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INVESTIGATION OF MECHANISMS OF HYDROGEN TRANSFER IN COAL HYDROGENATION

Semi-annual Technical Progress Report
for July-December, 1976
(Stage I, Phase I Report Period)

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ABSTRACT

This report presents progress being made in the study of hydrogen transfer in coal hydrogenation. Stage I consisting of establishing an inventory of model compounds, conducting preliminary experimentation to screen potential acceptors and donors, and establishing analytical techniques has been completed. Sources of model compounds have been established and the synthesis of tagged compounds is well underway. Preliminary donor-acceptor experiments have given a relative ranking of reactivities of acceptors and have established the specific donors along with reaction conditions to be used. Experimentation has also established the advantage of using a batch autoclave system with high temperature reactant charging over a packed-bed flow unit.

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 will be done using both tagged and untagged compounds as donors and acceptors. The tagged compounds include those containing stable (C^{13} and deuterium) or radioactive isotopes (C^{14} and H^3) or those having functionality that allows for isolation by extraction (tetrahydroquinoline). Experimentation is being conducted at conditions consistent with processes currently being developed to convert coal to liquids.

The project is divided into two phases, the first dealing with the study of model compounds, the second consisting of the application of these results to the study of coal and coal derived liquids. The following is a summary of the tasks to be covered in the initial phase of this project:

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.

SUMMARY OF PROGRESS TO DATE

The project is essentially progressing according to schedule. An inventory of commercially available model compounds has been established. The synthesis of tagged compounds is about 1 month behind the original schedule, but this will not interfere with the progress of experimentation. Operating conditions have been set for the deuteration of naphthalene to make deuterotetralin, and preparation of samples is now underway. The synthesis of ^{13}C tagged octahydrophenanthrene and dimethyl tetralin is also underway, and samples for experimentation should be available in 1 month. The preliminary hydrogen transfer experiments have been completed. Operating conditions have been established for planned detailed experimentation. Analytical procedures have also been established with some refinements being necessary as experimentation progresses.

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

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Stage 1. Preparative Work

a. Synthesis and procurement of model compounds:

With respect to establishing an inventory of model compounds, suppliers have been found for the commercially available donors and acceptors. Sufficient inventories of the selected compounds are on-hand for experimentation.

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.

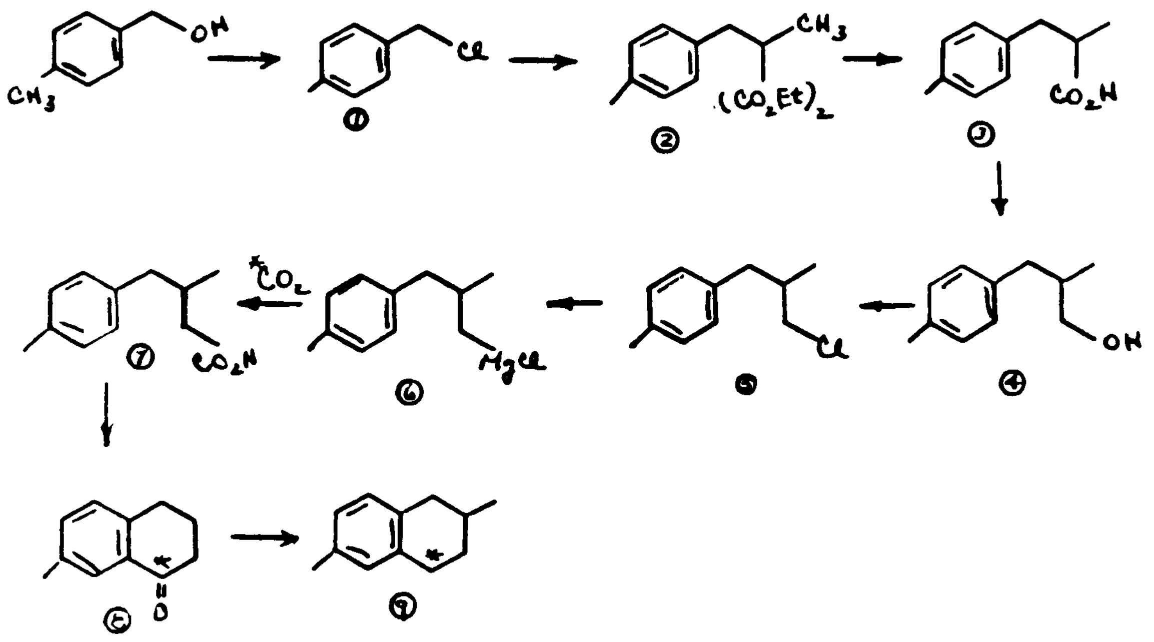
Experimentation is underway to establish reaction conditions for the reduction of naphthalene with deuterium to prepare a partially deuterated tetralin. Initial runs with hydrogen were made with a CoMo catalyst at temperatures to 410°C (770°F) and reaction times to 4 hours.

While these conditions were adequate for phenanthrene hydrogenation, insufficient naphthalene conversion was observed. A NiW catalyst (Nalco Sphericat 550) was substituted for the above and sufficient carbon disulfide added to maintain the catalyst in a sulfided state. At reaction conditions of 355°C (670°F) and 3 hours residence time, somewhat excessive conversion was observed (see Table 1). Several hydrogenation experiments will be done to reduce the conversion of naphthalene to decalin and yet retain high yields of tetralin. Deuterium will then be substituted for hydrogen in preparatory runs.

It is also noted that Professor E. J. Eisenbraun of Oklahoma State University is evaluating the deuteration of tetralin and its alkylated derivatives using a catalytic system with per-deuteroacetic acid solvent.

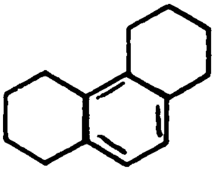
Dimethyl tetralin and octahydrophenanthrene are being synthesized with ^{13}C tags located in specific positions. This synthesis is being conducted in collaboration with Professor E. J. Eisenbraun.

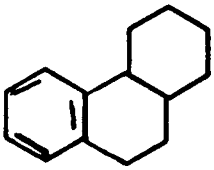
The preparation of 2,6-dimethyl-4C^{13}-tetralin was undertaken first. The synthesis route is represented as follows:



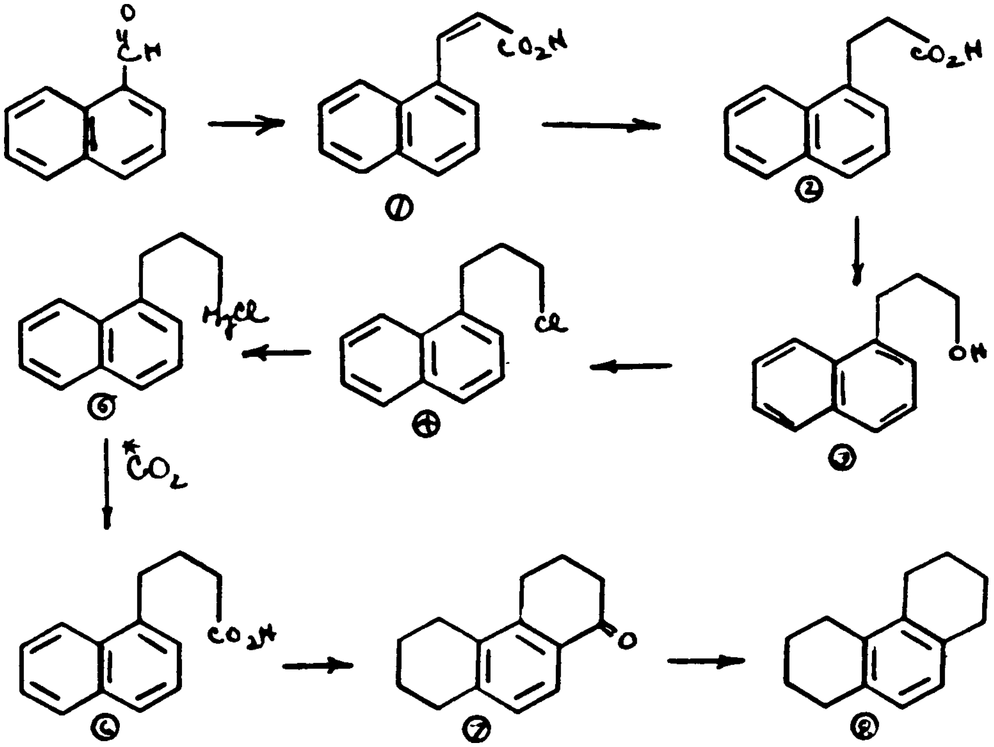
The above steps have been developed and essentially optimized through compound (5). Yields have been high. Experience is now being gained with "cold" CO_2. (Ba $^*CO_3$ has been secured as the source of $^*CO_2$.) A delay has occurred due to difficulties in securing correct fittings for the gas transfer system from the CO_2 generator. An all-metal system is considered necessary to ensure a quantitative transfer of expensive $^*CO_2$.

The second ^{13}C tagged compound, octahydrophenanthrene, can exist as either the symmetric (sym) or asymmetric (asym) isomer, as shown below:





As shown in the previous quarterly report (July-September, 1976), the asymmetric isomer was not sufficiently stable for experimentation at coal liquefaction conditions. Therefore, the decision was made to synthesize the symmetric isomer with the ^{13}C tag at C-4 position. This synthesis is also under the direction of Professor E. J. Eisenbraun and is proceeding as follows:



The steps have been optimized through step (4). When the CO_2 generator is functional, the remaining steps will be evaluated. It is noted that this synthesis is not reported in the literature, and that it represents a novel preparation.

b. Selection of analytical methods:

Little further experimentation appears necessary in the development of analytical methods. The applicable techniques include liquid chromatography (LC), gas chromatography (GC) and a combination of GC-mass spectrometry. In most of the donor-acceptor systems evaluated, a high resolution capillary GLC with a 100-foot SCOT column appeared to offer sufficient separation. When difficulties occurred, a medium resolution GC with a packed column was used with interfacing to a DuPont 21-491 mass spectrometer.

The analysis of tagged compounds will be accomplished with the use of a CEC-103 mass spectrometer and a Varian CFT-20 NMR (both hydrogen and ^{13}C). Apparently there is a possibility of using in the local vicinity an NMR with a deuterium probe. This will be checked into.

Another option is the use of a high performance liquid chromatograph being operated in both analytical and preparative modes. This apparatus primarily separates groups or classes of compounds.

c. Preliminary experimentation:

The conducting of preliminary donor/acceptor experiments has been completed and a selection of model compounds for detailed study has been made. In addition, the decision has been made to carry out the exchange reactions in a stirred autoclave with high temperature injection of the acceptor. The following is a discussion of the results of the screening of donors and acceptors at reaction conditions typical of coal liquefaction.

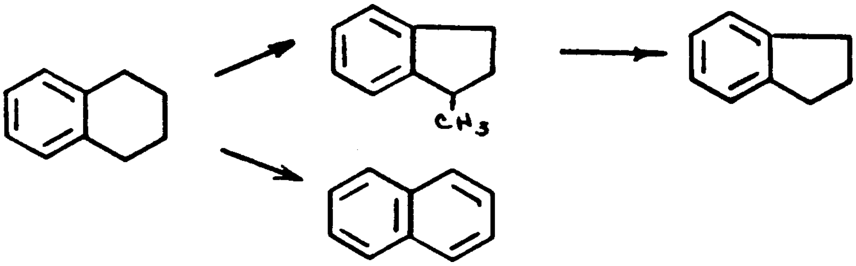
1) Experimental: The exchange reactions were done in both a micro-unit and a stirred batch autoclave. The micro-unit primarily consisted of a tubular reactor packed with inert quartz. The feed rate to this latter unit was typically controlled for nominal space times of 50 to 120 minutes. The second unit consisted of a 300 cc batch, stirred autoclave which was modified to provide for injection of reactants at elevated temperatures under pressure. The screening experiments were performed by charging 75 ml of donor to the reactor and rapidly heating it to the desired temperature (60-80 minutes were typically needed). At this temperature, 75 ml of a solution of 20% acceptor in donor was injected using nitrogen at 10.3 MPa (1500 psig). Samples were then taken periodically during the run.

In most cases, experiments were first made at 475°C (887°F). If a significant reaction was observed, lower temperatures were then used.

2) 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. Its primary disadvantages are 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 II

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 extract 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.

These 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 micro-unit at reactor conditions of 425° 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 to 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 2 and 3.

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 were 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 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).

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

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.

3) Acceptors: A summary of the results of both autoclave and micro-unit experiments with tetralin and various acceptors is given in Table II. A qualitative comparison of reaction rates of acceptors is given by the ranking A → D (upper case for the autoclave runs and lower case for the micro-unit runs). The rating is based upon distinct evidence (LC or GC-MS) of conversion of acceptors.

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

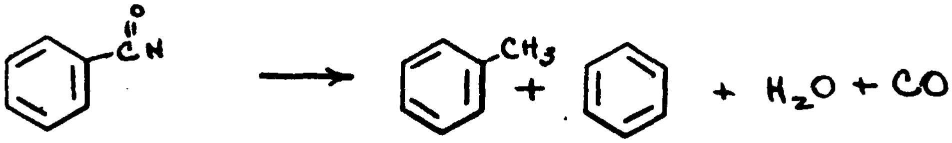
The time-temperature-conversion plots for the dibenzyl experiment in the autoclave is shown in Figure 4. At 400°C, the major product was toluene confirming that the β-cleavage to benzylic intermediate was occurring.

With the substitution of a heteroatom in the diaryl chain link (dibenzyl ether), a high reaction rate was observed at all temperatures. The conversion profile for the autoclave seen at 400°C is given in Figure 5.

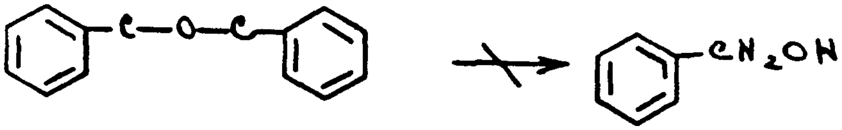
Studying the products from this overall reaction in the 375°-475°C range provided interesting clues as to the conversion path:

①

②



③



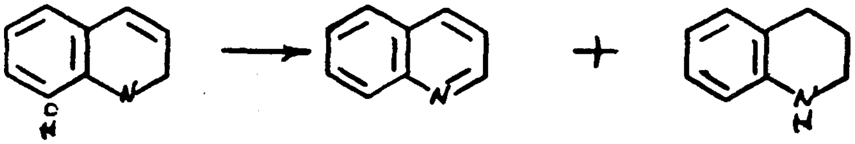
The cleavage of dibenzyl ether occurred at the β-position generating both the benzyl and benzyl alcohol radicals (assumed). Hydrogen was abstracted from tetralin to yield toluene. The oxygen radical did not stabilize itself in a similar manner, but apparently formed a high concentration of benzaldehyde intermediates. The presence of high concentrations of benzaldehyde was confirmed by GLC, GC-MS, and IR analyses. Carbon monoxide was detected in the gas product stream, but future work is required to differentiate the dehydration and decarbonylation reactions.

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 6 and 7 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.

d. Planned Research in Stage 2:

The primary objective of Stage 2 is that of arriving at a logical explanation of hydrogen transfer kinetics and developing mechanisms using experimentation with model compounds. This section is written to outline the research plans for the 12-month period covered in Stage 2. To a major extent, these plans are based upon the results of the above preliminary experiments. An outline of planned experimentation is given in Figure 8.

In summary, two research areas will be covered concurrently. The primary area will consist of in-depth experimentation of selected acceptors with a series of donors (with and without tags). Sufficient experimentation will be carried out with each acceptor to develop a kinetic model of the transfer reaction. The second area will consist of the study of background or scrambling reactions which may interfere with the above results.

The first acceptor to be evaluated is dibenzyl. Preliminary experimentation has indicated that this compound fractured in the presence of tetralin at reactor conditions typical of coal liquefaction processes. Specifically, little reaction was observed at 375°C, and essentially complete fracturing occurred at 475°C with a 1-hour residence time. The primary reaction product, toluene, can be separated from the donors and characterized by GC, MS, NMR, etc.

Dibenzyl experiments will consist of the following:

1. Three-hour batch autoclave runs (in duplicate) with tetralin at temperatures of 375°, 400°, 425°, and 450°C. Reactor contents will be periodically sampled. Acceptor concentrations between 10 and 50% will be tested at 425°C.

1a. A series of runs with deutero tetralin at 400° and 425°C to determine exchange reactions and sites.

2. A limited number of runs with dimethyl tetralin ("cold") to establish the effect of donor group substitution on hydrogen transfer.

2a. Repeat of (2) with deuterated dimethyl tetralin.

3. Sufficient experiments with octahydr-phenanthrene ("cold") to establish a kinetic model and provide a comparison with (1) above.

3a. Test labeled hydrophenanthrenes.

The second acceptor to be evaluated is dibenzyl ether. A similar schedule of experiments to those above is planned with the exception of using a lower temperature range (350°-425°C). The primary reaction products from the preliminary runs were toluene and benzaldehyde. Production of the latter compound was not anticipated; therefore, deuterium exchange reactions will probably be emphasized to develop an understanding of the reaction.

Depending upon the results of the dibenzylether studies, limited experimentation will be undertaken with dibenzyl sulfide.

To provide a further study of hydrogen transfer to oxygen-containing groups, tetralone and naphthol will be used. In these experiments, dimethyl tetralin is the preferred donor solvent to allow for differentiation of donor and acceptor reaction products.

It is anticipated that additional acceptors and donors will be included as experimentation progresses.

The second area of planned experimentation is that of examining "scrambling" reactions. Background exchange of deuterium between donors and acceptors may occur to a sufficient extent that interpretation of the transfer reaction is difficult. Measurement of this background exchange will be one of the first steps in experimentation with deuterated solvents.

It has been observed that tetralin undergoes rearrangement to methyl indane in the presence of potential acceptors, in spite of an apparent lack of change of these acceptors. This reaction is particularly amenable to study using deuterated or ^{13}C tagged tetralin. The depth of experimentation will depend upon initial results.

Experiments with ^{13}C tagged compounds are designed to provide insight into: (1) the fate of the donor solvent, (2) the importance of ring opening-closing reactions resulting in carbon scrambling, (3) degree of double bond isomerization at reaction conditions, and (4) the extent of carbon incorporation from the donor to acceptor. The analysis of products will be done using ^{13}C-NMR and precise mass measurements to determine position(s) and fate of the label. The supply of ^{13}C tagged material is limited and its use will depend upon data obtained during the donor/acceptor experiments.

A limited number of runs will be made with catalysts present. Plans will be set after the "scrambling" experiments are completed.

Figure 1

Program Schedule for Hydrogen Transfer Project

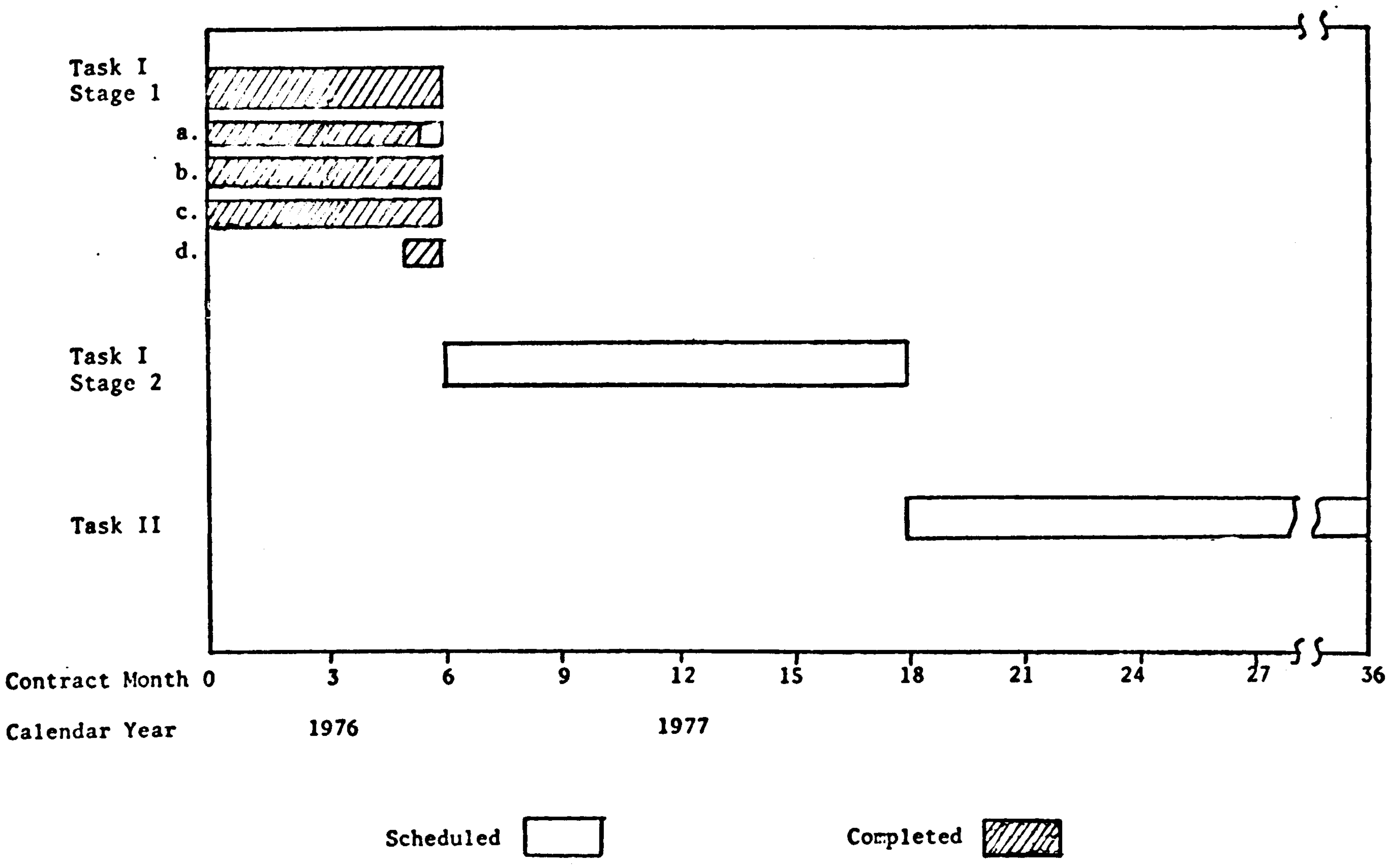


Figure 2

Tetralin Conversion as Functions of Temperature and Phenanthrene Level

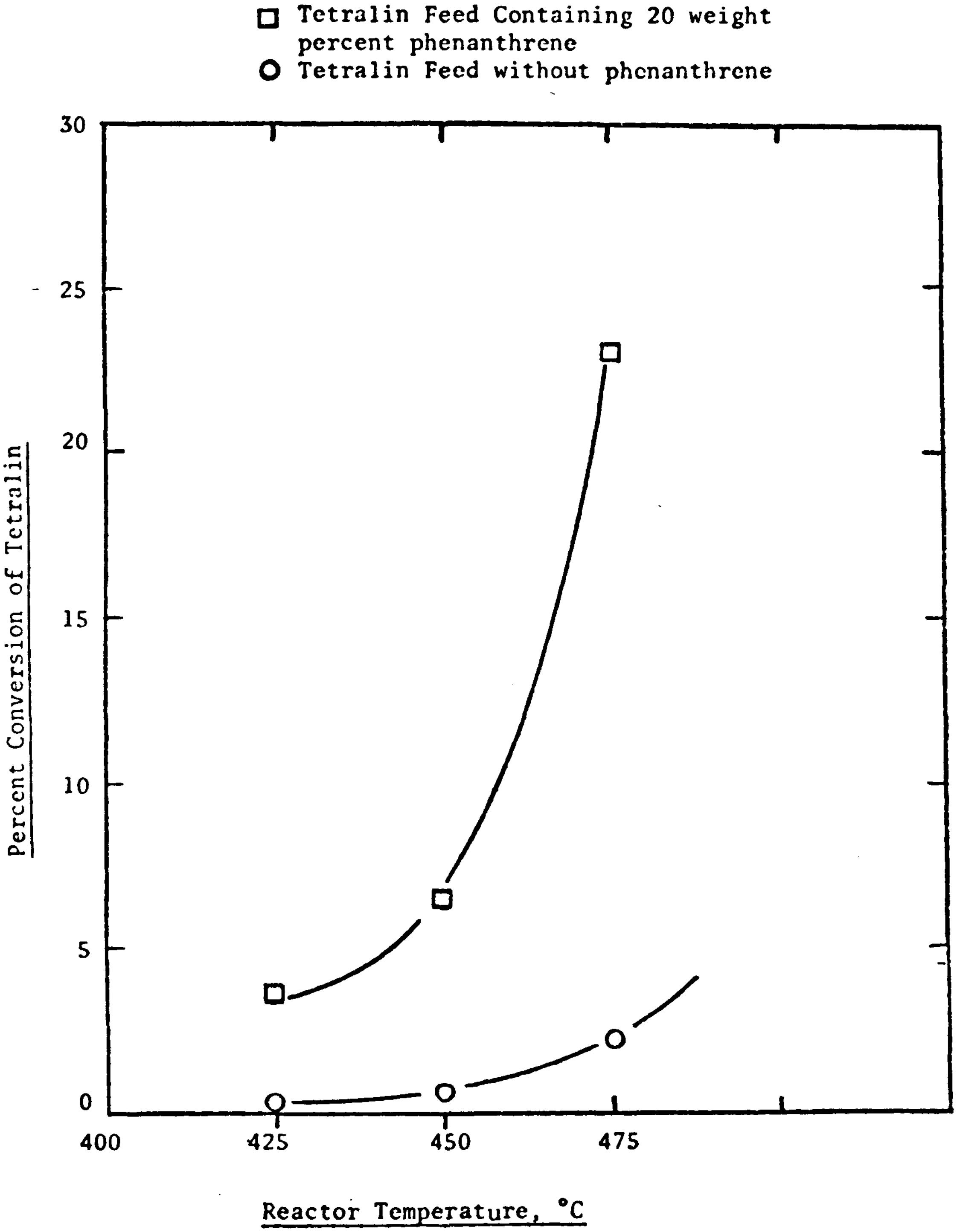


Figure 3

Effect of Phenanthrene Concentration upon Tetralin Conversion

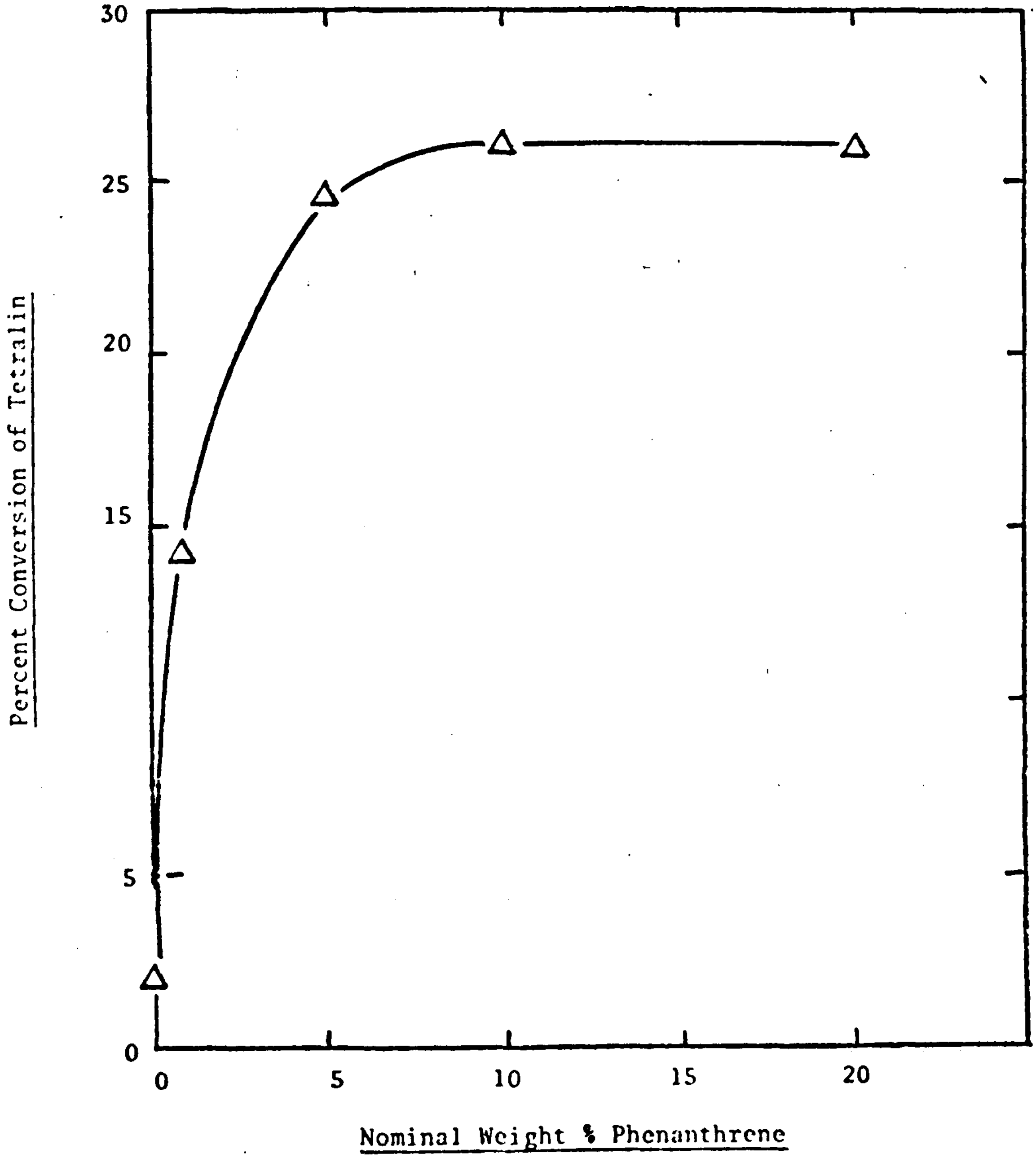


Figure 4

Dibenzy Conversion Profile
(400°C Maximum Temperature)

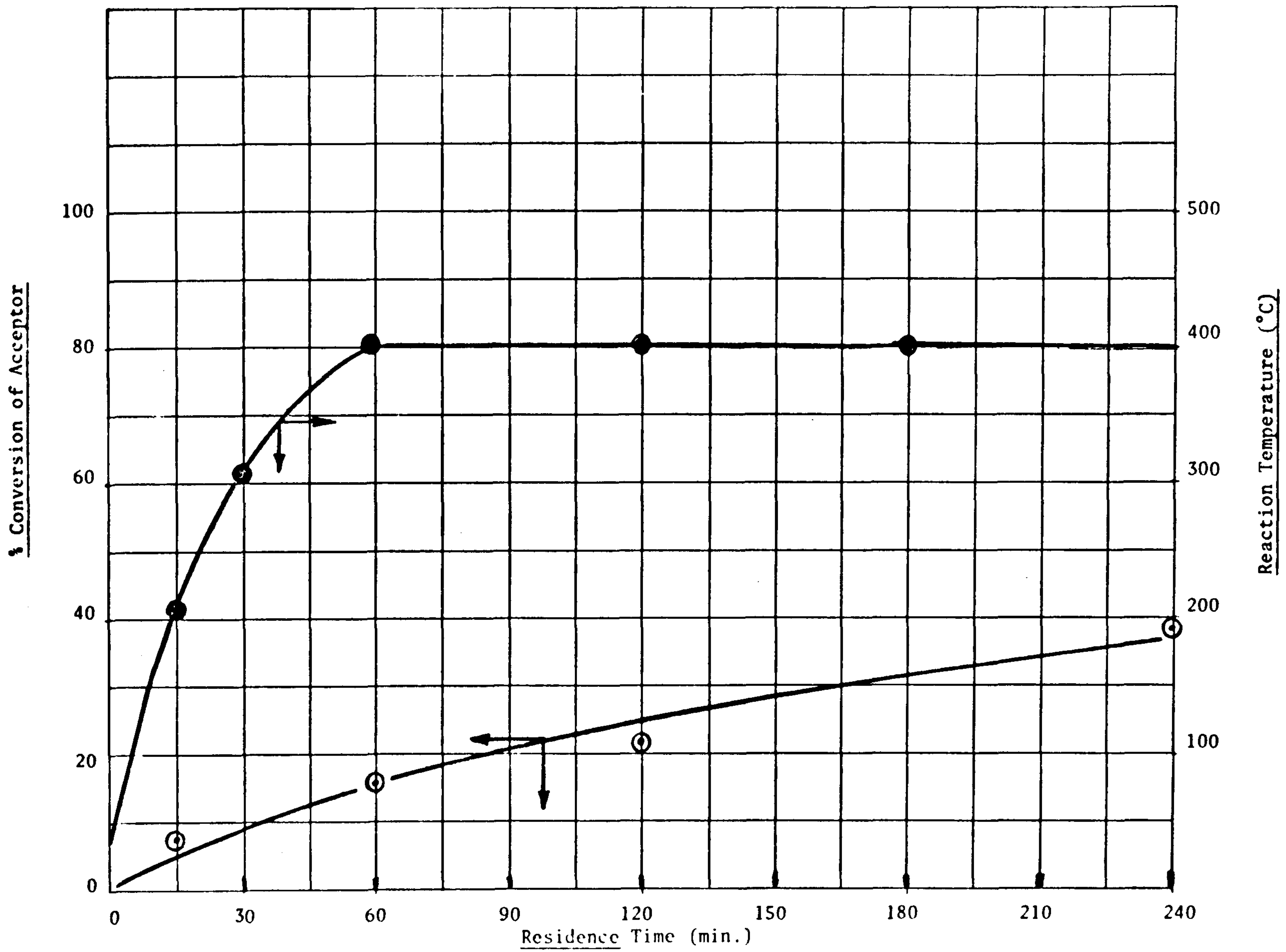


Figure 5

Dibenzyl Ether Conversion Profile
(400°C Maximum Temperature)

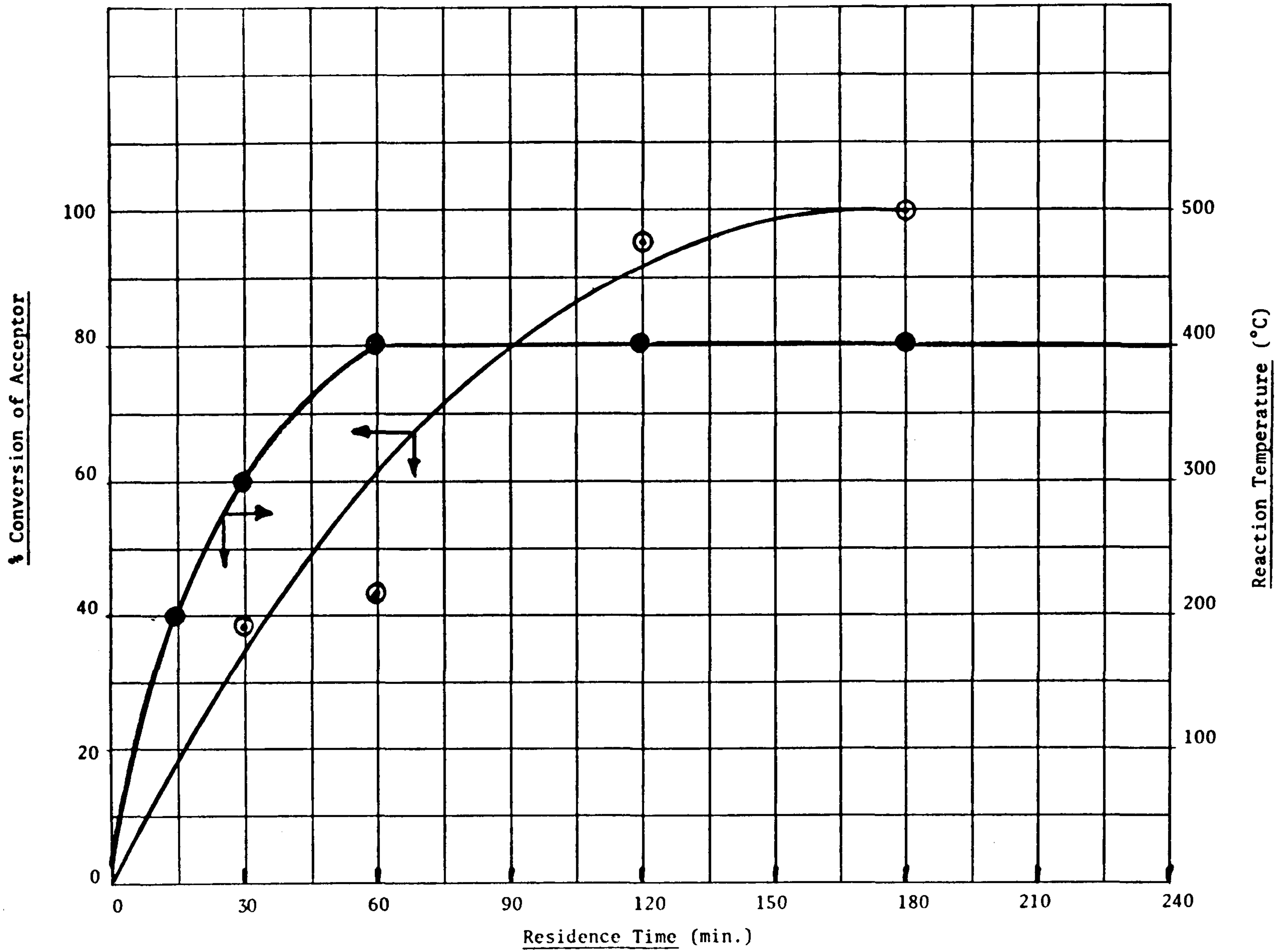


Figure 6

α Tetralone Conversion Profile

(400°C Maximum Temperature)

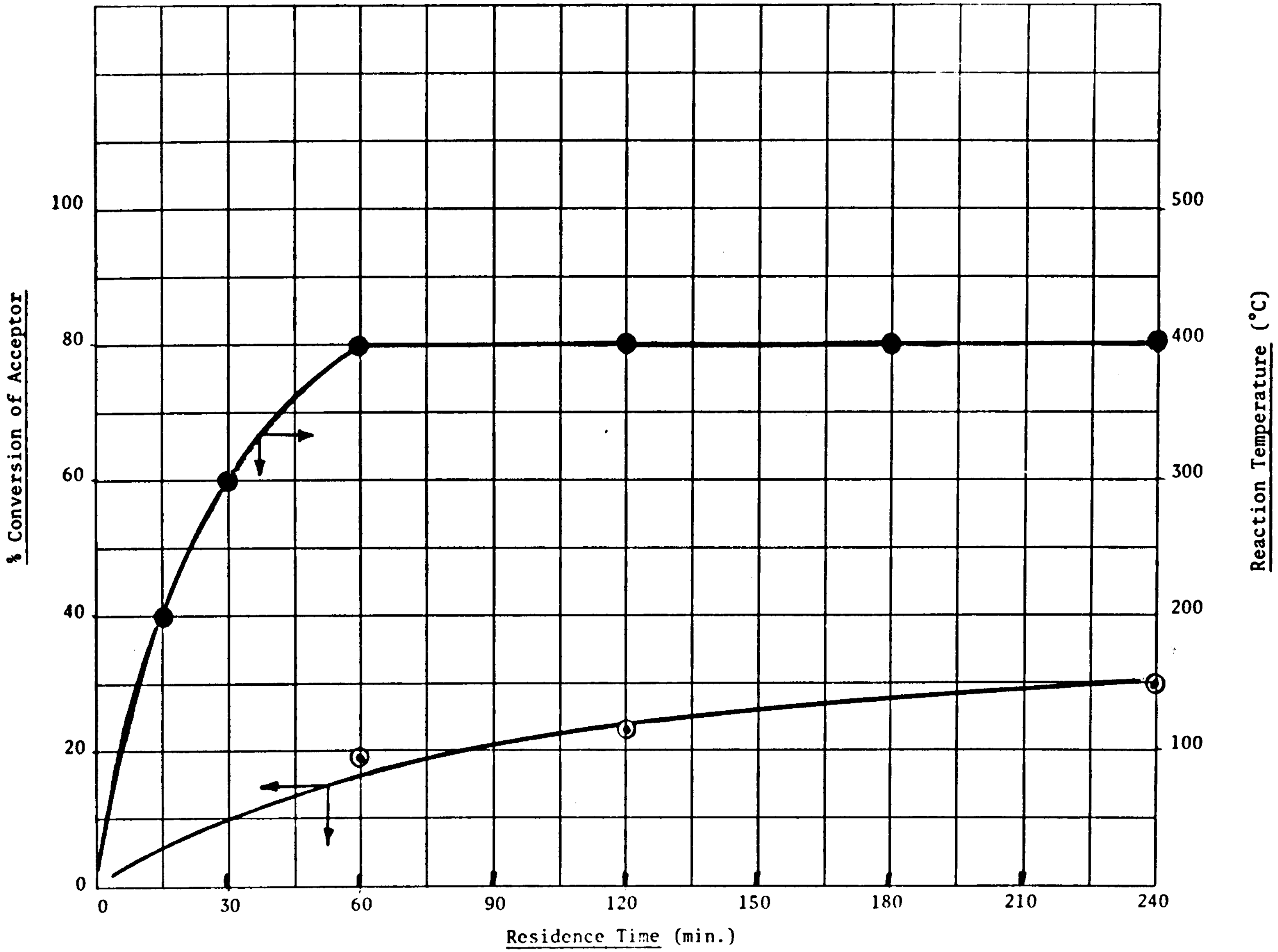


Figure 7

α Tetralone Conversion Profile
(475°C Maximum Temperature)

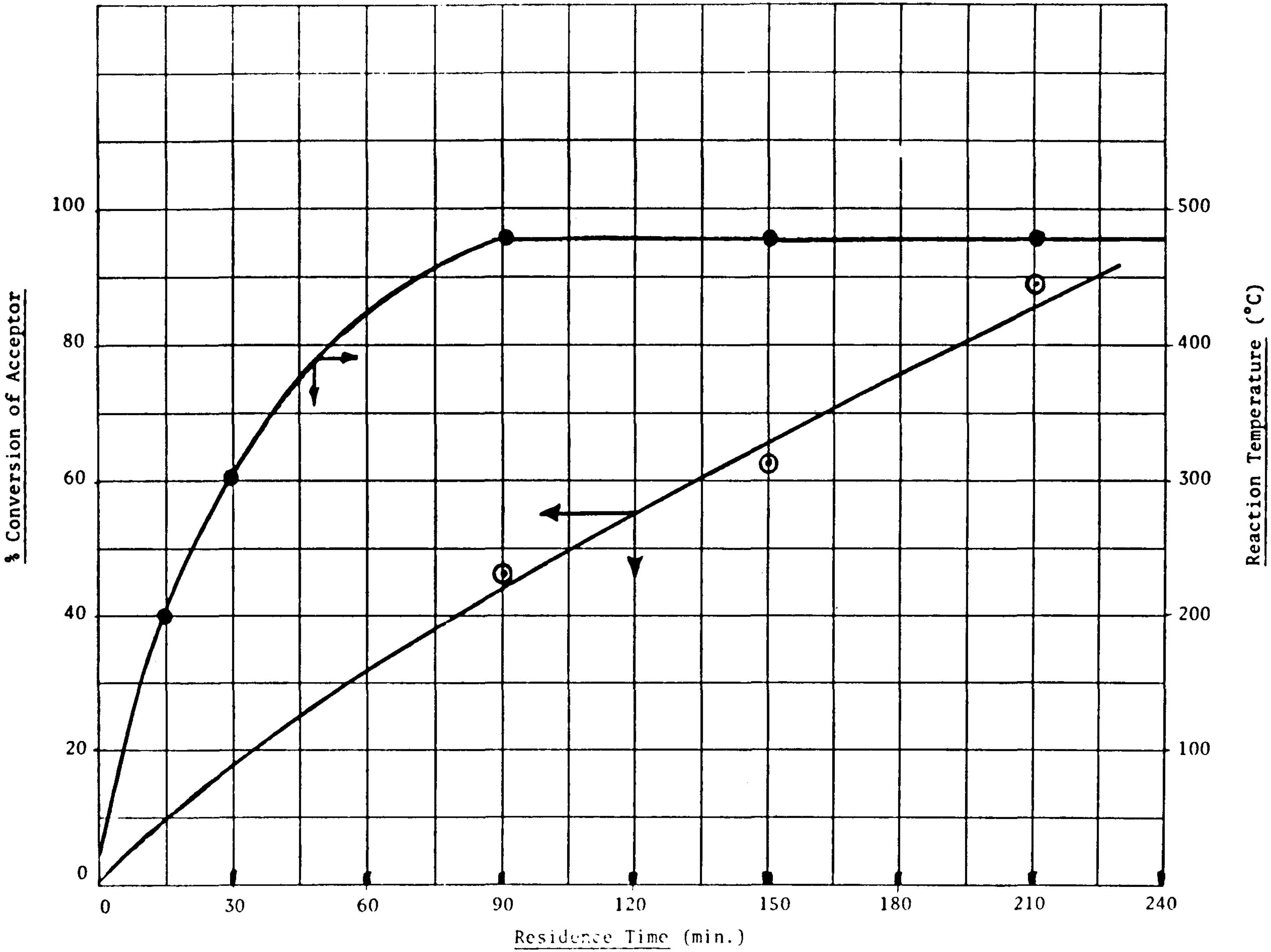
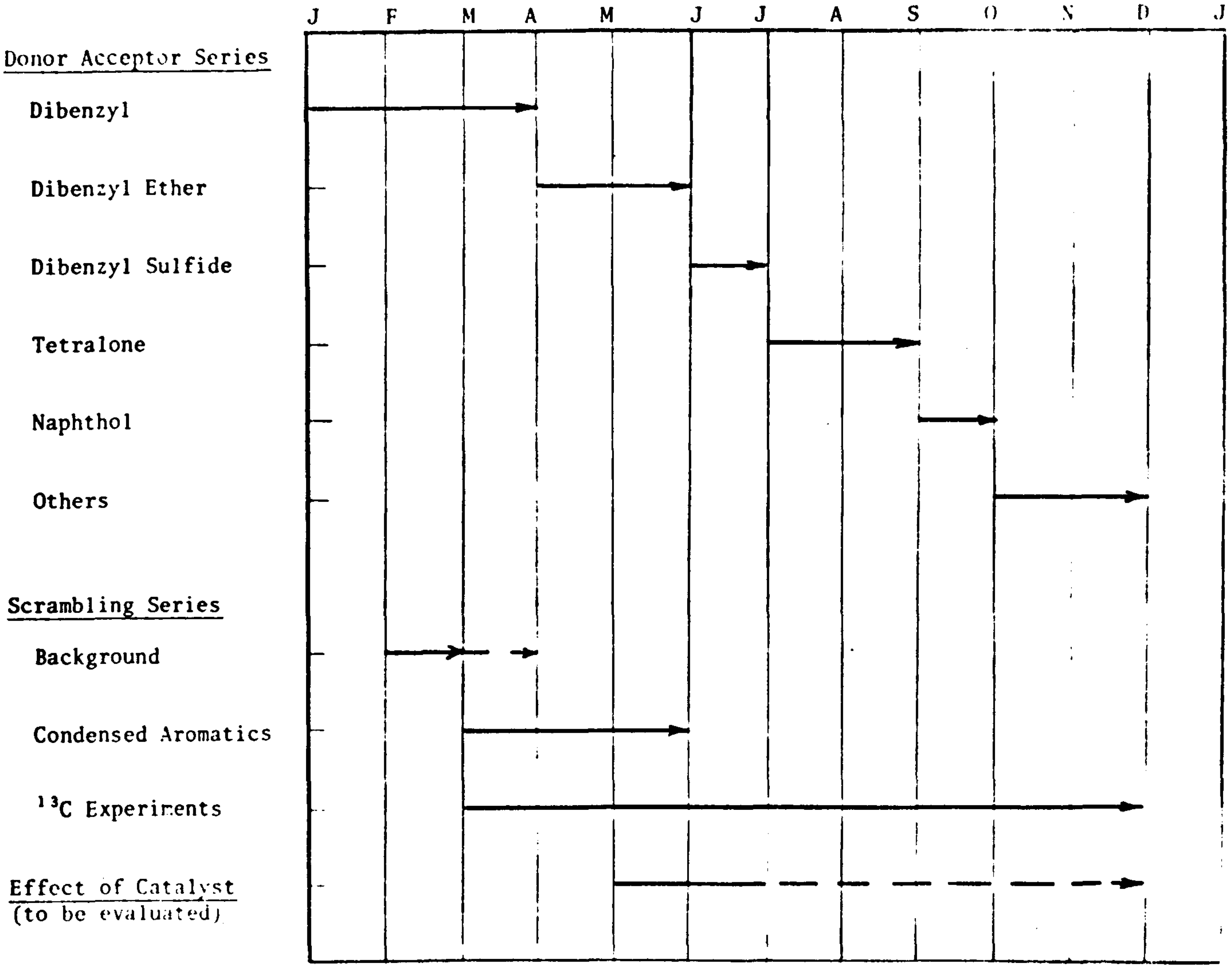


Figure 8

Planned Experiments: Stage 2



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

Table I

Hydrogenation of Naphthalene with NiW Catalyst

Reaction Conditions:

	Temperature (°C)	Time (hr)	Pressure (MPa/psig)
a) Presulfiding	200	2	1.6/235
b) Hydrogenation	356	3	12.4/1800
c) Heat-up & Cooling	---	3	---

Reactor Charge (grams):

Naphthalene	454.2 g
NiW Catalyst	22.0 g
CS_2	1.4 g

Reactor Product:

Total Products	487.3 g
Liquid Recovery*	442.9 g

Liquid Analysis (wt.%):

Benzene, toluene, ethyl benzene plus unknowns	0.3
Indane	0.04
Decalin plus methyl indane	8.6
Tetralin	88.0
Naphthalene	2.9
Heavy unknowns	0.2
	100.0

*No attempt was made to recover liquid remaining on the catalyst recovered by filtration.

Table II

Relative Ranking of Acceptor Reactions*

Temperature (°C)	375	400	425	475
Acceptors:				
1) Phenanthrene	---	D	---	C
2) Dibenzyl	cB	B	cA	bA
3) Dibenzofuran	---	---	---	cD
4) Dibenzothiophene	---	---	---	cD
5) N-Ethylcarbazole	---	---	---	dC
6) α-Tetralone	---	B	---	cA
7) Dibenzyl ether	B	B	aA	aA
8) Hexadecyl ether	---	---	---	A
9) Dodecyl ether	---	---	---	aA
10) Dodecyl sulfide	---	---	---	A
11) 8-Hydroxy quinoline	---	B	A	A
12) 2,6 Di-tert butyl 4-methyl phenol	b	b	a	a

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*Relative Ranking: A-very fast; D-no measurable reaction

Upper case - autoclave runs
Lower case - micro-unit runs