240
9/21/84 JS ②

DR-0416-2

DOE/ET/14700-18
(DE84013177)

Energy
FOSSIL

CHEMISTRY AND CATALYSIS OF COAL LIQUEFACTION: CATALYTIC AND THERMAL UPGRADING OF COAL LIQUID AND HYDROGENATION OF CO TO PRODUCE FUELS

Quarterly Progress Report for the Period
January—March 1984

By
Wendell H. Wiser

May 1984
Date Published

Work Performed Under Contract No. AC22-79ET14700

University of Utah
Salt Lake City, Utah

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A02
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA); Government Reports Announcements* and Index (*GRA* and I); *Scientific and Technical Abstract Reports (STAR);* and publication NTIS-PR-360 available from NTIS at the above address.

DOE/ET/14700-18
(DE84013177)
Distribution Category UC-90d

Chemistry and Catalysis of Coal Liquefaction Catalytic and Thermal Upgrading of Coal Liquid and Hydrogenation of CO to Produce Fuels

Quarterly Progress Report
for the Period Jan - Mar 1984

Dr. Wendell H. Wiser

University of Utah - Department of
Mining and Fuels Engineering
Salt Lake City, Utah 84112

Date Published - May 1984

Prepared for the United States Department
of Energy
Under Contract No. DE-AC22-79ET14700

CONTENTS

OBJECTIVE AND SCOPE OF WORK

I. The chemistry and Catalysis of Coal Liquefaction

Task 1 Chemical-Catalytic Studies

Coal will be reacted at subsoftening temperatures with selective reagents to break bridging linkages between clusters with minimal effect on residual organic clusters. The coal will be pretreated to increase surface area and then reacted at 25 to 350°C. Reagents and catalysts will be used which are selective so that the coal clusters are solubilized with as little further reaction as possible.

Task 2 Carbon-13 NMR Investigation of CDL and Coal

Carbon-13 NMR spectroscopy will be used to examine coal, coal derived liquids (CDL) and residues which have undergone subsoftening reactions in Task 1 and extraction. Improvements in NMR techniques, such as crosspolarization and magic angle spinning, will be applied. Model compounds will be included which are representative of structural units thought to be present in coal. Comparisons of spectra from native coals, CDL and residues will provide evidence for bondings which are broken by mild conditions.

Task 3 Catalysis and Mechanism of Coal Liquefaction

This fundamental study will gain an understanding of metal salt chemistry and catalysis in coal liquefaction through study of reaction known in organic chemistry. Zinc chloride and other catalytic materials will be tested as Friedel-Crafts catalysts and as redox catalysts using coals and selected model compounds. Zinc chloride, a weak Friedel-Crafts catalyst, will be used at conditions common to coal liquefaction to participate in well defined hydrogen transfer reactions. These experiments will be augmented by mechanistic studies of coal hydrogenation using high pressure thermogravimetric analysis and structural analysis. The results of these studies will be used to develop concepts of catalysis involved in coal liquefaction.

Task 4 Momentum Heat and Mass Transfer in CoCurrent Flow of Particle-Gas Systems for Coal Hydrogenation

A continuation of ongoing studies of heat and transport phenomena in cocurrent, co-gravity flow is planned for a one-year period. As time and development of existing work permits, the extension of this study to include a coiled reactor model will be undertaken. Mathematical models of coal hydrogenation systems will utilize correlations from these straight and coiled reactor configurations.

Task 5 The Fundamental Chemistry and Mechanism of Pyrolysis of Bituminous Coal

Previous work at the University of Utah indicates that coal pyrolysis, dissolution (in H-donor) and catalytic hydrogenation all have similar rates and activation energies. A few model compounds will be pyrolyze in the range of 375 to 475°C. Activation energies, entropies and product distributions will be determined. The reactions will assist in formulating the thermal reaction routes which also can occur during hydro-liquefaction.

II. Catalytic and Thermal Upgrading of Coal Liquids

Task 6 Catalytic Hydrogenation of CD Liquids and Related Polycyclic Aromatic Hydrocarbons

A variety of coal derived (CD) liquids will be hydrogenated with sulfided catalysts prepared in Task 10 from large pore, commercially available supports. The hydrogenation of these liquids will be systematically investigated as a function of catalyst structure and operating conditions. The effect of extent of hydrogenation will be the subject of study in subsequent tasks in which crackability and hydropyrolysis of the hydrogenated product will be determined. To provide an understanding of the chemistry involved, model polycyclic arenes will be utilized in hydrogenation studies. These studies and related model studies in Task 7 will be utilized to elucidate relationships between organic reactants and the structural-topographic characteristics of hydrogenation catalysts used in this work.

Task 7 Denitrogenation and Deoxygenation of CD Liquids and Related Nitrogen- and Oxygen-Containing Compounds

Removal of nitrogen and oxygen heteroatoms from CD liquids is an important upgrading step which must be accomplished to obtain fuels corresponding to those from petroleum sources. Using CD liquids as described in Task 6, exhaustive HDN and HDO will be sought through study of catalyst systems and operating conditions. As in Task 6, catalysts will be prepared in Task 10 and specificity for N- and O-removal will be optimized for the catalyst systems investigated. Model compounds will also be systematically hydrogenated using effective HDN/HDO catalysts. Kinetics and reaction pathways will be determined. A nonreductive denitrogenation system will be investigated using materials which undergo reversible nitridation. Conditions will be sought to cause minimal hydrogen consumption and little reaction of other reducible groups.

Task 8 Catalytic Cracking of Hydrogenated CD Liquids and Related Polycyclic Naphthenes and Naphthenoaromatics

Catalytic cracking of hydrogenated CD liquid feedstocks will be studied to evaluate this scheme as a means of upgrading CD liquids. Cracking kinetics and product distribution as a function of preceding hydrogenation will be evaluated to define upgrading combinations which require the minimal level of CD liquid aromatic saturation to achieve substantial heteroatom removal and high yields of cracked liquid products. Cracking catalysts to be considered for use in this task shall include conventional zeolite-containing catalysts and large-pore molecular sieve, CLS (cross-linked smectites) types under study at the University of Utah. Model compounds will be subjected to tests to develop a mechanistic understanding of the reactions of hydro CD liquids under catalytic cracking conditions.

Task 9 Hydropyrolysis (Thermal Hydrocracking) of CD Liquids

Heavy petroleum fractions can be thermally hydrocracked over a specific range of conditions to produce light liquid products without excessive hydrogenation occurring. This noncatalytic method will be applied to a variety of CD liquids and model compounds, as mentioned in Task 6, to determine the conditions necessary and the reactibility of these CD feedstocks with and without prior hydrogenation and to derive mechanism and reaction pathway information needed to gain an understanding of the hydropyrolysis reactions. Kinetics, coking tendencies and product compositions will be studied as a function of operating conditions.

Task 10 Systematic Structural-Activity Study of Supported Sulfide Catalysts for Coal Liquids Upgrading

This task will undertake catalyst preparation, characterization and measurement of activity and selectivity. The work proposed is a fundamental study of the relationship between the surface-structural properties of supported sulfide catalysts and their catalytic activities for various reactions desired. Catalysts will be prepared from commercially available. Supports composed of alumina, silica-alumina, silica-magnesia and silica-titania, modification of these supports to change acidity and to promote interaction with active catalytic components is planned. The active constituents will be selected from those which are effective in a sulfided state, including but not restricted to Mo, W, Ni and Co. The catalysts will be presulfided before testing. Catalyst characterization will consist of physico-chemical property measurements and surface property measurements. Activity and selectivity tests will also be conducted using model compounds singly and in combination.

Task 11 Basic Study of the Effects of Coke and Poisons on the Activity of Upgrading Catalysts

This task will begin in the second year of the contract after suitable catalysts have been identified from Tasks 6, 7 and/or 10. Two commercial catalysts or one commercial catalyst and one catalyst prepared in Task 10 will be selected for a two-part study, (1) simulated laboratory poisoning/coking and (2) testing of realistically aged catalysts. Kinetics of hydrogenation, hydrodesulfurization, hydrodenitrogenation and hydrocracking will be determined before and after one or more stages of simulated coking. Selected model compounds will be used to measure detailed kinetics of the above reactions and to determine quantitatively how kinetic parameters change with the extent and type of poisoning/coking simulated. Realistically aged catalysts will be obtained from coal liquids upgrading experiments from other tasks in this program or from other laboratories conducting long-term upgrading studies. Deactivation will be assessed based on specific kinetics determined and selective poisoning studies will be made to determine characteristics of active sites remaining.

Task 12 Diffusion of Polyaromatic Compounds in Amorphous Catalyst Supports

If diffusion of a reactant species to the active sites of the catalyst is slow in comparison to the intrinsic rate of the surface reaction, then only sites near the exterior of the catalyst particles will be utilized effectively. A systematic study of the effect of molecular size on the sorptive diffusion kinetics relative to pore geometry will be made using specific, large diameter aromatic molecules. Diffusion studies with narrow boiling range fractions of representative coal liquid will also be included. Experimental parameters for diffusion kinetic runs shall include aromatic diffusion model compounds, solvent effects, catalyst sorption properties, temperature and pressure.

III. Hydrogenation of CO to Produce Fuels

Task 13 Catalyst Research and Development

Studies with iron catalysts will concentrate on promoters, the use of supports and the effects of carbiding and nitriding. Promising promoters fall into two classes: (1) nonreducible metal oxides, such as CaO, K_2O, Al_2O_3 and MgO, and (2) partially reducible metal oxides which can be classified as co-catalysts, such as oxides of Mn, Mo, Ce, La, V, Re and rare earths. Possible catalyst supports include zeolites, alumina, silica, magnesia and high area carbons. Methods of producing active supported iron catalysts for CO hydrogenation will be investigated, such as development of shape selective catalysts which can provide control of product distribution. In view of the importance of temperature, alternative reactor systems (to fixed bed) will be investigated to attain better temperature control. Conditions will be used which give predominately lower molecular weight liquids and gaseous products.

Task 14 Characterization of Catalysts and Mechanistic Studies

Catalysts which show large differences in selectivity in Task 13 will be characterized as to surface and bulk properties. Differences in properties may provide the key to understanding why one catalyst is superior to another and identify critical properties, essential in selective catalysts. Factors relating to the surface mechanism of CO hydrogenation will also be investigated. Experiments are proposed to determine which catalysts form "surface" (reactive) carbon and the ability of these catalysts to exchange C and O of isotopically labelled CO. Reactions of CO and H_2 at temperatures below that required for CO dissociation are of particular interest.

Task 15 Completion of Previously Funded Studies and Exploratory Investigations

This task is included to provide for the orderly completion of coal liquefaction research underway in the expiring University of Utah contract, EX-76-C-01-2006.

Task 7

Catalytic Hydrodeoxygenation of Coal-Derived Liquids and Related Oxygen-Containing Model Compounds

Faculty Advisor: J. Shabtai
Graduate Student: Y. Shukla

Introduction

Coal-derived liquids are characterized by the presence of a considerable concentration of oxygen-containing components. Therefore, a systematic catalytic hydrodeoxygenation (HDO) study of coal-derived liquids and related model compounds is being carried out. This study provides information not only on the mechanism of HDO as related to the subject of catalytic upgrading of coal-derived liquids, but also on the role of oxygen-containing compounds in primary coal liquefaction processes.

Project Status

The catalytic HDO reactions of three representative aryl and arylalkyl ethers, i.e., dibenzyl ether, diphenyl ether, anisole and two furans, i.e., 2,3-benzofuran, dibenzofuran and 2-naphthol, as feeds are presently being investigated. Results obtained with anisole (25) as feed are presented in this report. This study observed the change in product composition as a function of experimental conditions, e.g., reaction temperature, hydrogen pressure and catalyst type. The experiments were performed in a shaken autoclave,[1] and the products obtained were identified and quantitatively analyzed by GC-MS and GC-available standard samples.

The reaction of 25 in the presence of the sulfided Co-Mo/γ-Al_2O_3 and Ni-Mo/γ-Al_2O_3 catalysts were investigated as a function of reaction temperature in the range of 170-350°C, a hydrogen pressure of 1000 psig with a reaction time of 0.5 hour. The results obtained with sulfided Co-Mo/γ-Al_2O_3 and Ni-Mo/γ-Al_2O_3 are summarized in Figures 1 and 2, respectively. As seen in Figure 1, the conversion of 25 increased slowly from 0.5% at 170°C to 11.50% at 260°C and then rapidly to 65.60% at 350°C. The main product at all temperatures was phenol (5). With an increase in temperature, the concentration of 5, first increased then slowly decreased, and the concentrations of benzene (3) and o-cresol (26) increased. Traces of cyclohexane (2), methylcyclopentane (1) and dimethyl phenol (36) were also observed.

With the sulfided Ni-Mo/γ-Al_2O_3 catalyst (Figure 2), the overall conversion varied from 0.5% at 170°C to 81.50% at 320°C. The main product at all temperatures was phenol (5). With an increase in temperature, the concentration of 5, first increased and then decreased, and the concentration of o-cresol (26) increased. Traces of cyclohexane (2), methylcyclopentane (1), p-cresol (27), benzene (3) and trimethyl phenol (31) were also observed.

The HDO reaction of 25 in the presence of the sulfided Co-Mo/γ-Al_2O_3 and Ni-Mo/γ-Al_2O_3 catalysts were also investigated as a function of hydrogen pressure in the range of 250-1500 psig at a reaction temperature of 260°C and a reaction time of 0.5 hour. The results obtained are summarized in Figures 3 and 4, respectively.

The change in product composition as a function of reaction temperature, hydrogen pressure and catalyst type can be rationalized in terms of the reaction network proposed in Figure 5. With both catalysts, the products observed were formed via reaction paths A and B. In reaction path A, 25 upon C (aliphatic)-O cleavage yielded phenol (5). With sulfided Co-Mo, 5 upon C-O cleavage yielded benzene (3) and traces of cyclohexane (3). With sulfided Ni-Mo, 5 upon hydrogenation followed by C-O bond cleavage yielded cyclohexane (2). In reaction path B, 25 by the converted mechanism[2] yielded θ-cresol (26) which upon transalkylation yielded dimethyl phenol (26) and trimethyl phenol (31).

Future Work

Kinetic studies of dibenzyl ether, diphenyl ether, dibenzofuran and 2-naphthol with commercial catalysts and catalysts synthesized in this laboratory will be continued.

References

1. G. Haider, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1981.

2. J.B. sonBredenberg *et al.*, *J. Catal.*, 77, 242 (1982).

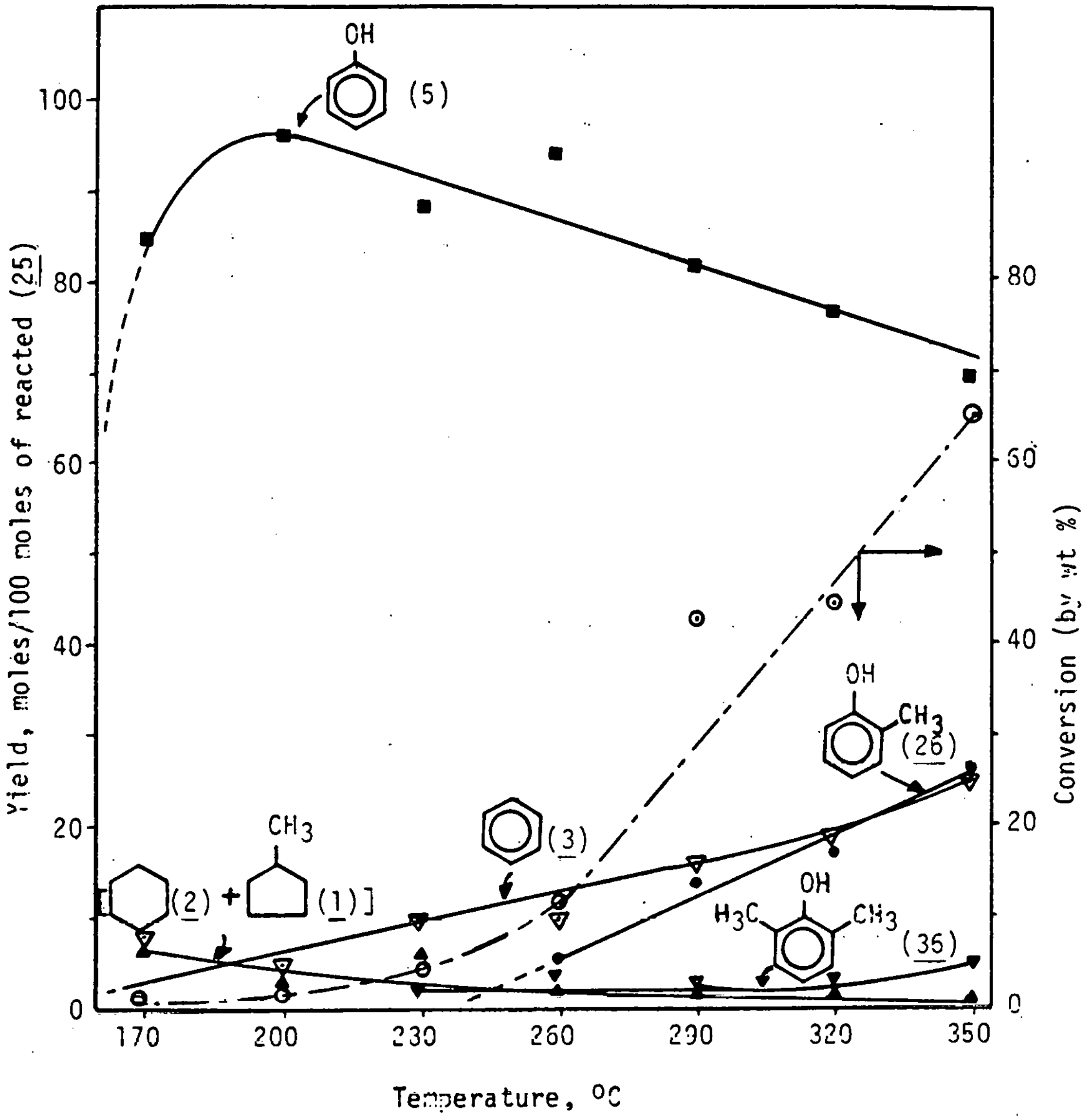

Figure 1. Change in product composition from hydrodeoxygenation of anisole (25) as a function of reaction temperature [catalyst, sulfided Co-Mo/γ-Al_2O_3 (Nalco #471); hydrogen pressure, 1000 psig; total reaction time, 0.5 hour].

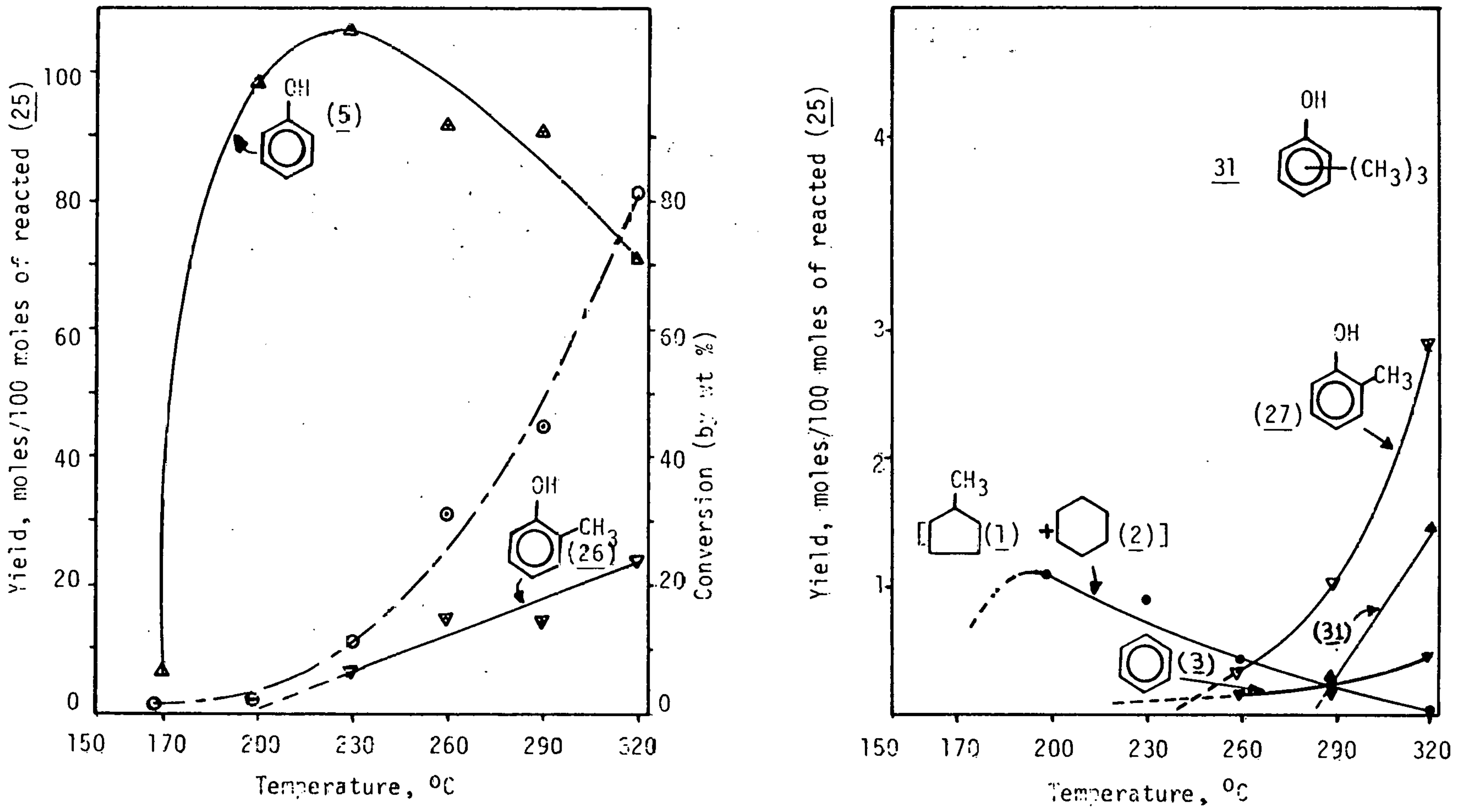

Figure 2. Change in product composition from hydrodeoxygenation of anisole (25) as a function of reaction temperature [catalyst, sulfided Ni-Mo/γ-Al_2O_3 (Nalco #504); hydrogen pressure, 1000 psig; total reaction time, 0.5 hour].

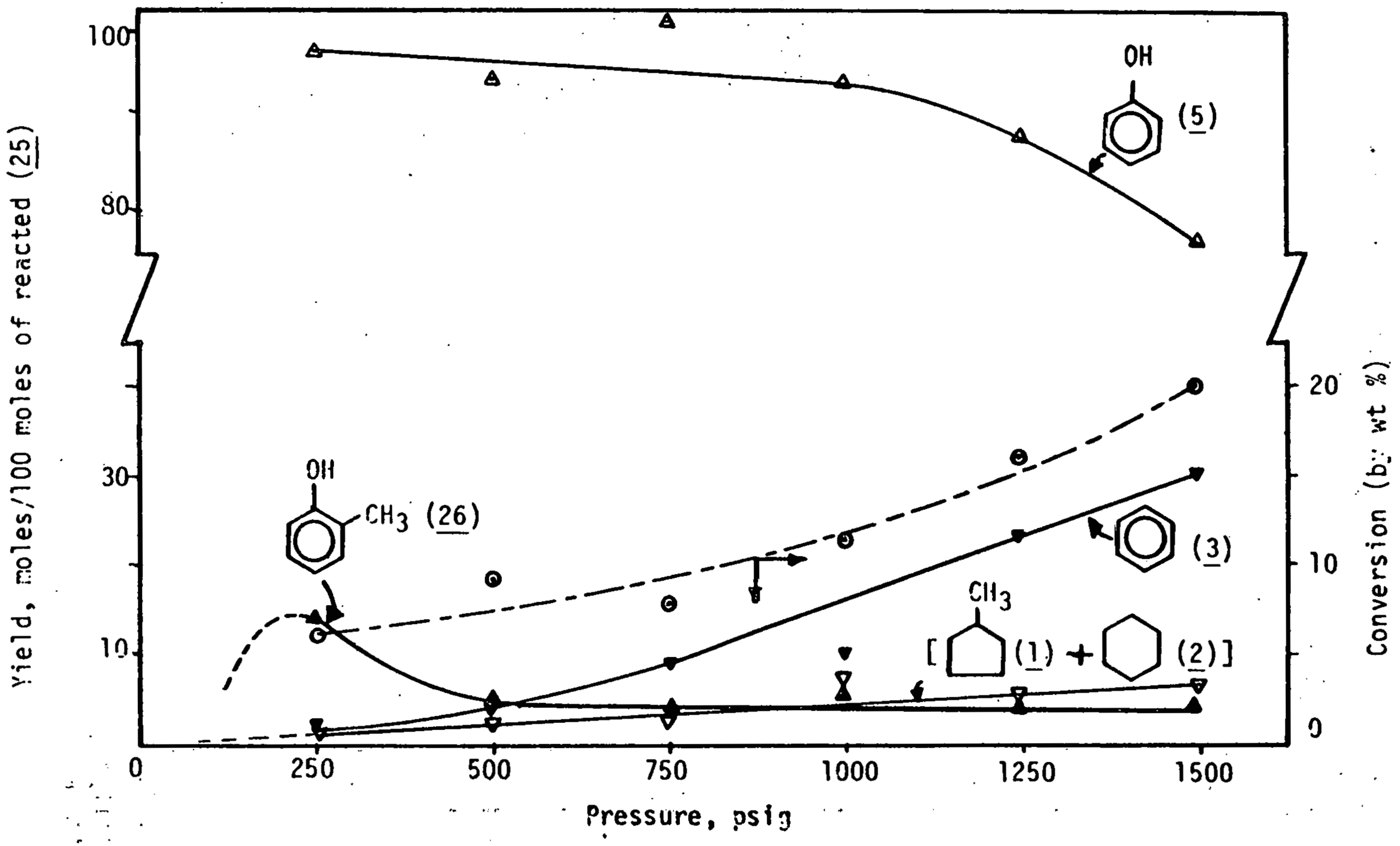

Figure 3. Change in product composition from hydrodeoxygenation of anisole (25) as a function of hydrogen pressure [catalyst, sulfided Co-Mo/γ-Al_2O_3 (Nalco #471); reaction temperature, 260°C; total reaction time, 0.5 hour].

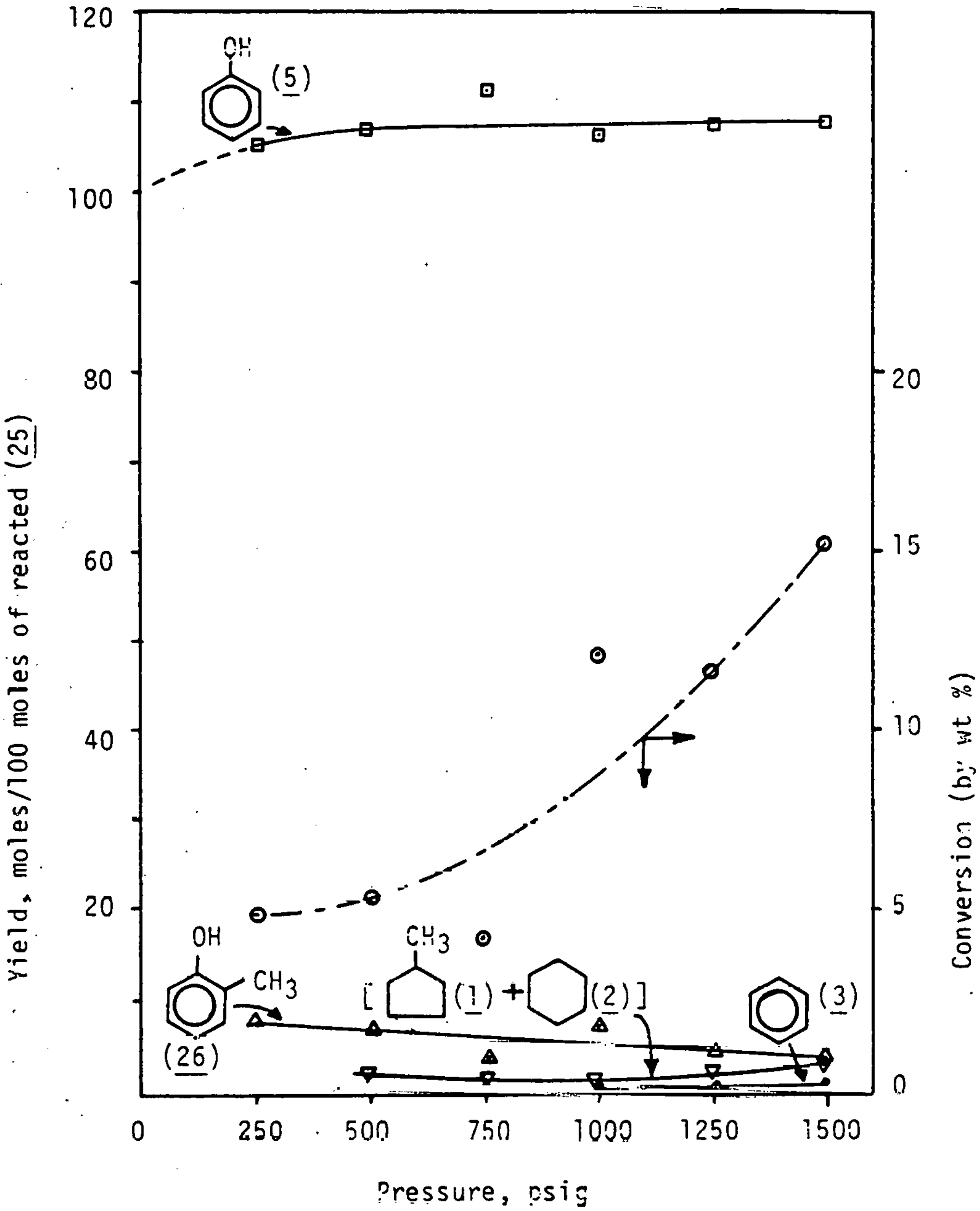

Figure 4. Change in product composition from hydrodeoxygenation of anisole (25) as a function fo hydrogen pressure [catalyst, sulfided Ni-Mo/γ-Al_2O_3 (Nalco #504); reaction temperature, 260°C; total reaction time, 0.5 hour].

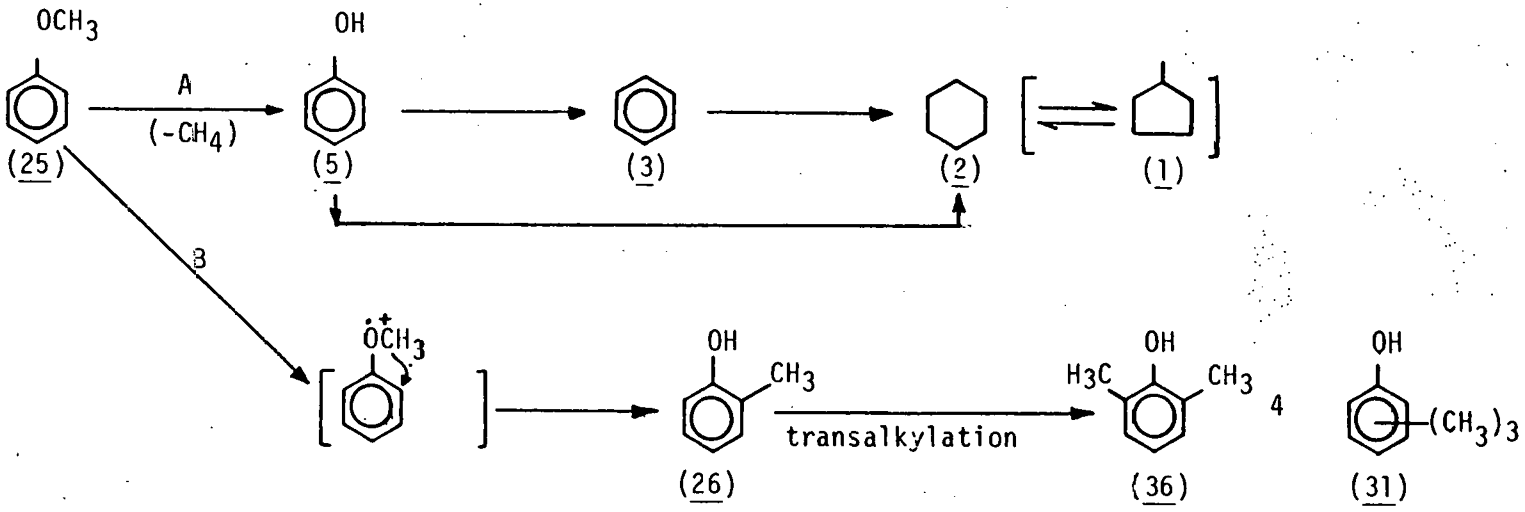

Figure 5. Reaction network of HDO reaction of anisole (25) with sulfided catalysts, (e.g., Co-Mo/γ-Al_2O_3, Ni-Mo/γ-Al_2O_3).

Task 7

Denitrogenation and Deoxygenation of CD Liquids and Related N- and O- Containing Compounds

Hydrodenitrogenation of Coal-Derived Liquids and Related N-Containing Compounds

Faculty Advisor: J. Shabtai
Graduate Student: J. Yeh

Introduction

The main objective of this research project is to develop effective catalyst systems and processing conditions for hydrodenitrogenation (HDN) of coal-derived liquids (CDL) in a wide range of nitrogen contents and structural type composition. This is of particular importance in view of the higher concentration of nitrogen-containing compounds in CDL as compared to that in petroleum feedstocks. For a better understanding of denitrogenation processes, the project includes systematic denitrogenation studies not only of CDL but also of related model N-containing compounds found in such liquids, e.g., phenanthridine, 1,10-phenanthroline, carbazoles, acridines, etc., as a function of catalyst type and experimental rate, mechanism and stereochemistry of HDN of structurally distinct N-containing aromatic systems in the presence of sulfided catalyts.

Project Status

The typical gas chromatograms of the products for N-ethylcarbazole and carbazole HDN are shown in Figures 1 and 2 respectively. The products were identified by GC with a nitrogen-sensitive detector, GC/MS, reference compounds and standard mass spectra.

An inert solvent, n-$C_{15}H_{32}$, was used for this study, No products appeared in the area where the solvent appeared. This was confirmed by trying n-$C_{12}H_{32}$ as the inert solvent (see Figure 3). Normal dodecane overlapped with one of the HDN products, therefore n-$C_{15}H_{32}$ was chosen as the inert solvent (Figure 3). Figures 1 and 2 show good product resolution.

The product distribution for N-ethyl-carbazole HDN as a function of reaction time at a hydrogen pressure of 2500 psig and a temperature of 320°C is shown in Figure 4. As seen in Figure 4, the concentration of N-ethylcarbazole (21) decreased as the reaction proceeded, but the concentration of 1,2,3,4-tetrahydro-N-ethyl-carbazole (22) increased first reaching a maximum, then decreased as the reaction proceeded. The concentrations of three HDN products (compounds 23, 24, and 25) increased during the reaction. Among these three, dicyclohexyl (23) was the largest compound, followed by hexylcyclohexane (25) and cyclohexylcyclopentylmethane (24). The product distribution for carbazole HDN (Figure 5) followed the same trends under the same conditions as those shown in Figure 4.

The proposed kinetic networks for HDN of N-ethylcarbazole and carbazole are shown in Figures 6 and 7, respectively. Table 1 summarizes pseudo-first-order rate constants at various temperatures for these two reactants. As is seen in Figure 6, the hydrogenation of one of the two benzene rings in N-ethylcarbazole (21) yielded 1,2,3,4-tetrahydro-N-ethylcarbazole (22) as the first step in the reaction. The subsequent HDN reactions of 1,2,3,4-tetrahydro-N-ethylcarbazole (22) went through different intermediates to yield three HDN products (23, 24 and 25). These three HDN products were not interconvertible. The reaction at the same conditions with a pure dicyclohexyl and n-$C_{15}H_{32}$ mixture shows that compounds 24 and 25 are not the products from the hydrocracking of dicyclohexyl.

The three parallel HDN reactions actually involved several reaction steps. Intermediates for those reaction were not seen during the reaction which indicates that the hydrogenation reaction of 1,2,3,4-tetrahydro-N-ethylcarbazole to the intermediates was much slower than the HDN reaction of the intermediates to different HDN products. The reaction rate constants $k_2 > k_3 > k_4$ indicate that dicyclohexyl (23) was the major product of these three HDN products, followed by hexylcyclohexane (25) and then cyclopentylcyclohexylmethane (24).

The HDN reaction network of carbazole (Figure 6) was similar to that of N-ethylcarbazole. Figure 6 indicates that the reaction network also included a hydrogenation reaction followed by three parallel HDN reactions. Table 1 shows that k_1 in the N-ethylcarbazole HDN network is smaller than k_1 in the carbazole HDN network, because the ethyl group hindered the flatwise adsorption of the benzene rings and slowed down the hydrogenation reaction. The k_2, k_3, k_4 in N-ethylcarbazole HDN network were higher than those in the carbazole HDN network. This indicates that the ethyl group tends to weaken the C-N bond and enhances three parallel HDN reactions.

From the rate constants obtained at various temperatures, the activation energy for each reaction step was calculated. Figure 8 shows an Arrhenius plot of first order rate constants for N-ethylcarbazole HDN. Table 2 summarizes the frequency factor and activation energy of each reaction step. The activation energies for the three parallel HDN reactions are the energies required for the overall reactions. The activation energies for k_3 and k_4 are higher than those for k_2, indicating that the HDN reactions of 1,2,3,4-tetrahydro-N-ethylcarbazole require more energy to yield compounds 4 and 5 than to yield dicyclohexyl (23).

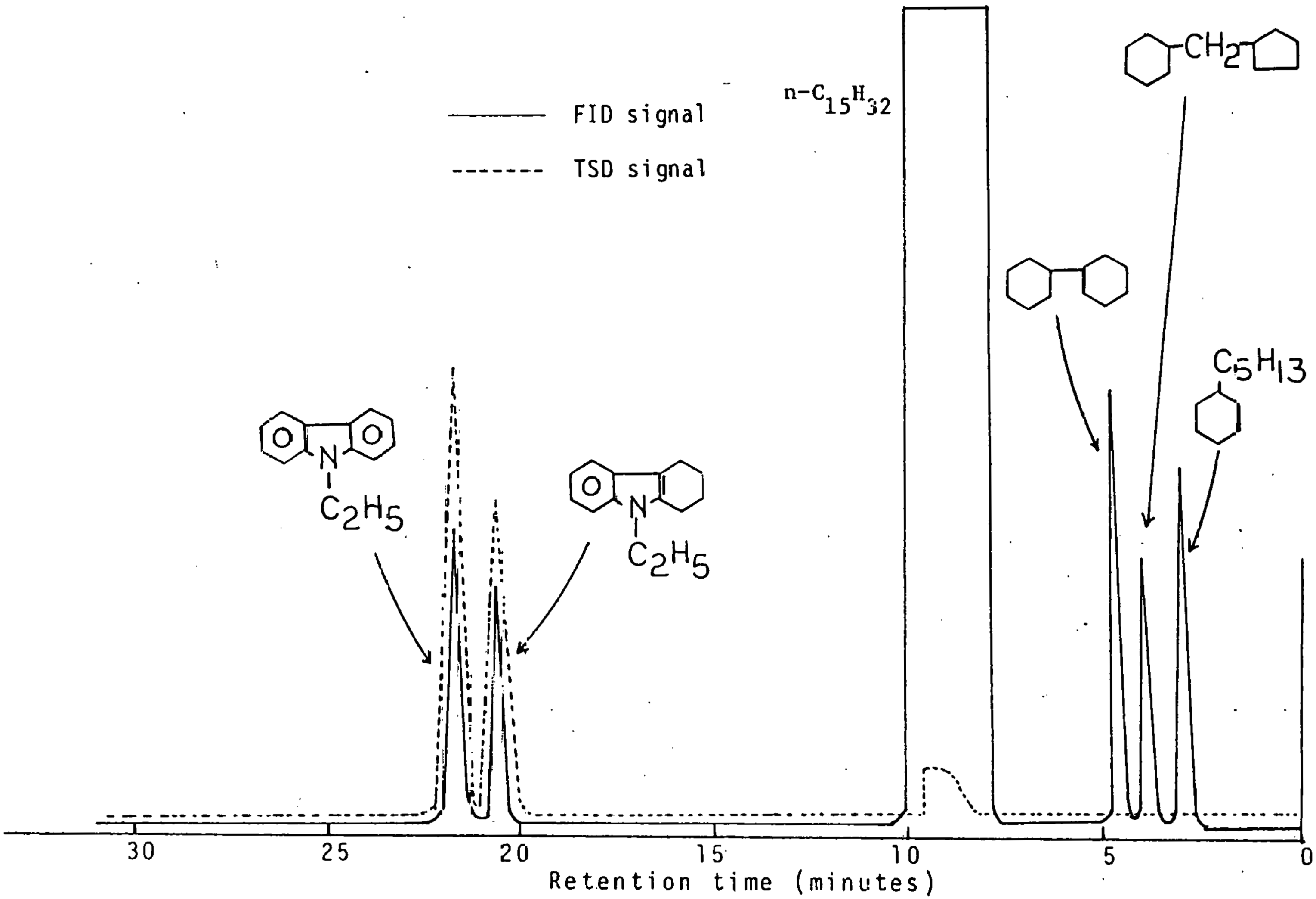

Figure 1. Gas Chromatogram of products of hydrogenation and hydrogenolysis reaction in N-ethylcarbazole HDN.

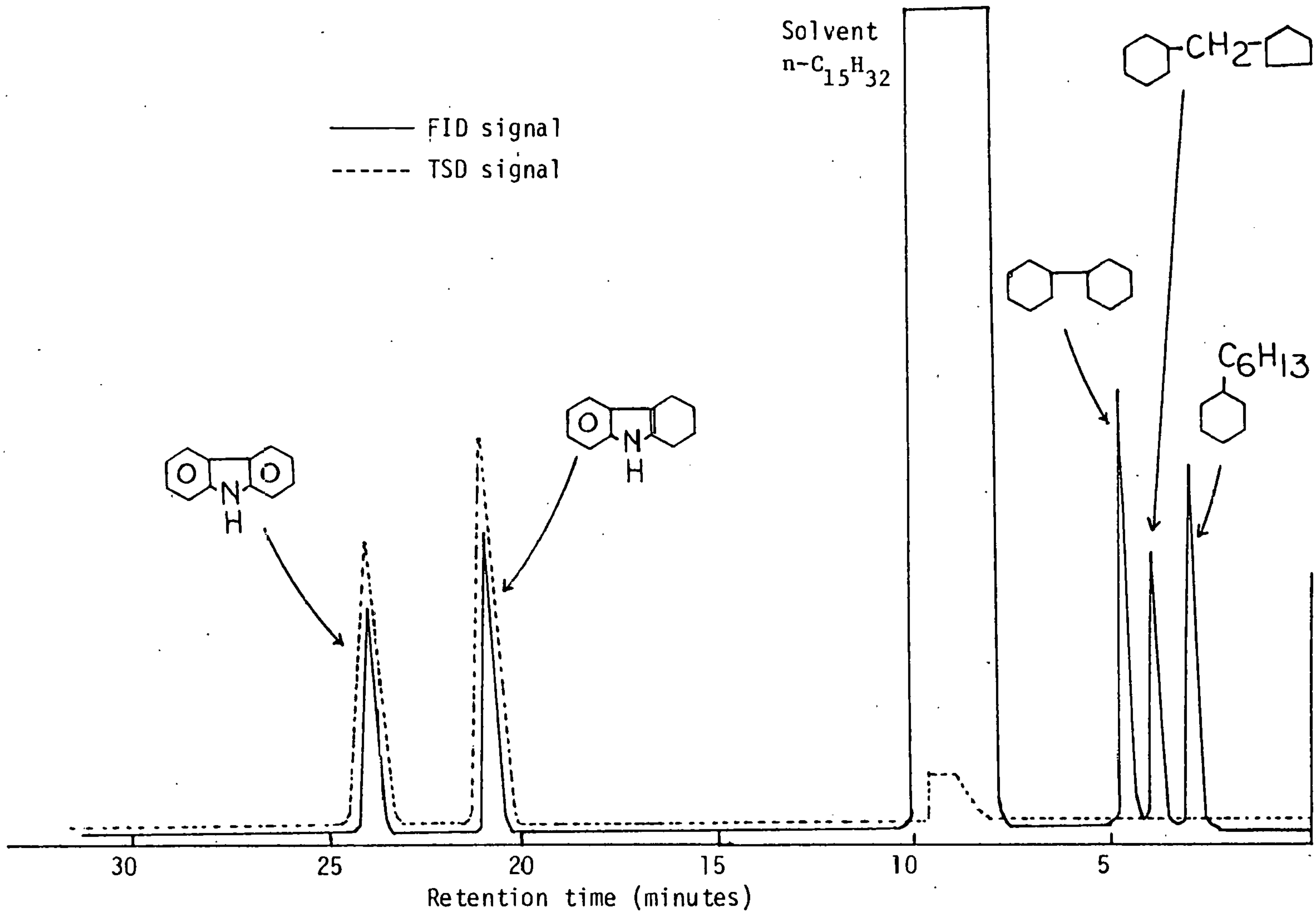

Figure 2. Gas Chromatogram of products of hydrogenation and hydrogenolysis reaction in carbazole HDN.

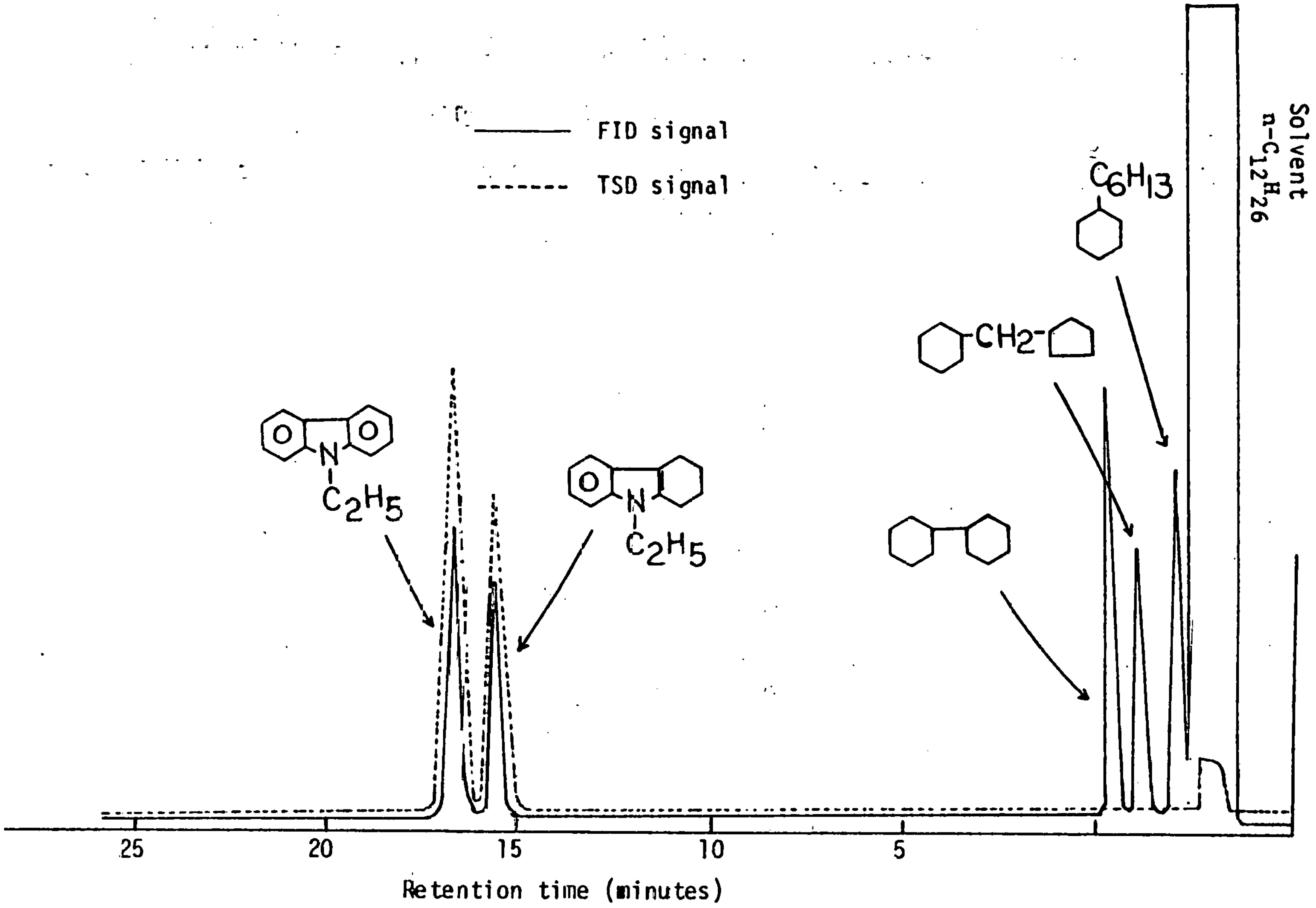

Figure 3. Gas chromatogram of products of hydrogenation and hydrogenolysis reactions in N-ethylcarbazole HDN

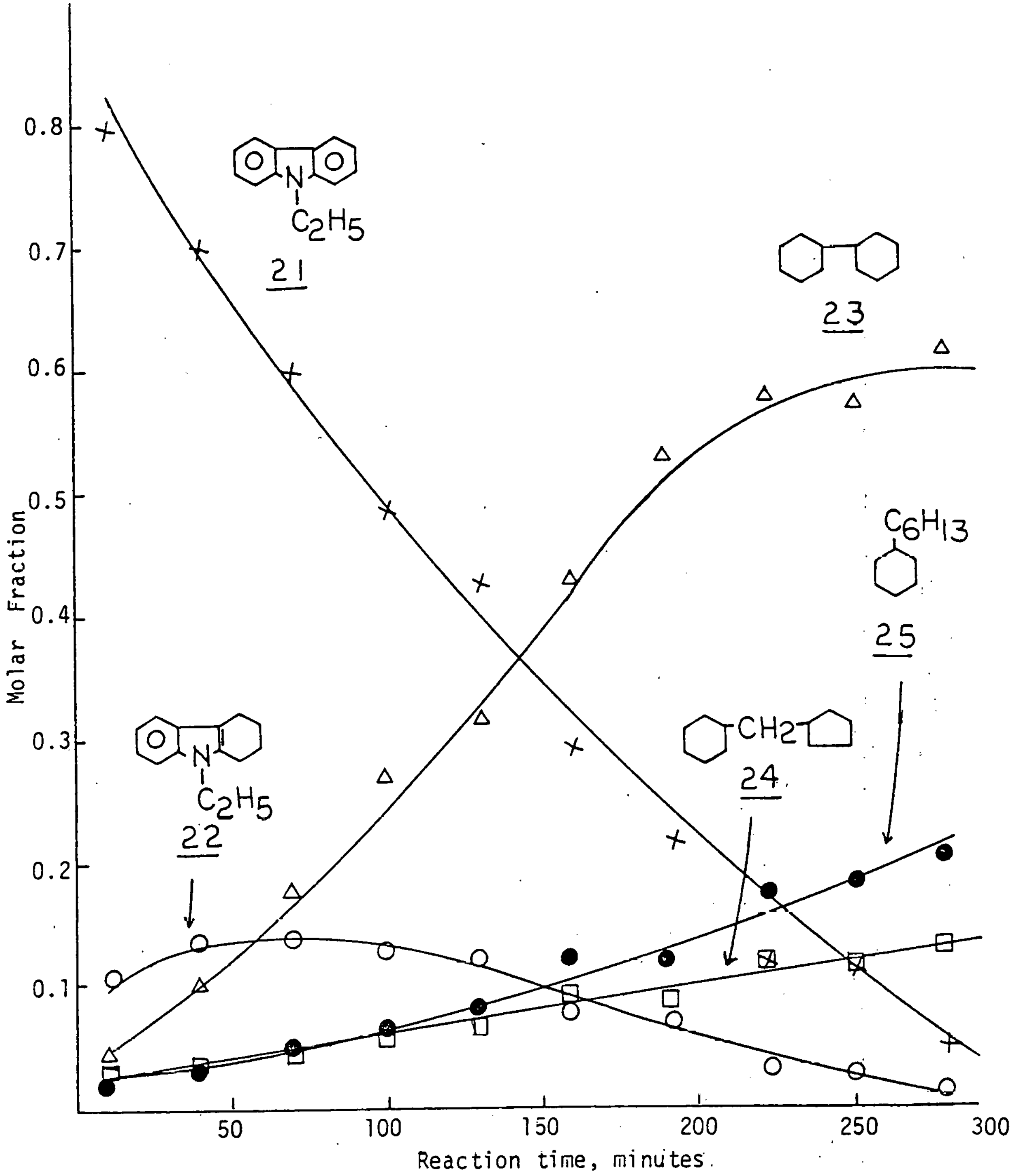

Figure 4. Products distribution as a function of reaction time in N-ethylcarbazole HDN.
H_2 pressure: 2500 psig. Temperature: 320°C

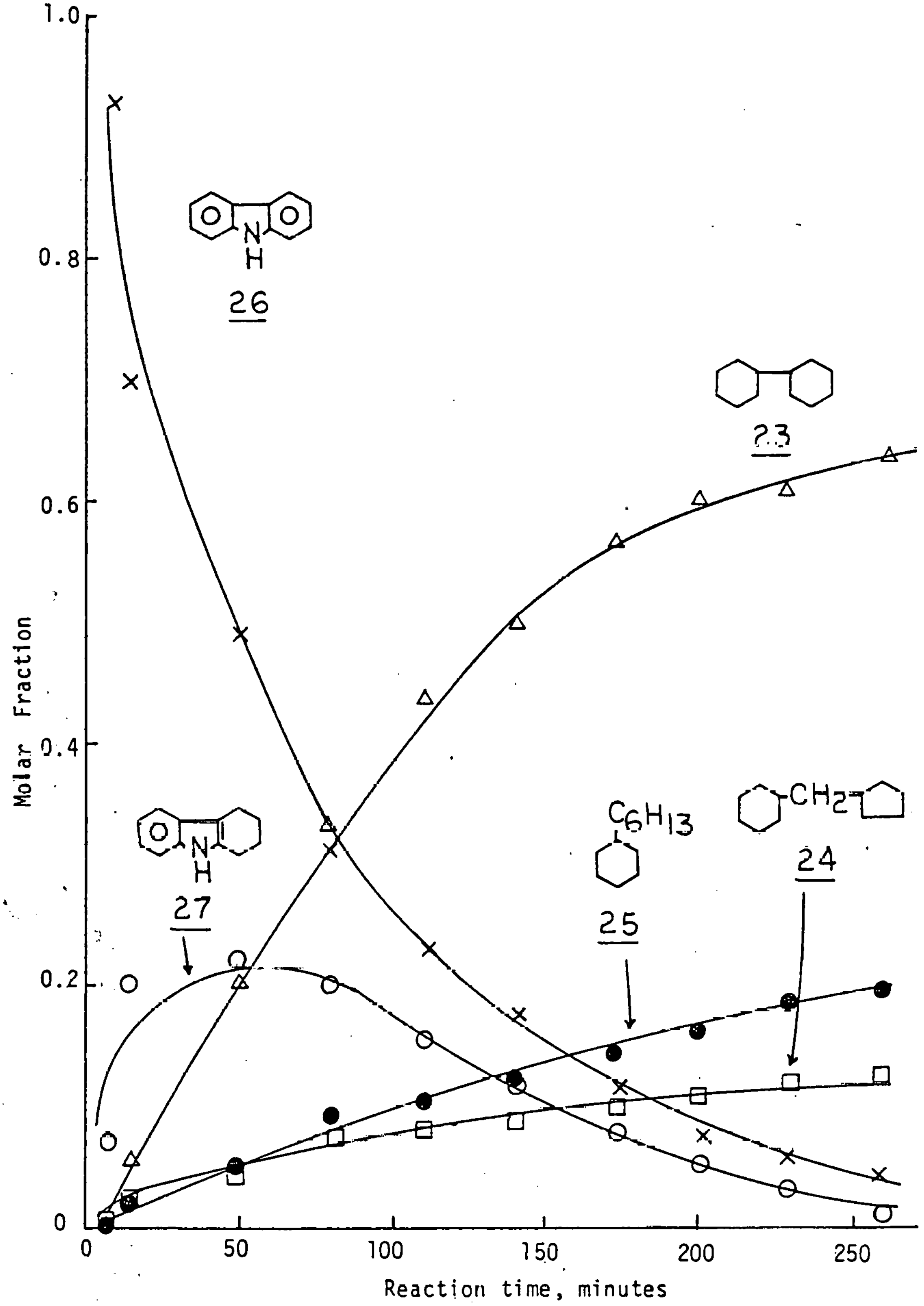

Figure 5. Products distribution as a function of reaction time in carbazole HDN.
H_2 pressure: 2500 psig. Temperature: 320°C.

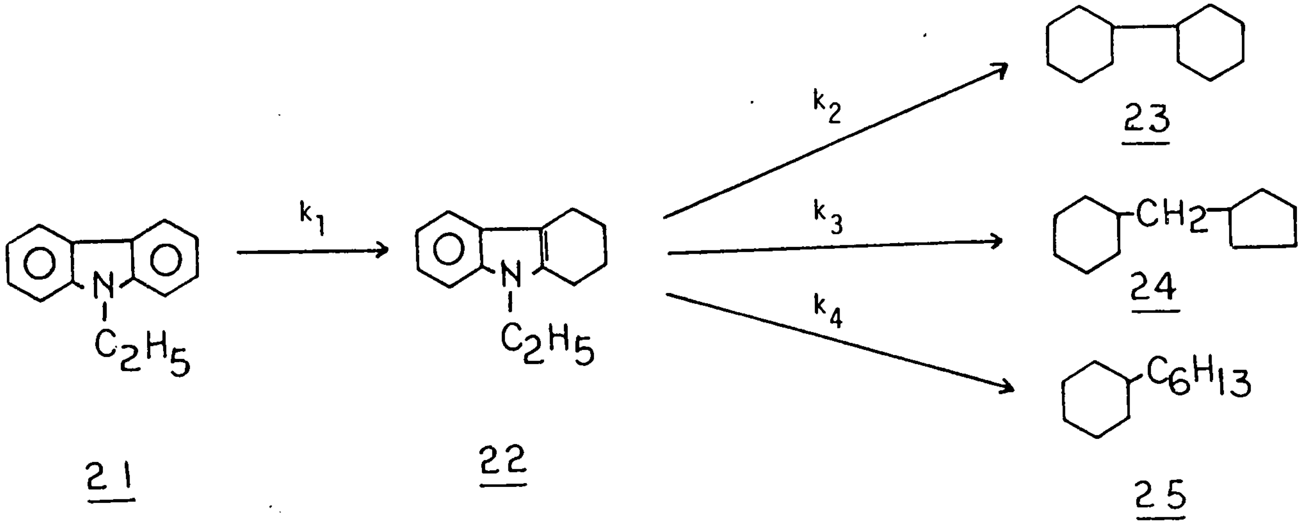

Figure 6. Proposed kinetics network for HDN of N-ethycarbazole

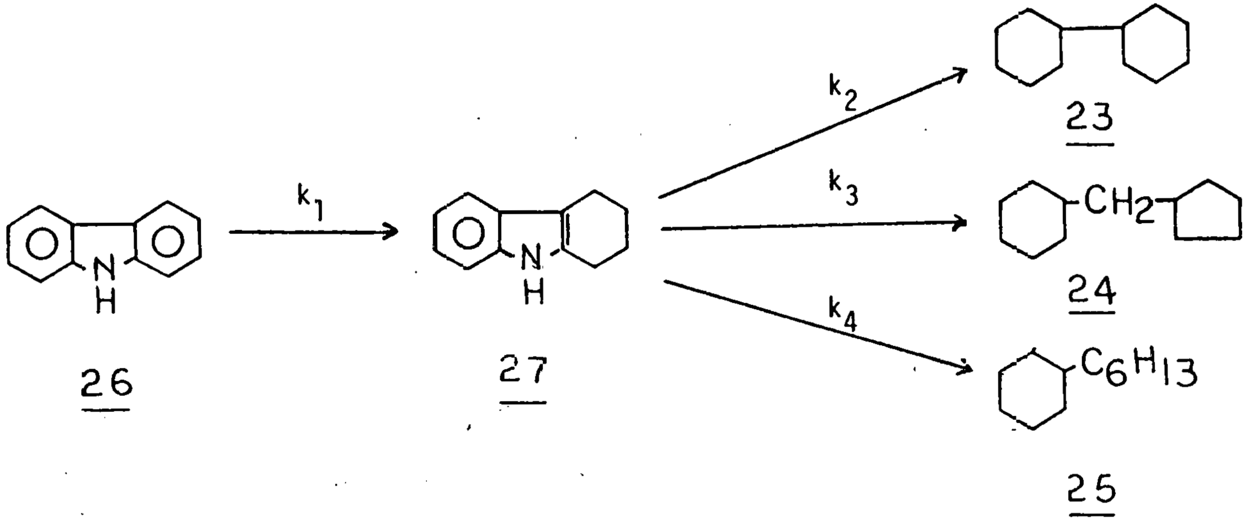

Figure 7. Proposed kinetic network for HDN of carbazole.

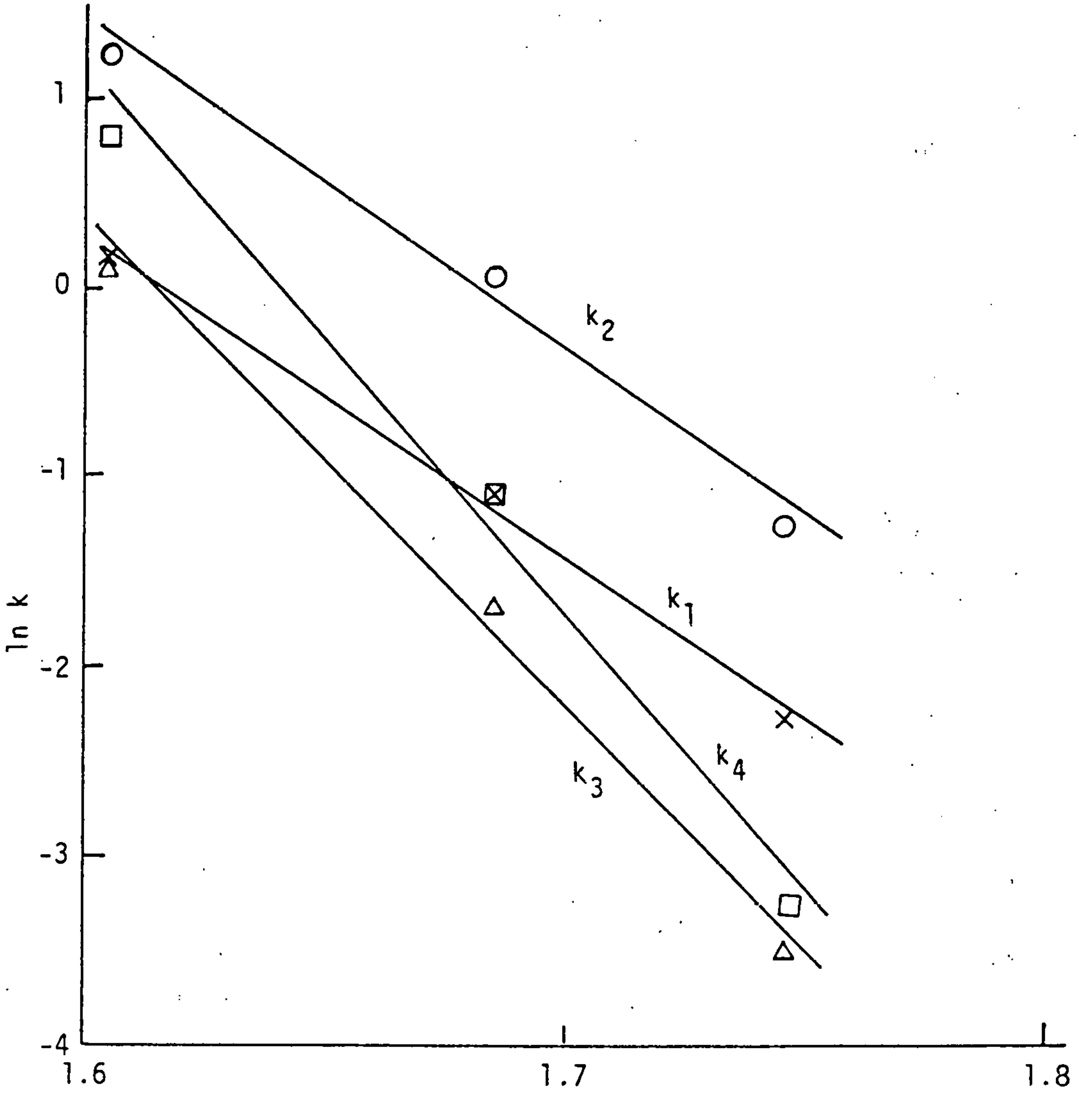

Figure 8. Arrhenius plot of first order rate constants of hydrogenation and hydrogenolysis reactions in N-ethylcarbazole HDN.

Table 1. Pseudo-first-order rate constants as a function of reaction temperature for N-ethylcarbazole and carbazole HDN at 2500 psig hydrogen pressure, unit: cc oil/g cat. min.

Reactant	Temperature, ^{o}C	k_1	k_2	k_3	k_4
N-ethyl-carbazole	300	0.102	0.282	0.029	0.035
	320	0.352	1.110	0.183	0.334
	350	1.150	3.433	1.042	2.142
Carbazole	320	0.476	0.812	0.133	0.244

Table 2. The frequency factors and activation energies of hydrogenation and hydrogenolysis reactions in N-ethylcarbazole HDN.

	k_o	E_a, kcal/mol
k_1	1.07×10^{12}	34.0
k_2	7.01×10^{12}	35.0
k_3	5.10×10^{17}	50.3
k_4	3.93×10^{20}	57.5

IV. Conclusions

Detailed conclusions are included in the reports for each task. No reports were submitted for Tasks 1 and 2. Task 4 is no longer funded and has been discontinued. Tasks 3, 5, 6, 8-11 have been completed. Tasks 12 and 14 are inactive. The theses for Task 13 are now being written.