



The pyrolysis of naphthacene  
by John Charles Philip

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE in CHEMICAL ENGINEERING  
Montana State University  
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**Abstract:**

The pyrolysis of naphthacene was studied in a Thermogravimetric Analysis (TGA) apparatus in order to obtain information which might be useful in the manufacture of commercial pyrolytic graphite.

During the pyrolysis runs, data was obtained concerning amount of weight loss, temperature, and rate of evolution of the gases produced by pyrolysis. Following the runs, the products were analyzed. The final temperature of all runs used for quantitative purposes was 625-630°C. The results of the product analysis were used to form a stoichiometric equation for the overall reaction of naphthacene.

Four compounds and unreacted naphthacene were found to be present in the condensate. One of these was 5,12-dihydronaphthacene. The other compounds appear to be two oxygenated compounds and one compound that maybe the result of further reaction of dihydronaphthacene.

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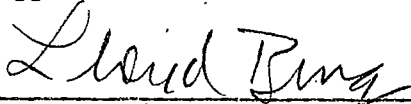
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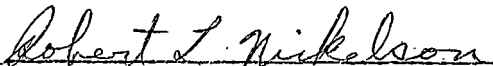
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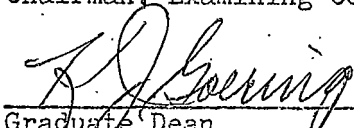
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## Abstract

The pyrolysis of naphthacene was studied in a Thermogravimetric Analysis (TGA) apparatus in order to obtain information which might be useful in the manufacture of commercial pyrolytic graphite.

During the pyrolysis runs, data was obtained concerning amount of weight loss, temperature, and rate of evolution of the gases produced by pyrolysis. Following the runs, the products were analyzed. The final temperature of all runs used for quantitative purposes was 625-630°C. The results of the product analysis were used to form a stoichiometric equation for the overall reaction of naphthacene.

Four compounds and unreacted naphthacene were found to be present in the condensate. One of these was 5,12-dihydronaphthacene. The other compounds appear to be two oxygenated compounds and one compound that may be the result of further reaction of dihydronaphthacene.

## Introduction

Pyrolysis or thermal decomposition is the process of breaking chemical bonds by means of thermal energy. Unless pyrolysis occurs in the presence of catalysts, it is known to proceed by a free radical mechanism and the products of pyrolysis may be predicted to some extent by means of the application of the knowledge of free radical chemistry.

The manufacture of pyrolytic graphite involves the pyrolysis of a feed stock that is primarily aromatic in character. The components of this feed that end up in the finished graphite are primarily polynuclear aromatic hydrocarbons or compounds which are capable of undergoing reactions which form this class of compounds. Lighter compounds will distill off during the process of heating the feed to the temperatures required to form graphite. Other classes of compounds besides polynuclear aromatic hydrocarbons can undergo pyrolysis and yield a high molecular weight carbonaceous residue, but ordinarily this residue will not yield a high-oriented graphite (1). There are two primary considerations which determine whether a given compound will give a well-oriented graphite. The first of these involves the structure of the original molecule. If the starting compound is not planar or has a great deal of steric crowding, it is not likely to form a well-oriented graphite. The second involves the melting point of the starting material. Brooks and Taylor found that well-oriented graphites did not result unless fusion of the starting compound occurred prior to the reactions producing graphite-like structures (2). For



these same reasons, if the mechanism of thermal decomposition for a molecule involves intermediates with the characteristics mentioned above, the compound is likely to form a graphite that is not well-oriented.

Compounds which form graphites react in the following manner: First, an aryl radical is formed by the rupturing of a carbon-hydrogen bond or by the attack of a radical on an aryl hydrogen. A diaryl molecule can then form in one of two ways. The first and least probable way is by combination of two aryl radicals. A more likely mechanism is the addition of an aryl radical to an aromatic molecule followed by the removal of hydrogen to give a diaromatic system. In order to get compounds with structures similar to that of graphite, cyclodehydrogenation takes place to give a more completely aromatic system. For example, in the tar formed by flow pyrolysis of anthracene at 700°C are 9,9'-bianthryl, 1,2:11,12-dibenzoperylene, and other compounds which could be formed by cyclodehydrogenation of the above or of compounds formed by some of the other possible radicals of anthracene (3). The structures of these compounds are shown in Table I.

The commercial manufacture of pyrolytic graphite involves a two-step process. During the first step of the process, a coke is formed by heating the feed stock slowly to approximately 800°F. During this heating period, the temperature may be allowed to level off at various intermediate points in order to help to remove impurities

which may be present in the feed. After the temperature reaches its final value, it is kept there for a predetermined length of time. The resultant coke is then made into electrodes and heated in an electric furnace to the 2500°C temperatures which are required in order to produce graphitic products (4).

At the present time it is not possible to tell in advance what the quality of the final graphite resulting from a given coker feed stock will be without taking a sample of the feed and actually making graphite from it. It would be desirable to be able to obtain enough information from the initial coking process to be able to tell what the ultimate graphite quality from the feed would be (4).

Most of the literature oriented toward the preparation of graphite from polynuclear aromatic hydrocarbons is based on work done by the Union Carbide Corporation for the Air Force Materials Laboratory. They took a large number of compounds and heated them to 750°C in a Differential Thermal Analysis (DTA) unit and classified these compounds as either thermally "reactive" or "unreactive", depending on whether they gave a measurable amount of carbonaceous residue at the end of the DTA run. These runs were made at atmospheric pressure (5). Out of those compounds which were found to be "reactive", they selected approximately 100 compounds to convert to graphite by heating to 3000°C. The orientation of the resultant graphite was then studied by means of x-ray diffraction. The 002 lattice spacing was selected to reflect the orientation of the graphite. The lower the value of this spacing, the

better is the orientation of the graphite (1). Graphites with a value for this spacing greater than 3.366 Angstroms are poorly oriented (1).

The purpose of this study was to study the reactions of compounds similar to those which would be found in coker feed stocks used in the manufacture of pyrolytic graphite with the hope that the information resulting might be useful in coker design and also might provide a useful way of testing a coker feed stock in order to predict how good a graphite it would make.

Two compounds were selected for this study: 1,2,5,6-dibenzanthracene and naphthacene. The first compound was selected because information available in the literature (6) indicated that the only gaseous products present in significant quantities after pyrolysis of this compound in a sealed glass ampoule were hydrogen and methane. This would make analysis and subsequent determination of kinetic information much simpler than if more gaseous products resulted. The chief disadvantage of this compound is that we wanted to know how well-ordered a graphite would result from the compounds selected and dibenzanthracene was classified in the work done by Union Carbide as thermally "unreactive" (5). DTA of this compound showed a boiling point at 520°C.

In the equipment used for this study, it was possible to obtain a 35% yield of carbonaceous residue based on original sample size when the pyrolysis of dibenzanthracene was being investigated. In the DTA work done by Union Carbide, the heating rate used was ten degrees per

## Equipment

A drawing of the equipment used to conduct the pyrolysis is shown in Figure 1. Basically, it consists of a stainless steel reaction chamber which is suspended from a continuous recording balance. The piece of tubing from which the reactor is suspended is also the thermowell for measurement of reactor temperature. The balance is the same one which R. A. Currie built for his study on the pyrolysis of acenaphthylene and bifulorenyl (7). Figure 1 shows the equipment as it appeared while Currie was doing his work. Figure 2 shows some of the modifications which were necessary in order to make the equipment perform satisfactorily for naphthacene. Comparison of Figures 1 and 2 shows that the design of the cap which fits over the heated zone was changed. This was done for two reasons. It was felt that the amount of oxygen getting to the reacting materials would be decreased sharply by increasing the length of the path required for its diffusion. The primary reason, however, for the change in design was to allow the installation of an additional heater. The purpose of this heater was to prevent the condensation of the heavier products which distilled off during the runs. In the early runs which were made on naphthacene, heavy solid products would condense on the thermowell and along the tube leading from the condenser to the reactor. This would result in the fouling of the balance. The heater was installed in order to raise the temperature of the gas coming in contact with these products to a value sufficiently high to prevent condensation from occurring until they reached the condenser region. The heater consisted of nichrome wire with ceramic bead insulation wrapped around this cap

and the beginning of the nipple leading away from the cap.

In addition to the equipment shown in Figures 1 and 2, there is a chromatograph built especially for this project hooked up to the outlet in order to analyze for the non-condensable gases produced. The chromatograph, which contains a thermal conductivity detector, uses a 1/4-inch diameter column that is packed with Porapak Q 100/120 to separate and analyze the gaseous products of naphthacene pyrolysis. This column is six feet six inches in length. Immediately before the chromatograph is located a glass wool filter to remove the last of the solid products from the gas stream and a tube of drierite to remove any water that may be contained in the stream. The carrier gas used in the chromatograph was nitrogen at 65 cc/min. The column temperature was 118.5°C. Nitrogen was used because helium, which is the preferred gas for methane and ethane chromatography, is very poor for hydrogen. Nitrogen is also inexpensive enough to use as a purge for the system.

The chromatograph was provided with an automatic sampling valve in order to have exactly the same sample size at every injection. This was very important since it was necessary to have information about absolute concentration of the individual components of the gas being analyzed. This uniformity in sample size can not ordinarily be achieved with a syringe.

The last piece of equipment used during the reaction was a positive displacement pump which was used to pull the gases leaving the condenser through the sample valve at a constant rate. It did this by

pumping water out of a sealed bottle which was connected to the outlet end of the sample valve at the required rate.

The remainder of the equipment is that which was used for analysis and identification of the products. An Aerograph 660 gas chromatograph equipped with a flame ionization detector was used to analyze the condensate. The column that was used was a 1/8-inch diameter, twenty-five foot column packed with 5% SE-30 on 50/60 mesh Anakrom ABS. The carrier gas was nitrogen at 25 cc/min. The column temperature was 242°C.

The infrared spectra used to identify one of the products and to aid in the characterization of one of the other products in the condensate were run in a Beckman IR-4 Infrared Spectrophotometer. The infrared spectra of another condensate fraction were run by Huffman Laboratories in Wheatridge, Colorado.

Ultraviolet spectra were run in a Beckman DK-2 Ultraviolet and Visible Spectrophotometer.

Preparative Chromatography was done in an Aerograph 200 gas chromatograph in a 1/4-inch column, fifteen feet long, packed with the same material as that used to analyze the condensate using hydrogen as carrier gas at 30 cc/min. The column temperature was 250°C.

## Experimental and Analytical Procedures

The sample size used in the pyrolysis runs under discussion here was between 0.9 and 1.1 grams. Prior to the beginning of the runs, the nitrogen supply to the reactor and that used to provide a continuous purge to the reaction chamber shown in Figure 1 was turned on. During the progress of the run, the rate of supply of nitrogen was kept slightly higher than the rate of its removal through the sample valve in order to help to cut down on the amount of oxygen entering the system.

On the day of the run, samples of the calibration gas were run through the sample valve at approximately the same rate at which the reaction gases would be pulled through the valve during the run in order to check the calibration curve and to provide a means of correction for the normal variation in atmospheric pressure that occurs.

The calculation of gas evolution rates was done by using the peak heights shown on the reaction-monitoring gas chromatograph. A calibration curve was made using a calibration gas purchased from the Matheson Company which contained 5.27 mol% hydrogen, 5.33% methane, and 5.43% ethane in nitrogen. The calibration curve was made by injecting samples of  $\frac{1}{4}$ , 1, 2, and 4 cc through the sampling valve at approximately the same rate at which the gases are pulled through it during the pyrolysis runs. This gas contains hydrogen, methane, and ethane at approximately the same concentrations in which they appear in the gaseous product mixture. Since the sample loop is not connected to carrier gas pressure until the moment of injection and the sample loop is outside

the chromatograph and far enough from the reaction area for the gases to cool to room temperature, the calibration curve was based on ambient temperature and pressure.

Twenty-five degrees centigrade was assumed as the temperature and the pressure was measured prior to every run in order to make corrections on the calibration curve. Since the calibration curve was based on a flow rate through the sample valve of 65 cc/min, it was necessary to correct for deviations from this value which occurred during the runs. The variations in ambient temperature were not corrected for since the original calibration curve was made using the assumption that sample valve temperature was the same as that in the chromatograph. The 4-cc sample loop was used during all of the runs. The gas evolution rate could then be calculated by means of the following equation:

$$\frac{\text{moles}}{\text{sample}} \times \text{flow rate} = \frac{\text{moles}}{\text{min}}$$

In this equation the flow rate must be expressed as the number of 4-cc samples per minute. The points used to make the calibration curve are shown in Table II. A computer program which was used to read the calibration curves is shown in Table III. The subroutine which will do the necessary interpolations is shown in Table IV. This subroutine takes the four points on the calibration curve nearest to the desired value and fits a fourth order polynomial through them and then calculates the desired intermediate value. The input to the curve reading program



includes calibration curve data taken from a graph which was drawn of the calibration for approximately every five units of peak height. It also includes the values of peak height for the gases taken during the run being analyzed.

Another program was written to integrate the gas evolution rate curves in order to obtain stoichiometric coefficients for the gases. It is shown in Table V that the output of this program was time, temperature, fraction of original sample corresponding to the amount of weight lost since the beginning of the run, total amount of gas evolved per gram of sample, and per gram of material remaining in the reactor. Gas evolution rate was expressed in both of these ways in order to decide which of the two values to present in the form of graphs. The values in the individual runs are affected by so many other variables other than temperature, such as the rate of temperature increase at the time at which the sample is taken, that the rates at a given temperature do not agree very well with those from other runs, no matter which basis is chosen as a means of expression of the rate. The rate per gram of sample was chosen as the expression to present. The rate per gram remaining in the reactor can easily be calculated from the other. The output of this program also provided the input to the program shown in Table VI which made the graphs shown in Figures 3-6.

During the progress of the runs, an attempt was made to keep the rate of temperature increase as close as possible to 1.67 degrees Centigrade per minute in order to get a better comparison between the re-

sults of the different runs. The rate of temperature increase prior to the temperature at which naphthacene melts ( $357^{\circ}\text{C}$ ) was found to be not critical since there does not appear to be any significant amount of reaction prior to that temperature.

After melting had occurred, the gas was sampled every five minutes until propane began to be evolved. It was then necessary to wait six minutes in order to allow the pen to get back to the baseline before injecting a new sample.

At the time of sample injection, a record was made of pumping rate. For the compounds which were used for this study, this was necessary because at the time during the run during which large quantities of condensate were coming off, ( $420\text{-}500^{\circ}\text{C}$ ) enough condensate would collect in the tubing leading to the chromatograph to cause a great increase in resistance to flow. Since the calibration curve which gives gas evolution rate from the chromatograph peak height is based on a constant flow rate of  $65\text{ cc/min}$ , any significant deviation from this flow rate must be corrected for.

The complete runs were terminated after the temperature of the reactor had remained constant at  $625^{\circ}\text{C}$  to  $635^{\circ}\text{C}$  for 15 minutes. The interrupted runs were terminated either after 15 minutes at some designated temperature if weight loss had not yet begun, or when the reactor had reached approximately constant weight.

After the runs had been completed, the final weight of the reactor was recorded and the carbonaceous residue was scraped out. This residue was extracted for 24 hours in a Soxhlet Extraction Apparatus to measure the amount of benzene-soluble material present in the residue.

The condensate was first separated manually into two fractions: unreacted naphthacene and other condensate. It was necessary to make this separation before chromatography because the chromatograph column used would not resolve naphthacene and some of the other compounds present in the condensate. This separation could be made with little difficulty, provided that enough condensate was present, since an interface forms in the condenser between naphthacene, which is red, and one of the other compounds, which forms yellow crystals. The fraction from which the naphthacene had been removed was then analyzed in the chromatograph.

Additional work was done on the condensate from some of the runs in order to identify some of the products.

The most important thing that was done was manual preparative chromatography, which allowed condensate samples to be separated into fractions containing some of the compounds making up the condensate in high purity. Some of these were sent to Huffman Laboratories for analysis of molecular weight and carbon and hydrogen content. Infrared and ultraviolet spectra and melting point were taken with equipment available on this campus. The infrared spectra that were obtained

were run in approximately 1% concentration in KBr micropellets in a Beckman IR-4 Infrared Spectrophotometer. The ultraviolet spectra were run in an approximately saturated solution in ethanol in a Beckman DK-2 Spectrophotometer.

## Results and Discussion

A total of 13 pyrolysis runs were made on naphthacene. Eleven of these were terminated at 625-630°C. The last two runs were made to intermediate temperatures in order to obtain information about when different reactions were occurring. For the complete runs (termination temperature 625-630°C), the supplier of the naphthacene was K & K Chemical Company. The supplier for the interrupted runs (those terminated at intermediate temperatures) was the Distillation Products Division of the Eastman Kodak Company. It was not possible to use the same supplier for all of the runs because K & K ran out of naphthacene shortly before the time that the naphthacene required for the interrupted runs was ordered. Only the last four of the complete runs will be discussed here since information obtained in these last four runs indicated that the results of the first six runs was not truly representative of the reaction of naphthacene at the measured temperatures of reaction.

The main problem which had to be solved in order to get data representing a true picture of the reactions occurring at the indicated temperatures was getting the high molecular weight vaporizable compounds produced by the pyrolysis into the condenser region without condensing prematurely or undergoing further reaction. When the equipment was set up as shown in Figure 1, the temperature of the gases entering the condenser region was only 140°C, well below the melting points of all but one of the compounds which were isolated during this study. This resulted in the condensation of the solid products as soon

as they left the hot reaction zone. The products would then collect on top of the reactor, on the walls of the passageway leading to the condenser, and on the outside of the thermowell. Eventually enough of them would collect to foul the balance and no meaningful weight loss data could be obtained. This problem was first solved by putting an additional resistance heater around the cap, as shown in Figure 2. With this heater it was possible to raise the gas temperature to  $318^{\circ}\text{C}$ , which was sufficient to get all of the solid products at least as far as the nipple leading away from the cap. Unfortunately, the surface temperature of the cap necessary to produce this gas temperature introduced some materials problems. This temperature was high enough to produce scale on the surface which was difficult to keep from dropping into the product when cleaning the apparatus at the end of the run. Evidence was also obtained that the cap was hot enough so that the unreacted naphthacene which distilled off and collected in the nipple continued to react and give off products. The final solution came from the installation of another preheater external to the apparatus. This made it possible to heat the gases entering the condenser to  $270^{\circ}\text{C}$  without making the nipple region hot enough to cause the continuation of pyrolysis there.

The information obtained during the complete runs is shown in Figures 3-6. The same information is presented in tabular form in Tables VII-X. The gas evolution rates which were obtained directly from the chromatograms made during the runs are underlined.

On a qualitative basis, the results obtained during the runs are quite similar. They all show maxima in hydrogen evolution rate at 425-435°C and a smaller maximum toward the end of the run near where the temperature began to level off. The curves for methane show maxima at 470-485°C and one run (Ex-NA-7) shows another maximum at 518°C. (Note that the value of moles of gas/min. gm of sample at the first maximum for this run was considerably lower than that for the other runs. All of the runs show maxima in ethane evolution rates at 460-485°C. In addition to the results shown on these graphs, there is a maximum evolution rate for propane at 460-475°C (although Ex-NA-8 showed its propane maximum at 485°C) and for ethylene at 450-460°C. There was also good agreement between the runs in the temperatures at which a weight loss first appeared. Weight loss in all runs except Ex-NA-11 began at 403-404°C. It began at 407°C in Ex-NA-11. This could easily be due to the lower sample size in this run since the balance has a finite sensitivity and the lower sample size could result in a longer lag until the balance was able to detect a change in weight. It should be mentioned here that in all of the runs, some material had appeared in the glass filter located just ahead of the chromatograph at least ten degrees before the balance first showed a loss. After the runs, the residue was put into a Soxhlet extraction apparatus using benzene for solvent for 24 hours. None of the runs taken to completion showed a significant quantity of benzene-soluble material present in the carbonaceous residue.

In addition to the gases mentioned above, a small amount of propylene was observed. Propane, propylene, and ethylene were not analyzed quantitatively since they were present in much smaller amounts than the others. A chromatogram which is typical of those taken during the portion of the run when all of the gases by propylene are present (when propylene is present it appears as a shoulder on the propane peak) is shown in Figure 7. Peak 1 is at an attenuation of 100 x.

Hydrogen, methane, and ethane were identified by means of comparison of retention time with that resulting from injection of a sample containing these compounds in approximately the same composition as that resulting from reaction. Propane and propylene were identified by comparison of retention time with that of pure samples. The difference in retention time between propane and propylene was used to identify ethylene by analogy by comparing the retention time observed for the peak suspected to be ethylene with that for ethane. Peak 1 was found to be hydrogen, peak 2 was methane, peak 3 was ethylene, peak 4 was ethane, peak 5 was propane. These same gases are reported in the literature as products when naphthacene is pyrolyzed at 475°C in a sealed glass ampoule (6). This same reference listed CO and CO<sub>2</sub> as products and there are unidentified peaks between peaks 2 and 3. Water was also given off and was removed from the stream ahead of the chromatograph because it has the same retention time in the column used as does propane.



A chromatogram similar to that which results from chromatography of the condensate after the unreacted naphthacene is removed is shown in Figure 8. The actual resolution which results is much better than that indicated. The only purpose of this figure is to indicate the peaks that result. The order of retention times is read from left to right. The first peak is solvent, the second is an unidentified light compound and the peaks labeled I, II, III, and IV are the ones which were used to obtain quantitative results.

Some of the compounds represented by these peaks were isolated for further study. Compound I appears in the condensate far enough separated from the other components that it was readily available in sufficiently high purity for further analytical work. The sample of it that was obtained showed only one peak in the 1/8-inch column which was used for condensate analysis. Peak II was isolated by means of preparative chromatography. Peaks III and IV were obtained in the same fraction by preparative chromatography and were then separated by hand since the 1/4-inch column used for the preparative work was not capable of resolving these two compounds.

Figure 2 shows the regions in which unreacted naphthacene, compound I, and compound II collect when passing through the condenser. Compounds III and IV collect primarily in the tubing leading from the condenser to the chromatograph and in the glass wool filter at the end of this tubing.

The problem of identification of these compounds proved to be very difficult. The only compound appearing in the condensate which was positively identified besides unreacted naphthacene was 5,12-dihydronaphthacene. The structure of this compound is shown in Table XII. It is reported in the literature as one of the pyrolysis products of naphthacene (5).

A considerable amount of information was obtained to aid in the characterization of compound I. It has a melting point of 145-150°C. The molecular weight measured by Huffman Laboratories by the Rast method indicated that it has the same number of carbon atoms as naphthacene. The result of the carbon and hydrogen determination which was also done by Huffman Laboratories is: carbon, 92.5%; hydrogen, 7.5%. Calculated values for benzyl naphthalene and methyl-benzyl-naphthalene are 6.46 and 6.94% H. The ultraviolet and infrared spectra of this compound are presented in Figures 10 and 11. The infrared appears to be similar to that of a disubstituted naphthalene. It is also quite similar to that for 2-benzyl-naphthalene. The structure of 2-benzyl-naphthalene is shown in Table I. The ultraviolet spectrum also appears to be similar to that of 2-benzyl-naphthalene and calculation of extinction coefficient for this compound indicate two or more fused rings. An attempt was made to run a NMR spectrum of this compound but not enough material was available to get a good spectrum.

Compound II was positively identified as 5,12-dihydronaphthacene. The melting point of compound II was measured in our labora-

tory as 205-210°C. The melting point reported in the literature for 5,12-dihydronaphthacene is 206°C. Huffman Laboratories ran a carbon and a hydrogen determination on compound II and reported 93.55% carbon and 6.22% hydrogen. The calculated value for dihydronaphthacene is 6.08% hydrogen. The molecular weight by the Rast method also agrees with that expected for dihydronaphthacene. The most conclusive evidence, however, comes from infrared spectroscopy. The spectrum for compound II shown in Figure 9 is identical to that reported in the literature for 5,12-dihydronaphthacene (8).

The part of the condensate identified as unreacted naphthacene is identical in appearance, retention time on the chromatograph, and infrared spectrum to that for the starting material.

Some information was obtained about the natures of compounds III and IV. Both compounds appear to have approximately the same molecular weight as naphthacene. Compound III is yellow and sublimes at 241-242°C without leaving a residue. Its infrared and ultraviolet spectra are shown in Figures 12 and 14. The curve marked "C" in Figure 14 is that for compound III. Compound IV is red and sublimes at 260-270°C, leaving a carbonaceous residue. Its infrared and ultraviolet spectra are shown in Figures 13 and 14. The curve marked "B" in Figure 14 is that for compound IV. The column used will not resolve either of these compounds from naphthacene. According to Huffman Laboratories, both of these compounds appear to be esters.

The method of calculation of the stoichiometric coefficients for the gaseous products was mentioned in the previous section. The points which went into the program for integration of gas evolution rate data in order to get the total amount of the gas which had been given off during the run came from smoothed data obtained from the various runs. The results from the different runs were compared in order to determine which points were to be thrown out. From this smoothed data, gas evolution rates, temperature, and amount of weight loss since the beginning of the run was obtained at intervals of one minute. In order to integrate the gas evolution curves it was assumed that the curves were linear over the one-minute intervals.

The method which was used to obtain the stoichiometric coefficients for the solid products is probably not the best method to use, but it was the only one which was capable at all of giving any idea of what the composition of the reaction products was. The first major weakness of the method is that it depends on the manual separation between the 5,12-dihydronaphthacene and the unreacted naphthacene. The reason that it was necessary to make this separation manually is that naphthacene is so much less soluble than the other components of the condensate in the  $CS_2$  used as solvent for the work done with the flame detector, that if the solution contained a representative amount of naphthacene, it would be so dilute in the other components that they would not show up at all due to the tailing of the peaks which becomes very pronounced if the amount of a component in the sample falls below

a certain value. The result of a poor separation between unreacted naphthacene and 5,12-dihydronaphthacene may be seen in Table XI. The sample size in Ex-NA-11 was approximately 25% less than in the other runs which resulted in the amount of condensate being much less. When there was less condensate, it was more difficult to make the separation accurately and evidently some of the 5,12-dihydronaphthacene was included with the unreacted naphthacene, resulting in a calculated conversion to 5,12-dihydronaphthacene that was much lower than that found for other runs. This run was not included in the average values used for the stoichiometric coefficients.

Even if it can be assumed that the manual separation was exact, there is still some weakness in the calculation method itself. Since for a flame ionization detector, peak area is proportional to carbon number and the products found in the condensate have approximately the same molecular weight and contain over 90% carbon, it was assumed that area fraction was proportional to weight fraction. In order to check this assumption, a known amount of 9,10-dimethylantracene was added to a sample of one of the condensates and run through the chromatograph. The sample was 4.44 weight percent dimethylantracene and two samples run through the chromatograph showed 3.54% and 4.06% dimethylantracene by area. This agreement is as close as the certainty with which the weight of the dimethylantracene was known, since the sample only contained 0.2 milligrams of dimethylantracene.

The chief problem with using the chromatograph to do quantitative analysis of this type of compound is that they appear to be adsorbed quite strongly which results in peak broadening and decreased resolution. A silanized support was used to try to reduce this effect, but it was still quite pronounced. If the samples were diluted enough some of the peaks would be broadened enough so that they didn't show at all.

A great deal of the time which was spent on this project was spent in trying to find a gas chromatograph column which would be useful for separating polynuclear aromatic hydrocarbons. The first column that was tried was a fifteen-foot, 1/8-inch diameter column packed with 20% LiCl on Chromosorb W. This column was recommended in the literature (9). For the pyrolysis products of naphthacene, however, it did not work very well. The main problem was that unless it was operated at quite high temperatures, it would adsorb all of the sample, especially naphthacene. When it was operated at sufficiently high temperatures (greater than 300°C), resolution was not very good, retention time was still quite high for naphthacene, and the high temperature was very hard on equipment. The column that was finally used was 5% SE-30 on 50/60 mesh Anakrom ABS. This column could be operated at lower temperatures at lower carrier gas flow rates and still allow all of the sample to come out in thirty minutes. The actual operating conditions that were used were a column temperature of 242°C, injector temperature of 330°C and a nitrogen flow rate of 25 cc/min. The same support and

operating conditions were used in a 1/4-inch column for preparative chromatography. It was also found that the detector temperature could be as low as 200°C without causing flooding of the detector.

The 1/8-inch column used for condensate analysis gave good resolution for all of the products in the condensate except between compounds III, IV, and naphthacene. The 25-foot column did not do any better at this job than did the 15-foot column which was originally tried. The most interesting thing that was discovered while working on the chromatography of the condensate is that if naphthacene is added to the condensate in large quantities, compounds II, III, and IV form one peak. The retention time of compound II is increased and that of III and IV is decreased. It appears that naphthacene may interact strongly with these compounds.

By means of the analytical methods which have been discussed, the stoichiometric equation shown in Table XII was calculated for the overall reactions of naphthacene to 625°C.

The stoichiometric coefficients shown in this equation were obtained by taking the arithmetic mean of the results of Runs 7-10. The value from Ex-NA-10 was not included in the calculation of the coefficient for ethane. The results from Ex-NA-11 were not included because the separation between unreacted naphthacene and 5,12-dihydronaphthacene was not made correctly and because the smaller sample size used for this run appeared to cause some of the differences.

Examination of Table XI and Figures 3-6 shows that there are some significant differences in the quantitative information obtained from the various runs. Before these are discussed, it should be pointed out that the minor differences between the runs in the location of the maxima in gas evolution rates is probably due to variation in heating rate, since this was controlled manually. The same reason would also explain the differences in value of evolution rate at the maximum except for the very large difference in the value of the hydrogen first maximum in Ex-NA-8 as compared to the values of this maximum rate in the other runs. A few possible reasons for this will be mentioned later. For reasons mentioned earlier in this paper, the results from Ex-NA-11 will not be counted. After the stoichiometric coefficients from Run 11 are discounted, there is pretty good agreement between the other runs in the methane coefficients. Comparison of the ethane curve from Ex-NA-10 with that of the other runs shows that its shape is different from that appearing for the others. This difference in shape could be corrected by throwing out the ethane evolution rate at 92 minutes for that run. This would result in an ethane coefficient more in line with that for other runs.

There is a possible explanation for the large hydrogen coefficient for Ex-NA-8 and for the unusually large value for the evolution rate at the maximum. Table XI shows that for this run, more of the naphthacene ended up in the condensate as unreacted naphthacene than in the other runs. The remainder of the condensate was less than



in the other runs. Since the analysis of the condensate indicates that the conversion of naphthacene to these compounds requires hydrogen, it appears that these results are related. A possible explanation might come from the free radical nature of the reactions which occur during pyrolysis. The production of hydrogenated compounds depends on the attack of hydrogen radicals on naphthacene or on some other compound present in the reaction mixture. It might have been possible for something to have been present during this run to cut down on the reactivity of the other compounds to hydrogenation by addition of a hydrogen radical. This would make abstraction of hydrogen from compounds present in the mixture by the hydrogen radicals more likely. Since this would result in more aromatic radicals, a larger conversion to carbonaceous material might be expected. The amount of carbonaceous matter present in the reactor at the end of Ex-NA-8 was greater than in the other runs. There is no real evidence, however, that this is what happened. The preceding discussion is only a possible explanation for what occurred.

Two interrupted runs were made in order to help determine when the compounds present in the condensate were produced. Ex-NA-12 was terminated at 405°C, shortly after the weight loss started. Ex-NA-13 was terminated at 450°C, shortly before the end of the weight loss. The residue from each of these runs was put into a Soxhlet extraction apparatus. The residue from the first run, which amounted to 89.5% of the original sample, contained 68% benzene-soluble material and required only 24 hours for the benzene around the thimble to become clear.

The residue from Ex-NA-12 appeared to contain carbonaceous material, unreacted naphthacene, and a yellow crystalline substance. Chromatography of the residue extract showed the presence of all four peaks labeled in Figure 8. The relative peak areas were similar to those resulting from chromatography of the complete runs except that peak IV was relatively smaller than it appeared in the chromatograms of the complete run condensates. The condensate appeared to contain unreacted naphthacene and a yellow powdery material.

Chromatography of the condensate showed some unidentified light compounds which only appeared because the sample used was much more concentrated than that used for chromatography of the complete run condensates and a large percentage of compound III. No 5,12-dihydro-naphthacene appeared to be present.

The residue from Ex-NA-13 was mostly carbonaceous material and contained some unreacted naphthacene. Chromatography of the extract showed the presence of the same compounds as in the previous run. The fraction of compound II appeared to be less in this run than in the previous and peak IV was more pronounced. The condensate from this run looked the same as that from the complete runs. Chromatography of the condensate showed the presence of some compound I, a small amount of compound II, and the remainder was compounds III and IV. There was more compound I present than compound II.

The data obtained in this work agree well with information available in the literature. The boiling point of dihydronaphthacene by

DTA is given as 420°C (5). The same reference shows that naphthacene has a weak exothermic reaction at 480°C which is close to the temperatures at which the evolution rates of methane and ethane had maxima. Dihydronaphthacene did not show up in the 405°C condensate but was present in the 450°C condensate.

From the data obtained from the interrupted runs, the following information about the course of the production of the solid materials present in the condensate may be concluded:

1. All of the compounds which appear in the condensate during the complete runs are first formed at some temperature below 400°C. This evidence indicates that production of these compounds is continuing in the temperature range of 400-450°C. Most of the production of compound IV occurs above 405°C.
2. Compounds I-IV still make up a significant part of the residue at 450°C, although most of the compound I has distilled off by this time.

These results indicate that since one of the major components of the residue that has not already reacted to form carbonaceous matter at 450°C is dihydronaphthacene, it might be possible for some of the non-condensable gases which begin to appear in the temperature range between the two interrupted runs to be formed by cracking of dihydronaphthacene (or of any of the other compounds found in the condensate).

The presence of such a large quantity of oxygenated compounds in the products resulting from the pyrolysis of a hydrocarbon in an inert atmosphere is quite puzzling. This has also occurred in pyrolysis studies appearing in the literature. For example, the gaseous products

of the pyrolysis of naphthacene in a sealed glass ampoule contain 1.5% CO and CO<sub>2</sub> (6). The presence of some oxygenated product is not too surprising since no method is provided for purging the reactor itself at the beginning of the run and polynuclear aromatic hydrocarbons form quinones quite readily. These quinones could undergo further reaction at high temperatures to form other oxygenated materials.

## Conclusions

The purpose of this work was to study the reactions occurring during the pyrolysis of naphthacene in order to help obtain a better understanding of how compounds which form a well-ordered graphite react.

Qualitatively, the results obtained from the four complete runs under discussion here agree with each other quite well. It is probable that the first peak in the hydrogen evolution curve is the result of the beginning of a period of rapid removal of hydrogen by reaction to form hydrogenated products. At the end of the runs, the evolution rate of the hydrogen was increasing as cyclodehydrogenation reactions forming graphite-like molecules probably was occurring in the residue. The methane, ethane, ethylene, propane, and propylene which were given off were products of cracking reactions of hydrogenated products formed earlier in the run.

The weight loss curves appear to be caused simply by distillation of products formed earlier in the run and do not reflect what is happening in the reactor at the time during which the loss is taking place.

Table I shows that there was considerable variation in the stoichiometric coefficients obtained from the different runs, so the averages presented elsewhere in this paper should not be regarded as exact values.

There is much room for future work to be done on this compound. Since the weight loss curves provide little information as to the rate at which reactions are occurring, more interrupted runs should be made. At least one run should be made to a temperature below 357°C, the melting point of naphthacene, in order to see whether reactions forming new products occur in the solid phase.

Some hydrogen evolution is evident at these lower temperatures but it could be due to small amounts of residue from previous runs which were not completely cleaned out. It would also be desirable to make a series of interrupted runs with K & K naphthacene and obtain stoichiometric coefficients for a number of intermediate temperatures. More runs should also be made to completion in order to obtain more valid values for the stoichiometric coefficients.

In order to get more information about the oxygenated compounds which were produced, some runs should be made in which a nitrogen purge is provided directly to the interior of the reactor prior to making the run. This would help to show the source of the oxygen.

Appendix































































































































