



A kinetic study of the pyrolysis reactions of acenaphthylene and bifluorenyl
by Robert Andrew Currie

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

The underlying purpose of this study was to provide kinetic design information to the commercial coking technology. Specifically, the study developed kinetic - correlations with the Arrhenius model from thermal gravimetric pyrolysis data. The pyrolysis studies were conducted under non-isothermal conditions on acenaphthylene and bifluorenyl.

These two compounds were selected because of their probable similarity to coker feed stocks and because acenaphthylene forms a high quality graphite while bifluorenyl forms a relatively poor graphite.

Thermal gravimetric analysis experiments provided the desired pyrolysis data while temperature was increased at a constant rate.

To correlate the major reactions kinetically, it was necessary to obtain and analyze weight-loss data, light hydrocarbon gas evolution rate data, and thermal data. An IBM digital computer was used for data reduction and also for certain statistical programs. Linear regression was used to correlate the data to obtain activation energies and frequency factors. A PACE TR-48 analog computer was used to study thermal pyrolysis data when the reaction did not involve appreciable weight loss or gas evolution.

Bifluorenyl and acenaphthylene each undergo three major reactions that can be analyzed kinetically based on the TGA experimental evidence. Bifluorenyl first reacts in a disproportionation reaction to form volatile fluorene. The remaining reactive material again reacts to form the more volatile fluorene during a second reaction. Both of these reactions are second order. The third major reaction prior to dehydrogenation is first order and forms hydrogen and methane. Acenaphthylene undergoes a first order polymerization step followed by a second order reaction in which the more volatile acenaphthene is formed. The third major reaction prior to dehydrogenation is pseudo first order and forms hydrogen, methane, and ethane. The energy of activation and frequency factor for each reaction prior to dehydrogenation was also determined.

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ACENAPHTHYLENE AND BIFLUORENYL

by

ROBERT ANDREW CURRIE

A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

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ABSTRACT

The underlying purpose of this study was to provide kinetic design information to the commercial coking technology. Specifically, the study developed kinetic correlations with the Arrhenius model from thermal gravimetric pyrolysis data. The pyrolysis studies were conducted under non-isothermal conditions on acenaphthylene and bifluorenyl. These two compounds were selected because of their probable similarity to coker feed stocks and because acenaphthylene forms a high quality graphite while bifluorenyl forms a relatively poor graphite.

Thermal gravimetric analysis experiments provided the desired pyrolysis data while temperature was increased at a constant rate. To correlate the major reactions kinetically, it was necessary to obtain and analyze weight-loss data, light hydrocarbon gas evolution rate data, and thermal data. An IBM digital computer was used for data reduction and also for certain statistical programs. Linear regression was used to correlate the data to obtain activation energies and frequency factors. A PACE TR-48 analog computer was used to study thermal pyrolysis data when the reaction did not involve appreciable weight loss or gas evolution.

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INTRODUCTION

In October of 1964, an agreement was entered into between Continental Oil Company and Montana State University, Bozeman, in which work was to be done at MSU on the kinetics of pyrolysis of certain high molecular weight aromatic hydrocarbons. It was intended that the research should provide additional technical information which could be pertinent to Conoco's commercial coke production process. To obtain the desired technical correlations, two pure compounds were selected which were representative constituents of coal and petroleum tars (1). The two compounds selected were acenaphthylene and bifluorenyl. By using representative feed stock compounds the kinetic correlations obtained from pyrolysis data will have direct use for chemical reactor design purposes. As stated in Levenspiel's Chemical Reaction Engineering (2), "Chemical kinetics is simply the study of the factors that influence the rate of reaction and the explanations for the rate of reaction. For the chemical engineer the kinetics of a reaction must be known if he is to make a satisfactory design for equipment in which these reactions are to be effected on a technical scale." If the design engineer has kinetic correlations available, he then has information on how much time the reaction will require to produce a certain level of conversion. Also, when Arrhenius kinetic models are used, the design engineer can obtain an estimate for the most desirable temperature of operation.

(2)

The selection of acenaphthylene and bifluorenyl was also based on information contained in the literature. Union Carbide Corporation has published a series of pertinent documents under contract with the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Most of their work applicable to the studies at MSU was brought up to date in a technical document published in September of 1964 (3). The earlier work done in 1962 was concerned with determining the coking value of various hydrocarbons and with the graphiticity of the resulting carbon (4,5). Later studies placed considerable emphasis on determining the mechanism of the reactions by electron spin resonance, nuclear magnetic resonance, and absorption spectroscopy (1,6). Two of the compounds consistently studied throughout Union Carbide's work were acenaphthylene and bifluorenyl. The studies reported in the literature were not concerned with the kinetics of the reactions involved in the coking sequence. However, the mechanisms reported have served as a guideline for developing the methods to be used in obtaining data for kinetic evaluation.

In the graphiticity studies conducted by Union Carbide (4,5) it was determined that the aromatic hydrocarbons could be placed in either category of "reactive" or "unreactive". The reactive hydrocarbons were thermally unstable and would react at one atmosphere pressure during pyrolysis to form new compounds, while unreactive compounds were simply distilled and did not undergo molecular structure changes. The reactive hydrocarbons were also studied to determine the quality of the carbon-

(3)

aceous residue and the coking value of the original compounds. To determine graphite quality, coke residues such as that produced in commercial coking processes are heated to approximately 3000°C before a quality determination is made.

The quality of graphite was determined by using x-ray diffraction equipment. The lattice spacing provides the desired information concerning the orientation of the graphite. The highly oriented synthetic graphite has a lattice spacing nearly the same as natural graphite. As the lattice spacing increases, the quality of graphite decreases since it becomes poorly oriented and nonplanar. Acenaphthylene produces a graphite in which the planes are well oriented and the lattice spacing is similar to natural graphite (3,7). Bifluorenyl produces a graphite that is highly nonplanar and is quite dissimilar from natural graphite.

Reactive compounds, by definition, leave a coke residue after pyrolysis. The amount of residue remaining at 700°C of the original weight determines the coking value. The properties of the final carbon and graphite depend to a large extent on the chemical constitution of the organic precursor. A listing of the thermally reactive hydrocarbons studied by Union Carbide has previously been reported (3,4,5). The coking value and the graphite quality are given for each reactive hydrocarbon.

(4)

The x-ray diffraction method for determining graphite quality is not sufficiently refined to report accurately variation of quality on a run-to-run basis. That is, on a set of pyrolysis experiments on a particular compound, the lattice spacings from run-to-run would not show sufficient deviation that meaningful correlations could be drawn. For this reason, no effort was made to obtain graphite quality determinations for the pyrolysis runs conducted at MSU. By selecting acenaphthylene and bifluorenyl, kinetic evaluation could be carried out for both a good and a poor graphite producing compound. Also, for this kinetic study it was desirable to choose compounds that produce sufficient volatile material so that weight loss data and gas evolution data could be obtained for use in kinetic evaluation.

During the initial planning phase it was decided to conduct the experimental work to obtain the most useful kinetic design information. In this connection, the pyrolysis was conducted at atmospheric pressure conditions while maintaining an inert environment around the reacting material and reaction products. The reacting material was heated from room temperature to essentially the same final temperature used in commercial coking operations. Because the temperature was continually increasing with time, the classical method of obtaining kinetic parameters under isothermal conditions could not be used. Instead, the temperature was increased at a constant rate and the theoretical kinetic expressions took temperature into consideration as an experimental variable. Data and correlations derived in this manner can then be used

for meaningful non-isothermal design relationships.

The data obtained for kinetic evaluation consisted of three general types. It was necessary to use differential thermal analysis data or similar thermal data to study reactions that were not characterized by weight loss or light hydrocarbon gas evolution. An example of this reaction would be vinyl type polymerization. For reactions that form volatile condensable intermediates, it was necessary to use thermal gravimetric data. For reactions that involve the formation of light-weight hydrocarbon gases, gas chromatography was used to obtain gas evolution rate data. By using all three data collection methods, it was possible to fully examine all the reactions of acenaphthylene and bifluorenyl over the temperature range normally associated with commercial coking processes.

The major reactions for both acenaphthylene and bifluorenyl are shown in Figure 1. This sequence of events is proposed because it is substantiated from MSU experimental results and from mechanism studies conducted by Union Carbide (4,5). The sequence of reactions for acenaphthylene and bifluorenyl provides a series of events as the temperature is increased. Furthermore, each compound has four major reactions. The fourth reaction in both cases involves only dehydrogenation. Dehydrogenation is initiated above temperatures of 550°C and continues to react at temperatures which exceed the capability of the TGA equipment. There is no corresponding measurable weight loss associated with the

(6)

dehydrogenation. This phase of pyrolysis is also very sensitive to temperature fluctuations. Since the temperature interval for the dehydrogenation exceeds the equipment capability, a kinetic study of this reaction was not feasible.

The three major reactions for both compounds shown in Figure 1 were studied in some detail. The proposed sequence does not mean that all of the reacting material must follow this set of reactions. As the pyrolysis proceeds, the exact composition of the reacting mass becomes more doubtful. The literature previously cited indicates that the pyrolysis products at higher temperatures have not been fully identified, although identification of the primary constituent was possible. The proposed reaction sequence was based on the identification of primary constituents and does not account for the formation of unidentified constituents. However, the probable molecular similarity between the identified and unidentified products gives the general reaction sequence additional significance.

RESEARCH OBJECTIVES

In a general sense, the basic purpose of the project was to contribute to the technical knowledge of the coking process. More specifically, the study was to develop kinetic correlations on the reactions of certain aromatic hydrocarbons during pyrolysis. The kinetic evaluation was to employ the Arrhenius expression which replaces the rate constant with a temperature dependent exponential term. Three parameters for each reaction need to be determined to fully define all terms in this kinetic model. The three unknown parameters are the order of the reaction, the frequency factor, and the energy of activation. By analyzing pyrolysis weight loss data, gas evolution data, and thermal data, kinetic analyses of the various major reactions can be made.

As a secondary objective it was intended that the kinetic results for acenaphthylene be compared with the results for bifluorenyl. This comparison would point out noticeable differences in their behavior during coking. However, this analysis must be qualitative in nature because many factors besides kinetic behavior affect ultimate graphite quality.

THEORETICAL DISCUSSION

Arrhenius Kinetic Model:

In the early phases of this project it became evident that the pyrolysis reactions of acenaphthylene and bifluorenyl do not lend themselves to experiments conducted under isothermal conditions. Unfortunately, non-isothermal kinetic data cannot be analyzed by the classical technique of plotting various concentration functions versus time. Since the sequence of reactions for the two compounds studied extend over a considerable temperature range, it was necessary to consider temperature as a variable in the kinetic models.

As discussed in Perry's Chemical Engineers' Handbook (8), Arrhenius in 1889 was able to rationalize the simple exponential function which adequately accounted for temperature effects on the rate of reaction. He arrived at the final form of his exponential equation by assuming an equilibrium situation to which he applied the van't Hoff thermodynamic equation:

$$\frac{d(\ln K)}{dT} = \frac{\Delta E}{RT^2}$$

where K is the ratio of the forward and reverse reaction-rate constants. Arrhenius noted from experimental data that the individual specific reaction rates followed relations of the form $k = k_0 e^{-E/RT}$ when the thermodynamic equation was integrated while holding E constant over the temperature interval of integration. This later equation is known as the

(9)

Arrhenius equation and E is the energy of activation and k_0 is the frequency factor. As stated by Perry (8), this equation "represents the effect of temperature so accurately that when deviations occur they are usually taken as evidence that the reaction is a composite one or that physical processes are important." For a simple irreversible reaction, the rate of conversion is directly related to the concentration of the reacting material. This relationship involves a rate constant and the concentration term raised to some applicable power. The power of the concentration term is known as the order of the reaction. The order is usually taken as first or second order when the general reaction kinetics are studied unless reaction mechanisms or other physical evidence dictates selection of different orders. Because there was no justification for greater discrimination between reaction orders, orders of reaction other than first or second were not considered. Also, the kinetics for each reaction involves an analysis of the general reaction that best describes the behavior in the applicable temperature interval. Therefore, all reaction orders are to be considered as pseudo orders.

The concentration terms in the kinetic model are dependent upon the volume of the reacting material. Even if the concentration terms were converted to moles of reactant, the volume must be considered as a variable. Since it was impossible to obtain accurate estimates of the volume of the reacting material at any time during pyrolysis, an assumption was made to simplify this analysis. It was assumed that the volume in the reactor varied directly with the weight remaining in the reactor.

(10)

This is the same as assuming that the density in the reactor remains constant, since the volume is equal to the weight in the reactor divided by the density. The values used for the density were determined from experimental analysis. By permitting the volume to vary directly with the weight, experimental weight-loss data was used for a continuous variable in the kinetic model. Also, this permitted the use of concentrations in all the calculations which simplified certain mathematical relationships for data conversion and analysis.

To obtain a temperature dependent kinetic model, the rate constant is replaced by an Arrhenius exponential temperature term. The Arrhenius term involves two unknown parameters which are the frequency factor k_0 and the energy of activation E . The kinetic model with the Arrhenius term has the form:

$$\frac{dC}{dt} = -k_0 e^{-E/RT} C^n$$

From experimental pyrolysis data the values for C , dC/dt , and T can be determined. Consequently, for each reaction the parameters k_0 , E , and n must be determined. The exponential term also involves the universal gas constant R .

Linear Regression:

The general approach for obtaining values of frequency factor and energy of activation was to use linear regression. The rate equation employing the Arrhenius exponential term was put into a different form

(11)

by taking the natural logarithm of both sides of the equation. Upon rearranging, the following is obtained:

$$\ln\left(-\frac{dC_A}{dt}\right) - n \ln C_A = \ln k_0 - E/RT$$

By arranging the experimental data into this form and by selecting the order of reaction to be studied, the left hand side of this equation can be combined into a new variable, Y. The term $1/RT$ can be converted into a new variable, X. In this manner the equation takes on the standard form for linear regression, which is $Y = B_0 + B_1X$ where B_0 is the intercept of the straight line and is the value for the logarithm of the frequency factor k_0 . The slope of the straight line, B_1 , is the value for the energy of activation E.

To perform the above regression analysis, an IBM 1620 digital computer program was used. This program permits rapid analysis of considerable quantities of experimental data which would be almost impossible to analyze if all the calculations were made by hand methods.

A multiple linear regression program was already written and available at Montana State University, consequently it was only necessary to program the computer to put the experimental data into the proper form for use in the regression program. This program determines the best fitting straight line by minimizing the sum of squares of the error. Once the computer fits the best fitting straight line, the desired values for the unknown parameters are defined.

Free Radical Reactions:

The reactions of acenaphthylene and bifuorenyl involve several major reactions besides the formation of some minor intermediate reaction products. Literature sources (3,5,6) indicate that all the major reactions involve free radicals. Lewis (5) indicates that the pyrolysis of reactive aromatic hydrocarbons is invariably accompanied by the formation of free radical species. It is felt that these radicals are transitory aromatic radicals formed by thermal dissociations of hydrogen at reactive ring sites by cleavage of substituent groups or by rearrangement. Energies of activation for some free radical reactions have been reported in the literature. Ethane has received considerable analysis over the past years. Recent references (9,10) give the energy of activation for the thermal decomposition of ethane to be greater than 70 K cal/mole. Steacie (11) indicates that energy required to get to the reactive transition state is dependent upon the singlet or triplet characteristics of the compound's transition state. If the CH_2 is in the triplet state, the process will be endothermic and 125 to 150 K cal/mole is a reasonable estimate of the activation energy. If the CH_2 reorganizes to the singlet state in the process, the reaction will be much less endothermic and 77 K cal/mole is not an unreasonable value. This argument shows that activation energies can vary over a large interval and that the mechanisms associated with the reaction are of considerable importance in explaining energy values.

(13)

TGA Thermal Data Analysis:

One reaction of acenaphthylene does not involve weight loss or gas evolution. This reaction is a vinyl type polymerization that is exothermic in nature. The kinetic study for this phase had to be based on thermal data from the TGA unit and from Conoco's DTA unit. The thermal data was obtained under non-isothermal conditions. The TGA data was analyzed by applying unsteady state heat transfer equations to the reacting mass. It was assumed that the material in the reactor behaved as a solid mass so that mixing effects were insignificant.

The partial differential equation relating the temperature to the time and position in a cylinder where end effects are negligible has the form:

$$\frac{\partial T}{\partial t} - \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial r^2} - \frac{k}{\rho C_p r} \frac{\partial T}{\partial r} = \frac{1}{\rho C_p} \frac{\partial Q}{\partial t}$$

where k is the thermal conductivity, C_p is the heat capacity, ρ is the density, and $\partial Q/\partial t$ is the rate of heat per unit volume generated by the reaction. This equation may be solved with appropriate boundary conditions to account for the heat transfer resistances at the boundary of the reacting mass.

The heat generated by the exothermic reaction is proportional to the rate of reaction. If the heat of reaction is known, the following substitution can be made in the differential equation:

(14)

$$\frac{\partial Q}{\partial t} = k_0 e^{-E/RT} C_A^n \Delta H$$

where ΔH is the heat of reaction on a mole basis.

To solve the partial differential equation the equation was transformed by using finite differences in the radial direction. Four radial increments were chosen so that cylinders were formed which had equal thickness of Δr . The partial differential equation under these transformations has the form:

$$\frac{\partial T_m}{\partial t} - \frac{k}{\rho C_p} \left[\frac{T_{m+1} - 2T_m + T_{m-1}}{(\Delta r)^2} + \frac{1}{r_m} \frac{T_m - T_{m-1}}{\Delta r} \right]$$
$$= \frac{1}{\rho C_p} k_0 e^{-E/RT_m} C_{A_m}^n \Delta H$$

and upon combining constants and rearranging, the equation becomes:

$$\frac{\partial T_m}{\partial t} = M T_{m+1} - M(2 - \frac{\Delta r}{r_m}) T_m + M(1 - \frac{\Delta r}{r_m}) T_{m-1} + \frac{\Delta H}{C_p} k_0 e^{-E/RT_m} C_{A_m}^n$$

After the model for the reacting mass was divided into concentric cylinders, the equation was used on each cylinder by choosing the proper subscripts. Since four radial increments were chosen, there are four ordinary differential equations of the type above that must be solved simultaneously.

(15)

Estimates for the value of various constants also have to be made for conditions involved. The remaining terms must come from experimental data.

Finally, the values for the frequency factor k_0 and the energy of activation were varied on an analog computer to best simulate the experimental temperature trace. An analog computer block diagram for this simulation is shown in Figure 2.

DTA Thermal Data Analysis:

The analysis of thermal data for evaluating reaction kinetics has been brought up to date recently by Reed, et al (12). This has proven to be of value in determining reaction kinetics from DTA data. Since DTA samples are very small and involve a large ratio of heat transfer area to sample volume, a perfectly mixed model can be assumed. This model again involves a heat balance where the exothermic reaction contributes heat based on the rate of reaction. The equation is:

$$\frac{dT}{dt} = \frac{hA}{\rho C_p V} (T_s - T) + \frac{k_0}{\rho C_p} e^{-E/RT} C_A^n \Delta H$$

where T_s is the reference temperature of the DTA unit and h is the heat transfer coefficient. The constants in this equation can be combined to simplify the form. The values for the combined constants were determined from experimental processes which involved simulation of the temperature on the analog computer. An analog block diagram for simulating the DTA curves is given in Figure 3.

EXPERIMENTAL CONSIDERATIONS

General:

After the first preliminary investigations on aromatic hydrocarbon pyrolysis, it became evident that a considerable amount of equipment had to be fabricated or purchased in order to obtain the necessary data for kinetic analysis. This equipment had to be able to operate at temperatures between ambient and 600°C, be able to monitor the weight loss of the pyrolysis sample, be able to collect and analyze all light hydrocarbon gaseous products, be able to monitor the temperature inside the reaction vessel, and also be able to maintain an inert atmosphere around the entire reaction chamber. The equipment used in this project generally consisted of a thermogravimetric analysis unit (TGA), differential thermal analysis (DTA), gas chromatograph, and miscellaneous support apparatuses.

Thermogravimetric Analysis Unit (TGA):

The TGA unit was fabricated at Montana State University. The basic concept for this unit was first reported by Ewald (13), while certain useful modifications were obtained from an article by McAdie (14). The automatic recording balance as used by Ewald (13) was a modification to a model R Leeds & Northrup automatic recording mechanism. Figure 4 shows the modification made to a Leeds & Northrup mechanism at MSU to make an automatic recording balance useful for the pyrolysis experiments. The balance worked very well throughout the duration of the experiments.

The balancing chain was selected so that a weight loss of one gram would give a movement on the recording pen of about nine inches. The unit was calibrated to obtain an exact conversion factor. The balance proved to be sensitive to changes in weight of less than 0.01 grams. Tests were also made which proved that altering experimental conditions on temperature and inert sweep gas flow rate had essentially no effect on the accuracy of the balance.

The reaction chamber was placed directly below one arm of the automatic recording balance. The entire reaction chamber was custom fabricated to best serve the experimental objectives, and this assembly is shown in Figure 5. The reaction chamber refers to all the miscellaneous equipment necessary to perform the pyrolysis in the reactor, collect all gaseous products, preheat sweep gas and maintain an inert atmosphere around the reactor vessel.

The design of the reaction chamber had to take into consideration four major concepts. First, it was necessary to collect all components that were driven out of the reactor without destroying the automatic balancing capability. The reactor vessel was designed with a small gas exit tube which came out of the top of the reactor parallel to the shaft suspending the vessel from the arm of the balance. The exit tube telescoped into a larger tube fabricated into the lid of the heating chamber. The tube in the lid passed through a water-cooled condenser and into a gas collection system. As the pyrolysis reactions forced gaseous pro-

ducts out of the vessel, all the products were pulled off. The heavier reaction products condensed in the water-cooled condenser while light hydrocarbon gases continued to flow toward the gas collection system.

Second, an inert gas atmosphere had to be maintained at all times. Nitrogen was chosen for this because it was used as a chromatograph carrier gas and also because of its presence in air. Again, the inert atmosphere criterion could not interfere with the recording balance. Consequently, sweep gas had to be allowed to flow freely out of the hole in the heating element lid used by the shaft to the recording balance. This problem was handled by forcing more pre-heated nitrogen into the bottom of the heating element than was drawn off through the condenser. In this way, all the reaction products were swept through the condenser at a given flow rate with nitrogen making up the balance of the exit gas flow stream.

Third, the heating element which freely surrounds the reactor vessel had to be adjustable in all three axes. The element was vertically adjustable to govern the telescoping of the reactor vessel exit tube and the heating element lid. The element was horizontally adjustable in order to permit the reactor to hang freely inside the heating element and also to pass freely through the shaft hole in the heating element lid. The heating element is cylindrical in shape and is housed in a stainless steel can. The nitrogen sweep gas and the heating element electrical leads both enter the bottom of the can. The top is removable and houses the gas exit tubes previously discussed.

Finally, the reactor had to be machined for special features. The vessel was made of stainless steel and had to be designed to minimize its weight. The top of the vessel unscrews for sample insertion and for removing the coke residue after pyrolysis. A thermocouple well extends through the head of the reactor and comes within a quarter of an inch from the bottom of the reactor. By using a continuous strip chart recorder in conjunction with the reactor thermocouple, a continuous record of the reaction temperature was made. However, bringing the thermocouple leads off of the balance without destroying the balance sensitivity required special consideration. It was necessary to solder light, flexible number 34 copper leads to the thermocouple leads to span between the balance and the TGA cabinet. The connection to the cabinet for completing the circuit to the recorder was made by using two glass vials filled with mercury. The fine copper leads were inserted into the mercury before each pyrolysis run.

During each pyrolysis experiment a check of the accuracy of the reactor thermocouple was possible. This check was possible when the initial reactor sample reached the melting point of either acenaphthylene or bifluorenyl. The temperature trace would produce a constant temperature plateau as long as the sample was melting. The melting point temperature obtained from the TGA consistently was within $\pm 2^\circ\text{C}$ of the melting point reported in the literature.

All of the equipment and parts that go together to make up the reactor assembly are housed in a cabinet just below the scales. Portions of the cabinet were water cooled. However, the main function of the cabinet was to provide an additional inert chamber around the reactor assembly. This additional nitrogen atmosphere was employed to minimize any oxygen diffusion around the balance shaft hole in the heating element lid. On early experiments it was noted that some oxygen diffused into the hot products gas stream causing carbon dioxide and water to be formed. As an additional precaution, the head of the heating element can was made of a stainless steel block 1-1/4 inches thick. The balance shaft hole was drilled through the block so that oxygen would have to diffuse a greater distance before coming into contact with the hot reaction products. After these modifications were made, oxygen contamination was not a problem. The diffusion block is shown in Figure 5.

The nitrogen used for sweep gas was first metered through a rotameter and then heated prior to entering the bottom of the heating element can. The heating element around the reactor vessel and the nitrogen pre-heater were controlled by Variacs. The head of the heating element can was clamped onto the can by two large C-clamps. An aluminum foil gasket was placed between the lid and the stainless steel can to minimize the amount of oxygen that could enter between these two pieces. The gas collection system used to pull a given flow rate of gas out of the reactor was controlled by a positive displacement pump. The pump

removed water from a large jar at a controllable rate. The water removed caused the gaseous reaction products and the nitrogen sweep gas to be drawn through the condenser and through a solenoid-operated, automatic sampling valve on the chromatograph. The sampling valve was actuated periodically to inject a sample into the chromatograph for analysis.

Gas Chromatograph:

During the planning phases for this project, it was anticipated that various hydrocarbon gases from methane to n-pentane would have to be analyzed as part of the pyrolysis products. After consulting literature sources it became evident that hydrogen and light hydrocarbon gases up through C₅ could not be analyzed at one time, with one sample, on one column. From information contained in chromatography catalogs it was decided to use a 24-foot partition column of 30% Bis (2-(2-methoxyethoxy) ethyl) ether on chromosorb. This partition column can separate most of the hydrocarbon gases between methane and n-pentane but does not separate hydrogen from methane. Since hydrogen and methane were known to be pyrolysis products, an additional column had to be used. Hydrogen can be separated from methane by using just molecular sieve in a six-foot column. However, the columns can not be used in series because hydrocarbon gases above ethane will not pass through the molecular sieve. Finally, a thermal conductivity chromatograph was modified by a series of quick-opening valves to permit one sample to be injected on molecular sieve for methane-hydrogen separation and analysis and then a second

sample could be injected on the partition column for hydrocarbon gas analysis. As it turned out, the pyrolysis of bifluorenyl only produced appreciable quantities of methane and hydrogen so that the sieve column was sufficient. On acenaphthylene, besides hydrogen and methane, significant quantities of ethane appeared. For this analysis the samples of gas were alternated between the sieve column and the partition column.

To determine the gas evolution rate from the pyrolysis reactions, peak heights on the chromatogram were used. To calibrate the column a gas mixture containing known percentages of hydrogen, methane, and ethane was ordered. These three gases each made up about five percent of the mixture, with the remainder being nitrogen. Since samples were injected into the columns by an automatic gas sampling valve, it was decided to obtain a peak height calibration curve by changing the sample loop size. Sample loops were obtained which had volumes of 1/4, 1, 2, and 4 ml. As each loop was used, a different concentration of standard gas was injected into the chromatograph. In this way it was possible to determine peak heights versus volume percent. Since the reaction products were passing through the system at a known flow rate metered by the gas collection system, the experimental peak heights represented gas evolution rate. A standard sweep gas flow rate of 65 cc/min was chosen. By using the ideal gas law, the calibration curve was plotted as gas evolution rate in moles per minute versus chromatogram peak height in strip chart recorder units.

The chromatograph used nitrogen as a carrier gas, since this carrier works well when hydrogen detection is required. Also, nitrogen was used as the reactor sweep gas and is quite inexpensive compared to most other carriers. The detector and columns were operated at 50°C, and the current to the detector was 200 milli-amperes. The carrier gas flow rate was approximately 110 cc/min at room temperature and 640 mm Hg. The peak heights were recorded on a Brown strip chart recorder at approximately five-minute intervals.

Differential Thermal Analysis, (DTA):

One reaction of acenaphthylene was characterized by an exothermic reaction that did not result in weight loss or gas evolution. To analyze this reaction, three DTA runs were made on Conoco's unit. The DTA unit was a Dupont 900 Differential Thermal Analyzer. This apparatus is capable of heating a sample under inert conditions at various heating rates from zero to 30°C per minute. The temperature of the reacting material is measured against the temperature of an inert sample and the temperature difference ΔT is monitored.

TGA Operating Procedures:

The stainless steel vessel reactor has a volume of just over 10 cubic centimeters. However, pyrolysis runs generally used only about one-third of this volume for the sample. Larger samples had a tendency to bubble out of the reactor as gaseous products were formed. Of importance in this connection was the free volume in the water-cooled condenser for

precipitating the condensable products. By keeping the samples small, plugging was not a problem. Also, the volume of light gaseous products did not exceed the gas collection sweep capability. Pyrolysis runs produced the best results when the voltage to the reactor heating element was increased at a given, predetermined rate. This procedure proved to be extremely important in obtaining reproducible, accurate, meaningful data.

By increasing temperature linearly at some determined rate, several errors are minimized. In this respect, the thermocouple temperature lag is kept approximately constant. The heat applied to the reactor maintains a more constant driving force and minimizes transient behavior. Reaction products are driven off at a constant rate providing smooth weight-loss traces and gas evolution curves for better analysis. To aid in maintaining a constant temperature rate, power was drawn from a constant voltage transformer to prevent line fluctuations. Data obtained in this manner proved to be more reliable and much easier to analyze.

The voltage rates used had to be determined from experience based on the compound under study. If the increase was too slow, the reaction took far too long to go to completion. If the increase was too rapid, the automatic balance could not keep up with the actual weight loss. Also, the rate of gas evolution would be increased causing the volume of the gas to exceed the capability of the gas collection system.

Early experiments were conducted without preheating the nitrogen sweep gas. It was later determined that the sweep gas did not become hot enough on passing through the reactor heating element. As the colder nitrogen came in contact with the volatile reaction products, the products tended to precipitate to the nearest surface. Often the condensed products remained in the telescoping gas exit tubes causing an inaccurate weight-loss trace. Upon preheating the nitrogen, all the volatile material was carried well into the condenser before condensing. The preheated nitrogen never exceeded 320°C prior to entering the reactor area.

Post-Pyrolysis Procedures:

After a pyrolysis experiment, the coke in the reactor is scraped out. The condensed products in the condenser are washed out with acetone and the solution is collected in a beaker. From the data available, a check is made on the overall material balance. The coke, condensed products, and light gases are all considered in the weight balance. After some early equipment modifications it was possible to obtain a material balance that accounted for 96 to 98% of the original sample weight. The major part of the missing material is lost from the condensable products during the acetone wash of the condenser. This is quite important since the weight-loss curve is then quite accurate for data correlation. That is, as long as the condensable products leave the reactor zone, the weight-loss trace will show the true pyrolysis weight data.

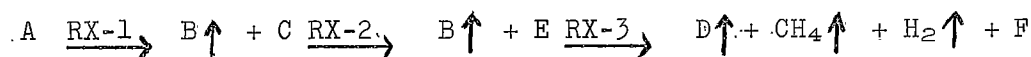
DISCUSSION AND RESULTS

General:

The sequence of reactions for acenaphthylene and bifluorenyl provides a natural series of events as temperature increases. Each compound has three major reactions that can be kinetically analyzed from TGA data. These three reactions for both acenaphthylene and bifluorenyl will be considered in some detail. The reactions of bifluorenyl will be discussed in sequence followed by a sequential analysis of acenaphthylene. Certain comparisons between the two compounds will be discussed last.

Kinetics of Bifluorenyl:

The mechanism studies reported in the literature were very valuable in planning and executing pyrolysis experiments. A set of pyrolysis mechanisms is contained in a Union Carbide Corporation report (3). Figure 6 shows the pyrolysis reactions of bifluorenyl which includes the formation of the bifluorylidene radical. In the pyrolysis of bifluorenyl three separate reactions make up the significant reactions prior to dehydrogenation. Figure 1 shows this main sequence of events as it applies to the kinetic study. The thermal gravimetric data (TGA) substantiates that three reactions are kinetically significant prior to high temperature dehydrogenation. The general reaction sequence and the compound designations are as follows:



In this equation, A represents bifluorenyl, B is fluorene, C is bifluorylidene, D is predominately tetrabenzonaphthalene, E is unreacted tetrabenzonaphthalene or one of its homologs, and F is the carbonaceous material. The molecular structures for these compounds are given in Figure 6. Tetrabenzonaphthalene is shown in this sequence of reactions because Union Carbide was able to identify this compound as part of the reacting mass. A pyrolysis weight-loss trace is depicted in Figure 7, which shows the weight loss associated with each sequence of the pyrolysis. The corresponding temperature trace is also shown on Figure 7.

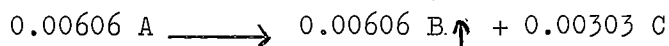
There is one alternate possibility for the third reaction which will be discussed later. Also, more exacting equations with stoichiometric coefficients will be presented with the discussion of each reaction. Table I is a complete listing of all the pyrolysis experiments conducted on bifluorenyl. A brief description of the applicability of each experiment is also given in this table.

The yield of carbonaceous material for bifluorenyl pyrolysis runs conducted at MSU average about 28%. The yield for each run is given in Table I. This yield is comparable to the yield reported in a Union Carbide document (1), which was about 30%. In other work performed by Union Carbide (4) the yield was reported to be as low as 5.8%; however, experimental conditions were not discussed. The carbon yields resulting from MSU pyrolysis runs indicate that the run-to-run variations are quite low.

First Reaction of Bifluorenyl (RX-B-1):

The first reaction of bifluorenyl is a disproportionation to yield reactive fluorene radicals which can abstract hydrogen atoms to form volatile fluorene or dimerize to bifluorylidene. From experimental data the disproportionation begins at about 347°C. The final temperature for this reaction overlaps with the beginning of the second pyrolysis reaction. This overlapping occurs at temperatures greater than approximately 405°C. The volatile fluorene is condensed as a solid in the condenser during pyrolysis. Chromatography has been used to compare a known fluorene sample with the condensate from pyrolysis. Fluorene has thus been identified as the major constituent in the condenser after pyrolysis.

Since the first reaction of bifluorenyl involves disproportionation, the stoichiometric equation in moles based on a two-gram initial sample is:



where A, B, and C are bifluorenyl, fluorene, and bifluorylidene, respectively. The one-to-one mole ratio between A and B simplifies the data conversion equations for concentration. The exact form of the data conversion equations are given later with the applicable computer program.

The kinetic correlations were first studied using a PACE TR-48 analog computer. The general approach was to place the experimental data on the analog function generators and also simulate the desired

kinetic model on the computer. Certain parameters of the chosen model could be varied by adjusting potentiometers. When the simulated model agreed well with the experimental data, the potentiometer settings were recorded. From the settings, best values for the various parameters could be determined.

Considerable effort was spent to make use of mathematical techniques suggested for use on the analog computer in an article by Steinmetz (15). The method employed the concept of steepest descent to provide the optimum values for the unknown parameters. This method did not work well when a kinetic model was anything but simple in nature. The Arrhenius expression presented several problems when this technique was used. The method requires almost twice as much analog equipment as less sophisticated programs. The TR-48 computer at MSU did not have sufficient equipment for the Arrhenius steepest descent program. Secondly, the steepest descent program was quite complicated and consequently lost its versatility rather quickly. Each time a slight change was made in the model or the anticipated value for certain parameters, the program needed considerable revision. Finally, error introduced within the analog equipment also made the results questionable. However, this method made use of some analog techniques that worked very well when combined with other programs. One of the most useful analog techniques that was incorporated in other programs was the use of repetitive operation.

(30)

The analog program which proved to be most successful for non-isothermal data required manual adjustment of potentiometers to obtain the best data simulation. Experimental data from Run EX-B-12 was chosen for simulation because of the smooth increase in the temperature during the weight loss. The weight-loss data was placed on one variable diode function generator (VDFG) and the corresponding temperature placed on the second VDFG. A complete analog block diagram for this simulation is shown as Figure 8. For better usage on the analog computer, the Arrhenius equation was put into a form using logarithms to the base ten. The following equations indicate how the Arrhenius expression was handled.

$$\frac{1}{V} \frac{dN_A}{dt} = -k_0 e^{-E/RT} \left(\frac{N_A}{V} \right)^n$$

Assume constant density in the reactor so that $V = \frac{W_r}{\rho_0}$

where: $\rho_0 = .957$ grams/cc (from experimental data)

$W_0 = 2.00$ grams bifluorenyl

M.W. fluorene = 166

M.W. bifluorenyl = 330

$E = \alpha E_0$ (for computer reasons) calories/mole

$R = 1.987$ calories/mole °K

W_r = weight in reactor at any time

$k_0 = \text{sec}^{-1}$ 1st order; cc/mole sec. 2nd order

$N_A = W_0/330 - (W_0 - W_r)/166 = W_r/166 - 0.00599$

(moles bifluorenyl)

r = scaling factor for analog

(31)

$$\text{Let: } \frac{k}{r} = \frac{k_0}{r} e^{\alpha E_0/RT}$$

For analog usage:

$$1/2 \log 100 \left(\frac{k}{r} \right) = 1/2 \log \frac{100}{r} (k_0) - \frac{40 \left(\frac{\alpha}{80} \right) E_0/400}{2.303 R (T/400)}$$

The scaled differential equations solved by the computer were:

1st Order:

$$\left[\frac{dN_A}{.01 dt} \right] = - r \left[\frac{k}{r} \right] \left[\frac{N_A}{.01} \right]$$

2nd Order:

$$\left[\frac{dN_A}{.01 dt} \right] = - .005 \rho_{or} \left[\frac{k}{r} \right] \left[\frac{N_A}{.01} \right]^2 / \left[\frac{W_r}{2} \right]$$

The optimization is carried out by adjusting the potentiometers for the terms $(1/20)(\log 100/r)(k_0)$ and $-40 (\alpha/80)/2.3 R$. However, the computer introduces a certain amount of error when certain analog components are used. The VDFG units which are used for the experimental data memory can use only ten experimental data points. The VDFG unit then puts a straight line segment between each consecutive pair of data points. This means that a smooth continuous function like a weight-loss curve is simulated by ten consecutive straight line segments. Also, the logarithm generator works on essentially the same idea as the VDFG unit and, consequently, this unit also introduces a certain amount of error. In addition to the above two potentiometers, a third one had to be ad-

justed to provide the scaling factor r . The adjustment of the factor made changes in the error from the logarithm generator. The optimization is dependent upon matching the segmented curve to the theoretical concentration curve, consequently varying the scaling factor does not affect the optimization. The use of a third potentiometer considerably complicates finding the true minimum error.

The error term is generated by taking the difference between the experimental concentration curve (stored on the VDFG) and the theoretical concentration curve (generated from the Arrhenius expression). This term is squared and integrated over the applicable time period to produce a final value for the total error. The value for the total error is read on a voltameter.

The weight loss data for the Run EX-B-12 was tried using this method for both first and second order kinetics. The procedure worked quite well within the capability of the equipment. The exact point at which a minimum value of the error occurred could not be determined; instead it was necessary to determine an interval within which the minimum error occurred. For example, the first order reaction gave minimum error values between an energy of activation of 42,500 and 48,200 cal/mole. It was necessary to treat the second order reaction in the same manner. After determining kinetic values for EX-B-12, Run EX-B-2 was chosen because of its different temperature profile. The minimum error range was determined for this run and the results of this

study are given in Table II. From this analog study it was not possible to determine if a first or second order kinetic model fit the data best. Neither visual comparisons nor the final value for the error made it possible to distinguish the proper order of reaction.

After studying Run EX-B-12 and Run EX-B-2 data on the analog computer, it was decided to investigate the possibilities of programming the IBM 1620 digital computer to perform the desired data analysis. Changing computers became necessary when the analog provided a range of acceptable values for each set of data instead of the best value. Besides being a slow, time-consuming analysis, the error generated in the analog equipment may have affected the results to the point of losing the true optimum value.

The general approach for the digital computer was to convert experimental data to applicable concentration and temperature data, obtain rate of reaction data, combine terms and then use linear regression to determine the best values for kinetic parameters. The experimental data was punched directly onto IBM cards in the units used by the strip chart recorders. The computer was then programmed to use conversion factors and stoichiometric equations to convert the experimental data to units of concentration (moles/cc), temperature ($^{\circ}$ K), and time (sec). However, the Arrhenius expression also requires rate data (moles/cc sec). To obtain rate data, the computer was used to fit a polynomial to the concentration and time data. After trying polynomial orders of three

through seven, a sixth order polynomial gave the best fit. The polynomial program provides a value for the sum of squares of the errors and this value was used to determine the degree of the polynomial to use. A print out of the polynomial data was also checked against each set of pyrolysis data. Once the coefficients of the sixth order polynomial were determined, the derivative of the polynomial was taken for each experimental data point (one minute intervals). After this program, the computer rearranged the experimental data into a form for use in a linear regression program. The linear regression program then provided the best values for the energy of activation and the frequency factor. The regression program was run twice, once for a first order reaction and once for a second order reaction. A simplified flow diagram of this procedure is given in Figure 9. A listing of the computer programs for data conversion and rearrangement is given in Table III. The linear regression concept was previously discussed in the Theoretical Considerations section of this thesis.

Five weight-loss pyrolysis experiments were correlated using the digital computer. The experimental data for these five TGA runs are listed in Tables IV through VIII. Table IX lists the five runs and the corresponding results obtained from the regression analysis. Also given is the correlation coefficient for each regression analysis. The correlation coefficient is an indication of the goodness of fit between the regression line and the experimental data. Correlations above 0.90 are

