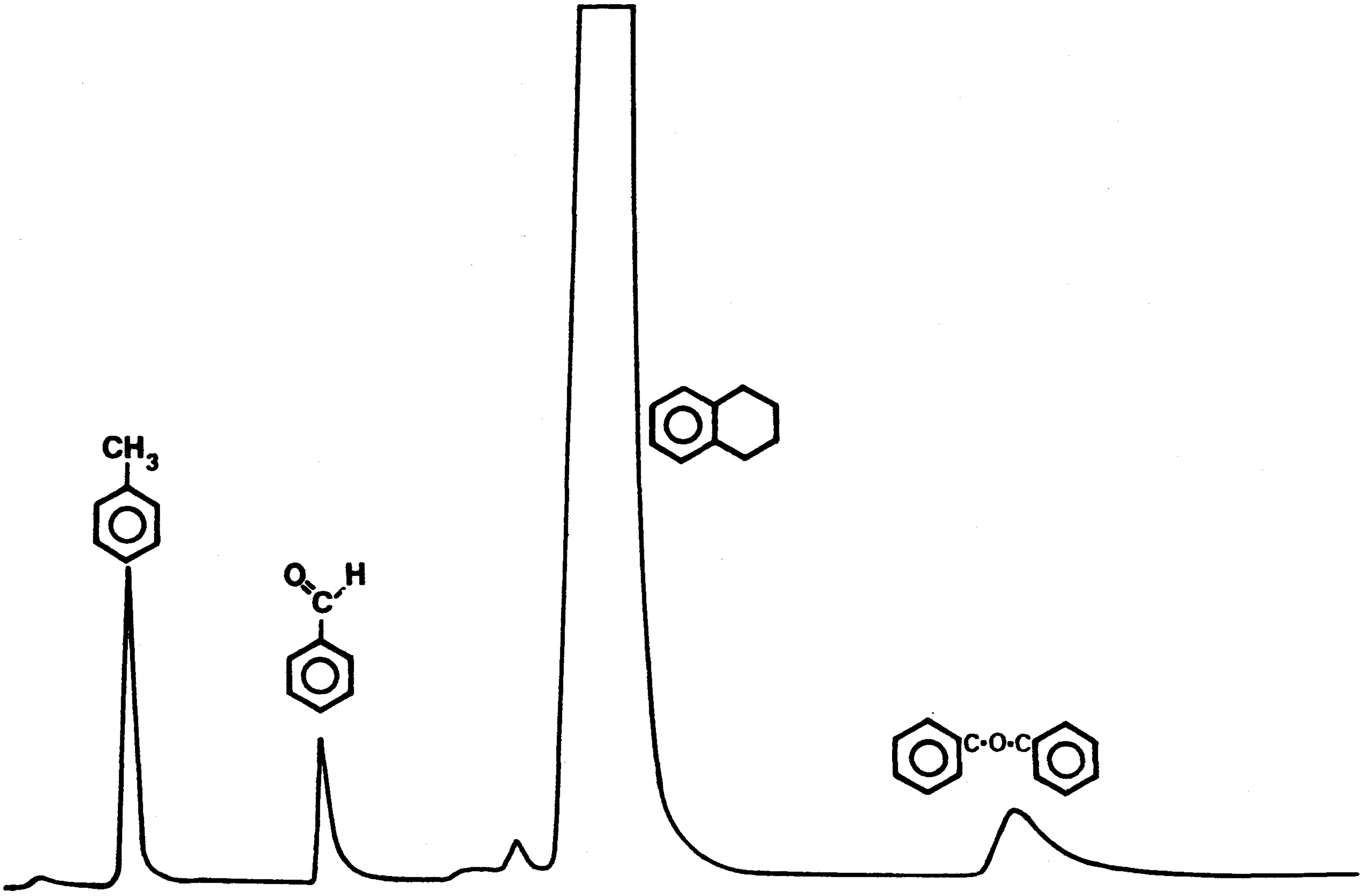


Figure 30: Gas-liquid chromatograph of dibenzyl ether hydrogen-transfer cracking products

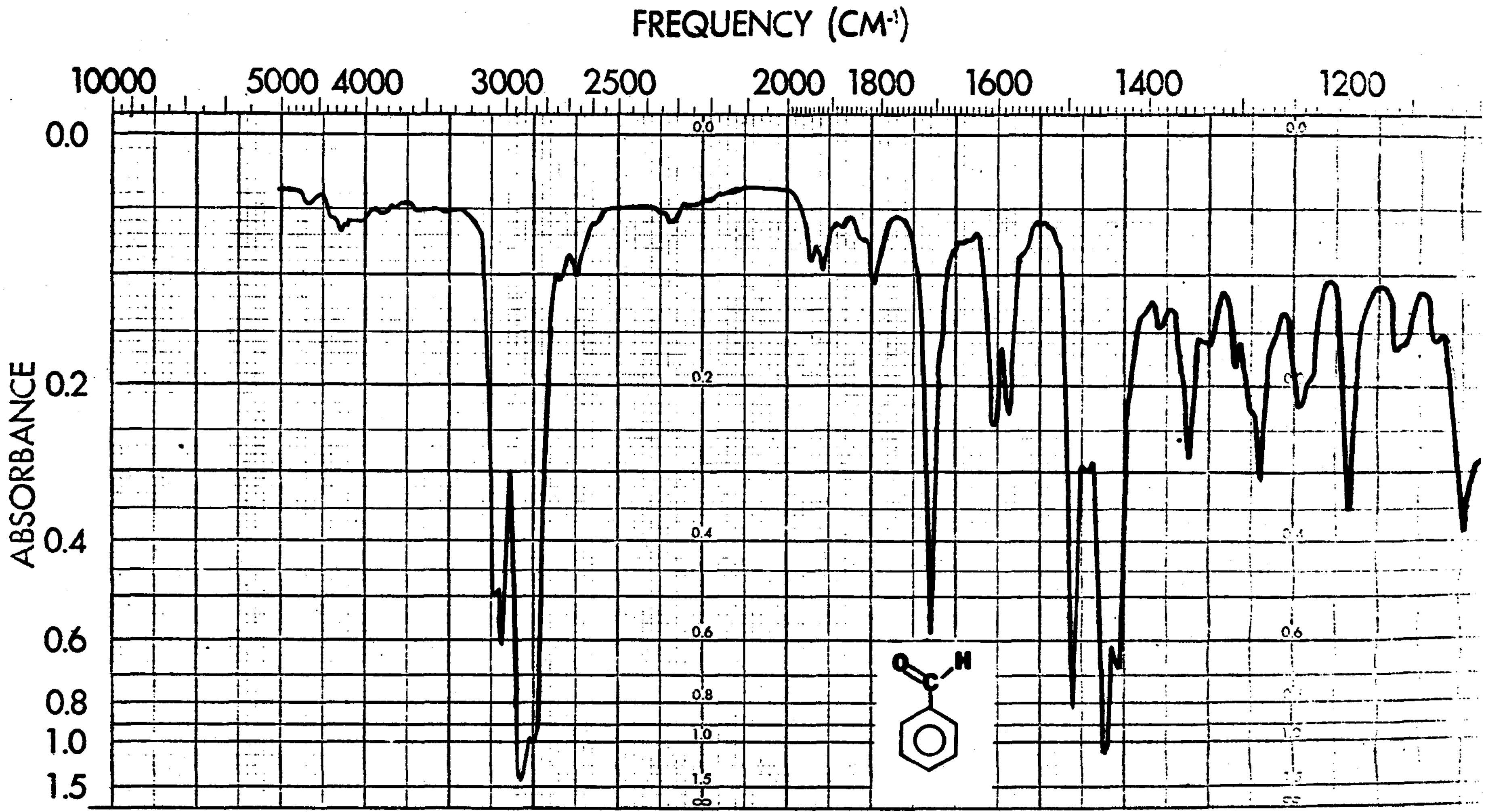
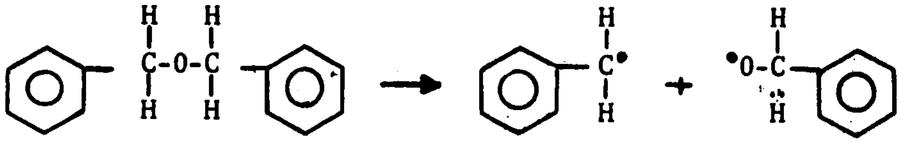


Figure 31: Dibenzyl ether products at 400°C after 30 minutes reaction time

Two dibenzyl ether experiments were done with mesitylene as a solvent at 350°C using both nitrogen and hydrogen atmospheres. These runs showed that conversion to toluene and benzaldehyde again resulted without hydrogen transfer but at a slightly slower rate than that observed with tetralin. No polymerization of mesitylene was observed.

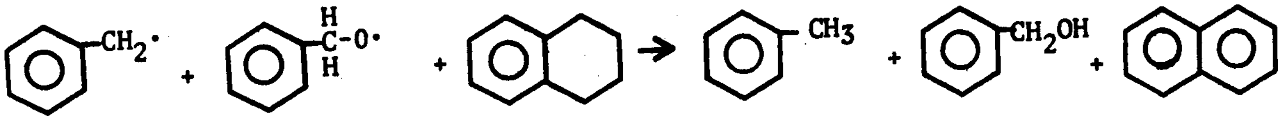
These various experiments suggest that conversion can occur by two routes: (1) intermolecular hydrogen transfer and (2) intramolecular hydrogen transfer. The overall reactions are proposed as follows:

(1) Intermolecular: thermal cleavage to yield free radicals:

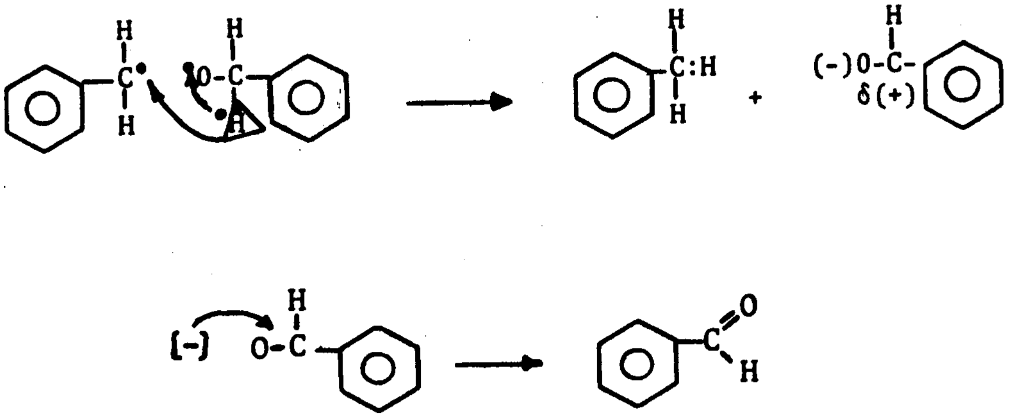


(18a)

(18b)

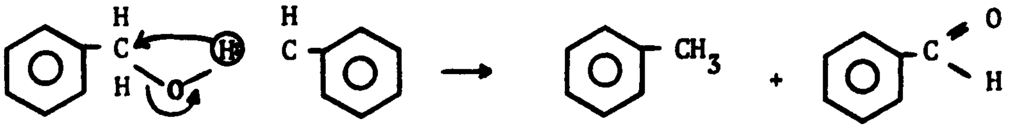


(2) Intramolecular hydride transfer: generate toluene and benzyloxy anion by the thermal cleavage of the C-O bond which is then stabilized by rearrangement to the aldehyde.



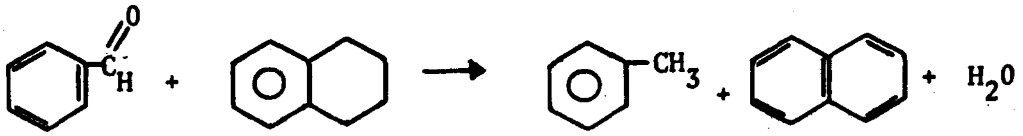
(19a)

or this can be illustrated by a simple hydride transfer without a free radical intermediate:



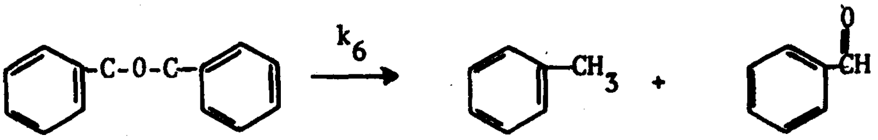
(19b)

The intramolecular rearrangement is apparently favored in poor (non-donor) solvents and at low temperatures (<365°C). However, the overall conversion of dibenzyl ether is enhanced by tetralin at any temperature by providing a source of hydrogen sites and by the fact that benzaldehyde can react as follows:



(20)

The overall dibenzyl ether (tetralin reaction) is assumed to progress as follows:



(21)

A satisfactory fit of the data to the following rate equation was achieved:

$$\frac{d\ C_{DBE}}{dt} = -k_6\ C_{DBE} \tag{22}$$

where C_{DBE} is the concentration of dibenzyl ether (in weight percent) in tetralin. As shown in the Arrhenius plot, Figure 38, the activation energy of k_6 was 36 440 calories/gram mole. If the first-order rate expression is valid, then the conversion of C_{DBE} should be independent of the feed composition. At 350°C, percentage conversions of DBE were measured for four different DBE feed concentrations (i.e., 10%, 15%, 30%, and 42%.) These results are summarized in Figure 39. The results indicate that the assumption of first-order reaction mechanism for DBE conversion is valid. This also indicates that, of the two routes mentioned above, the intramolecular reaction route is most likely to be valid. Experimentation with deuterium further confirms this in that little deuterium is transferred from the donor solvent to the reaction products.

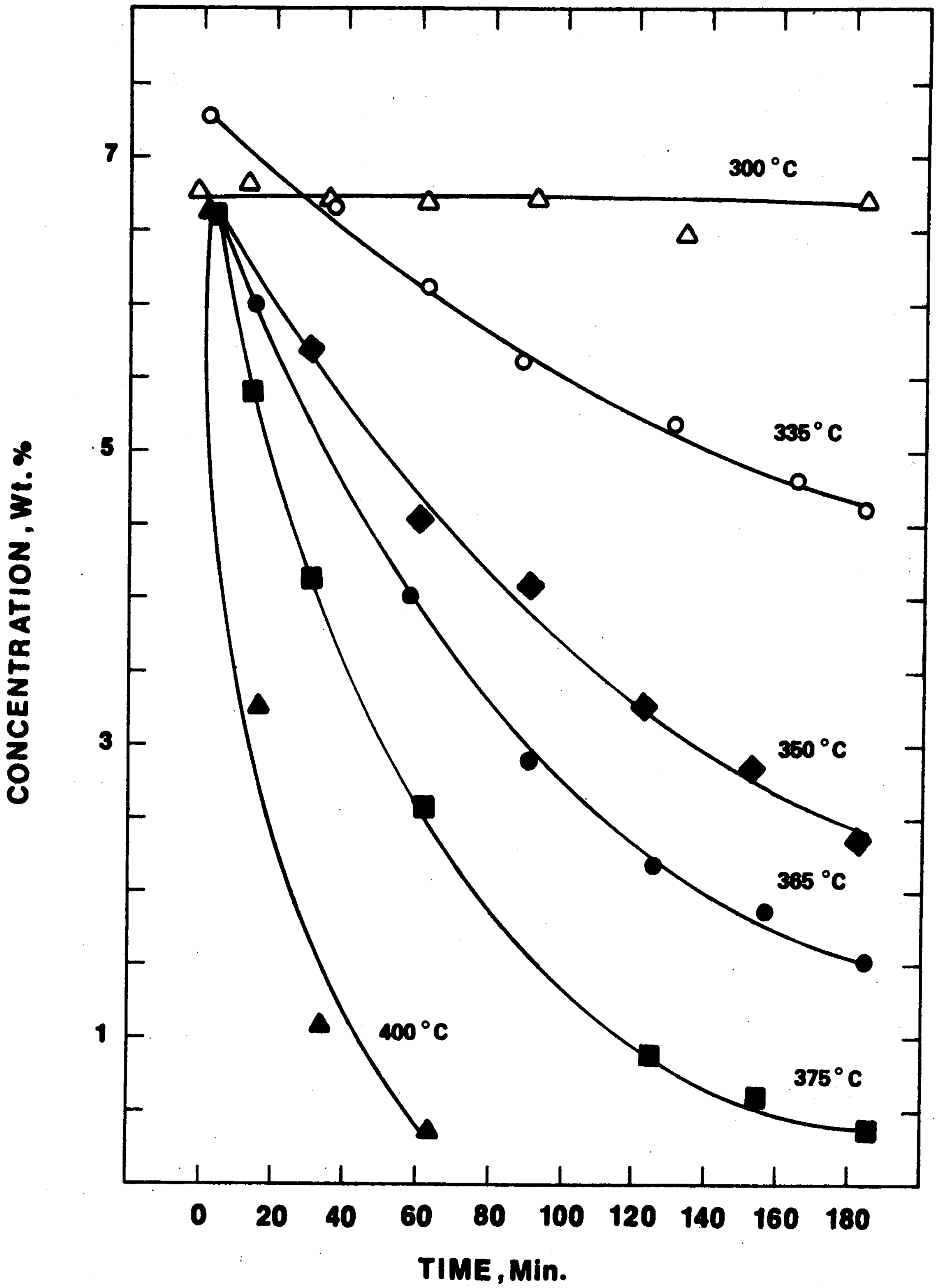


Figure 32: Dibenzyl ether concentration versus time for a feed of 10% dibenzyl ether with 90% tetralin in a nitrogen atmosphere

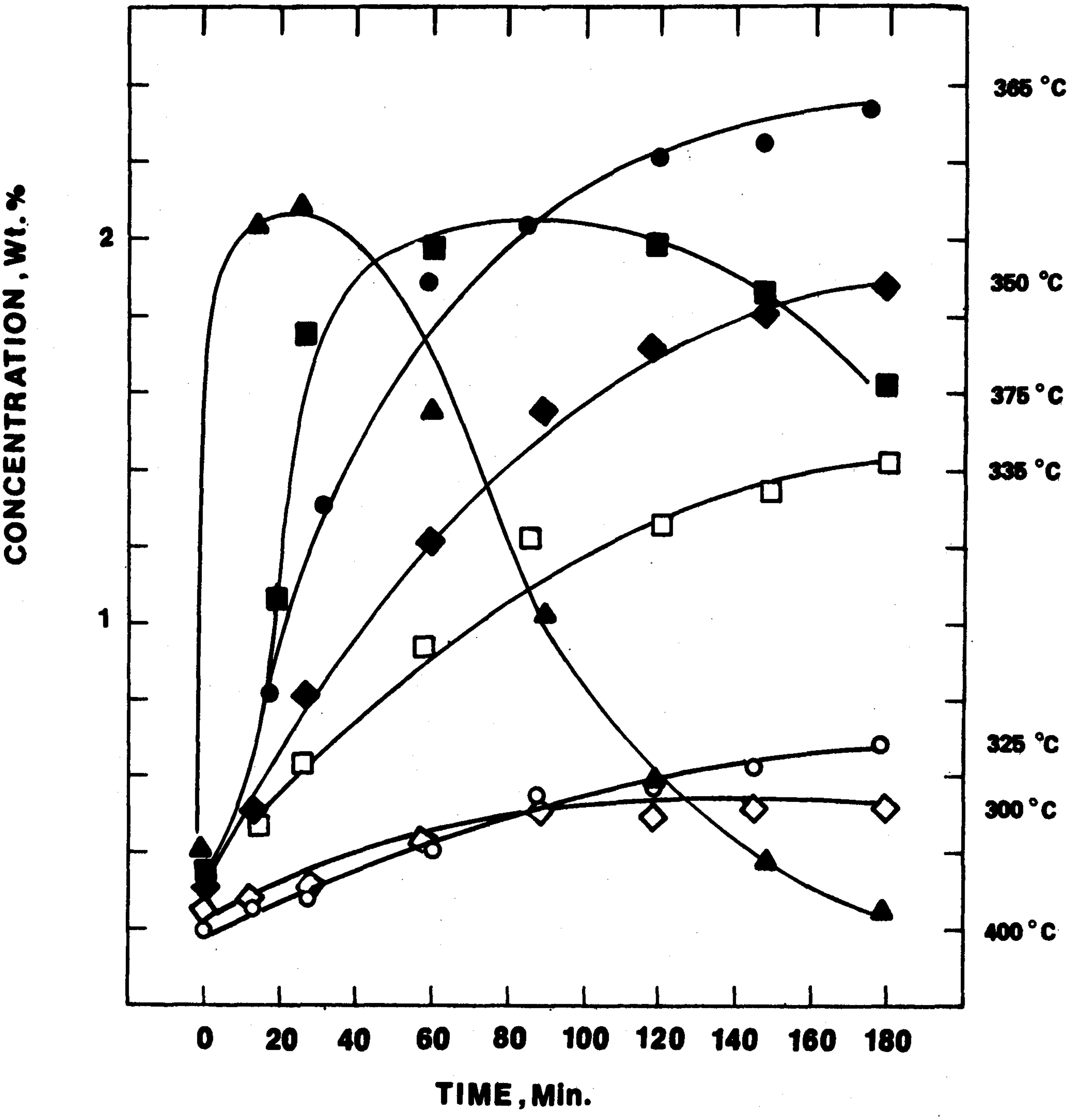


Figure 33: Benzaldehyde concentration versus time for a feed of 10% dibenzyl ether with 90% tetralin in a nitrogen atmosphere

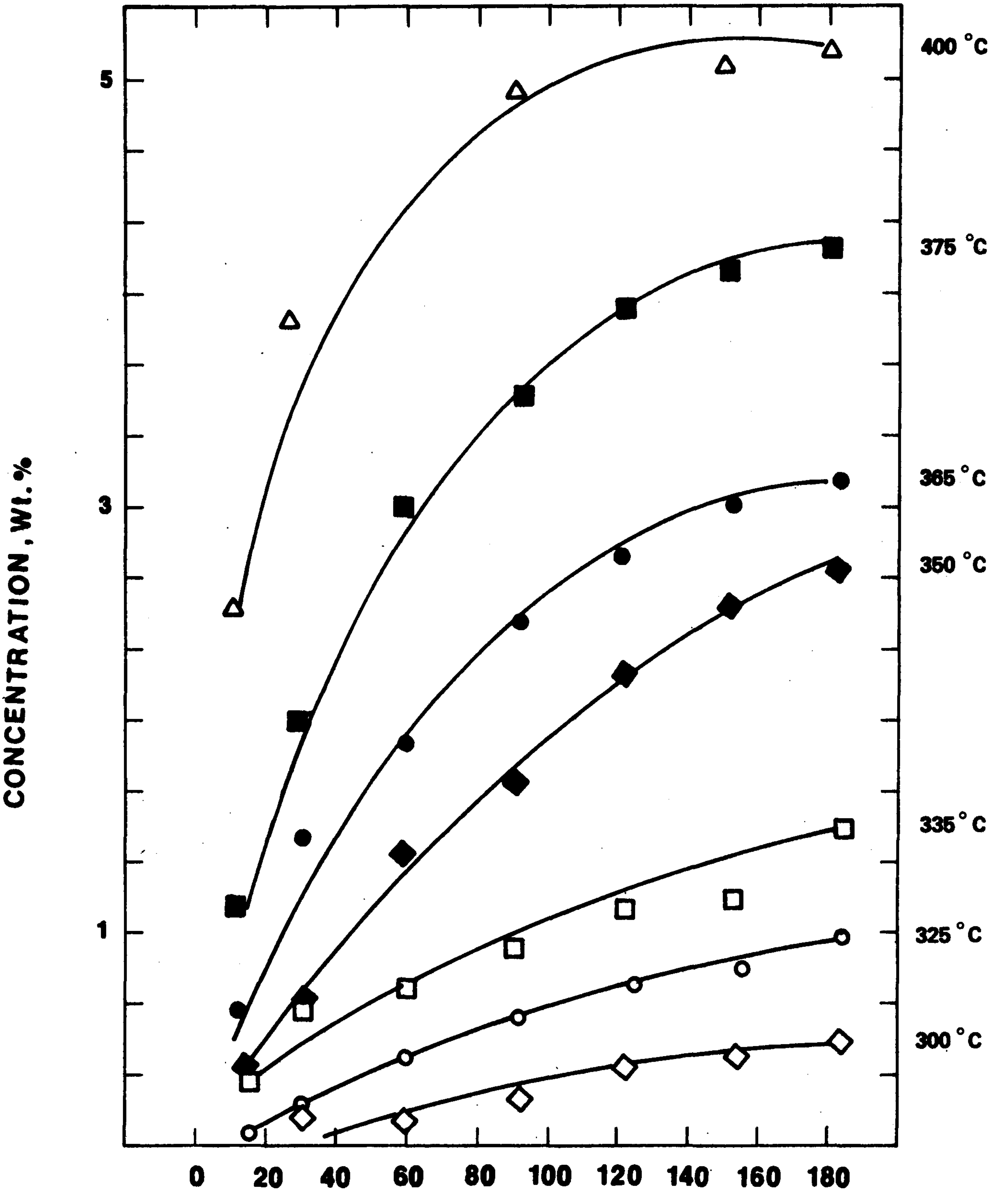


Figure 34: Toluene concentration versus time for a feed of 10% dibenzyl ether with 90% tetralin in a nitrogen atmosphere

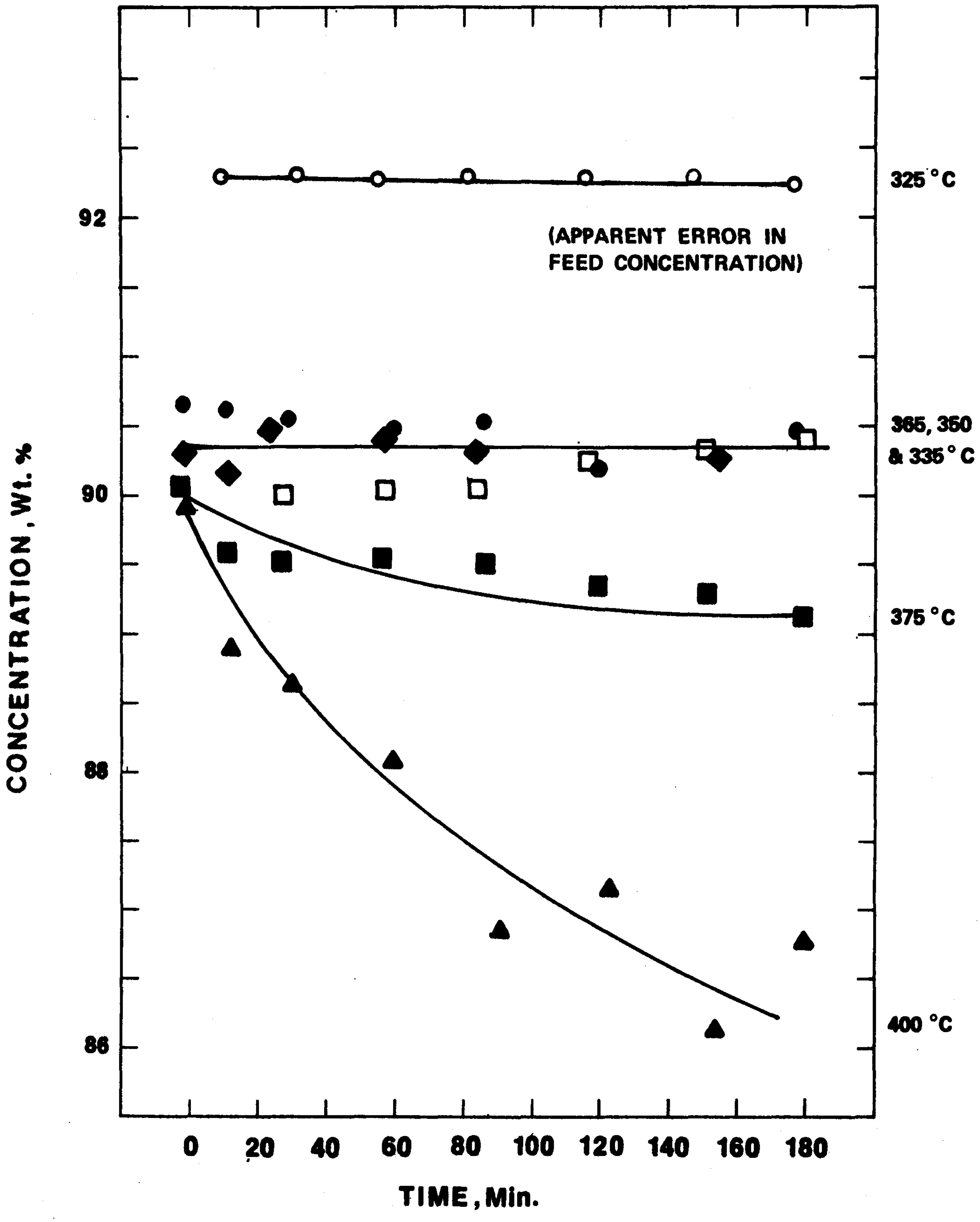


Figure 35: Concentration of tetralin versus time for a feed of 10% dibenzyl ether with 90% tetralin in a nitrogen atmosphere

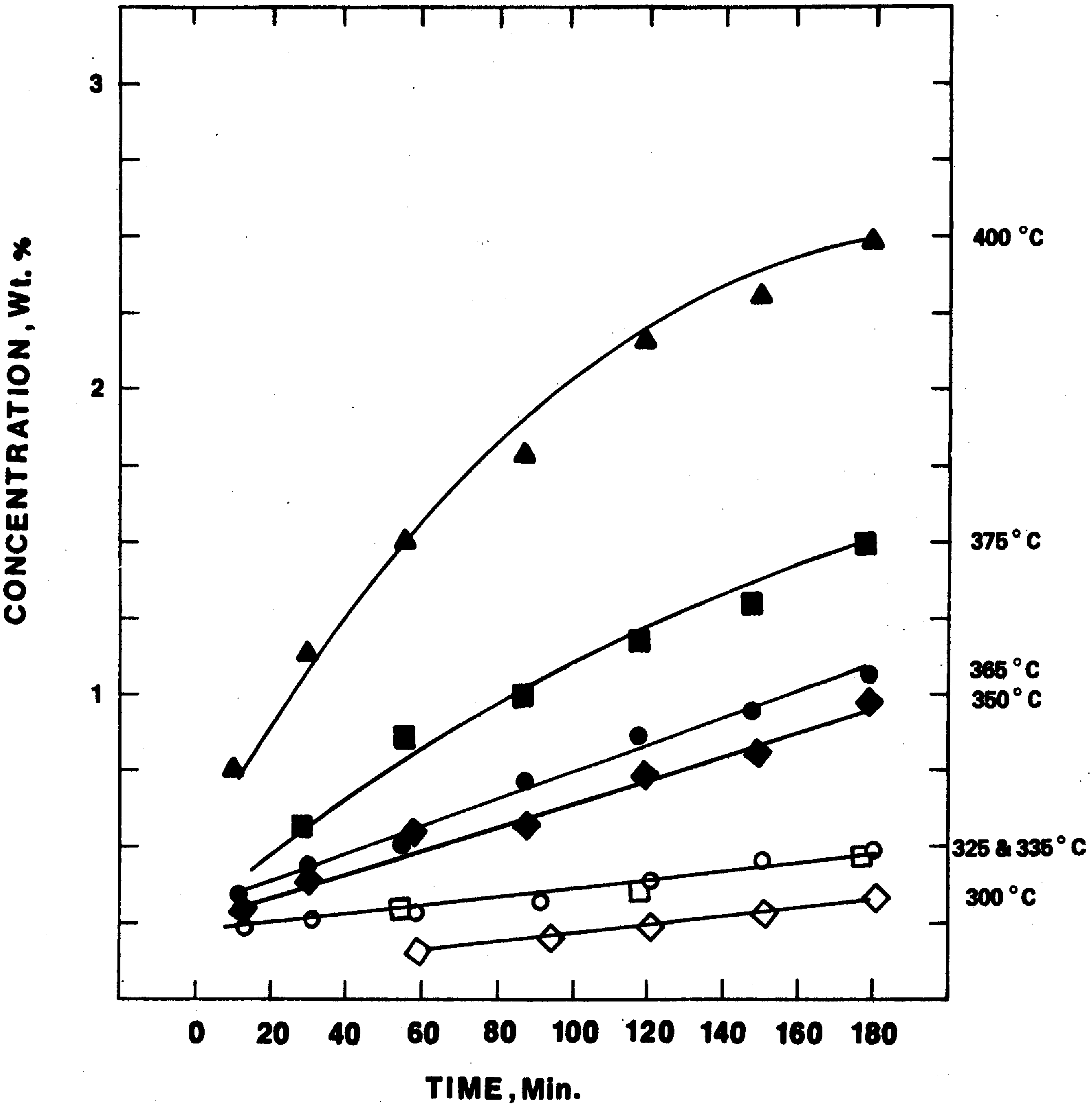


Figure 36: Concentration of naphthalene versus time for a feed of 10% dibenzyl ether with 90% tetralin in a nitrogen atmosphere

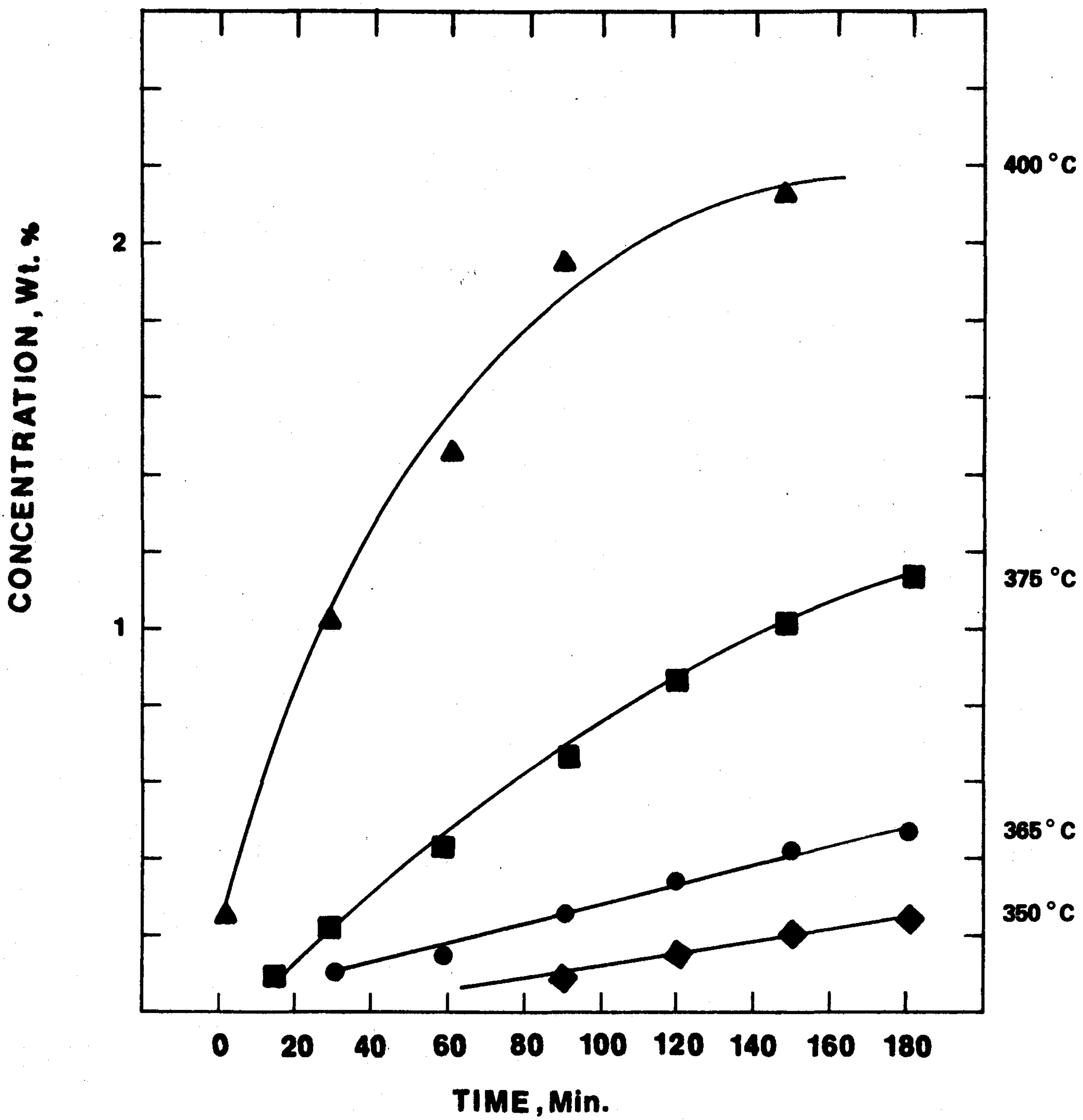


Figure 37: Concentration of benzene versus time for a feed of 10% dibenzyl ether with 90% tetralin in a nitrogen atmosphere

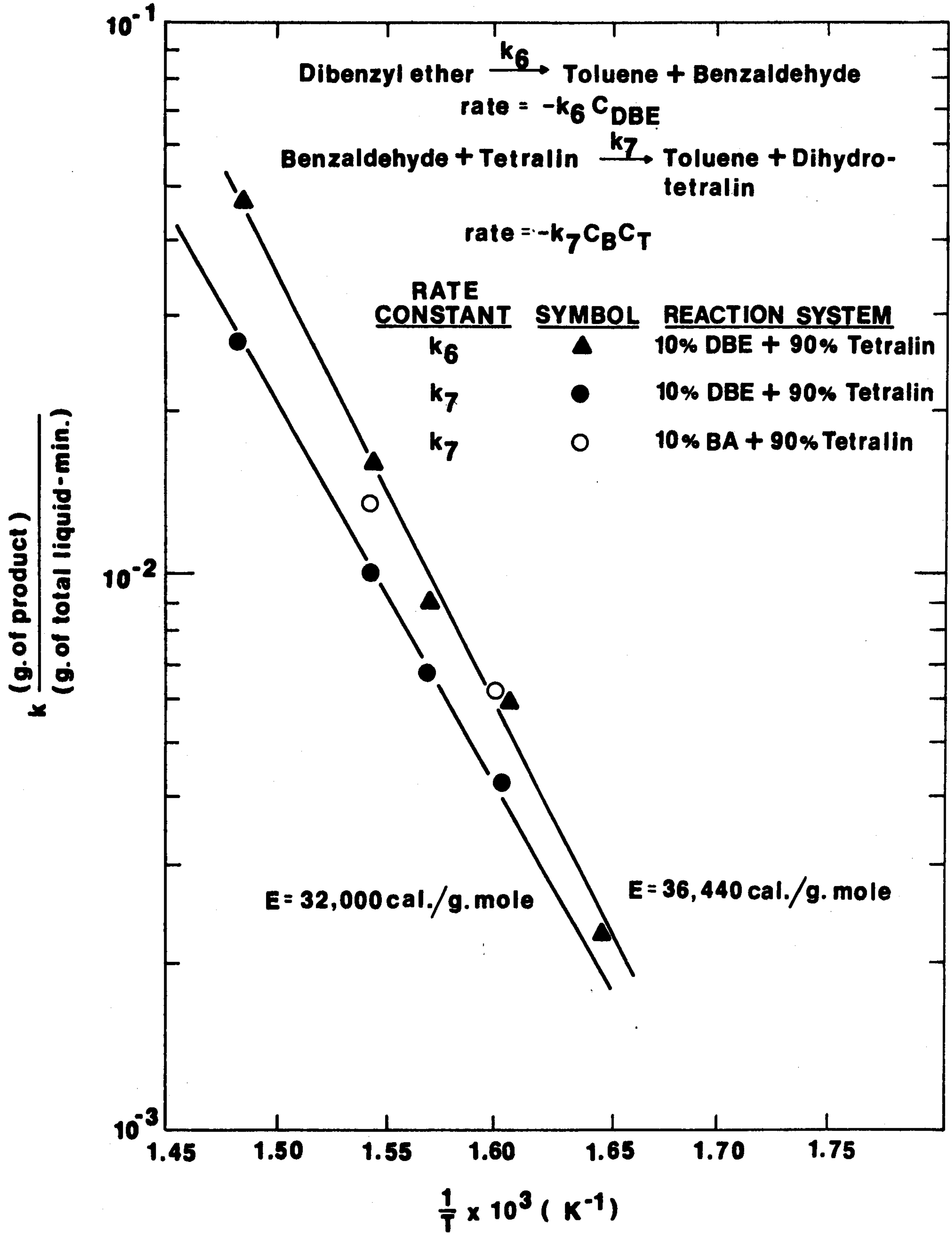


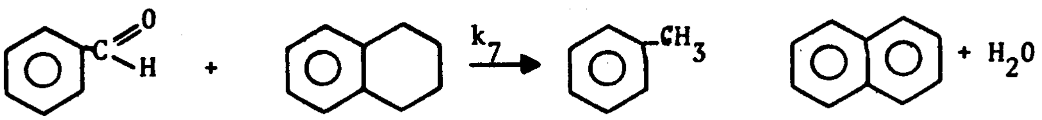
Figure 38: Arrhenius plots for the dibenzyl ether and benzaldehyde reactions

Because there was no marked effect of catalyst on the cracking of dibenzyl, only two catalytic runs were made with dibenzyl ether. In this case, the use of a 5 wt.% charge of Nalcomo 477 catalyst promoted the ether cracking reaction at 350°C so greatly that essentially no ether was left by the 15-minute sample period. The run was repeated and only trace levels were found at 5 minutes. It was beyond the scope of this project to explore this reaction further, but it is obvious that each cracking reaction in coal liquefaction is much differently affected by the presence of a catalyst. As a generalization (only), there is an indication that intramolecular hydrogen transfer may be promoted by a catalyst to a greater extent than intermolecular reactions.

2. Benzaldehyde

The formation of benzaldehyde as a major intermediate in the cleavage of dibenzyl ether with donor solvents was surprising considering the reported work of Brucker and Kolling.(7) If aldehydes can be generated by the thermal cleavage of ethers, their presence in coal liquids would be expected. They would, therefore, abstract hydrogen from solvents during liquefaction. The analysis of coal liquids has indicated that only low levels of carbonyls, including aldehydes, are present in typical liquefaction products (see Reference 9). Therefore, the aldehydes must be relatively reactive at liquefaction conditions. In order to better delineate the chemistry of dibenzyl ether acceptors, several hydrogen transfer experiments were performed with benzaldehyde.

In good donor solvents (tetralin), benzaldehyde readily converts to toluene:



(23)

From an analysis of the disappearance of benzaldehyde during dibenzyl ether cracking, the reaction of benzaldehyde with tetralin was shown to fit the following rate equation:

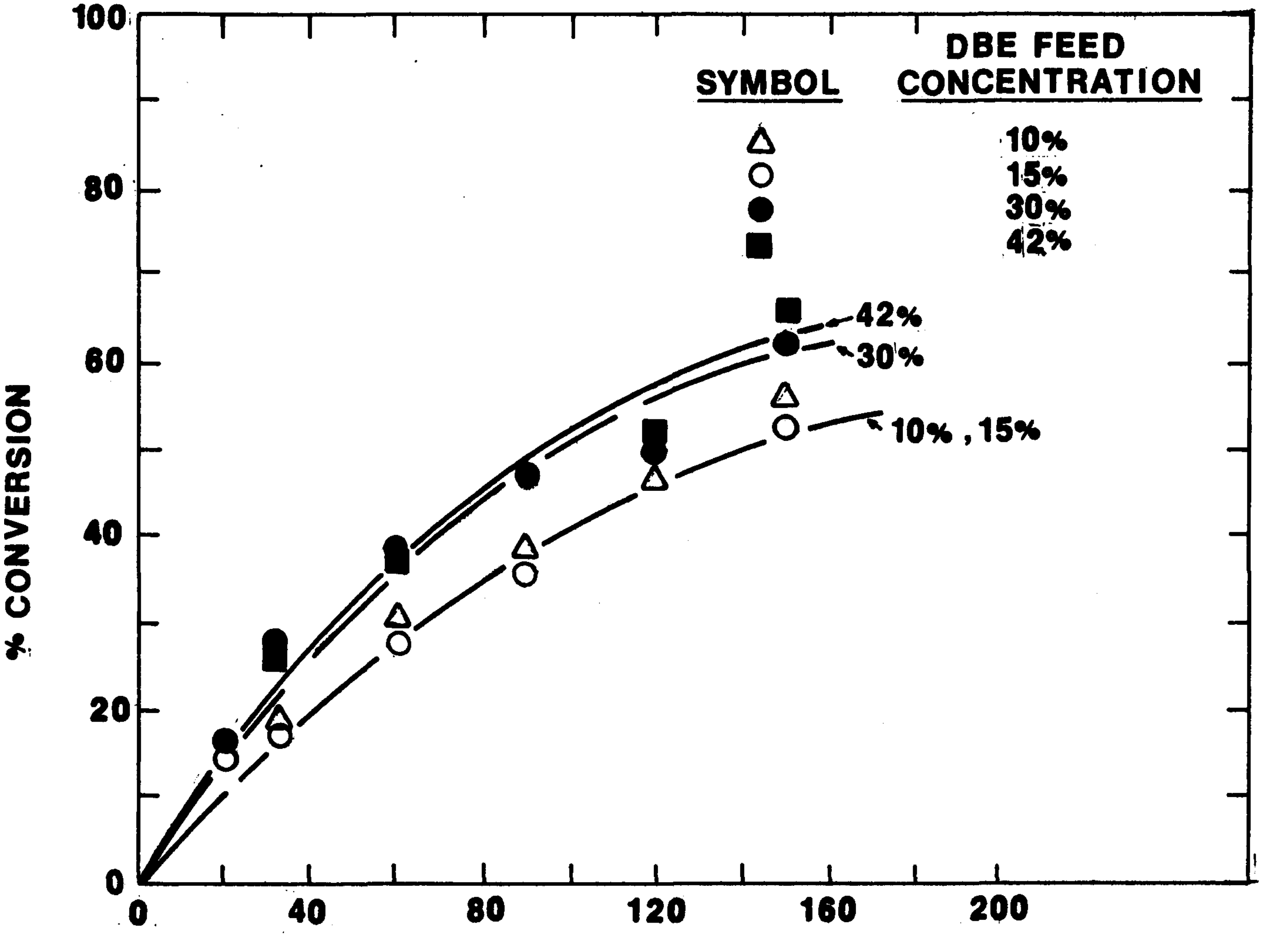


Figure 39: Dibenzyl ether conversion as a function of time and concentration

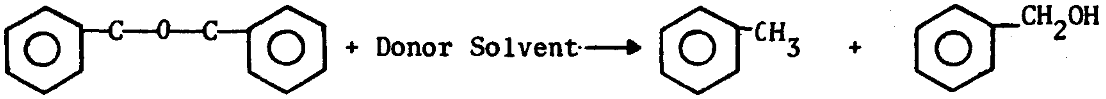
$$\frac{dC_{BA}}{dt} = -k_7 \; C_{BA} \; C_T \tag{24}$$

where C_{BA} and C_T are the concentrations of benzaldehyde and tetralin in weight percent. At high tetralin concentrations, the reaction is pseudo-first order with respect to benzaldehyde. Individual runs were made with benzaldehyde (10%) and tetralin (90%) at 350° and 375°C. The rate constants were essentially the same as those obtained from the series reaction of dibenzyl ether → benzaldehyde → toluene. The results are shown in the Arrhenius plot given in Figure 38. The activation energy of this reaction is 32 000 cal/g mole.

The reduction of benzaldehyde is analogous to stilbene in that a double bond (C=O) is initially reduced. A poor donor solvent (mesitylene) was found not to reduce the double bond. This is indirect evidence for the need of participation by a good hydroaromatic structure in the reaction. In poor solvents or at high aldehyde concentrations, benzaldehyde reacts with itself forming benzoic acid as a major product. The other product presumably is toluene-analysis of a sample from such a run was not attempted due to the existance of solids. The instability of oxygen compounds at moderate to high concentrations in poor donor solvents is a common observation and may be particularly relevant to the liquefaction of low rank coals.

3. Benzyl Alcohol

The study of benzyl alcohol was undertaken because of questions arising in the dibenzyl ether work. The literature(7,8) has indicated that, with donor solvents such as tetralin and tetrahydroquinoline, dibenzyl ether clearly converts to equal moles of toluene and benzyl alcohol.



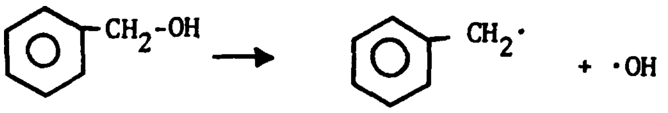
(25)

This implies that thermal cleavage of a benzyl ether bond generates both a benzyl and benzyloxy free radical which are stabilized by abstraction of hydrogen from the hydroaromatic solvent. However, only trace levels of benzyl alcohol were found in the dibenzyl ether reaction products. On the other hand, benzaldehyde is always observed as a stable but transitory intermediate in this reaction. Considering the possibility that the alcohol may, itself, be functioning as a hydrogen acceptor and donor, a series of experiments at various concentrations, temperatures, and solvents was performed.

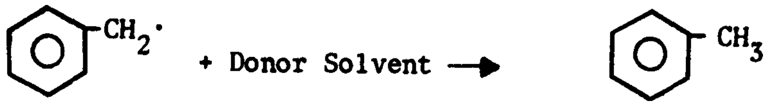
Benzyl alcohol can thermally react in many solvents to form products such as benzaldehyde, toluene, dibenzyl ether, dibenzyl, and stilbene as well as solvent adducts, as discussed in Section I. The primary reaction in good donor solvents appear to be the reduction of the alcohol to toluene. A secondary reaction is the formation of aldehyde which is subsequently reduced to toluene. Reference is made to Figures 43 and 44. Benzyl alcohol always forms benzaldehyde, whose concentration seems to be quite dependent on both temperature and reaction time. As was observed with dibenzyl ether, the benzaldehyde intermediate continues to react with donor solvent to form toluene. The benzyl alcohol/benzaldehyde reaction appears to be reversible as observed from the deuterium experiments. Specifically, when D_4-tetralin was used with benzaldehyde, some deuterium was incorporated in the benzaldehyde.

For further reference, a reaction mechanism is being proposed assuming free radical intermediates. The primary and secondary reactions can be rationalized as follows:

Primary Reaction:

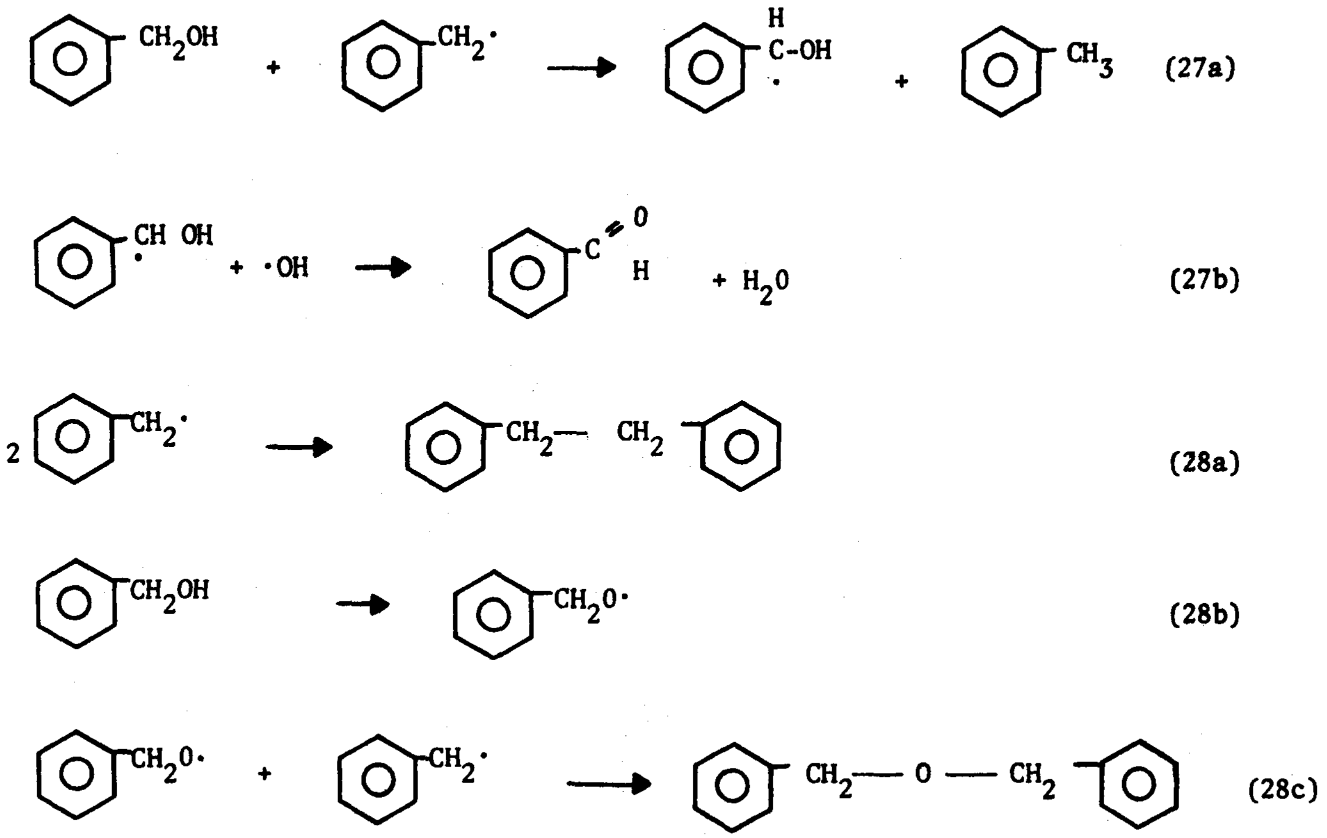


(26a)



(26b)

Secondary Reaction:



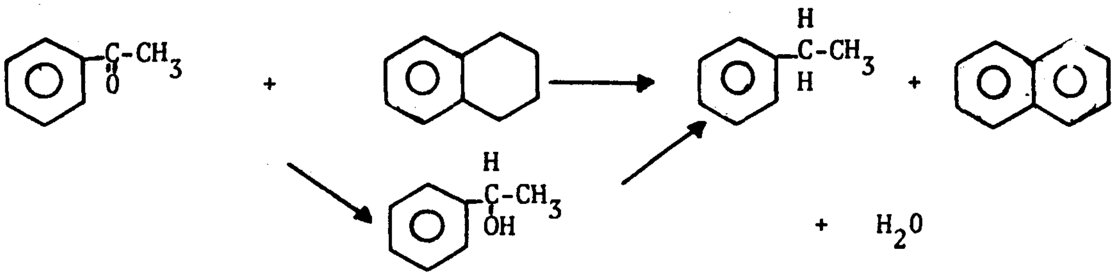
Benzyl alcohol may thermally form several free radicals depending on which bonds are broken or on which hydrogen is abstracted. The primary product, toluene, requires the generation of stable benzyl free radicals which react with any good donor solvent, as discussed in earlier sections. Benzyl radicals may also react with an alcohol to abstract an α-hydrogen (27a) which subsequent expels water and forms benzaldehyde (27b). Benzyl radicals can also react with each other to form dibenzyl which is stable under 400°C. The observation of traces of dibenzyl ether in reaction products also suggests the existence of an oxy radical (28c), as found recently by Ernest.(10)

Figures 40 and 41 show plots of the disappearance of benzyl alcohol in various solvents and the rate constants associated with each. The initial reactions appeared to be first order. This is further suggested by the similar equal rate constants being observed at 33 and 10% alcohol levels. In the absence of a solvent, the disappearance of alcohol also followed a first-order correlation; however, the reaction rate constant was much lower, indicating a different reaction mechanism. An Arrhenius plot of the various rate constants is shown in Figure 42. The higher reactivity of alcohol in THQ over tetralin is pointed out. For reference, a plot of aldehyde and toluene concentration in the liquid samples versus time and temperature for a feed of 10% alcohol in tetralin is given in Figures 43 and 44, respectively.

4. Acetophenone

The study of benzaldehyde indicated that carbonyl groups are excellent hydrogen acceptors but the study should be extended to other carbonyl-containing compounds. Acetophenone was chosen for reasons of availability, stability, and ease of product determination.

By analogy to benzaldehyde, the following reaction with tetralin should occur:



(29)

If the reaction occurs step-wise, the intermediate alcohol should form. Initial reactions done at 350°C (as with benzaldehyde) in fact show the presence of the alcohol intermediate and were confirmed by D-incorporation from D_4-tetralin. A chromatographic technique was developed to resolve aldehyde-alcohol mixtures for similar systems, but reference samples were not readily available for this system. However, it was observed that

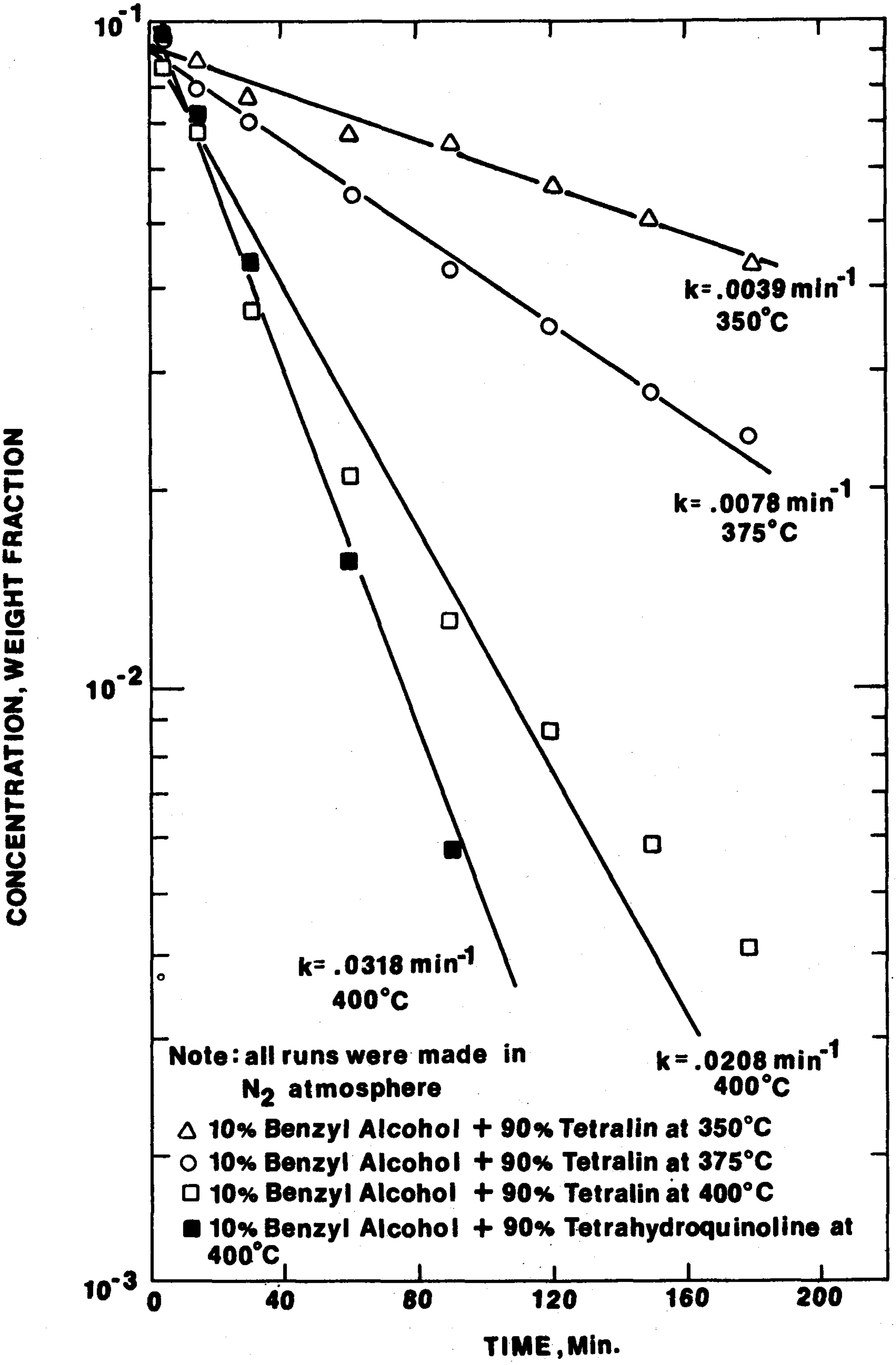


Figure 40: Benzyl alcohol reaction in tetralin: concentration versus time for a feed of 10% alcohol

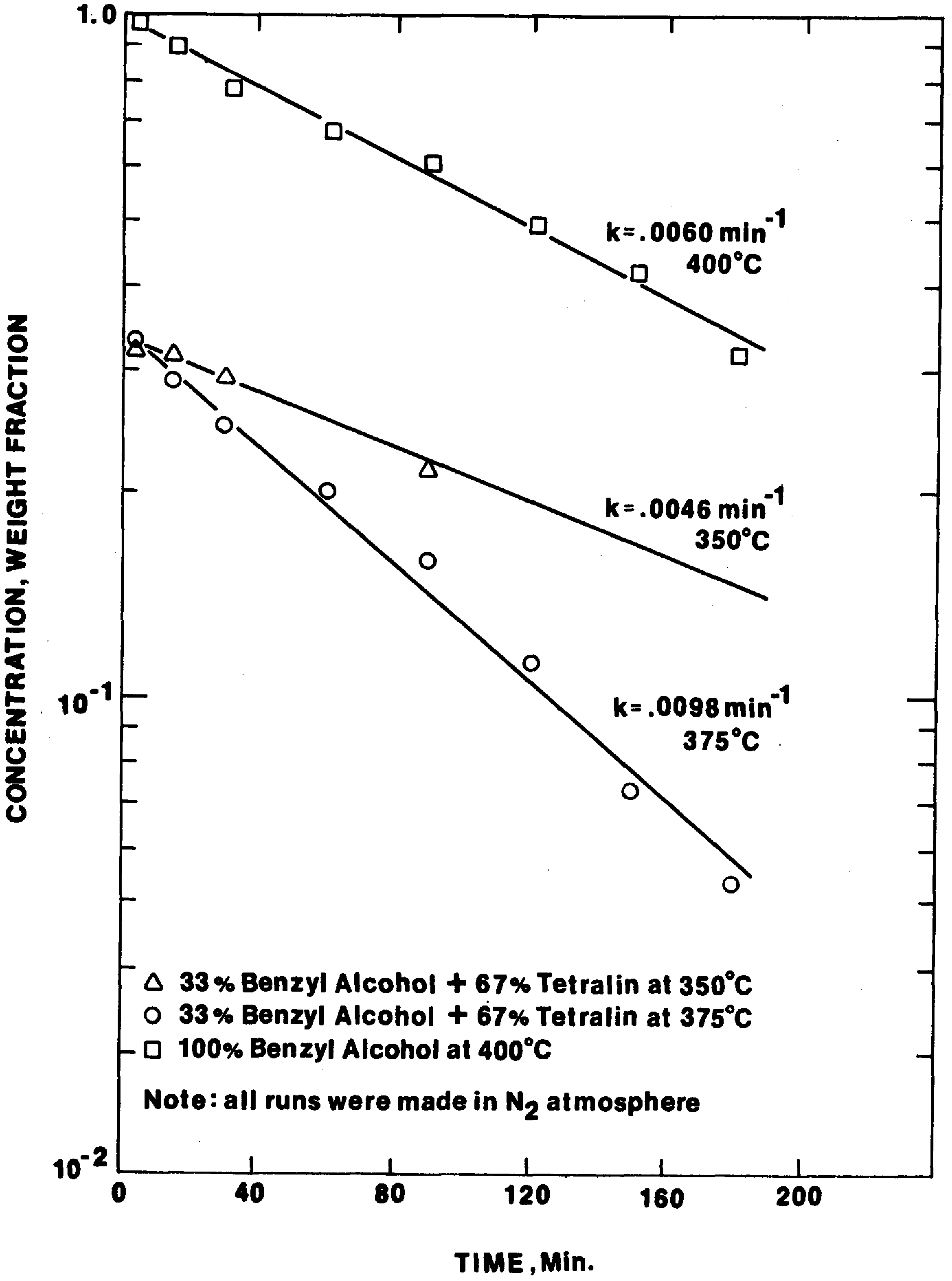


Figure 41: Benzyl alcohol reaction in tetralin: concentration versus time for feeds of 33 and 100% alcohol

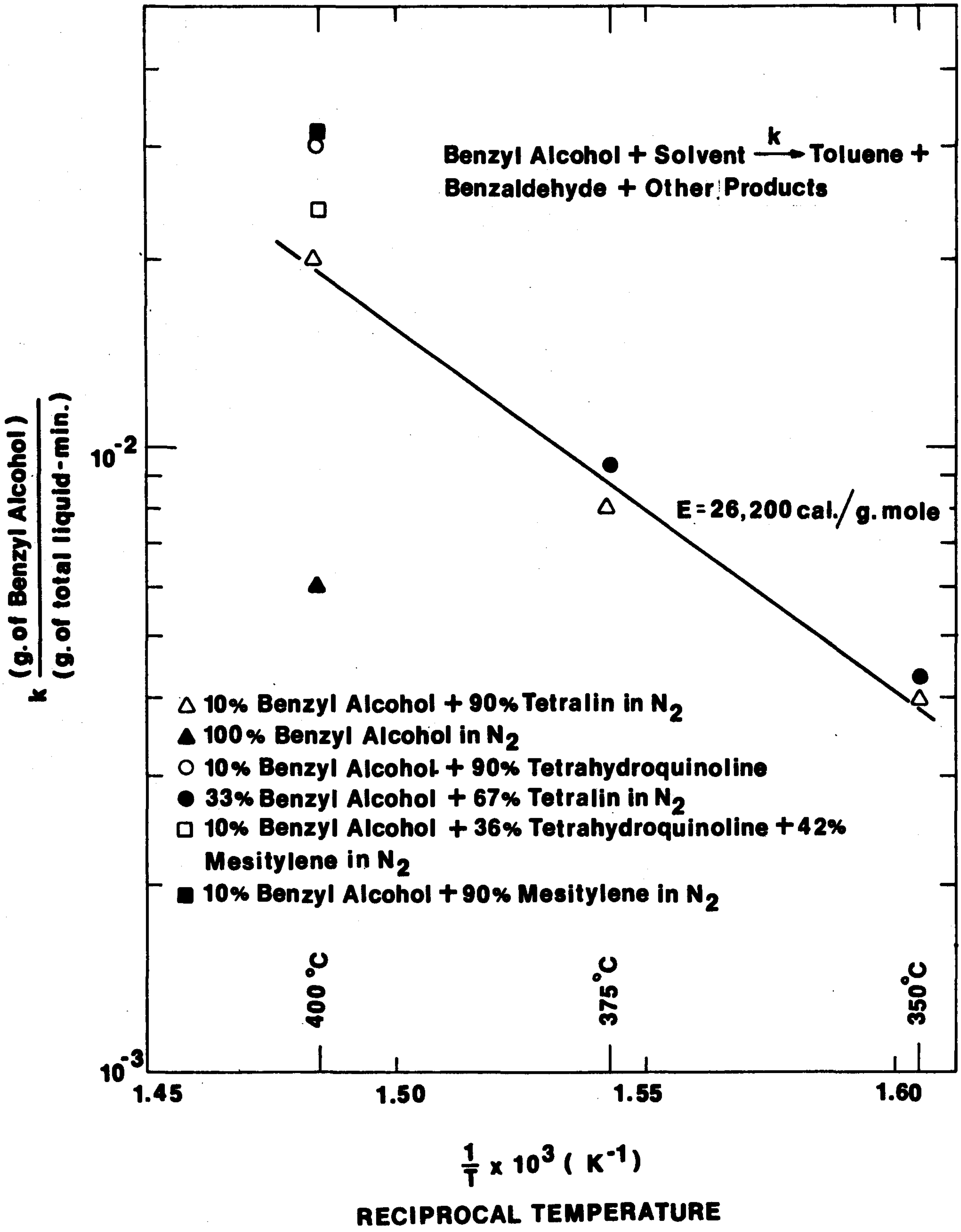


Figure 42: Arrhenius plot for the benzyl alcohol reaction

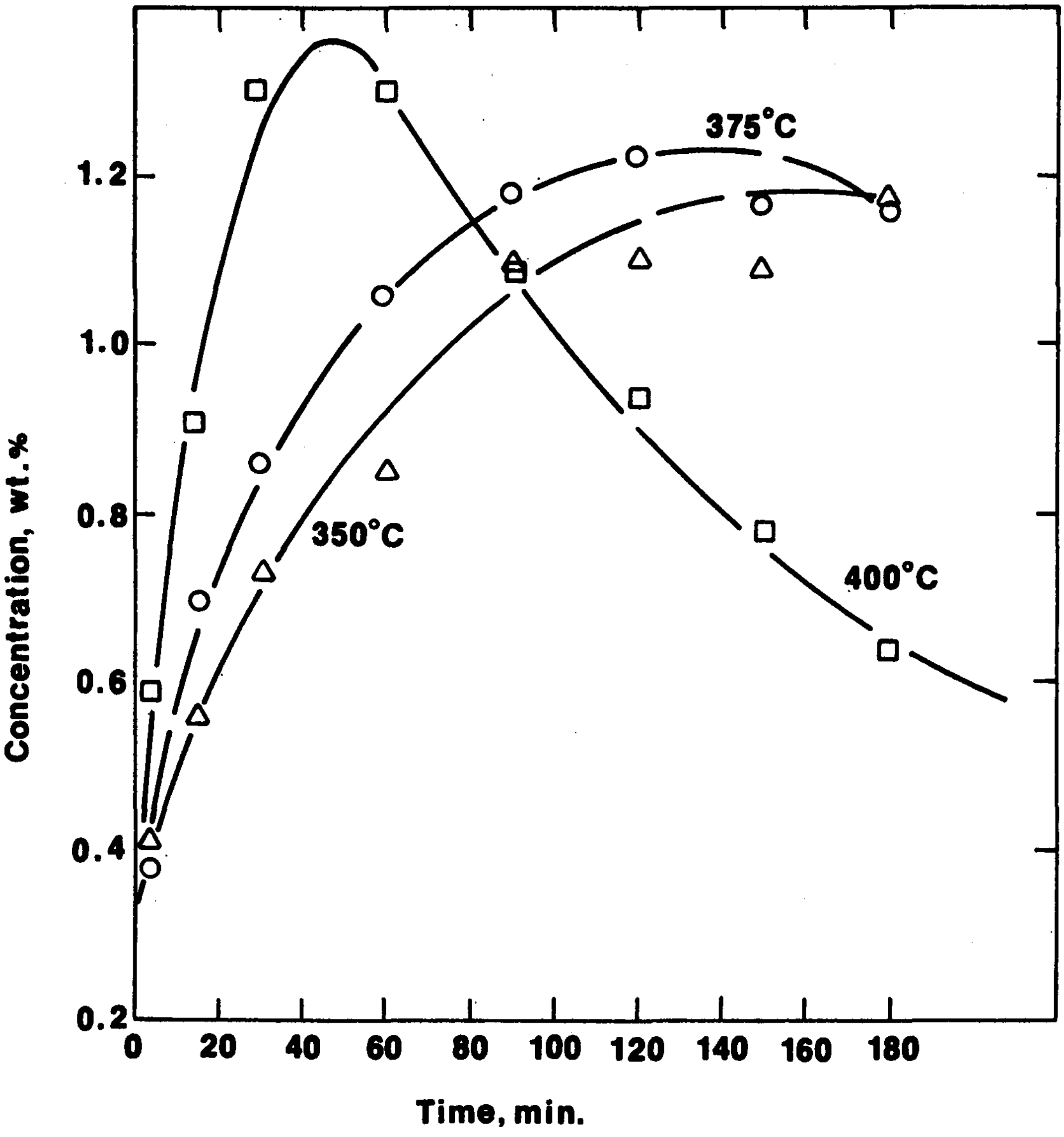


Figure 43: Benzaldehyde concentration versus time for a feed of 10% benzyl alcohol with 90% tetralin in a nitrogen atmosphere

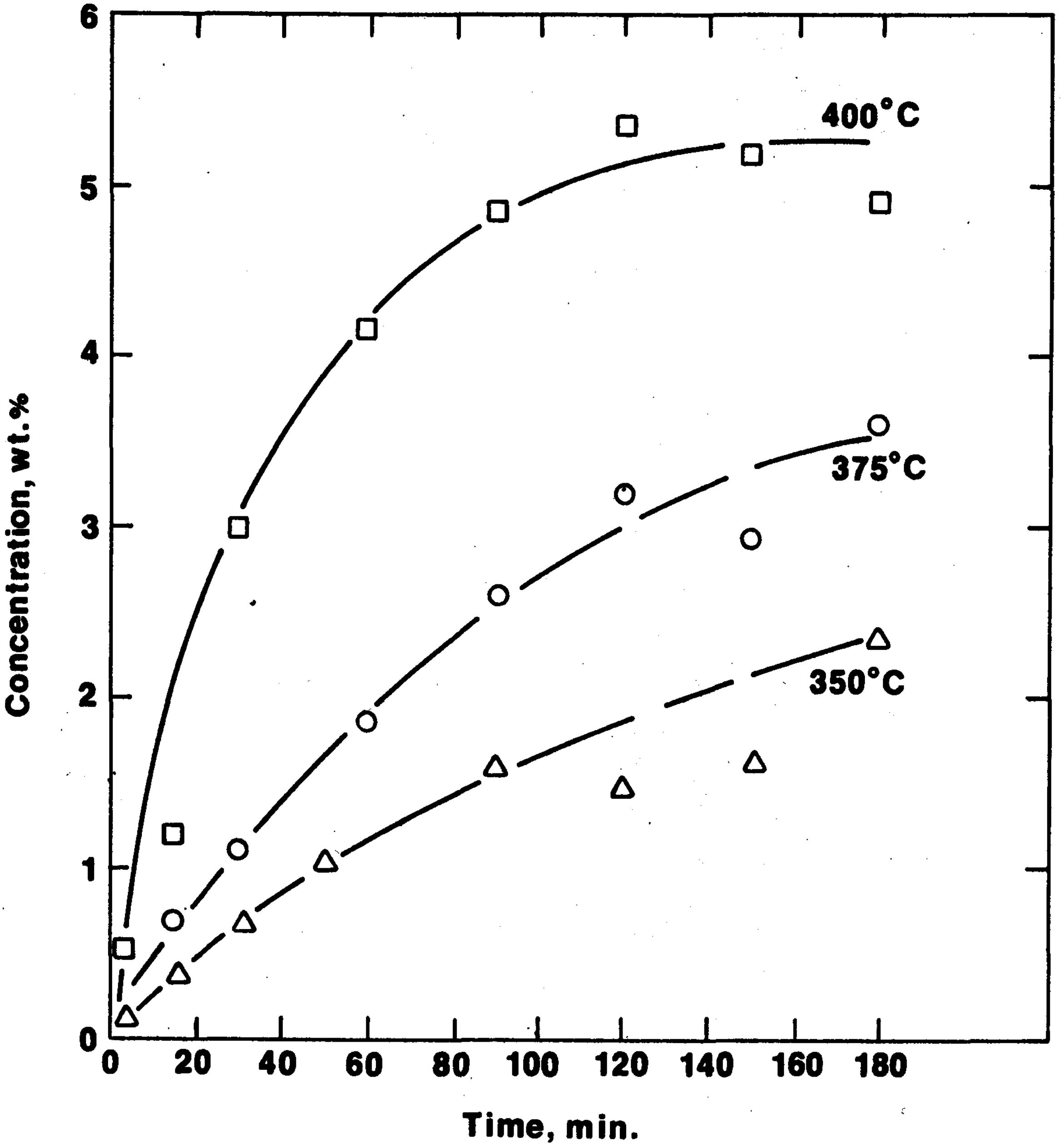


Figure 44: Toluene concentration versus time or a feed of 10% benzyl alcohol with 90% tetralin in a nitrogen atmosphere

the acetophenone peak reduced with reaction time, and another peak, presumably alcohol, formed. It was also observed that only moderate reduction to ethylbenzene occurred.

The rate of the dehydration step is low at temperatures below 400°C. This implies that the first step (addition to double bond C=0) is quite fast but cleavage of the carbon-oxygen bond is much slower, and rate-determining.

Kinetic experiments were performed in the 400-450°C range. As shown in Figure 45, an excellent fit of the data was obtained for first-order rates for the disappearance of acetophenone. A minor side reaction occurs at higher temperatures to yield toluene which is an example of the high reactivity of benzylic free radicals. Figure 46 shows the Arrhenius plot for the primary reaction from which an activation energy of 33 500 cal/g mole is calculated. It is interesting that acetophenone is considerably more stable than benzaldehyde in tetralin-consonant with the former's greater steric requirements for donation.

5. α-Tetralone

The study of carbonyl functional groups as hydrogen acceptors was extended a step further to include cyclic α-tetralone. It was found to be more stable than benzaldehyde and is more representative of coal structures than acetophenone. Screening studies had indicated that α-tetralone would react with tetralin in the 400-475°C range.

Kinetic experiments have been done in tetralin, 2,6-dimethyltetralin, and mesitylene solvents. α-tetralone reacts in each of these solvents with the eventual formation of naphthalene. Kinetic modeling can be done by following the disappearance of tetralone. Figure 47 shows that the data fit a first-order reaction quite well. The Arrhenius plot is given in Figure 48.

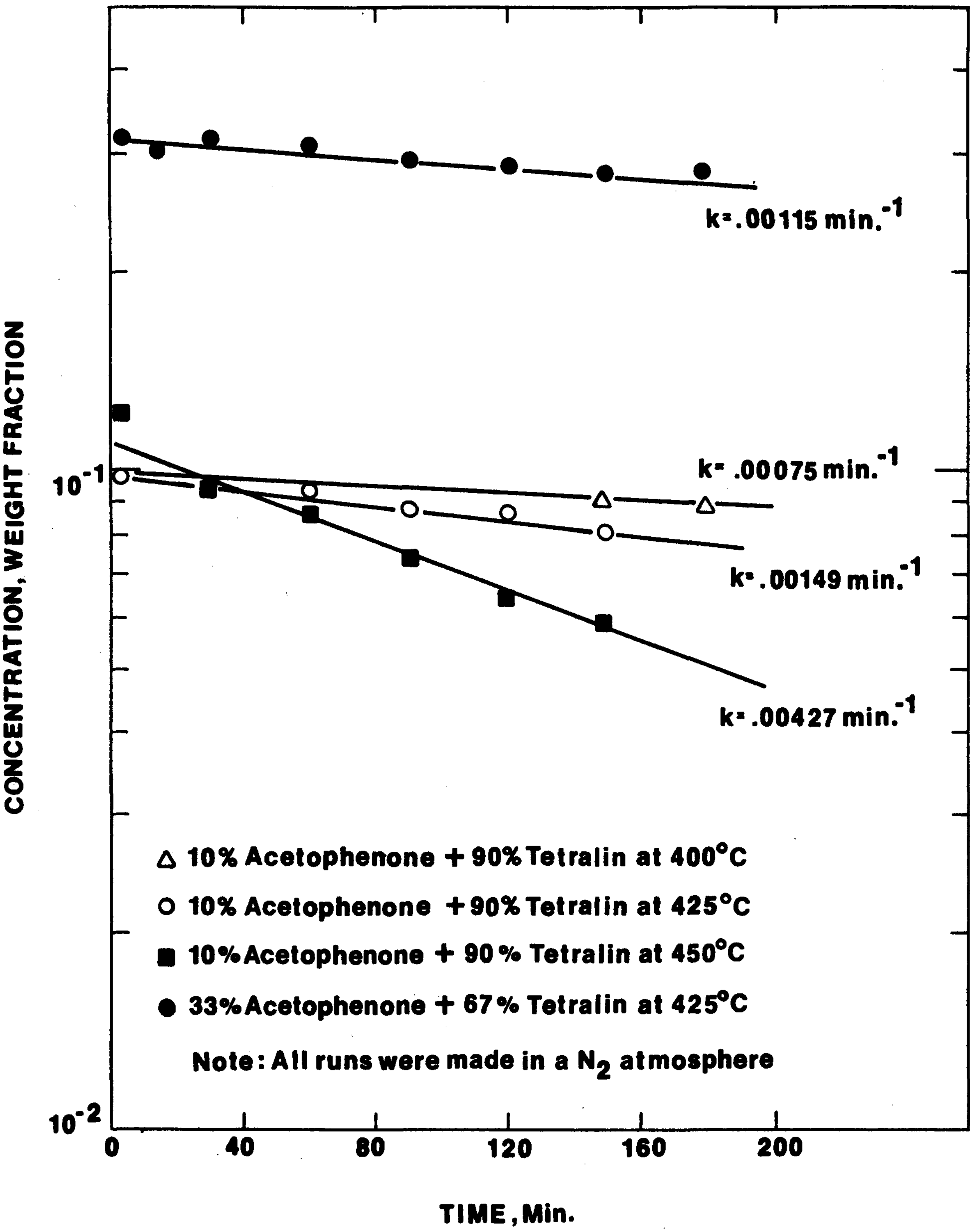


Figure 45: Acetophenone reaction in tetralin: concentration versus time

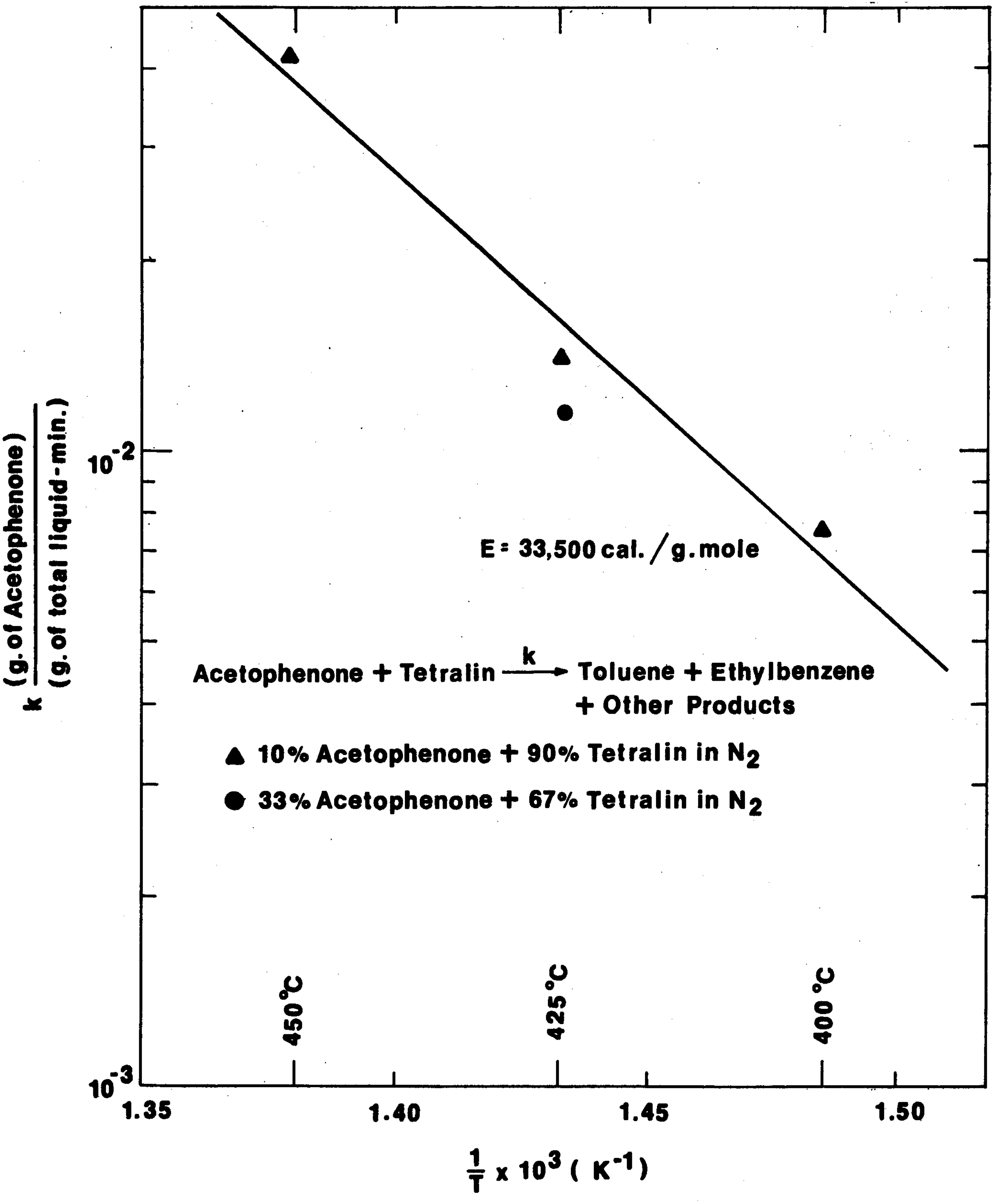


Figure 46: Arrhenius plot for the reaction of of acetophenone in tetralin

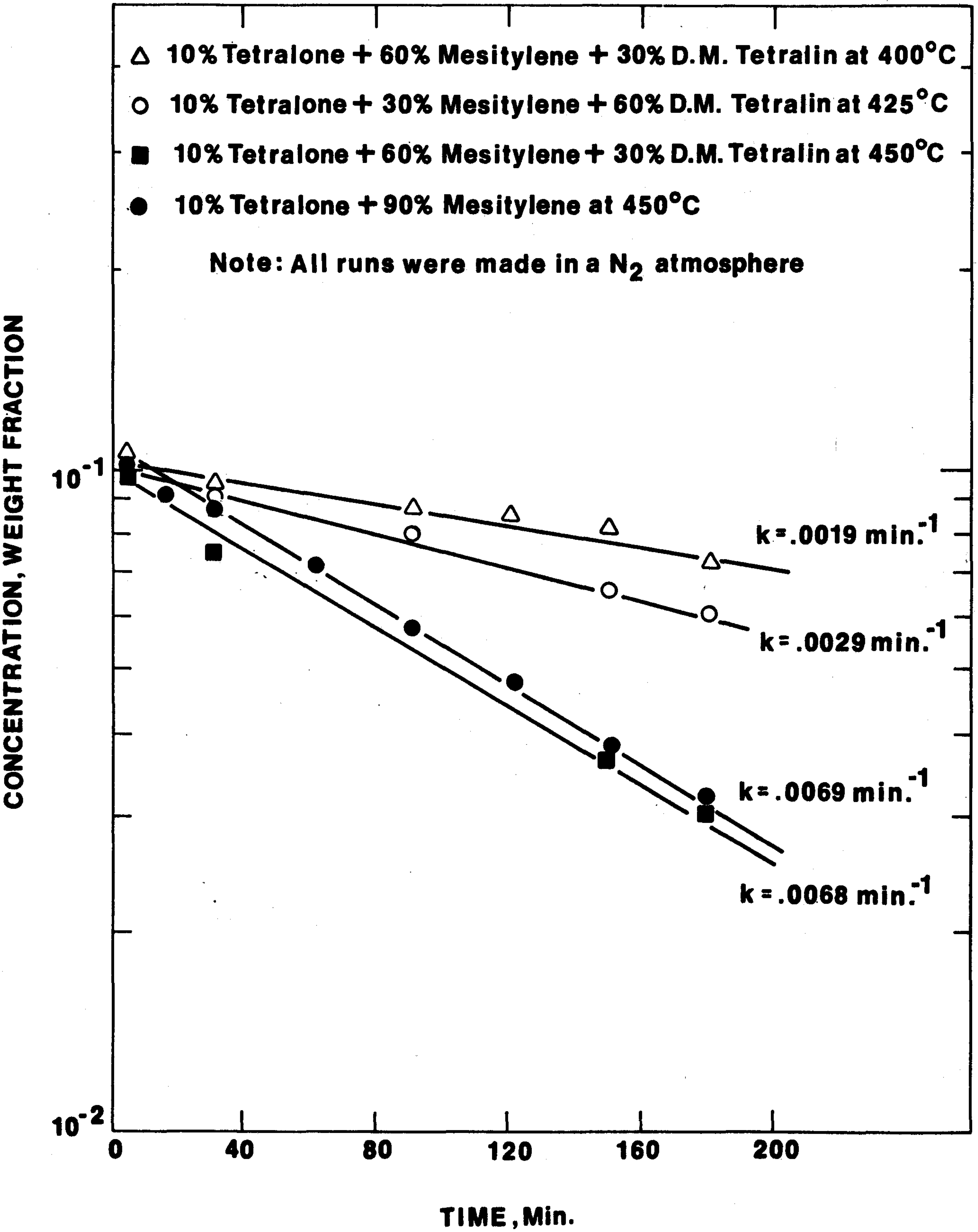


Figure 47: Tetralone reaction in mesitylene and dimethyl tetralin: concentration versus time

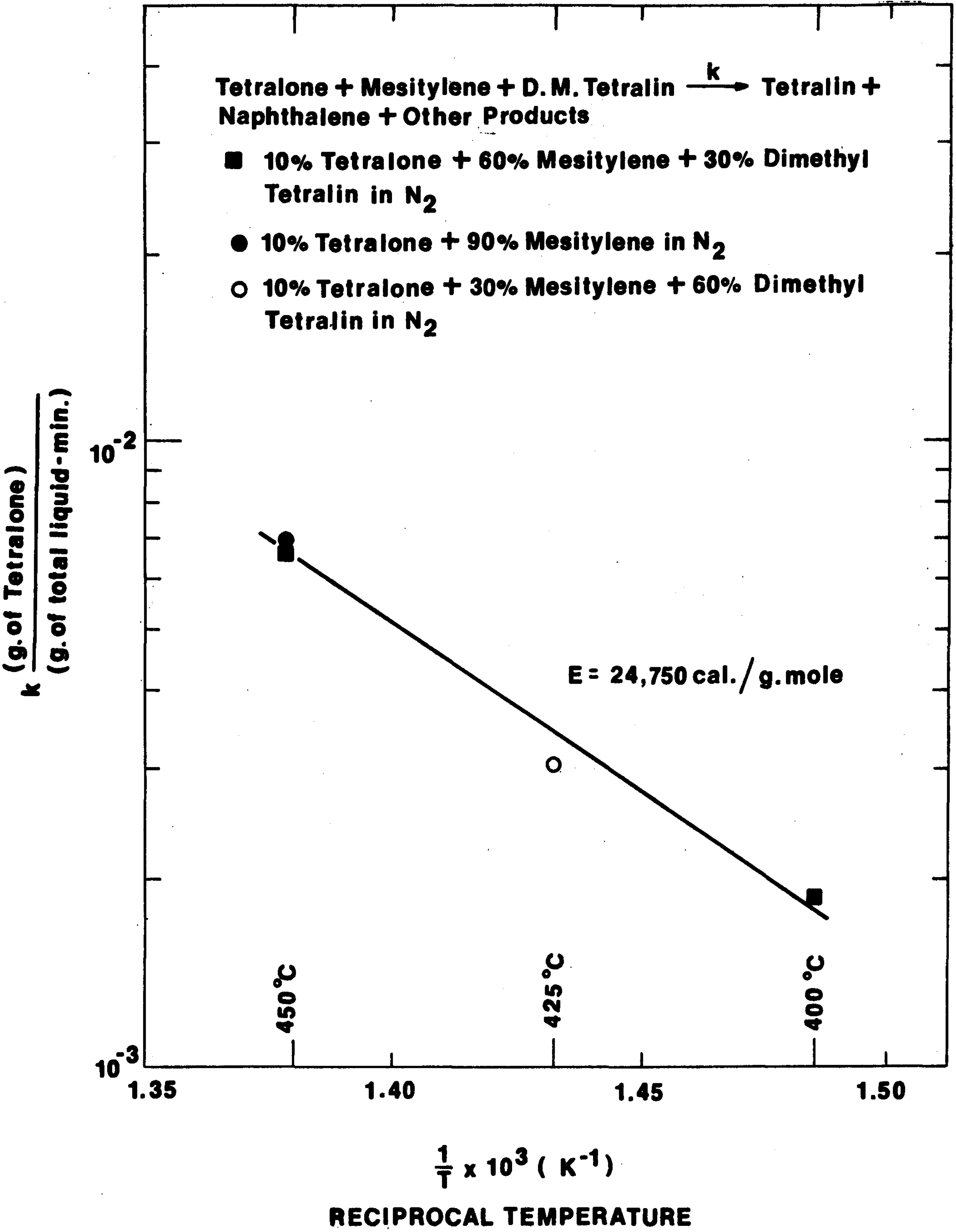
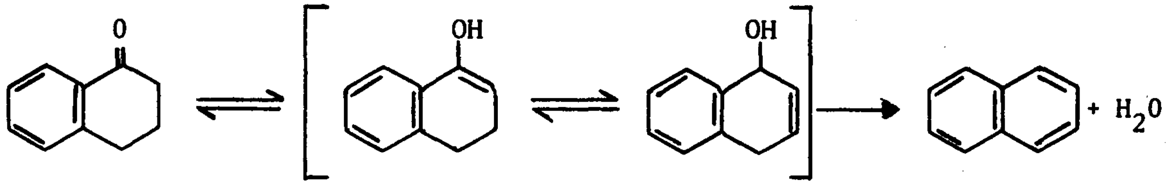


Figure 48: Arrhenius plot for the reaction of tetralone in mesitylene and dimethyl tetralin

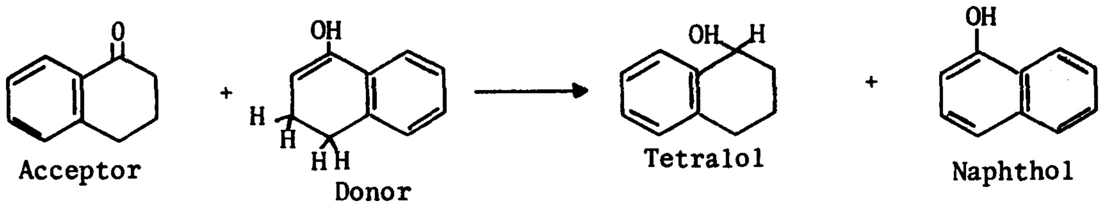
Contrary to benzaldehyde and acetophenone, tetralone reduces in the absence of a good donor solvent without any serious side reactions. This can be attributed to two factors. First, α-tetralone can be thermally dehydrated via the -enol structure, as follows:



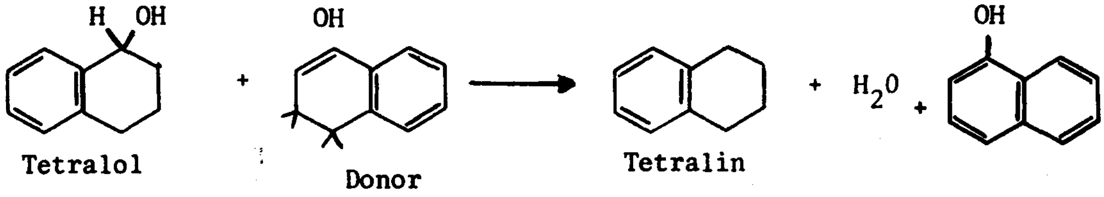
(30)

While this type reaction would occur at high temperatures (7400°C), it is known to proceed at lower temperatures in the presence of alkali or noble metal catalysts.(11) It would appear likely that the mineral matter present in coal would also promote the reaction.

Secondly, dehydration can be the result of true hydrogen transfer in which one molecule of tetralone can function as a donor solvent and another molecule function as an acceptor. If this was the prevailing reaction, the products would be an equal mixture of tetralol or tetralin and naphthol depending on extent of reaction:

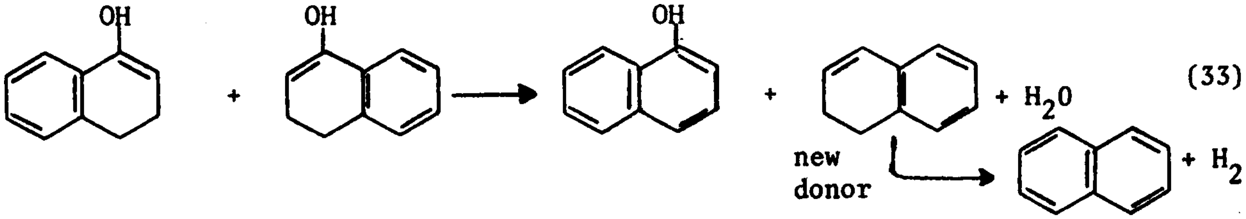


(31)



(32)

Analysis of products by GLC-MS indicates that with all solvents used, the formation of naphthalene and naphthol predominates with traces of dihydronaphthalene. The absence of tetralol and tetralin can be rationalized in terms of the -enol tautomer acting as a donor and its isomer behaving as an acceptor.



(33)

6. Aromatic Phenols (Naphthol and Xylenol)

After observing how readily benzyl alcohol dehydroxylates in good donor solvents (350-400°C) and tetralones in either poor or good solvents (400-450°C), we chose to study the reactivity of completely aromatic phenols.

The dimethyl phenols (either 2,6- or 3,5-) appear to be essentially unreactive up to 450°C in tetralin. At 450°C, it is estimated that the reaction rate constant is less than 3×10^{-4} min^{-1}; there was no means of estimating the activation energy of the reaction.

α-Naphthol reacts with the donors tetralin, 2,6-dimethyltetralin, and tetrahydroquinoline to form naphthalene. As with the other reactions, mesitylene also served as a donor solvent. The conversion of α-naphthol as a function of time and temperature is shown in Figure 49. The Arrhenius plot is given in Figure 50.

The reaction of α-naphthol in tetrahydroquinoline is particularly smooth because the water that is formed is readily absorbed by the solvent. This is reflected in a slightly higher rate of reaction. No particular side reactions are observed in these dehydroxylations.

7. Summary (Oxygen Groups)

The most common heteroatoms in coal are those containing oxygen, particularly in coals of low rank. The specific functional group determines the temperature and the extent of reaction with donor solvents. To remove oxygen, it must first be reduced to a C-O form. This reduction usually occurs quickly in the temperature range of 300° to 375°C. For the cleavage of the C-O bond, higher temperatures are then needed.

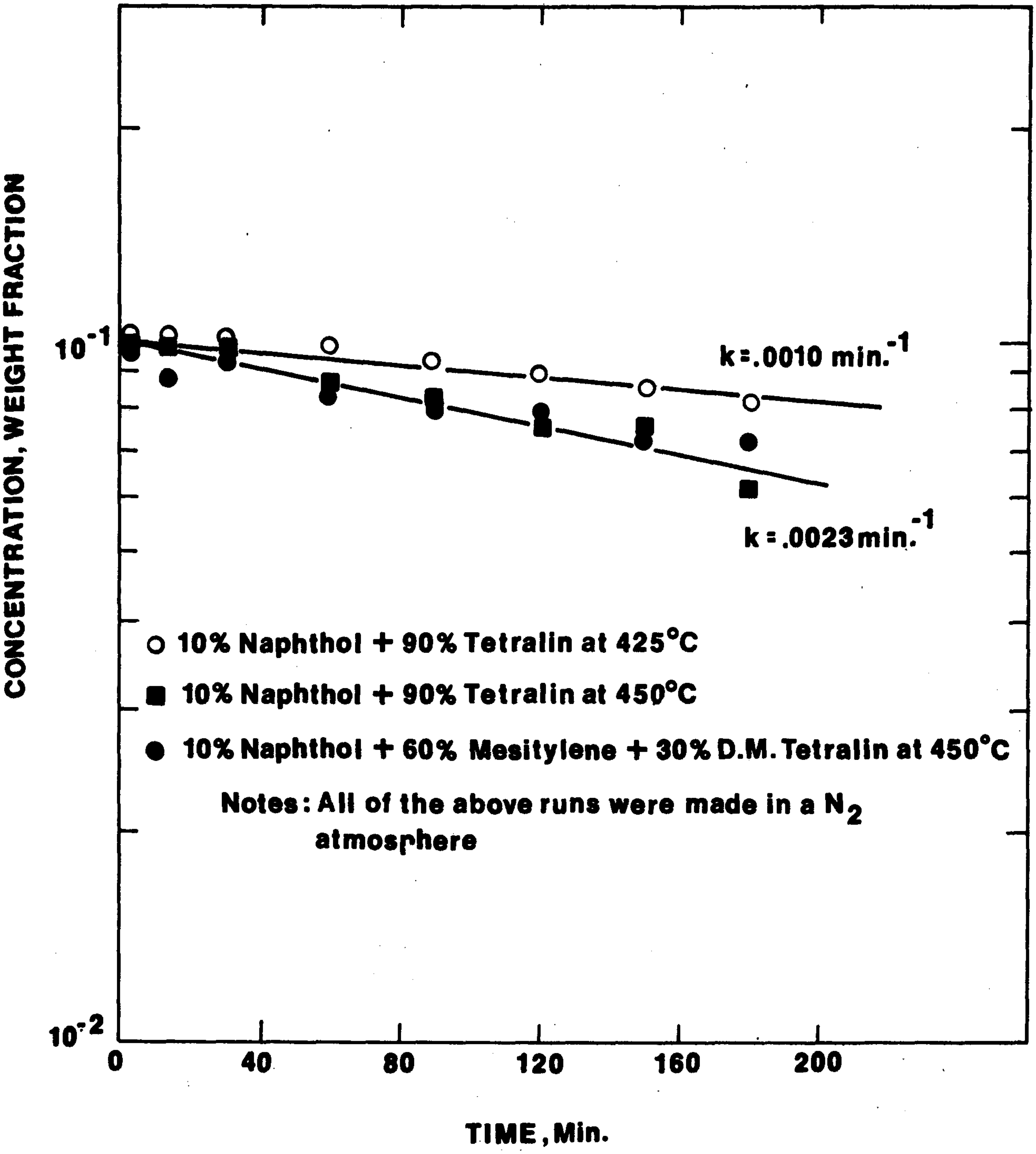


Figure 49: Naphthol reaction in solvent: concentration versus time

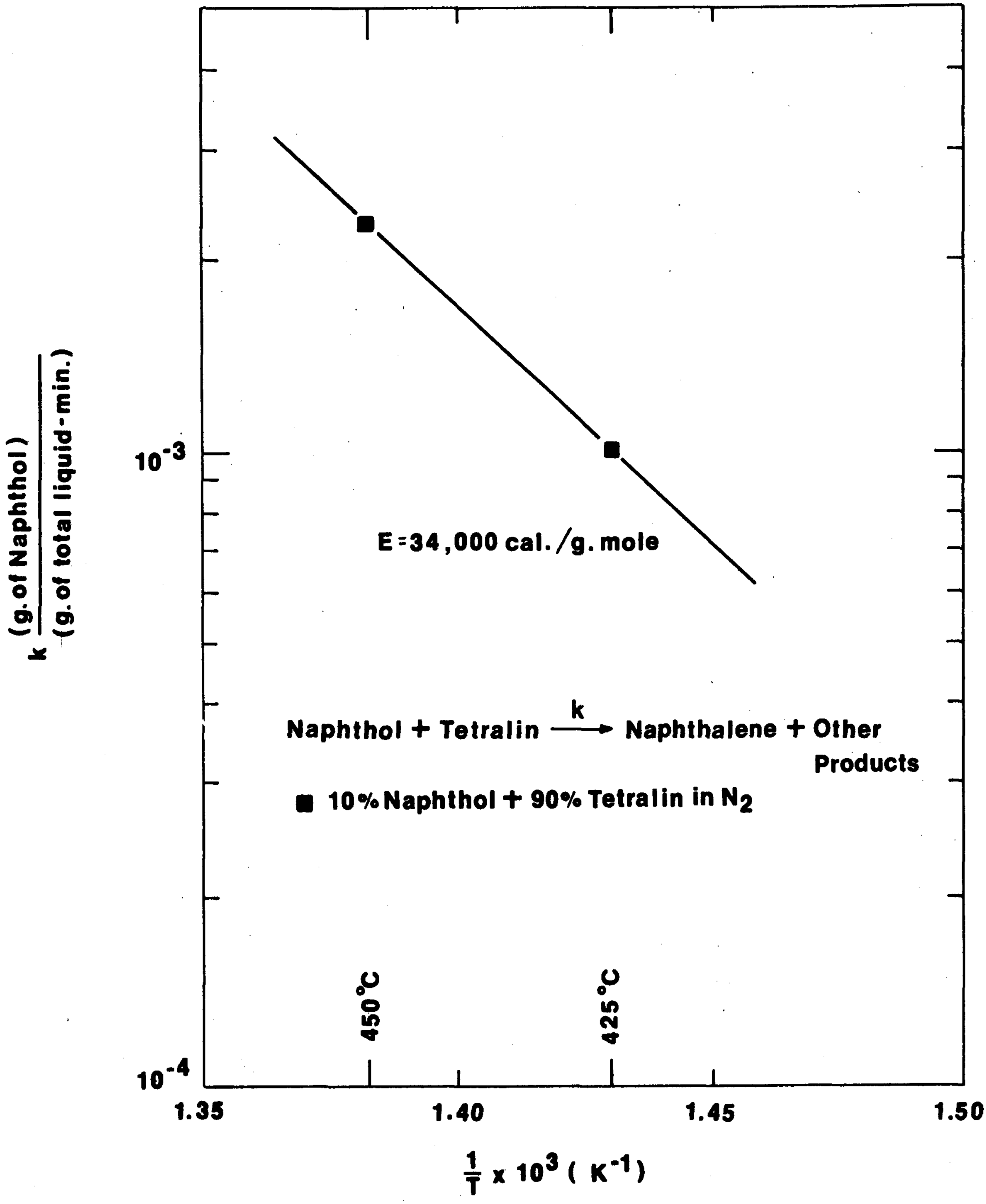


Figure 50: Arrhenius plot for the reaction of α-naphthol in tetralin

If an oxygen is directly attached to an aromatic ring, additional stabilization of the C-O bond is observed; phenols are very stable but naphthols react very slowly with donor solvents. As the oxygen-containing group is further removed from the aromatic ring, it becomes increasingly easy to deoxygenate. The high reactivity of non-aromatic oxygen (and sulfur) compounds can generate new intermediates that may not be naturally present in the original coal. For example, chain ethers (and thioethers) can create olefins, alcohols, and thiols which can then function as new hydrogen acceptors. The high reactivity of oxygen-containing groups also means that hydrogen need not always be abstracted from a good donor solvent to maintain a reaction. The hydrogen can be supplied by intramolecular rearrangements from poor donor solvents or from other hydrogen containing components of coal.

The relative order of reactivity of oxygen functional groups was found to be the following:

Benzofuran < aromatic phenols < ketones < aldehydes < chain ethers

(Thioethers are more reactive than chain ethers.)

These studies suggest that low rank coals should be very reactive to good donor solvents in the 300-400°C range with reasonable removal of oxygen and organic sulfur. Phenolic and furan oxygens are likely to remain unaffected during the liquefaction process unless a catalyst is present. Of course, some mineral matter present in coal can serve as a catalyst.

The work also suggests that when coal slurries are pumped through a preheater, a reasonable amount of solvation and molecular weight reduction occurs at low temperatures due, in part, to the fracturing of C-O bonds. However, with the presence of free radicals at these low temperatures, adduction reactions can occur that tie up a portion of both the cracked coal products and donor solvent (particular reference is made to the preheater).

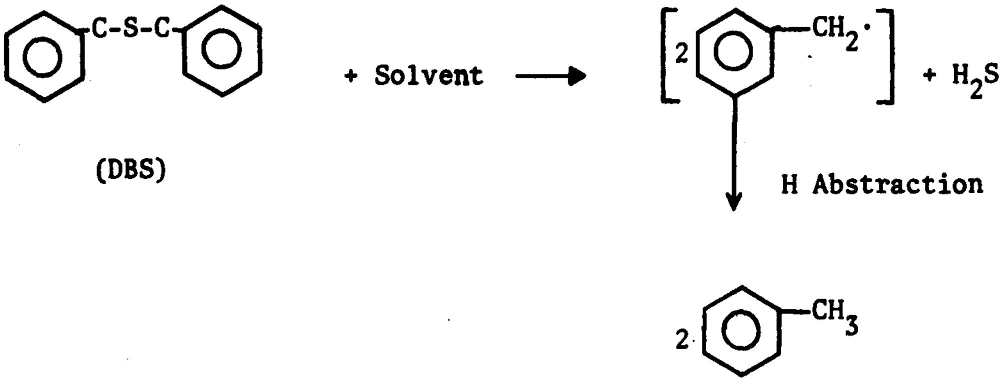
While there appeared to be little or no effect of a catalyst on dibenzyl cracking (C-C bond rupture), the cracking of dibenzyl ether was greatly promoted. This effect of a catalyst on C-0 bond cracking should be of direct interest to coal liquefaction, and it should be studied further.

I. Hydrogen Transfer to Sulfur-Containing Compounds

Due to the low reactivity of dibenzothiophene, the study of acceptors was extended from dibenzyl to dibenzyl ether to dibenzyl sulfide to observe the effect that different heteroatoms had on rates of reaction and products.

The sulfide reacts readily in either mesitylene or tetralin at very low temperatures (∿300°C) to yield primarily toluene and hydrogen sulfide. This results from the cleavage of DBS to the benzyl radical which is stabilized by hydrogen abstraction from any solvent or another molecule of dibenzyl sulfide.

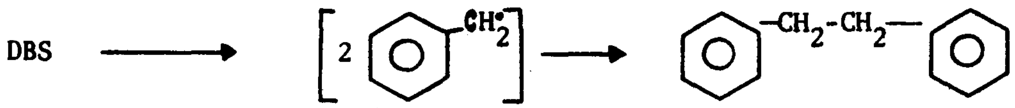
Primary Reaction of DBS to Form Toluene:



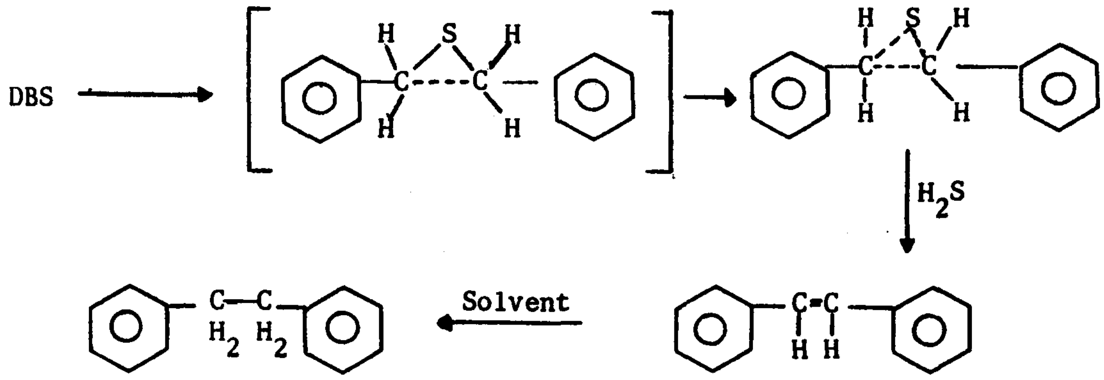
(34)

However, a significant amount of both stilbene and dibenzyl can form as side products. This formation may be attributed to the high lifetime of the benzyl radicals or to the participating of a three-membered ring intermediate. These side products can result from a hydride transfer reaction similar to that show in pages 79 and 92 for the corresponding ether. Alternate schemes are shown below:

Secondary Reactions:



(35)



(36)

Dibenzyl

Stilbene

When D_4-tetralin was used as the solvent, we observed more deuterium incorporated in both stilbene and dibenzyl than in the original sulfide. Therefore, the latter reaction (36) may not be reversible and can proceed with the participation of a donor solvent. The yield of stilbene and dibenzyl is always greater in a poor solvent (mesitylene). Specifically, about 30% of the dibenzyl sulfide was converted to dibenzyl when mesitylene was used as the solvent as opposed to only trace levels being formed when tetralin was used.

The fact that dibenzyl sulfide reacts much faster than either dibenzyl ether or dibenzyl is attributed to the relative strength of the bonds being cleaved:

$$C\text{-}C > C\text{-}O > C\text{-}S$$

It should be noted that this specific comparison is valid since each has an attached benzylic group which makes these bonds particularly easy to cleave. Although not studied quantitatively in this project, we have observed that completely aliphatic C-O and C-S bonds are much more difficult to cleave, even in good donor solvents. The differences in C-C, C-O, and C-S bond strengths may not be so marked in this case.

Due to the high reactivity of dibenzyl sulfide, the kinetics were difficult to model. A plot of dibenzyl sulfide concentration as a function of time and temperature is shown in Figure 51. As observed in the semi-log plot, Figure 52, only the initial conversion data were used in calculating the reaction rate constants. The activation energy was calculated as 18 800 cal/g mole (see Figure 53). This activation energy is significantly lower than the 30 000 cal/g mole of the oxygen-containing compounds and the 43 000 cal/g mole of dibenzyl.

J. The Formation of Solvent/Acceptor Adducts

1. High Temperature (>400°C) Reactions

The primary reaction between good donor solvents, such as tetralin and octahydrophenanthrene, and acceptors can give rather "ideal" products. For example, at moderate concentrations (10-20%), dibenzyl is converted only to toluene in these solvents. However, when solvents are mixtures of good and poor donors, secondary reactions may become quite important, in that undesirable and "non-ideal" products are recovered. The type of secondary reaction products may not only be determined by solvents used, but can also be influenced by the temperature of reaction and the structure of acceptor molecules. The secondary reactions may well compete with primary reactions to such an extent that kinetics become distorted and difficult to model.

When the dibenzyl acceptor system was modeled (Section C), it was shown that the rate of reaction was primarily independent of the type of solvent. In a poor solvent (mesitylene), hydrogen abstraction is as fast as with a good solvent. At these high temperatures, benzyl radicals are very reactive and can be stabilized by either hydrogen abstraction or recombination with other free radicals.

When mesitylene donates hydrogen, an aromatic radical results having the following possible structures:

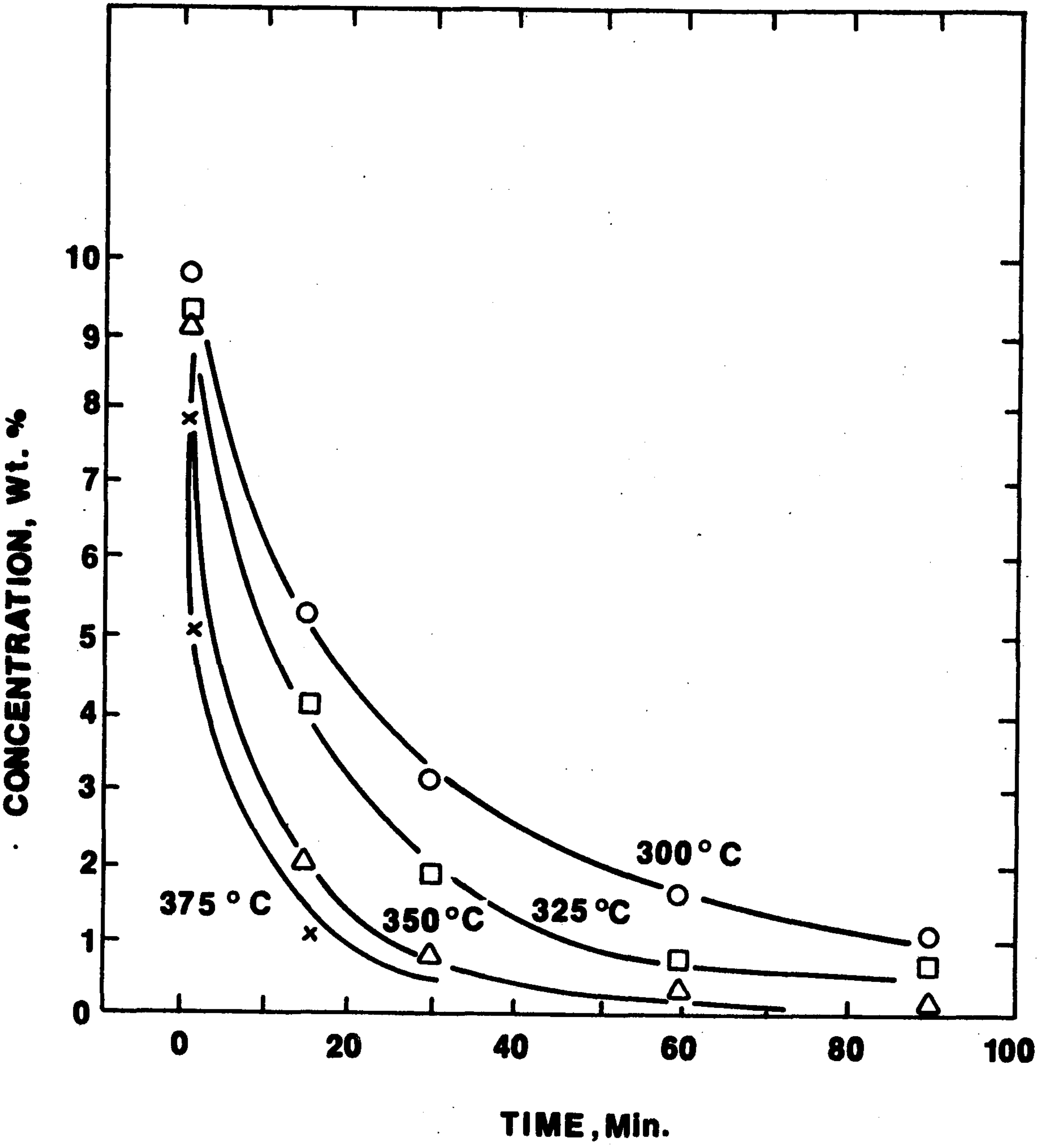


Figure 51: Dibenzyl sulfide concentration versus time for a feed of 10% sulfide with 90% tetralin in a nitrogen atmosphere

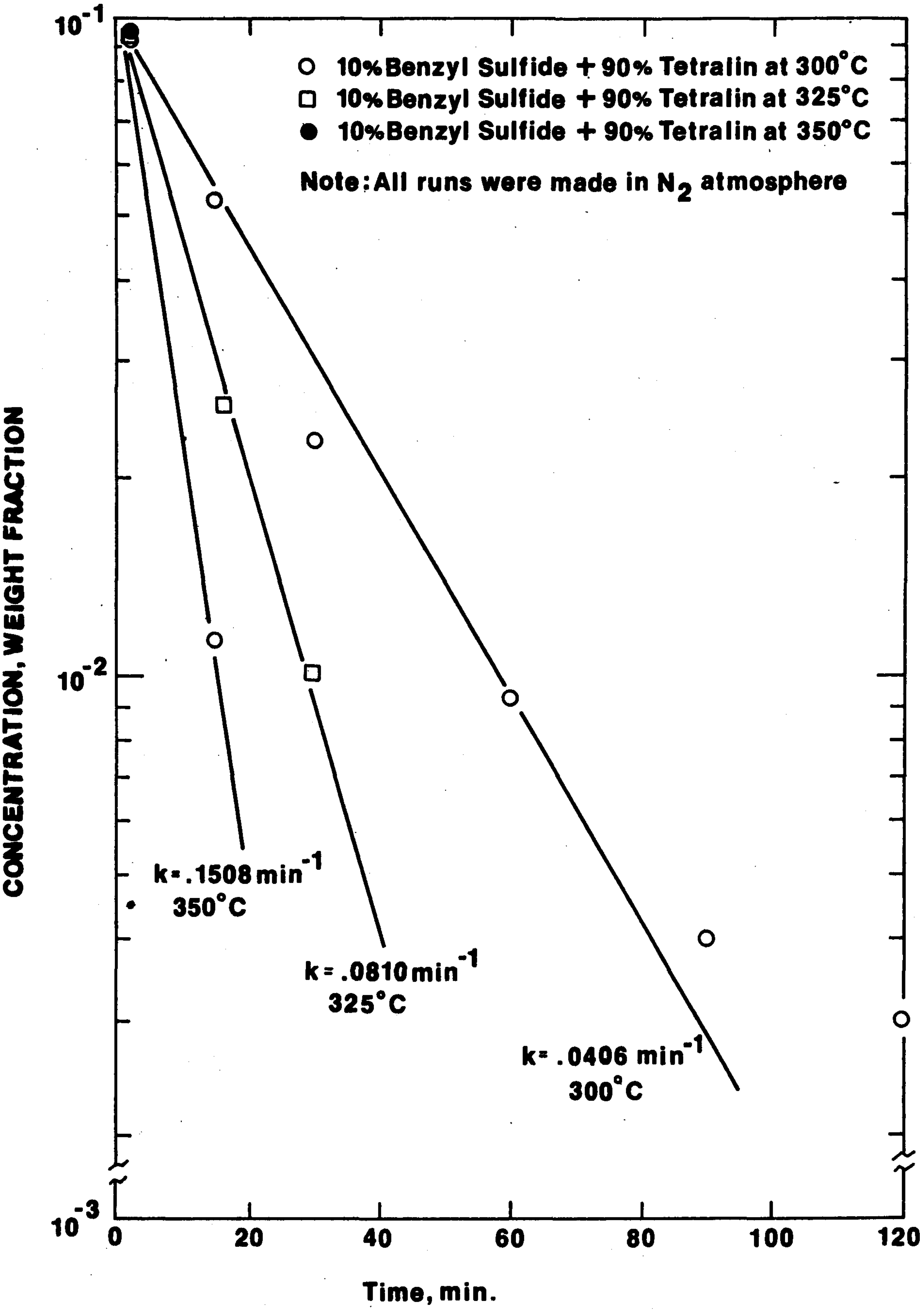


Figure 52: Semi-log plot of selected dibenzyl sulfide reactions

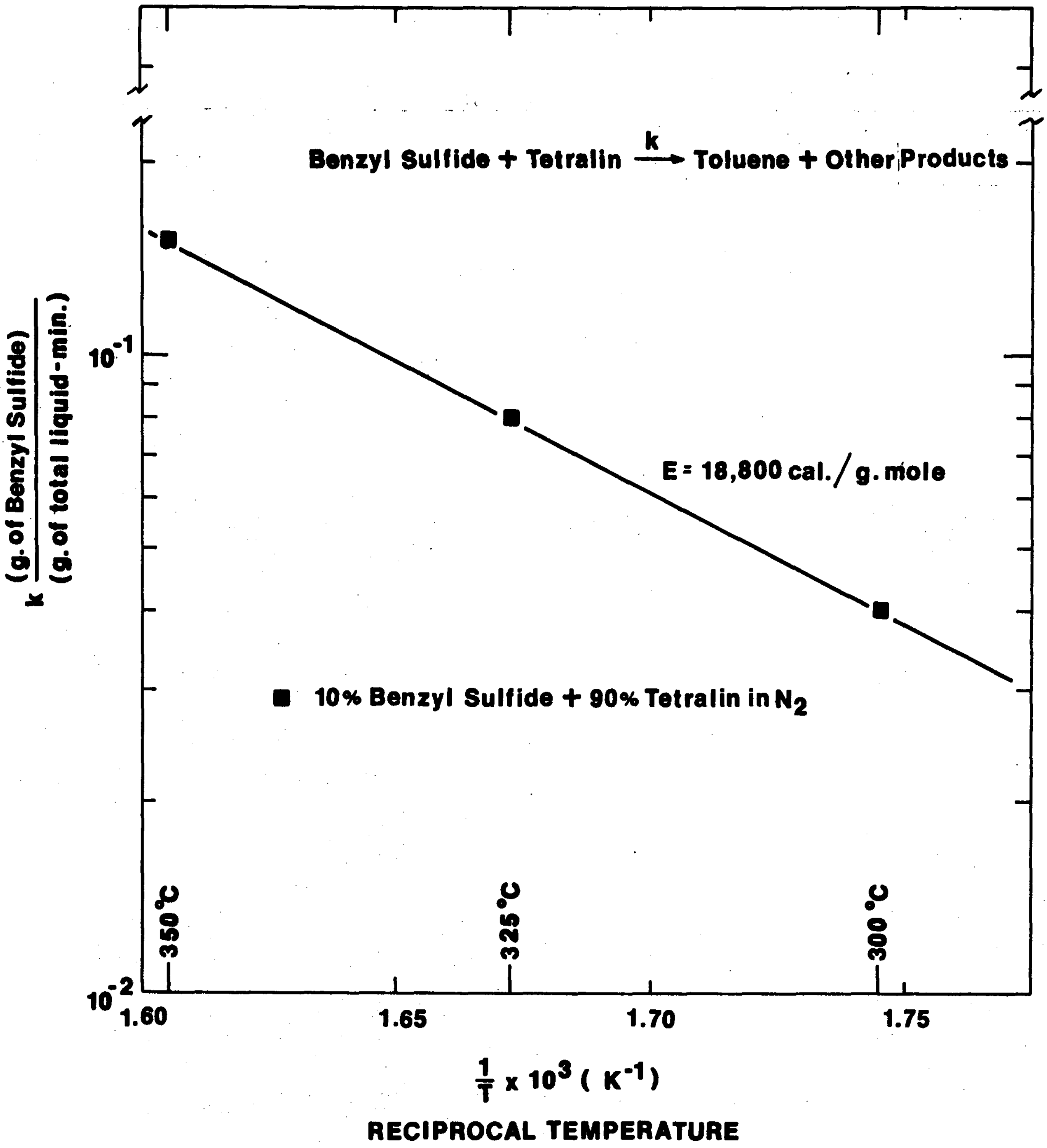
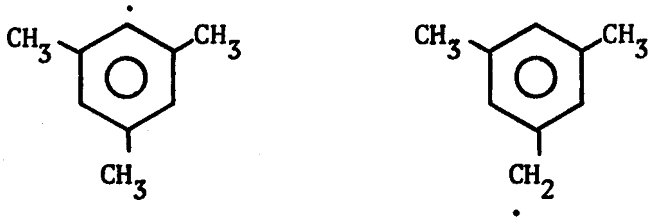


Figure 53: Arrhenius plot of dibenzyl sulfide cracking

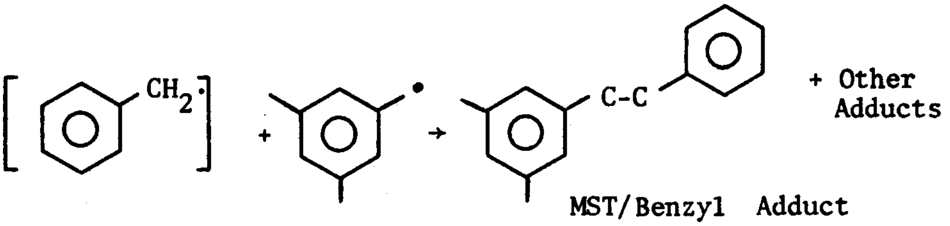


As reaction time increases, the concentration of mesityl free radicals increases, thereby, resulting in a greater potential to form adducts. The ultimate stabilization of all free radicals by recombination results in a very complex mixture of products. Dimers or adducts are, therefore, expected with poor donor solvents.

For the dibenzyl system, the following reaction may occur:

$$2\ [\text{Benzyl}\cdot] + 2\ \text{Mesitylene} \xrightarrow{N_2} 2\ \text{Toluene} + \text{Dimer} \tag{37}$$

Since the products actually vary, the following reaction is also possible.



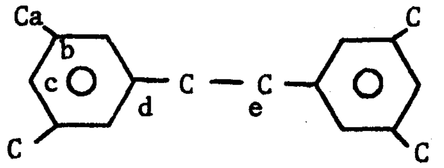
(38)

Experimental data indicate that these reactions may not be first order with respect to mesitylene concentration. These types of secondary reactions result in "adducts" which we define as any kind of radical-radical interaction of solvent molecules with or without the participation of acceptors, which result in higher molecular weight products. In the case of the above reaction, the presence of hydrogen actually promotes cracking of mesitylene and forms xylene radicals which further complicates the mixture of adducts.

The adduct product from the reaction of the dibenzyl/mesitylene system in either a hydrogen or nitrogen atmosphere is a family of oligomers, nearly all which incorporate mesitylene or xylene. The distribution of adducts or oligomers is dependent upon the reaction time, atmosphere (N_2 or H_2), concentration of acceptor radicals and concentration of other solvent (good donors) molecules.

The above dependence is illustrated by observing several GLC curves of products from the reaction of a feed blend of 10% tetralin, 30% dibenzyl, and 60% mesitylene. Figure 54 shows the product distribution after 30 mintues of reaction time in a hydrogen atmosphere at 450°C. Toluene, naphthalene, and adducts are present. Although tetralin is still present in high concentration, adducts begin to form, indicating that the rate of hydrogen abstraction from a good donor is not much faster than that from a poor donor. Adducts are not observed when pure tetralin is used as solvent proving that the secondary reaction is indeed related to mesitylene. Figure 55 shows the final products after three hours of reaction time; tetralin is absent, the dibenzyl concentration is low, and a large variety of adducts are present.

Figure 56 shows the typical product distribution for the dibenzyl/mesitylene reaction under a nitrogen atmosphere. Again, toluene and adducts are the primary products. It is noted that, in this case, one particular adduct is preferentially formed. This adduct has been isolated by preparative GLC and identified (MS, NMR) as 3,3',5,5'-tetramethyl dibenzyl, which is the primary mesitylene dimer. Figure 57 shows the ^{13}C-NMR spectrum of this polymer. Line assignments fit the following structure.



Mass Spec: m/1 238 (P, 25%)
m/1 119 (P 119, 100%)

Designated Carbon	a	b	c	d	e
C-NMR Assignment, ppm	21.25	137.79	127.5	142.05	38.09

The above adduct is simply a tetra-substituted dibenzyl.

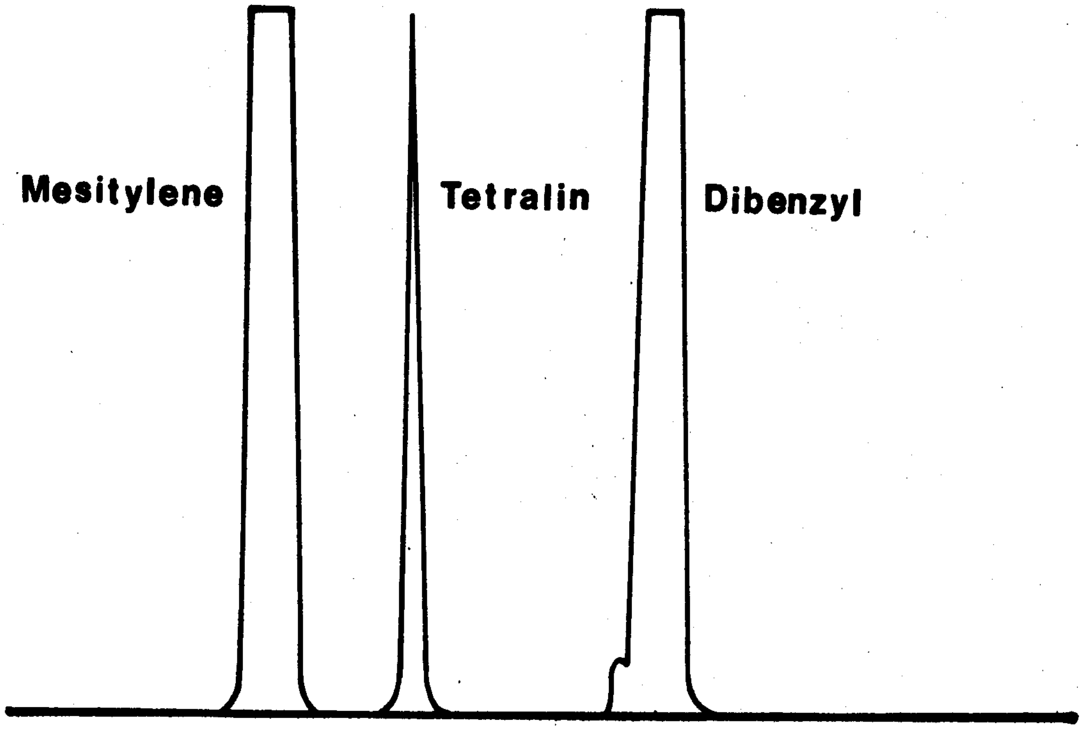


Figure 54a: Dibenzyl/mesitylene system in a hydrogen atmosphere

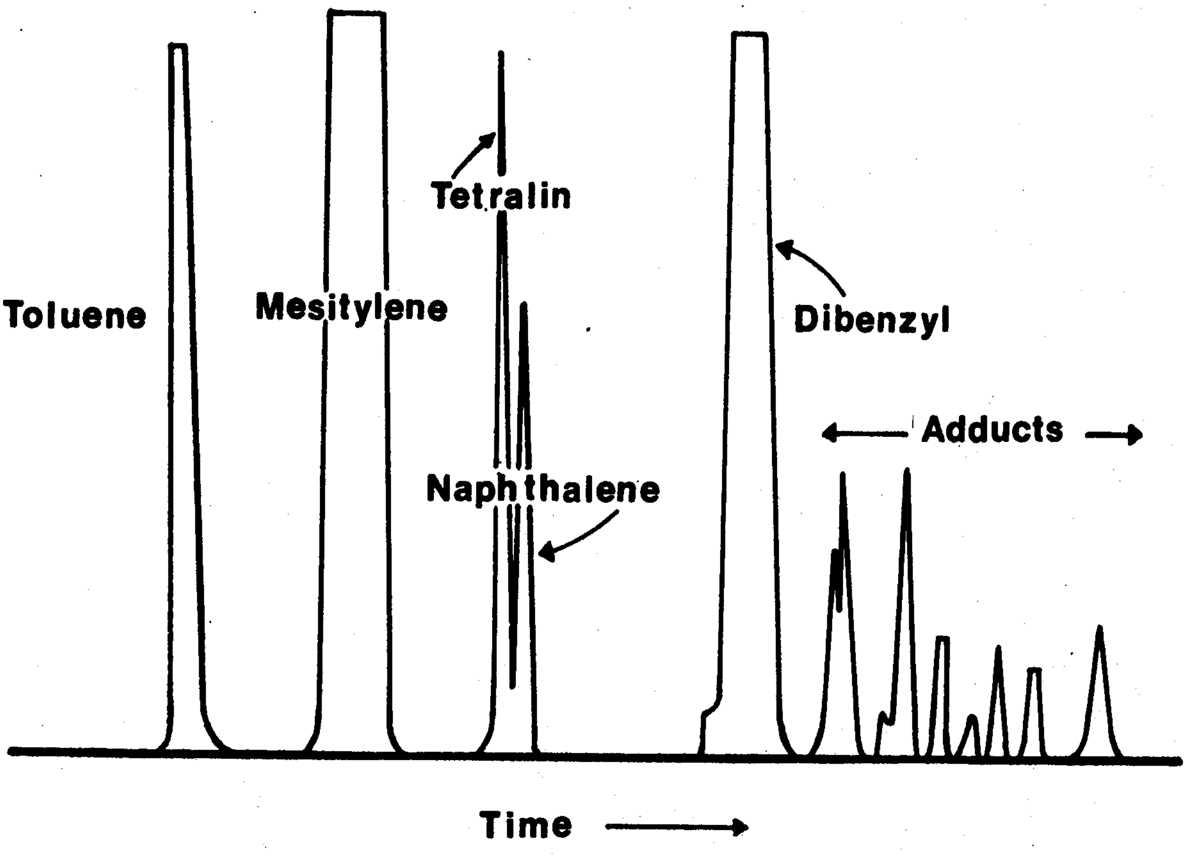


Figure 54b: Dibenzyl/mesitylene system in a hydrogen atmosphere: 30 minute reaction time

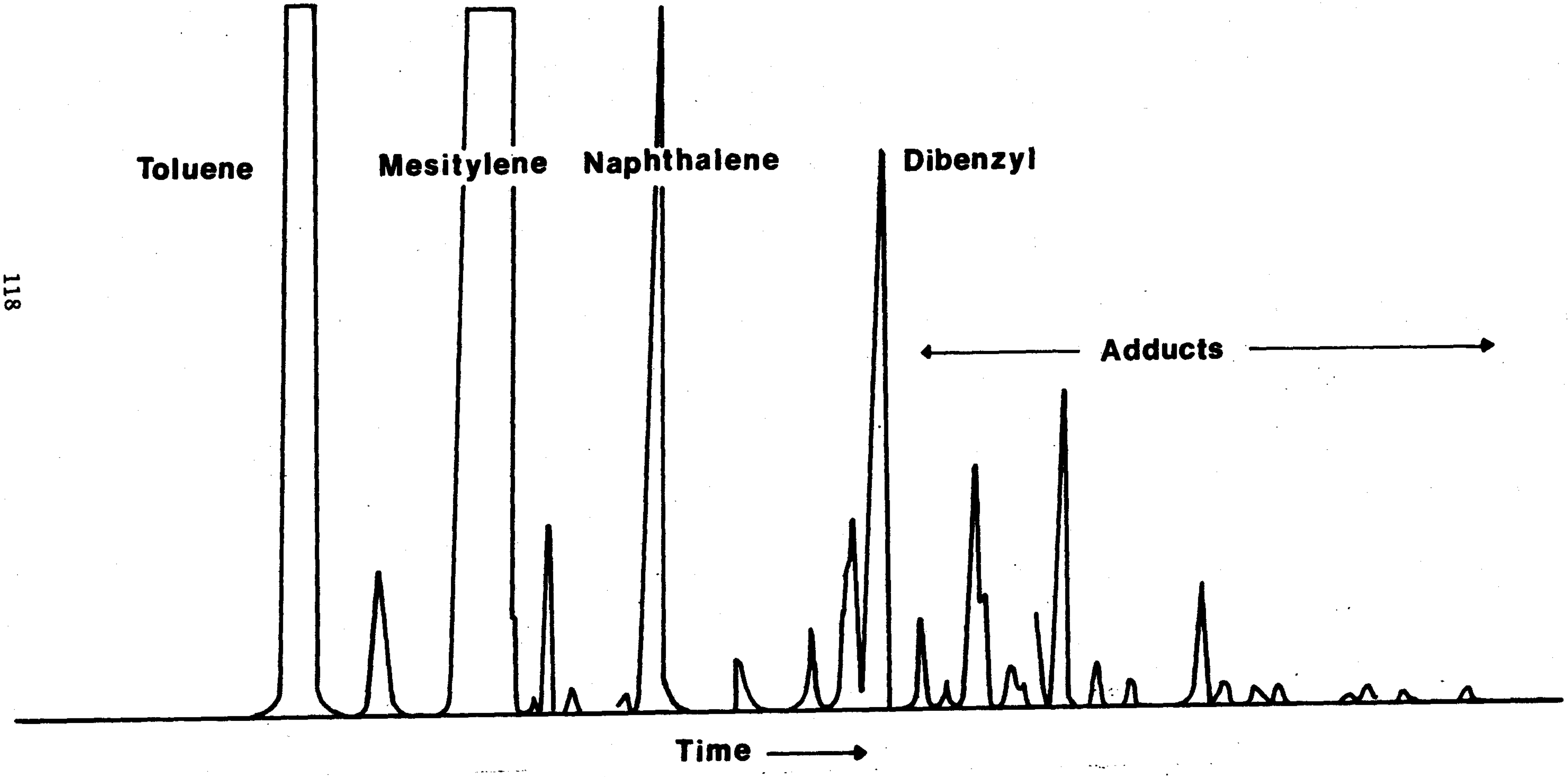


Figure 55: Dibenzyl/mesitylene system in a hydrogen atmosphere: 3-hour reaction period

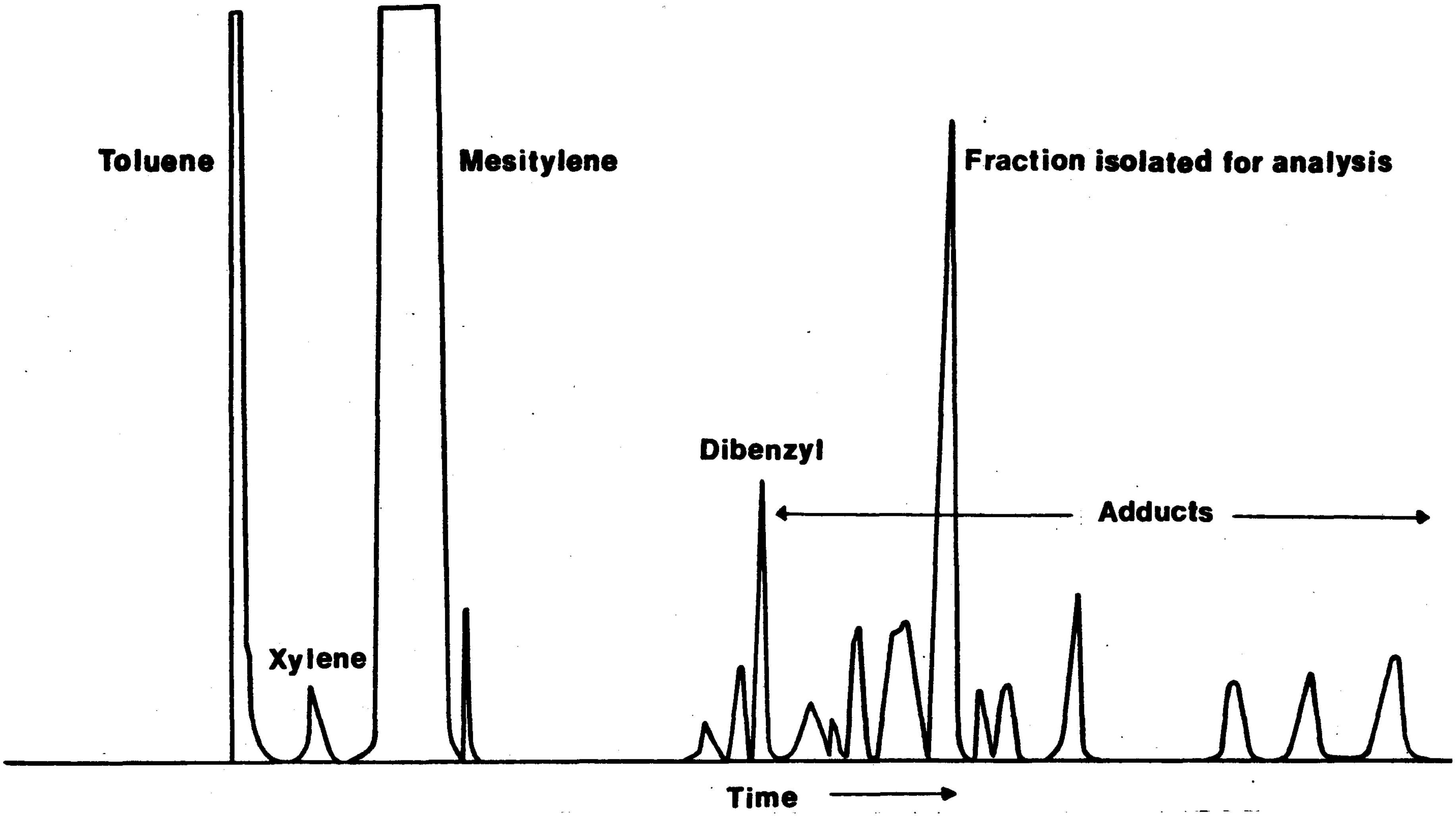


Figure 56: Dibenzyl/mesitylene system in a nitrogen atmosphere: 3-hour reaction period

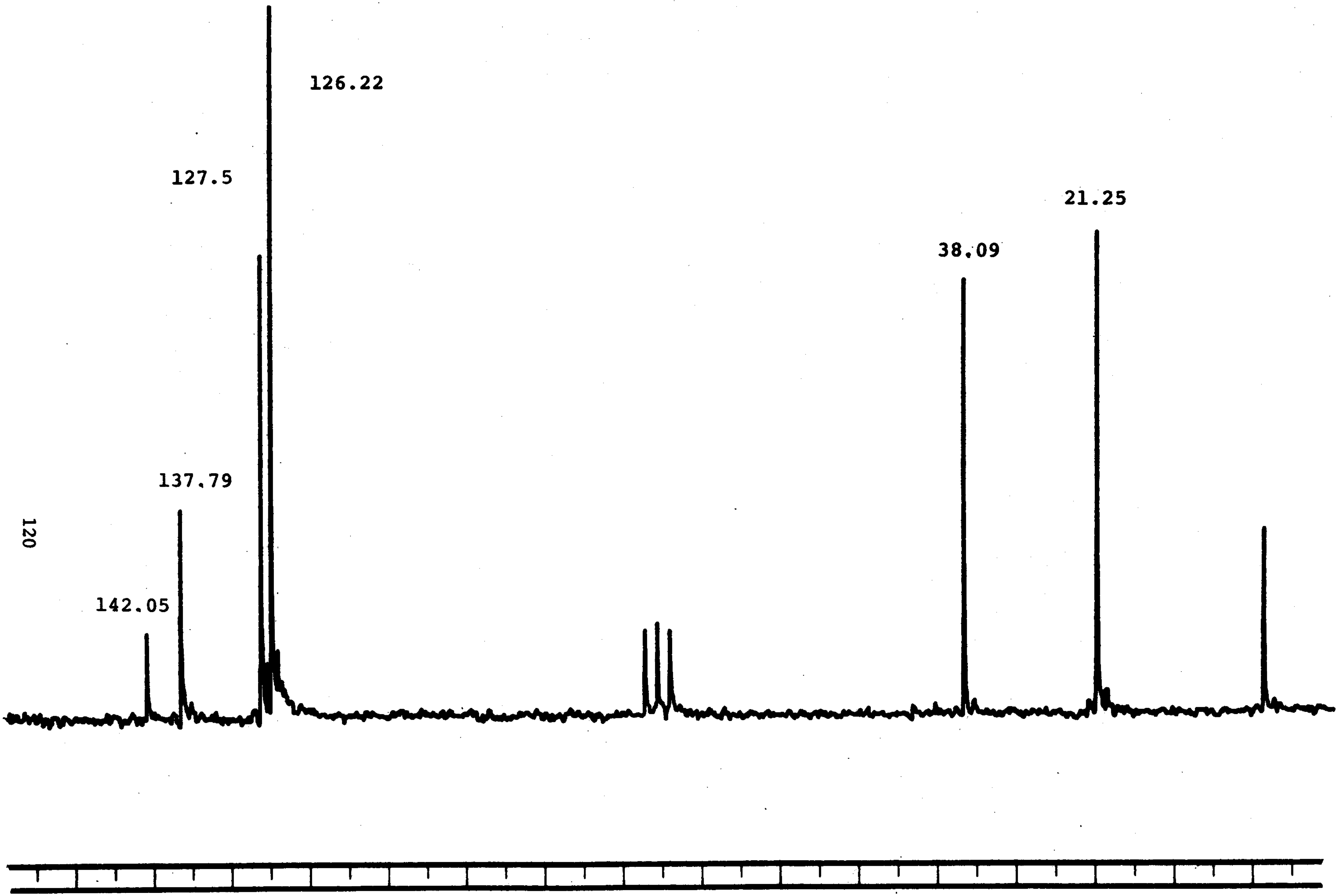


Figure 57: ^{13}C-NMR spectrum of isolated 3,3',5,5'-tetramethyl dibenzyl

Many of the remaining adducts are isomers where the link is either a diphenyl or diphenylmethane type. To our knowledge, this is the first confirming evidence that hydrogen is readily abstracted from either a methyl group or an aromatic ring by an acceptor free radical, thereby, forming these types of polymers. From other studies (Section D), it was learned that the latter structures are very stable at 450°C in the presence of tetralin. In a subsequent experiment, a sample of isolated high boiling components (primarily adducts) was reacted with tetralin at 450°C. The primary product was 1,3,5-trimethylbenzene (mesitylene) which indicated that the placement of methyl groups on the benzene rings of dibenzyl does not affect the basic cleavage of the dibenzyl but does reduce the reaction rate. The fact that alkylation increases stability of the dibenzyl system is implicit from the manner in which it is formed. However, additional experiments would be required to determine the effect of rings alkylation on the reaction kinetics. (This was outside the scope of the present project.)

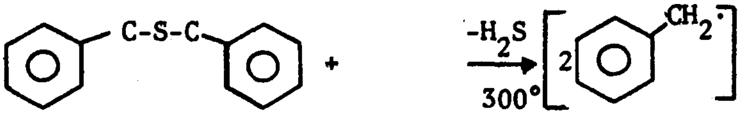
Conclusions. The studies of adduct formation-decomposition with dibenzyl acceptors were most valuable in establishing that under conditions of coal liquefaction both solvent molecules and acceptor fragments can and do interact to form higher molecular weight products. At temperatures above 400°C, these "adducts" are most likely to involve only poor donor solvents and that their formation can only be avoided by providing sufficient "transferable hydrogen" from hydroaromatic molecules to satisfy the requirements of all acceptor radicals generated by the solute (coal).

2. Low Temperature (<400°C) Reaction

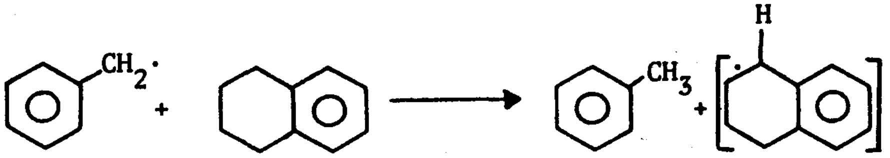
After completing the dibenzyl studies, effort was directed to other acceptors which demonstrated signficiant reaction with tetralin at mild temperatures. These acceptors included benzaldehyde, benzylalcohol, dibenzylether and dibenzyl sulfide. The results are discussed in other sections of this report. These studies showed that hydrogen transfer can occur at 300°C, if an acceptor free radical can be generated. These studies also indicated that the mesitylene polymers could be formed at these low temperatures. This is firm evidence that abstraction by acceptor radicals is the most correct view of the stabilization process. It is noted that both mesitylene and tetralin are completely stable up to 400°C.

The most surprising observation from the low temperature reaction was the formation of adducts between good donor solvents (tetralins, octahydrophenanthrene, tetrahydroquinoline) and acceptor radicals. The donor adducts are quite complex and are not of a single predominant structure. In reactions with tetralin, mass spectral studies (GLC-MS) indicate that the tetralin is bonded to phenyl-, benzyl-, benzyloxy-, or phenoxy-groups. Smaller amounts of the same groups bonded to naphthalene are also observed. When D_4-tetralin is used as a solvent (see Section J), the adducts always contain deuterium, further confirming the incorporation of solvent molecules.

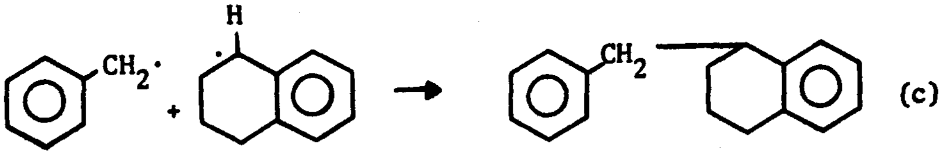
Bonding is assumed to be predominantly on the hydroaromatic ring since this should be the most reactive site of tetralin donors; but, based on mesitylene experiments, some bonding on the aromatic ring also occurs. Isolation and analysis of the adducts indicated that at low temperatures free radical lifetimes can be reasonably long permitting competition between H· and C· for stabilization. The following equations represent how these may occur:



(39a)



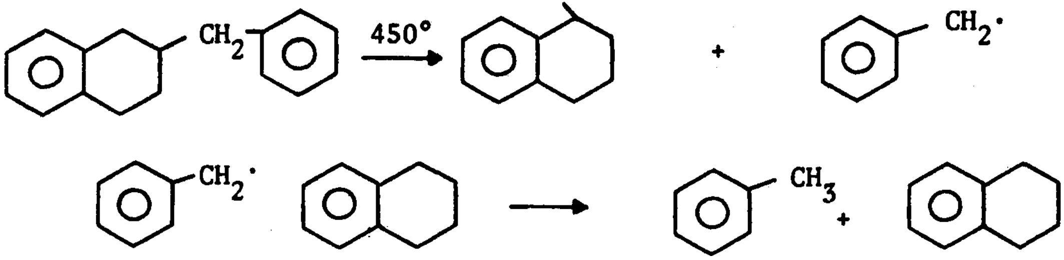
(39b)



(40)

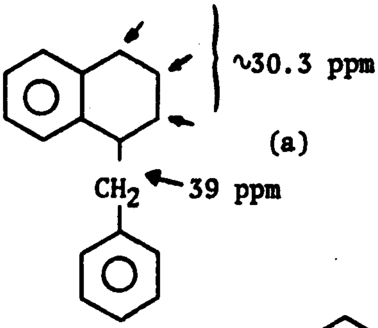
As the reaction proceeds, concentrations of both (a) and (b) increase, thereby, creating a greater probability of (40). The analytical data always show increasing concentration of adducts (c) with reaction time and with increasing concentration of the initial acceptor or (a).

It appears that the formation of benzyltetralin occurs during the hydrogen-transfer reactions at low temperatures (300°-400°C). If the adduct was attached at the hydroaromatic ring, a certain degree of "depolymerization" could be achieved by isolation the polymer and reacting it with fresh tetralin at 450°. From the previous studies with dibenzyl polymers, one would predict that cleavage would occur at high temperatures, as follows:

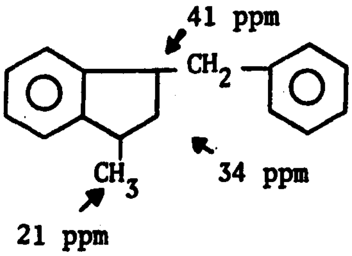


When this was done, less than fifty percent of the adduct "depolymerized" as shown. The remainder did not react (GLC-MS). Although the major adducts had the same molecular weight and similar fragmentation (large P-15 ion), the ^{13}C-NMR showed that significant rearrangement had occurred.

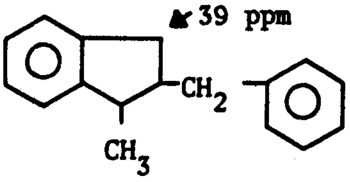
Figures 58 and 59 show the partial C-NMR spectra of both original and 450°C thermally treated adducts. Each fraction is a mixture of isomers. The lines at 34.2, 38.7, 39.1, and 41 ppm are indicative of five-membered rings, while the strong line at 21.2 is indicative of a CH_3-group on a saturated ring. The following structures would be typical of these signals:



(a)



(b)



(c)

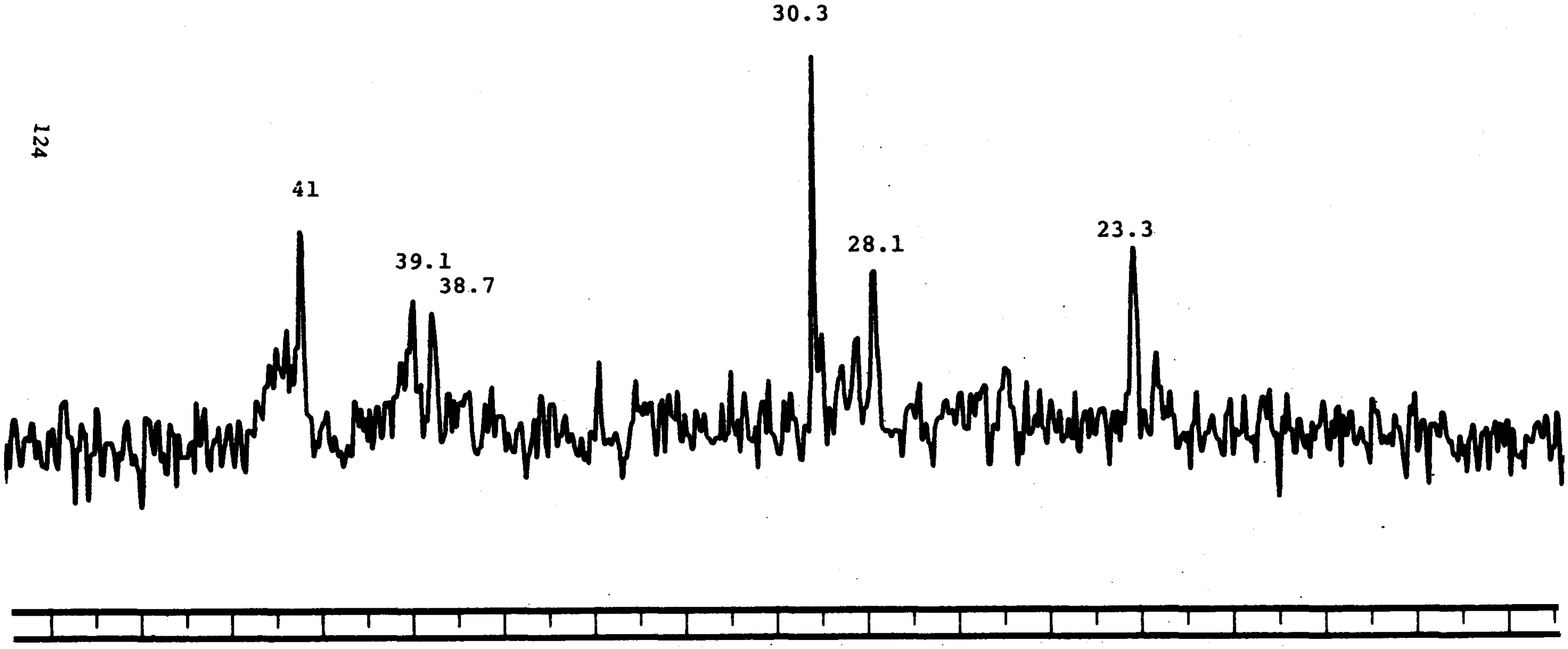


Figure 58: Partial ^{13}C-NMR spectrum of tetralin adducts formed at low temperatures

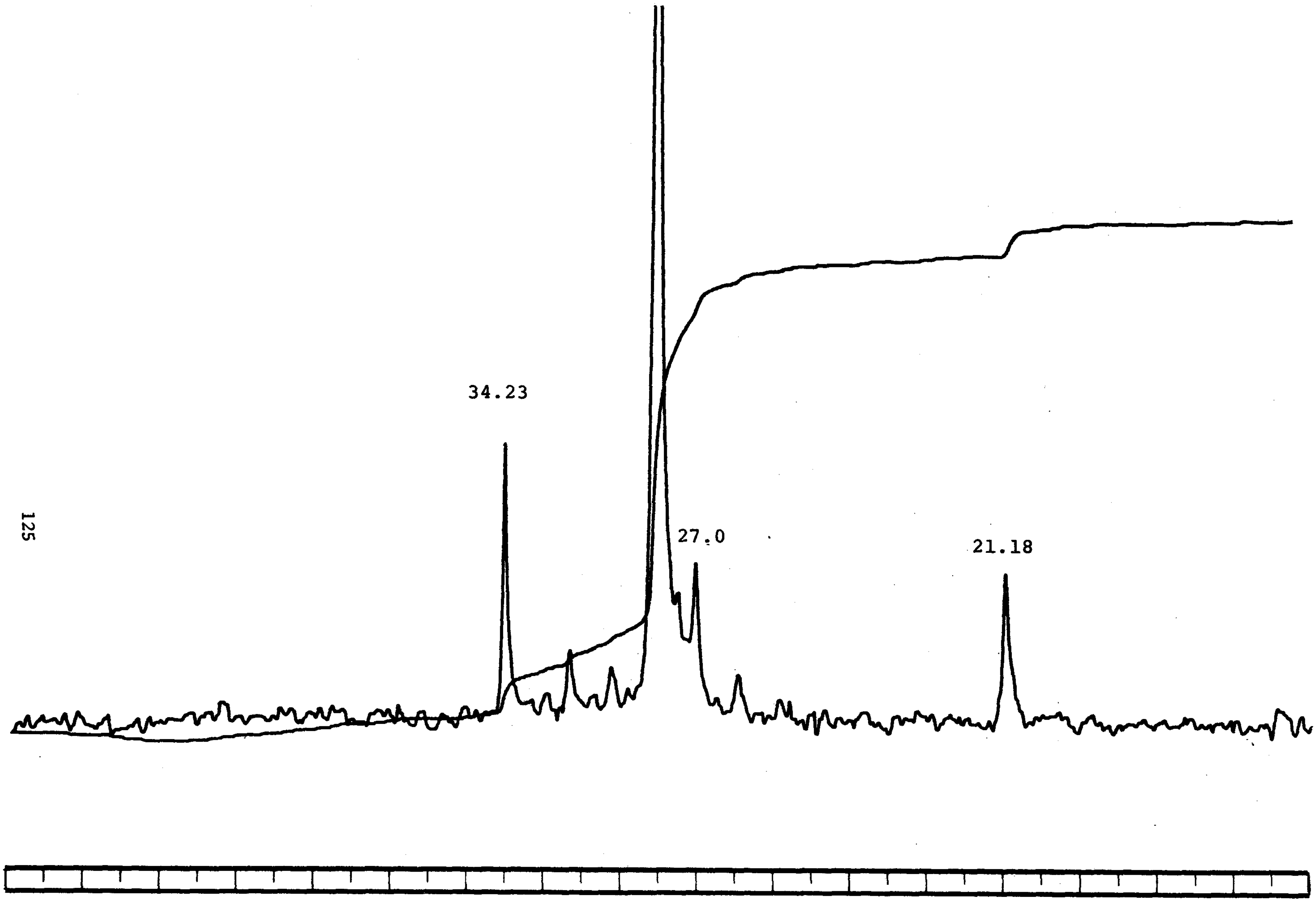


Figure 59: Partial ^{13}C-NMR spectrum of thermally stable tetralin adducts

The strong line at 30.0 ppm in both spectra indicate that the six-membered ring is intact and that, when certain positions are substituted by benzyl groups, they resist cleavage as in Section D. The fact that lines at 38, 39, and 41 ppm disappear upon heating at 450° suggest that those particular structures are cleaved (unlikely if they are in a five-membered ring) or rearranged to a more stable form. Finally, the observation that benzyl naphthalenes are also present confirm that isomer (a) is present and that it can still function as a donor after adduction.

The adduction reactions discussed are not limited to benzyl-type radicals nor to tetralin solvents. They have been observed with long chain thioether acceptors and donor solvents including dimethyltetralin, octahydrophenanthrene, and tetrahydroquinoline. Donors using a D or ^{13}C label have been used to provide further confirmation that the solvent was incorporated in adducts. Additional studies could be carried out using preparative GLC and micro NMR techniques to isolate purer fractions of these adducts which, together with the ^{13}C labels, would provide more definitive information on their structures.

Conclusion. These observations on adducts forming at low temperatures (300°-400°C) have a very significant impact on coal liquefaction chemistry and hydrogen transfer mechanisms. The results confirm that good donor solvents, having an ideal hydroaromatic system, can become irreversibly adducted to acceptor radicals which can be generated from coal. The presence of oxygen and sulfur functions on the radicals seems to enhance the formation of these adducts. Adduct formation with a donor solvent appears to be enhanced by high radical concentrations such as produced from the acceptor, dibenzyl sulfide, at relatively low temperatures (300-350°C) and long reaction times. Therefore, solvent incorporation can begin in the preheater and continue at all stages of coal liquefaction. Short reaction times are preferred to minimize this problem.

The similarity of structures of thermally stable adducts and rearranged solvents suggest that the mechanism of hydrogen transfer is unavoidably tied to donor solvent structure and stability. Therefore, good detailed analysis is necessary to determine hydrogen transfer levels at various operating conditions with different coals.

K. Experimentation With Deuterium Tracers

The study of reactions using deuterium tracers was undertaken to develop an understanding of the mechanisms of hydrogen transfer in reactions with model compounds. This experimentation is designed to lead into follow-up work with coal and coal-derived compounds. The following discussion is divided into sections dealing with the background experiments, the preparation of deuterated tetralin, and experimentation with model compounds.

1. Background Experimentation

A number of experiments were performed with D_4-tetralin to determine the fate of deuterium under conditions of hydrogen transfer cracking. Thermal studies using mesitylene as solvent indicated that the label was fairly stable up to 425°C. However, above 425°, the label became randomly incorporated in the solvent. The exchange was likely associated with the thermal dissociation of tetralin, since onset of rearrangement to methyl indane and dehydrogenation to naphthalene has been shown to occur in this temperature range.

When dibenzyl was reacted with D_4-tetralin, deuterium was incorporated in the toluene product but was randomly distributed. All products contained deuterium, indicating that no selectivity could be observed over the scrambling background. If scrambling can indeed be eliminated by performing reactions below 400°C, more reactive acceptors, such as oxygen and sulfur compounds, would be suitable for studying the selectivity of the hydrogen transfer process. As indicated in other sections of this report, olefins, oxygen, and sulfur compounds react with tetralin in the 300-400°C range. A series of experiments were made using oxygen and sulfur compounds with both D_4-tetralin and unlabeled tetralin in a deuterium atmosphere. The runs were successful and are decribed in a following section. It is also noted that experiments have established that scrambling does not occur between mesitylene and D_4-tetralin at 350°C.

2. Synthesis of Deuterium-Tagged Tetralin

Reaction conditions have been established for the reduction of naphthalene with deuterium to prepare partially deuterated tetralin. Bulk quantities have been prepared using a batch autoclave. A typical charge consisted of naphthalene (450 g), pulverized Nalco Sphericat 550 nickel/ tungsten catalyst, (22 g) and sufficient carbon disulfide (1.4 g) to maintain the catalyst in a sulfided state. Effective results were obtained at reaction conditions of 350°C (602°F), a total pressure of 10.5 MPa (1500 psig), and a 3.0-hour residence time. Typical conversion levels of naphthalene have been above 95% with the yield of tetralin being between 88 and 90%. The bulk reaction product subsequently distilled in a Podbielniak Mini-cal unit packed with Heli-Pak and operated with a 20/1 reflux ratio. A center-cut of about 75% was retained for the experiments.

As shown in Table IV, a typical product consisted principally of D_3 to D_6 derivatives. However, the deuterium had been scrambled into both the aromatic and hydroaromatic rings, as indicated by NMR. In addition, the vent gas from the reactor consisted of about equal concentrations of H_2, HD, and D_2. In summary, the above NiW catalyst, when sulfided, is effective for the reaction of naphthalene with deuterium, but its use promotes scrambling. Based on random scrambling of the deuterium between the aromatic and hydroaromatic rings, it is estimated that 38% of the donatable "hydrogen" is deuterium.

More selective means of preparing deuterated tetralin are available, but the time and cost of preparation are high. It did not appear to be warranted at this time. In particular, the more interesting

TABLE IV

Incorporation of Deuterium Into Tetralin

(D_x-Tetralin Distillate Cut)
93% Tetralin by GLC
3% Naphthalene
4% Me Indanes

Deuterium Addition	Intensity
0	0.9
1	3.4
2	9.3
3	17.0
4	21.7
5	20.5
6	14.5
7	8.0
8	3.4
9	1.3
	100.0

DCC:WPC
GR&DC
CR&CD
3/22/78

hydrogen transfer experiments were made with untagged tetralin and deuterium reaction atmosphere. The methods of preparing selective deuterated tetralin were reviewed by L. Heredy and R. P. Showronski at the July 16, 1977, ERDA contractors' meeting [Contract No. E(49-18)-2328].

3. Deuterium Experiments With Model Compounds

Due to the reaction temperature limitation of 400°C, hydrogen transfer experiments with deuterium were undertaken with the following acceptors: dibenzylether, benzaldehyde, benzylalcohol, acetophenone, dimethylphenol, and dibenzyl sulfide. To separate the role of the donor solvent from that of dissolved gas, parallel experiments were made with acceptors and D_4-tetralin in a nitrogen atmosphere or with unlabeled tetralin in a deuterium atmosphere. The series of experiments was made at 350°C (662°F) with a total pressure of 10.3 MPa (1500 psig). Due to high reactivity, the dibenzyl sulfide runs were at lower temperatures.

The reaction products were analyzed using a combination of procedures. First, the routine periodic samples (15, 30, 60, 90, etc., min) were quantitatively analyzed by GLC. It was shown that the reaction profiles were essentially identical to those of the kinetics experiments discussed earlier. Secondly, selected samples were analyzed by GLC-MS from which the incorporation of deuterium was calculated.

The level of deuterium was calculated by measuring the M^+ and $M^+ + 1$ peak heights and making a comparison with those from a "natural," or completely unlabeled system. These were then expressed as percentages from:

$$\text{Isotope Ratio} = \frac{M + 1}{M} \times 100\% \qquad (42)$$

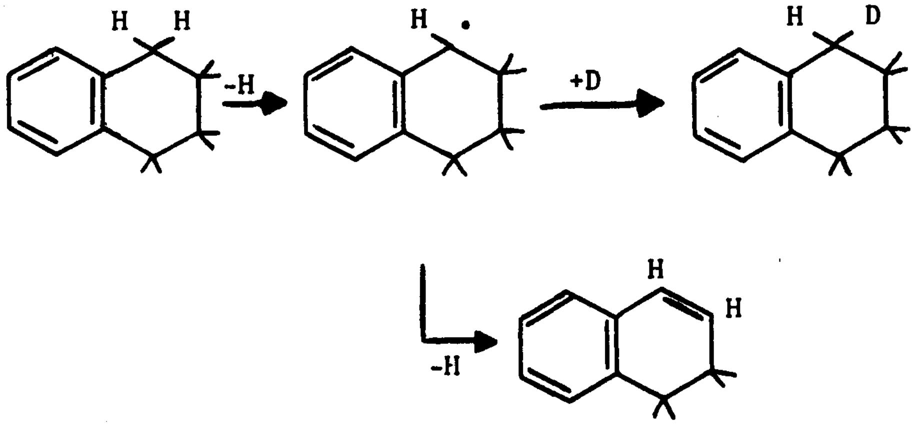
Since the "natural abundance" M+1 peak is due to ^{13}C isotopes, levels greater than this must be due to the incorporation of deuterium. The level of ^{13}C isotopes has been taken into account in the levels of incorporated deuterium reported below.

It is noted that no measurable amounts of $M^+ + 2$ ions were observed. Therefore, essentially only one deuterium was transferred per average acceptor molecule.

The following is a discussion of the results of the experiments with deuterium or deuterium-tagged tetralin. The data dealing with deuterium being incorporated in adducts or isomers are discussed in the appropriate section.

Benzaldehyde: When benzaldehyde is reduced with tetralin, the primary reaction products are toluene and benzene. As shown in Table V, a significant amount of deuterium was incorporated in both of these products, but the level was dependent upon the source of donor. In the case of benzaldehyde reduction with H_{12}-tetralin in a deuterium atmosphere, the resulting toluene had a deuterium level of 25% of the hydrogen added to produce toluene. Therefore, about one-fourth of the hydrogen came from the dissolved gas and three-fourths from the donor solvent. In this run, essentially no deuterium was found in the benzene; therefore, the radicals had been stabilized by abstracting hydrogen from the donor solvent or by rearrangement when decarbonylation occurred.

There was some deuterium incorporated into tetralin, presumably as a result of "re-hydrogenation" after some hydrogen had been donated to the acceptor. Specifically, the carbon free radical can be stabilized with dissolved deuterium and aromatization does not necessarily occur.



(43)

TABLE V

D_2·Tagged Transfer Experiments: Benzaldehyde Systems

I. Reaction in a Deuterium Atmosphere (HT77-103)

	Deuterium Incorporation(1)		
Reaction Time (min)	60	120	240
Compound:			
Benzaldehyde	2.7	3.9	5.2
Toluene	27.0	24.0	20.6
Benzene	2.0	0.5	2.3
Tetralin	0.0	3.5	11.3

II. Reaction with Deuterium-Tagged Tetralin in a Nitrogen Atmosphere (HT77-97)

	Deuterium Incorporation(1)		
Reaction Time (min)	60	120	240
Compound:			
Benzaldehyde	14.5	7.9	4.7
Toluene	19.8	22.0	24.1
Benzene	16.5	15.2	19.1
Tetralin	-----(approx. 450%)------		

III. Distribution of Reaction Products (I and II above)

	Wt. % Component in Reactor		
Reaction Time (min)	60	120	240
Compound:(2)			
Benzaldehyde	6.0	4.3	2.4
Toluene	1.2	2.0	3.4
Benzene	0.8	1.4	2.4
Tetralin	88	87	86

Note (1): Deuterium incorporation is calculated as the (M+1)/M ratio less natural abundance due to ^{13}C; expressed as % of a deuterium atom incorporated (i.e., C_6H_5D is 100%).

Note (2): Naphthalene, adducts, and unidentified components are not included.

DCC:WPC
GR&DC
CR&CD
3/22/78

Because this deuterium incorporation into tetralin occurs after the primary transfer reaction is under way and its level is relatively low, little of the deuterium in the toluene would have been the result of the secondary series of reactions of tetralin being deuterated and then deuterium being transferred to reacting benzaldehyde.

With the reduction of benzaldehyde with D_4-tetralin, the resulting toluene showed a deuterium incorporation of 22%. This is lower than the estimated level of donatable deuterium (38%) in the D_4-tetralin. However, due to mass and higher resonant energy of hydrogen over deuterium, it would be anticipiated that hydrogen transfer would be preferred by a ratio of about $\sqrt{2}$. The 22% level is, therefore, reasonable. It is interesting that deuterium incorporation in benzene product of this run was about 17%, indicating that much of the "hydrogen" was transferred from the donor solvent.

Dibenzyl Ether: As noted in Table VI, when dibenzyl ether was cracked in tetralin ($C_{10}H_{12}$) in a deuterium atmosphere, only about 6% deuterium was introduced into the primary cracked products, toluene and benzaldehyde. Even when deuterium-tagged tetralin (considered to contain about 38% donatable hydrogen as deuterium) was used, only 3% deuterium was introduced into the benzaldehyde and 12% into the toluene. Therefore, it appears that most of the hydrogen necessary to satisfy free radicals from the C-O bond breaking of dibenzyl ether comes from internal rearrangement reactions. No D-H exchange in the tetralin of a run with deuterium atmosphere was observed; this further indicates that internal rearrangement during dibenzyl ether cracking occurs. A trace level of dibenzyl was detected in the products from the run in a deuterium atmosphere. Again, only a low level of deuterium incorporation was observed.

Benzyl Alcohol: The results of the runs with benzyl alcohol reduction are given in Table VII. When the alcohol was heated with tetralin ($C_{10}H_{12}$) in a deuterium atmosphere, little incorporation of deuterium was observed in the benzaldehyde and toluene products, namely

TABLE VI

D_2·Tagged Transfer Experiments: Dibenzyl Ether Systems

I. Reaction in a Deuterium Atmosphere (HT77-101)

	Deuterium Incorporation(1)		
Reaction Time (min)	60	120	240
Compound:			
Dibenzyl ether	Nil	Nil	Nil
Benzaldehyde	4.3	6.4	3.2
Toluene	5.3	5.7	8.3
Benzene	-	0.3	-
Dibenzyl	(1.4)	9.3	-
Tetralin	Nil	Nil	Nil

II. Reaction with Deuterium-Tagged Tetralin in a Nitrogen Atmosphere (HT77-94)

	Deuterium Incorporation(1)		
Reaction Time (min)	60	120	240
Compound:			
Dibenzyl ether	Nil	Nil	Nil
Benzaldehyde	3.4	1.7	2.3
Toluene	9.5	10.2	16.3
Benzene	40.4	31.7	20.4
Dibenzyl	-	-	-
Tetralin	-----(approx. 450%)-------		

III. Distribution of Reaction Products (I above)

	Wt.% Component in Reactor		
Reaction Time (min)	60	120	240
Compound:			
Dibenzyl ether	4.9	3.3	1.7
Benzaldehyde	1.2	1.6	1.8
Toluene	1.2	2.0	3.2
Benzene	0.1	0.2	0.3
Dibenzyl	Trace	Trace	Trace
Tetralin	90	89	88

Note (1): Deuterium incorporation is calculated as the (M+1)/M ratio less natural abundance due to ^{13}C; expressed as % of a deuterium atom incorporated (i.e., C_6H_5D is 100%).

Note (2): Naphthalene, adducts, and unidentified components are not included.

TABLE VII

D_2·Tagged Transfer Experiments: Benzyl Alcohol Systems

I. Reaction in a Deuterium Atmosphere (HT77-104)

	Deuterium Incorporation(1)		
Reaction Time (min)	60	120	240
Compound:			
Benzyl alcohol	10.7	8.8	4.8
Benzaldehyde	2.3	2.0	3.3
Toluene	2.7	3.5	10.3
Tetralin	Nil	Nil	10.4

II. Reaction with Deuterium-Tagged Tetralin in a Nitrogen Atmosphere (HT 78-1)

	Deuterium Incorporation(1)		
Reaction Time (min)	60	120	240
Compound:			
Benzyl alcohol	2.7	38.5	40.8
Benzaldehyde	15.7	29.7	30.6
Toluene	7.7	9.6	7.8
Tetralin	------(approx. 450%)------		

III. Distribution of Reaction Products (I above)

	Wt.% Component in Reactor		
Reaction Time (min)	60	120	240
Compound:			
Benzyl alcohol	6.8	5.6	3.5
Benzaldehyde	0.7	0.8	0.8
Toluene	1.6	2.1	4.1
Tetralin	------(approx. 90%)-------		

Note (1): Deuterium incorporation is calculated as the (M+1)/M ratio less natural abundance due to ^{13}C; expressed as % of a deuterium atom incorporated (i.e., C_6H_5D is 100%).

Note (2): Naphthalene, adducts, and unidentified components are not included.

DCC:WPC
GR&DC
CR&CD
3/22/78

about 4%. Again, little was incorporated in the tetralin. This indicates that dissolved gas (deuterium) plays only a minor role in the reduction of an alcohol.

In the case of the reaction of the alcohol with D_4-tetralin, interesting results were observed. The unreacted benzyl alcohol and product aldehyde had significant levels of deuterium, namely 30-40%. This indicates either the reversibility of the aldehyde/alcohol reaction or an H/D exchanger with the deuterated solvent. It is also noted that the toluene product had a low level of deuterium, 9%. This shows the redox behavior of the alcohol since the deuterium was attached to the hydroxyl group. Reference is made to the previous section of this report dealing with reaction mechanisms and kinetics.

3,5-Dimethylphenol: To be consistent with the above work, dimethylphenol was heated with tetralin ($C_{10}H_{12}$) in a deuterium atmosphere at 350°C (see Table VIII). Essentially no reduction of the phenol was observed, but a high level of deuterium incorporation (52%) occurred. The hydrogen on the hydroxyl group is very labile and H/D transfer with dissolved gas occurs quickly. This ease of transfer is consistent with phenols being considered at hydrogen donors in coal liquefaction. It is noted that this phenol underwent little reduction even at temperatures up to 450°C. For reference, essentially no deuterium was incorporated in the tetralin confirming its thermal stability at 350°C and the lack of the phenol reaction.

Acetophenone: At 350°C, little reduction of acetophenone occurs (see Table VIII); however, some H/D transfer was observed with dissolved deuterium. This is probably related to the keto-enol equilibrium reaction. The level of deuterium incorporation in the acetophenone fraction (isolated in the GC-MS instrument) was 34%. Only a low level of deuterium (7%) was found in tetralin.

Dibenzyl Sulfide: Dibenzyl sulfide cracks and reduces readily in the presence of tetralin at 350°C. The primary product is toluene from the hydrogen transfer cracking at the C-S bond. Apparently, a second route exists through the abstraction of sulfur with the formation of stilbene

TABLE VIII

D_2 Tagged Transfer Experiments: Acetophenone & Dimethyl Phenol Systems

I. Acetophenone Reaction in a Deuterium Atmosphere (HT77-105)

Note: At 350°C, only a very low level of acetophenone reaction was observed; therefore, only the 240 minute sample was analyzed by GC/MS.

Compound	Deuterium Incorporation	Wt% Component in Reactor
Acetophenone	34.4	9.1
Tetralin	6.6	∿90

II. 3,5-Dimethylphenol Reaction in a Deuterium Atmosphere(HT77-106)

Note: As in I above, only the 240 minute sample was analyzed by GC/MS.

Compound	Deuterium Incorporation	Wt% Component in Reactor
3,5-Dimethylphenol	52.3	9
Tetralin	3.5	∿90

DCC:bjs
GR&DC
CR&CD
3/22/78

and then dibenzyl. At 350°C, little cracking of dibenzyl occurs. Considering the above, deuterium incorporation was measured in toluene, dibenzyl, and unreacted dibenzyl sulfide. The results are given in Table IX. Reference is also made to a previous section in which the mechanism and kinetics of the reactions are discussed.

As with the other acceptors, essentially no deuterium incorporation in the toluene product occurred when unlabeled tetralin and deuterium gas were used. This also appeared to be the case when D_4-tetralin was used. This latter low level is consistent with that of the dibenzyl ether experiments, in that a portion of the hydrogen comes from internal rearrangement. In the run with D_4-tetralin, the anticipated level of deuterium was present in the dibenzyl product fraction. It is noted that only a low level of dibenzyl was observed; therefore, the direct cracking of dibenzyl sulfide to form toluene is preferred over the abstraction of sulfur with the formation of stilbene which then reduces forming dibenzyl.

<u>Summary of Deuterium Experiments</u>: The use of deuterium-tagged donor-solvents appears to be an effective means of studying hydrogen-transfer experiments below 400°C. One of the most interesting observations is that dissolved deuterium gas does not effectively transfer to free radicals when a donor solvent such as tetralin is present. The highest level of deuterium incorporation was 25% in the case of benzaldehyde reduction; with benzyl alcohol reduction and the cracking of dibenzyl ether and sulfide, it was only about 5%.

In the above runs with deuterium gas, there appeared to be a significant "re-hydrogenation" of the tetralin with deuterium after some hydrogen had been donated to the acceptor. Therefore, the role of a hydrogen gas in a coal liquefaction reactor appears to be that of providing hydrogen for regenerating the donor. Obviously, other roles are played such as reducing coke deposition on available catalyst sites (such as minerals).

When dibenzyl ether and sulfide were cracked in the presence of partially deuterated tetralin, little deuterium was also incorporated in the products. This indicates that much of the hydrogen comes from internal

TABLE IX

D_2 Tagged Transfer Experiments: Dibenzyl Sulfide Systems

I. Reaction in a Deuterium Atmosphere (HT77-102)

Note: Reaction Temperature 300°C

	Deuterium Incorporation		
Reaction Time (min)	60	120	240
Compound:			
Dibenzyl sulfide	4.9	7.9	14.6
Toluene	2.0	3.3	6.1
Dibenzyl	9.0	15.0	--
Tetralin	1.7	5.0	21.8

II. Reaction with Deuterium Tagged Tetralin in a Nitrogen Atmosphere (HT77-96)

Note: Reaction Temperature 325°C

	Deuterium Incorporation		
Reaction Time (min)	60	120	240
Compound:			
Dibenzyl sulfide	4.1	6.2	7.9
Toluene	4.3	7.5	14.9
Dibenzyl	6.8	15.2	32.4
Tetralin	-- (approx. 450%) --		

III. Distribution of Reaction Products at 300°C

	Wt% Compound in Reactor		
Reaction Time (min)	60	120	240
Compound:			
Dibenzyl sulfide	0.9	0.3	Tr
Toleune	∿7	∿8	∿8
Dibenzyl	Tr	Tr	Tr
Tetralin	-- (approx. 90%) --		

Note (1): At 350°C, only a very low level of acetophenone reaction was observed; therefore, only the 240 minute sample was analyzed by GC/MS.

Note (2): As in 1 above, only the 240 minute sample was analyzed by GS/MS.

DCC:bjs, GR&DC, CR&CD, 3/22/78

rearrangement during cracking. This is consistent with hydrogen being exchanged internally during coal liquefaction.

It was interesting to note that a high level of H/D exchange occurred during the heating of 3,5-dimethylphenol in a deuterium atmosphere. This occurred in spite of essentially no reduction of the hydroxyl group. This indicates that hydroxyl hydrogens are labile and may serve as transfer agents in coal liquefaction. This is of particular significance due to the high level of hydroxyl functionality in coal.

One complication in the above work was that of using partially deuterated tetralin as the donor solvent. While the tetralin had about 38% transferable deuterium and 62% hydrogen, the resulting products had about 22% deuterium incorporation. Due to its reduced mass and higher energy, hydrogen was perferentially transferred. Little data are readily available on H/D reactivity at the reaction conditions used herein. It would have been preferable to use D_{12}-tetralin; however, the cost would have been prohibitive. In addition, due to the individual reactions and temperatures studied (<400°C), extrapolation to liquefaction at about 450°C would not justify the cost.

PROPOSED SCHEDULE OF WORK OF PHASE II

Project: Investigation of Mechanisms of Hydrogen Transfer in Coal Hydrogenation.

Objective: To develop an understanding of the mechanisms of hydrogen transfer to coal in the basic coal liquefaction reaction environment used in processes currently being developed to convert coal to liquid.

Phase II: Coal and Coal-Derived Compounds Investigation (period of January 1978 - June 1979).

1. Asphaltene Studies

Following the study of model compounds (Phase I), it is logical to progress to the study of the primary intermediate formed during coal liquefaction, namely, the asphaltene fraction. This fraction is soluble in aromatics (toluene), and the study of hydrogen transfer reactions can be done without extensive development of analytical techniques. The results can be compared to those from model compounds and those which we plan to obtain from experiments with coal.

The series of experiments are divided into the stages described below. (Most of the runs will be made with the autoclave unit used in Phase I.)

a. Preparation: Samples high in asphaltene content will be obtained from two sources. SRC-type products have been requested from the Tacoma facility and the GR&DC pilot plant. Samples of the specific coals used in the SRC runs are also ordered for experiments listed in Section B-2. The second source of asphaltenes will be that of recovering heavy product fractions from the liquefaction runs of Section B. Emphasis will be placed upon using asphaltenes generated from liquefaction runs of low reaction severity. The samples will be extracted with pentane to remove oils. The residue will then be extracted with toluene to recover an asphaltene fraction.

b. Preliminary Asphaltene Experiments: A short series of time/temperature runs (350-475°C, 5-180 minutes) will be made with tetralin solvent to measure overall reaction rates and prepare samples for characterization.

c. Testing Analytical Techniques to Characterize Asphaltenes: The applicability of existing analytical techniques to this study will be confirmed. Techniques for determining the following properties will be tested with asphaltene samples: (1) molecular weight, number and weight averages with a molecular weight profile; (2) functionality - ^{13}C NMR of product oils, H NMR, and oxygen groups; and (3) hydroaromatic content.

d. Detailed Experiments: Based upon background developed in Phase I, detailed hydrogen transfer experiments will be done with a wide range of reactor residence times, temperatures and solvents of varying donor capability. Analytical techniques tested in Section A.3 will be used to characterize reaction products. At least two "standard" asphaltenes will be studied. Particular emphasis will be shown to using asphaltenes that have experienced different levels of hydrogenation (for example, collecting asphaltenes from liquefaction runs of increasing temperature.) Runs will also be done with catalysts (coal ash/mineral matter and pulverized commercial CoMo type). Consideration is being given to adding back mineral matter to selected samples of asphaltenes. The goal of this phase is to define the role of the donor solvent and its effect upon the characteristics of the reaction products.

Experimentation will include the use of deuterium, ^{13}C- and ^{14}C-tagged solvents. Due to high levels of hydrogen/deuterium scrambling above 400°C, emphasis will be placed upon experimentation below this temperature. Therefore, only the initial stages of asphaltene reactions will be studied. The extent of deuterium transfer to the products and the comparison of intra- versus intermolecular transfer during the fracturing of asphaltenes will be studied. Due to limitations on the supply of deuterium (primarily cost), experimentation will be done in a batch autoclave.

Runs will be made with tagged solvents to measure the extent of solvent/asphaltene reaction resulting in the formation of adducts. Specifically, it is desired to measure the loss of donor solvents into the high boiling or asphaltene fractions. Techniques have been developed to do this with ^{14}C-tagged solvent. ^{13}C NMR is also available to observe changes of structure of previously prepared ^{13}C-tagged solvents (dimethyl tetralin and octahydrophenanthrene).

2. Coal Studies

The results and conclusions derived from the study of model compounds and asphaltenes will be tested against those derived from the study with coal.

Experimentation will primarily be done in bench-scale liquefaction units capable of continuous feed and product withdrawal. A unit is being modified to handle coal feed slurries of between 0.7 and 7 lb/hr (nominal space times of 0.1 to 1.0 hour).

The following is a summary of the stages of experiments to be made with coal.

a. Preliminary Experiments: A short series of time/temperature runs with appropriate coals and the solvent tetralin will be made to confirm unit operability and to provide samples to test analytical techniques. This will be followed by a series of liquefaction runs made at low temperatures (325°C-400°C) to observe the interaction between donor solvent and coal. This is of use in providing a comparison of reaction kinetics with those derived for the model compounds, specifically those containing oxygen and sulfur functionality. Asphaltene samples will also be prepared for use in Section A.1.

b. Detailed Experiments: Hydrogen transfer experiments will be done with a range of residence times, temperatures, and solvents. Runs will be done with both hydrogen and nitrogen atmospheres. A limited number of batch autoclave runs will also be done with deuterium. Experiments will also be done with catalysts in a manner similar to those in the asphaltene series. In all of these runs, emphasis will be placed on correlating donor solvent capability against the molecular weight and chemical functionality of the liquefaction products. The consumption of hydrogen will also be studied.

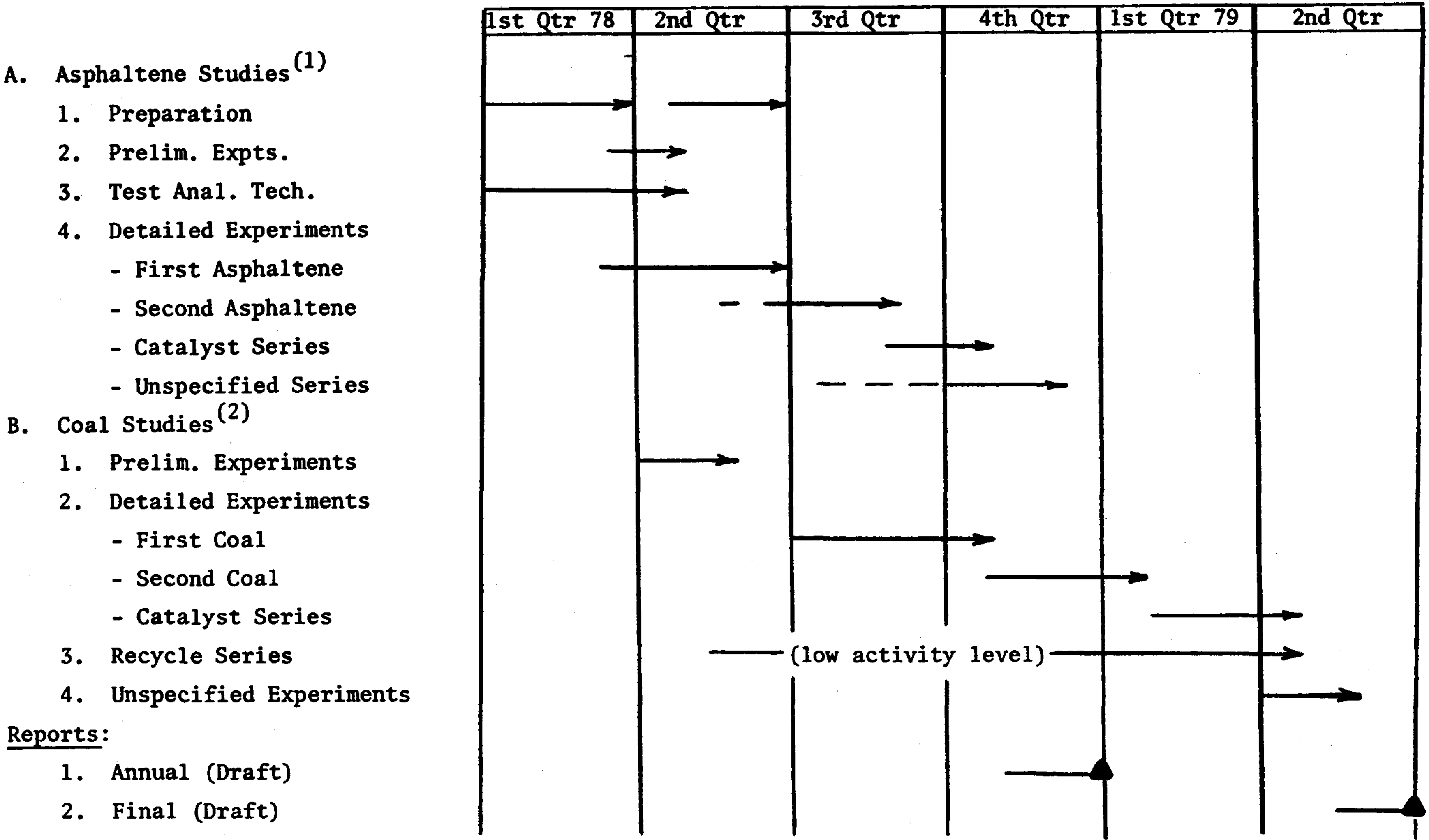
Experimentation with deuterium, ^{13}C- and ^{14}C-tagged solvents will follow the same line of reasoning presented for the asphaltene series (Section A). The experiments with the tagged solvents will be spaced in with other experimentation so that individual results can be analyzed before progressing to the next.

c. Recycle Series: A very significant level of isomerization of hydroaromatic donors to indane type non-donors was observed in the experiments with model compounds. This implies that a donor solvent will lose its effectiveness with recycle. Therefore, it is planned to recover selected solvent cuts from the above experiments and recycle these solvents. The hydrogen donating capability of these solvents will be examined along with the results of the liquefaction runs. These latter experiments will be spaced in with the series of primary runs.

d. Unspecified Experiments: Time is being set aside to expand upon the above work or to undertake interesting new aspects that should develop. One alternate is the study of a low ranked coal (lignite) and its asphaltene intermediate product.

Phase II Schedule

Coal and Coal-Derived Compounds Investigation



NOTES: (1) Lab-scale unit

(2) Bench-scale unit(s)

DCC:bjs, GR&DC, CR&CD, 3/22/78

ACKNOWLEDGMENTS

We wish to acknowledge our indebtedness to K. S. Seshadri for performing the ^{1}H and ^{13}C-NMR and providing aid in structural characterization; J. C. Suatoni, H. T. Best, and J. T. Swansiger for chromatographic and spectroscopic analysis; W. C. Edmunds, W. M. Diethorn, P. B. Rude, and T. R. Byer for experimental assistance; and Professor E. J. Eisenbraun and his staff of Oklahoma State University for technical assistance and the preparation of selected model compounds.

REFERENCES

1. Horrex, C. and Miles, S.E., Discussions Faraday Soc. 10, 187 (1951).

2. Curran, G.P., Struck, R.T., and Gorin, E., I&EC Process Design and Development 6 (No. 2), 166 (1967).

3. Whitehurst, D.D., et al., Annual Report entitled "The Nature and Origin of Asphaltenes in Processed Coal," Project 410-1 of the Electric Power Research Institute, July 1977, Report No. EPRI AF-480.

4. Goodman, A.L. and Eastman, R.H., JACS 86, 908 (1964).

5. Ruberto, R.G., Cronauer, D.C., Jewell, D.M., and Seshadri, K.S., Fuel 56, 25 (1977).

6. Jewell, D.M., et al., Anal. Chem.

7. Brucker, R. and Kolling, G., Bren. Chemie 46, 41 (1965).

8. Reifarth, K., University of Berlin, Ph.D. Thesis entitled, "Reaction of Tetralin and Dibenzyl Ether" (1977).

9. Ruberto, R.G. and Cronauer, D.C., "Oxygen and Oxygen Functionalities in Coal and Coal Liquids," paper presented at ACS National Meeting, Chicago, IL, August 28-September 2, 1977.

10. Emert, J., Goldenberg, M., Chiu, G.L., and Valeri, A., J. Org. Chem. 42, 2012 (1977).

11. Eisenbraun, E.J., et al., J. Org. Chem. 35, 1260 (1970) and ibid. 36, 686 (1971).

APPENDICES

A. SUMMARY OF EXPERIMENTS: HYDROGEN TRANSFER STUDIES

B. SYNTHESIS AND PURIFICATION OF DONOR SOLVENTS

by E.J. Eisenbraun, C.E. Brown, D.L. Bymaster
E.H. Vickerg, T.K. Dobbs

C. CARBON-13 NMR SPECTRA OF SYNTHESIZED SOLVENTS

by K.S. Seshadri, D.M. Jewell, E.J. Eisenbraun

D. STRUCTURAL FEATURES OF HYDROPHENANTHRENES

APPENDIX A

SUMMARY OF EXPERIMENTS: HYDROGEN TRANSFER STUDIES

Run No.	Time Hrs.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77- 1	2	400	Tetralin	150	-	-	-	-
77- 2	3	400	Tetralin	120	-	-	-	-
			2,6 Di Tert Butyl-4 Methylphenol	30	-	-	-	-
77- 3	3	400	Tetralin	120	-	-	-	-
			4 Methyl 1 Tetralone	30	-	-	-	-
77- 4	3	400	Tetralin	120	-	-	-	-
			Benzyl Sulfide	30	-	-	-	-
77- 5	3	400	Tetralin	135	-	-	-	-
			Dibenzyl	15	-	-	-	-
77- 6	3	400	Tetralin	75	Tetralin	60	Dibenzyl	15
77- 7	3	425	Tetralin	75	Tetralin	60	Dibenzyl	15
77- 8	3	450	Tetralin	75	Tetralin	60	Dibenzyl	15
77- 9	3	475	Tetralin	75	Tetralin	60	Dibenzyl	15
77-10	3	400	Tetralin	75	Purified Tetralin	60	Dibenzyl	15
77-11	3	425	Tetralin	75	Tetralin	60	Dibenzyl	15
77-12	3	450	Tetralin	75	Tetralin	60	Dibenzyl	15
77-13	3	475	Tetralin	75	Tetralin	60	Dibenzyl	15
77-14	3	437	Tetralin	75	Tetralin	60	Dibenzyl	15
77-15	3	463	Tetralin	75	Tetralin	60	Dibenzyl	15
77-16	3	437	Tetralin	75	Tetralin	60	Dibenzyl	15
77-17	3	463	Tetralin	75	Tetralin	60	Dibenzyl	15
77-18	3	450	Decalin	150	-	-	-	-
77-19	3	450	Decalin	75	Decalin	-	Dibenzyl	30
77-20	3	450	Decalin	75	Tetralin	75		
77-21	3	450	Decalin	75	Tetralin	60	Dibenzyl	15
77-22	3	450	Tetralin	75	Tetralin	75	Dibenzyl	30
77-23	3	450	Tetralin	50	Tetralin	50	Dibenzyl	50
77-24	1	450	Mesitylene (Incomplete)	144	-	-	-	-
			Dibenzyl	16				

Run No.	Time Hrs.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77-25	3 3/4	400	Mesitylene	135	-	-	-	-
		425	DiMethyl-Tetralin	15	-	-	-	-
(1000 psig,		437						
nitrogen)		450	(1/2 hour at each temperature)					
		463						
		475						
77-26	3	400	Tetralin	135	-	-	-	-
			Stilbene	15				
77-27	3	450	Tetralin	135	-	-	-	-
			Stilbene	15	-	-	-	-
77-28	3	450	Tetralin	75	Dimethyl Tetralin	60	Dibenzyl	15
77-29	3	450	Mesitylene	75	H_8P	60	Dibenzyl	15
77-30	3	400	Mesitylene	135	-	-	-	-
			Octahydrophenanthrene	15				
77-31	3	450	Tetralin	70	Tetralin	56	Dibenzyl	14
77-32	3	400	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-33	3	375	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-34	3	350	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-35	3	325	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-36	3	300	Tetralin	75	Tetralin	60	Dibenzyl ether	15
77-37*	3	425	Mesitylene	75	Mesitylene	60	Dibenzyl	15
77-38*	3	450	Mesitylene	75	Mesitylene	60	Dibenzyl	15
77-39*	3	475	Mesitylene	75	Mesitylene	60	Dibenzyl	15
77-40*	3	450	Tetralin	113	Tetralin	22.2	Dibenzyl	14.8
77-41	1 1/2	400	Mesitylene	100	D_4 Tetralin	50	-	-
	1 1/2	450	Mesitylene	100	D_4 Tetralin	50	-	-

Note: *Hydrogen atmosphere (1500 psig total pressure), all others nitrogen unless noted.

Run No.	Time Hrs.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77-42	3	400	Mesitylene	65	D_4 Tetralin	39	Dibenzyl	30
77-43	3	425	Mesitylene	65	D_4 Tetralin	39	Dibenzyl	30
77-44	3	450	Mesitylene	65	D_4 Tetralin	39	Dibenzyl	30
77-45	2	450	Pseudo-Cumene-Dibenzyl	170	-		-	
	1	475	Pseudo-Cumene-Dibenzyl	170				
77-46	3	450	Pseudo-Cumene-H_8Ph	150	-		-	
77-47	1	400	Pseudo-Cumene-H_8Ph	150	-		-	
	1	450	Pseudo-Cumene-H_8Ph	150	-		-	
77-47	1	400	Pseudo-Cumene-Octahydro-phenanthrene	150	-		-	
	1	450						
77-48	3	400	Tetralin	75	Tetralin	60	Benzil	15
77-49	3	450	Tetralin	75	Tetralin	60	Benzil	15
77-50	3	350	Tetralin	75	Tetralin	60	Benzaldehyde	15
77-51	3	375	Tetralin	75	Tetralin	60	Benzaldehyde	15
77-52	3	350	Tetralin	75	Tetralin	60	Dibenzyl Sulfide	15
77-53	3	375	Tetralin	75	Tetralin	60	Dibenzyl Sulfide	15
77-54	1	400	Pseudo-Cumene and Cycloparaffin	150	-		-	
	2	450	Pseudo-Cumene and Cycloparaffin	150				
77-55	3	450	Pseudo-Cumene	50	Dibenzyl	15		
					Cycloparaffin	60		
					Pseudo-Cumene	25		
77-56	3	425	Mesitylene	75	Tetralin (Fisher)	75		
77-57	3	450	Mesitylene	75	Tetralin (Fisher)	75		
77-58	3	425	Mesitylene	75	Mesitylene	60	Dibenzyl	15
77-59	3	437	Mesitylene	75	Mesitylene	60	Dibenzyl	15
77-60	3	450	Mesitylene	75	Mesitylene	60	Dibenzyl	15
77-61	3	450	Mesitylene	75	Dibenzyl	60	Tetralin	15
77-62	3	450	Mesitylene	75	Tetralin	60	Phenanthrene	15
77-63	3	425	Mesitylene	75	Tetralin	60	Phenanthrene	15
77-64	3	450	Mesitylene	150	-		-	
77-65*	3	450	Mesitylene	150				
77-66*	3	350	Mesitylene	75	Mesitylene	60	Dibenzylether	15
77-67	3	350	Mesitylene	75	Mesitylene	60	Dibenzylether	15
77-68	3	335	Tetralin	75	Tetralin	60	Dibenzylether	15
77-60	3	365	Tetralin	75	Tetraline	60	Dibenzylether	15

Note: *Hydrogen atmosphere (1500 psig total pressure), all others nitrogen unless noted.

Run No.	Time Hrs.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77-70	3	450	Mesitylene	75	Tetralin	60	Phenylhexane	15
77-71	3	450	Mesitylene	75	Tetralin	60	1,4 Diphenyl-butane	15
77-72	3	450	Mesitylene	75	Tetralin H_8Ph	50 10	Dibenzyl	15
77-73	3	375	Tetralin	75	Tetralin	60	Benzil	15
77-74	3	325	Tetralin	75	Tetralin	60	Dibenzyl Sulfide	15
77-75	3	300	Tetralin	75	Tetralin	60	Dibenzyl Sulfide	15
77-76	3	450	Tetralin	75	Tetralin	60	Dibenzyl Methane	15
77-77	3	450	Tetralin	75	--	-	Dibenzyl	75
77-78	3	450	Tetralin	75	Tetralin	60	Dibenzyl	15
			(additional 4 1/4" x 8 1/4" price of 316SS, 80 mesh screen (16.2 gm)					
77-79	3	350	Tetralin	75	Tetralin	60	Benzyl alcohol	15
77-80	3	375	Tetralin	75	Tetralin	60	Benzyl Alcohol	15
77-81	3	450	Mesitylene	75	Mesitylene	60	H_8Ph (cold) H_8Ph (hot)	13.5 1.5
77-82	3	450	Mesitylene	50	Dibenzyl	10	H_8Ph (cold) (hot)	 4.0
77-83	3	365	Mesitylene	50	Dibenzyl ether	10	H_8Ph (cold) (hot)	36 4.0
77-84	3	300	Mesitylene Tetralin (D4)	112.5 12.5				
77-85	3	350	Mesitylene Tetralin	112.5 12.5				
77-86	3	450	Tetralin	75	Tetralin	67.5	HT77-60 Polymer	7.5
77-87	3	365	Tetralin	75	Tetralin	58.5	Dibenzyl Ether Tetrahydroquinolin	15.0 1.5
77-88	3	365	Tetralin	75	Tetralin	52.5	Dibenzyl Ether Tetrahydroquinolin	15.0 7.5
77-89	3	350	Tetralin	75	Tetralin	45	Dibenzyl Ether	30.0
77-90	3	350	Tetralin	75	Tetralin	25	Dibenzyl Ether	50.0
77-91	3	350	Tetralin	75	Dibenzyl Ether	75		
77-92	3	300	Mesitylene	105	D4-Tetralin	30	Benzyl Sulfide	15.0
77-93	3	350	Mesitylene	105	D4-Tetralin	30	Benzyl Ether	15.0
77-94	3	350	D4-Tetralin	80	Dibenzyl Ether	20		
77-95	3	300	Tetralin	75	Tetralin	60	Di-n-Dodecyl ether	15.0

Run No.	Time Hr.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77-96	3	325	D4-Tetralin	68.7	Benzyl Sulfide	20	D4 Tetralin	11.3
77-97	3	350	D4 Tetralin	90	Benzaldehyde	10		
77-98	3	350	Mesitylene	120	Mesitylene	15	Benzyl Sulfide	15.0
77-99	3	300	Mesitylene	120	Mesitylene	15	Benzyl Sulfide	15.0
77-100	4	350	Tetralin	150				
77-101**	4	350	Tetralin	135				
			Dibenzyl Ether	15				
77-102**	4	350	Tetralin	135				
			Benzyl Sulfide	15				
77-103**	4	350	Tetralin	135				
			Benzaldehyde	15				
77-104**	4	350	Tetralin	135				
			Benzyl Alcohol	15				
77-105**	4	350	Tetralin	135				
			Acetophenone	15				
77-106**	4	350	Tetralin	75	Tetralin	60	2,6,Dimethylphenol	15
77-107	3	400	Tetralin	75	Tetralin	60	Benzyl Alcohol	15
77-108	3	350	Tetralin	100.5	Benzyl Alcohol	49.5		
77-109	3	375	Tetralin	100.5	Benzyl Alcohol	49.5		
77-110	3	300	Tetralin	78.8	Tetralin	21.7	Dibenzyl Sulfide	49.5
77-111	3	400	Tetralin	75	Tetralin	60	Acetophenone	15
77-112	3	425	Tetralin	75	Tetralin	60	Acetopheneon	15
77-113	3	450	Tetralin	75	Tetralin	60	Acetophenone	15
77-114	3	425	Tetralin	100.5	Acetophenone	49.5		
77-115	3	350	Tetralin	100.5	Benzaldehyde	49.5		
77-116	3	425	Tetralin	75	Tetralin	60	Phenol Ethyl	15
77-117	3	425	Mesitylene	75	Mesitylene	60	DLB-I-88	13.5
77-118	3	450	Mesitylene	75	Mesitylene	60	DM Tetralin (cold)	13.5
							DM Tetralin (hot)	1.5
77-119	3	400	Mesitylene	90	DM Tetralin (cold)	41	DM Tetralin (hot)	4.0
							Tetralone	15

**Deuterium atmosphere; all others nitrogen, unless noted.

Run No.	Time Hr.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77-120	3	425	Mesitylene	90	DM Tetralin (cold)	41	DM Tetralin (hot)	4.0
							Tetralone	15
77-121	3	450	Mesitylene	90	DM Tetralin (cold)	41	DM Tetralin (hot)	
							Tetralone	15
77-122	3	450	Mesitylene	90	Mesitylene	45	Tetralone	15
77-123	3	450	Mesitylene	90	3,5-Dimethylphenol	15	DM Tetralin (cold)	41
							DM Tetralin (hot)	4
77-124	3	450	Mesitylene	90	Naphthol	15	DM Tetralin (cold)	41
							DM Tetralin (hot)	4
77-125	3	450	Mesitylene	75	Mesitylene	60	Naphthol	15
77-126	Postponed							
77-127	3	400	Tetralin	75	Tetralin	60	3,5-Dimethylphenol	15
77-128	3	425	Tetralin	75	Tetralin	60	3,5-Dimethylphenol	15
77-129	3	450	Tetralin	75	Tetralin	60	3,5-Dimethylphenol	15
77-130	3	450	Tetralin	51	Tetralin	49.5	3,5-Dimethylphenol	49.5
77-131	3	450	Mesitylene	75	Mesitylene	60	3,5-Dimethylphenol	15
77-132	3	450	Tetralin	75	Tetralin	60	Naphthol	15
77-133	3	425	Tetralin	75	Tetralin	60	Naphthol	15
77-134	3	450	Mesitylene	50	Mesitylene	40	Polymer	10
77-135	2	400	Mesitylene	50	Mesitylene	50	Tetrahydroquinoline	50
	2	450	Mesitylene	50	Mesitylene	50	Tetrahydroquinoline	50
77-136	3	450	Mesitylene	90	Tetrahydroquinoline	45	Dibenzyl	15
77-137	3	350	Mesitylene	90	Tetrahydroquinoline	45	Dibenzyl ethyl	15
77-138	3	400	Mesitylene	90	Tetrahydroquinoline	45	Benzyl alcohol	15
77-139	3	450	Mesitylene	90	Tetrahydroquinoline	45	Naphthol	15
77-140	3	400	Mesitylene	75	Mesitylene	52.5	Benzyl alcohol	22.5
77-141	3	400	Benzyl alcohol	75	Benzyl alcohol	75		
77-142	1-1/2*	350	Benzaldehyde	75	Benzaldehyde	75		
77-143	3	350	Tetralin	75	Tetralin	60	Benzoic acid	15
77-144	3	350	Tetrahydroquinoline	70	Tetrahydroquinoline	20	Benzyl ether	10
77-145	3	400	Tetrahydroquinoline	50	Tetrahydroquinoline	35	Benzyl alcohol	15
77-146	3	350	Mesitylene	75	Mesitylene	60	Benzaldehyde	15
77-147	3	450	Tetralin	36.25	HT77-108 Residue	36.25		
77-148	3	350	Tetralin	75	Tetralin	60	n-Dodecyl sulfide	15

---

*Recovery Plugged

**Deuterium atmosphere; all others nitrogen unless noted.

Run No.	Time Hr.	Temp. °C	Reactor Charge	Grams	Feed Tank Charge (Solvent)	Grams	Feed Tank Charge (Acceptor)	Grams
77-149	3	375	Tetralin	75	Tetralin	60	n-Dodecyl sulfide	15
77-150	3	400	Tetralin	75	Tetralin	60	n-Dodecyl sulfide	15
77-151	3	400	Tetralin + 7.5 g Cat.	75	Tetralin	60	Dibenzyl	15
77-152	3	425	Tetralin + 7.5 g Cat.	75	Tetralin	60	Dibenzyl	15
77-153	3	425	Tetralin + 7.5 g Kaolin	75	Tetralin	60	Dibenzyl	15
77-154	3	425	Tetralin + 7.5 g NiW	75	Tetralin	60	Dibenzyl	15
77-155	3	425	Tetralin + 7.5 g Nuchar Charcoal	75	Tetralin	60	Dibenzyl	15
77-156	3	350	Tetralin + 7.5 g 5N2-13DG	75	Tetralin	60	Dibenzyl ether	15
78-1	3	350	D_4 tetralin	50	D_4 tetralin	40	Benzyl alcohol	10

APPENDIX B

THE SYNTHESIS AND PURIFICATION OF 1-^{13}C-1,2,3,4,5,6,7,8-OCTAHYDROPHENANTHRENE AND 4-^{13}C-2,6-DIMETHYL-1,2,3,4,-TETRAHYDRONAPHTHALENE AND THE CORRESPONDING UNLABELLED HYDROCARBONS

by

E.J. Eisenbraun, C.E. Brown, D.L. Bymaster, E.H. Vickerg, T.K. Dobbs

INTRODUCTION

One of the objectives of our study of hydrogen transfer was to utilize tagged donor solvents to better delineate the overall fate of hydroaromatic structures in the transfer reaction. Due to the lack of availability of tagged solvents, an effort to synthesize reasonable quantities (1 kg) of both 1-^{13}C-2,6-dimethyltetralin and 1-^{13}C-sym-octahydrophenanthrene. These particular compounds have unique structural features which may have an effect on the hydrogen transfer reactions. These features include:

(a) the presence of alkyl groups on the hydroaromatic ring which may exhibit steric effects on the transfer step,

(b) both have readily assigned ^{13}C-NMR spectra,

(c) both have higher boiling points than the typically used solvent, tetralin,

(d) sym-octahydrophenanthrene has a greater number of transferable hydrogens per molecule than tetralin.

The purpose of this report is to document the important aspects of the syntheses. To our knowledge, the preparation of the ^{13}C-labeled compounds has never appeared in the open literature. The ^{13}C-NMR and mass spectra of many of the intermediates involved are also included. These syntheses were conducted under the direction of Dr. E.J. Eisenbraun of Oklahoma State University.

Reference is made to the attached figures (Schemes I through III) for identification of individual compounds.

EXPERIMENTAL

The preparation of the title compounds is divided into the synthesis of 1-^{13}C-1,2,3,4,5,6,7,8-octahydrophenanthrene (10), the synthesis of 4-^{13}C-2,6,-dimethyl-1,2,3,4-tetrahydronaphthalene (24), and the preparation and purification of the corresponding unlabelled hydrocarbons.

At the onset of this work, some effort was made to synthesize as-octahydrophenanthrene (shown as 9 in Scheme I). A small amount of this hydrocarbon was prepared and subjected to testing, but when it was learned that the thermal stability of 9 is inadequate, we began the synthesis of the symmetric isomer (10). Trial studies had shown that unlabelled 10 has better thermal stability.

Of the various synthesis routes considered for 10, we selected Scheme I based primarily on experience and the reported reliability of the reactions as well as our being able to introduce the expensive ^{13}C label at a comparatively late stage of the synthesis. Also this synthesis could utilize ^{13}C barium carbonate, which is one of the cheaper and more readily available forms of labelled starting material. The success of this reaction scheme, particularly the critical carbonation step, has amply justified this synthesis program.

Scheme II shows alternate routes which could provide 10 from 2a or 6. Some exploratory work has been done and there is good indication that either of these routes could be effective, e.g., a favorable ratio 12:13 (72:28) is obtained on hydrogenation in the presence of Pd/C in acetic acid solvent. Carboxylic acid 12, mp 133-6°C, crystallizes preferentially. However, this information was gained late in the synthesis work, so we have not actively pursued this reaction scheme. Should it become necessary to prepare additional 10, it may be advisable to further explore these new routes.

The reactions of Scheme I are straightforward, the initial step being a modified Knovenagel reaction,[1] which is easily carried out in good yield. Catalytic hydrogenation of 2a to 3a is also a straightforward reaction. The conversion of the ester 3b to either the bromide 5a or the chloride 5b caused no difficulty. However, in our attempt to utilize the cheaper and more conveniently prepared chloride, 5b, we found that the initiation of the Grignard reagent was slow and unpredictable and that the insolubility of the subsequently formed chloro Grignard reagent was a considerable disadvantage. Data gained from subsequent studies in Scheme III indicate that the chloride could be used provided care is exercised in selection of solvent. However, since the bromide 5a was effectively used in preparing 6, we are satisfied that this is an adequate step.

As pointed out previously, we were concerned about the carbonation step, which leads to 6 of Scheme I. The importance of developing this step into a high-yield, efficient procedure was realized, since the expensive ^{13}C label would be involved. Accordingly, we thoroughly re-examined the carbonation of Grignard reagents.[2] To improve this reaction, we developed an efficient procedure which became possible through the construction of a convenient and effective Grignard carbonation reactor. This apparatus is capable of carrying out Grignard reactions under a modest pressure (1-2 atm) and with the chance of accidental loss of expensive ^{13}C label greatly reduced. The critical components of our apparatus were constructed of metal rather than of glass. Once this apparatus was built, we were able to carry out carbonation reactions on an increased scale (to 0.5 mol) with ease and without great concern over loss of expensive label. A detailed description of this carbonation apparatus and its use in converting 5a to 6 is described in Appendix A.

The cyclization of 6 to 7 is readily carried out as shown in Scheme I. In the subsequent steps of converting 7 to 10, we noted that if Pd/C hydrogenolysis is carried out at 60° in a Parr shaker at 50-60 psi in acetic acid, reduction proceeded to a mixture of 9:10 (40:60). When Pd/C hydrogenolysis was carried out in a glass apparatus[3] at 80-90° in acetic acid at 1 atm, it was possible to halt the process after 7 had been converted to 8. Filtration and addition of Rh/C catalyst enabled hydrogenation to a mixture of 9:10 (15:85). Unfortunately, this ratio could not be duplicated with the Parr apparatus. In practice, we fractionally distilled the mixture of 9 and 10 to remove the more volatile 9. Those cuts containing an acceptable concentration of 10 (greater than 95%) were retained. The remaining material consisting distilled the mixture of 9 and 10 was dehydrogenated to 1-^{13}C-phenanthrene (11) by heating in the presence of Pd/C at 300° for 3.5 hr. This hydrocarbon was subsequently catalytically hydrogenated as shown in Scheme I to a mixture of 9 and 10, which were again fractionally distilled. The necessary sample of labelled hydrocarbon 10 was obtained from these combined fractions.

To obtain a 1-kg sample of unlabelled 10, commercial phenanthrene (11) was recrystallized from ethanol until gas chromatography analysis (1.5% OV-17 + 1.95% QF-1/Chrom Q 80/100 mesh, 6-ft x 1/4-in. copper tubing; analysis was run at 200°C with helium flow of 120 ml/min) showed the phenanthrene to be of acceptable purity. This sample of phenanthrene was then desulfurized by treating with Raney nickel catalyst in boiling ethanol. Subsequent catalytic hydrogenation of 11 with Pd/C catalyst at 60° and 30 psig for 24 hr provided a mixture of 9:10 (40:60) from which 10 was obtained by fractional distillation at 82° (0.15 mm) using a 20-cm x 4-cm column of 1/4" perforated steel saddles.

The synthesis of 4-^{13}C-2,7-dimethyl-1,2,3,4-tetrahydronaphthalene (24) is shown in Scheme III. This synthesis has similarities to that of Scheme I. It also employs carbonation of a Grignard reagent as a late stage to introduce the ^{13}C label. There are, however, some important differences. We learned that preparation of pure alkyl halides 21b and 21c was difficult, since the presence of the neighboring tertiary hydrogen caused undesirable elimination to alkene. However, with use of triphenylphosphene and bromine, a satisfactory procedure for preparing the alkyl bromide 21b was developed.

Use of the alkyl chloride 21c was hampered by slow initiation of the Grignard reagents and poor solubility in ether solvent. These objections to the use of the chloride 21c were overcome by changing the solvent in the preparation of the Grignard reagent to a mixture of benzene:THF (9:1). In another experiment, it was learned that the bromide 21b functioned more efficiently than the chloride 21c in this solvent mixture.

EXPERIMENTAL

E-2-(1-Naphthyl)propenoic Acid (2a). To 500 g (3.21 mol) of 1-naphthaldehyde (1) in 3.50 l. of pyridine was added 500 g (4.81 mol) of malonic acid and 25 ml of piperidine. The solution was stirred at 25° under N_2 for 48 hr, warmed to 100° for 3 hr, cooled, and then poured into a mixture of ice and hydrochloric acid. The precipitated acid was filtered and then dissolved in sodium carbonate solution. After extraction with ether, the carbonate solution was acidified and the precipitated acid was filtered and dried to give 555 g (87%) of 2a, mp 206-209°. A sample recrystallized from acetone had mp 211-212° (lit.[4] 212°); ^{1}H NMR (DMSO-D_6) δ 6.81 (d, J=16 Hz, 1, C=CHCO$_2$H), 7.50-8.20 (m, 7, naphthyl H), 8.57 (d, J=16 Hz, 1, C=CHAr); ir (KBr) 3000 (-OH), 1675 (CO), 790, 770, 765, (1-naphythyl) cm^{-1}; mass spectrum m/e (rel intensity) M$^+$ 197.92 (1), 194.90(2), 177.94(6) 164.9(13), 153.9(86), 152.97(100), 140.99(58).

Methyl E-2-(1-naphythly)propenoate (2b). A solution of 220 g (1.11 mol) of 2a in 2.5 1. of methanol containing 40 ml of sulfuric acid was refluxed for 4 hr and then methanol was distilled off. The residue was dissolved in ether and washed with saturated sodium carbonate solution. The ether extract was dried (MgSO$_4$), concentrated, and the residue was distilled to give 230 g (97%) of 2b 140° (0.4 mm) (lit.[5] 123-124° at 0.1 mm); ^{1}H NMR (CDCl$_3$) δ 3.72 (s, 3, -OCH$_3$); 6.37 (d, J=16 Hz, C=CHCO$_2$C$_3$); 7.14-8.06 (m, 7, ArH); 8.41 (d, J=16 Hz, C=CHAr); ir (neat) 1700 (CO), 800, 775, 720 (1-naphthyl) cm^{-1}; mass spectrum m/e (rel intensity) M$^+$ 212.11(32) 181.12(20), 153.12(100), 152.10(65), 151.1(16).

Methyl 2-(1-Naphythly)propanoate (3b). To a solution of 23.9 g (1.12 mol) of 2b in 1.5 l. of ethanol was added 10 g of 5% Pd/C and the mixture was hydrogenated at 60° and 40 psi until H_2 uptake slowed (110% of theoretical H_2 volume). Filtration, evaporation of the solvent, and distillation of the residue gave 235 g (98%) of 3b; bp 127° (1 mm); mp 34-36° (lit.[6] 35-36.5°); ^1H NMR ($CDCl_3$) δ 2.58 (t, J=8 Hz,2, $-C\underline{H}_2CO_2CH_3$), 3.30 (t, J=8 Hz, 2, $-CH_2Ar$), 3.52 (s, 3, OCH_3), 7.18-7.92 (m, 3,ArH); ir (neat) 1725 (CO), 795, 730 (1-naphthyl) cm^{-1}; mass spectrum *m/e* (rel intensity) M^+ 213.83 (100), 154.99 (37), 153.98 (81), 153.01 (44), 151.97 (28), 114.99 (31). The ^{13}C-NMR assignments for both 3a and 3b are shown in Table I.

3-(1-Naphthyl)-1-propanol (4). To a solution of 300 g (2.10 mol) of diisobutylaluminum hydride in 3.0 l. of benzene was added a solution of 214 g (1.0 mol) of 3 in 600 ml of benzene at a rate sufficient to maintain the temperature at 45°. After addition, the solution was stirred for 2 hr, then cooled and excess reagent was destroyed by adding 30 ml of methanol. The cool solution was poured on ice and hydrochloric acid (caution/foaming) and then stirred for 1 hr. The layers were separated, the water layer was extracted once with ether, and the combined organic extracts were washed with 5% hydrochloric acid, 5% sodium carbonate, and saturated sodium chloride. After drying ($MgSO_4$), the solvent was removed under reduced pressure and the residue was distilled to give 182 g (98%) of 4, bp 155° (1.0 mm) (lit.[7] 130° at 0.5 mm); ^1H NMR (CCL_4) δ 1.83 (m, J=7 Hz, 2, $-C\underline{H}_2-$), 2.96 (t, J=7 hz, 2, $ArCH_2$), 3.52 (t, J=6 Hz, 2, $-C\underline{H}_2OH$), 4.12 (s, 1, $O\underline{H}$), 7.04-7.96 (m, 7, ArH); ir (neat), 725, 775, 790 (1-naphthyl), 3300 (OH) cm^{-1}; mass spectrum *m/e* (rel intensity) M^+ 186.02 (22), 168.04 (25), 153.07 (32), 141.96 (43), 141.01 (100), 115.08 (24). The ^{13}C NMR assignments are shown in Table II.

1-Bromo-3-(1-Naphthyl)propane (5a). To a solution of 275 g (1.58 mol) of 4 in 300 ml of benzene at 5° was added 167 g (0.62 mol) of phosphorous tribromide over 2 hr. The temperature was kept below 10° during addition. After stirring overnight at 25°, the solution was poured into water, extracted with ether, and the ether extract was washed with 5% sodium carbonate, saturated sodium chloride, and then dried ($MgSO_4$).

Removal of the solvent under reduced pressure and distillation of the residue gave 248 (63%) of 5a; bp 124° (4 mm) (lit.[7] 160° at 5 mm); ^1H NMR (CCl_4) δ 1.97 (m, 2, $-CH_2\underline{CH_2}CH_2$), 2.92 (t, J=7 Hz, 2, $ArCH_2-$), 3.06 (t, J=7 Hz, 2,$-\underline{CH_2}$ Br); 7.06-7.84 (m, 7, ArH); ir (neat) 790, 775, 725 (1-naphthyl) cm^1; mass spectrum *m/e* (rel intensity).

1-Chloro-3-(1-Naphthyl)propane (5b). To a solution of 184 g (0.99 mol) of 4 in 86 g (1.09 mol) of pyridine at -5° was added 130 g, (1.08 mol) of thionyl chloride. The temperature was kept below 10° during addition. After addition, the mixture was stirred for 30 min, then cautiously warmed to 100° for 30 min. After cooling, the solution was poured onto a mixture of ice and hydrochloric acid and then extracted with ether. The ether extract was washed with 10% hydrochloric acid, cool 5% sodium carbonate, dried ($MgSO_4$), filtered, and concentrated by evaporation under reduced pressure. The residue was distilled to give 174 g (86%) of 5b, bp 125° (1.0 mm) (lit.[7] bp 108° at 1.0 mm); ^1H NMR (CCL_4) δ 1.9. (m, 2, $-CH_2-$), 2.98 (t, J=7 Hz, 2, $ArCH_2-$), 3.25 (t, J=7 Hz, 2, $\underline{CH_2}Cl$), 7.02-7.90 (m, 7, ArH); ir (neat) 790, 775, 730 (1-naphthyl) cm^{-1}; mass spec *m/e* (rel intensity M^+ 203.91 (28), 152.93 (11), 141.87 (18), 140.84 (100), 138.85 (9), 173.54 (19). The ^{13}C-NMR assignments for both the bromo and chloro derivatives are given in Table III.

1-^{13}C-4-(1-Naphthyl)butyric Acid (6). The ^{13}C-labeled acid 6 was prepared as described in Appendix A in approximately 87% yield by carbonation[8] of Grignard reagents. This preparation was accomplished via the Grignard reagents derived from the alkyl bromide 5a and the alkyl chloride 5b. In the latter case, the Grignard reagent was poorly soluble in ether. Therefore, the alkyl bromide was the major source. The ^{13}C-NMR assignments for both the labeled and unlabeled acids are given in Table IV.

1-^{13}C-3,4-Dihydro-1(2H)-phenanthrenone (7). To a mixture of 94 g (0.44 mol) of acid 6 in 500 ml of benzene contained in a 1-liter, round-bottomed flask was added 103 g (0.50 mol) of powdered PCl_5 in portions with stirring and cooling in ice water.[9] The flask was protected from moisture by a calcium chloride tube which was removed only during the addition of reagents. Heat and hydrogen chloride evolve during the vigorous reaction, and on standing at room temperature for an hour, nearly all the acid and phosphorus pentachloride dissolved. The mixture was warmed on the steam bath for about five minutes, in order to ensure complete reaction, and then was chilled until benzene showed signs of beginning to solidify. At this point, a solution of 112 ml (0.98 mol) of anhydrous stannic chloride in 112 ml of dry benzene was added rapidly with stirring, whereupon an orange-yellow complex separated. After standing for 15 min in ice water, the mixture was hydrolyzed by the addition of ice followed by 300 ml of concentrated hydrochloric acid. A small amount of ether (50 ml) was added to hasten the hydrolysis of the $SnCl_4$ addition complex (which is soluble in ether), and the mixture was shaken until all the complex was dissolved. After separation, the organic layer was washed with several portions of 5% hydrochloric acid, water, 5% aqueous sodium hydroxide, and finally again with water. After evaporation of the solvent, the residue was crystallized from methanol, giving 79 g (92%) of colorless ketone, 7, mp 94-95°C; mass spectrum m/e (rel. intensity) M^+ 196.8(100), 168.9(73), 139.9(99). The ^{13}C-NMR assignments of both labeled and unlabeled ketone are given in Table V.

1-^{13}C-cis-1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (9) and 1-^{13}C-1,2,3,4,5,6,7,8-Octahydrophenanthrene (10). To a solution of 180 g (0.92 mol) of 7 in 1500 ml of acetic acid was added 15 g of 5% Pd/C and the mixture was hydrogenated at 60-70°C and 40 psig.[10] The reaction was monitored by GLC studies and it was stopped after complete conversion of 7 to a mixture of 9 and 10 (1:1.2). The mixture was cooled and filtered through Dicalite. The acetic acid filtrate was evaporated and the residue was dissolved in isohexane[11] and then eluted through a column of basic alumina and evaporated. The concentrate was vacuum-distilled through a 2.0-cm x 20-cm column of packed metal helices at 75°C (0.2 mm) to give 75 g of 10 (purity 98%): mp 15° (lit.[12] 16.7°); ^1H NMR ($CDCl_3$) δ 1.5-1.9 (m, 8, $-CH_2-$), 2.30-2.54 (m, 4, $ArCH_2-$), 2.54-2.78 (m, 4, $ArCH_2-$), 6.70 (s, 2, ArH); ir (neat 2900 (ArH), 795 (1-naphthyl) cm^{-1}; mass spectrum m/e (rel. intensity) M^+ 186(100%), 184(25%), 171(5.5%), 158(68.7%). ^{13}C-NMR assignments are shown in Table VI.

1-^{13}C-Phenanthrene (11). To 60.3 g of 6 was added 6.5 g of 5% Pd/C, and the mixture was heated under N_2 at 1 atm for 3.5 hr at 300°. After cooling, the mixture was dissolved in ether, filtered through Dicalite, and the filtrate was concentrated to give 57 g (99%) of 11; mp 95-97°. A sample recrystallized from ethanol had mp 97-99°; ^{1}H NMR was identical to phenanthrene. The melting point of a mixture of 8 with phenanthrene showed no depression. Mass spectra of 11 are *m/e* (rel. intensity) 178.9(100), 177.9(17), 151.9(7). C-NMR assignments are given in Table VII.

Hydrogenation of 1-^{13}C-Phenanthrene (11). A solution of 55.9 g (0.31 mol) of 11 in 500 ml acetic acid containing 3.5 g at 5% Pd/C was hydrogenated and the product then distilled as described above to give 24 g (41%) of 10.

Diethylmethyl(4-Methylphenylmethyl)malonate (18). In a 12-1. fluted flask equipped with a turbine stirrer, addition funnel, heating mantle, Dean-Stark trap, thermometer, and nitrogen bubbler was placed 1300 ml of anhydrous ethanol. Sodium (76 g, 3.3. g atom) was added slowly over 30 min with stirring. The solution was maintained at reflux until all of the sodium had reacted, then 600 ml of ethanol was removed by distillation and 3 1. of dry toluene was added. Diethylmethylmalonate (523 g, 3.0 mol) was added to the solution over 15 min, after which the toluene/ethanol azeotrope was removed until the temperature reached 108°C with sufficient toluene being added to maintain a homogeneous solution. *p*-Methylbenzylchloride (450 g, 3.2 mol) was added to the solution over 30 min and the addition funnel was rinsed with toluene. Subsequently toluene was removed by distillation until the temperature reached 110° C. The mixture was then cooled, acidified with conc. HCl, and the organic layer was washed twice with water. The organic layer was dried ($MgSO_4$), filtered, concentrated by rotary evaporation, and then vacuum-distilled at 115-130° (0.1 mm) [lit.[13] 220° (20 mm)] to give a 79% yield (662 g, 2.38 mol) of diester (18). Ir (neat) 1730 cm^{-1} (C=0). The ^{13}C-NMR assignments are given in Table VIII.

Methyl(4-Methylphenylmethyl)malonic Acid (19). In a 5-l., 1-neck flask equipped with reflux condenser was placed 355 g (1.27 mol) of the diester 18. Ethanol (1500 ml) and 10% NaOH (2500 ml) were also added and the solution was stirred at reflux for 4 hr. The reflux condenser was then replaced with a distillation head and ethanol was removed by distillation. The distillation residue was cooled and extracted with ether, poured over ice, and acidified (conc. HCl) to give white crystals of diacid, 19, mp 170-171° (dec). Recrystallization from ethyl ether afforded a 97% yield (275 g, 1.24 mol) of the diacid 19, mp 173-174°C (dec). Ir (KBr) 3000 (-CO$_2$H), 1725 (C=O) cm^{-1}. The mass spectra m/e (rel. intensity) are M$^+$ 193.02(21), 131.96(100), 116.96(14); ^{13}C-NMR assignments are given in Table IX.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.00; H, 6.35.

2-Methyl-P-Tolylpropionic Acid (20). To a 500-ml flask equipped with thermometer, Vigreux column, and gas bubble tube was added 127 g (0.57 mol) of diacid, 19. The temperature was raised until at 140°, CO$_2$ was evolved. Heating was continued until at 220°C, CO$_2$ evolution ceased. The residue was Kugelrohr-distilled (110°C, 0.1 mm Hg) to give 98% (99 g, 0.56 mol) of monocarboxylic acid, 20, as white crystals, mp 39-41°C. Ir (KBr) 3278 (CO$_2$H), 1695 (C=O) cm^{-1}.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.31; H, 8.00.

2-Methyl-3-P-Tolyl-1-Propanol (21a). To a solution of 353 g (2.5 mol) of diisobutylaluminumhydride in 1 l. of dry toluene was added a solution of 127 g (0.71 mol) of monoacid 20 in 300 ml of toluene over a 1-hr period at 30°C. After addition was complete, excess reducing agent was destroyed by the addition of 82 ml of ethyl acetate. The solution was poured carefully over 3 kg ice, and acidified with 1.5 l. of concentrated HCl. The mixture was placed in a separatory funnel and the organic layer was removed. The aqueous layer was extracted twice with toluene, the organic layers were combined, washed twice with water, dried ($MgSO_4$), and filtered. Kugelrohr distillation (103°, 0.1 mm) afforded an 84% yield (98 g, 0.60 mol) of alcohol 21a.[14] Ir (neat) 3333 (OH), 1036 (C=O) cm^{-1}; ^1H NMR (acetone-d) δ 7.05 (s, 4, ArH), 3.45 (d, J=6 Hz, 2, $-CH_2O-$), 2.85-2.21 (m, 2, $ArCH_2$), 2.3 (s, 3, $ArCH_3$), 1.9 (octet), J=6 Hz, 1, 3° H), 0.88 (d, 3, J=6 Hz, R-CH_3). Mass spectra m/e are (rel. intensity) M^+ 163.91(90), 130.90(100), 145.93(43). The ^{13}C-NMR assignments are given in Table X.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C,80.16; H, 9.79.

2-Methyl-3-P-Tolyl-1-Bromopropane (21b). To a CCl_4 solution containing 149 g (0.91 mol) of alochol 21a was added 261 g (1.0 mol) of $P(C_6H_5)_3$.[14] Through an addition funnel was added 160 g (1.0 mol) of Br_2. The reaction mixture was allowed to stir overnight under N_2. The subsequent precipitate was filtered and washed with CCl_4, then twice with H_2O. The CCl_4 wash was filtered through $MgSO_4$ and concentrated under vacuum. The residue was fractionally distilled at 75°C (0.13 mm) to give an 86% yield (177 g, 0.78 mol) of bromide 21b.[15]

2-Methyl-3-P-Tolyl-1-Chloropropane (21c). To a cooled (ice bath) solution containing 100 g (1.27 mol) of pyridine and 118 g (0.72 mol) of alcohol 21a was slowly added 107 g (0.9 mol) of thionylchloride. The solution was stirred for an additional 15 min, then the ice bath was removed and the mixture was heated to 60°C.

The mixture was then poured into a separatory funnel and extracted with ethyl ether. The ether extract was then washed with 10% HCl, then twice more with 800 ml portions of H_2O. The organic layer was dried (Na_2SO_4), filtered, and the solvent concentrated to yield 110 g (0.6 mol) of chloride 21c.

The residue was distilled (85°, 0.1 mm) to yield 74 g (0.404 mol) (56.2%) of chloride 21c. Mass spectra (rel. Intensity) are M^+ 181.95(11), 139.98(4), 105.06(100), 77.10(9); the ^{13}C-NMR assignments are given in Table X.

Anal. Calcd for $C_{11}H_{15}Cl$: C, 72.33; H, 8.22. Found: C, 72.45; H, 8.20.

1-^{13}C-3-Methyl-4-P-Tolylbutanoic Acid (22). Labeled carbon dioxide[8] ($^{13}CO_2$, 0.22 mol) was generated using the apparatus described in Appendix A by adding 200 ml of H_3PO_4 to an aqueous slurry of 48.5 g of $Ba^{13}CO_3$ (92% ^{13}C).[8]

Preparation of the Grignard reagent was accomplished using the Grignard apparatus described in Appendix A. In the 3-necked flask was placed 7.1 g (0.29 mol) of Mg turnings and 300 ml of 9:1 benzene:THF solution. This solution was brought to reflux as 60 g (0.26 mol) of bromide, 17b, was added slowly through the addition funnel. After the reaction was initiated, reflux was maintained for an additional 45 min after which almost all the Mg had dissolved.

The Grignard reagent was transferred via siphoning to a previously prepared stainless steel reactor. After cooling the vessel to liquid nitrogen temperature, CO_2 was sublimed into the stainless steel reactor, and the system was allowed to warm to room temperature overnight, after which unreacted CO_2 was recovered.

The stainless steel vessel was then removed, and its contents poured over 500 g of ice. The mixture was acidified with conc. HCl and extracted three times with ethyl ether. The combined ether layers were washed two times with saturated Na_2CO_3 (ca. 1 l.), then filtered through $MgSO_4$ and concentrated to give 9.0 g of neutral product.

The Na_2CO_3 extracts containing the labeled acid were acidified with conc. HCl followed by extraction (two times) with ethyl ether. The organic layer was filtered through $MgSO_4$ and concentration of the ether fraction yielded 40.5 g (0.23 mol) of ^{13}C-labeled acid, 22 (94.5%).

Kugelrohr distillation of the product (0.13-mm, 113°C) [lit.[16] 180-181° (15 mm)] afforded 39.3 g (0.22 mol) of 22 in 92% yield. The mass spectra (rel. intensity) for unlabeled acid are M^+ 192.00 (22), 173.97 (8), 132.01 (100); the ^{13}C-NMR assignments are given in Table XI.

1-^{13}C-3,7-Dimethyl-3,4-Dihydro-1(2H)-Naphthalenone (23). To 485 g of polyphosphoric acid was added 54 g (0.28 mol) of labeled carboxylic acid, 22. The mixture was heated at 95-105°C for 1 hr, then poured over ice and stirred to yield greenish-white crystals. The product was extracted with ether, filtered through $MgSO_4$, concentrated, and vacuum-distilled at 80°C (0.1 mm) [lit.[16] 140-150° (15 mm for unlabelled ketone)] to give a 97% yield (47 g, 0.27 mol) of labeled ketone, 23, as white crystals, mp 49-50° [lit.[16] 52-53° for unlabeled ketone]. The mass spectra (rel. intensity) are M^+ 175.11(71), 160.06(53), 132.98(100), 103.99(80); ^{13}C-NMR assignments are given in Table XII.

4-^{13}C-2,6-Dimethyl-1,2,3,4,-Tetrahydronaphthalene (24). A solution of 30.9 g (0.18 mol) of labeled ketone, 23, in 500 ml of acetic acid containing 3 g of 5% Pd/C was hydrogenated at 70-75° at 35 psi. Hydrogen uptake ceased after 25 psi H_2 was consumed. The solution was filtered, concentrated, neutralized with Na_2CO_3, extracted with isohexane and dried ($MgSO_4$). Kugelrohr distillation at 57° (0.1 mm) gave a 73% yield (20.7 g, 0.13 mol) of labeled hydrocarbon, 24. The mass spectra (rel. int.) are M^+ 161.05(62), 146.04(37), 118.(100); the ^{13}C-NMR assignments are given in Table XII.

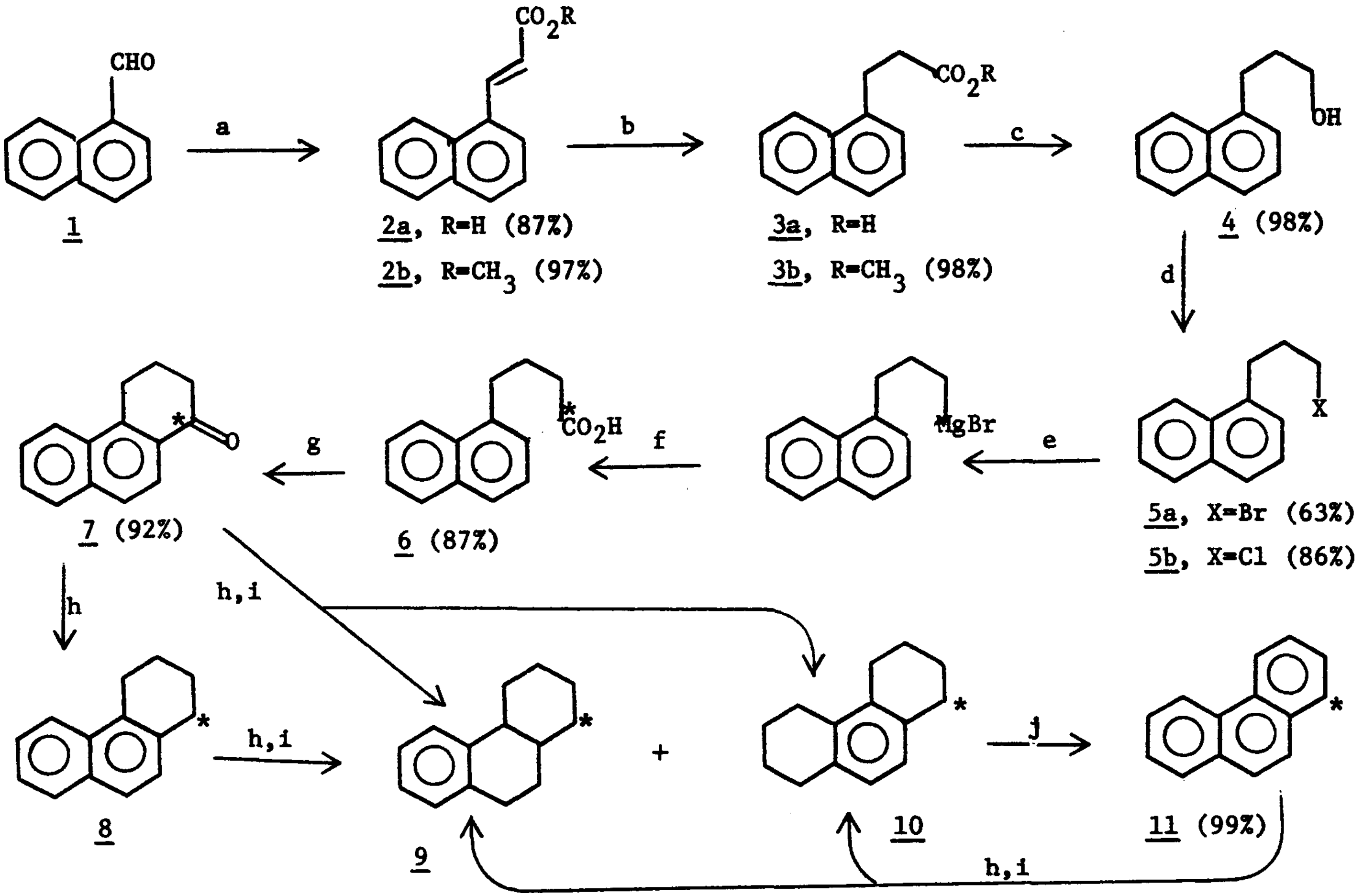
ACKNOWLEDGMENTS

The technical assistance of the following is gratefully acknowledged: C. E. Browne, D. L. Bymaster, K. D. Cowan, T. K. Dobbs, E. H. Vickery. We also thank Gulf Research & Development Company for support of this work through DOE Project E(49-18)-2305, and Messrs. M. W. Atkins and H. Hall for their help in design and construction of the apparatus. J. A. Browne is also thanked for preparation of the sketches.

REFERENCES

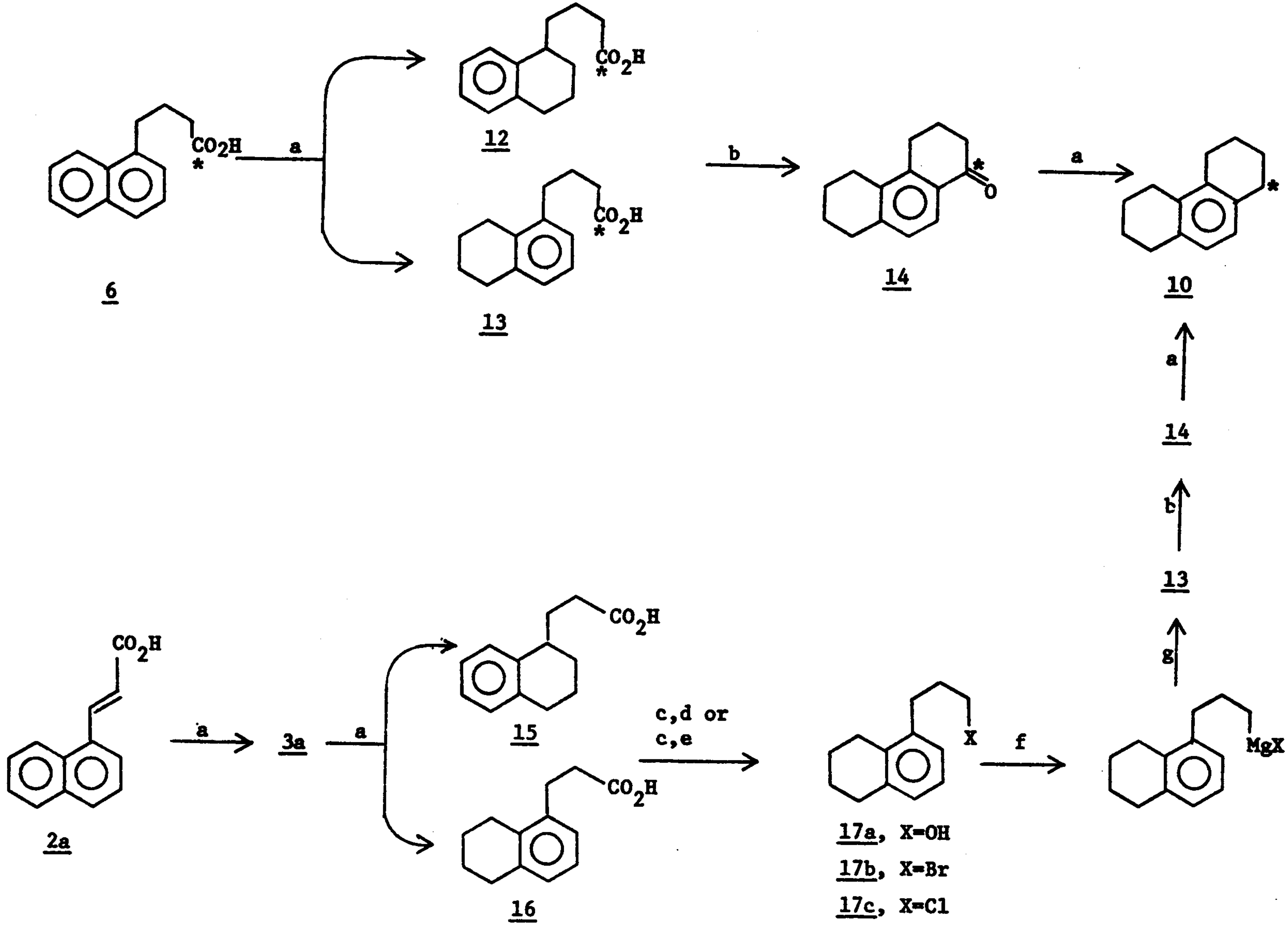
1. G. Jones, *Org. React.*, 15, 204 (1967).
2. References to the carbonation of Grignard reagents may be found in Appendix A.
3. K. D. Cowan and E. J. Eisenbraun, *Chem. Ind.* (London), 221 (1976).
4. K. A. Jenson, A. Kjaer, and S. C. Linholt, *Acta Chem. Scand.* 6, 180 (1952).
5. M. K. Hoffman and E. Berliner, *J. Org. Chem.* 35, 745 (1970).
6. L. F. Fieser and M. D. Gates, *J. Am. Chem. Soc.*, 62, 2335 (1940).
7. A. Marei, A. A. Sammoui, and T. Kassem, *J. Chem. U.A.R.*, 12, 323 (1969).
8. The $^{13}CO_2$ as 90% Ba$^{13}CO_3$ was obtained by Gulf Research & Development Co. from Mound Laboratory, Miamisburg, Ohio 45342.
9. W. S. Johnson, *Org. React.*, 2, 136 (1949).
10. J. W. Burnham and E. J. Eisenbraun, *J. Org. Chem.*, 36, 737 (1971).
11. Phillips Chemical Co., Isohexane, bp. 52-61°.
12. G. Schroeder, *Ber.*, 57, 1990 (1924).
13. J. P. Trivedi and J. J. Trivedi, *J. Ind. Chem. Soc.*, 35, 687 (1958).
14. L. Horner, H. Oediger and H. Hoffmann, *Ann.*, 626, 26 (1959).
15. L. Ruzicka and M. Liquori, *Helv. Chim. Acta*, 15, 3 (1932).
16. F. Mayer and G. Stamm, *Ber.*, 56, 1424 (1923).

SCHEME I



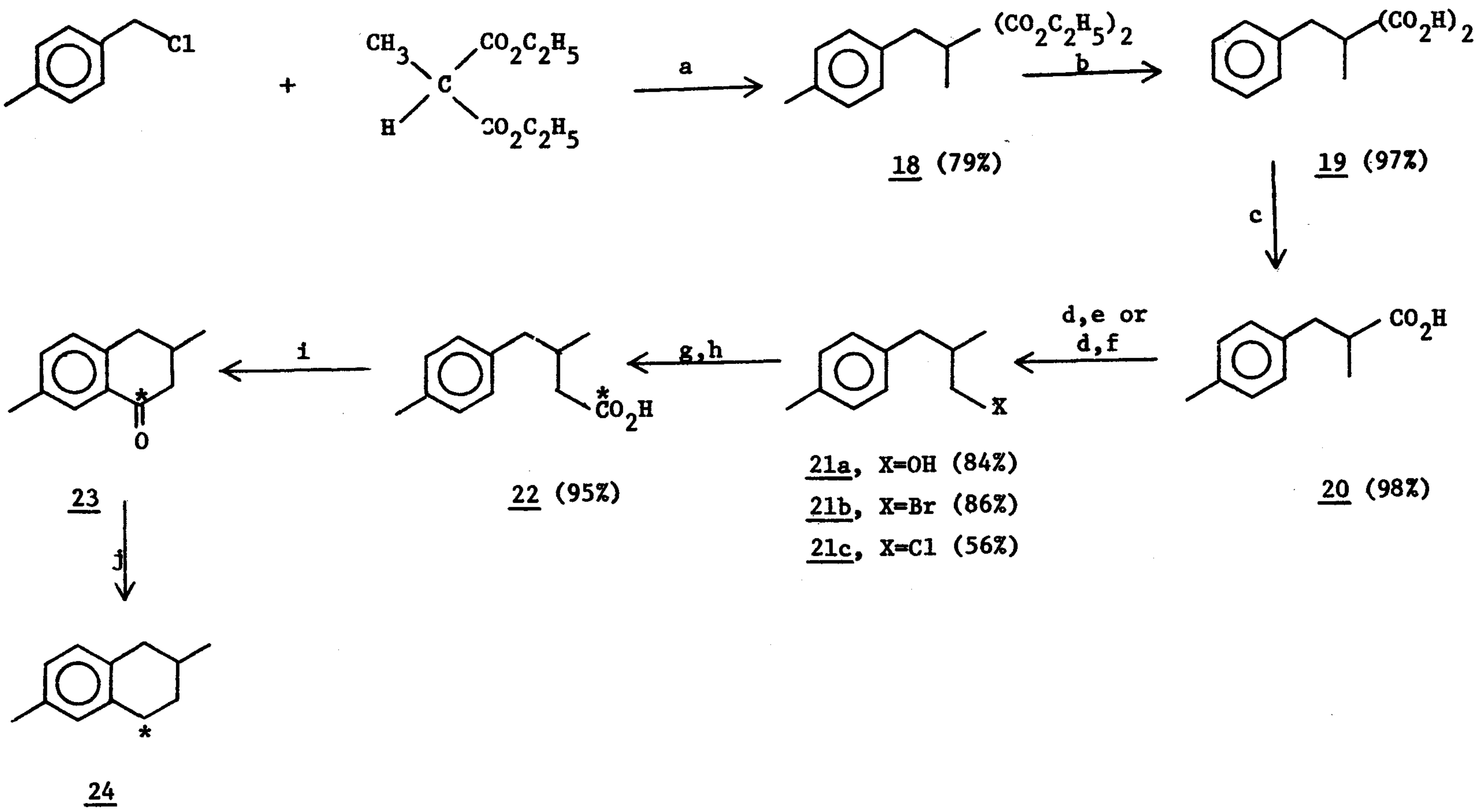
^{a}Piperidine, pyridine, malonic acid. ^{b}Pd/C, H_2, ethanol. ^{c}$(i\text{-}C_4H_9)_2AlH$, C_6H_6. ^{d}PBr_3. ^{e}Mg, ether. f $^{13}CO_2$. ^{g}PCl_5; $SnCl_4$, Δ. ^{h}Pd/C, H_2, HOAc. ^{i}Δ. ^{j}Pd/C, Δ.

SCHEME II



^{a}Pd/C, H$_2$, HOAc, Δ. ^{b}PPA, Δ. ^{c}(ibu)$_2$AlH, C$_6$H$_5$CH$_3$. ^{d}PBr$_3$. ^{e}SOCl$_2$, C$_6$H$_6$, Py. ^{f}Mg, I$_2$, ether. g ^{13}CO$_2$, H$^+$.

SCHEME III



$^{a}C_2H_5O^-$, $C_6H_5CH_3$, Δ. $^{b}OH^-$, Δ; $H_3\overset{+}{O}$. ^{c}Δ. $^{d}(iC_4H_9)_2AlH$, $CH_3C_6H_5$. $^{e}(C_6H_5)_3P$, Br_2, Δ. $^{f}SOCl_2$, C_6H_6, Py. ^{g}Mg, THF, C_6H_6 (1:9). ^{h} $^{13}CO_2$. ^{i}PPA, Δ. $^{j}H_2$, Pd/C, HOAc, Δ.

ATTACHMENT A

A METAL APPARATUS FOR LARGE-SCALE REACTION OF GRIGNARD REAGENTS WITH $^{13}CO_2$

Carbonation of carbanions is an effective method for preparing carboxylic acids, and if labeled carbon dioxide is used, the tag is introduced at the site.[1,2] Most labeling via tagged carbon dioxide has been done with glass apparatus designed for millimole reactions[1] and because the sensitivity of ^{14}C detection allows use of a low isotope concentration, the need for a more robust apparatus did not develop. The toxicity and accountability for ^{14}C also contributed to the small scale of ^{14}C labeling.

The advent of $^{13}CO_2$ has provided a new dimension in labeling.[3] With absence of toxicity and because ^{13}C detection is considerably less sensitive, large-scale synthesis of ^{13}C labeled compounds seems inevitable. We recently undertook the synthesis of molar quantities of ^{13}C-labeled compounds and were forced to re-examine the capabilities of methods used in carbonation to accommodate larger scale reactions. Carbonation as a means of introducing ^{13}C label was selected because of cost. Bubbling $^{13}CO_2$ through the Grignard reagent[4a] was prohibitive, nor did it seem advisable to add the Grignard reagent to solid $^{13}CO_2$[4b] because this lessens opportunity for contact. Since use of conventional carbonation apparatus[1] in labeling would have required innumerable runs, we decided to redesign the equipment to suit our needs which included an increased scale and some reduction of anxiety over possible loss of valuable $^{13}CO_2$ in the event of glass breakage or stopcock failure during large runs.

To overcome the deficiencies of a glass apparatus, metal was used in those areas in which high pressure might result, particularly in the event of accidental pressure surges.

Since carbonation proceeded readily under pressure, we decided to add $^{13}CO_2$ to the performed Grignard reagent rather than in the inverse manner.[4b] Thus the metal components shown in Figures 2 and 4 have importance other than safeguarding expensive labeling material.

An outline of the steps used in the ^{13}C carbonation of a Grignard reagent is listed below. A description of the individual steps and other experimental details are presented as well.

1. Generation of $^{13}CO_2$ (Fig. 1)
2. Transfer and storage of $^{13}CO_2$ (Fig. 2)
3. Preparation of Grignard reagent (Fig. 3)
4. Transfer of Grignard to reactor (Fig. 4)
5. Transfer of $^{13}CO_2$ to reactor, allowing carbonation reaction to proceed.
6. Recovery of any unreacted $^{13}CO_2$ and isolation of carbonation product.

EXPERIMENTAL

Generation of $^{13}CO_2$. To the 500-ml flask of the apparatus shown in Fig. 1 was added 65.6 g of ^{13}C-barium carbonate[5] and 65 ml of H_2O. The dropping funnel was charged with 100 ml of 85% phosphoric acid. The apparatus of Fig. 1 and Fig. 2 were connected and the gas collection bottle was alternately evacuated by opening nv-1, nv-6, and nv-7, and then filled with N_2 by closing nv-1 and opening nv-4. The system was evacuated by closing nv-4 and opening nv-1. This process was repeated three times, and at the end of the final evacuation, nv-1 and nv-6 were closed, nv-2, nv-8, nv-9, and tsc-1 were opened and the entire system was purged with N_2. Nv-2 and tsc-1 were closed and the system evacuated to 400 mm by opening nv-1 and nv-5.

The gas collection bottle was chilled in liguid N_2. Phosphoric acid was slowly added to the magnetically stirred $Ba^{13}CO_3$ slurry and the pressure was maintained below 1 atm by slowly opening nv-6. After complete addition of H_3PO_4, the flask contents were stirred 10 min and then tsc-1 was opened slowly to admit N_2 until the pressure in the system reached 1 atm. This insured complete transfer of the $^{13}CO_2$. Nv-6, nv-8, and nv-9, as well as tsc-1, were closed and the liquid N_2 coolant was removed from the gas collection bottle.

1-^{13}C-4-(1-Naphthyl)Butyric Acid. The apparatus of Figures 2, 3, and 4 were used. To the 1-l. flask (rbf-2) was added 8.8 g (0.36 mol) of magnesium, the dropping funnel (df-2) was charged with a solution of 93.5 g (0.36 mol) of 1-bromo-3-(1-naphthyl)propane[6] in 500 ml anhydrous ether, and the system was purged with N_2 by opening stopcocks tsc-2 and tsc-3. To frb-2 was added 50 ml of the ether solution and the reaction was initiated by warming. The remainder of the solution was then added at a rate sufficient to maintain reflux (1 hr total addition time). The reaction flask was heated at reflux temperature for 20 min. Stopcock (tsc-2) was closed and tsc-4, nv-2, nv-2, nv-8, nv-9, and nv-10 were opened in that order, respectively, to allow transfer of the Grignard to the reaction vessel of Fig. 4. Nv-2 and nv-10 as well as tsc-3 and tsc-4 were closed and the reaction vessel then cooled in liquid N_2. The system was evacuated to 200 mm by opening nv-1 and nv-5. These valves were then closed and $^{13}CO_2$ was transferred to the reaction vessel by opening nv-6 and warming the gas collection bottle. Nv-6 was closed and the liquid N_2 bath removed from the reaction vessel. Nv-3 was opened to observe the reaction pressure (45 psig max.) and stirring was initiated while the reaction vessel warmed. A decrease in pressure occurred as the reaction proceeded. Stirring was continued for 4 hr, then unreacted $^{13}CO_2$ was vented through nv-2 into saturated barium hydroxide by opening tsc-3, tsc-4, nv-2, and nv-10. The reaction vessel was disassembled, 10% hydrochloric acid was added, and the reaction vessel contents were transferred to a 1-l. separatory funnel. The mixture was extracted with ether (3x), the layers were separated, and the ether solution was washed with H_2O (2x). The ether solution was then thoroughly extracted with saturated sodium carbonate and the aqueous layer was washed with ether. Acidification, filtration, and drying gave 54.9 g (88% based on charged $Ba^{13}CO_3$) of 1-^{13}C-4-(1-naphthyl)butyric acid; mp 106-109° (lit.[7] mp 107.5-108.5°.

The above procedure and apparatus were used in the preparation of ^{13}C-labeled 3-methyl-4-(4-methylphenyl)butanoic acid in 95% yield. Both the alkyl chloride[6] and bromide[6] were used in this case.

REFERENCES

1. A. Murray and D. L. Williams, "Organic Synthesis with Isotopes," Part I, 1958, New York; Interscience Publishers, p. 86 and p. 317.

2. L. F. Fieser and Mary Fieser, "Reagents for Organic Synthesis," Vol. 5, 1975, New York; John Wiley and Sons, p. 94.

3. E. J. Eisenbraun, and L. P. Varga, Pollution Technology International, 1972, 6, p. 34.

4. (a) D. E. Pearson and D. Cowan, Org. Syn., 1973, Coll. Vol. V, p. 890;
   (b) R. B. Woodward and E. C. Kornfeld, ibid., 1955, Coll. Vol. III, p. 413.

5. Purchased from U. S. Energy Res. and Dev. Administration, Mound Lab, Monsanto Research Corp, P.O. Box 32, Miamisburg, Ohio 45342 as 90% $BaCO_3$ (92.1% ^{13}C).

6. To be published.

7. Nathan L. Drake and Warren C. McVey, J. Org. Chem., 1939, 4, p. 464.

8. E. J. Eisenbraun and H. Hall, Chem. & Ind., 1970, p. 1535.

LEGEND FOR FIGURES 1, 2, 3, AND 4

c	condenser, water-cooled, § 35/20
cf	coarse frit
ct	cold trap, 250-ml, § 50/30 O-ring joint and § 18/9 O-ring joint side arm
df-1	dropping funnel, pressure equalizing, 150-ml, Teflon stopcock and § 35/20 O-ring joints
df-2	dropping funnel, pressure equalizing, 500-ml, Teflon stopcock and § 35/20 O-ring joints
dt	drying tube, 75-ml with § 28/15 O-ring joint at top and § 18/9 O-ring joint at bottom
frb-1	flask, round-bottom, 500-ml, 2-neck, § 35/20
frb-2	flask, round-bottom, 1-1., 2-§ 35/20 and siphon tube; adapter constructed from Ace Glass, Inc. thread connector #5027
gb	gas collection bottle, 1-1., 1/4" pipe
j-1b	joint, brass, § 18/9, Ace Glass, Inc., #7659-02, P.O. Box 688, Vineland, NJ 08360; O-ring added locally
j-1g	joint, O-ring ball and socket, glass, § 18/9, Quartz Glass Corporation, 12440 Exline Street, El Monte, Calif. 91732
j-1s	joint, socket, stainless steel, § 18/9, Ace Glass, Inc., #7658-22
j-2g	joint, O-ring ball, glass, § 35/20, Quartz Glass Corp.
j-2s	joint, socket, stainless steel, § 35/20, Ace Glass, Inc., #7548-40
m	to manometer
ms	magnetic stirrer
msb-1	magnetic stirring bar, Teflon-enclosed, egg-shaped, 12x36 mm
msb-2	magnetic stirring bar, Teflon-enclosed, egg-shaped, 25x70 mm
n	to nitrogen
nv-1,2,4,5,6,7,8	needle valve, brass, 1/4" pipe, 1/4" Swagelok
nv-3	needle valve, brass, 1/4" pipe

LEGEND (Cont'd)

nv-9	needle valve, brass, 1/4" Swagelok
nv-10	needle valve, stainless steel, 1/2" pipe, or needle valve, ss, 3/8" pipe and 2 each 3/8" to 1/2" pipe reducer
pc	pipe cross, brass, 1/4" female
pg	pressure gauge, 0-200 psig, 1/4" pipe
pt	pipe T, brass, 1/4" female
rv	reaction vessel, stainless steel, 1700 ml; see reference 8 for construction details of a similar vessel
st	siphon tube and threaded bushing. Ace Glass, Inc. #5029
tsc-1 through tsc-4	Teflon stopcock, 2-mm
v	to vacuum

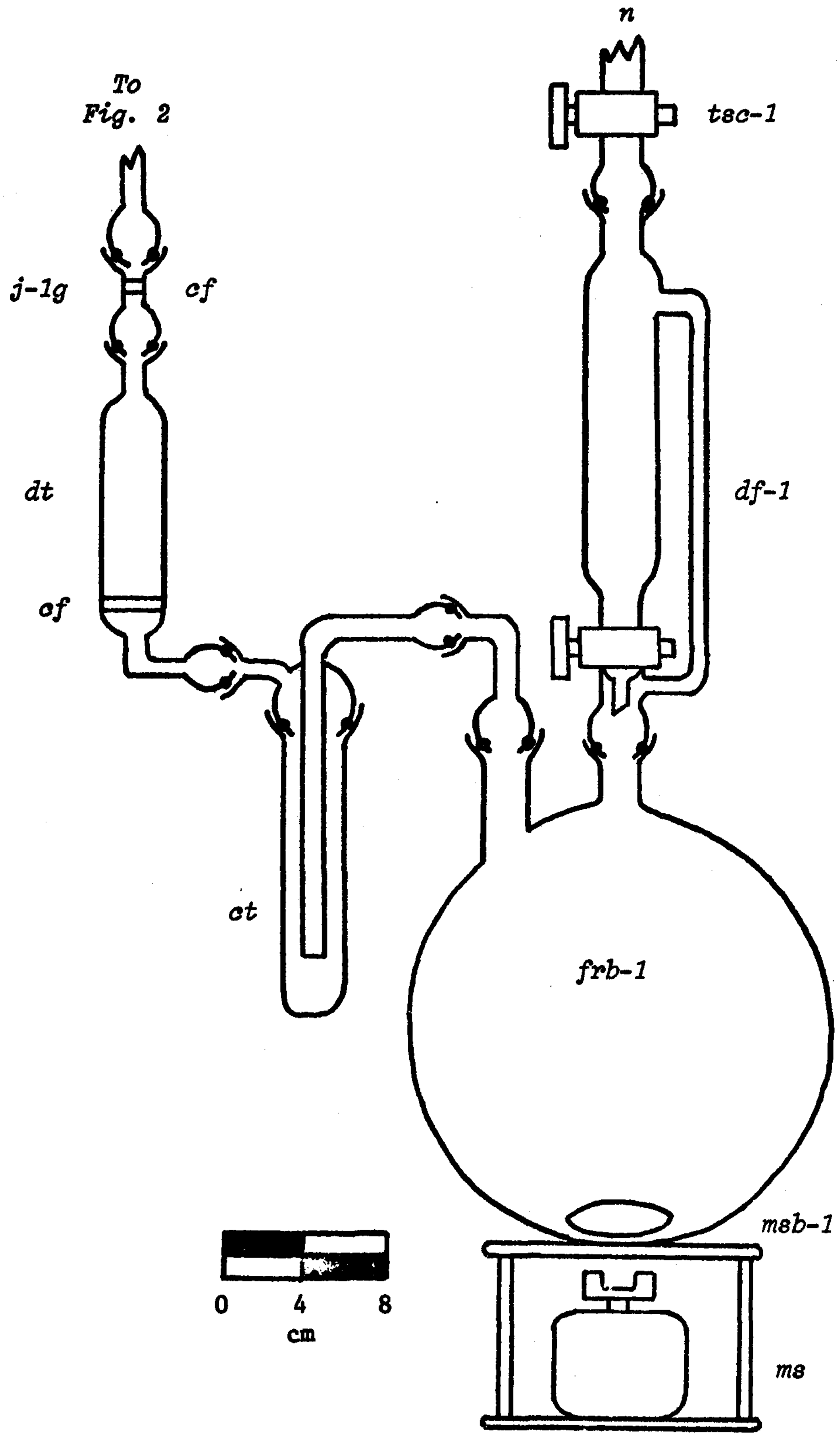


Figure 1. $^{13}CO_2$ Generator

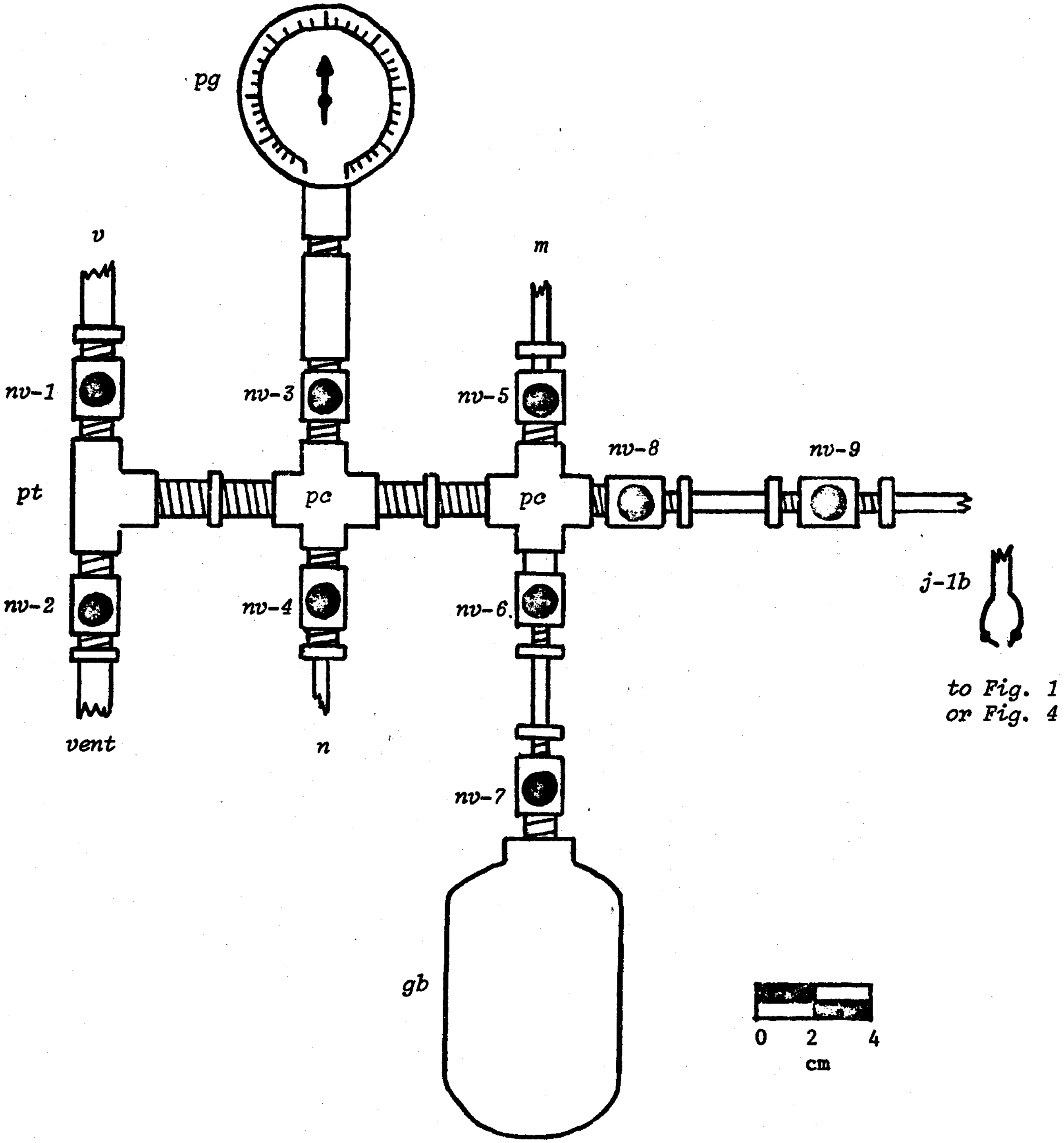


Figure 2. Gas Manifold, Metal

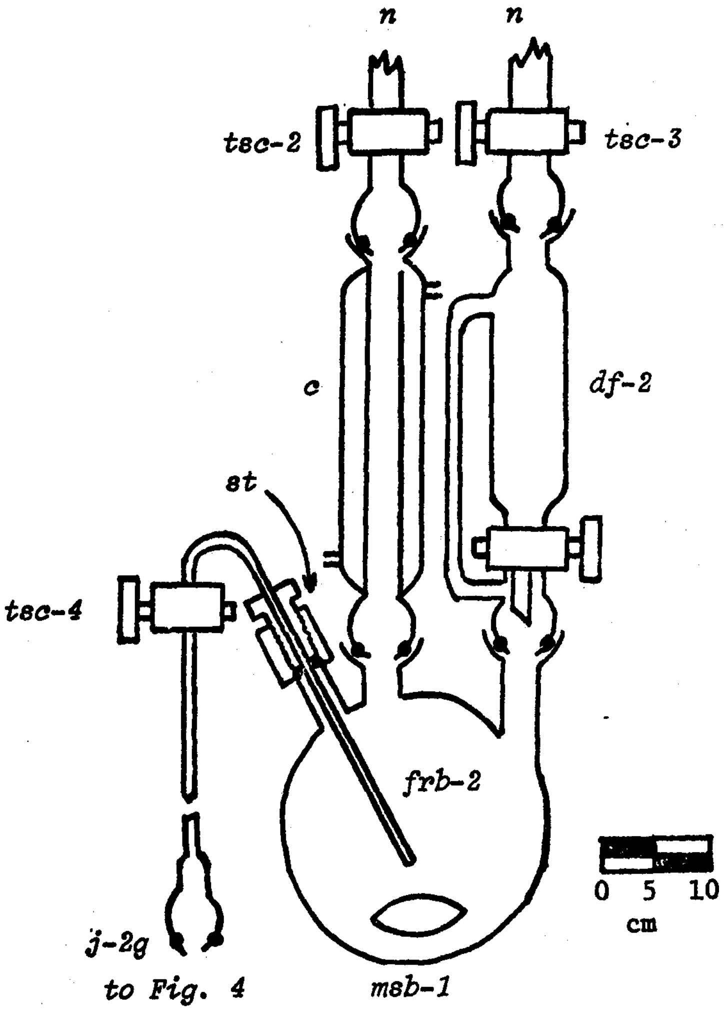


Figure 3. Apparatus for Generating Grignard Reagent

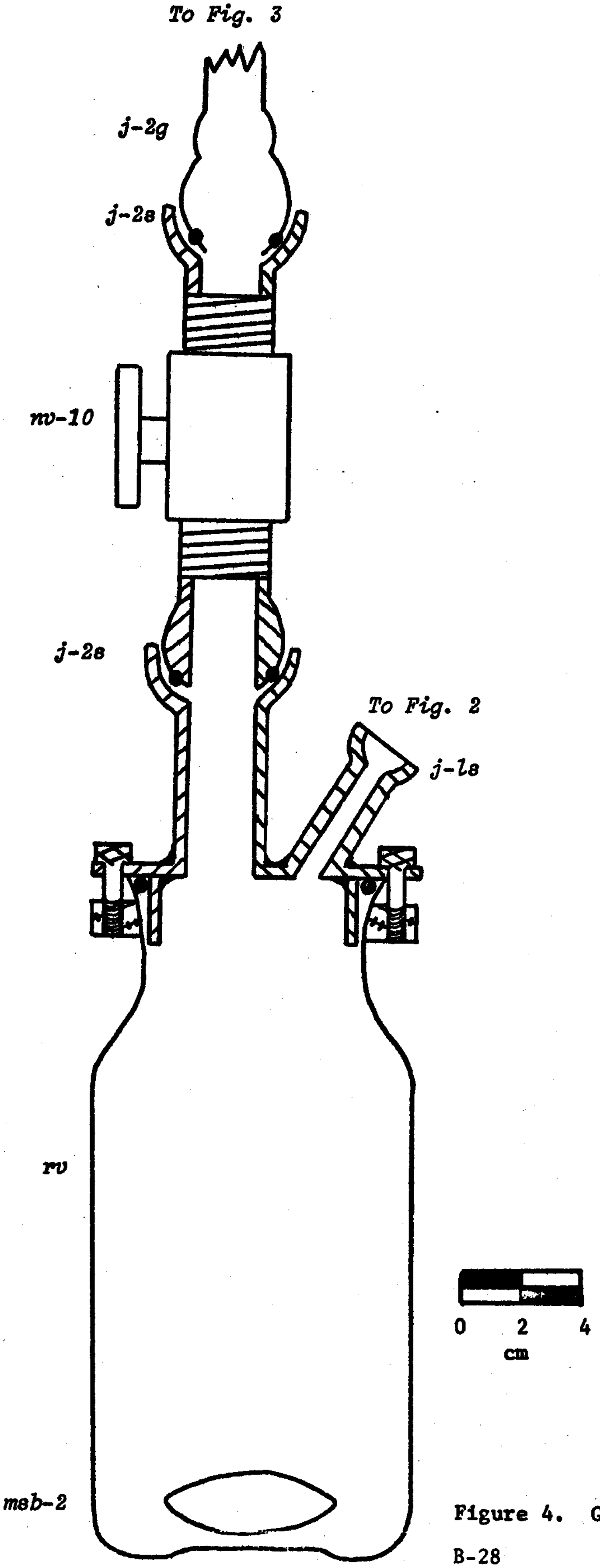


Figure 4. Grignard Reaction Vessel

Table I

C-NMR ASSIGNMENTS FOR
2-(1-NAPHTHYL)PROPIONIC ACID AND METHYL ESTER

	3a	3b
1	137.8	136.5
2	126.8	126.0
3	126.7	125.8
4	127.7	127.1
4a	134.8	133.9
5	129.5	128.8
6	126.4	125.5
7	126.4	125.5
8	124.2	123.3
8a	132.5	131.6
$\alpha(CH_2)$	28.5	28.0
$\beta(CH_2)$	35.4	34.8
CH_3		51.4
C>=0	174.7	173.1

Table II

C-NMR ASSIGNMENTS FOR 3-(1-NAPHTHYL)-1-PROPANOL

	4
1	137.9
2	125.8
3	125.6
4	126.5
4a	133.8
5	128.6
6	125.4
7	125.3
8	123.6
8a	131.7
α	28.9
β	33.2
γ	61.9

Table III

C-NMR ASSIGNMENTS FOR 1-BROMO-(AND -CHLORO-)-3-(1-NAPHTHYL)PROPANE

	B	Cl
1	136.4	136.6
2	126.2	126.1
3	125.8	125.8
4	126.8	126.8
4a	133.8	133.8
5	128.7	128.7
6	125.3	125.4
7	125.3	125.4
8	123.4	123.4
8a	131.6	131.7
α	33.34	29.6
β	33.20	33.0
γ	30.9	44.4

Table IV

C-NMR ASSIGNMENTS FOR LABELED AND UNLABELED 1-NAPHTHYL BUTYRIC ACID

Carbon	unlabeled δ^c(Tris)	labeled
1	138.7	-
2	126.8	127.0
3	126.5	126.6
4	127.4	127.5
4a	134.8	-
5	129.4	129.5
6	126.2	126.4
7	126.2	126.4
8	124.5	124.7
8a	132.6	-
$CH_2(\alpha)$	26.7	26.9
$CH_2(\beta)$	32.7	32.9
$CH_2(\gamma)$	33.8	34.1
>C=0	175.0	174.6

Table V

C-NMR ASSIGNMENTS FOR LABELED AND UNLABELED 3,4-DIHYDRO-1-(2H)-PHENANTHRENE

	unlabeled	labeled
Carbon No.	δ^C(TMS)	7
1	198.2	198.4
2	38.2	38.4
3	22.6	22.7
4	25.3	25.5
4a	135.5	-
4b	131.2	-
5	122.5	122.4
6	126.5	126.7
7	126.7	126.7
8	128.1	128.2
8a	129.7	-
9	124.7	-
10	128.6	128.7
10a	142.8	-

Table VI

C-NMR ASSIGNMENTS FOR 1-^{13}C-1,2,3,4,5,6,7,8-OCTAHYDROPHENANTHRENE

1	30.1
2	23.6
3	23.6
4	26.3
4a	134.2
4b	134.2
5	26.3
6	23.6
7	23.6
8	30.1
8a	135.1
9	126.5
10	126.5
10a	135.1

Table VII

C-NMR ASSIGNMENTS FOR 1-^{13}C-PHENANTHRENE

1	128.5
2	126.5
3	126.5
4	122.6
4a	-
4b	-
5	122.6
6	126.5
7	126.5
8	128.5
8a	-
9	126.8
10	126.8
10a	-

Table VIII

C-NMR ASSIGNMENTS FOR METHYL (4-METHYLPHENYLMETHYL) MALONIC ACID AND ITS DIETHYL ESTER

Carbon Position	δ^c(TMS) Ester	δ^c(TMS) Acid
1	133.3	134.3
2	130.2	130.9
3	128.9	129.5
4	136.3	136.8
5	128.9	129.5
6	130.2	130.9
>C=0	171.7	173.6
CH_3(α to ring)	20.9	21.0
CH_2(α to ring)	40.9	41.3
C	54.9	54.9
CH_3	19.7	20.0
CH_3(Ester)	14.0	-
CH_2(Ester)	61.1	-

Table IX

C-NMR ASSIGNMENT FOR 2-METHYL-3-β-TOLYLPROPIONIC ACID

1	136.0
2	129.1
3	128.9
4	135.8
5	128.9
6	129.1
>C=0	183.0
CH_3(α to ring)	21.0
CH_2	38.9
CH	41.4
CH_3	16.4

Table X

C-NMR ASSIGNMENTS FOR 2-METHYL-3-b-TOLYL-1-PROPANOL AND 2-METHYL-3-p-TOLYL-1-CHLOROPROPANE

Carbon Position	δ^c(21a)	δ^c(21C)
1	137.6	136.6
2	129.0	129.0
3	128.9	129.0
4	135.0	135.4
5	128.9	129.0
6	129.0	129.0
CH_3(α to ring)	20.9	21.0
CH_2(α to ring)	39.2	39.7
CH	37.8	37.5
CH_3	16.4	17.6
CHx	67.2	50.2
	x=OH	x=Cl

Table XI

C-NMR ASSIGNMENTS FOR LABELED AND UNLABELED METHYL -4-p-TOLYBUTANOIC ACID

Carbon Position	δ^c	
1	136.9	136.9
2	129.1	129.0
3	129.1	129.0
4	135.4	135.4
5	129.1	129.0
6	129.1	129.0
>C=0	180.0	180.0
CH_3(α to ring)	20.9	21.0
CH_2(α to ring)	40.8	39.4
CH	32.1	32.1
CH_3	19.5	19.5
CH_2	42.5	42.4

Table XII

C-NMR ASSIGNMENTS FOR 1-^{13}C-3,7-DIMETHYL-3,4-DIHYDRO-1(2H)-NAPHTHALENONE, LABELED AND UNLABELED 2,6-DIMETHYL-1,2,3,4-TETRAHYDRONAPHTHALENE

	Compound δ^c (TMS)		
Carbon Position	24(a)	23	24
1	129.0	128.8	128.9
2	134.5	134.4	134.5
3	126.3	127.1	126.3
4	128.9	128.6	128.8
4a	133.6	134.4	133.6
5	37.8	37.7	37.7
6	29.5	36.6	-
7	31.7	48.2	-
8	29.3	198.6	29.3
8a	136.2	134.4	136.4
$CH_3(2)$	20.9	20.9	20.9
$CH_3(6)$	22.01	21.2	22.1

24(a) is unlabeled 2,6-dimethyltetralin

APPENDIX C

CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF 2,6-DIMETHYLTETRALIN AND OF REACTION INTERMEDIATES IN ITS SYNTHESIS FROM p-TOLYLCHLOROETHENE

by K.S. Seshadri, D.M. Jewell, E.J. Eisenbraun

INTRODUCTION

Solvent depolymerization of coal is by hydrogen transfer from the hydroaromatic compounds to free radicals generated during the thermal cracking of the polymeric structure of coal. In model studies the solvents employed are tetralin, sym-octahydrophenanthrene, and other hydroaromatic hydrocarbons. The methyl derivatives of these hydroaromatic hydrocarbons are also effective hydrogen donors. To understand the reaction mechanism and the kinetics of depolymerization of coal, we have undertaken the study of several model reactions in which the hydrogen donor molecules of 2,6-dimethyltetralin and sym-octahydrophenanthrene with enriched ^{13}C in an appropriate location in each molecule. The synthesis is complex and costly. Therefore, it was necessary to monitor each step of the reaction. This was accomplished by analyzing the ^{13}C NMR spectra of reaction intermediates. The reaction intermediates are derivatives of benzene and napthalene and, to our knowledge, they have not been studied by ^{13}C NMR. Our results are novel. In this paper, the results on the derivatives of benzene are presented. In a subsequent paper, the spectra of napthalene derivatives will be discussed. Also, the enriched samples at 10% dilution are under study to measure ^{13}C-^{13}C coupling constants.

RESULTS AND DISCUSSION

The structures for the compounds included in the present study are presented in Figure 1. Only the ring carbon nuclei are numbered. The rest of the carbons are appropriately identified in tables. Structural determination by NMR spectroscopy largely depends on the ability to predict chemical shifts for a given compound. A variety of techniques are available to accomplish the assignments. For several substituted benzenes, the aromatic carbon chemical shifts are predicted by the additivity of substituent effects. In addition, the spectral features, particularly in the off-resonance decoupling experiments, are used in the assignment of resonance positions.

The chemical shifts measured for the malonate, malonic, and propionic derivatives are collected in Table I. The results for the chloropropane, chloroethane derivatives are given in Table II. Table III has the values for the propanol and butanoic acid derivatives and Table IV that of 2,6-dimethyltetralin. These results are discussed in turn in the following sections, along with the shielding trend exhibited by the aryl, the alkyl, and the carbonyl carbon nuclei. The results are considered mainly in terms of the known structural effects on ^{13}C shieldings.

Diethyl Methyl (4-methylphenylmethyl) Malonate

The ^{13}C spectrum of this compound has three resonance positions which retain their singlet structure in the off-resonance experiment. The low-field singlets are at 136.3 and 133.3 ppm. In a benzene molecule, with a propyl group on C-1 and a methyl group on C-4, reasonable values for the shielding of C-1 and C-4 are, respectively, 140 ppm and 135.0 ppm. However, the carboxyl group on the propyl chain, besides α and β effects, has a significant shielding γ-effect.(2) The magnitude of this shielding effect is between 2 to 3 ppm. The added effect of two carboxyl groups would substantially decrease the shielding of C-1 and, therefore, we have assigned the value of 133.3 ppm to it and 136.3 ppm to C-4. This choice is supported by the resonance positions of quarternary centers in 2-methyl-3-p-tolylpropionic acid, which has, in the corresponding position, one carboxyl group instead of two. Actually, there is no significant difference in the α, β, γ, and δ effects, due to -COOH and -COOR groups. Therefore, we should expect that by replacing the two ester groups by one acid group, C-1 should be deshielded by about +2.5 ppm. If the value of 136.4 ppm is assigned to C-1 instead of 133.3 ppm, in the transition from structure I to structure III, the shielding of C-1 should decrease by +2.5 ppm. The observed value is either 135.8 or 136.0 ppm, substantiating the assignment of the peak at 133.3 ppm to C-1 in I.

The resonance positions arising from the other aromatic carbon nuclei are at 128.9 and 130.2 ppm. The one at the lower field is assigned to C-2 and C-6 and the other to C-3 and C-5. In the absence of the ester groups on the propyl chain, one would expect the chemical shift of C-3 and C-5 to be at a slightly lower field than that of C-2 and C-6. However, the carboxyl group has significant deshielding δ-effect,(3) thereby shifting the shielding of C-2 and C-6 to a lower field.

The carboxyl substituent effects along the alkyl chain by comparison with the shieldings of the corresponding alkanes have been derived by examining the published results on acids and esters. The variation of the shielding of the carbon α to the carboxyl group is dominated by the electro negativity of the group. The average effects are:(3) α, +21.0; β, +2.5; γ, -2.0, and δ, +1.0 ppm. This information along with the relative intensities of resonance portions and the splitting pattern in the off-resonance experiment have been utilized in assigning values to side chain carbons.

The shieldings of carbons in the propyl cahin are influenced by the aromatic ring and by the two carboxyl groups. The resonance position at 54.9 ppm retains its singlet structure in the off-resonance experiment and, therefore, it is assigned to the quarternary carbon in the propyl chain. The rest of the assignments are straightforward and unequivocal. However, the value of 19.7 ppm assigned to the methyl carbon in the propyl chain needs to be justified. In propylbenzene, the shielding of $-CH_3$ carbon is 14.0 ppm. It is experiencing the β-effect from the two carboxyl groups. Therefore, its shielding is likely to be decreased by about +5 ppm, placing its chemical shift closer to 19 ppm than to 21 ppm.

Methyl (4-methylphenylmethyl) Malonic Acid

The shieldings of aromatic carbons of this molecule differ slightly from those in the malonate. The difference is probably due to the slight differences in the long-range effects of the acid and ester groups. However, the significant difference is in the shielding of carboxyl carbon. The ester carbonyl carbon is shielded by -2.0 ppm compared to the acid carbonyl carbon. Formation of the methyl ester of aliphatic acid causes a consistent upfield shift in the carboxyl shielding. In the examples known, the change is about -7.0 ppm,(4) which is attributed to the elimination of hydrogen bonds upon esterification. We observe the same trend here, but the magnitude of the change is much less. Complete assignments are in Table I.

2-Methyl-3-p-tolylpropionic Acid

The shieldings of carbons in this molecule follow the expected trend and substantiate some of the assignments in I and II. The resonance position at 183.0 ppm has been assigned to the carboxyl carbon. As the chain length is increased in aliphatic acids, carboxyl carbon experiences a deshielding β-methyl effect, which is about +3 ppm.(2) The carboxyl carbon in the present compound is experiencing β-effects due to a methyl and methylene group and, therefore, its shielding is shifted about 6 ppm downfield from acetic acid. Actually, the chemical shift observed here is identical to that reported for isopropionic acid.(5) The magnitude of the γ-effect due to the carboxyl group should be less at C-1 than in the corresponding dibasic acid derivative. The resonance positions of the two quarternary centers of this molecule are at 136.0 and 135.8 ppm. If either of them are assigned to C-1, the assignment is consistent with the reduced γ-effect due to the carboxyl group at C-1, compared to II. The value of 136.0 ppm is assigned to C-1 and 135.8 ppm to C-4. Perhaps they could be reversed. The magnitude of the δ-effect is less, due to the replacement of two carboxyl groups by one. Therefore, the shieldings of C-2 and C-6 are shifted upfield in comparison to II.

The shielding of the carbon in the methyl group of the propyl side chain is altered from that in n-propane by the phenyl group and also by the carbonyl group. The shielding γ-effect of the phenyl group is compensated by the deshielding β-effect of the carboxyl group, placing its chemical shift almost in the same position as in n-propane. The rest of the assignments are straightforward. The deshielding α- and β-effects of the carboxyl group are less than in the corresponding dibasic acid.

2-Methyl-3-p-tolyl-1-chloropropane and p-tolychloroethane

The interesting features of the ^{13}C spectrum of these two compounds are the resonance portions in the high field end of the spectrum. This region is analyzed by considering the effects due to the chlorine atom and the phenyl group, along a hydrocarbon chain. Alkyl halides have been studied in sufficient detail(6) and the chlorine atom markedly deshields the α- and β-carbons along the chain. The γ-carbon is shielded. The average α, β, and γ affects, respectively, all +31.2, +10.5, and -4.6 ppm. The corresponding effects of a phenyl group are +23.0, +9.5, and -2.0 ppm.(7) Due to the combined effect of these two functions, the expected chemical shift values for the methylene carbon α to the aromatic ring and that of the other methylene carbon α to the chlorine atom are, respectively, 43 and 54 ppm. The observed values are 39.7 and 50.2 ppm, which are in fairly good agreement with the calculated values. The calculated values for the methine and the methyl carbons are 43 and 18 ppm and the observed values are 37.5 and 17.6 ppm. The additivity parameters that have been derived by studying a series of alkyl halides and alkylbenzenes appear to be satisfactory in arriving at the assignments. However, the final proof has been obtained by examining the splitting pattern in the off-resonance experiment.

The spectrum of p-tolylchloroethane has, at the high field end of the spectrum, two resonance portions: one at 46.1 ppm and the other at 21.0 ppm. The former is twice as intense as the latter, while it splits into a triplet and the other into a quartet in the off-resonance experiment. The additivity parameters mentioned above suggest that the two methylene carbons should have different shielding, indicating that these parameters are useful for predictive purposes, particularly when the substituent is under the influence of two functional groups. The chemical shift values for the aromatic carbons are given in Table II.

2-Methyl-3-p-tolyl-1-propanol

The assignment of values to saturated carbons in this molecule can be accomplished by considering the effect of a phenyl group along 2-methylpropanol.(8) The predicted values for the methylene carbon α to the ring, the methine carbon β to the ring, methyl carbon, and the methylene carbon adjacent to oxygen, respectively, are 42, 41, 17, and 67.0 ppm. The observed values in the same sequence are 39.2, 37.8, 16.4, and 67.2. The agreement is similar to that which has been observed in similar compounds in this study. Again, we have utilized the information in the off-resonance experiment to arrive at the final assignments. In this compound, as in other cases, the additive parameters have proved useful in distinguishing the resonance positions due to the two methyl groups, one α to the aromatic ring and the other in the branched propyl chain. The assignment of values to aromatic carbons is straightforward, and they are given in Table III.

3-Methyl-4-p-tolylbutanonic Acid

The ^{13}C spectrum of this compound has similar features to those of IV and VI but with interesting differences. The resonance positions of the two methyl group carbons are close to each other, unlike IV and VI. The γ-effective to the carboxyl group is less than that of the chlorine atom and the hydroxyl group. Therefore, the shielding of methyl carbon close to the carboxyl group is shifted downfield by about 3 ppm compared to the corresponding methyl group in structures IV and VI, placing its chemical shift close to that of the methyl group on the ring. The resonance position at 180.0 is assigned to the carboxyl carbon and this value is close to that which has been observed in n-propionic and n-butyric acid, suggesting that the carbon α and β to the acid group have significant effects on the shielding of carboxyl carbon, while the γ-effect is negligible. The complete assignment is in Table III.

2,6-Dimethyltetralin

So far, we have considered the ^{13}C spectrum of the reaction intermediates in the synthesis of 2,6-dimethyltetralin. The synthetic route was devised to obtain the ^{13}C-enriched 2,6-dimethyltetralin. We have recorded the ^{13}C spectrum of the enriched final product and some of the intermediates. They have to be studied at greater dilution to understand the spectral features, which we have postponed for the time being.

The ^{13}C spectrum of tetralin has been studied by Retcofsky and co-workers(9) and by Johnson and Jankowski.(10) The values assigned by Retcofsky for the shielding of C-1 and C-2 are 129.6 and 126.0 ppm, respectively, whereas this assignment has been revised by Johnson and Jankowski. Our study of the homolog of tetralin confirms the assignments of Retcofsky.

The changes in the shieldings of carbon nuclei in 2,6-dimethyltetralin compared to tetralin follow the expected rules. Methyl substitution on an aromatic carbon normally decreases the shielding of the substituted carbon by about 9.2 ppm, and therefore the value of 134.5 ppm is assigned to C-2. The <u>para</u> effect at C-4a would increase its shielding, and therefore the value of 133.6 is assigned to it. The magnitude of these changes is similar to those observed in toluene compared to benzene.

The shieldings of saturated ring carbons follow the same bend as in methylcyclohexane compared to cyclohexane.(11) C-5 and C-7 experience a downfield shift of +8.4 ppm and C-6 a downfield shift of +6.1 ppm, compared to the corresponding values in tetralin. These changes are similar to the β and α effects observed in methylcyclohexanes.

The changes in the shieldings of aromatic carbons, in particular that of C-2, are in agreement with the chemical shift values assigned to C-1 and C-2 by Retcofsky. If C-2 is assigned the value of 129.0, a resonance position characteristic of a quarternary center should have been observed around 138.2 ppm. We have not observed any resonance absorption at fields higher than that corresponding to 136.2 ppm, which incidentally is due to one of the bridgehead carbons. Although the values assigned to C-6 and C-8 could be reversed, by examining the splitting pattern in the off-resonances spectrum, we have concluded that the value of 29.5 ppm is more appropriate to C-6 than to C-8. Complete assignment is in Table IV.

The structure of the compounds that are included in this report is by no means complex. Unambiguous assignments, particularly for saturated carbons, have been possible by examining the spectral features in the off-resonance decoupling experiment. The assignments have been explained by considering the structures, with the exception of 2,6-dimethyltetralin as an alkane chain of three or four carbons, with a p-tolyl group on one end and an electronegative group on the other end. The effect of these two groups along the chain has been examined. The effect is not exactly additive. However, the additivity parameters that have been derived by an accumulation of ^{13}C spectra of several classes of compounds have provided a reasonable guideline for arriving at the assignments. At present, we do not have a satisfactory explanation for the lack of exact additivity effect of the two functional groups along the chain.

EXPERIMENTAL

Materials

Compounds I through VIII were synthesized by the procedure given in Reference 1.

Spectra

Nuclear magnetic resonance spectra of ^{13}C in natural abundance were obtained by the pulsed FT technique at 20 MHz on a Varian CFT-20 spectrometer, which is equipped with 620/L computer with 16 K memory. The free induction decays, after a sufficient number of transients have been accumulated, were smoothed with an exponential function and Fourier transformed. Samples were studied in 8 mm O.D. tubes at a concentration corresponding to about 200 mg in a total volume of 1.3 ml and at a probe temperature of 36°C. The solvents, depending on the sample, were $CDCl_3$ and acetone-acetone-d_6. The deuterated solvent served to obtain field-frequency lock, and chemical shifts are in ppm downfield from internal TMS.

ACKNOWLEDGMENT

Funding of this research study was provided by the U.S. Energy Research & Development Administration under Project E(49-18)-2305. We wish to also acknowledge our indebtedness to L. Kindley (DOE), D. C. Cronauer, and A. Bruce King for helpful suggestions.

REFERENCES

1. E. J. Eisenburn, et al.
2. R. Hagen and J. D. Roberts, J. Amer. Chem. Soc. 91, 4504 (1969).
3. J. B. Stothers, "Carbon-13 NMR Spectroscopy," p. 148, Academic Press, New York, New York, 1972.
4. Ibid., p. 299.
5. D. H. Marr and J. B. Stothers, Can. J. Chem. 47, 3601 (1967).
6. T. D. Brown as cited in Ref. 3, p. 133.
7. As cited in Ref. 3, p. 98.
8. J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, J. Amer. Chem. Soc. 92, 1338 (1970).
9. H. L. Retcofsky and R. A. Friedel in "Spectroscopy of Fuels," (R. A. Friedel, ed.), p. 90, Plenum Press, New York, 1970.
10. L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," Wiley-Interscience, New York, 1972.
11. D. K. Dalling and D. M. Grant, J. Amer. Chem. Soc. 94, 5318 (1972).

Table I

^{13}C Shieldings for Ring and Side Chain Carbons in I-III (δ^{C} from TMS)

	Compound		
Ring Position	**I**	**II**	**III**
C-1	133.3	134.3	136.0
C-2	130.2	130.9	129.1
C-3	128.9	129.5	128.9
C-4	136.3	136.8	135.8
C-5	128.9	129.5	128.9
C-6	130.2	130.9	129.1
Carbons in Substituents			
CH_3 (α to ring)	20.9	21.0	21.0
CH_2 (α to ring)	40.9	41.3	38.9
C/CH	54.9	54.9	41.4
CH_3	19.7	20.0	16.4
CH_3 (ester group)	14.0	--	--
CH_2 (ester group)	61.1	--	--
>C=0	171.7	173.6	183.0

KSS:smm
CR&CD
GR&DC
3/22/78

Table II

^{13}C Shieldings for Ring and Side Chain Carbons in IV and V (δ^{C} from TMS)

	Compound	
Ring Position	IV	V
C-1	136.6	138.0
C-2	129.0	129.3
C-3	129.0	128.5
C-4	135.4	134.6
C-5	129.0	128.5
C-6	129.0	129.3
Carbons in Substituents		
CH_3 (α to ring)	21.0	21.0
CH_2 (α to ring)	39.7	46.1
CH	37.5	--
CH_2	50.2	46.1
CH_3	17.6	--

KSS:smm
CR&CD
GR&DC
3/22/78

Table III

^{13}C Shieldings for Ring and Side Chain Carbons in VI and VII (δ^{C} from TMS)

	Compound	
Ring Position	VI	VII
C-1	137.6	136.9
C-2	129.0	129.1
C-3	128.9	129.1
C-4	135.0	135.4
C-5	128.9	129.1
C-6	129.0	129.1
Carbons in Substituents		
CH_3 (α to ring)	20.9	20.9
CH_2 (α to ring)	39.2	40.8
CH	37.8	32.1
CH_3	16.4	19.5
CH_2	67.2	42.5
>C=0		180.0

KSS:smm
CR&CD
GR&DC
3/22/78

Table IV

^{13}C Shielding for Ring and Side Chain Carbons in VIII

Ring Position	δ^C (TMS)
C-1	129.0
C-2	134.5
C-3	126.3
C-4	128.9
C-4a	133.6
C-5	37.8
C-6	29.5
C-7	31.7
C-8	29.3
C-8a	136.2
CH_3(2)	20.9
CH_3(6)	22.0

KSS:smm
CR&CD
GR&DC
3/22/78

APPENDIX D

STRUCTURAL FEATURES OF HYDROPHENANTHRENES

As part of the study of rearrangement reactions of hydroaromatic donor solvents (Section F), methods were established to determine the structural features of hydrophenanthrenes. Emphasis was placed upon the analyses of specific LC fractions using ^{13}C-NMR and MS. The following is a discussion of the means of identifying the individual compounds.

A sample of hydrogenated phenanthrenes was separated into seven fractions, designated A through G. Each fraction was examined by mass spectrometery and ^{13}C-NMR, and structures were assigned by correlating this information with that from reference compounds. The ^{13}C-NMR stick spectra are shown in Figures 1 and 2. Table 1 illustrates the mass spectra of these fractions. The intensities of major ions (m/e) are expressed as percent of the base peak where P represents the molecular ion. If more than one molecular ion is suspected, P^1, P^2, etc., is used.

Reference Hydrophenanthrenes - Pure tetrahydrophenanthrene and octahydrophenanthrene were used for both C-NMR and mass spectrometry in order to have a "reference base" from which to compare isomers. This information appears at the bottom (H) of Figures and Both pure compounds have molecular ions as their base (100%) peak in their mass spectra. Tetrahydrophenanthrene is similar to tetralin in that the P-28 ion is the major fragment peak.

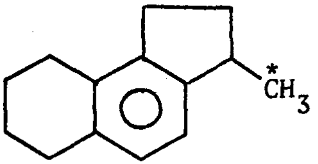
As in the case of tetralin/methyl indane, the most significant spectral features to observe are the relative percentages of P, P-15, and P-28 ions. The P-15 ion is due to the loss of a CH_3 group evolved during rearrangement promoted by electron impact. In the absence of any additional alkyl substituents, an increase in P-15 ion concentration indicates the natural presence of a methyl group.

The ^{13}C-NMR data of each reference compound show a distinct signal for each of the four saturated carbons. For symmetry reasons, the two saturated rings in H_8Ph are equivalent. The most important spectral features to observe are that in each compound the hydroaromatic carbons always have signals between 23-30 ppm. This is specific for the six-membered rings. Five-membered rings, such as indanes, do not have signals in this region.

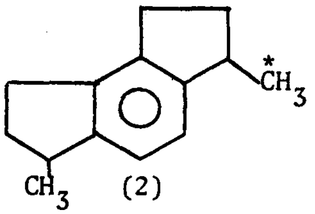
The isomers are listed arbitrarily, but A, D, E, F, and G are all derived from a 1-^{13}C labeled pure H_8Ph. Isomers B and C are derived from unlabeled H_8Ph. The carbons bearing the ^{13}C label are intense and are identified with a strong broken line in Figure 1. The position of the signal for the ^{13}C label in pure reference H_8Ph is at 30.2 ppm.

Fraction A - Isomer A is a monoaromatic derivative since its P is 186 and its UV spectrum is purely benzenoid. The fact that the P-15 ion is base peak indicates that one or more CH_3 groups are present. NMR shows that the label has completely rearranged from a CH_2 to a CH_3 group (20.2 ppm). Weaker signals between 19.0 and 21 ppm indicate that the non-labeled hydroaromatic ring has also rearranged to produce new CH_3 groups.

Fraction B - Isomer B is also monoaromatic. In comparing both mass spectra and line positions of NMR, it is very similar to isomer A. The predominant CH_3 group is also at 20.3 ppm. The new lines at 34.4 and 39.3 ppm in both A and B indicate the position of the CH_3 substituent is identical in each. These lines of equal intensities are due to the CH_2 groups of a five-membered ring. Considering the original position of the label, we conclude that both A and B have the following structures:



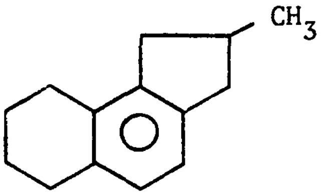
(1)



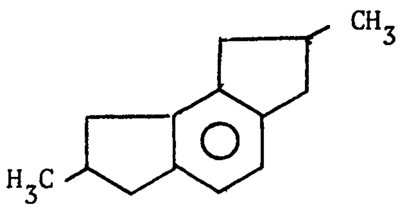
(2)

These structures account for the positions of the label on a CH_3 group, a five-membered ring, and the high intensity of a P-15 fragment in the mass spectrum. However, a reasonable concentration of structure (1) must exist to account for the remaining hydroaromatic carbons in a six-membered ring. Calculations show that the level of transferable hydrogen has been reduced by about 50% in B. This is consistent with an "average structure" as in (1). Both A and B also contain some hexahydro derivative as indicated by a m/e of 184 and a line at 120.4 ppm. The olefin group is not in the labeled ring, but too little is known about these derivatives to speculate on possible structures.

Fraction C - This isomer is monoaromatic, unlabeled, and contains some hexahydro derivatives. The very intense P-15 and P-45 fragments also indicate a high degree of rearrangement to methyl derivatives. The ^{13}C-NMR lines at 19.1 (CH_3-) and 34.0 + 37.0 ppm indicate that these are position isomers of A and B. This is evidence for the following structures:



(3)



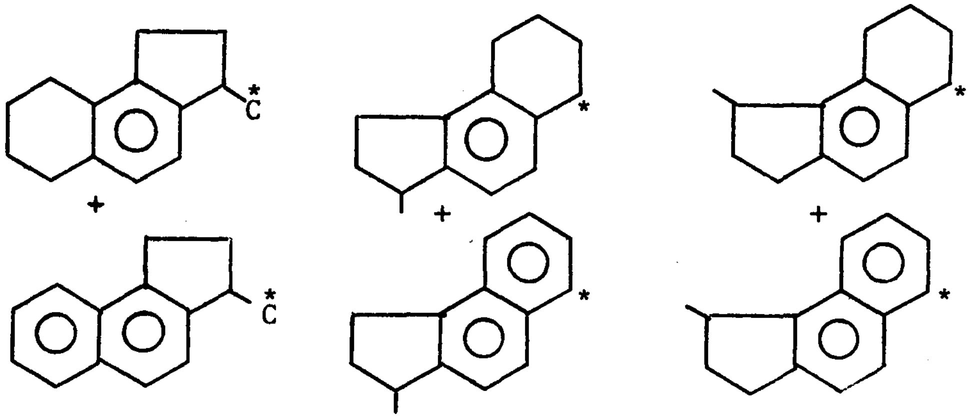
(4)

Calculations again show that about 50% of transferable hydrogen has been lost, indicating that one six-membered ring is present as in (3).

Fraction D - This isomer is essentially pure tetrahydrophenanthrene, with little rearrangement. The ^{13}C label is equally distributed between the hydroaromatic ring (30 ppm) and aromatic ring (128.3 ppm), indicating no preference for which ring dehydrogenates or hydrogen transfers. The presence of very weak signals at 20.5 ppm and 32 ppm indicates little isomerization. This is confirmed by mass spectra.

Fraction E - This compound is tetrahydrophenanthrene with the label equally distributed, as in Fraction D.

Fraction F - This fraction is a mixture of octahydro-, hexahydro- , and tetrahydrophenanthrenes P^3, P^2, P^1, respectively), but the H_4Ph is highest in concentration (mass and UV spectra). The prevalence of $-CH_3$ groups is indicated by a large P-15 ion, strong lines in the 19-21 ppm region, as well as the existence of five-membered rings (31-39 ppm). The ^{13}C label is equally distributed between CH_3 and the original CH_2 six-membered rings. The level of isomerization is quite similar to that of isomer A. The additional CH_3 lines at 20-21 ppm and at 30-31 ppm indicate that a reasonable amount of isomerization also involved positions 4 and 5 of the original H_8Ph. Therefore, this mixture may contain the following structures:



Fraction G - This fraction is completely monoaromatic and contains only trace amounts of rearranged isomers. With only few exceptions, the positions of major C-NMR lines are identical to pure $^{13}C-H_8Ph$.

Table I

MASS SPECTRAL DATA OF ISOLATED HYDROPHENANTHRENES

	m/e (% Base Peak)										
Isomer	186	184	182	180	178	171	169	167	158	154	141
A	P (53)					P-15 (100)			P-28 (18.9)		
B	P^1 (81)	P^2 (34.7)				P^1-15 (100)			P^1-28 (37)		P^1-45 (35)
C	P^1 (93)	P^2 (98)				P^1-15 (63)					P^1-45 (100)
D			P (100)					P-15 (35)		P-28 (67)	P-41 (27)
E			P (100)					P-15 (27)		P-28 (69)	
F	P^2 (23)	P^3 (10)	P^1 (42)					P^1-15 (100)			P^1-41 (15)
G	P (100)					P-15 (76)			P-28 (56)		
Pure tetrahydro-phenanthrene			P (100)					P-15 (15)		P-28 (78)	P-41 (34)
Pure octahydro-phenanthrene	P (100)					P-15 (68)			P-28 (30)		P-45 (33)

DCC:smm
CR&CD
GS&TC
3/17/78

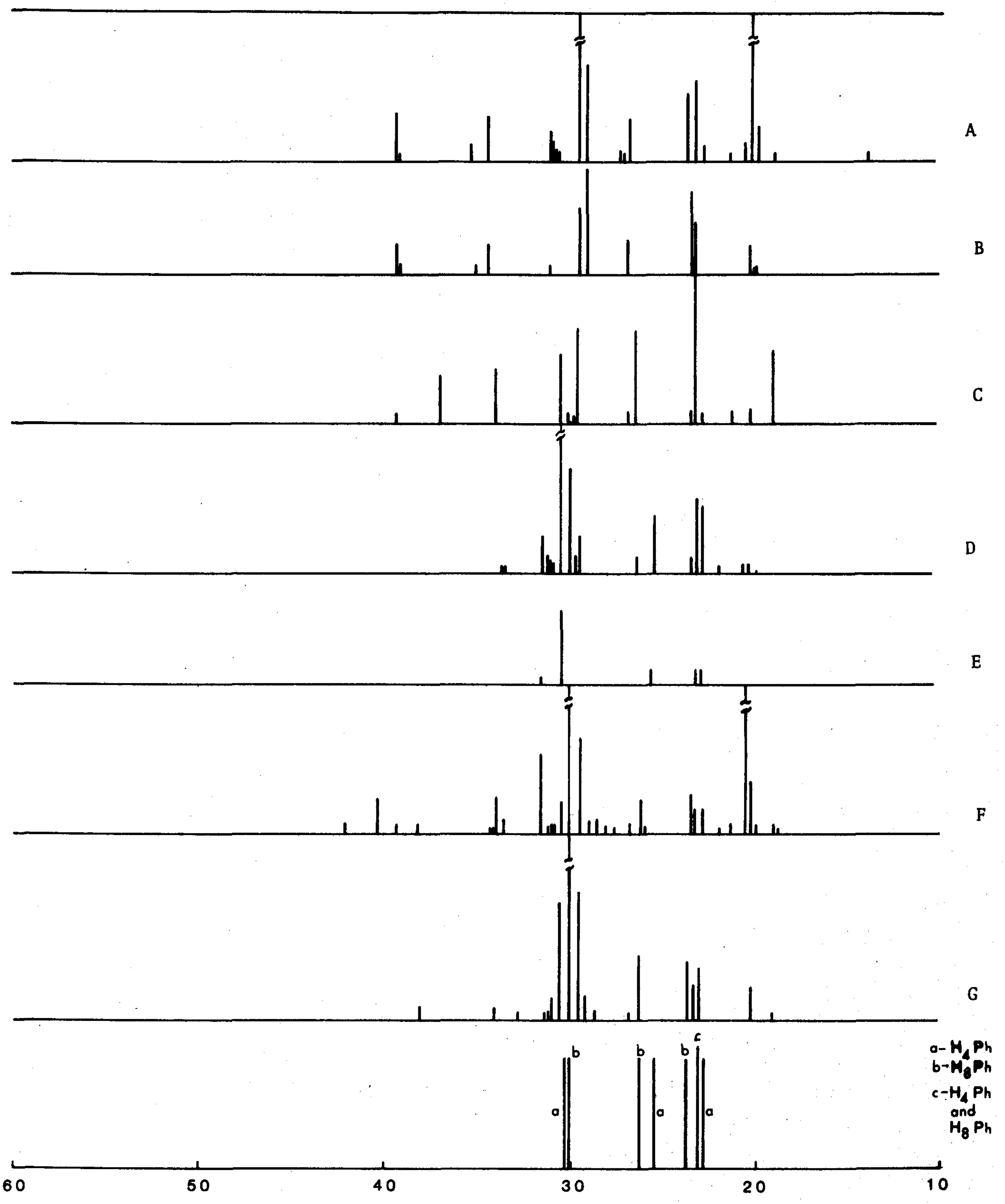


Figure 1 ^{13}C-NMR Spectra of Hydrophenanthrenes: Saturate Region

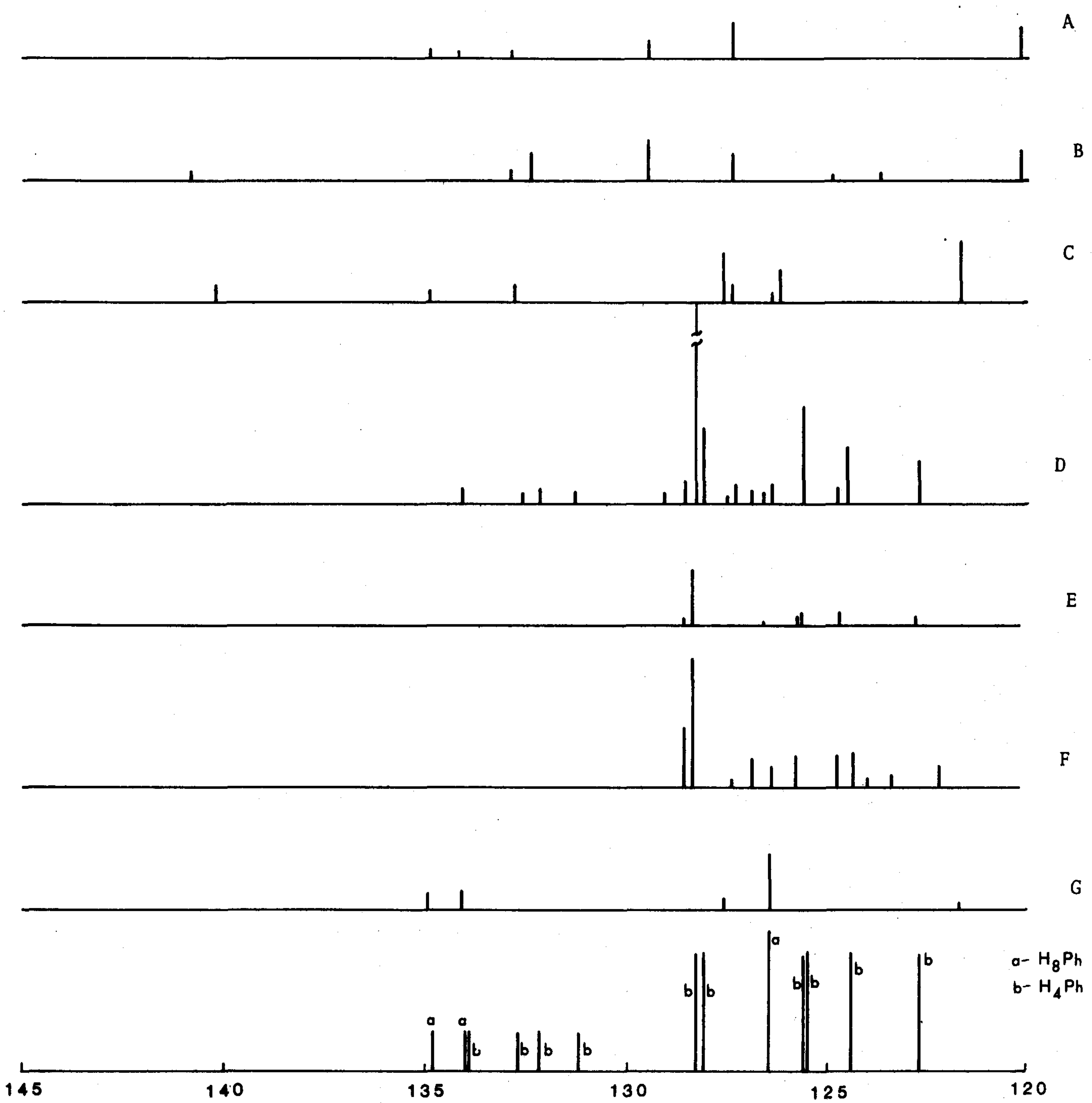


Figure 2 ^{13}C-NMR Spectra of Hydrophenanthrenes: Aromatic Region

☆U.S. GOVERNMENT PRINTING OFFICE: 1979 -640-014 4529 REGION NO. 4