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INVESTIGATION OF MECHANISMS OF HYDROGEN TRANSFER IN COAL HYDROGENATION

Annual Progress Report
for July 1976 to June 1977

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FOR JULY 1976 - JUNE 1977

ABSTRACT

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 at coal liquefaction conditions. 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. Aromatic ethers, sulfides and compounds having carbonyl, alcohol and hydroxylic 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 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 rearranged to form methyl indane-type compounds, thereby, resulting in a solvent of reduced hydrogen donor capacity. The study of hydrogen transfer using deuterium-tagged donor was not successful at temperatures above 400°C due to scrambling. It is anticipated that this latter experimentation will be successful at lower temperatures.

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.

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 is being carried out with each acceptor to develop a kinetic model of the transfer reaction. The second area consists of 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:

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.

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 schedule of experimentation is included herein as Figure 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 separate the role of dissolved hydrogen. Catalytic runs will also be made using finely divided catalyst and a high degree of agitation.

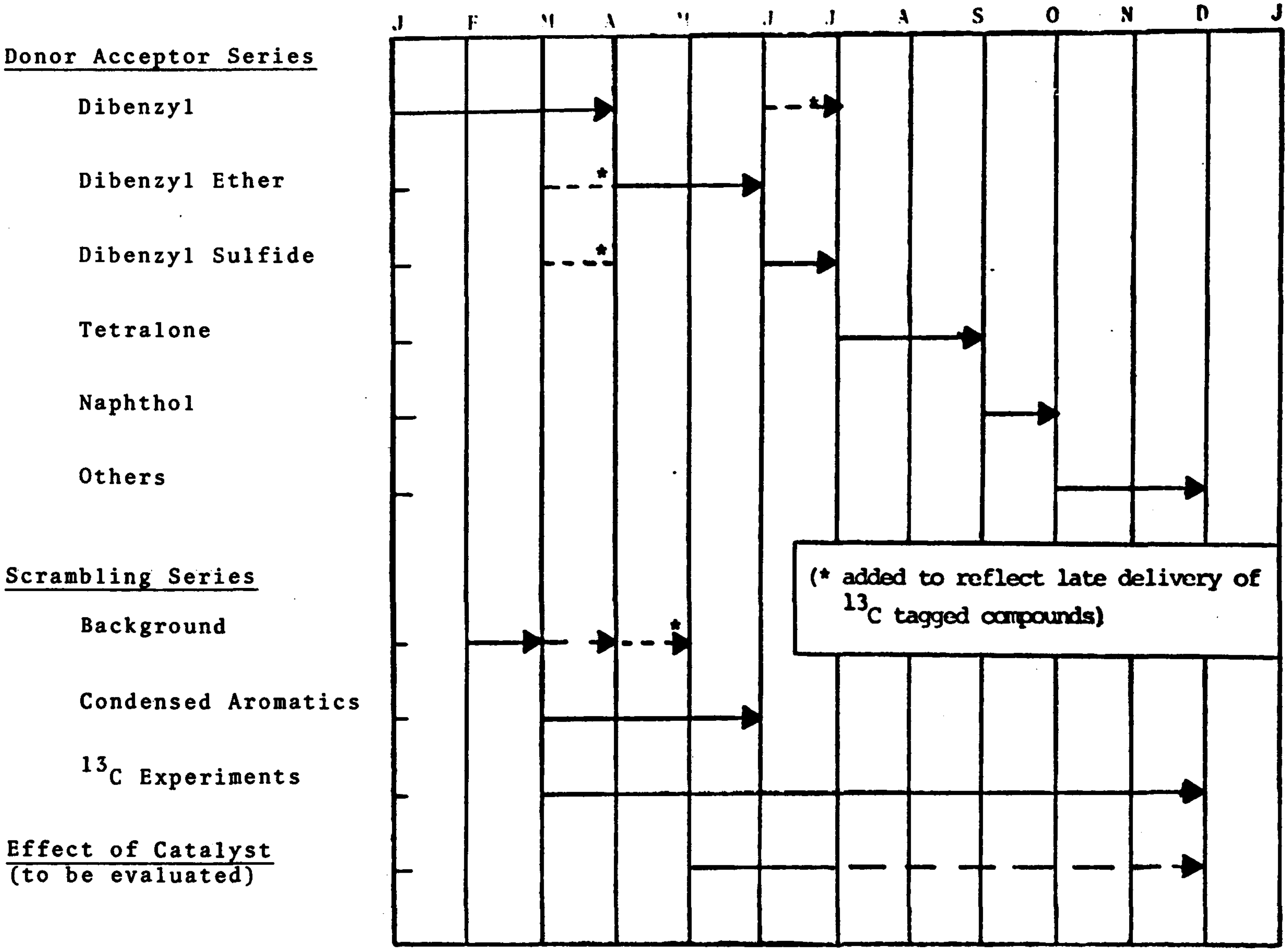
b. Perform necessary analytical work.

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.

Figure 1

Planned Experiments: Stage 2



(* added to reflect late delivery of ^{13}C tagged compounds)

NOTE: The above schedule is that of experimentation; additional time may be necessary to complete analysis.

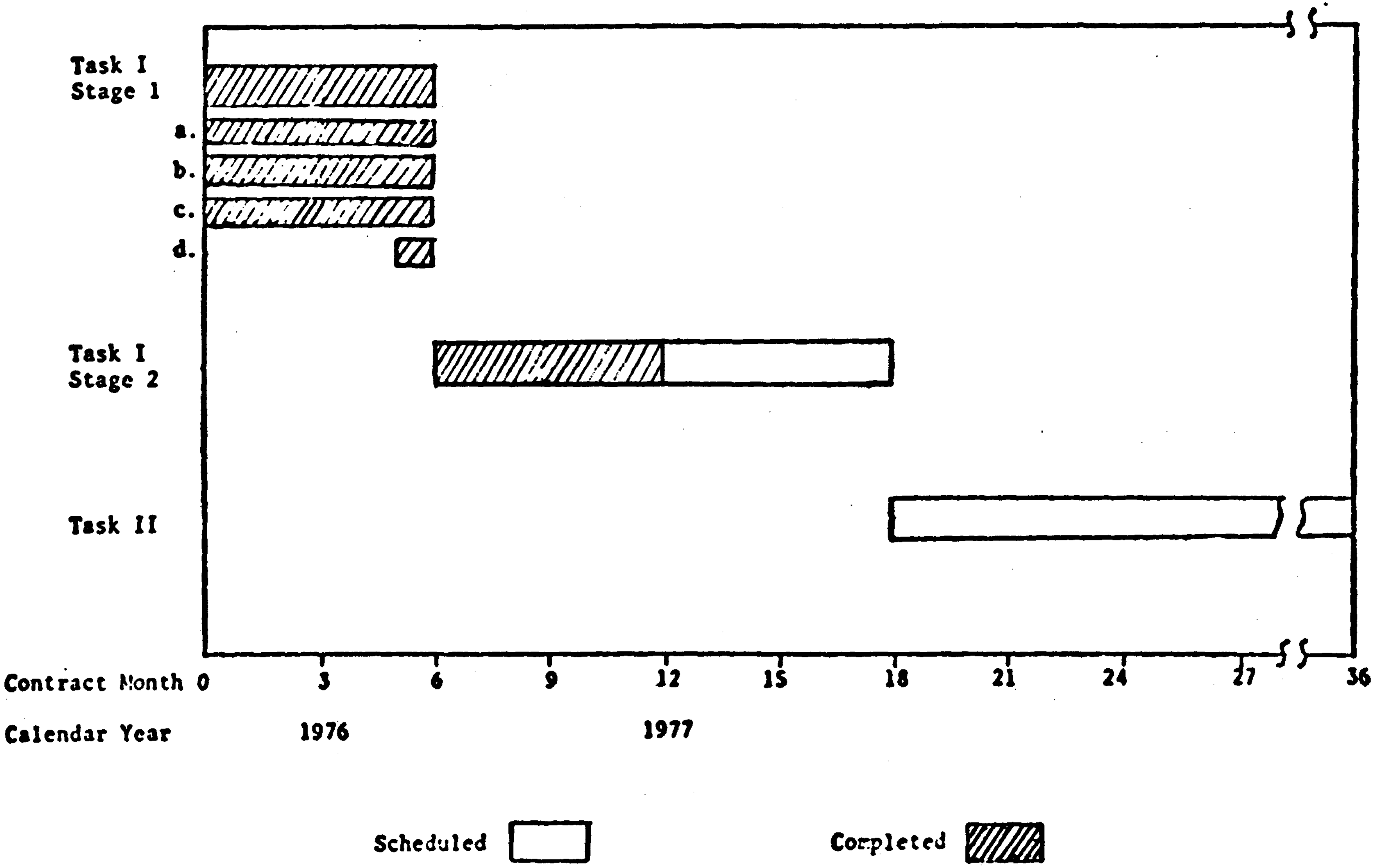
SUMMARY OF PROGRESS TO DATE

The project is continuing essentially on schedule. The screening experiments of Stage 1 were completed and reported in the Semi-annual Report. With respect to Stage 2, hydrogen-transfer experimentation with the system of dibenzyl with various donors has been completed. The data have been reduced to a form necessary to establish a reaction model. The resulting model fits the data very satisfactorily over the range of conditions studied. With the exception of three follow-up runs, hydrogen-transfer experimentation with the acceptor dibenzyl ether and isolated intermediate reaction products has also been completed. Kinetic expressions for the later reactions have been formulated. Experiments reacting deuterium-tagged tetralin with dibenzyl ether are under way. Some delays in operation of the analytical equipment had created a problem, but these have apparently been resolved. The preparation of most of the ^{13}C tagged donor solvent has been completed and experimentation is getting under way.

A copy of the program schedule is included as Figure 2. Reference is again made to Figure 1 for further details.

Figure 2

Program Schedule for Hydrogen Transfer Project



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 primarily consisted of a feed burette, Milton-Roy mini-pumps, a tubular reactor, a vapor/liquid separator, and let-down valves. The tubular reactor was 0.8 cm (5/16") inside diameter by 9.0 cm (35") length. It was packed with 10 to 40 mesh quartz beads. The feed rate was typically controlled for nominal space times of 50 to 120 minutes. Liquid feed was introduced at the bottom of the reactor. A schematic of the unit is shown in Figure 3.

The second unit consisted of a 300 cc batch stirred autoclave. The unit also had a 300 cc heated feed tank to provide for injection of reactants at elevated temperatures under pressure. A schematic of the experimental set-up is shown in Figure 4. In most of the runs, the desired amount (typically 75 grams) of donor was charged to the reactor and rapidly 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 heated 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 liquid chromatography as well as HPLC techniques.

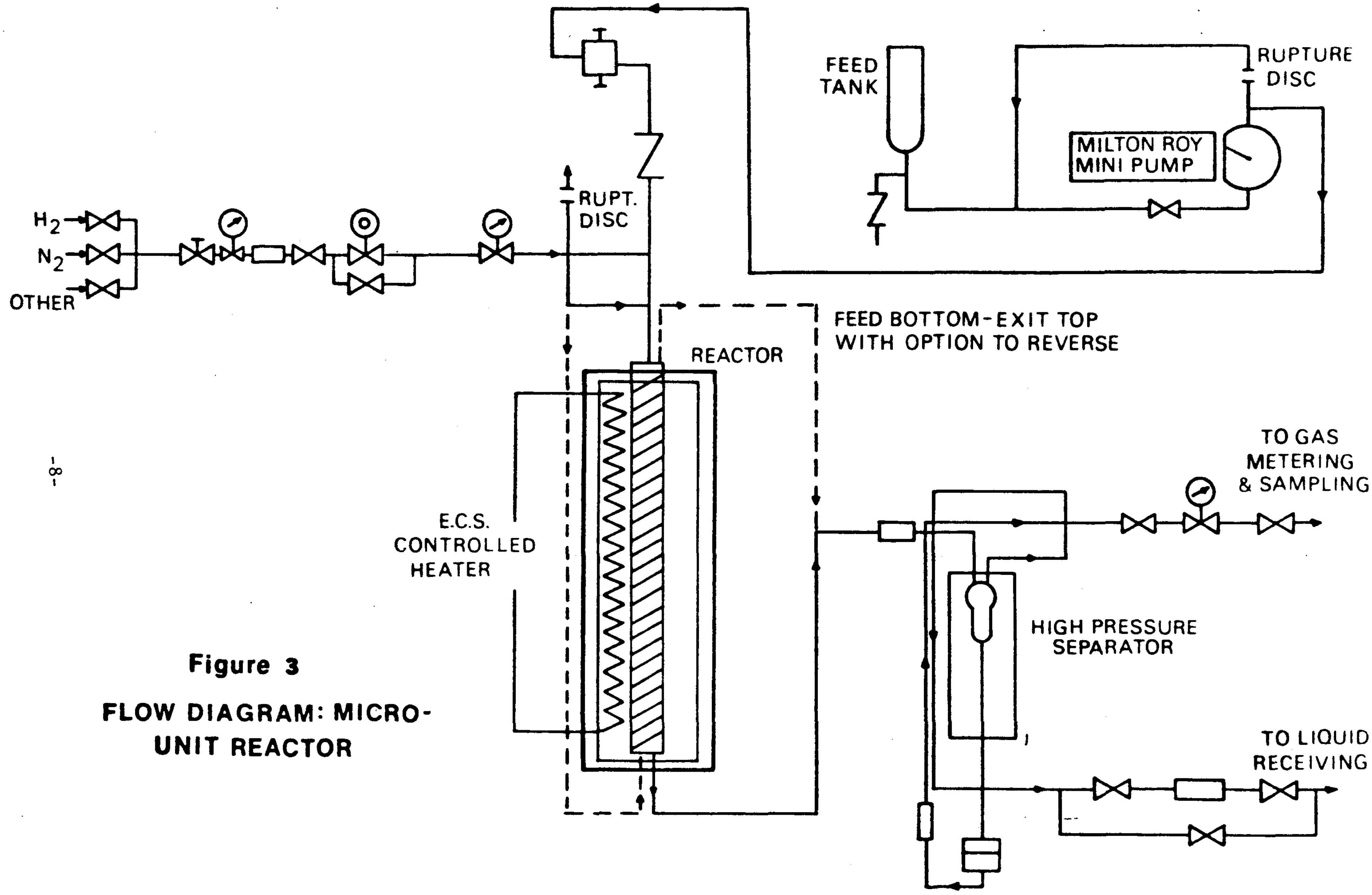
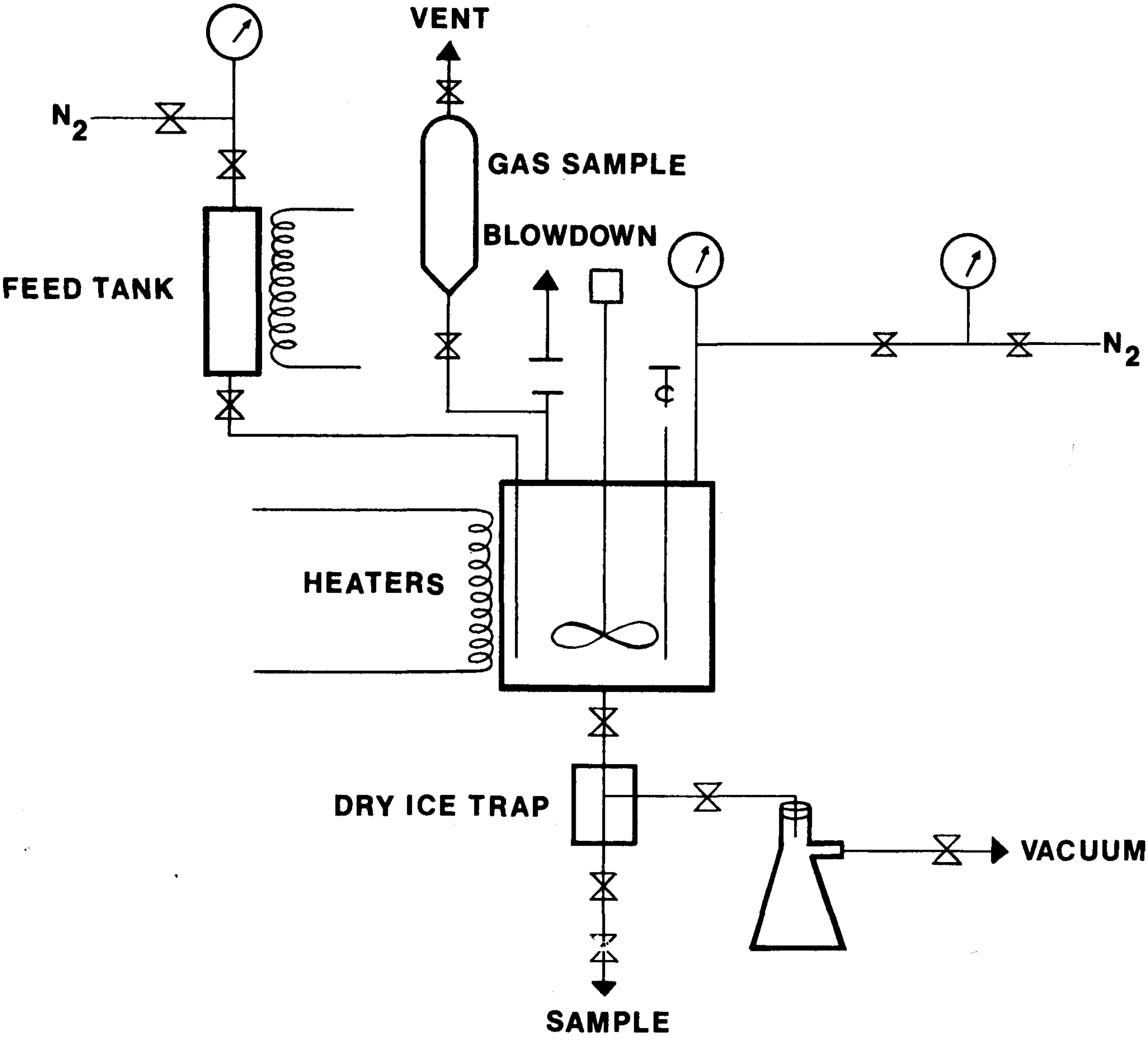


Figure 3

FLOW DIAGRAM: MICRO-UNIT REACTOR

Figure 4

SCHEMATIC OF EXPERIMENTAL UNIT



Further analysis of isolated products was carried out using a CEC-103 low voltage mass spectrometer and a CFT-20/FT NMR instrument with both hydrogen and carbon-13 probes. It is noted that low-voltage mass spectra were normally obtained only when a sufficient number of samples accumulated. The Isotron had to be replaced frequently when operating under conditions of low voltage.

For reference, a list of the experiments carried out in both the micro and autoclave units is included in Sections 1 and 2 of the Appendix.

B. Screening of Donors and Acceptors

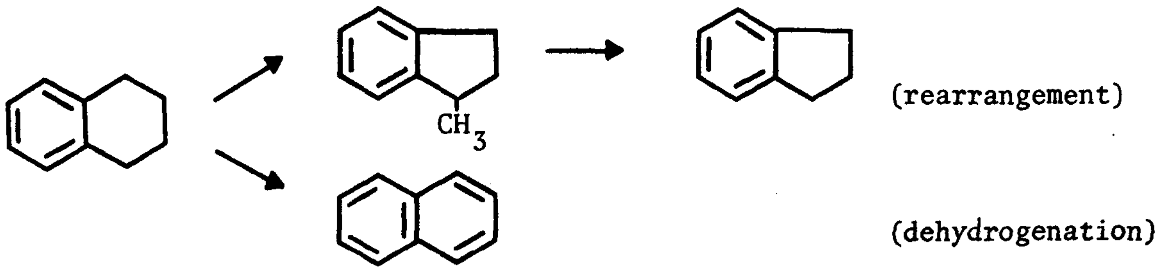
During the first six months (Stage 1) of experimentation, screening experiments were made to choose model donor and acceptor compounds that would be subsequently studied in depth. In this section of the report, the results of these initial runs are summarized.

1. Donors

The primary characteristics considered in the choice of donors were the following: (a) the known ability to donate hydrogen, (b) their existence in typical coal liquids, (c) availability and cost, and (d) 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.



To determine the extent of tetralin rearrangement, the reactor contents of batch autoclave experiments at 475°C and 3 hours residence time were analyzed. The results from runs with four acceptors are summarized in the following table.

Table I

Analysis of Residual Solvent and Products

(Batch Autoclave Runs: 3 hours at 475°C)

Component	Acceptor			
	N-Ethylcarbazole	Dibenzyl	Hexadecylether	Dodecyl ether
Indane	3.1	3.0	4.3	2.9
Methyl Indane	22.5	22.2	24.7	22.5
Tetralin	53.0	49.1	39.5	49.0
Naphthalene	10.5	12.8	18.0	12.9
Methyl Naphthalene	--	--	1.3	1.1
Acceptor + Others	10.9	12.9	12.2	11.6
Total	100.0	100.0	100.0	100.0

Considering that the initial reactor charge contained 90% tetralin, a sizable conversion to naphthalene and methyl indane occurred during the reaction period. With N-ethylcarbazole, very little hydrogen transfer was observed; therefore, solvent decomposition appeared to be primarily thermal. Dibenzyl, hexadecyl ether, and dodecyl ether appeared to abstract hydrogen from tetralin as indicated by higher naphthalene yields. The latter two "acceptors" also generated alkyl radicals which became attached to the naphthalene/tetralin system yielding stable methyl and dimethyl naphthalene products.

The above results are consistent with those observed during initial micro-unit experiments. In these runs, analytical techniques were still under development; therefore, unidentified peaks were combined and tetralin concentration changes were reported in terms of conversion:

$$\%\ \text{Conversion} = \frac{\%\ \text{in Feed} - \%\ \text{in Product}}{\%\ \text{in Feed}} \times 100$$

With the feeding of "purified" tetralin to the mico-unit at reactor conditions of 425°C and 450°C at space times of 105 minutes, conversion of tetralin to by-products was low (ca. 0.5 wt%). At 475°C, conversion increased to 2.3%. With the addition of phenanthrene (20 wt%), tetralin conversion increased to 3.5% at 425°C and 23% at 475°C. Apparently, 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. This rearrangement appears to occur even if essentially no detectable change of the acceptor is observed. The effect of temperature and acceptor concentration is shown in Figures 5 and 6.

As a result of the above experiments, an in-depth study of the rearrangement, cracking, and dehydrogenation reactions of tetralin in the presence of dibenzyl was undertaken. These experiments are discussed later in the 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 asymmetric isomer

FIGURE 5.

TETRALIN CONVERSION AS FUNCTIONS OF TEMPERATURE AND PHENANTHRENE LEVEL

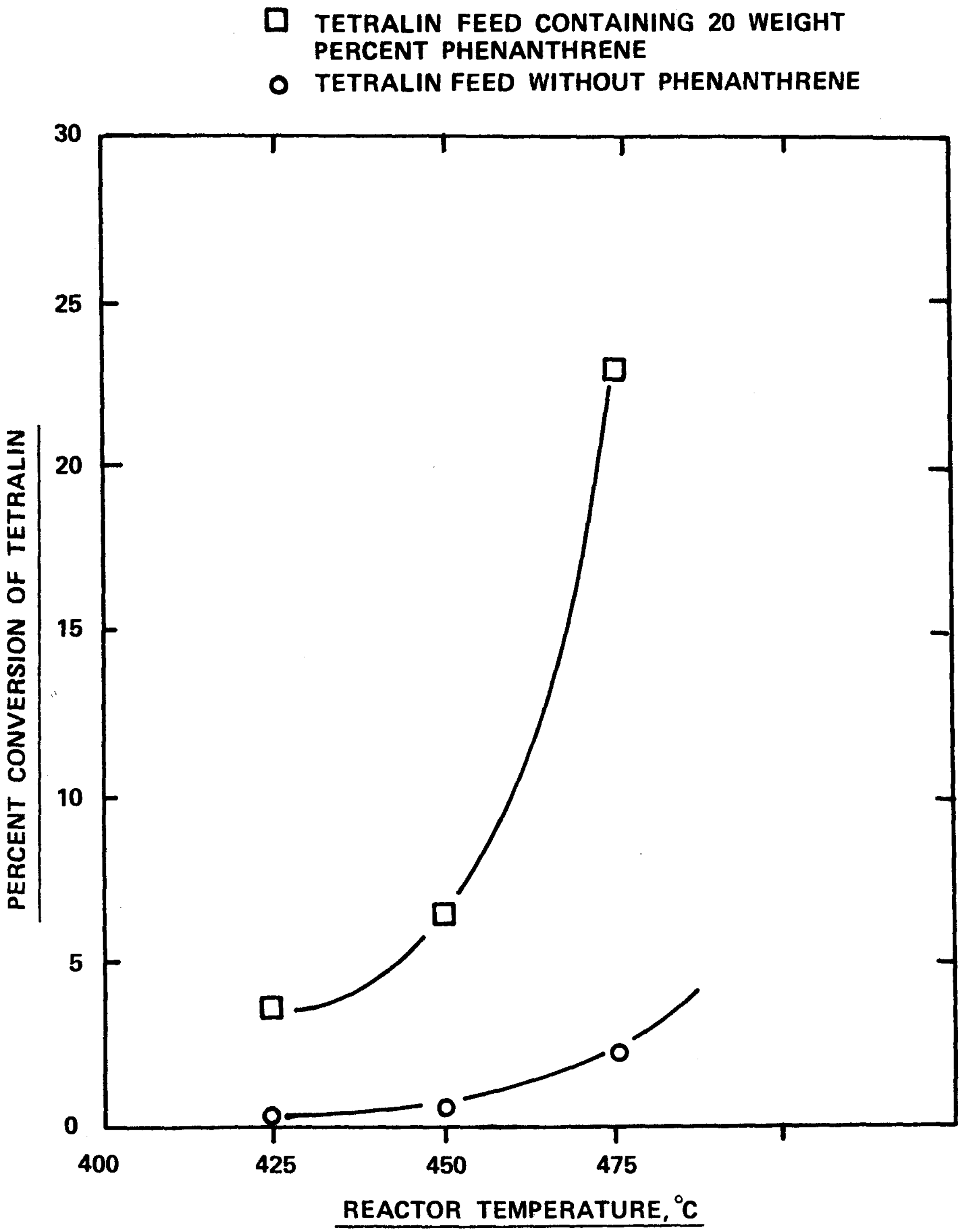
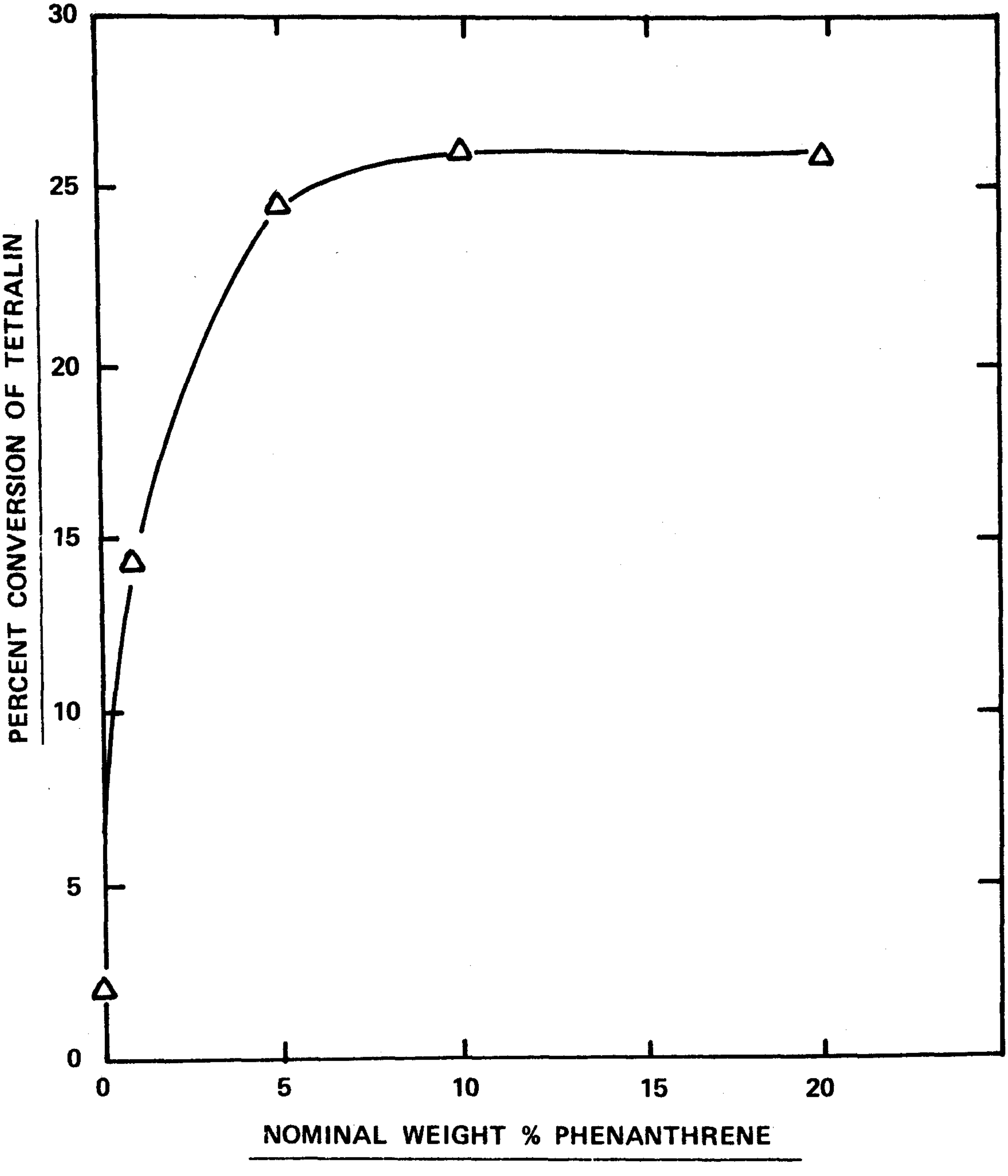


FIGURE 6

EFFECT OF PHENANTHRENE CONCENTRATION UPON TETRALIN CONVERSION



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, sub-bituminous coal, greater than 90% MAF solvation 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 < 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 Semi-annual report 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. Phenanthrene was converted to hydroaromatic derivatives at a level of 5-10% at 475°C. No cracking was observed. At lower temperatures, essentially no reaction was detected. Dibenzofuran and dibenzothiophene appeared to be inert in the autoclave experiments. No evidence of hydro-derivatives was detected. The N-ethylcarbazole underwent rearrangement to alkyl derivatives by migration of $-C_2H_5$ to ring positions; this was purely thermal and not due to any hydrogen transfer phenomena.

In the micro-unit experiments, limited conversion of the dibenzofuran and dibenzothiophene was observed. Specifically, about 10% reduction in dibenzofuran concentration was recorded at 475°C, and trace unknown product peaks were detected in the dibenzothiophene run.

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 reactor systems. The conversion levels in the micro-unit at nominal residence times of about 80 minutes were the following:

Temperature (°C)	375	425	475
Concentration, wt%			
Feed	10.5	10.5	9.0
Product	10.0	8.9	3.1

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.

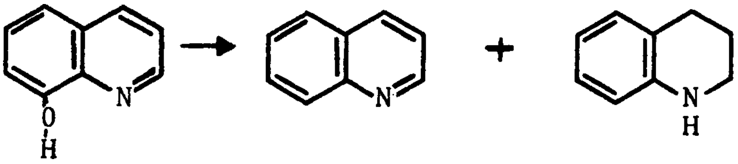
With the substitution of a heteroatom in the diaryl chain link (dibenzylether), high conversion levels were observed at temperatures over 400°C. The primary reaction products from the ether reaction were toluene and benzaldehyde.

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 quenching the cracking process.

d. α-Tetralone: This compound was chosen as an example of a carbonyl group which is probably present in coals. Figures 7 and 8 show the time-temperature-conversion plots of tetralin/tetralone reactions at 400° and 475°C. With the marked change in reaction rates, this will be a good oxygen-containing compound to study in developing the theory of hydrogen transfer mechanisms.

Analytical techniques have progressed to the stage of detecting low levels of an intermediate -OH group. GLC results indicated that α-tetralone is being directly dehydrated to tetralin with only minor conversion proceeding through an intermediate alcohol.

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, 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 in view of the presumed presence of hydroxy-quinoline structures in coal. This may be part of the reason why there appears to be a concentrating of basic functionality in asphaltene fractions.

C. Kinetics of Hydrogen-Transfer Cracking of Dibenzyl in Tetralin and Related Solvents

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

FIGURE 7

α TETRALONE CONVERSION PROFILE

(400 °C MAXIMUM TEMPERATURE)

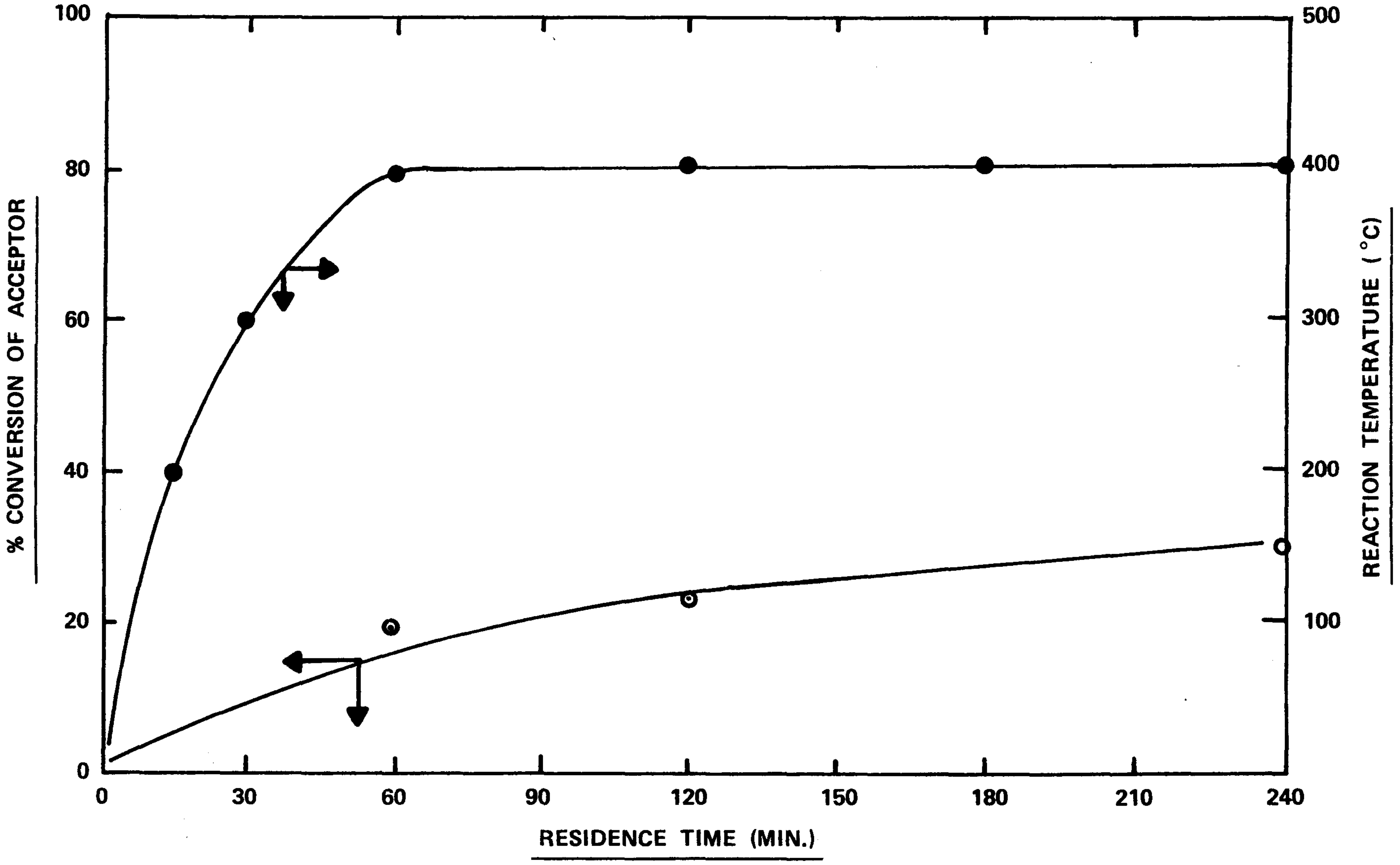
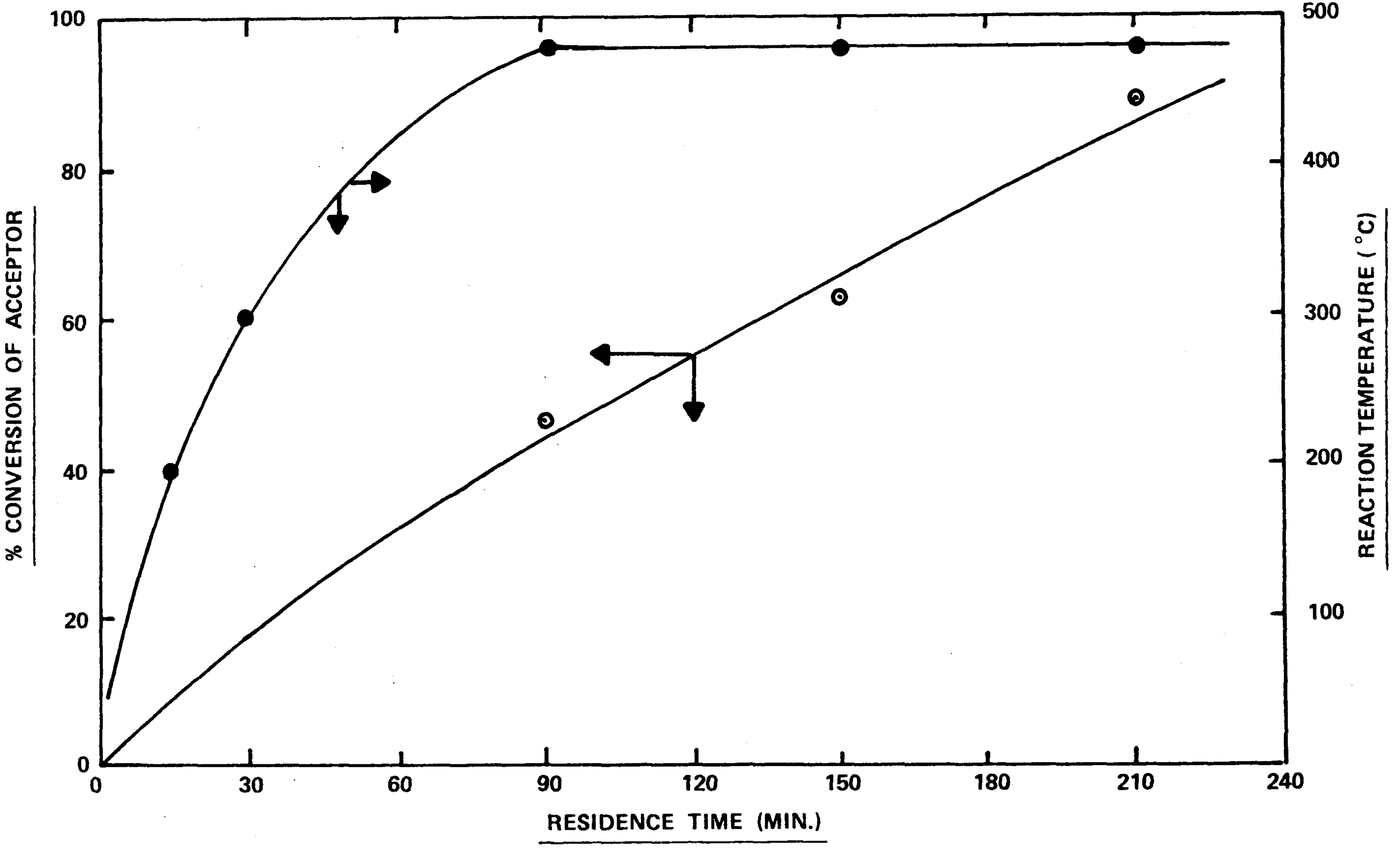


FIGURE 8

α- TETRALONE CONVERSION PROFILE

(475 °C MAXIMUM TEMPERATURE)



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

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

- 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 specific 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. The operating procedures discussed in Section A were used in these runs.

The wall of the reactor did not catalyze the reaction. As was verified for a typical case of 10% dibenzyl and 90% tetralin in nitrogen atmosphere at 450°C by adding mesh screens of the same material as the reactor wall. The conversions of both dibenzyl and tetralin did not change by the increase in metal surface area. The kinetic study reported here is, therefore, believed to be one of purely thermal hydrogen transfer reactions.

1. <u>Primary Reaction</u>

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

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

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

TABLE II

LIST OF EXPERIMENTAL SYSTEMS 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 + N_2	450
HT77-42-44	Dibenzyl (22%)	D_4 Tetralin (29%) + MST (49%) + N_2	400, 425, 450

where [Benzyl] represents the active benzyl free radical. As seen subsequently with each donor solvent, a number of secondary reactions also occur producing a variety of products. The mechanisms for these secondary reactions are more complex and differ with each solvent. They may involve the formation of more free radicals and a series of chain transfer reactions consisting of initiation, propagation, and termination steps. 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 dibenzyl conversion. However, if the first reaction is comparatively slower, the overall reaction, namely

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

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

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

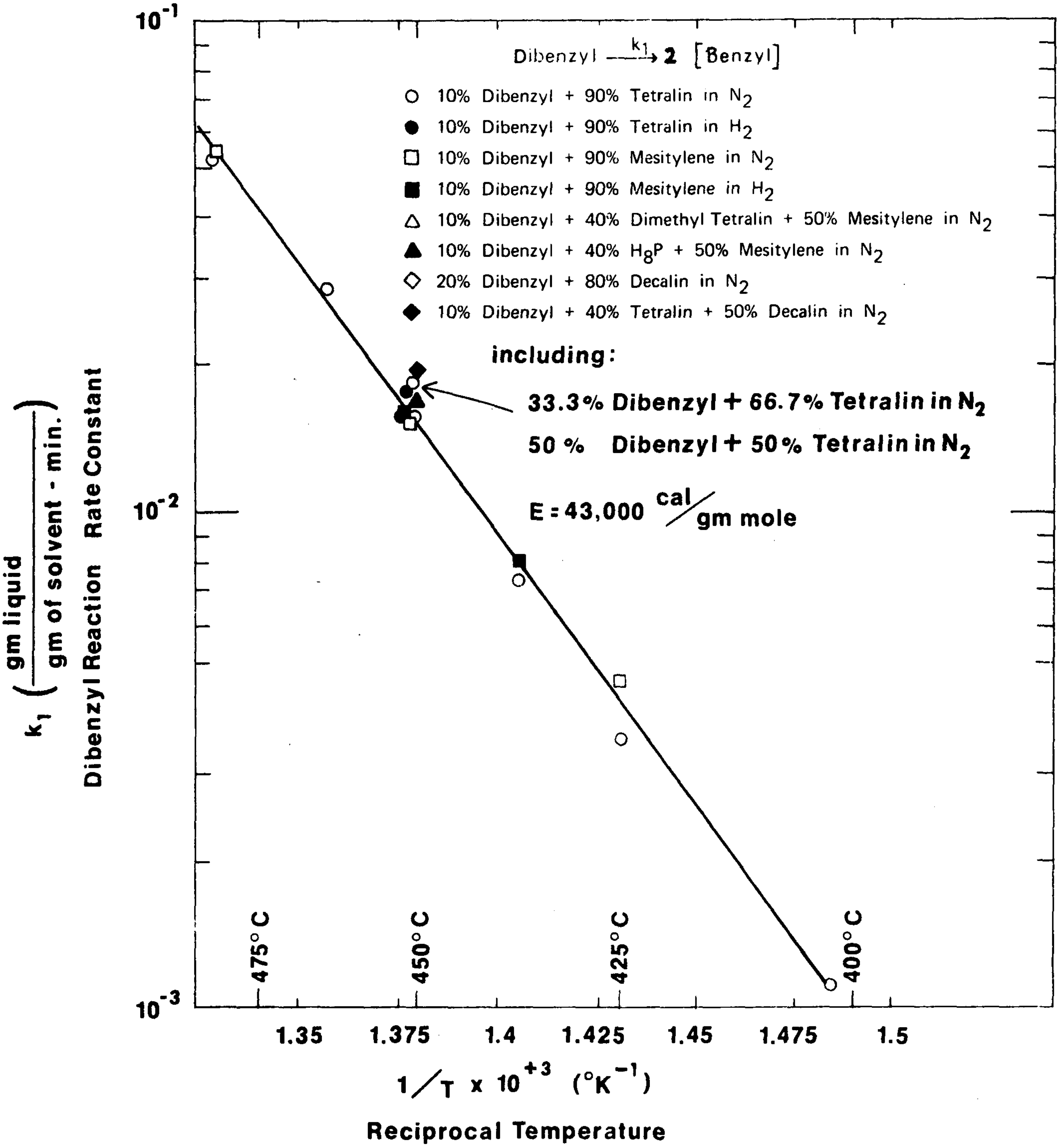
$$\frac{dC_B}{dt} = -k_1 C_B \qquad (4)$$

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 9. The activation energy for k_1 was found to be approximately 43,600 cal/gm mole. The fact that Equation (4) correlated the experimental data for all systems well implies that the benzyl free radical is very active and it readily reacts with any available solvent. Furthermore, recombination of benzyl free radicals does not occur at a significant rate. Combination of the benzyl radical with mesitylene radicals, however, can be a significant reaction

FIGURE 9

ARRHENIUS PLOT FOR THE PRIMARY DIBENZYL REACTION



in the absence of sufficient hydroaromatics. Combination of benzyl radicals with good donor solvent molecules, such as tetralin and octahydrophenanthrene, was not observed.

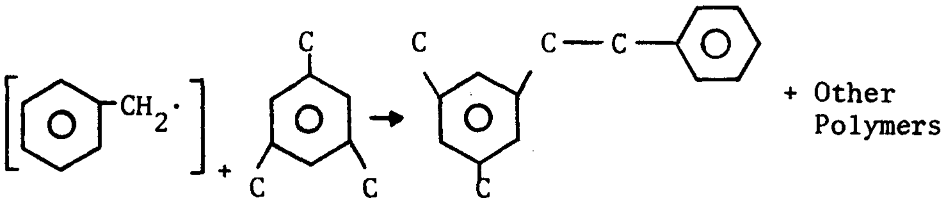
2. Secondary Reactions

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

a. Reactions with Mesitylene in Nitrogen: When mesitylene is used with dibenzyl in 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 products from this reaction may vary. Mesitylene can also react with benzyl radicals to form other polymer products:



(6)

[Benzyl] mesitylene MST/Toluene Adduct

Experimental data indicate that this reaction (6) may not be first order with respect to mesitylene concentration.

GC-MS studies were performed to identify major products. Some typical toluene and dimer concentrations obtained in these studies are shown in Figures 10 and 11. 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 in a nitrogen atmosphere [see reaction (5)]. The other secondary reaction (6) also occurs. Unlike the previous case, the presence of hydrogen

FIGURE 10

CONCENTRATION OF TOLUENE VERSUS TIME FOR A FEED OF 10% DIBENZYL WITH 90% MESITYLENE IN A NITROGEN ATMOSPHERE

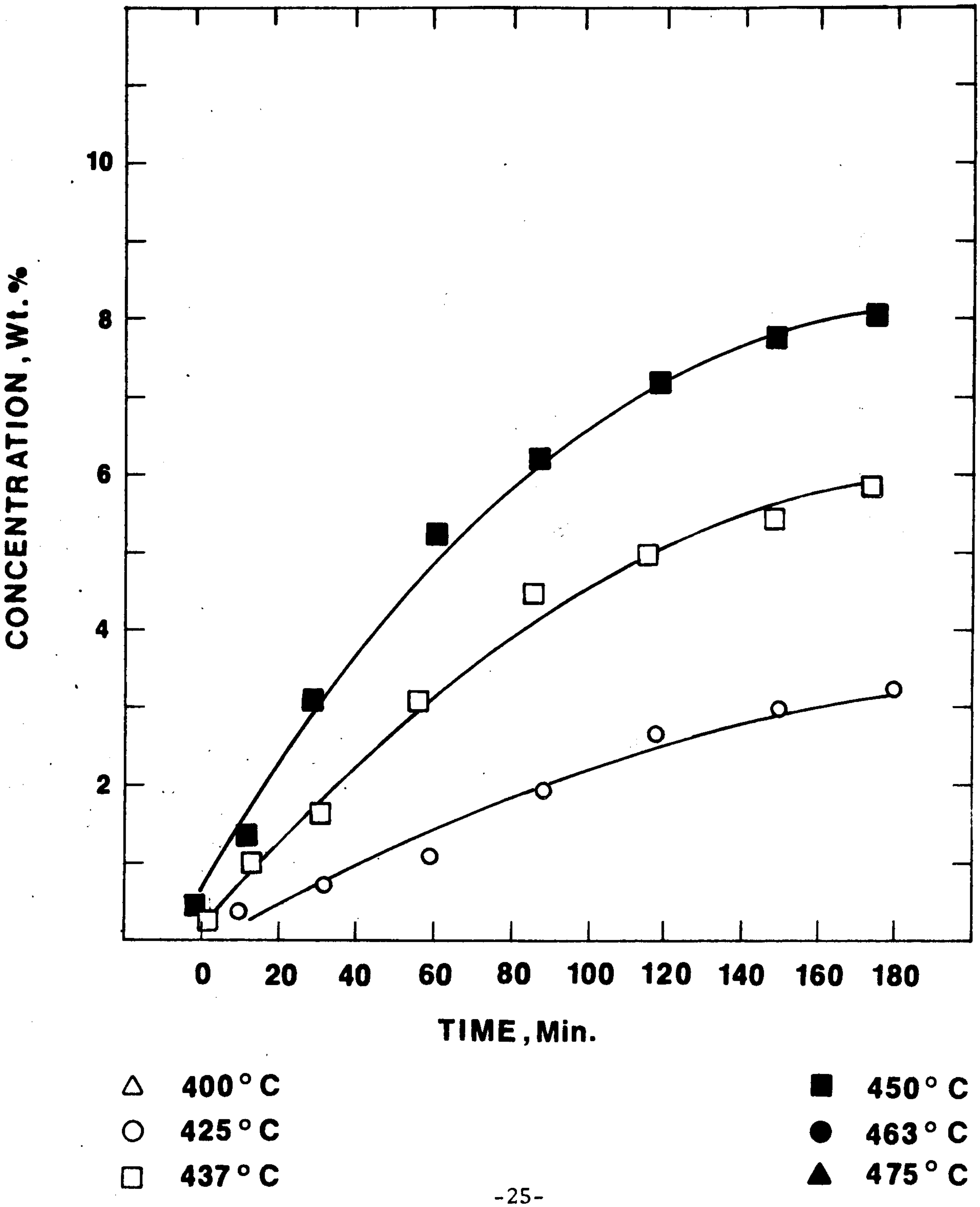
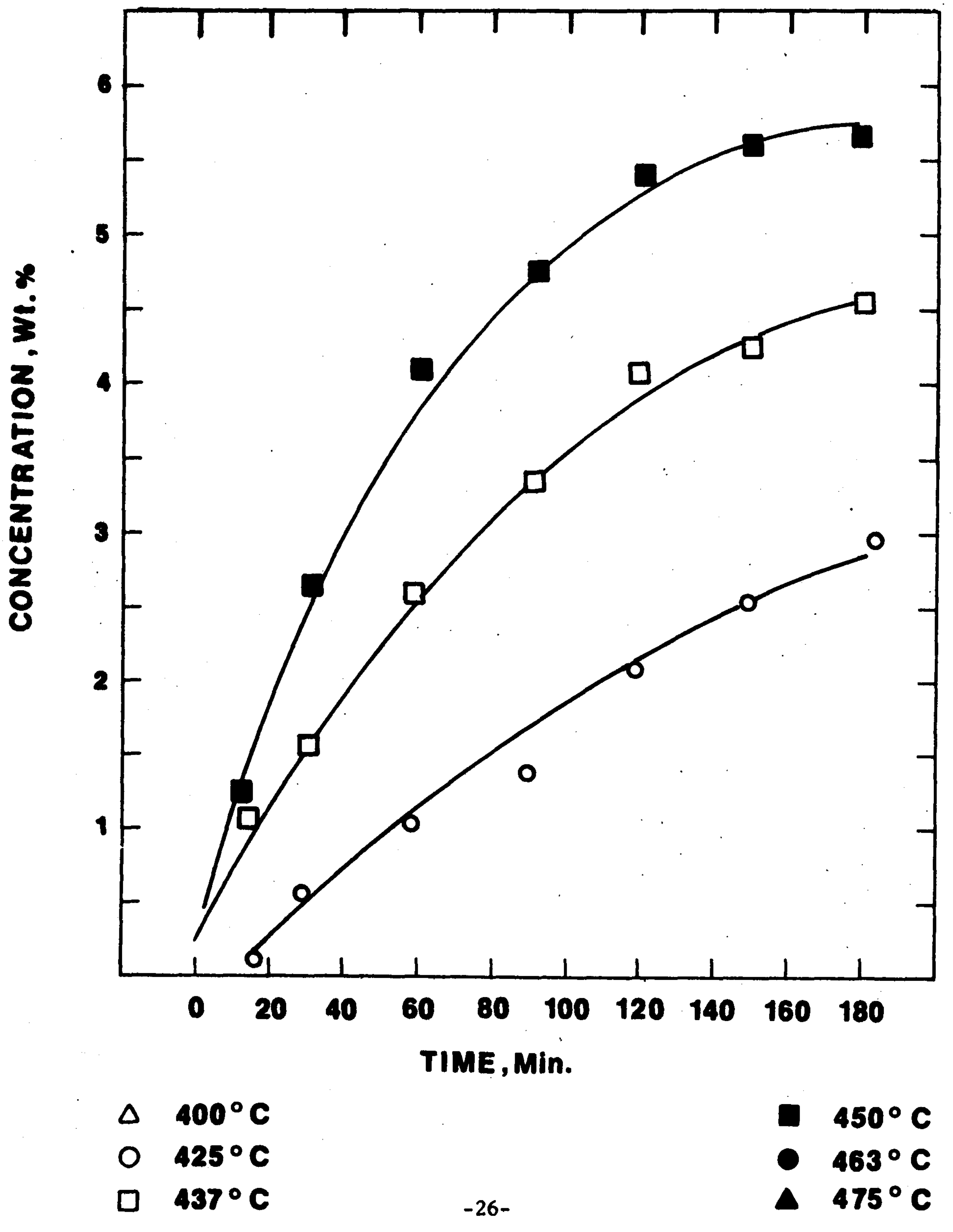


FIGURE 11

CONCENTRATION OF DIMER VERSUS TIME FOR A FEED OF 10% DIBENZYL WITH 90% MESITYLENE IN A NITROGEN ATMOSPHERE

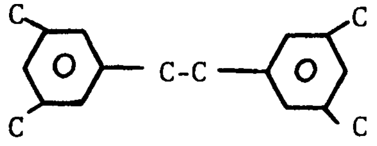


promotes cracking of mesitylene to form xylenes. Typical concentrations of cracked products in this system are illustrated in Figure 12.

The polymer product for the dibenzyl/MST system in either H_2 or N_2 is a family of polymers. Nearly all the polymers incorporate mesitylene or mesitylene fragments (xylene). The distribution of polymers 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 $-CH_3$ group.

The above dependence is illustrated by observing several GLC curves. Figure 13a represents an initial blend of 10% tetralin, 30% dibenzyl, and 60% mesitylene. Figure 13b shows the products of this blend after 30 minutes of reaction time in hydrogen atmosphere at 450°C. Toluene, naphthalene, and polymer products are present. Although tetralin remains, polymers begin to form. Polymers are not observed when tetralin is the only solvent. Figure 14 shows the final products after three hours of reaction time; tetralin is absent, the dibenzyl concentration is low, and a large variety of polymer products are present.

Figure 15 shows the typical product distribution for the dibenzyl/mesitylene system with a nitrogen atmosphere. Again, toluene and polymers are the primary products. It is noted that, in this case, one particular polymer is preferentially formed. This polymer has been identified as 3,3',5,5'-tetramethyl dibenzyl, which is the primary mesitylene dimer.



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

FIGURE 12

CONCENTRATION OF CRACKED PRODUCTS (BENZENE + ET.– BENZENE + XYLENES + LIGHT UNKNOWNS) VERSUS TIME FOR A FEED OF 10% DIBENZYL WITH 90% MESITYLENE IN A HYDROGEN ATMOSPHERE

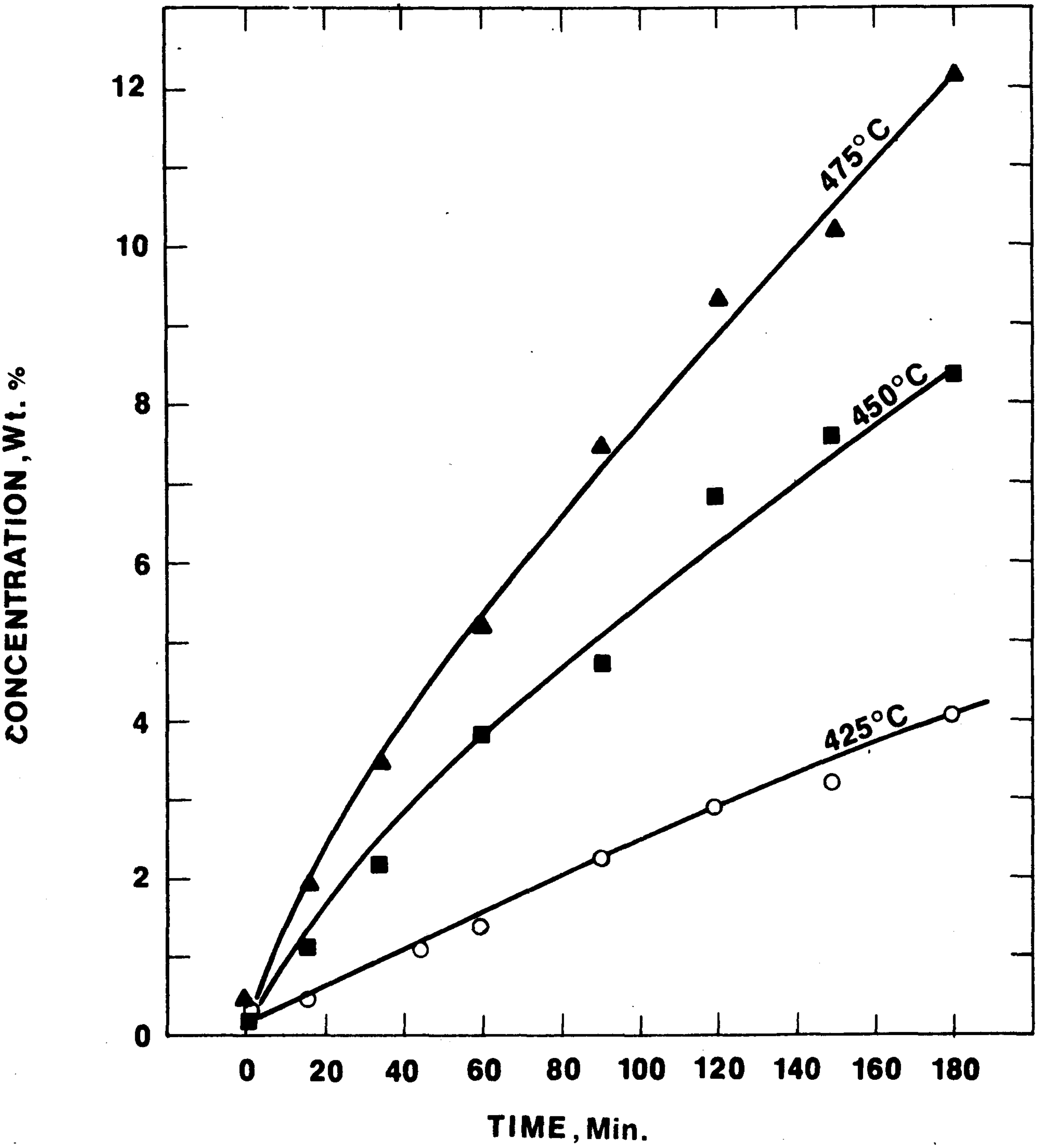


FIGURE 13A

DIBENZYL/MESITYLENE SYSTEM IN HYDROGEN ATMOSPHERE

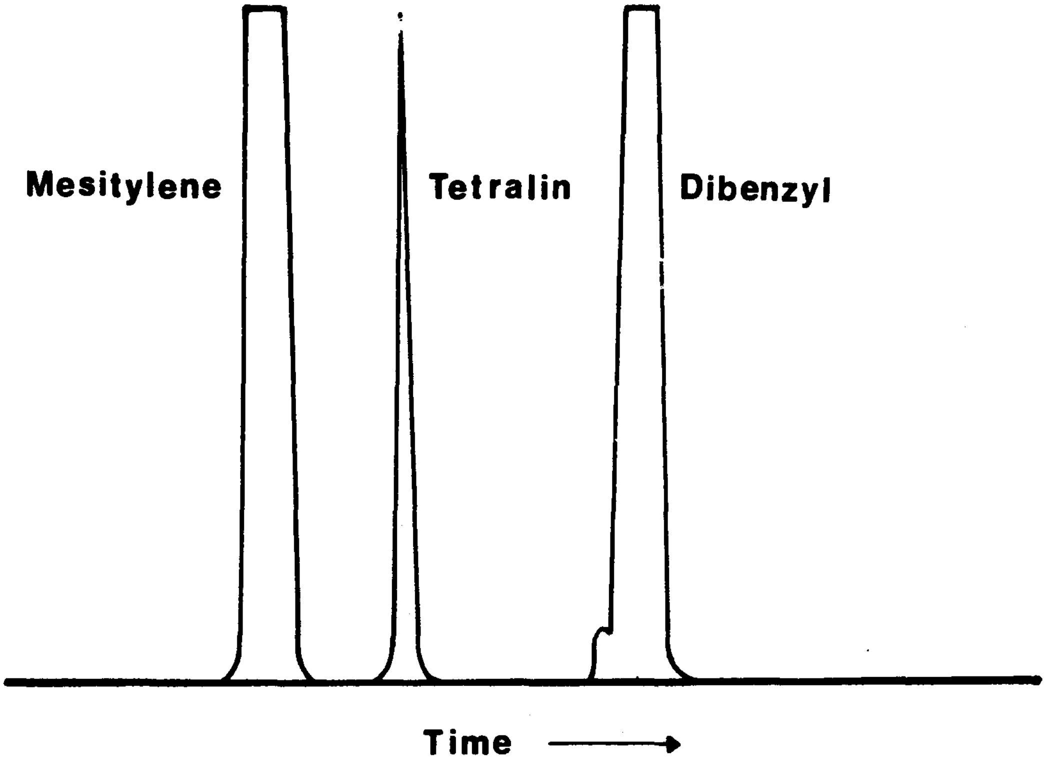


FIGURE 13B

DIBENZYL/MESITYLENE SYSTEM IN HYDROGEN ATMOSPHERE – 30 MINUTE REACTION PERIOD

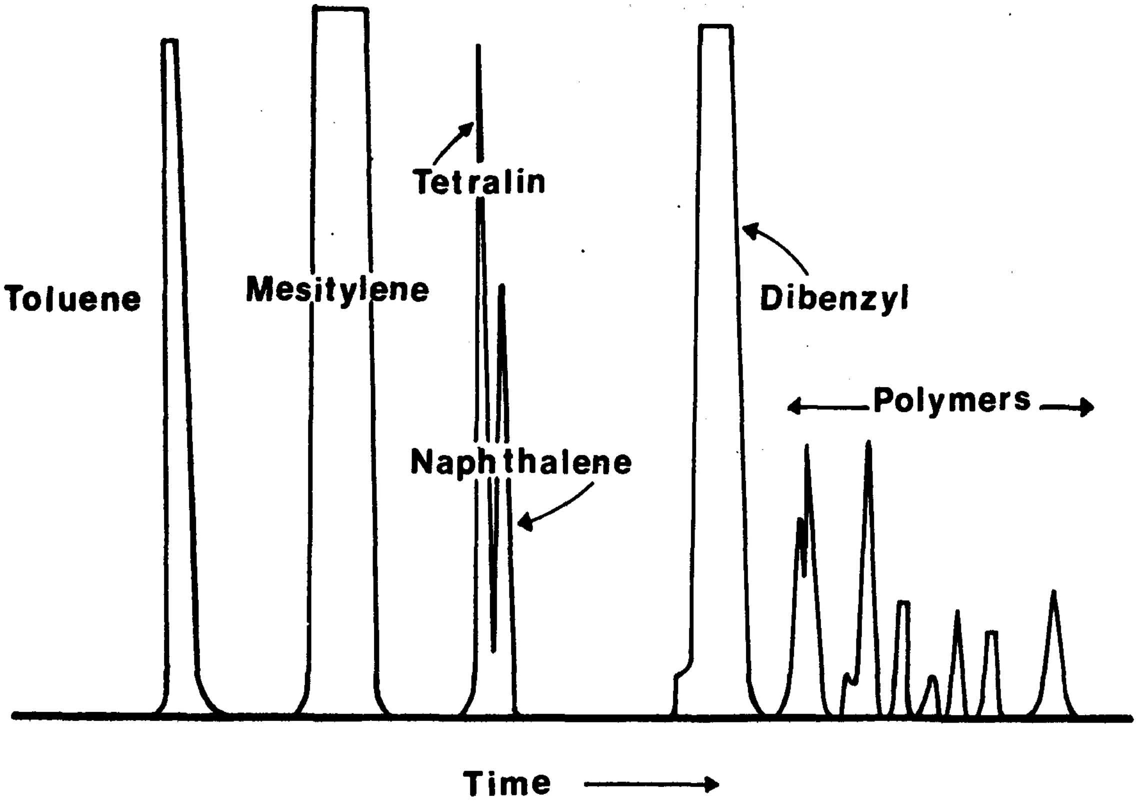


FIGURE 14

DIBENZYL/MESITYLENE SYSTEM IN HYDROGEN ATMOSPHERE – 3 HOUR REACTION PERIOD

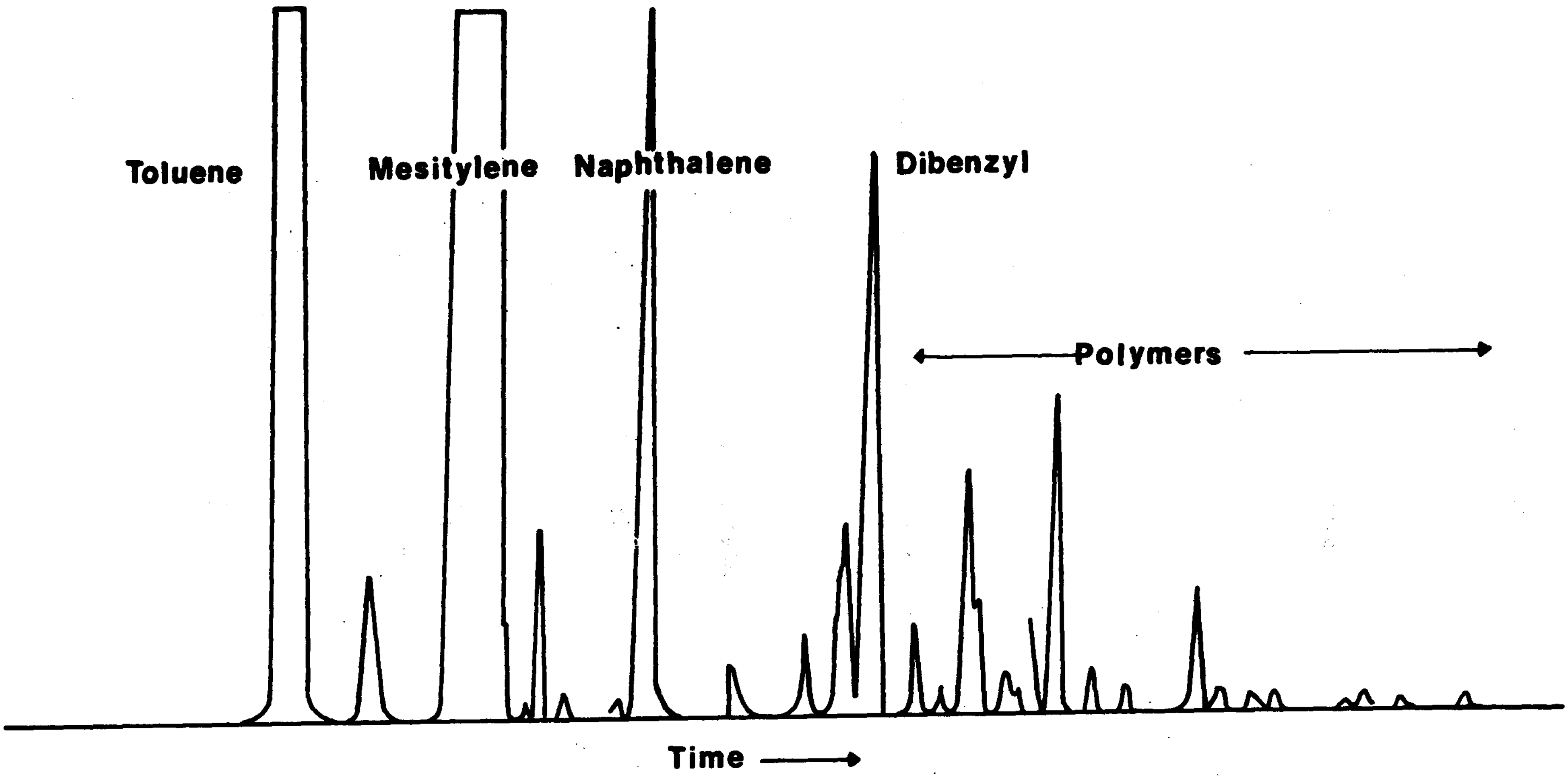
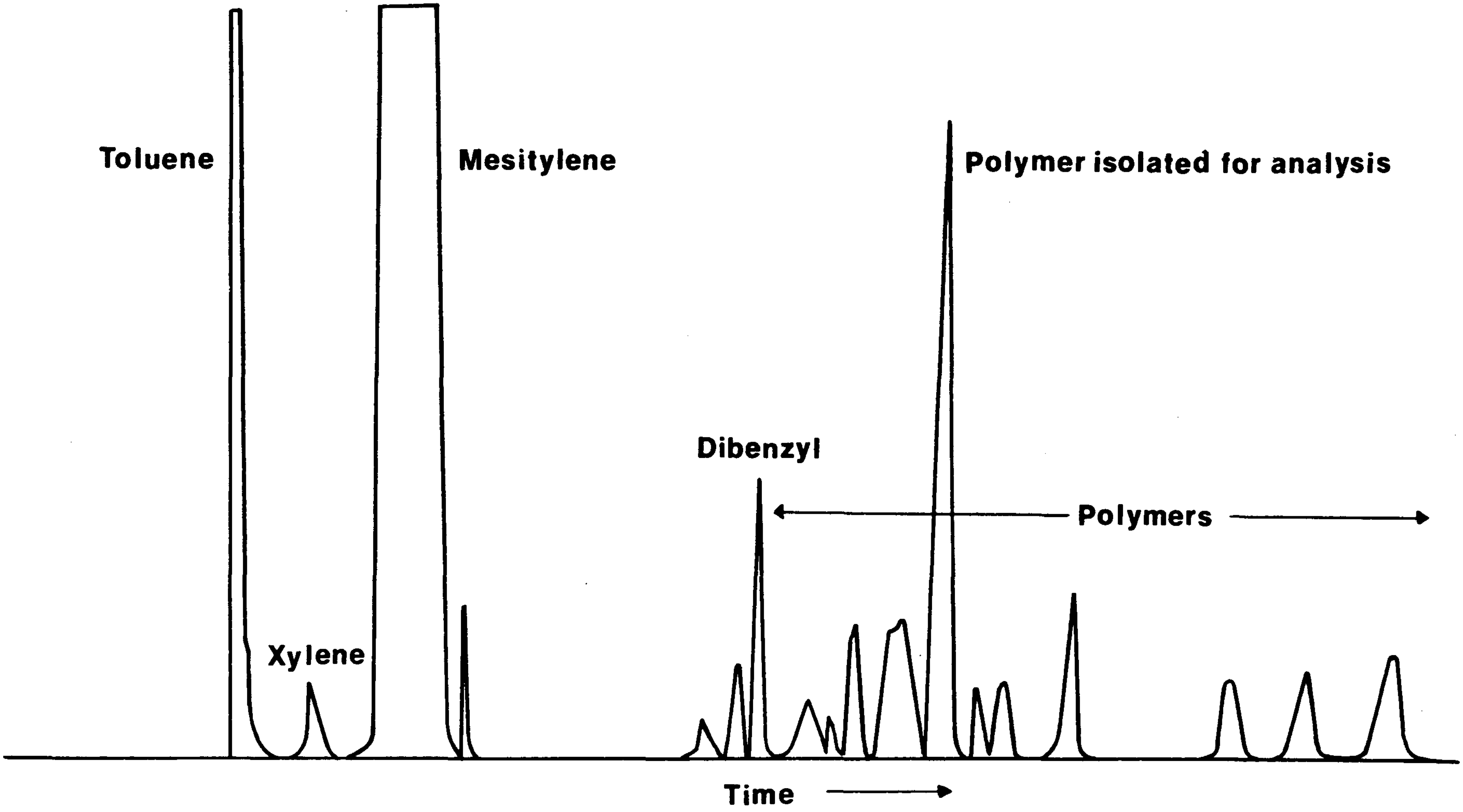
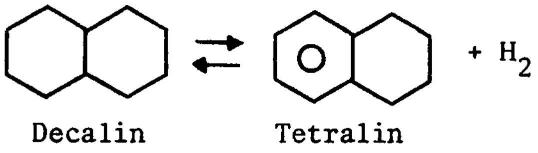


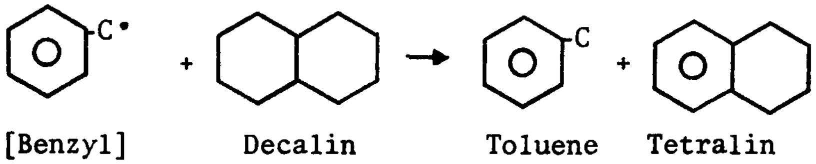
FIGURE 15

DIBENZYL/MESITYLENE SYSTEM IN NITROGEN ATMOSPHERE – 3 HOUR PERIOD

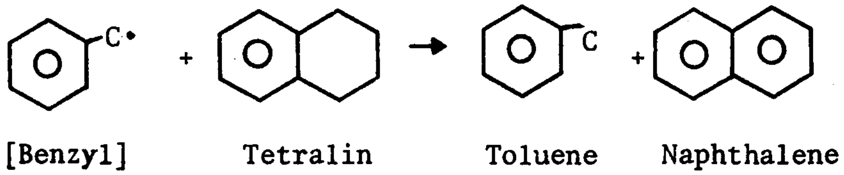




(7)



(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 the first route.

Results from experiments at 450°C and 3 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 16). These results imply that reaction (8) is considerably faster than the combination of reactions (7) and (8). Therefore, the controlling reaction for the dibenzyl/decalin system is reaction (8).

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 16). This implies that reaction (9) is more favorable than reaction (8), and tetralin is a better hydrogen source than decalin for the benzyl free radical. This is further substantiated by examining the productions of toluene illustrated in Figure 17. As shown in this figure, for a temperature of 450°C, the toluene production for the dibenzyl/tetralin system is very similar to the one for dibenzyl/tetralin/decalin system. However, both of these are considerably different from the one observed in dibenzyl/decalin system.

FIGURE 16

FORMATION OF NAPHTHALENE USING DIFFERENT FEEDS AT 450 °C

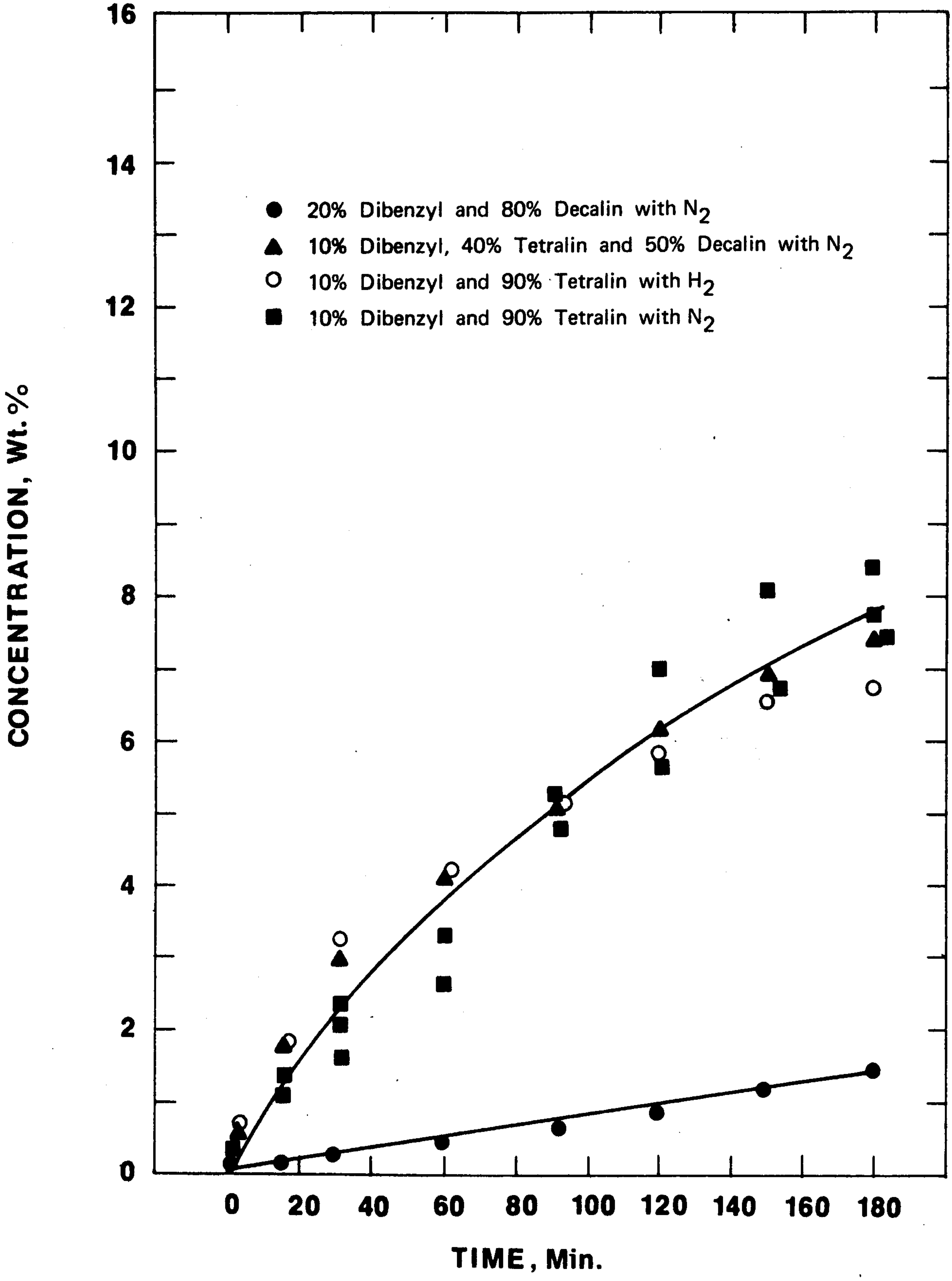
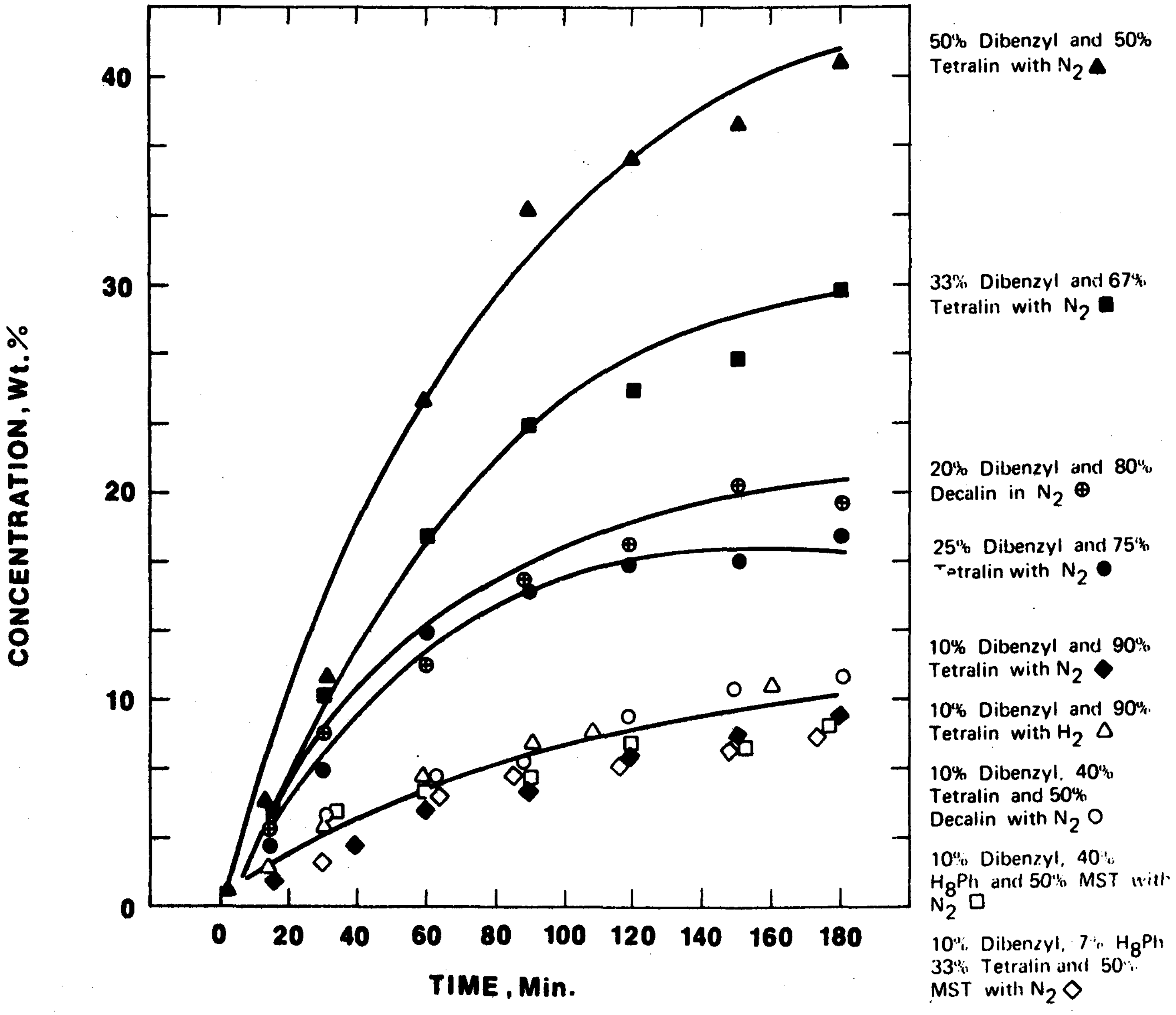


FIGURE 17

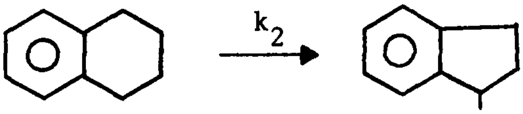
FORMATION OF TOLUENE USING DIFFERENT FEEDS AT 450 °C



The dibenzyl/decalin system produces more cracked products than the dibenzyl/tetralin system. This is illustrated in Figure 18 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 hydrogen atmosphere.

D. Rearrangement Reactions

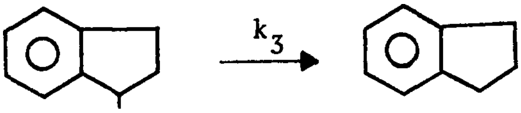
One of the most undesirable rearrangement reactions that occurs in the tetralin/dibenzyl system is



(10)

Tetralin Methyl Indane

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



(11)

Methyl Indane Indane

In the absence of reliable information, reaction (10) was assumed to be first order with respect to tetralin concentration. This model fit the experimental data very well. Figure 19 shows Arrhenius plots of k_2 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 hydrogen. The graph shows that while the presence of phenanthrene slightly alters the value of k_2, dibenzyl increases the rate constant by an order of magnitude. Therefore, the rearrangement to methyl indane is significantly promoted by benzyl free radicals.

FIGURE 18

CONCENTRATION OF CRACKED PRODUCTS (BENZENE + ET.–BENZENE + XYLENES + LIGHT UNKNOWNS) VERSUS TIME FOR DIFFERENT FEEDS AT 450 °C

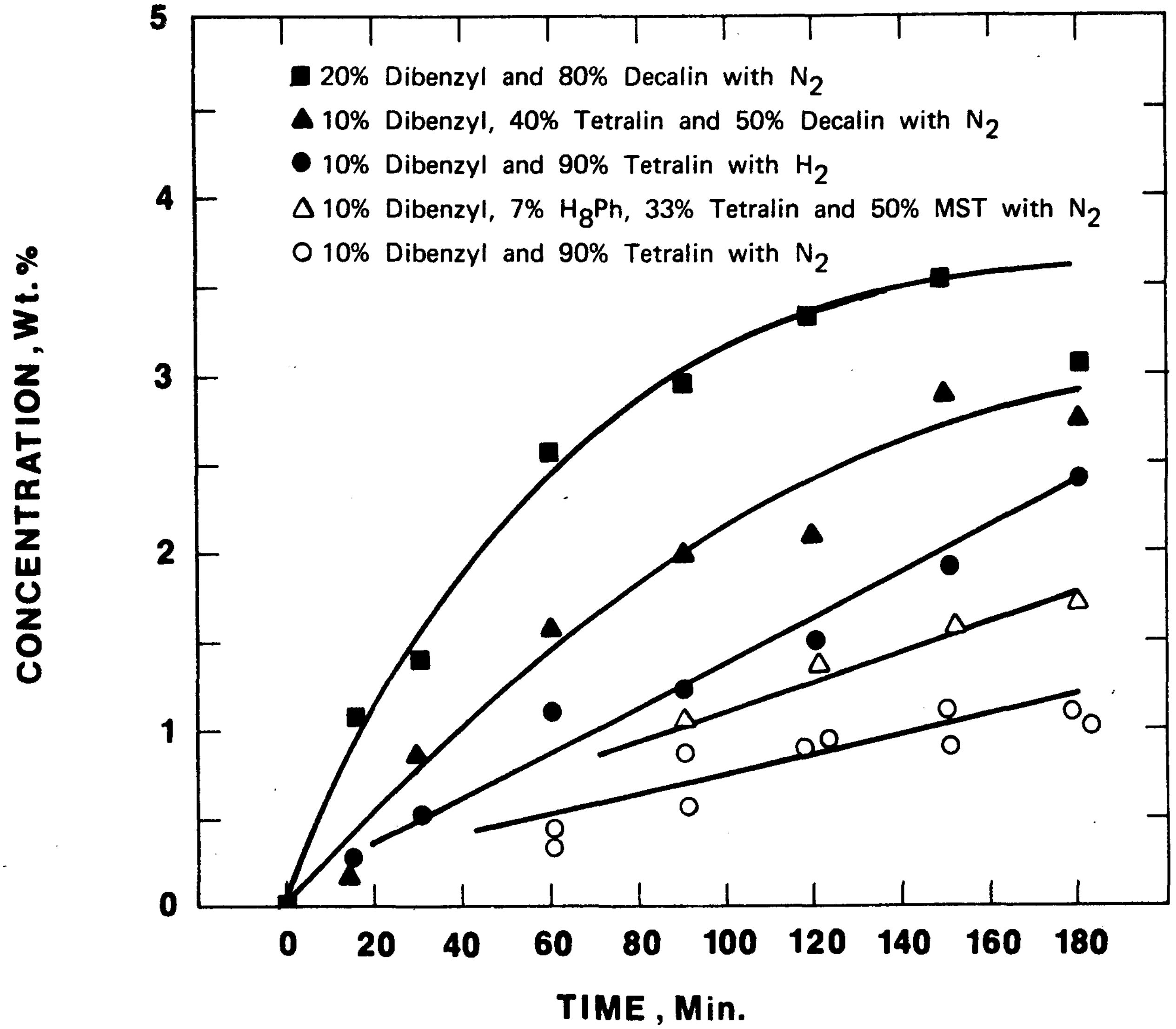
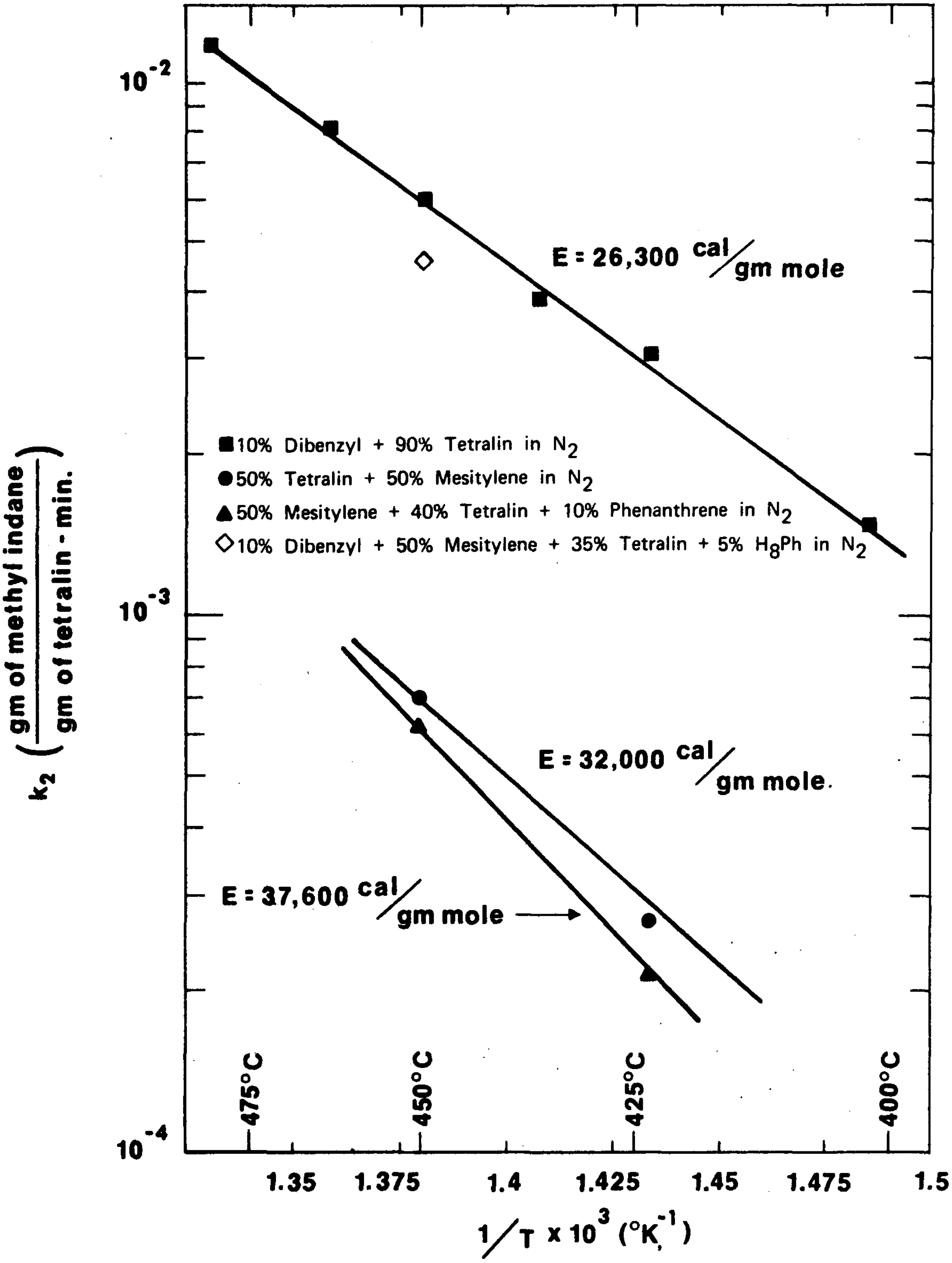


FIGURE 19

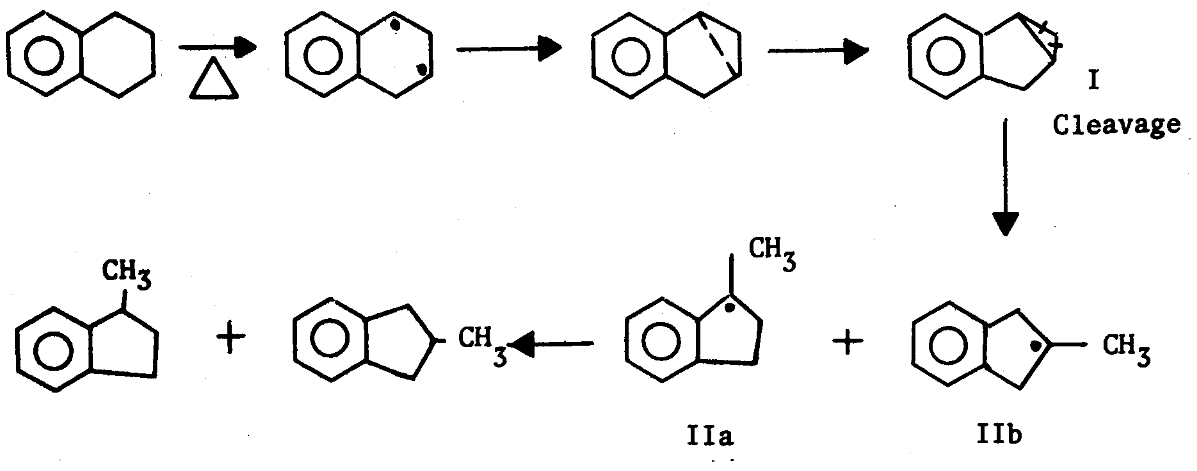
ARRHENIUS PLOT FOR THE TETRALIN FORMING METHYL INDANE REACTION

$$\text{Tetralin} \xrightarrow[k_2]{} \text{Methyl Indane}$$

First order with respect to Tetralin

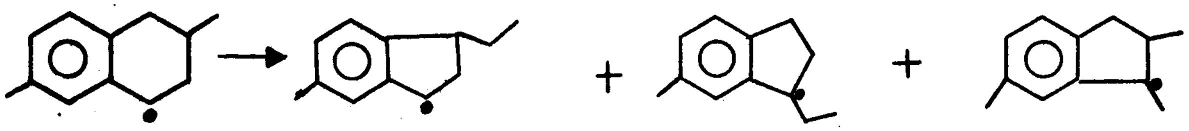


Tetralin rearrangements can be depicted as proceeding through three-membered ring intermediates:



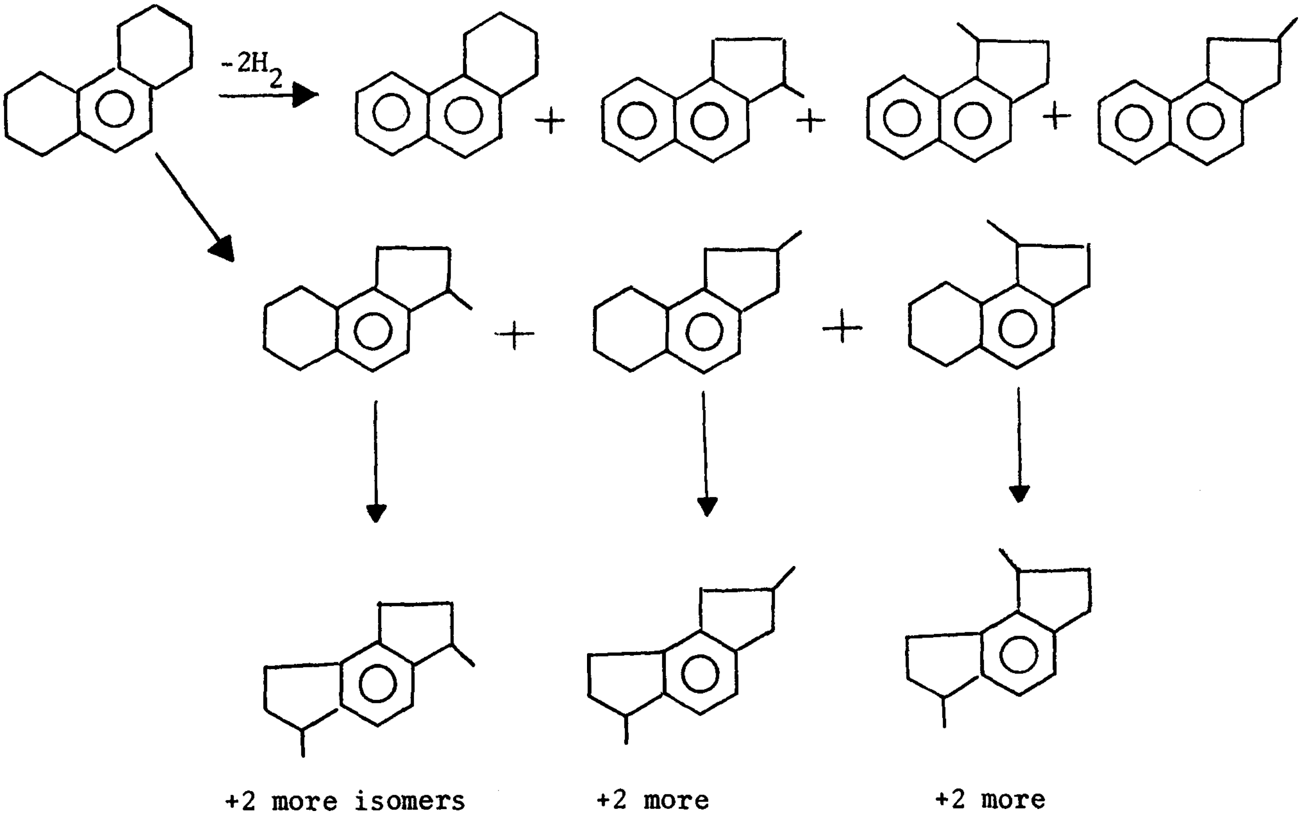
Although intermediate-I is a known compound,(2) the three-membered ring will cleave at 400°C to generate radicals IIa or IIb and finally the methyl indanes. The common observation of the 1-methyl indane isomer can be attributed to greater stabilization of the benzyl radical IIa.

Due to the importance of this rearrangement to donor solvent chemistry, these reactions are being studied with a substituted tetralin and octahydrophenanthrene. Assuming that the above mechanism is applicable, 2,6-dimethyl tetralin may rearrange to the following major products:



This reaction has been made, and a number of products observed. Isolation and identification by liquid chromatography and C-NMR techniques are under way. Since a ^{13}C label has been placed on C-4, the assignment of all carbons in the NMR spectra should be simplified.

sym-Octahydrophenanthrene (H$_8$Ph) 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 are now being carried out. The following structures are possible products:



The fact that sym-H$_8$Ph is indeed unstable at 450°C is illustrated by Figure 20 which shows that after 3 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.

By combining liquid chromatography, GLC-MS, and C-NMR, partial identifications have been made. Figure 21 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 C-NMR evidence for methyl groups on the β-positions of the five-membered rings has been obtained. These studies are continuing with the ^{13}C-labeled H$_8$Ph to better understand and

FIGURE 20

STABILITY OF OCTAHYDROPHENANTHRENE AT 450 °C

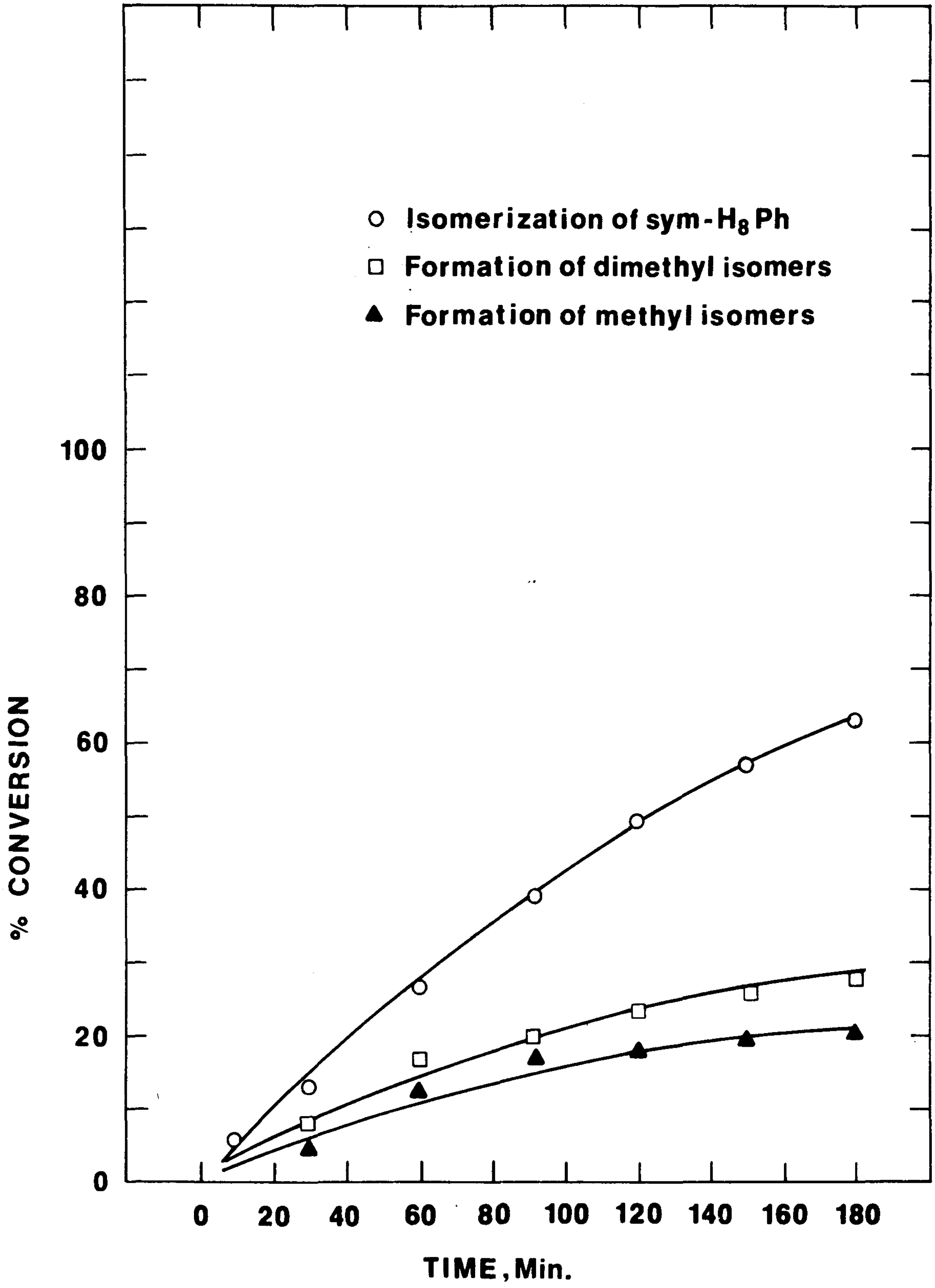
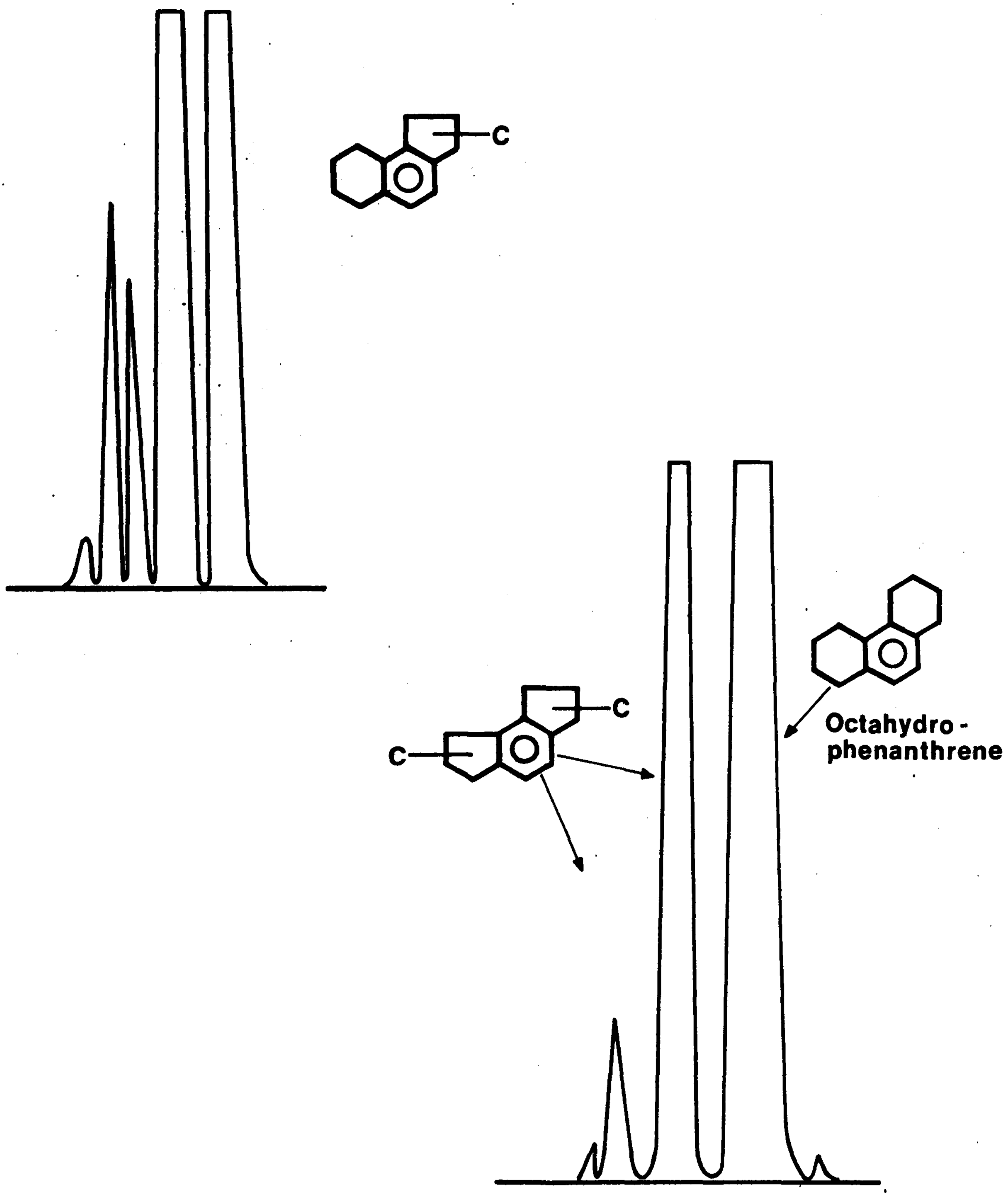


FIGURE 21

ISOMERS OF OCTAHYDROPHENANTHRENE SEPARATED BY LIQUID CHROMATOGRAPHY AND GAS–LIQUID CHROMOTOGRAPHY

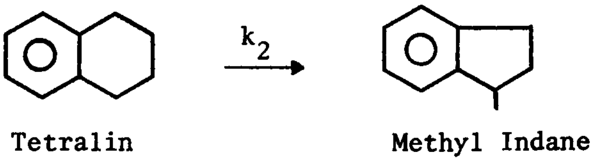


assign the structures. ^{13}C-NMR spectra of pure sym-H_8Ph, ^{13}C labeled sym-H_8Ph, the monomethyl rearranged derivative and the di-methyl rearranged derivative are shown in Figures 22 through 25.

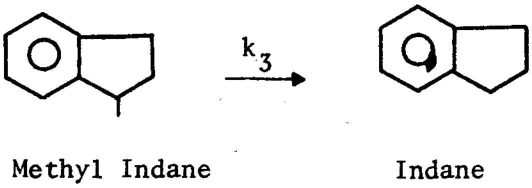
These studies are particularly relevant to coal liquefaction processes that depend on good donor solvents. The rearranged hydroaromatics are very stable to further dehydrogenation (do not transfer hydrogen) and readily dealkylate. The reactions are, for practical purposes, irreversible. Since the products are isomers, mass spectrometry cannot detect the non-donor species. These reactions imply that with either high temperatures, long reaction times, or recycle operations, the composition of donor solvent will not be constant.

E. Thermal Stability of Donor Solvents

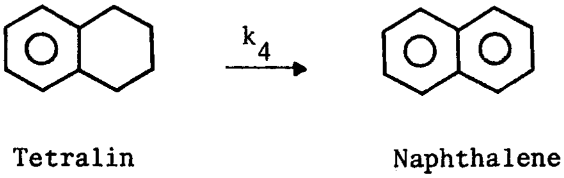
The following reactions can occur because of the instability of tetralin above 400°C.



(10)



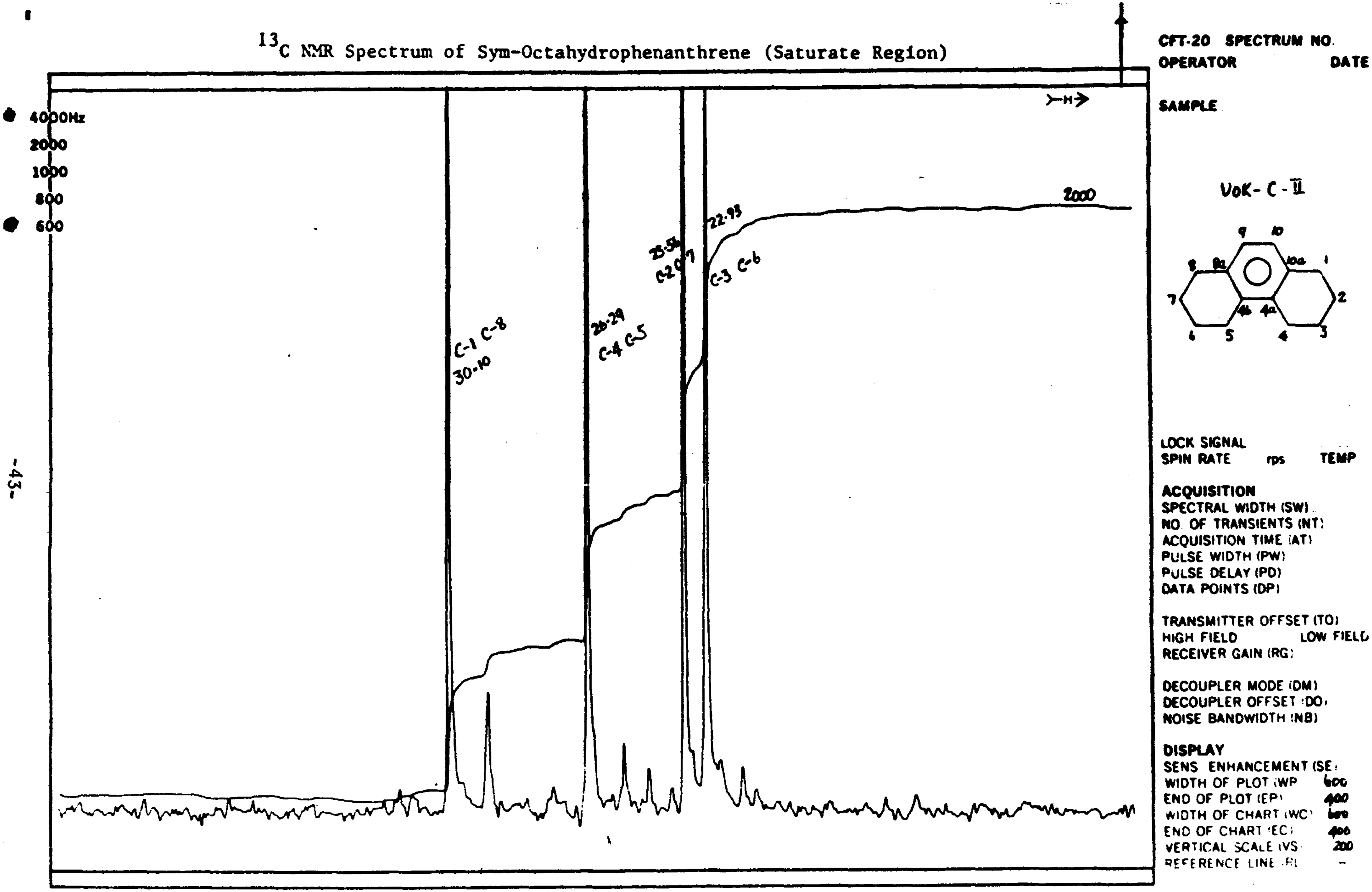
(11)



(12)

Figure 22

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



CFT-20 SPECTRUM NO.
OPERATOR DATE

SAMPLE

LOCK SIGNAL
SPIN RATE rps TEMP

ACQUISITION
SPECTRAL WIDTH (SW)
NO OF TRANSIENTS (NT)
ACQUISITION TIME (AT)
PULSE WIDTH (PW)
PULSE DELAY (PD)
DATA POINTS (DP)

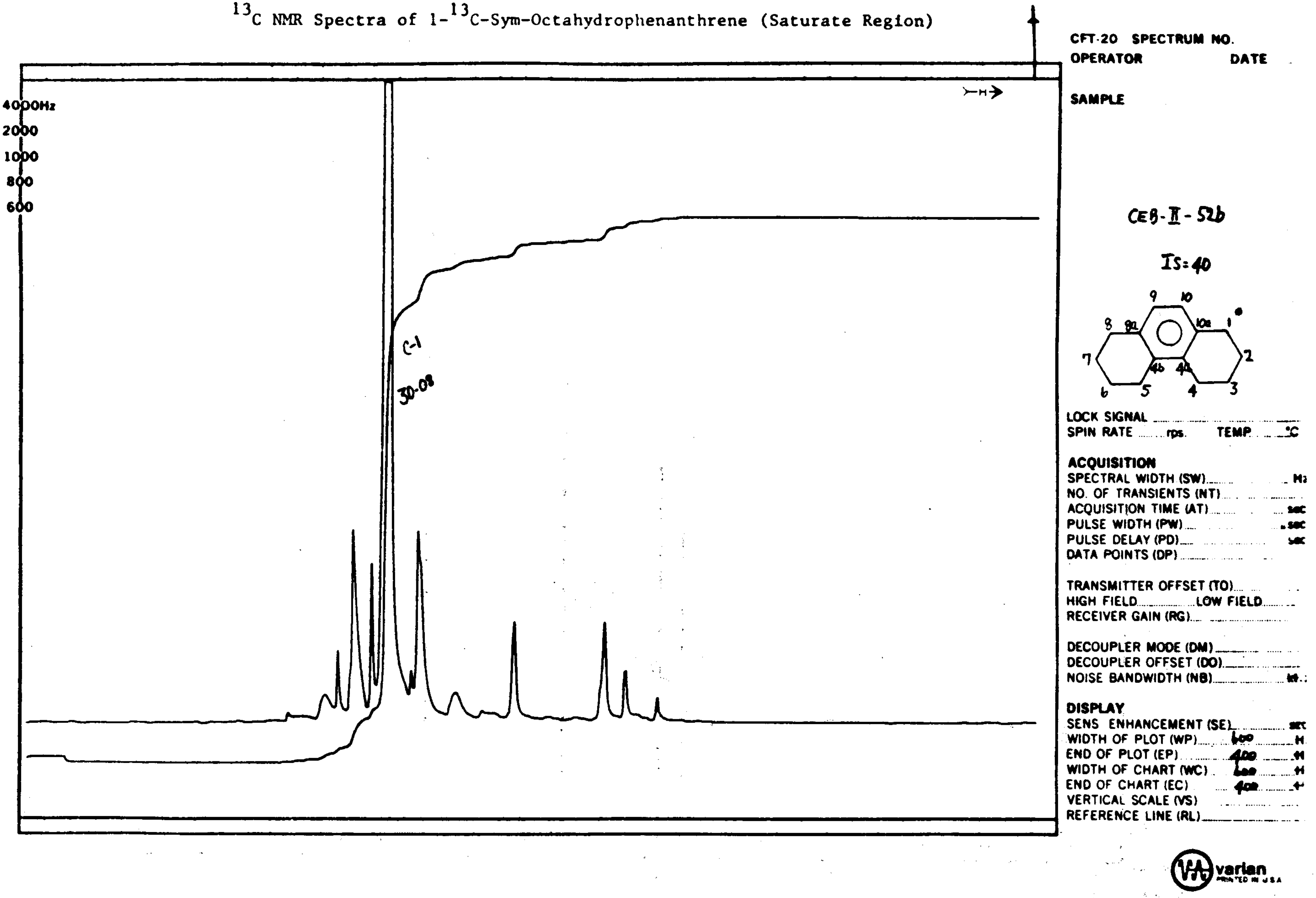
TRANSMITTER OFFSET (TO)
HIGH FIELD LOW FIELD
RECEIVER GAIN (RG)

DECOUPLER MODE (DM)
DECOUPLER OFFSET (DO)
NOISE BANDWIDTH (NB)

DISPLAY
SENS ENHANCEMENT (SE)
WIDTH OF PLOT (WP) 600
END OF PLOT (EP) 400
WIDTH OF CHART (WC) 600
END OF CHART (EC) 400
VERTICAL SCALE (VS) 200
REFERENCE LINE (RL) –

Figure 23

^{13}C NMR Spectra of 1-^{13}C-Sym-Octahydrophenanthrene (Saturate Region)



CFT-20 SPECTRUM NO.
OPERATOR DATE
SAMPLE

CEB-II-52b

Is:40

LOCK SIGNAL
SPIN RATE rps. TEMP °C

ACQUISITION
SPECTRAL WIDTH (SW) Hz
NO. OF TRANSIENTS (NT)
ACQUISITION TIME (AT) sec
PULSE WIDTH (PW) sec
PULSE DELAY (PD) sec
DATA POINTS (DP)

TRANSMITTER OFFSET (TO)
HIGH FIELD LOW FIELD
RECEIVER GAIN (RG)

DECOUPLER MODE (DM)
DECOUPLER OFFSET (DO)
NOISE BANDWIDTH (NB) Hz

DISPLAY
SENS ENHANCEMENT (SE) sec
WIDTH OF PLOT (WP) 600 H
END OF PLOT (EP) 400 H
WIDTH OF CHART (WC) 600 H
END OF CHART (EC) 400 H
VERTICAL SCALE (VS)
REFERENCE LINE (RL)

Figure 24

^{13}C NMR Spectrum of Monomethyl Isomers of Rearranged Octahydrophenanthrene

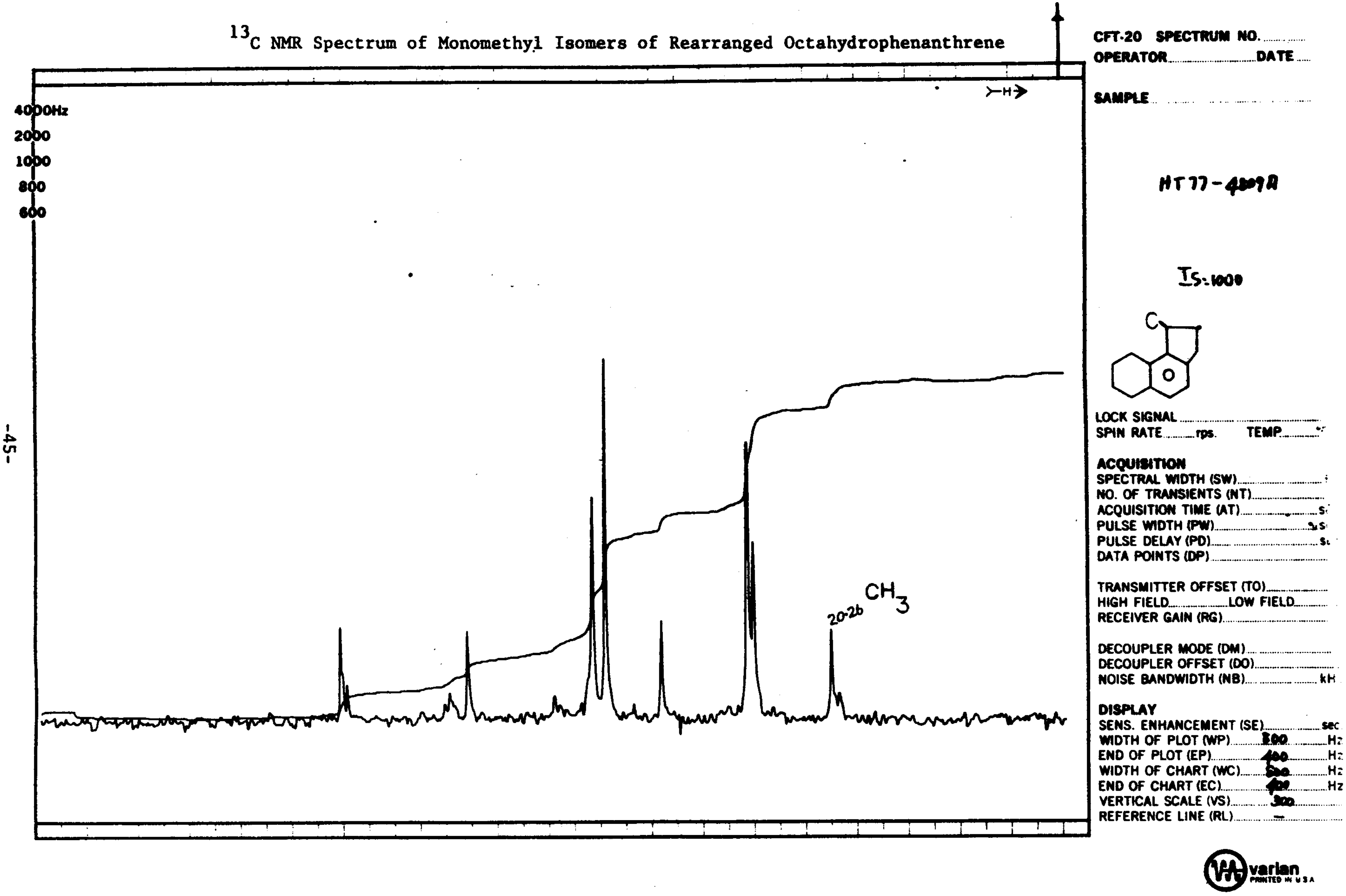
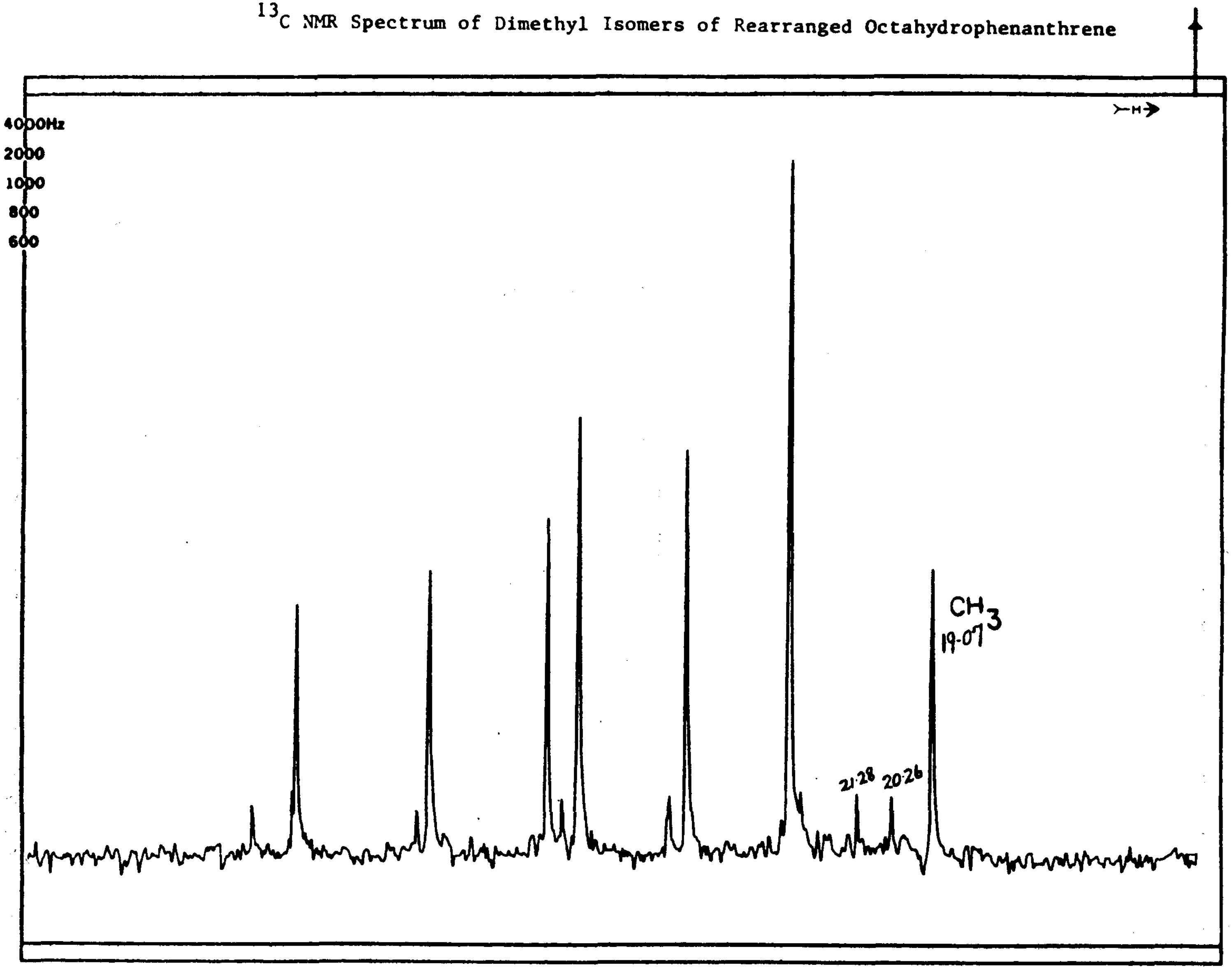


Figure 25

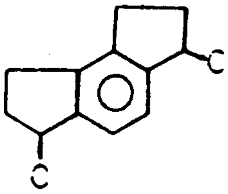
^{13}C NMR Spectrum of Dimethyl Isomers of Rearranged Octahydrophenanthrene



CFT-20 SPECTRUM NO.
OPERATOR DATE

SAMPLE

HT71-4609B



LOCK SIGNAL
SPIN RATE rps TEMP °C

ACQUISITION
SPECTRAL WIDTH (SW) Hz
NO. OF TRANSIENTS (NT)
ACQUISITION TIME (AT) sec
PULSE WIDTH (PW) µsec
PULSE DELAY (PD) sec
DATA POINTS (DP)

TRANSMITTER OFFSET (TO)
HIGH FIELD LOW FIELD
RECEIVER GAIN (RG)

DECOUPLER MODE (DM)
DECOUPLER OFFSET (DO)
NOISE BANDWIDTH (NB)

DISPLAY
SENS ENHANCEMENT (SE)
WIDTH OF PLOT (WP) 700
END OF PLOT (EP) 400
WIDTH OF CHART (WC) 700
END OF CHART (EC) 400
VERTICAL SCALE (VS) 200
REFERENCE LINE (RL)

varian

Other reactions such as tetralin forming toluene or tetralin and naphthalene forming cracked products are also possible but are normally slow and appear to be negligible.

The data indicate that for the system of 50% mesitylene with 50% tetralin in nitrogen, methyl indane dealkylation, reaction (11), is of zero order. The Arrhenius plots for k_3 are shown in Figure 26. The presence of dibenzyl significantly increases the rate of reaction (11). 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 ($\geq$25%) indicate that for these systems, reaction (11) is no longer zero order. In these cases, the reaction (11) is most likely first order with respect to methyl indane concentration. Also, the rate of indane production with a 90% tetralin plus 10% dibenzyl in hydrogen system and 20% dibenzyl plus 80% decalin in nitrogen is double that of 10% dibenzyl and 90% tetralin in a nitrogen atmosphere (see Figure 27).

The experimental data indicate that tetralin dehydrogenation, reaction (12), is of zero order for the following 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 Arrhenius plots for k_4 are shown in Figure 28. The rate constant, k_4, is only mildly increased by the presence of an acceptor (dibenzyl). Phenanthrene appears to somewhat hinder the reaction (12).

F. Hydrogen-Transfer Cracking of Non-Condensed Aromatic Analog 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.

FIGURE 26

ARRHENIUS PLOT FOR METHYL INDANE FORMING INDANE REACTION

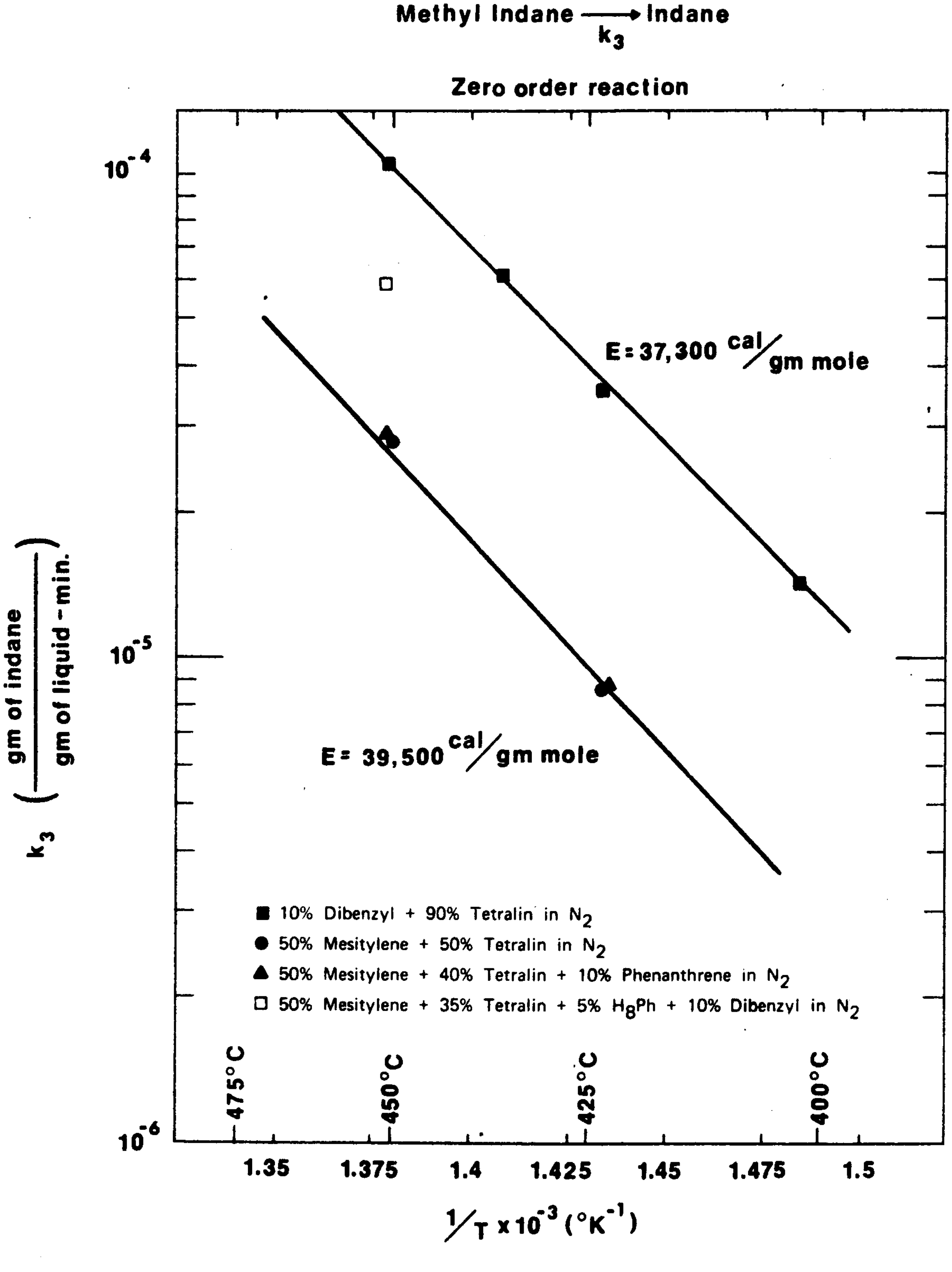


FIGURE 27

INDANE CONCENTRATION VERSUS TIME FOR DIFFERENT FEEDS AT 450 °C

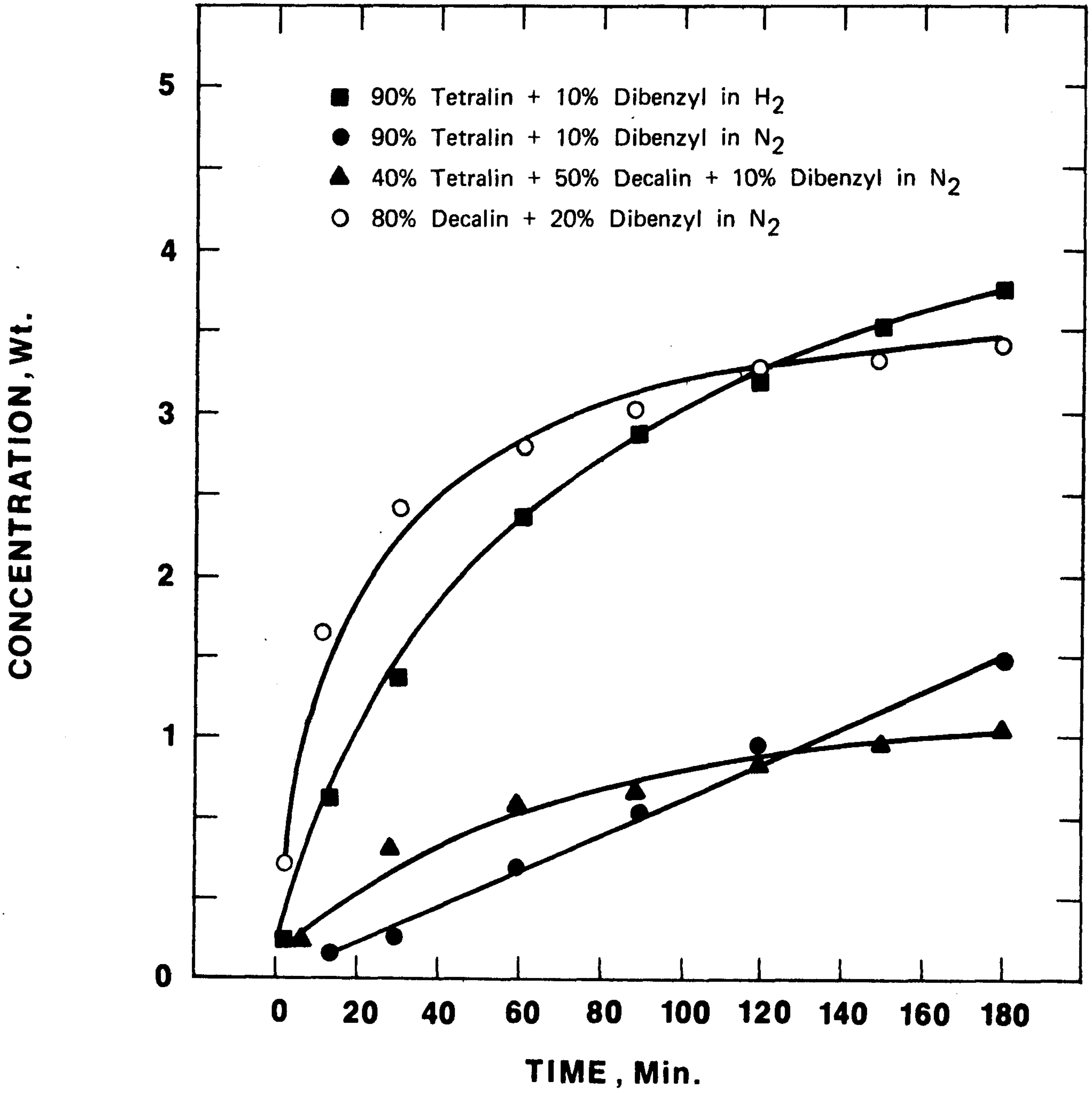
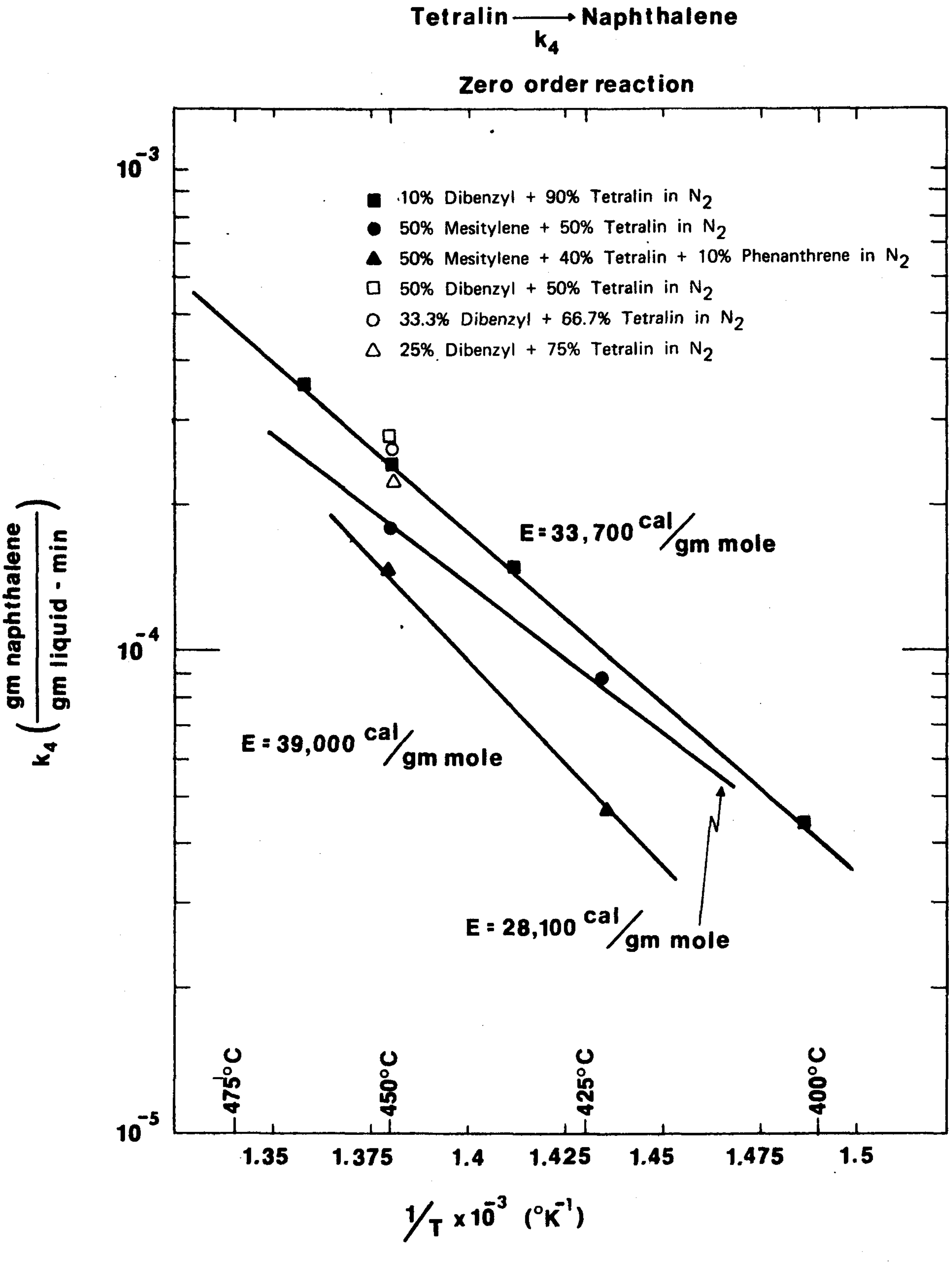


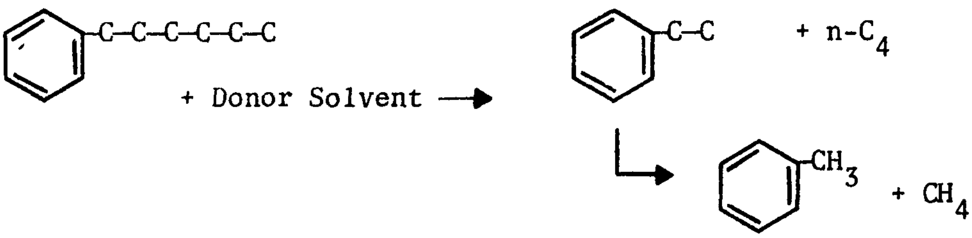
FIGURE 28

ARRHENIUS PLOT FOR THE TETRALIN FORMING NAPHTHALENE REACTION



The conversion profiles of these reactions and that of dibenzyl are shown in Figure 29. Each compound was more stable than dibenzyl. Diphenyl methane was essentially unreactive; this is due to aromatic resonance stabilization. 1-Phenylhexane converted at 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 30 and 31. No evidence was found for propyl- or butylbenzene in the liquid phases of the runs with 1-4,diphenylbutane and 1-phenylhexane. The major gaseous products were n-butane and methane in the latter run. This is consistent with a step-wise reaction as follows:



(13)

(14)

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

G. Hydrogen-Transfer to 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, tetralin, and toluene are given in Figures 32 through 35.

FIGURE 29

CONVERSION OF DIFFERENT ACCEPTORS AT 450 °C

▲ 10% Dibenzyl with 40% Tetralin and 50% Mesitylene
■ 10% Phenylhexane with 40% Tetralin and 50% Mesitylene
● 10% 1,4 Diphenylbutane with 40% Tetralin and 50% Mesitylene
○ 10% Diphenylmethane with 40% Tetralin and 50% Mesitylene

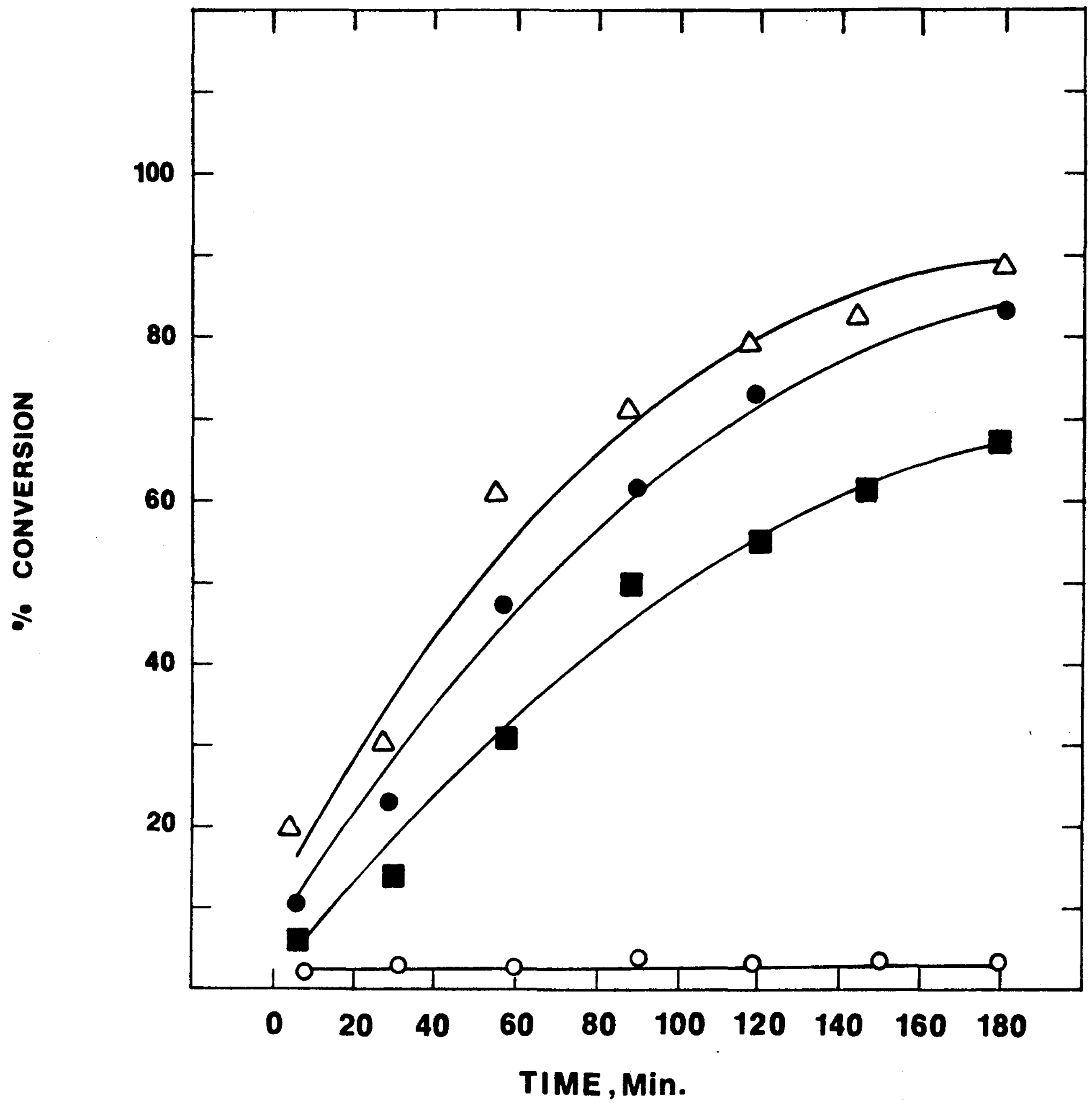


FIGURE 30

FORMATION OF ETHYL BENZENE VERSUS TIME FOR DIFFERENT ACCEPTORS AT 450 °C

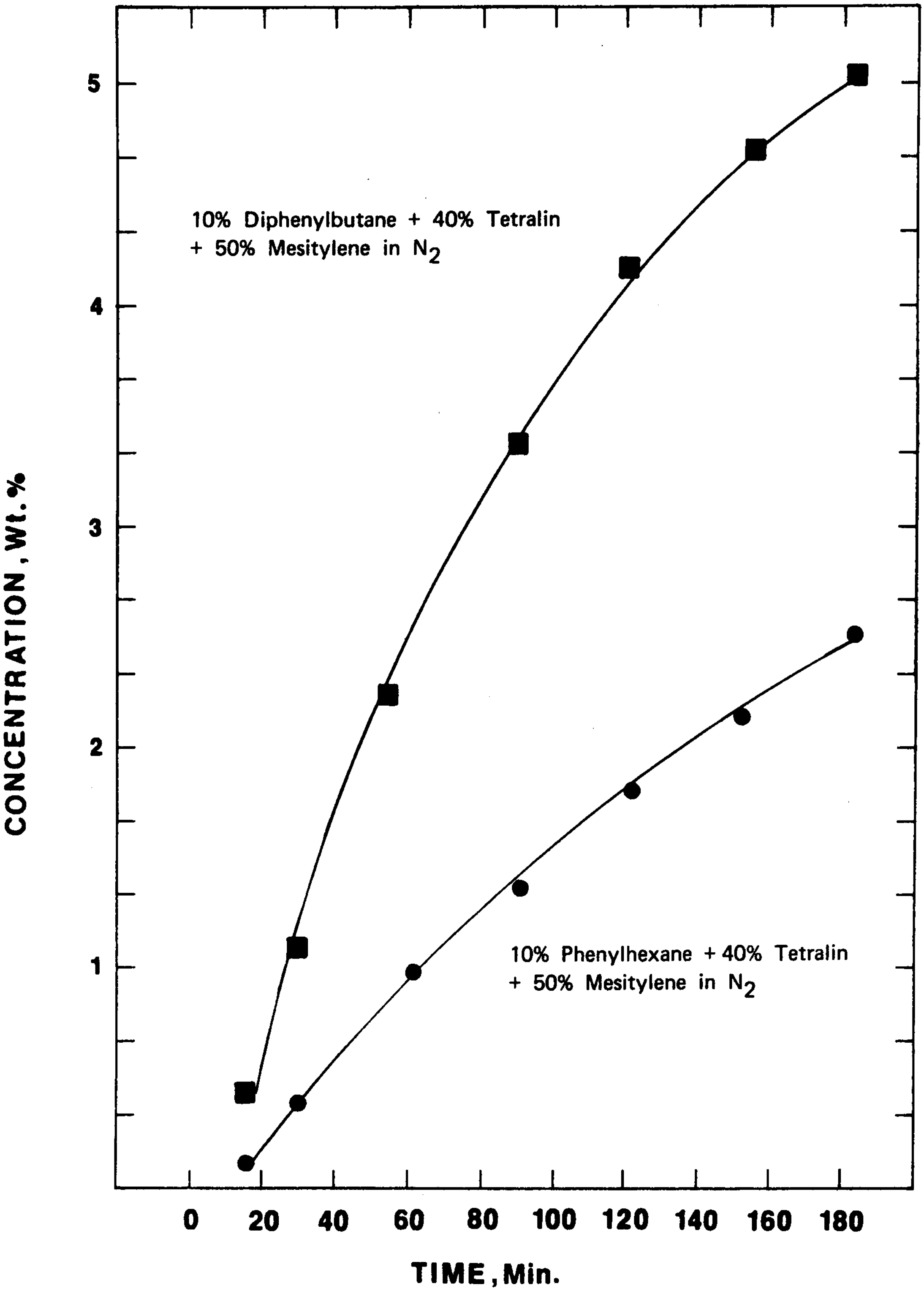


FIGURE 31

FORMATION OF TOLUENE VERSUS TIME FOR DIFFERENT ACCEPTORS AT 450 °C

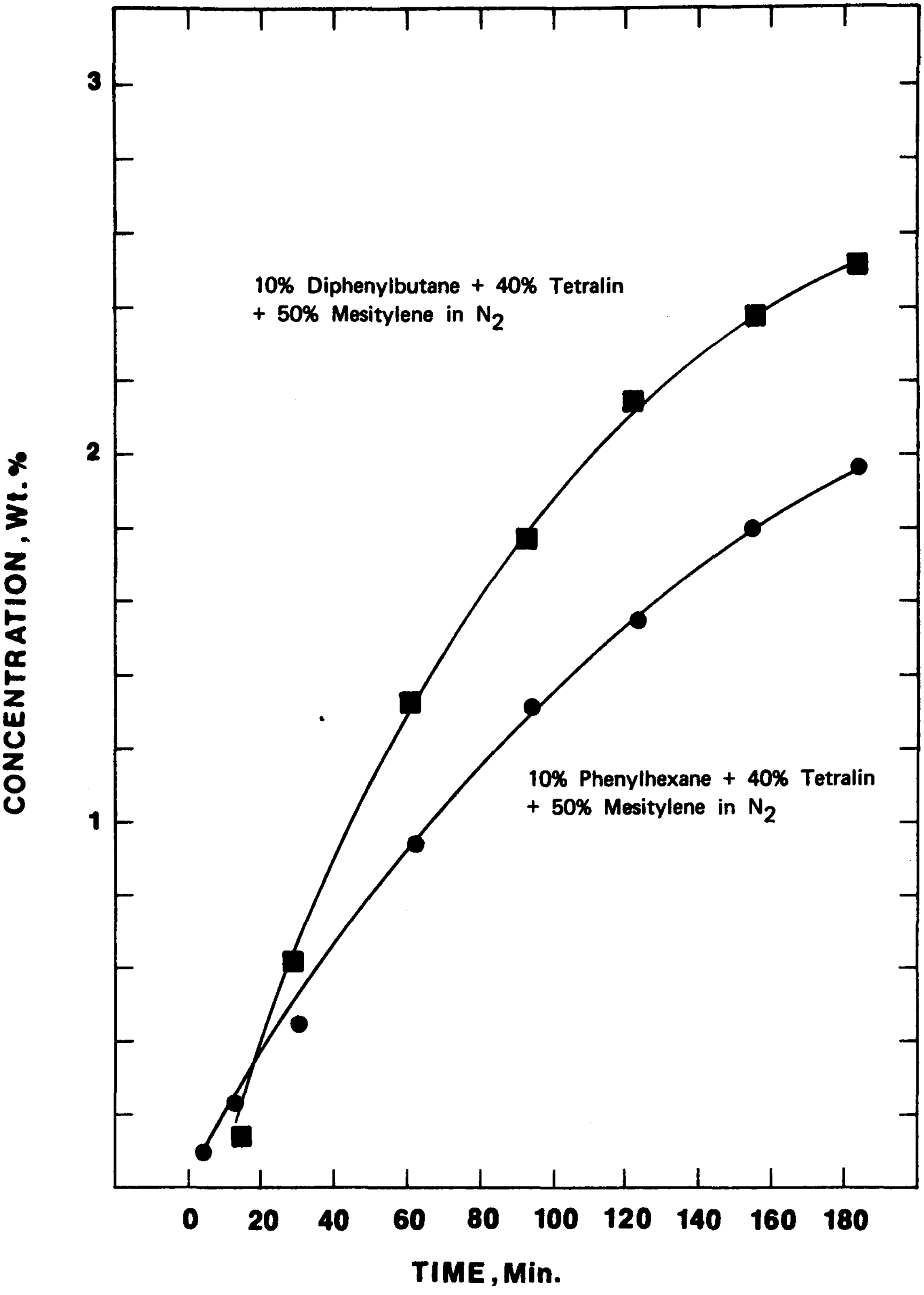


FIGURE 32

STILBENE CONCENTRATION VERSUS TIME FOR A FEED OF 10% STILBENE WITH 90% TETRALIN IN NITROGEN ATMOSPHERE

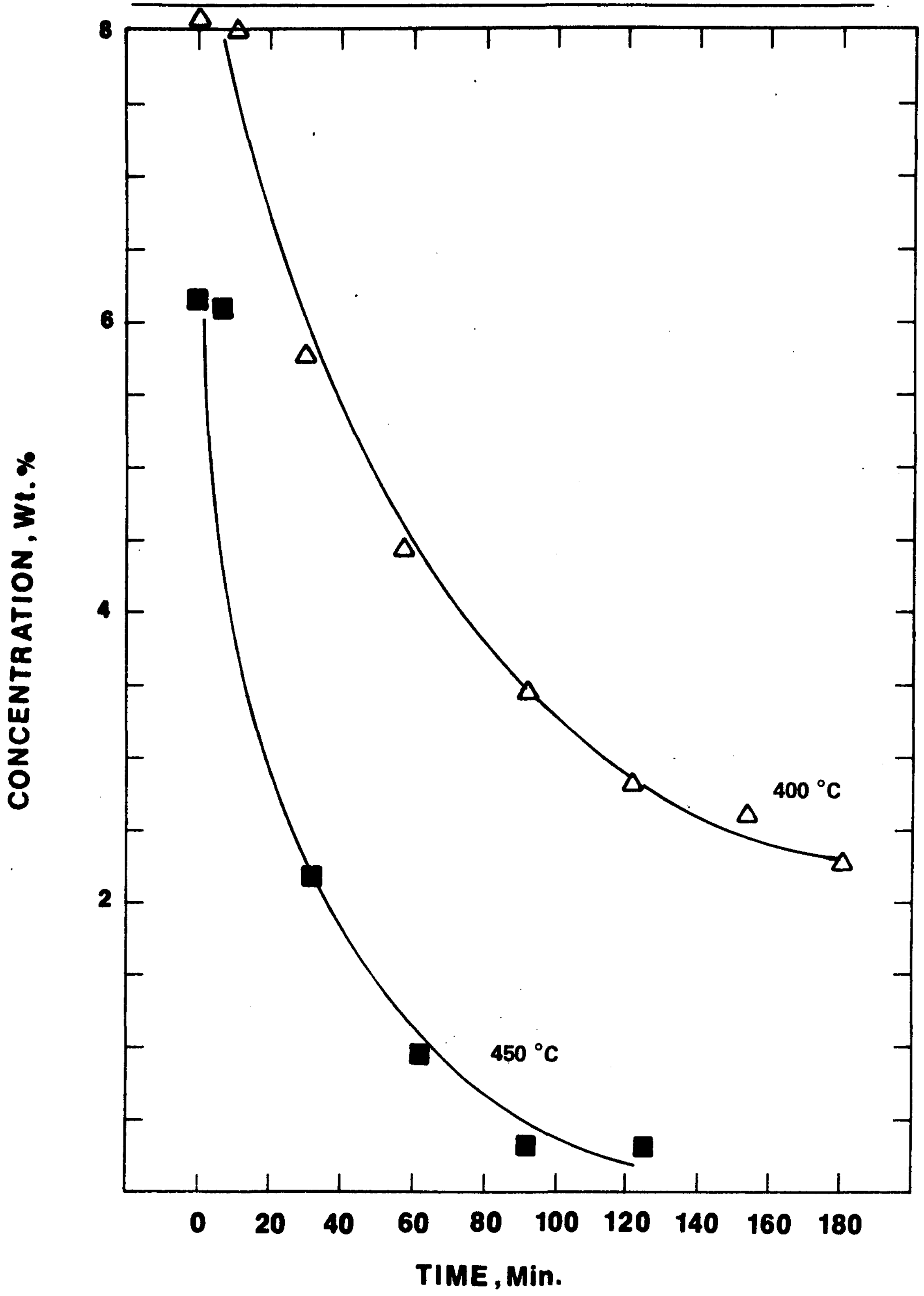


FIGURE 33

DIBENZYL CONCENTRATION VERSUS TIME FOR A FEED OF 10% STILBENE WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE

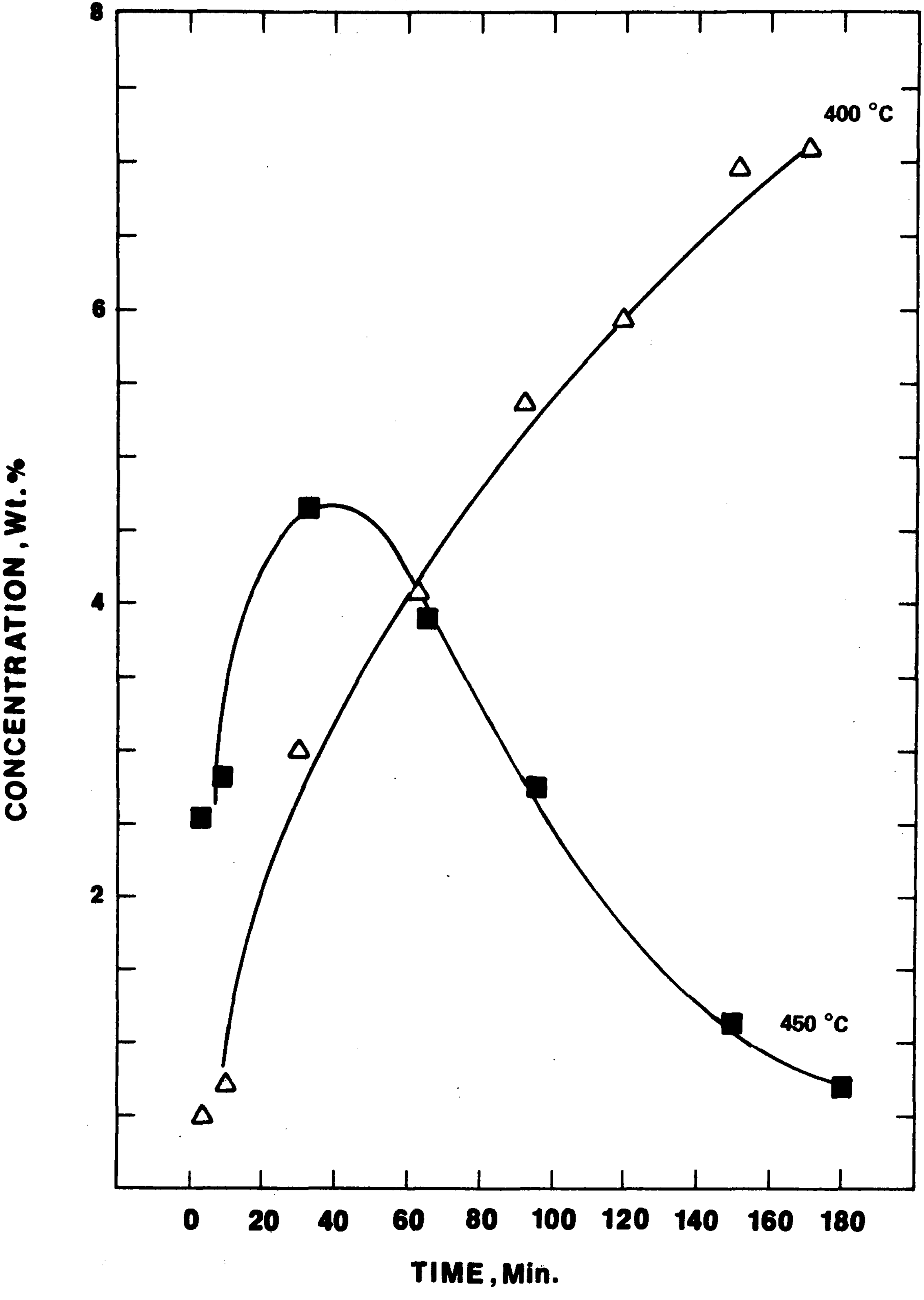


FIGURE 34

TETRALIN CONCENTRATION VERSUS TIME FOR A FEED OF 10% STILBENE WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE

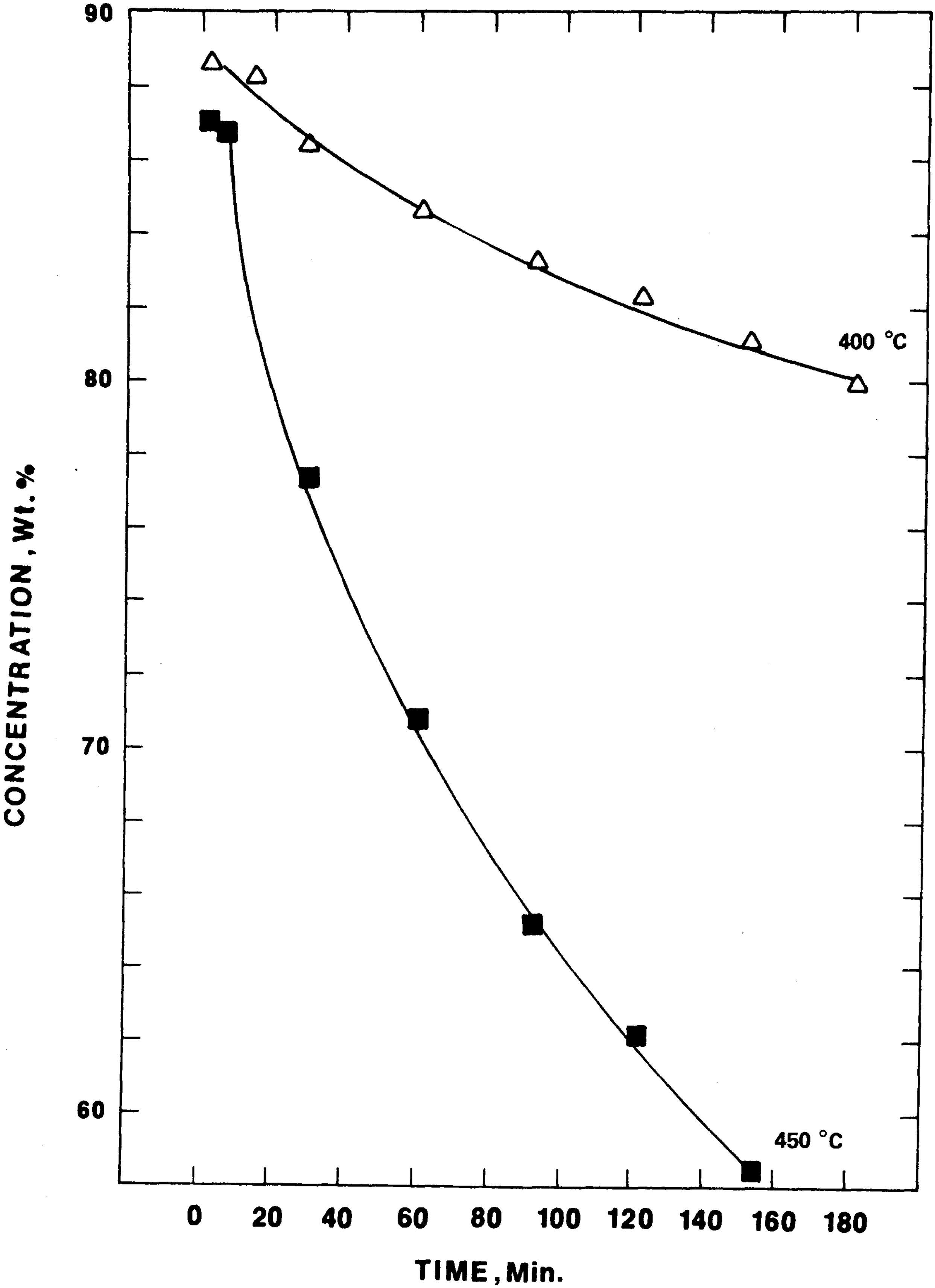
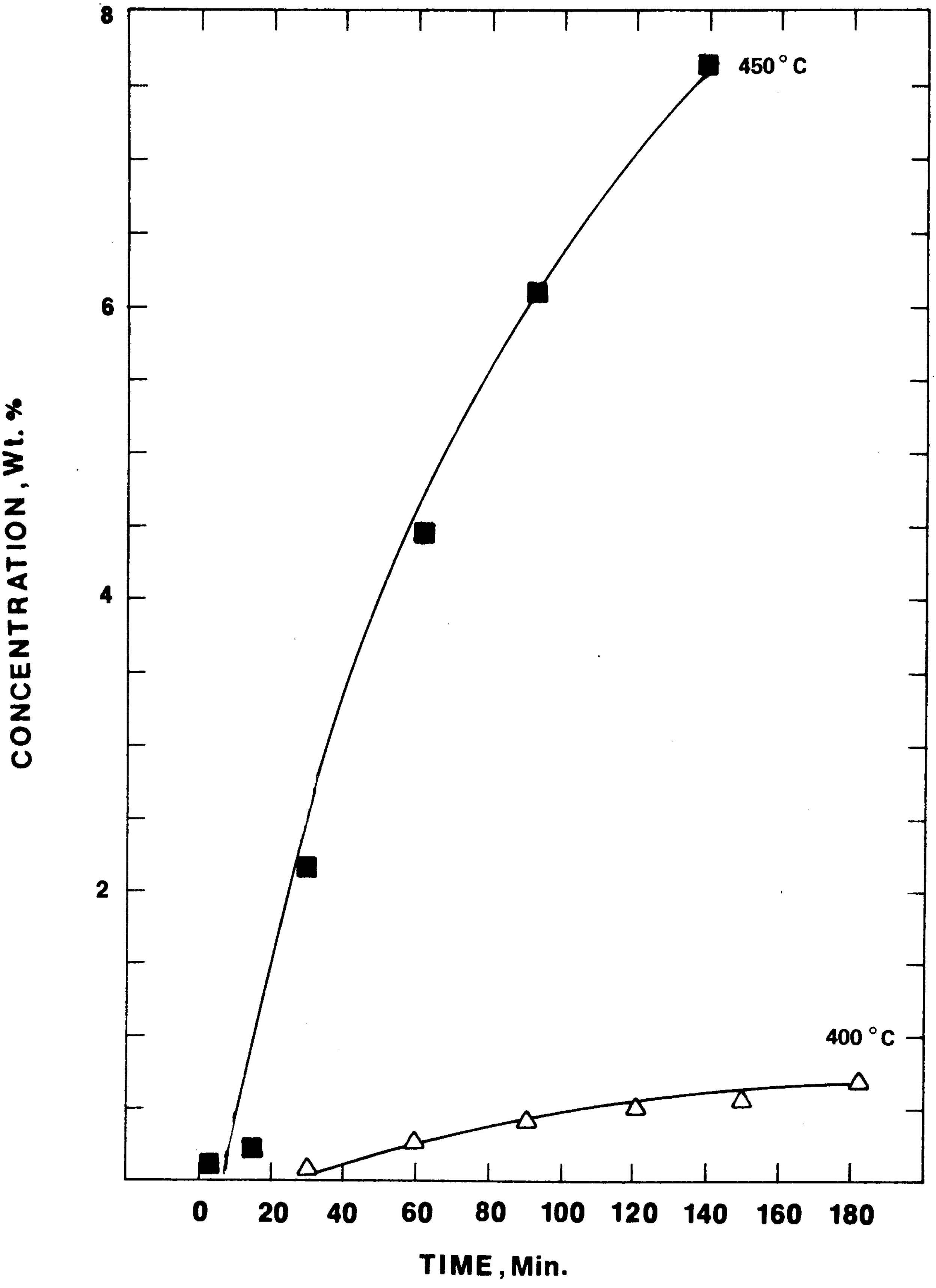
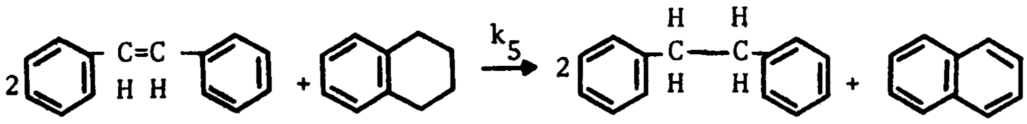


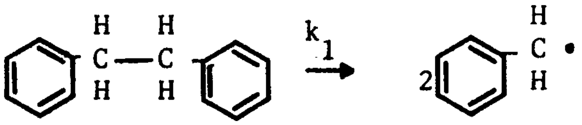
FIGURE 35

TOLUENE CONCENTRATION VERSUS TIME FOR A FEED OF 10% STILBENE WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE



The following reaction sequence was assumed:


(15)


(1)

The rate constant of reaction (15) was best fit by the expression

$$\frac{d\,C_s}{dt} = -k_5\, C_s\, C_t$$

where C_s and C_t are stilbene and tetralin concentrations in weight %. The Arrhenius plot, Figure 36, indicates an activation energy of 28,400 calories/gram mole.

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.

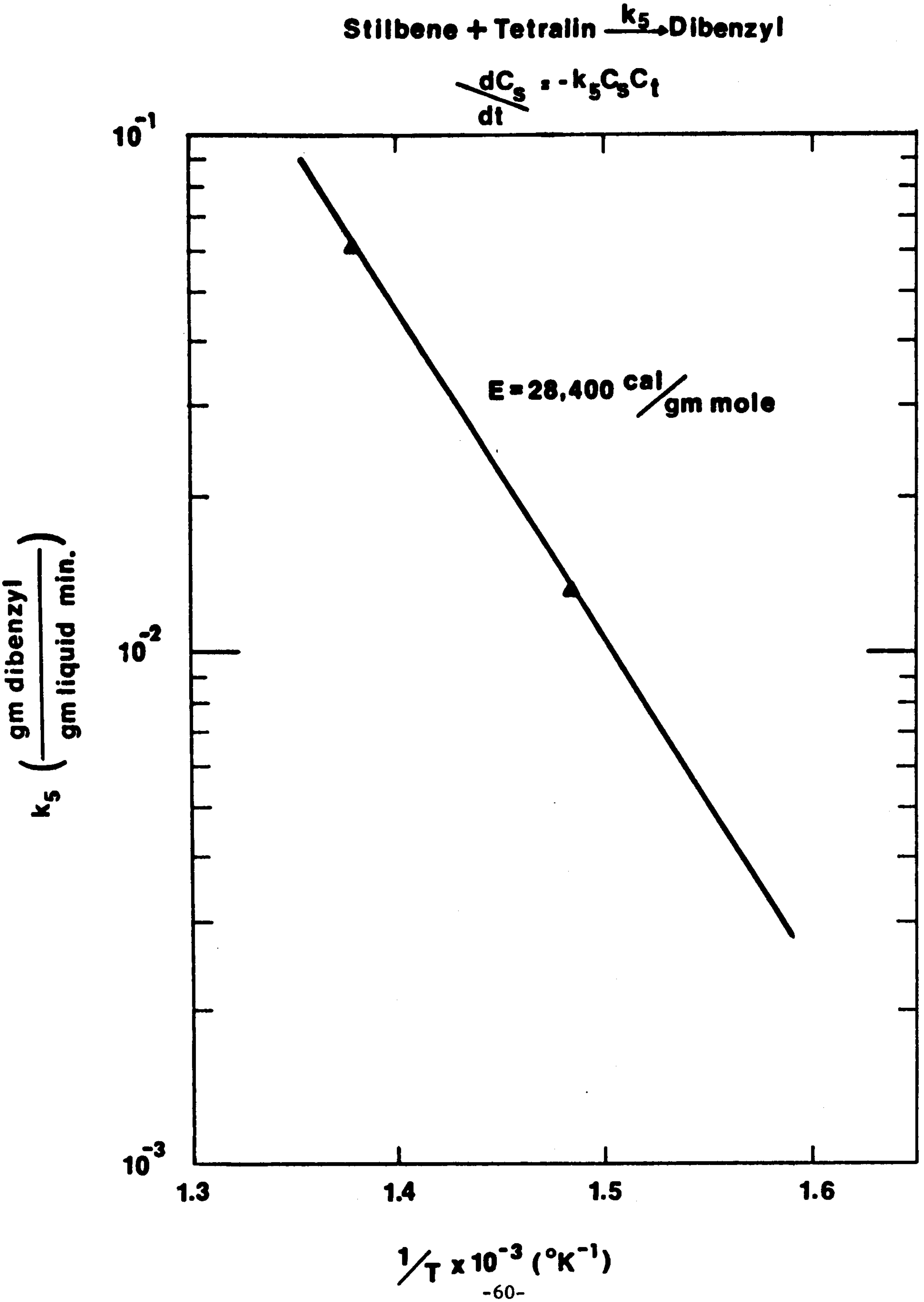
The chemistry of these four-centered reactions may be better understood with the use of deuterium-tagged solvents. In addition, carbonyl reductions should parallel the stilbene reduction reaction.

H. Hydrogen-Transfer Reactions With Dibenzyl Ether

Since preliminary screening experiments showed a rapid conversion of ethers above 400°C, a temperature range of 300-400°C was chosen for the dibenzyl ether reactions. This study was made using tetralin and mesitylene as solvents. Since tetralin was essentially stable below 400°C, this provided a system to evaluate hydrogen-transfer with a minimum of ring contraction to methyl indane.

FIGURE 36

ARRHENIUS PLOT FOR THE STILBENE TO DIBENZYL REACTION



Assuming that dibenzyl ether will thermally cleave at the β-position, similar to dibenzyl, the initial intermediates are expected to be Ph-CH_2· and Ph-CH_2O· 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(3) for the solvent tetrahydroquinoline.

However, our analyses (GLC, MS, IR) have shown that benzaldehyde was formed in place of benzyl alcohol. Figure 37 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 38.

Calculation of the major component concentrations from these experiments confirmed that benzaldehyde was a reaction intermediate (see Figures 39 through 44). In particular, Figure 40 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 (see Figure 45). Figure 42 indicates that, within analytical experimental error, little net change in tetralin concentration occurred in the 300-365°C range. Figure 43, however, shows that a limited amount of naphthalene was being formed by direct hydrogen transfer.

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) intramolecular hydrogen-transfer and (2) intermolecular hydrogen-transfer. The overall reactions are proposed as follows:

FIGURE 37

GAS–LIQUID CHROMATOGRAPH OF DIBENZYL ETHER HYDROGEN TRANSFER CRACKING PRODUCTS

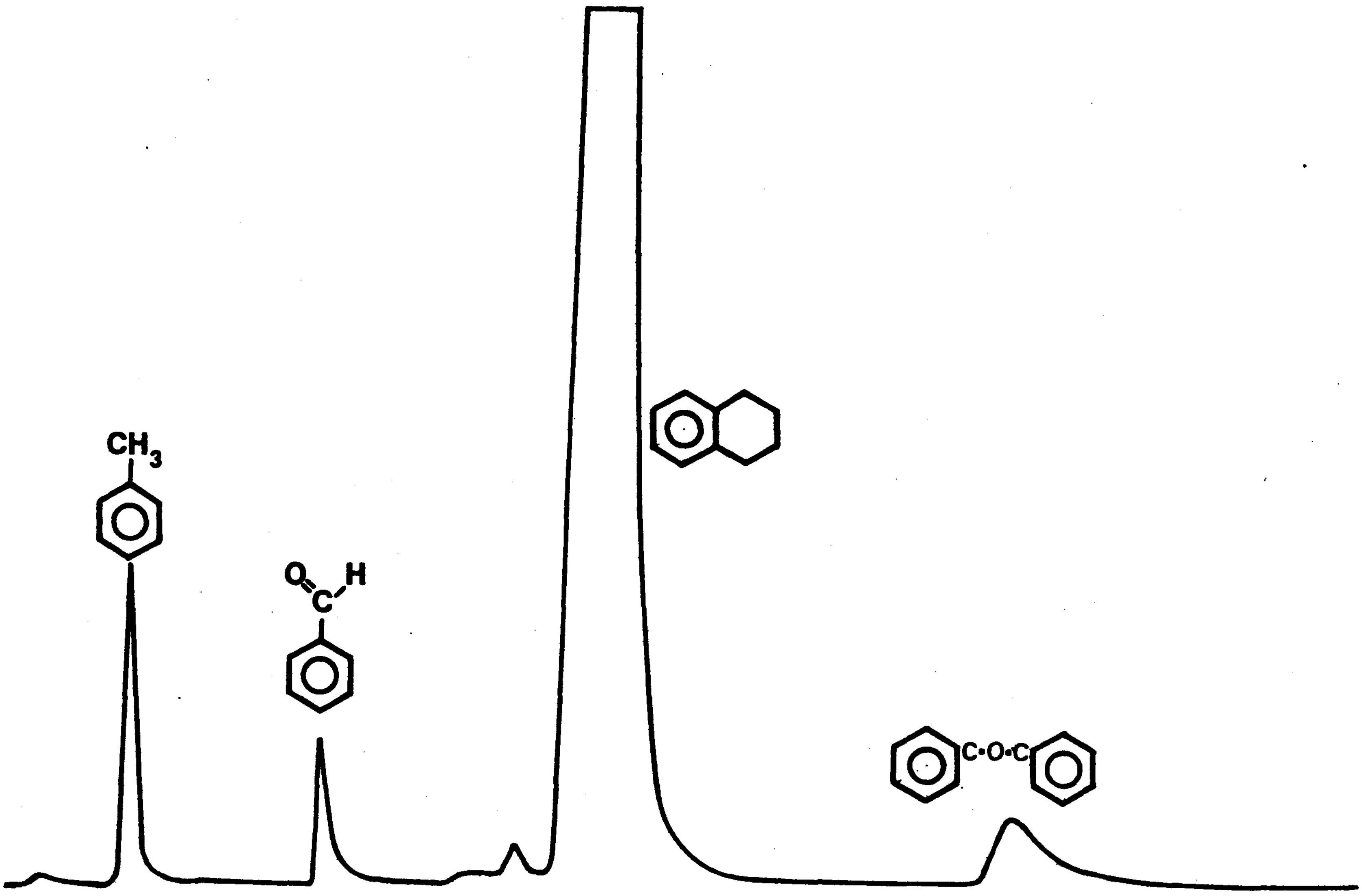


Figure 38

DIBENZYL ETHER PRODUCTS AT 400° C AFTER 30 MINUTES REACTION TIME

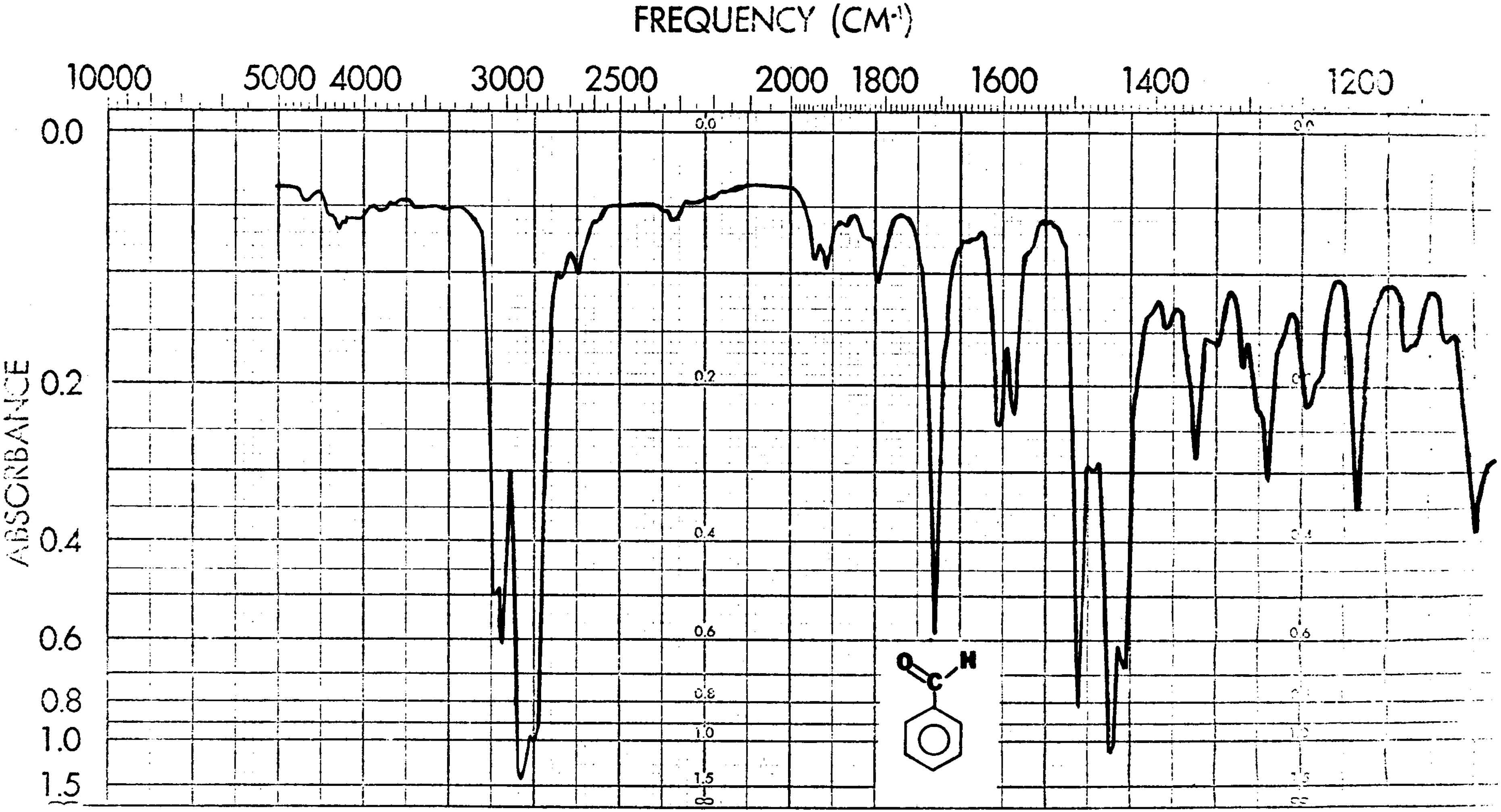


FIGURE 39

DIBENZYL ETHER CONCENTRATION VERSUS TIME FOR A FEED OF 10% DIBENZYL ETHER WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE

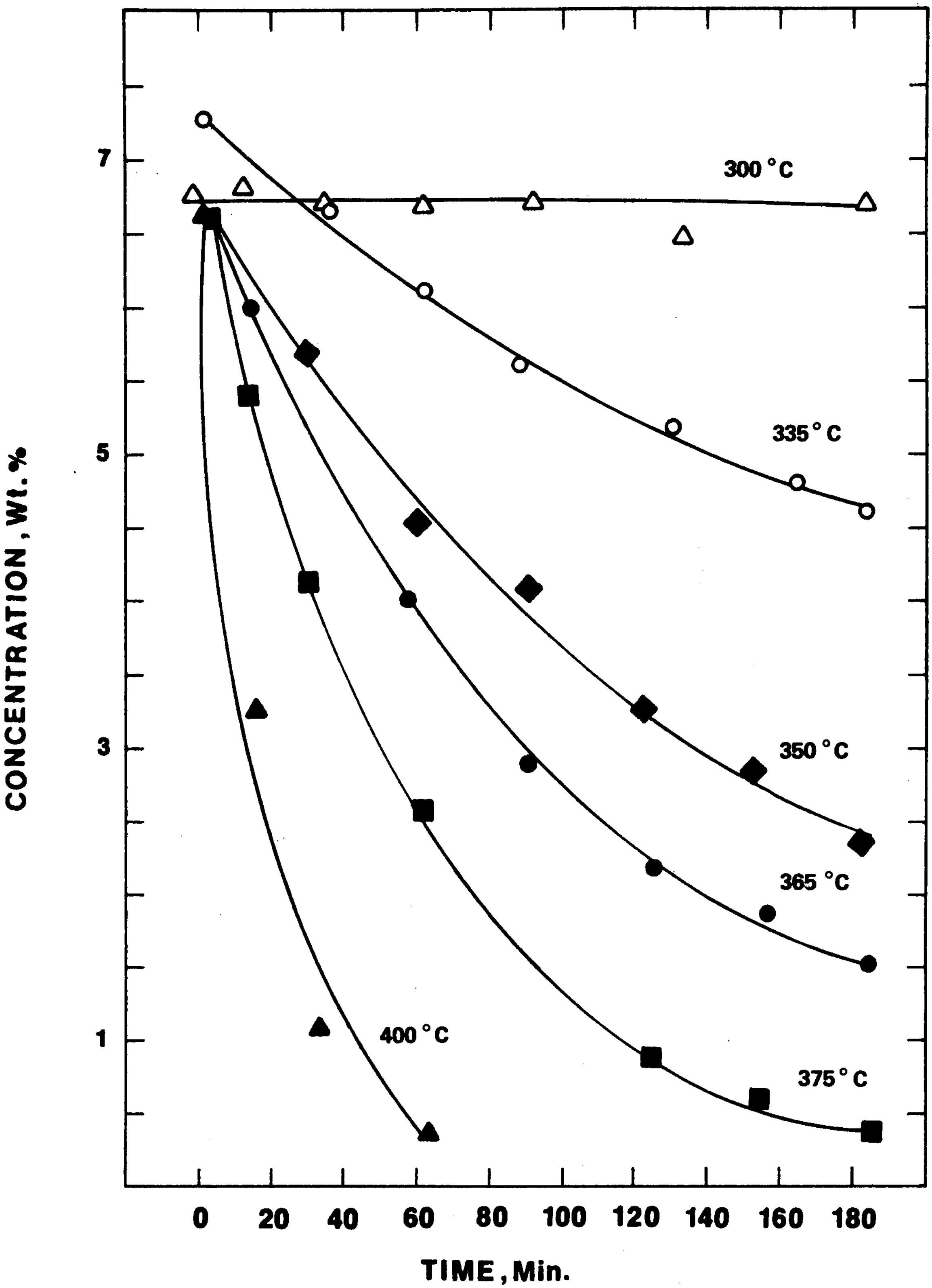


FIGURE 40

BENZALDEHYDE CONCENTRATION VERSUS TIME FOR A FEED OF 10% DIBENZYL ETHER WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE

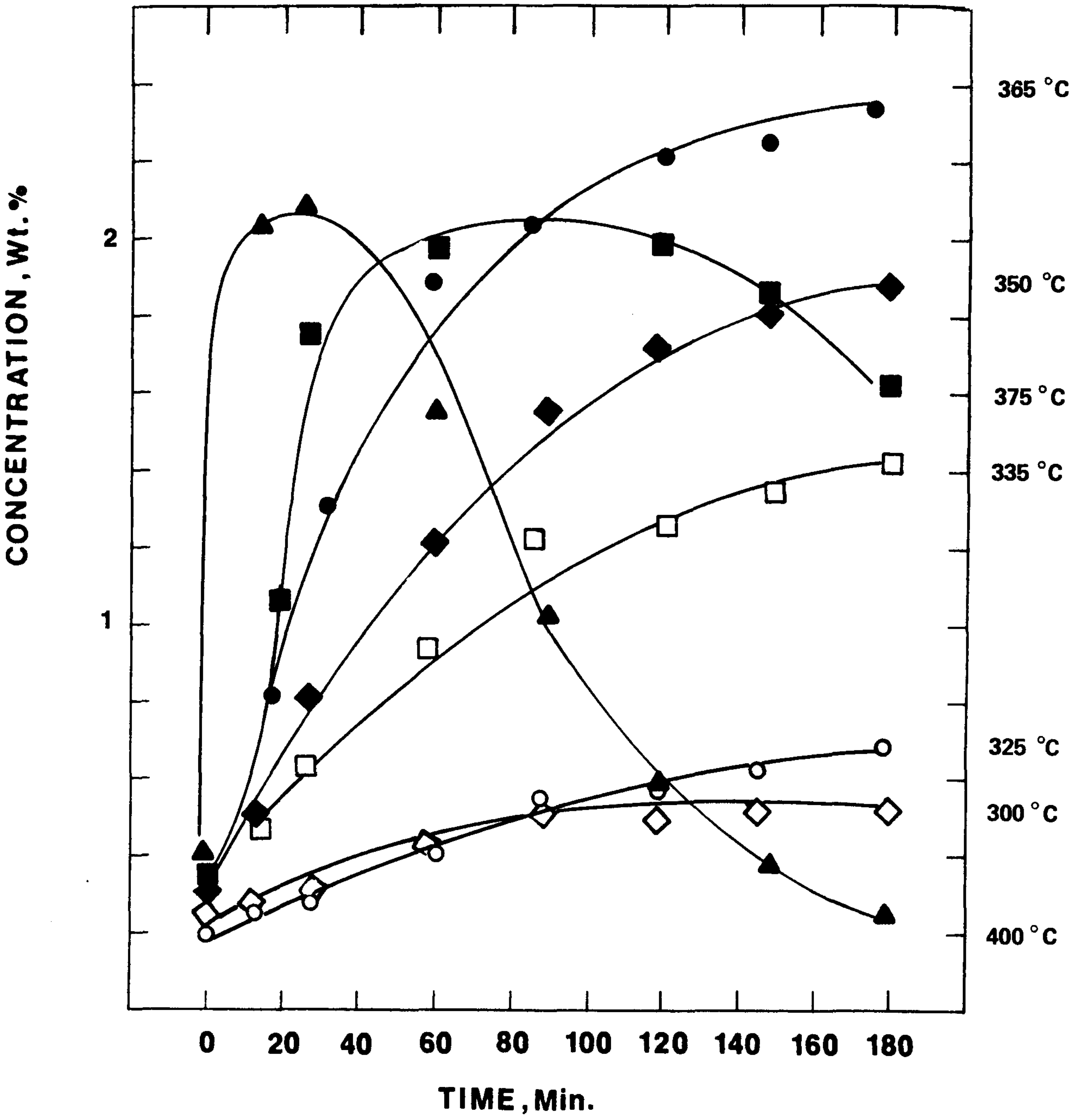


FIGURE 41

TOLUENE CONCENTRATION VERSUS TIME FOR A FEED OF 10% DIBENZYL ETHER WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE

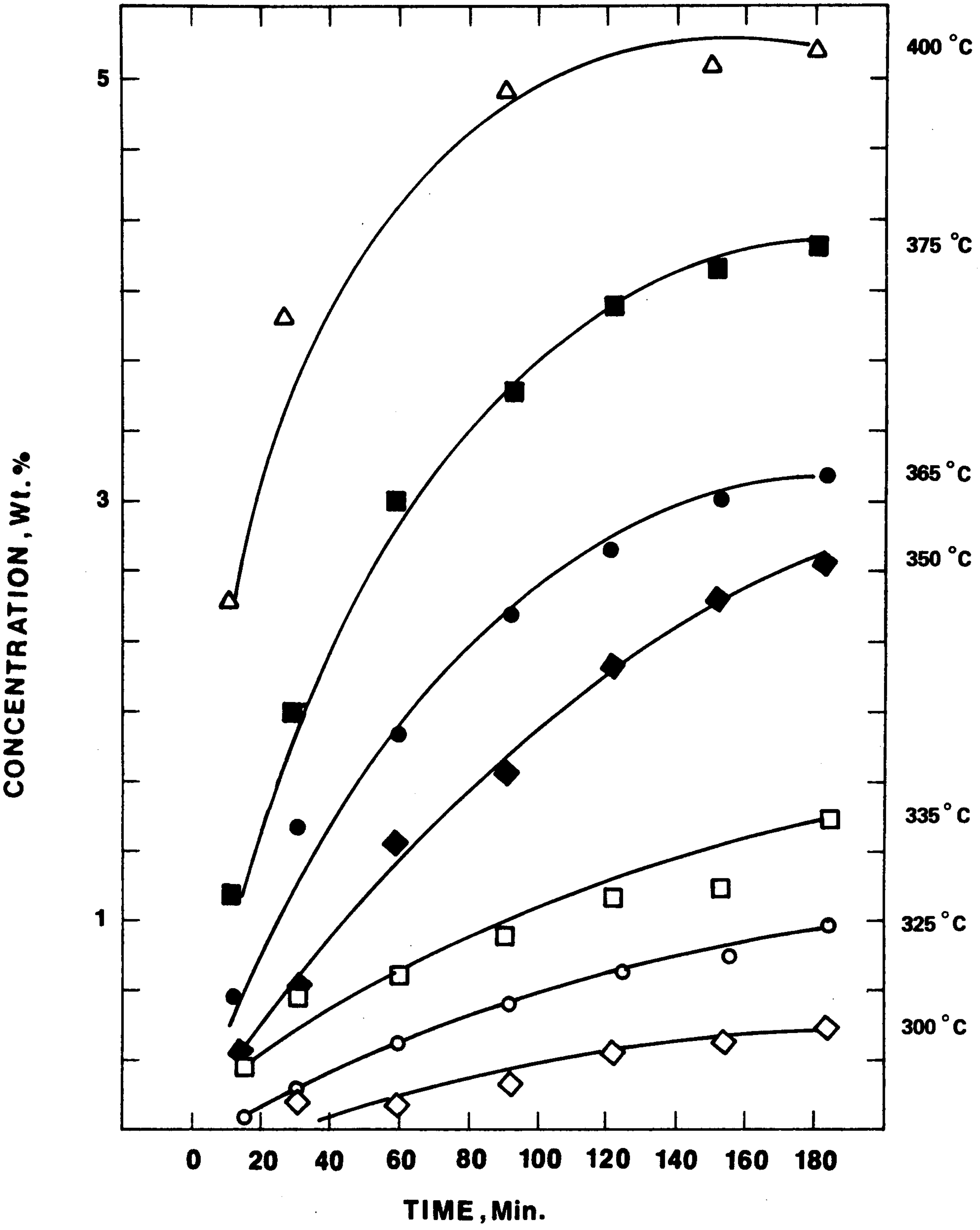


FIGURE 42

CONCENTRATION OF TETRALIN VERSUS TIME FOR A FEED OF 10% DIBENZYL ETHER WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE

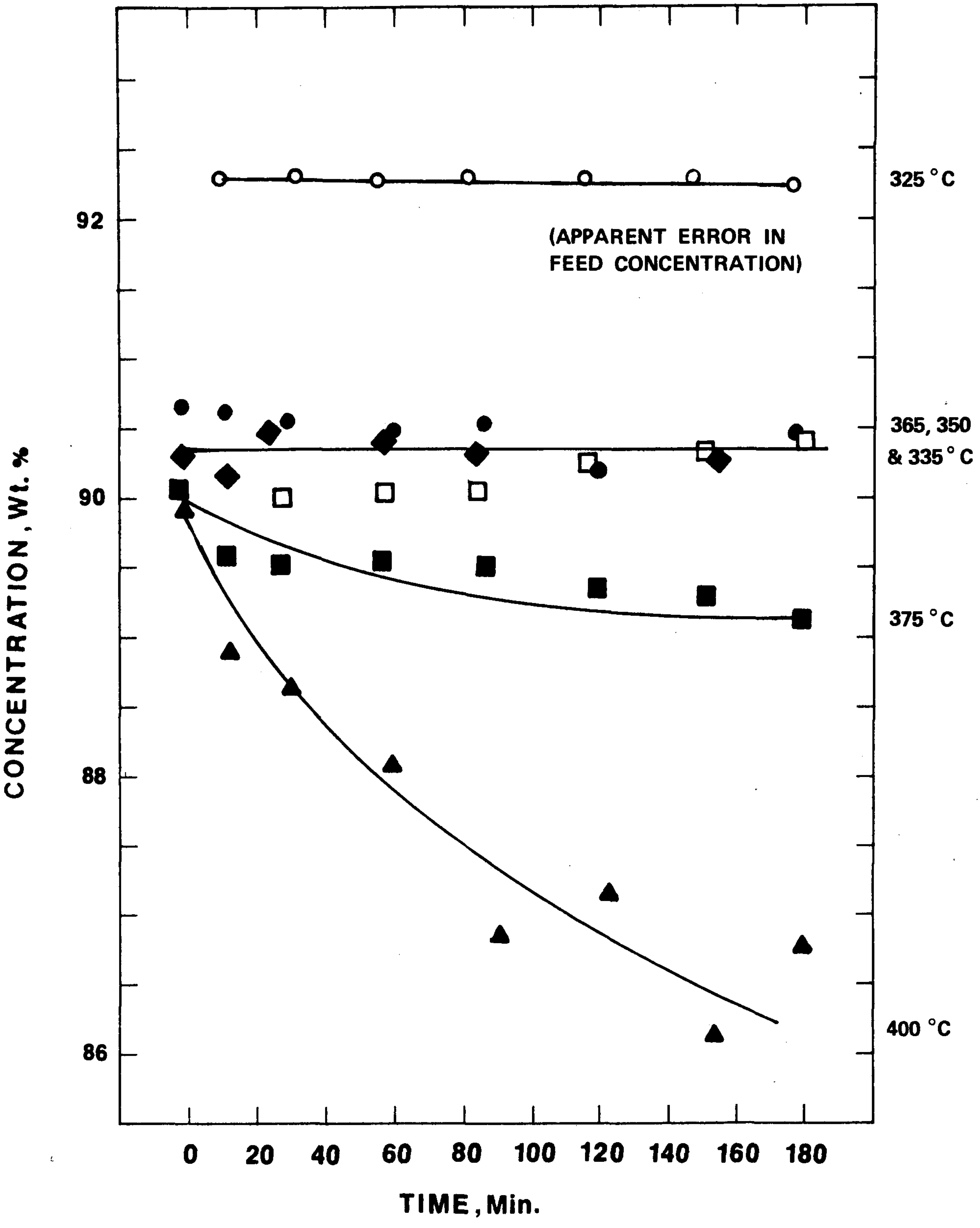


FIGURE 43

CONCENTRATION OF NAPHTHALENE VERSUS TIME FOR A FEED OF 10% DIBENZYL ETHER WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE

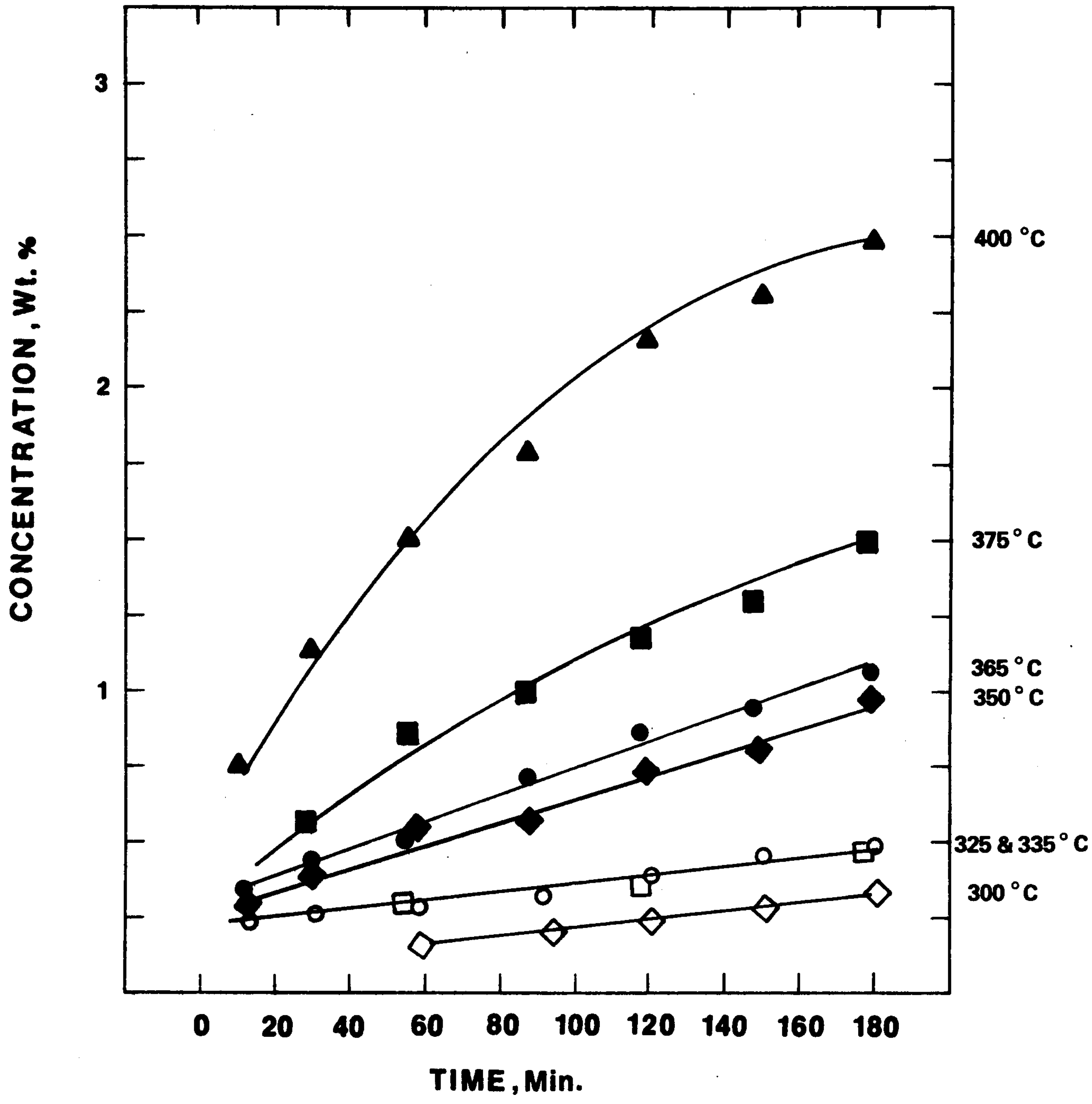


FIGURE 44

CONCENTRATION OF BENZENE VERSUS TIME FOR A FEED OF 10% DIBENZYL ETHER WITH 90% TETRALIN IN A NITROGEN ATMOSPHERE

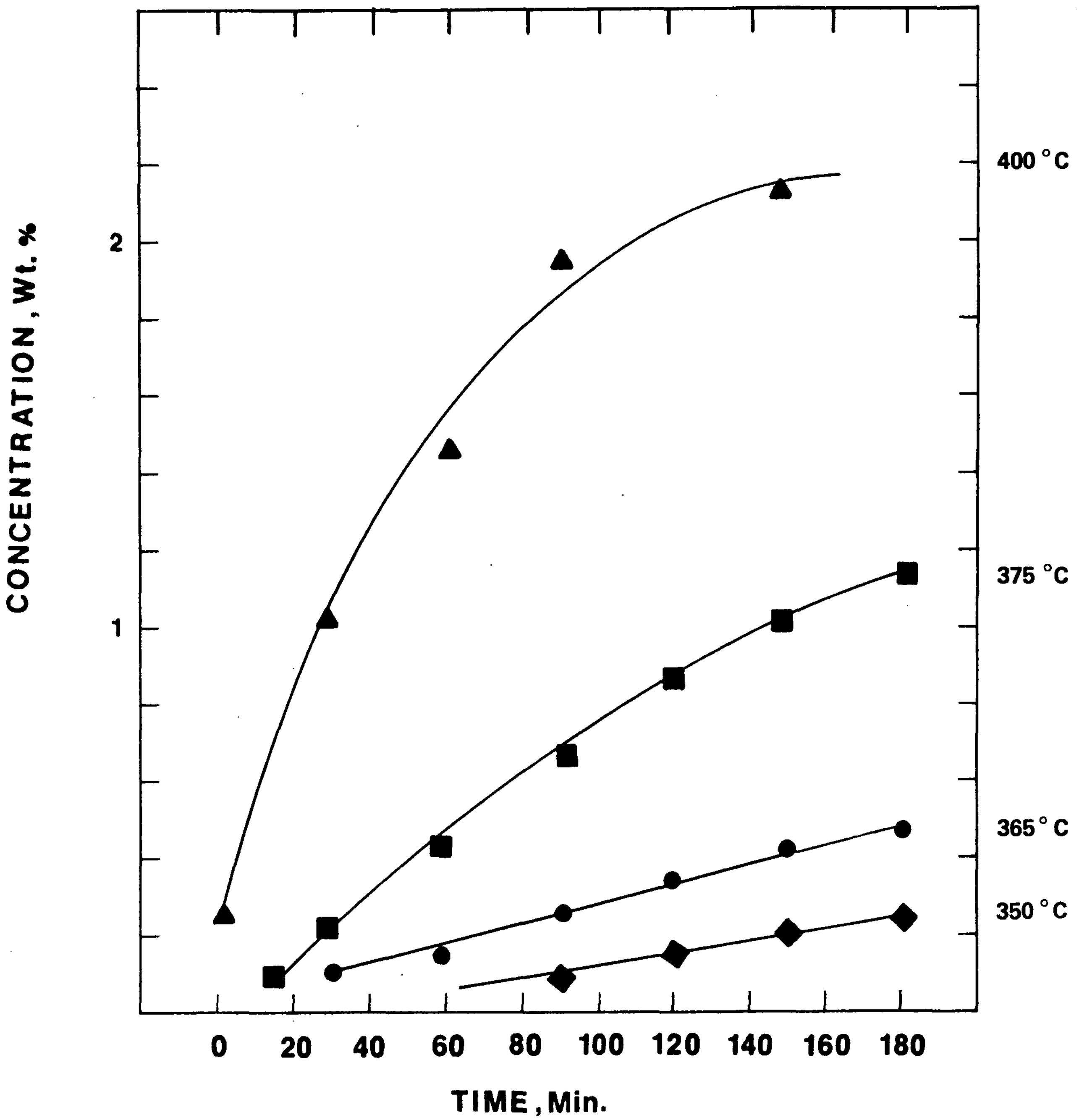
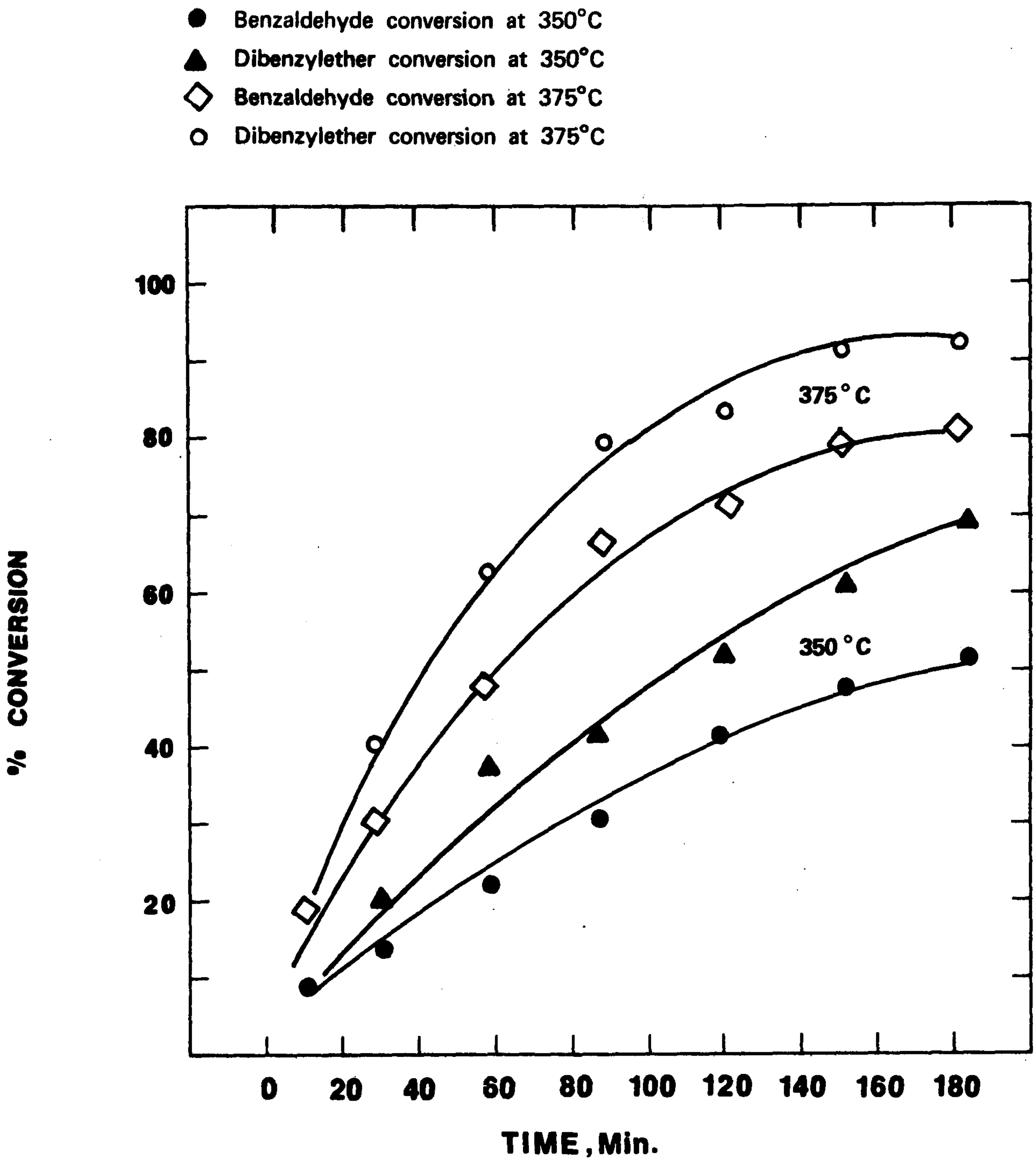
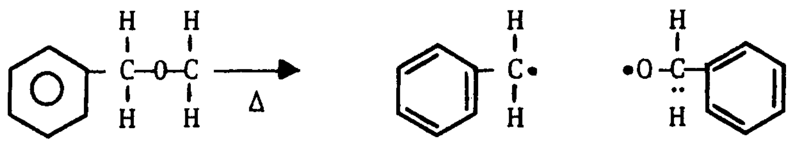


FIGURE 45

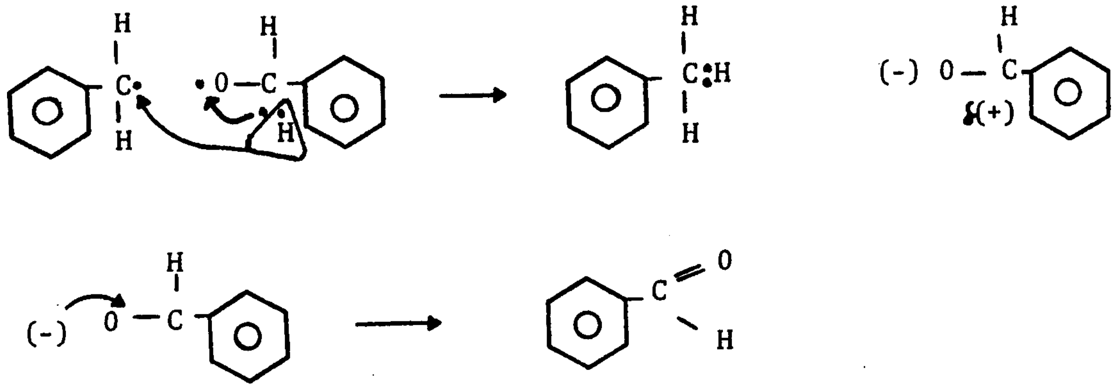
CONVERSION OF OXYGEN CONTAINING COMPOUNDS IN TETRALIN



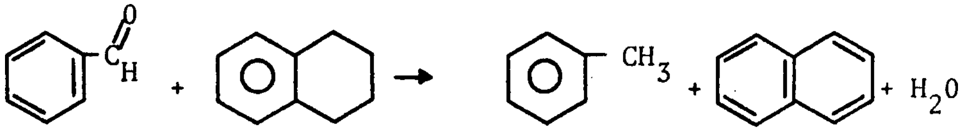
(1) Intermolecular: thermal cleavage to yield free radicals:



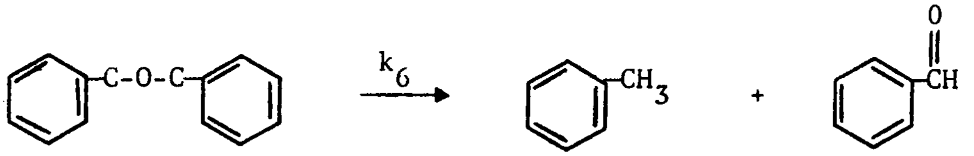
(2) Intramolecular (internal): generate toluene and benzyloxy anion which is then stabilized by rearrangement to the aldehyde.



The intramolecular rearrangement is more favorable in poor (non-donor) solvents and at low temperatures (< 365°C). However, the overall conversion of dibenzylether is enhanced by tetralin at any temperature by providing a source of hydrogen sites and by the fact that a secondary reaction of benzaldehyde can occur:



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



(16)

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

$$\frac{d\left(C_{DBE}\right)}{dt} = -k_6\left(C_{DBE}\right)$$

where C_{BDE} is the concentration of dibenzyl ether in weight percent. As shown in the Arrhenius plot, Figure 46, the activation energy of k_6 was 36,440 calories/gram mole. Based on the above data, the intramolecular reaction route is most likely to be valid.

The reaction of benzaladehyde with tetralin best fits the rate expression:

$$\frac{d\ C_{BA}}{dt} = -k_7\ C_{BA}\ C_T$$

where C_{BA} and C_T are the concentrations of benzaldehyde and tetralin in weight percent. The activation energy for k_7 is 32,000 calories/gram mole.

Future experiments will be done with deuterium-tagged tetralin and at low temperatures using deuterium gas in an effort to confirm the above reaction mechanism.

I. D_4-Tetralin Studies

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.

FIGURE 46

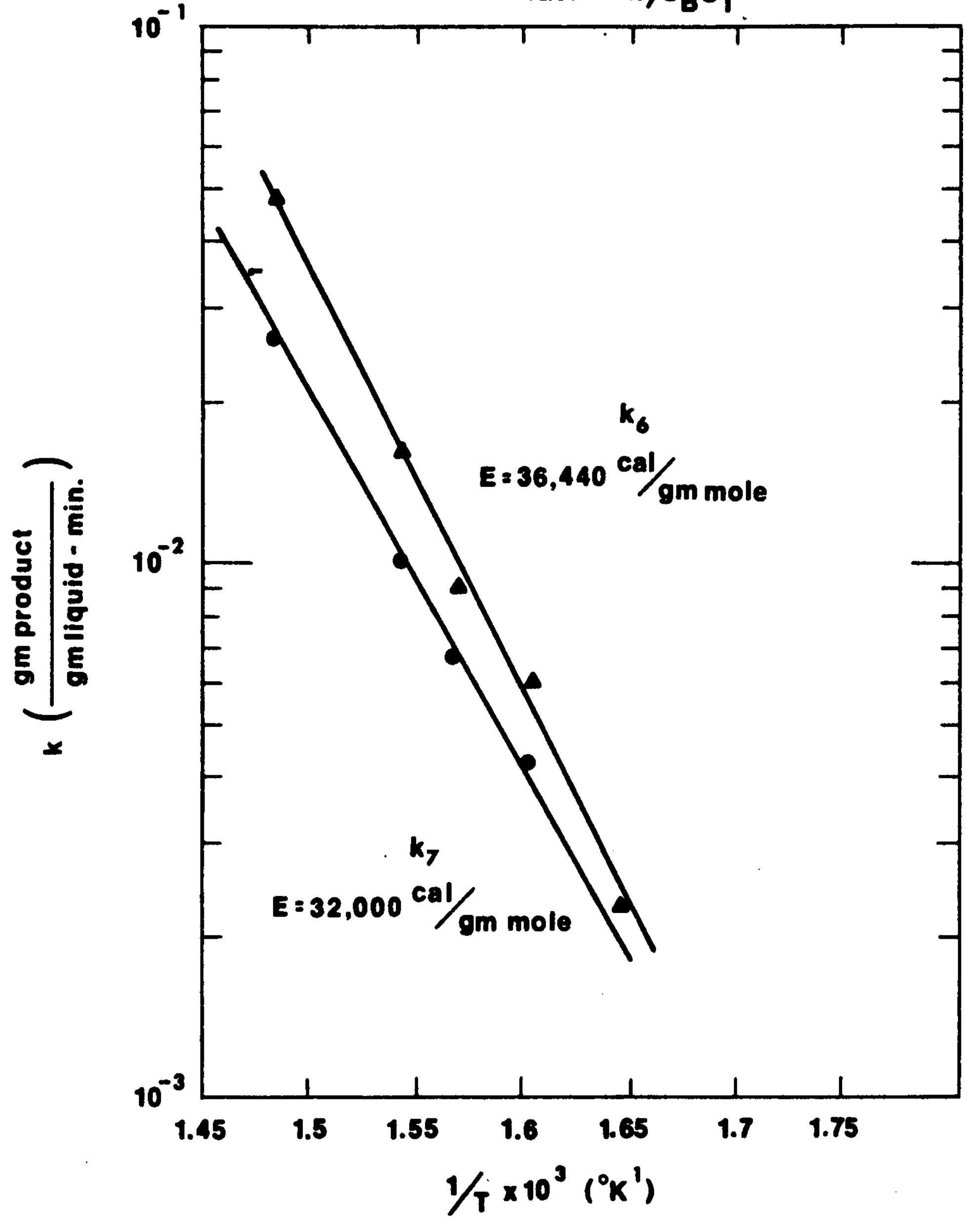
ARRHENIUS PLOTS FOR THE DIBENZYL ETHER AND BENZALDEHYDE REACTIONS

$$\text{Dibenzyl ether} \xrightarrow{k_6} \text{Toluene} + \text{Benzaldehyde}$$

$$\text{rate} = -k_6 C_{DBE}$$

$$\text{Benzaldehyde} + \text{Tetralin} \xrightarrow{k_7} \text{Toluene} + \text{Dihydrotetralin}$$

$$\text{rate} = -k_7 C_B C_T$$



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, should 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. Current studies are employing 350°C, dibenzylether and dibenzylsulfide as acceptors for studying the selectivity of D-transfer. Recent experiments have established that scrambling does not occur between mesitylene and D_4-tetralin at 350°C.

J. Synthesis of Labeled Donor Solvents

In the preparation of tagged compounds, experimentation can be categorized into the deuteration of donor solvents and the synthesis of ^{13}C-tagged dimethyl tetralin and octahydrophenanthrene.

1. 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 (660°F), a 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 was 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.

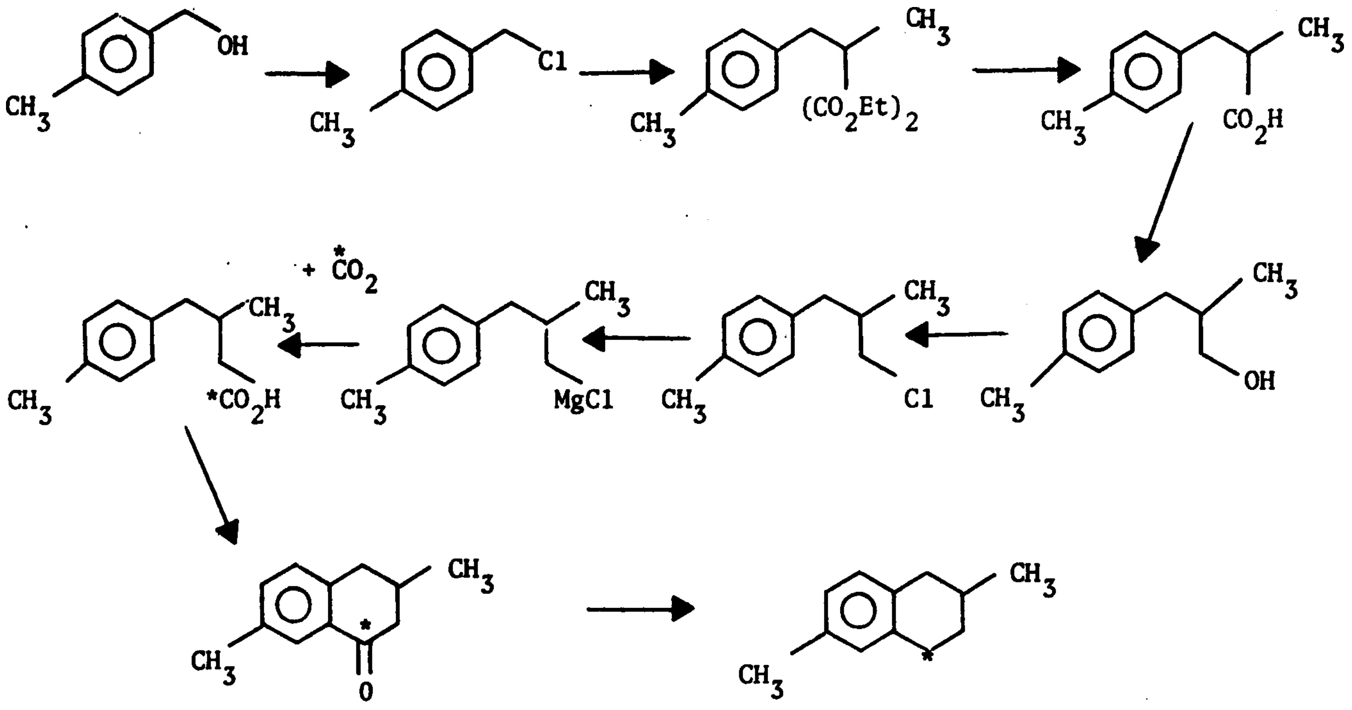
As shown in Table D of Appendix II, a typical product consisted principally of D_4 and D_5 derivatives. However, the deuterium had been scrambled into both the aromatics and hydroaromatic rings. In addition, the vent gas from the reactor had consisted of about equal concentration of H_2, HD and D_2. In summary, a NiW catalyst is effective for the reduction reaction, but its use promotes scrambling. More selective means are available and will be used if warranted. In particular, this reaction can be done with a more active catalytic system with per-deuteroacetic acid as solvent. Reference is also made to the work of L. Heredy and R. P. Skowronski reported at the July 16 ERDA contractors' meeting [Contract No. E(49-18)-2328].

2. ^{13}C Labeled Compounds

Experiments with ^{13}C-tagged compounds are designed to provide insight into: (a) the fate of the donor solvent, (b) the importance of ring opening-closing reactions resulting in carbon scrambling, (c) degree of double bond isomerization at reaction conditions, and (d) the extent of carbon incorporation from the donor to acceptor. The specific compounds chosen for the ^{13}C experiments were 2,6-dimethyl tetralin and sym-octahydrophenanthrene. The compounds have unique structural features which may have an effect on the mechanism of hydrogen transfer. These are: (a) the presence of alkyl groups on the hydroaromatic ring may result in changes due to steric effects, (b) both have readily assigned ^{13}C-NMR spectra, (c) both have higher boiling points than the typically used solvent, tetralin, and (d) sym-octahydrophenanthrene (H_8Ph) has a greater number of transferable hydrogens per molecule than tetralin.

Since neither compound is commercially available in quantities needed for this project, routes for their synthesis were developed. These syntheses were conducted under the direction of Dr. E. J. Eisenbraun of Oklahoma State University. They required substantial innovation to ensure high yields and selectivity due to the expense of the ^{13}C tag.

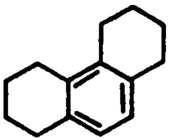
a. 2,6-Dimethyl-4-^{13}C Tetralin: The step-wise schematic for preparing this compound is represented as follows:

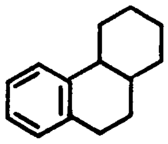


The $^*CO_2$ is generated from purchased Ba $^{13}CO_3$. An all-metal system was designed for performing the Grignard and CO_2 insertion steps such that quantitative transfer was achieved.

A sample of 100 g of labeled tetralin has been prepared with 97% ^{13}C purity. One kg of the unlabeled compound has been prepared by catalytic hydrogenation of 2,6-dimethylnaphthalene. Hydrogen-transfer experiments will utilize solutions of about 10% ^{13}C concentration.

b. Octahydrophenanthrene: This compound can exist as either the symmetric (sym) or asymmetric (asym) isomer:


Sym


Asym

As noted earlier in this report, the symmetric isomer was chosen for experimentation due to its stability.

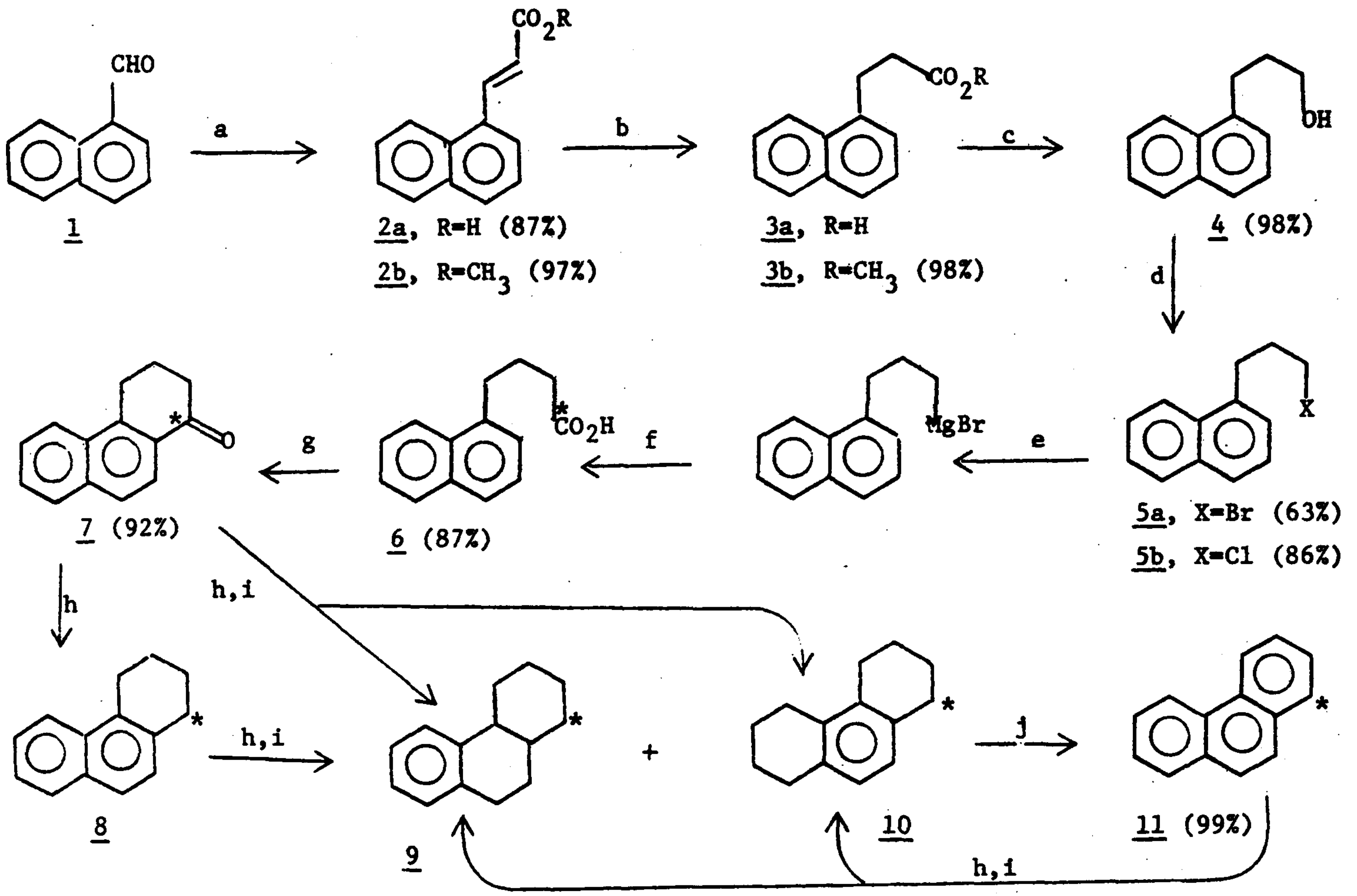
The procedure for the preparation of the sym-isomer with the ^{13}C label at one of the benzylic positions is outlined in Figure 47. The major reagents are also shown.

A 100 g sample of pure ^{13}C sym-isomer has been prepared; 1 kg of the unlabeled sym-isomer has been prepared by catalytic hydrogenation of phenanthrene. Experimentation is under way using a 10% concentration of ^{13}C-containing material.

DCC:WPC

Figure 47

PREPARATION OF OCTAHYDROPHENANTHRENE



[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.

REFERENCES

1. Ruberto, R.G., Cronauer, D.C., Jewell, D.M., and Seshadri, K.S., Fuel 56, 25, January 1977.

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

3. Brucker, R., and Kolling, G., Brem-Chemie 46, 41 (1965).

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APPENDIX I.

Summary of Hydrogen Transfer Experiments

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

APPENDIX II.

Table A

SUMMARY OF POTENTIAL HYDROGEN ACCEPTORS SCREENED AND CONDITIONS FOR RUN SERIES 923

Feed Description						
Acceptor (10 Wt%)	Donor (90 Wt%)	Temperature, °C	Run No.	Average Feed Rate cm^3/hr	Average Product Rate, G/hr	Average Gas Rate SCFH
Phenanthrene	a	475	923A	10.28	9.63	0.159
Dibenzofuran	a	475	923B	10.28	10.04	0.138
Dibenzothiophene	a	475	923C	10.28	9.77	0.137
N-Ethyl Carbazole	a	475	923D	9.98	9.88	0.152
Dibenzyl	a	475	923E	9.89	9.73	0.136
Dibenzyl Ether	a	475	923F	9.91	9.53	0.140
Hexadecyl Ether	a	-	-			
α-Tetralone	a	475	923H	10.18	9.91	0.175
Dodecyl Ether	a	475	923I	10.08	9.59	0.206
Dodecyl Sulfide	a	-	-			
Phenanthrene	a	475	923K	9.63	9.41	0.164
Phenanthrene	b	475	923L	9.83	9.78	0.142
Phenanthene	c	475	923M	9.92	10.70	0.120
Phenanthrene	d	475	923N	10.22	10.54	0.112
Phenanthrene	e	475	923O	10.20	10.72	0.116
Phenanthrene	a	475	923P	10.03	9.82	0.131
Dibenzyl Ether	a	425	923Q	10.18	9.25	0.189
Dibenzyl Ether	a	375	923Q	10.28	8.33	0.165
Dibenzyl	a	375	923R	10.06	9.78	0.107
Dibenzyl	a	425	923R	10.06	9.85	0.134
2,6-Di-Tert. Butyl-4-Methyl Phenol	a	475	923S	9.99	9.17	0.111
2,6-Di-Tert. Butyl-4-Methyl Phenol	a	425	923S	9.99	9.25	0.163
2,6-Di-Tert. Butyl-4-Methyl Phenol	a	375	923S	10.22	9.44	0.130

(a) Tetralin, 98% Nominal Purity, Chemical Sample Co.
(b) Tetralin, 95% Nominal Purity, Fisher.
(c) Tetralin, X9308A7 10% Cur
(d) Tetralin, X9352A07 10% Cur
(e) Tetralin, X9352A06 Cur 6

RUN SERIES 923 RESULTS

Acceptor	Temp., °C	Gas Chromatography Analyses, Wt% Feed Donor	Gas Chromatography Analyses, Wt% Feed Acceptor	Gas Chromatography Analyses, Wt% Product Donor	Gas Chromatography Analyses, Wt% Product Acceptor	Conversion of Donor (Tetra.)%	Conversion or Acceptor %	Average Nominal Hold Time, Minutes
Dibenzyl Ether	375	91.20	7.03	90.10	3.12	1.21	55.62	78
	425	91.20	7.03	87.40	-	4.17	100.0	79
	475	91.06	7.26	84.07	-	7.68	100.0	81
Dibenzyl	375	90.62	7.96	88.85	9.36	1.95	(b)	80
	425	90.62	7.96	84.69	6.62	6.54	16.83	80
	475	88.93	9.40	73.69	3.04	17.14	67.66	81
α-Tetralone	475	90.73	7.34	88.23	6.09	2.76	17.03	79
Dibenzofuran	475	90.54	7.91	85.26	7.02	5.83	11.25	78
2,6,-Di-Tert, Butyl-4-Methyl Phenol	375	87.57	7.94	92.34	2.50	-	68.51	79
	425	87.57	7.94	92.46	1.28	-	83.33	81
	475	87.57	7.94	84.89	0.37	3.06	95.34	81
Phenanthrene	475	89.57	8.00	82.69	4.96	7.68	38.00	78
	475	88.99	8.71	80.80	5.74	9.20	34.10	84
	475	90.05	6.29	79.89	5.88	11.28	6.52	80
Phenanthrene	475	88.86	6.11	77.22	7.33	13.10	(b)	82
	475	86.71	8.97	81.35	7.07	6.18	21.18	81
	475	86.45	5.42	82.48	6.52	4.59	(b)	79
	475	89.24	5.13	82.95	5.53	7.05	(b)	79
Dibenzothiophene	475	91.40	(c)	83.00	(c)	9.19	(b)	77
N-Ethyl Carbazole	475	91.15	(c)	66.46	(c)	27.09		81
Phenanthrene	475	87.13	9.46	64.51	7.66	25.96	19.03	105

(a) Previous run series.

(b) Product percentages greater than feed percentages.

(c) Multiple GC peaks.

Table C

RUN SERIES 923 - TETRALIN CONVERSION/REARRANGEMENT COMPOSITIONS

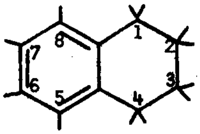
Acceptor	Temperature, °C	Partial Product Composition, Wt%			
		Indane	Methyl Indane	Tetralin	Naphthalene
Dibenzyl Ether	375	-	0.39	90.10	0.95
	425	0.27	1.21	87.40	3.43
	475	0.60	3.46	84.07	4.49
Dibenzyl	375	-	0.26	88.85	0.60
	425	0.24	1.99	84.69	2.32
	475	1.08	6.55	73.69	7.24
α-Tetralone	475	0.26	1.93	88.23	2.45
Dibenzofuran	475	0.40	3.26	85.26	2.72
2,6-Di-Tert. Butyl-4-Methyl Phenol	375	-	0.28	92.34	0.62
	425	-	0.80	92.46	1.16
	475	0.56	4.83	84.89	4.46
Phenanthrene	475	0.72	4.63	82.69	4.51
	475	0.80	5.65	80.80	4.22
	475	0.86	6.31	79.89	4.03
Phenanthrene	475	0.98	6.32	77.22	4.98
	475	0.42	2.91	81.35	5.89
	475	0.28	2.80	82.48	5.06
	475	-	3.05	82.95	4.52
Dibenzothiophene	475	-	6.68	83.00	3.01
N-Ethyl Carbazole	475	-	10.81	66.46	10.01

Table D

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