



A study of the thermal decomposition of 1, 8-dinaphthylenethiophene
by William Thomas War

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 reaction of 1,8-dinaphthylenethiophene heated at an average rate of 3.69°C per minute up to 600°C was studied using a thermogravimetric analysis unit. This unit was capable of indicating temperature, weight loss, and amounts of gaseous products produced as a function of time. The study showed that hydrogen, methane, ethane, hydrogen sulfide, and traces of ethene were liberated during the reaction. Also, naphthalene, acenaphthylene, and acenaphthene were identified as products of reaction. The structures of other condensable products were discussed but not identified.

Interrupted reactions were performed, and the percent sulfur in the residues reported. The amount of sulfur in the final residue was 1.42%. Twenty-eight percent of the sulfur lost was attributable to hydrogen sulfide; the remainder to thiophene-based aromatic compounds.

From the chromatographic analysis of the condensable material, rates of gas liberation, weight and temperature traces, and material balances, a possible reaction path was proposed.

A STUDY OF THE THERMAL DECOMPOSITION OF

1,8-DINAPHTHYLENETHIOPHENE

by

WILLIAM THOMAS WAR

A thesis submitted to the Graduate Faculty in partial

fulfillment of the requirements for the degree

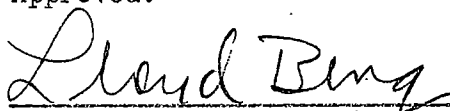
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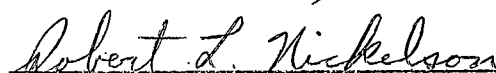
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VITA

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ABSTRACT

The pyrolysis reaction of 1,8-dinaphthylenethiophene heated at an average rate of 3.69°C per minute up to 600°C was studied using a thermogravimetric analysis unit. This unit was capable of indicating temperature, weight loss, and amounts of gaseous products produced as a function of time. The study showed that hydrogen, methane, ethane, hydrogen sulfide, and traces of ethene were liberated during the reaction. Also, naphthalene, acenaphthylene, and acenaphthene were identified as products of reaction. The structures of other condensable products were discussed but not identified.

Interrupted reactions were performed, and the percent sulfur in the residues reported. The amount of sulfur in the final residue was 1.42%. Twenty-eight percent of the sulfur lost was attributable to hydrogen sulfide; the remainder to thiophene-based aromatic compounds.

From the chromatographic analysis of the condensable material, rates of gas liberation, weight and temperature traces, and material balances, a possible reaction path was proposed.

INTRODUCTION

The element sulfur appears in the starting material of many fuels and, as a result, often in the fuels themselves. This sulfur leads to problems of pollution, corrosion, and contamination.

Sulfur, as it occurs in coal as various forms, has been studied quite extensively in the past (2, 9, 10, 20, 21). These studies show that the sulfur in coal occurs mostly in organic form with the remainder being inorganic, pyrites or free sulfur. Because gases containing sulfur are liberated during combustion of this coal, the sulfur becomes an undesirable constituent.

Sulfur is also a problem in petroleum coke. Some background may help explain why this problem has occurred. The residual oils in a refinery consist of the heavy ends of the distillation processes. Previously this residual oil was used as fuel for oil burning steam locomotives and steamships. With consumers such as these, restrictions were very lenient on the sulfur content of the residual oils. However, with the trend toward diesel engines, inland refiners found it uneconomical to ship their residual oil to seaport consuming points for use as steamship fuel. Thus, refiners found they needed a new outlet for their residual stock.

In 1955, Humble Oil and Refining Company started up their fluid coker in Billings, Montana (6). This coker was designed to convert 3,900 bpd of residual feed into gasoline, heating oil, and coke, using a purely thermal process.

At the present time, Humble has a large stockpile of petroleum coke at their Billings refinery. The primary reason for the stockpile is that the petroleum crude refined at Billings has a high sulfur content. Thus, the coke produced contains approximately 6% sulfur (23). Also, the coke contains very little volatile matter. As a result of the high sulfur content, the coke is not suitable for producing electrodes for aluminum production, it can not be used in the coking furnaces of steel mills, and it can not be used as a source of carbon in phosphorous production. Finally, because of its low content of volatile matter, it makes a poor fuel.

Previous work has shown (5) that the sulfur can be removed from this petroleum coke by heating in the presence of air to approximately 3,000°F, thus essentially burning off the sulfur. This method, however, is not economically feasible because of the excessive heat required.

Justification of Research Topic

Throughout the course of the refining process many aromatic compounds are formed. Some of these aromatics will form polynuclear molecules during the heating processes. Many of the heavier aromatic and polynuclear compounds terminate in the bottoms, and become part of the residual oil. Thus, it is reasonable to assume that much of the sulfur present in petroleum coke is combined in some manner as organic sulfur in heterocyclic or polynuclear form.

These facts prompted a preliminary study of several heterocyclic and polynuclear sulfur containing compounds. These compounds were chosen on the basis of molecular structure, boiling point, and commercial availability. The molecular structure should be representative of the type of compound that may be found in coker feed stock. Also, the compound must decompose before its boiling point is reached; otherwise, no carbonaceous product results. Finally, it was not desired to synthesize the compound and thus commercial availability was a necessary condition.

Research Objectives

The primary objective in this research project is to trace the sulfur throughout the course of the carbonization reaction of a material typical of the type of sulfur compound found in coker feed stock. In doing this, products of reaction both condensable and non-condensable will be identified. Finally, possible reaction paths will be suggested and supported by experimental data.

It is felt that this general knowledge in the field of pyrolysis of sulfur-bearing heterocyclic compounds will lead the way to further study in this area and may possibly suggest methods for modifying the coking process so that the coke resulting has a lower sulfur content than the coke now being produced. Also, it will produce general knowledge in the area of reactions of organic sulfur taking place in coal during carbonization.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Equipment previously constructed (8) at Montana State University was used for the pyrolysis study of 1,8-Dinaphthylene-thiophene. This equipment generally consists of a thermogravimetric analysis unit (TGA), differential thermal analysis unit (DTA) capable of detecting major exotherms and endotherms, a gas chromatograph, and miscellaneous support apparatus. Figure 1 shows the modifications made to a Leeds and Northrup temperature recorder mechanism at Montana State University (8) to make an automatic recording balance useful for the pyrolysis studies. The balancing chain responds to a weight change of one gram by moving the recording pen approximately nine inches. The unit has been calibrated to obtain an exact conversion factor and the balance is sensitive to weight changes of less than .01 gram. Also, tests were made and previous work shows (8) that altering temperature and sweep gas flow rate over the range of interest has essentially no effect on the accuracy of the balance.

The reaction chamber is suspended from one arm of the automatic recording balance. Figure 2 shows the reaction chamber. Also shown is the oven used to heat the chamber from ambient temperature to 600°C, the inert gas preheater, and the condenser.

With this design, all volatile compounds are driven from the reactor without destroying the automatic balancing capability of the mechanism. As volatile products are formed in the reaction, they are pulled through the water-cooled condenser by maintaining a constant

suction rate on the line leading from the condenser. The condensable products are trapped here, while the non-condensable vapor is pulled through the system to the on-stream chromatograph.

Since this is a pyrolysis study, it is necessary to blanket the reaction area with an inert gas throughout the course of each pyrolysis reaction. Nitrogen is used as this inert gas because of its inexpensive availability and because nitrogen serves as the carrier gas for the chromatograph column.

The heating oven surrounding the reactor is adjustable in all three axes. Thus, it can be aligned to allow the reactor to be suspended completely free, assuring accurate weight traces during the reaction course.

As is pointed out (8), the reactor itself is specially designed to meet certain requirements. The vessel is made of stainless steel and designed to minimize its weight. The top of the vessel can be unscrewed for sample insertion and removal of carbonaceous residue. A thermocouple well extends through the reactor head, and is positioned one-fourth inch from the bottom of the reactor. By using a strip chart recorder in conjunction with this thermocouple, a continuous temperature profile can be generated.

The above mechanism is housed in a metal cabinet as shown in Figure 1. Besides the condenser being water-cooled, the plate directly above the oven and below the balancing pans is also water-

cooled. This eliminates the circulation of warm gas and consequent instability of the balancing mechanism.

Gas Chromatograph

It was found in initial experimentation that the gas chromatograph previously used (8) would not suffice for this experimental work. The chromatograph oven was highly unstable to ambient air temperature changes, thus causing considerable base line drift on the recorder. In addition, it contained two chromatograph columns in parallel used to separate hydrogen, methane, and ethane. Because of the necessity for two columns, elaborate piping was necessary which proved troublesome from the standpoint of performance and maintenance. Still further, two samples had to be injected to obtain one representation of the reaction gas (8).

With advanced technology in chromatograph column packing, it became feasible to use one column in the place of two. Therefore, a new on-stream chromatograph was designed and built with the oven and injection apparatus being contained in a separate compartment from the electronic equipment.

The oven (Figure 3) is constructed primarily of wood and transite and is well insulated to protect against temperature fluctuations due to ambient air temperature changes. A thermistor serves as the sensing device to maintain any constant temperature up to 120°C.

The electronic cabinet contains the circuit used to provide constant temperature to the oven, the constant voltage supply, and various attenuation and on-off switches. Plug-in terminals are provided on the panel of this electronic cabinet to allow easy connection of the recorder, detector, thermistor, and power output to the oven.

A solenoid-operated, 2-way sampling valve allows the injection of samples into the chromatograph column. Porapak type Q (100-120 mesh) is used as column packing, and the sensing device is a thermal conductivity detector. The column is constructed of a 6½-foot length of ¼-inch aluminum tubing. Aluminum is used to reduce corrosion by sulfur compounds. Porapak Q will separate hydrogen, methane, ethane, and sulfur-containing gases such as hydrogen sulfide.

The chromatograph yields extremely reproducible gas data, very stable operation, and has reduced maintenance considerably.

Materials

Phenyl disulfide, 2,5-diphenyl-p-dithiin, and S-trithiane were purchased from Eastman Organic Chemicals. These are reagent grade chemicals. Di-p-tolydisulfide and 1,8-dinaphthylenethiophene were purchased from K & K Chemicals. They are listed to be 95-99% pure. The chemicals were used in the condition received.

The calibration gas which was purchased from and analyzed by the Matheson Company contained 5.06% methane, 4.60% hydrogen, 5.67% ethane, and 7.48% hydrogen sulfide. The remaining 77.19% is nitrogen.

Operating Procedures

To explain the operating procedures used for this research, a typical TGA run will be described in detail.

1) In preparation for a run, the reactor is cleaned and weighed. The starting material is then inserted into the reactor and it is re-weighed to determine the amount of starting material. The reactor is then suspended freely from the pan of the balance (Figures 1 and 2), and the thermocouple connected. The pen is adjusted by the addition of weight to the opposite pan so as to allow for adequate chart to record the weight loss during the reaction. Silver Goop is used as a thread lubricant and seal for the top of the reactor. All other thread fittings in the vapor line between the reactor and the chromatograph are sealed with teflon tape. Aluminum foil serves as a gasket between the reactor and the diffusion block (Figure 2). After all the tubing between the reactor and the sampling valve has been secured and the reactor adjusted, the water bottle is filled. This water jug serves as a vacuum source for drawing the reaction gases through the system. Water is pumped at a constant rate of 65 cc/min from the bottle. The chromatograph oven and detector must be at steady state to assure reproducible peak heights and to eliminate base line drift.

2) Once these steps have been taken, the front door of the cabinet is closed and nitrogen blankets the reaction system. Nitrogen is injected into the reactor oven at 65 cc/min to correspond with the

pumping rate of gases from the reaction area. Thus, when volatile material leaves the reactor, it is all pulled through the condenser area. Also, when no volatile material is being evolved, essentially no atmosphere outside the reactor oven is pulled into the condenser.

At this point the reactor temperature and the nitrogen preheater temperature have been allowed to reach steady state with the variacs set at 10 volts, corresponding to 50°C and 30 volts, corresponding to 70°C, respectively. This is considered time zero in the reaction time.

At time zero the reactor oven variac is set to 30 and the nitrogen preheater variac is set at 120 volts, where it remains throughout the course of the reaction. From this point on the reactor oven temperature is increased by increasing the variac setting 2 volts every 5 minutes, corresponding to an average heating rate of 3.7°C/min. Also, every 5 minutes a gas sample is injected into the chromatograph. At the termination of the reaction all the variacs are shut off and the system cools in a nitrogen atmosphere.

3) Once the reaction area is cooled, all auxiliary equipment is shut down. The condensate in the vapor line, filter, and condenser is extracted with carbon disulfide and the carbonaceous residue is drilled from the reactor. These materials are saved for quantitative and qualitative analysis.

Qualitative Analysis

The materials other than carbonaceous residue that are formed in the reaction can be categorized as condensables and non-condensables.

The non-condensable products are detected by gas chromatography. The gaseous compounds produced were positively identified by comparative retention times of known compounds (H_2 , CH_4 , C_2H_6 , H_2S) with the unknowns. The presence of hydrogen sulfide was verified also by odor.

The condensable products were analyzed by infrared spectroscopy, molecular weight determination, carbon and hydrogen content, and melting points. Since these condensable compounds could be obtained only in very small quantities, Huffman Laboratories, Wheatridge, Colorado performed much of the micro-analytical work necessary to determine the nature of these compounds.

For determining melting points above the capability of the Fisher melting point apparatus, a hot plate was constructed with an iron-constantan thermocouple attached. The temperature was recorded with a strip chart recorder. This apparatus provided for melting point accuracy of $\pm 5^\circ C$. Special analytical methods suggested by Sawicki et al (18) for detection of hetero-substituted aromatic derivatives and aromatics were also used.

Problems that accompanied these analyses were primarily ones of product separation and small sample sizes. Manual preparative gas

chromatography was used to separate the products obtained as condensables. The chromatograph contained a thermal conductivity detector with a 15-foot, 1/4-inch aluminum column packed with 5% Se-30 on Anakrom 50/60 ABS, and operated at temperatures from 175 to 250°C. As each product peak appeared, the sample was collected in a 3mm glass tube cooled to 0°C in ice water.

Quantitative Analysis

The amounts of non-condensable gases liberated were determined by using a calibration gas of known concentration. By varying the sample loop size between 1/4, 1, 2, and 4 ml, a calibration curve of moles of gas vs. peak height is obtained for each gas (Figures 4, 5, and 6 and Table I). For future calculation purposes it was desired to obtain an equation to represent the portion of these calibration curves that corresponded with the physical data. For hydrogen, methane, and ethane, the lower part of the curves is all that was used, and therefore a linear fit could be used. For the hydrogen sulfide evolution a curve fit program written by Paul E. Simacek, a graduate student at Montana State University, was used. Several equations of the type $x = y^2$ and $y = ax + b$ were used to fit the entire calibration curve.

During actual experimentation each gas peak height is measured. This value is converted to moles of gas per minute per gram of starting material (Table II). Total moles of each gas liberated during a

reaction is determined by measuring the area under the curve of moles per minute per gram of starting material vs. minutes with a planimeter and multiplying this value by the number of grams of starting material.

Initially the condensables were extracted with carbon disulfide, the solvent evaporated and the residue weighed. Using this method on several runs to complete the material balance, only approximately 90% of the starting weight could be recovered. It was found that during the evaporation process of the carbon disulfide, some of the materials in the condensate were subliming rapidly and making an exact material balance impossible. Thus, the quantity of total condensables liberated is determined by difference in the material balance. The amount of the condensables which is actually starting material is determined by gas chromatographic analysis. Since all condensables except starting material pass through the Se-30 column at a given temperature, a material balance is established by injecting a known amount of condensable products into the column, collecting that fraction which comes out and weighing it. The difference is starting material.

DISCUSSION OF RESULTS

Preliminary Results

On the basis of molecular structure, boiling point, and commercial availability, several compounds were studied. Table III shows the results of this initial study which had the purpose of determining the feasibility and practicality of further study of the molecules.

It is obvious from Table III that S-trithiane essentially boils away before the temperature can get high enough to initiate a pyrolysis reaction. Phenyl disulfide, 2,5-diphenyl-p-dithiin and di-p-toly-disulfide produce some carbonaceous residue, indicating that they are reactive compounds as defined by Union Carbide (11, 12, 13). 1,8-dinaphthylenethiophene proved to be reactive and also yields a high percent of carbonaceous residue.

Mechanism studies have been made on several of the compounds (4) and differential thermal analysis (DTA) has been performed on 1,8-dinaphthylenethiophene by Union Carbide (19). This DTA shows that 1,8-dinaphthylenethiophene undergoes an exothermic reaction or exothermic reactions between 495 and 540°C. Union Carbide also reports 68% carbonization with mostly starting material condensed during the course of the reaction.

As a result of this initial study of sulfur compounds and with DTA data reported by Union Carbide for 1,8-dinaphthylenethiophene, this material was chosen as a compound for study. 1,8-dinaphthylene-

thiophene is believed to be a compound representative of sulfur compounds possibly found in coal and petroleum coke feeder stock and it yields a high percent of carbonaceous residue upon carbonization.

DISCUSSION OF RESULTS OF PYROLYSIS OF 1,8-DINAPHTHYLENETHIOPHENE

In the carbonization or pyrolysis reaction of 1,8-dinaphthylene-thiophene, several separate reaction are believed to occur. From these reactions are liberated compounds, some of which will condense and others which will not condense at cooling water temperatures.

Condensable Products

The condensable products, as was mentioned, were separated and purified using preparative chromatography. Table IV shows the amounts of materials collected using this method.

Table IV. Amounts of Materials Collected from the Condensable Products of Runs 1,8-D VII, -VIII, -IX, and -X.

<u>Material Number</u>	<u>Amount Collected, grams</u>
2	.0030
4	.0044
6	.0020
7	.0022
8	.0102
9	.0021

The materials numbered above represent the materials collected by preparative chromatography. A typical chromatogram is sketched in Figure 7 and the compounds are identified and molecular structure described in Table V.

The small amounts collected can be attributed to several factors. The material handling technique is not without shortcomings. Each time a particular material was detected, the same collection tube was used to gather it. Thus, the hot carrier gas would sublime some of the material already present in the tube and carry it through to the air. Also, since purity was essential, only the top of each peak was collected. The purity of the samples was verified by chromatographic analysis using the more sensitive flame ionization detector. This purity verification step consumed more of the sample.

As was mentioned, this chromatographic analysis shows that nine materials (Figure 7) including the starting material are formed as condensable products of the reaction. Of these, 39.5% is distilled 1,8-dinaphthylenethiophene. The remainder of the condensable products are decomposition products of the starting material (Table V).

Compound Number 2 was positively identified on the basis of infra-red spectroscopic analysis to be naphthalene.

Materials numbered 3 and 5, as can be seen from Figure 8, are present in trace amounts and no attempt was made to collect in pure form or identify these materials.

Material Number 4, however, is one of the major products of the reaction. It consists of at least two separate compounds as can be noted by the shoulder on Number 4 peak (Figure 7). It is a clear white liquid at room temperature. Huffman Laboratories reports this material to have a molecular weight of 165. Its infrared spectra shows $-\text{CH}_2-$ and CH_3- stretching bands, and indicates the presence of C-S groups. With these considerations, and examining the structure of 1,8-dinaphthylenethiophene in relation to probable sulfur-containing products, it is believed (7) that the most likely possibility for material Number 4 is, at least in part, a thiophene-based aromatic compound.

Material Number 6 appears as a clear liquid. The infrared spectra of this compound shows the presence of $-\text{CH}_2$ and $-\text{CH}_3$ groups with C=C and C-H out of plane bending on an aromatic nucleus. Conclusions reached are that this is a naphthalene system with aliphatic substitution.

Material Number 7, another of the major constituents making up the condensate, has a molecular weight of 178. It appears to be one compound on the basis of chromatographic analysis and its infrared spectra shows $-\text{CH}_2-$, CH_3 , aromatic C=C, and C-S, and aromatic C-H out of plane modes. It can again be reasonably assumed, as with material Number 4, that this compound is most likely a thiophene-based aromatic. As will be shown, a mechanism consideration also helps substantiate this assumption.

Material Number 8, which appears to be one compound by chromatographic analysis, has a carbon content of 93.2% and a hydrogen content of 6.3%. Its molecular weight is 156 and it melted at 93°C.

A study of the infrared spectrograph of this material, along with the other data, shows that it is mostly acenaphthylene containing possible traces of acenaphthene. (Satler IR Spec #178).

Material Number 9 is present in very small quantities. It is a heavy oil, appearing to be two compounds. The colors of these oils are light yellow and dark orange.

Non-Condensable Products of Reaction

The non-condensable products of reaction, identified by using retention time, are hydrogen, methane, ethane, hydrogen sulfide, and traces of ethane.

The liberation of hydrogen from the reaction mass begins at approximately 345°C. Hydrogen sulfide, which is first observed at 430°C, is the next gas to appear in abundance. Methane and ethane evolution begins to increase sharply at 510°C. Tables VI through XIII list the evolution rates of these gases throughout the course of interrupted runs 1,8-DQ III, -IV, -V, -VI, -VII, -VIII, and -XII. Also listed in these tables is the percent weight loss of the reaction mass as the reaction proceeds. It can be seen (Figure 8) that the initial weight loss begins around 275°C. As the temperature approaches 400°C, the weight loss curve begins to increase rapidly until a temperature of 580°C is reached. At this temperature the slope of the

curve again decreases, indicating the weight being lost is becoming less significant.

Figures 9 and 10 show the rate of evolution of hydrogen, methane, ethane, and hydrogen sulfide as the reaction proceeds. The hydrogen liberation curve indicates that there are at least three separate reactions occurring below 600°C which result in hydrogen liberation. Hydrogen is liberated at a steadily increasing rate up to the temperature of 430°C. Here, hydrogen evolution rate begins to level off for a short time and then increases until the temperature of 510°C is reached. At 510°C, the rate of hydrogen evolution again tends to level off momentarily and then increases until a maximum rate of hydrogen evolution is reached at approximately 530°C. The hydrogen evolution rate then decreases sharply through 600°C.

The methane and ethane rate, unlike hydrogen, shows only one major period of evolution. At 510°C, methane and ethane evolution begins and the rate increases until 530°C is reached. At 530°C, as with hydrogen, the gas evolution rates decrease through the rest of the reaction.

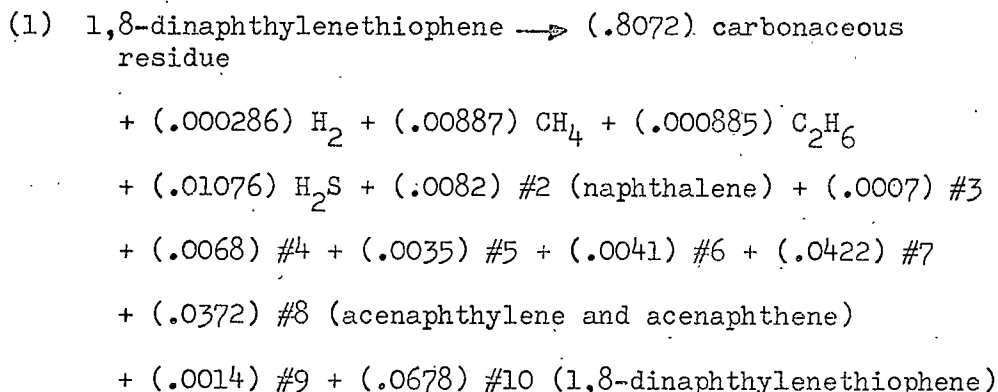
Hydrogen sulfide shows only one major evolution period. At 430°C it appears in substantial quantities and reaches its maximum evolution rate at 480°C, at which temperature it decreases rapidly.

By studying the gas data above, it appears that the following three reactions are occurring. The first liberates only hydrogen as

a non-condensable gas. The second results in hydrogen and hydrogen sulfide, and the third reaction liberates hydrogen, methane, and ethane.

Material Balance

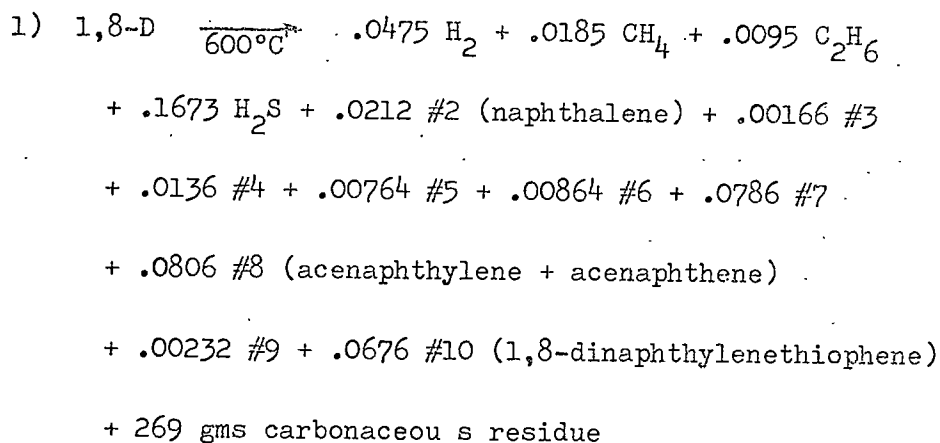
If a material balance is calculated for the pyrolysis reaction up to 600°C, several interesting facts about the reaction can be learned. From one gram of 1,8-dinaphthylenethiophene (Table XIII), .000286 grams of hydrogen, .00887 grams of methane, .000885 grams of ethane, and .01076 grams of hydrogen sulfide, plus .1719 grams of condensable material are produced. As was stated earlier, the amount of condensables is determined by difference. The remaining .8072 grams are carbonaceous residue formed in the reaction. If the condensable products alone are considered, chromatogram areas give a good approximation of the amount of each material present (Table XIV). Knowing this, a complete material balance can be obtained (in grams):



Stoichiometry

From Table XV it can be seen that one mole of 1,8-dinaphthylenethiophene yields .0475 moles hydrogen, .0185 moles of methane, .0095

moles of ethane, and .1673 moles of H_2S when the final reaction temperature is $600^\circ C$. Also, using the material balance and the information on the molecular weight of condensate materials (Table V), the stoichiometry of the reaction can be written as:



The molecular weights of materials numbered 3, 5, 6, 9 are approximated by comparison of their positions on the chromatogram (Figure 7) with the positions of the compounds of known molecular weight. They were estimated to be 130, 150, 155, and 220, respectively.

The Gravimetric Curve

Comparing the weight loss as a function of temperature (Figure 8) with hydrogen evolution as a function of temperature (Figure 9), it appears as though major weight loss periods accompany maximum rates of hydrogen evolution. As the hydrogen evolution rate begins to increase rapidly at $410^\circ C$, so does the percent weight loss. At approximately $435^\circ C$, the rate of hydrogen evolution has leveled

off slightly, along with the rate of weight loss. Another dip in the hydrogen evolution and weight loss curves is apparent at 510°C. At 530°C, where the hydrogen evolution rate reaches its maximum value and drops sharply, the weight loss curve becomes almost horizontal, indicating very little weight loss occurring past 530°C.

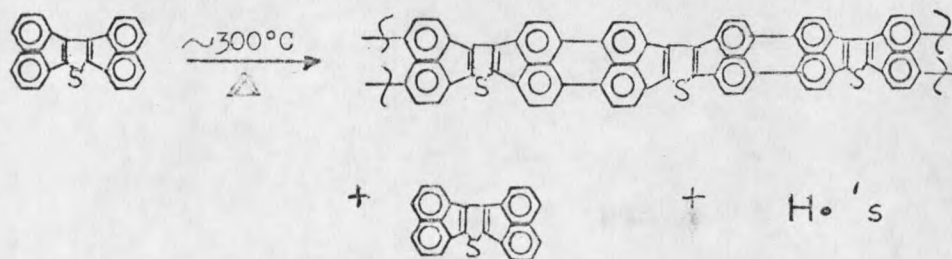
This gravimetric curve also suggests that three reactions are taking place up to 530°C. The initial loss of weight, immediately following the melting point of 260°C, can be attributed to vaporizing 1,8-dinaphthylmethiophene before reaction occurs.

A Possible Reaction Mechanism

From the experimental results of gravimetric analysis, thermal analysis, product identification, and quantitative analysis, a possible reaction path can be postulated.

1) The initial reaction believed to occur consists of the intermolecular hydrogen transfer between reacting molecules (9 11, 12, 13, 15, 22). This would be considered a polymerization step.

1(A)

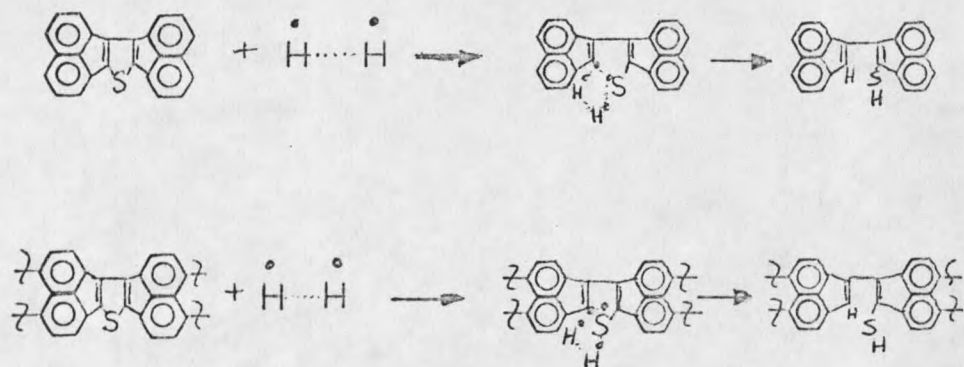


Reactions such as these are believed important in pure thermal uncatalyzed carbonization reactions (13). This type of reaction can occur around 200-350°C (9, 13), and the hydrogen liberated at these temperatures will be reactive with active sites in the reaction mass. Since there are so many more reactive sites than there are hydrogen atoms, the least likely thing to occur would be for the hydrogen to combine to form hydrogen gas (7). Therefore, it can be said that the more likely event would be the combination of hydrogen with reactive sites on the molecule and the liberation of very little hydrogen gas. Thus, this first reaction would not appear as one that would result in significant weight loss or hydrogen evolution.

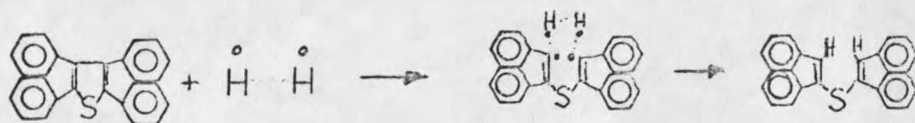
From the data obtained, the reaction temperature may be estimated. Since hydrogen begins to appear at approximately 330°C and the 1,8-dinaphthylenethiophene melts at 260°C, the reaction temperature can be estimated to be around 300°C.

2) Following this polymerization step, at temperatures between 300 and 430°C, hydrogen evolution and slow weight loss are all that is occurring. It can be hypothesized that during this period, hydrogen liberated in reaction 1(A) is attacking the reactive sites of the molecule in the following manner:

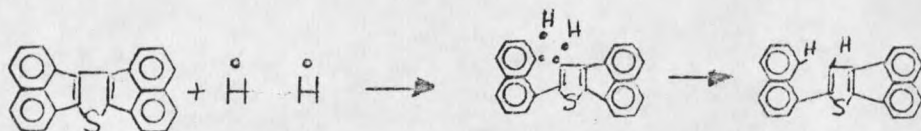
2(A)



2(B)

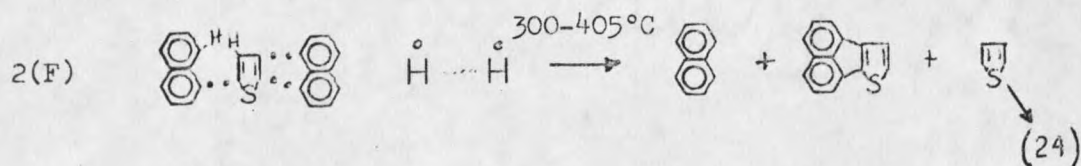
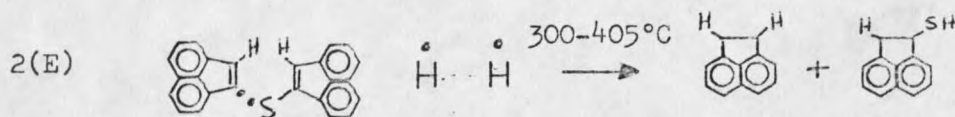
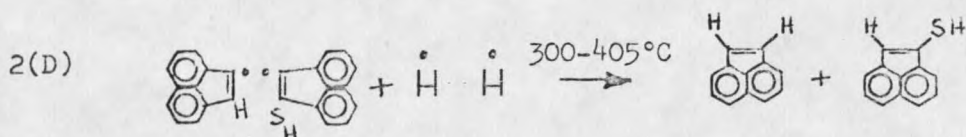


2(C)



Reactions of this type can occur on the polymer chain suggested in Reaction 1(A) or on the 1,8-dinaphthylthiophene molecule itself. It is possible that a depolymerization step exists or, more likely, that all the molecules do not take part in the polymerization step of 1(A).

However, when molecules of this type are formed, they consist of a large bulky group fastened in the middle by one weak bond. This bond is thus highly strained and becomes a very likely site for attack by more hydrogen.



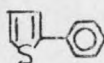
By the time 405°C is reached, materials numbered 2, 4, 5, 6, 7, and 8 (Tables XVI and XVII) are present in the condensable material. These facts suggest that the above sequence must occur between 300 and 405°C. Also, hydrogen is now appearing as a product of reaction, indicating that the polymerization step described in Step 1 is still occurring between these molecules being formed. This fact is further substantiated in Table XVII where it can be seen that the extract

from the residue which was pyrolyzed to 405°C shows the presence of many compounds as heavy as, or heavier, than 1,8-dinaphthylene-thiophene but only traces of the compounds appearing to be formed in reactions 2(D), 2(E), and 2(F).

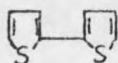
A word can be said here about materials numbered 4 and 7, believed to be thiophene-based compounds. Upon the occurrence of reaction 2(F), thiophene and thiophene-based compounds would be formed. Also, if thiophene itself is pyrolyzed (24), these compounds are formed:



thionaphthene



phenylthiophenes



bithiophenes



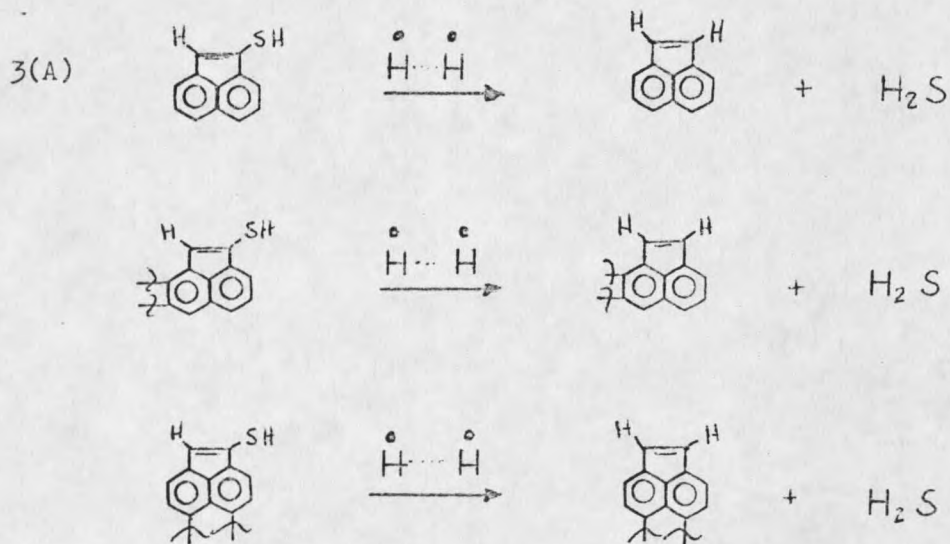
thiophenes



naphthalene

Compounds of this type are believed the probable constituents of Materials 4 and 7.

3) At approximately 430°C, hydrogen sulfide is liberated from the reaction (Figure 10). Also, at this temperature, hydrogen evolution rate starts to level off. It is reasonable to assume that, as the hydrogen sulfide is formed, the necessary moles of hydrogen consumed by the formation of hydrogen sulfide would account for the leveling off in the hydrogen evolution rate.



By the time 405°C is reached, the reaction mass contains 7.01% sulfur. Since the starting material contains 9.63% sulfur, 25.1% of the original sulfur is removed from the reaction mass. Since hydrogen sulfide is not observed until 430°C, all the sulfur thus far removed must be accounted for in the condensate. As can be seen from Table XVI, compounds 4 and 7 account for a large portion of the condensable material.

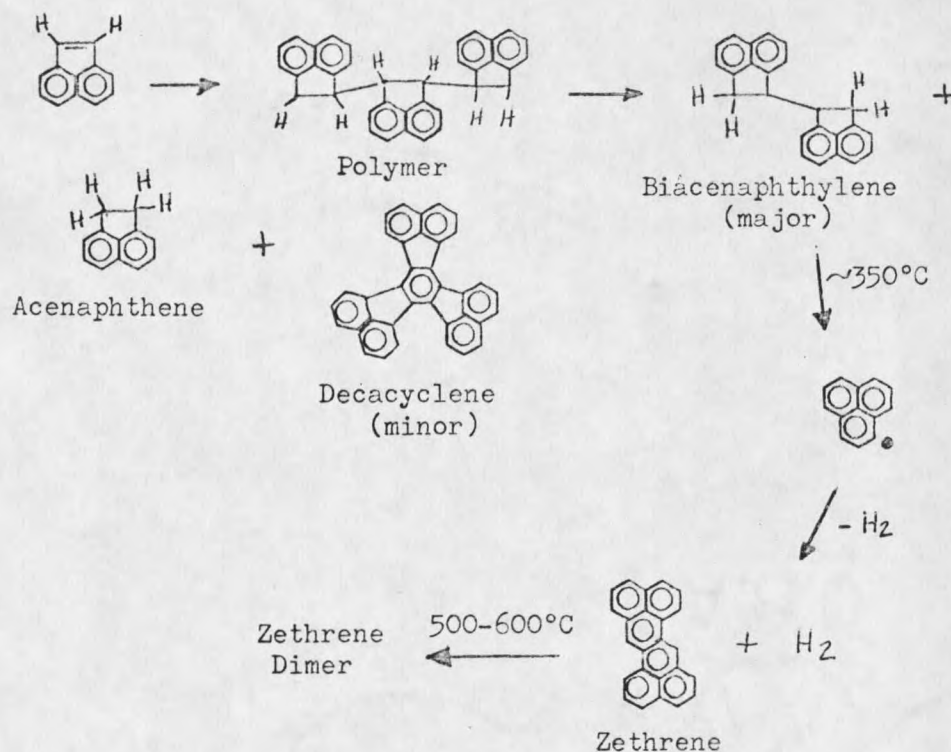
By the end of Step 3, the major portion (79.5%) of the sulfur present in the starting material has been liberated (Table XVIII). However, all of this sulfur does not appear as hydrogen sulfide. In fact, only about .25 moles total of hydrogen sulfide are liberated per mole of starting material by the end of the reaction. Therefore, considering the sulfur that is lost as a basis, only 28% of this can

be accounted for by H_2S evolution. For this reason it is logical to assume that compounds formed in reactions of the type 2(F) account for the greatest portion of the sulfur lost during the pyrolysis reaction.

Once all of the -SH reactive groups have been removed by combination with hydrogen, the hydrogen evolution rate again begins to increase.

4) At approximately 530°C , hydrogen evolution takes a sharp rise. Along with hydrogen, methane, ethane, and traces of ethene are liberated.

In order to pursue the course of the reaction further, it is necessary to look at the compounds already formed by previous steps. Acenaphthylene, the major product in suggested reaction thus far, has been studied extensively under pyrolytic conditions (8, 11, 12, 13, 17, 19). Once acenaphthylene is formed, it will undergo the following reactions:



The total polymerization step of this reaction would not be likely to occur since free radicals are already present by the time acenaphthylene is formed.

If the gas evolution during the pyrolysis of acenaphthylene is studied (8), it can be seen that hydrogen and methane evolution rates reach a maximum at about 530°C, the same temperature as they do in the pyrolysis of 1,8-dinaphthylenethiophene. This fact seems to support the argument that when acenaphthylene is formed, it is indeed pyrolyzed in the reaction.

The carbonaceous residue at the final temperature of 600°C contains 1.42% sulfur. The majority of this sulfur is probably contained in the reaction mass as combined C-S-C groups, as any -SH group would be very susceptible to reaction with hydrogen. During the polymerization step 1(A), thiophene groups remain intact in the large complex system formed. Some of the polymer material will break down during the continuation of the reaction and consequently some of the thiophene sulfurs will be attacked by hydrogen. However, some of these sulfur atoms may become part of a complex molecule and thus make attack by hydrogen almost impossible. The same process is possible with compounds formed in the reactions of the type 2(F).

Tables XIX and XX present a summary of all reactions performed with 1,8-dinaphthylenethiophene. Table XIX shows the results of primary studies, listing sample sizes, final temperature reached, percent carbonaceous residue, and remarks about each particular run. Table XX includes the same listings but the reactions were productive runs liberating quantitative data.

Melting points of the residues from the interrupted runs can be seen in Table XVII. The melting point profile indicates that as the temperature increases, the size and complexity of the molecules is also increasing.

CONCLUSIONS

From this initial study of the carbonization reaction up to 600°C of 1,8-dinaphthylenethiophene, several conclusions can be formed. The reaction liberates hydrogen, methane, ethane, hydrogen sulfide, and traces of ethene as non-condensable products of reaction. The temperatures at which these compounds reach a maximum liberation rate is 530°C for hydrogen, methane, and ethane, and 745°C for hydrogen sulfide. The methane, ethane, and hydrogen sulfide show single evolution peaks but the hydrogen evolution profile indicates several reactions occurring during the heating period. The weight trace follows a similar pattern on the hydrogen evolution curve, indicating that major weight loss periods accompany major hydrogen evolution periods.

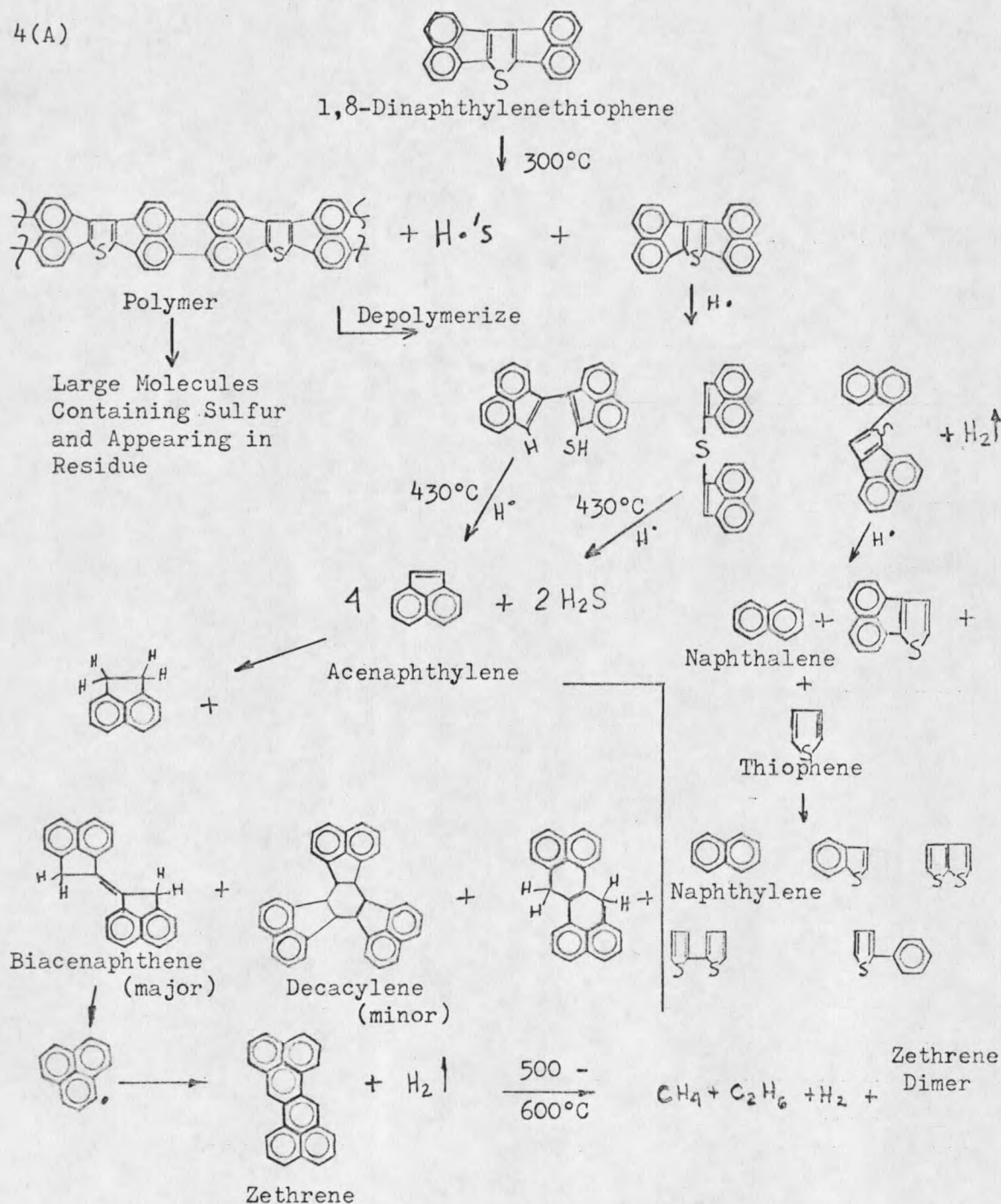
Nine condensable products of reaction are formed. Of these, four are in major proportions. Naphthalene, acenaphthylene, and acenaphthene are positively identified products of the reaction. Thiophene-based aromatics are believed to make up the other major products. The minor condensable products are believed to consist of substituted naphthalene compounds.

The starting material consists of 9.63% sulfur; 25.1% of this original sulfur is lost by evolution of thiophene-based aromatics by the time 405°C is reached. At 505°C, 79.5% of the original sulfur is lost. Between 405°C and 505°C, hydrogen sulfide is liberated. However, only 28% of the sulfur lost can be attributed to H₂S. The

remainder of the sulfur lost is most likely liberated as thiophene-based aromatics. At the final carbonization temperature, the material has lost 19.28% of its original weight and contains only 1.42% sulfur.

The results suggest a possible reaction path (Figure 12). At approximately 300°C, a polymerization step occurs liberating hydrogen-free radicals. These free radicals are free to attack active sites on the molecule or combine to form hydrogen gas. Since, at the initiation of polymerization there are more active sites than hydrogen-free radicals, they will initially attack the active sites in the reaction mass. In doing so, the sigma bonds connecting the naphthalene structure to the thiophene center are broken along with the thiophene C-S bond and the thiophene C-C bond. At this point, hydrogen is liberated indicating continuing polymerization. Once molecules of this type are formed, the hydrogen-free radicals present in the system will immediately shear off any available -SH groups to produce acenaphthylene and hydrogen sulfide. Along with these compounds, thiophene and thiophene-based aromatics are formed. Thiophene itself will be pyrolyzed to thiophene-based polynuclear and heterocyclic compounds. These types of compounds, along with sulfur trapped from the polymerization step, are believed to be the origin of sulfur in the residue. The acenaphthylene formed continued in a known reaction mechanism (8) to form carbonaceous residue.

4(A)



POSSIBLE REACTION MECHANISM

Figure 12. Possible Mechanism for the Pyrolysis of 1,8-Dinaphthylenethiophene.

RECOMMENDATIONS

It was noticed during the course of this research that at temperatures above 600°C, hydrogen sulfide again appeared in the non-condensable products. Also, the percent sulfur in the residue was less for the 625°C residue (1.25) than it was for the 600°C residue (1.42). For this reason, a study of the reaction at higher temperatures would yield interesting results. Modifications in the apparatus would be necessary to accomplish this study.

Also, attempts should be made to alter reaction conditions and thus affect the final amount of sulfur contained in the residue. For example, the temperature might be maintained at the temperature corresponding to that of maximum hydrogen sulfide evolution in an attempt to remove more reactive -SH groups before continued combination of molecules trap these groups. Altering rate of temperature increase should also affect the final amount of sulfur appearing in the residue.

To make the runs more reproducible and less tedious, the apparatus could be put on an automatic basis. To accomplish this it would be necessary to devise a method to increase the reactor temperature linearly with time, to take samples automatically and mark the temperature profile every time a sample was taken.

Finally, attempts should be made to determine the kinetics of the reaction.

APPENDIX

Table I. IBM Computer Program to Calculate Calibration Curve.

```

ZZJOB 5                                BILL WAR 158-67
ZZFORX5
*LIST PRINTER
C    CALIBRATION CURVES FOR MOLES OF GAS VS. PEAK HEIGHT
    DIMENSION VOL(4), GAS(4), PK(4,4,4)
C    GAS 1 = METHANE
    GAS(1) = .0506
C    GAS 2 = HYDROGEN
    GAS(2) = .0460
C    GAS 3 = ETHANE
    GAS(3) = .0567
C    GAS 4 = HYDROGEN SULFIDE
    GAS(4) = .0748
C    GAS 5 = NITROGEN
    GAS(5) = .7719
    VOL(1) = .25
    VOL(2) = 1.00
    VOL(3) = 2.00
    VOL(4) = 4.00
    READ 10, T,P
10  FORMAT (2F7.2)
    TEMP = T + 293.16
C    R = 62396 ((MM. HG.)(CC))/((GM. MOLES)(DEG. K))
    R = 62396.00
20  FORMAT (29H MOLES OF GAS VS. PEAK HEIGHT///)
    PRINT 20
    READ 30, (((PK(J,K,I), J=1,4), K=1,4), I=1,4)
30  FORMAT (10F8.2)
    DO 45 K=1,4
    DO 45 I=1,4
    V = VOL(I)*GAS(K)
    XMOLS = (P*V)/(R*TEMP)
40  FORMAT(16H    GAS NUMBER IS I2//)
41  FORMAT(10H    MOLES= E14.8)
42  FORMAT(18H    PEAK HEIGHT= F8.2)
    PRINT 40,K
    PRINT 41, XMOLS
    DO 44 J=1,4
44  PRINT 42, PK(J,K,I)
    PKA = (PK(1,K,I)+PK(2,K,I)+PK(3,K,I)+PK(4,K,I))/4.
43  FORMAT (26H    AVERAGE PEAK HEIGHT= F7.2)
    PRINT 43, PKA
45  CONTINUE
    CALL EXIT
    END

```

Table II. IBM Computer Program for Data Conversion of 1,8-Dinaphthyl-
enethiophene Reactions, 1,8-DQ III through 1,8-DQ XII

```

ZZJOB 5
ZZFORX5
**BILL WAR 158-67
  1 FORMAT(5F12.4)
    READ 1,PP,CT,CR,SR,W
C   ATMOSPHERIC PRESSURE = PP, CHROMATOGRAPH COLUMN TEMP.
C   1= CT
C   CARRIER GAS FLOW RATE = CR, SWEEP GAS FLOW RATE = SR
C   INITIAL WT. OF 1,8-DINAPHTHYLENETHIOPHENE = W
C   OTIME=T, REACTOR TEMP=TM, SQUARES OF WT. LOSS= SQ, HYD
C   1ROGEN PEAK HEIGHT=H
C   METHANE PEAK HEIGHT= XME, ETHANE PEAK HEIGHT=ETH,
C   HYDROGEN SULFIDE PEAK HEIGHT=HS
C   WT = PER CENT WEIGHT LOSS
C   MOLES/MIN/WT OF STARTING MATERIAL HYDROGEN = B
C   MOLES/MIN/GM OF STARTING MATERIAL METHANE = C
C   MOLES/MIN/GM OF STARTING MATERIAL ETHANE = D
C   MOLES/MIN/GM OF STARTING MATERIAL H2S = E
  2 FORMAT (33H1          ATMOSPHERIC PRESSURE IS,F8.2, 7H
    1 MM.HG.)
  3 FORMAT (38H          CHROMATOGRAPH COLUMN TEMP IS,F8.
    12,10H DEGREES C)
  4 FORMAT (34H          CARRIER GAS FLOW RATE IS,F8.2,12
    1H CC.PER MIN.)
  5 FORMAT (32H          SWEEP GAS FLOW RATE IS,F8.3,12H
    1CC.PER MIN.)
  6 FORMAT (54H          INITIAL WT. OF 1,8-DINAPHTHYLENE
    1THIOPHENE IS,F8.4,6H GRAMS//)
    1F8.4,6H GRAMS//)
    PRINT 2,PP
    PRINT 3,CT
    PRINT 4,CR
    PRINT 5,SR
    PRINT 6,W
  7 FORMAT (59H          RATE
    1 OF GAS EVOLUTION)
  16 FORMAT (59H          MULT
    1IPLIED BY (10**8))
  8 FORMAT(66H          TIME TEMP. WT LOSS      MOLES/(MIN)
    1(GM. STARTING MATERIAL))
  90FORMAT(68H          MIN. DEG.C PERCENT HYDROGEN ME
    1THANE ETHANE HYDROGEN)
    1E HYDROGEN)
  17 FORMAT(67H
    1 SULFIDE//)
    PRINT 7

```

Table II (continued)

```
PRINT 16
PRINT 8
PRINT 9
PRINT 17
10 FORMAT (2F5.0,F7.3,4F8.2,F3.0)
11 READ 10,T,TM,SQ,H,XME,ETH,HS,END
   IF(END) 50,13,13
13 WT = 100. - (((W-(.01105*SQ))*100.)/W)
   HMOL = .08245*H
   B = (10150.*(HMOL/PP))/W
100 XMMOL = .3555*XME
   C = (10150.*(XMMOL/PP))/W
200 ETMOL = .84*ETH
   D = (10150.*(ETMOL/PP))/W
300 X = HS - 4.0
   IF (X) 20,20,21
20 HSMLS = 2.48 * HS
   GO TO 30
21 Y = HS - 8.5
   IF (Y) 22,22,23
220 HSMLS=(-.05274+SQRTE((.05274**2)+(4.*.00011)*(4.06379
   1-HS)))/(-.00022)
   GO TO 30
23 Z = HS - 10.2
   IF (Z) 24,24,26
240 HSMLS=(-.02437+SQRTE((.02437**2)+(4.*.00003)*(6.34049
   1-HS)))/(-.00006)
   GO TO 30
26 HSMLS =9.17*HS + 133.
30 E = (10150.*(HSMLS/PP))/W
25 FORMAT (6X,F5.0,2X,F5.0,2X,F7.2,2X,F7.2,3X,F7.2,3X,F7
   1.2,2X,F8.2)
   PRINT 25,T,TM,WT,B,C,D,E
   GO TO 11
50 CALL EXIT
END
```


Table III. Initial Study of Several Polynuclear and Heterocyclic Sulfur Compounds Using a Thermogravimetric Analysis Unit (TGA).

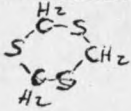
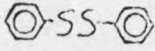
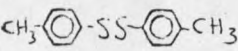
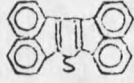
Name	Molecular Formula	Observed Exothermic Regions	Observed Endothermic Regions	% Residue
S-Trithiane		None	215°C 275°C	1.74
Phenyl Disulfide		350°C	60°C 315°C	9.57
2,5-Diphenyl-p-Dithiin		200°C	115°C 415°C	12.3
Di-p-Tolyl Disulfide		None	45°C 315°C	28.1
1,8-Dinaphthyleneethiophene		Slight at 540°C	260°C	81.0

Table V. Qualitative Analysis of Compounds Contained in the Condensable Material Formed in the Pyrolysis of 1,8-Dinaphthylene-thiophene.

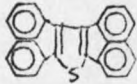
Compound Number	Identification	Description
1	Carbon Disulfide	Solvent
2	 -Naphthalene	Positive Identification
4		Colorless liquid at 25°C, IR Spec shows -SH, -CH ₃ , -CH ₂ , -C-S modes. Appears to be two compounds. MW = 165.
6		A naphthalene system with aliphatic substitution.
7		-CH ₂ -, CH ₃ -, C=C, C-S & C-H (IR spec). Possibly a thiophene-based compound. MW = 178.
8	 Acenaphthene	Positive Identification.
	 Acenaphthylene	Positive Identification.
10	1,8-Dinaphthylene-thiophene 	39.5% of condensables is starting material.
3, 5, 9		These materials appear in very small quantities, and no attempts at identification were made.

Table VI. Results of Reaction 1,8-DQ III.

ATMOSPHERIC PRESSURE IS 623.20 MM.HG.
 CHROMATOGRAPH COLUMN TEMP IS 119.00 DEGREES C
 CARRIER GAS FLOW RATE IS 65.00 CC.PER MIN.
 SWEEP GAS FLOW RATE IS 65.000 CC.PER MIN.
 INITIAL WT. OF 1,8-DINAPHTHYLENETHIOPHENE IS .6990 GRAMS

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	RATE OF GAS EVOLUTION MULTIPLIED BY (10**8)			
			MOLES/(MIN)(GM. STARTING MATERIAL)			
			HYDROGEN	METHANE	ETHANE	HYDROGEN SULFIDE
.	50.	0.00	0.00	0.00	0.00	0.00
5.	56.	0.00	0.00	0.00	0.00	0.00
10.	68.	0.00	0.00	0.00	0.00	0.00
15.	76.	0.00	0.00	0.00	0.00	0.00
20.	92.	0.00	0.00	0.00	0.00	0.00
25.	112.	0.00	0.00	0.00	0.00	0.00
30.	131.	0.00	0.00	0.00	0.00	0.00
35.	153.	0.00	0.00	0.00	0.00	0.00
40.	174.	0.00	0.00	0.00	0.00	0.00
45.	197.	0.00	0.00	0.00	0.00	0.00
50.	221.	0.00	0.00	0.00	0.00	0.00
55.	242.	0.00	0.00	0.00	0.00	0.00
60.	260.	0.00	0.00	0.00	0.00	0.00
65.	282.	.31	0.00	0.00	0.00	0.00
70.	312.	.79	0.00	0.00	0.00	0.00
75.	330.	1.26	4.80	0.00	0.00	0.00
80.	348.	1.58	5.76	0.00	0.00	0.00
85.	367.	1.89	10.56	0.00	0.00	28.89
90.	386.	2.05	24.97	0.00	0.00	57.78
95.	406.	2.52	64.35	2.48	0.00	69.34
100.	423.	3.31	109.50	4.14	0.00	69.34
105.	438.	4.58	184.42	8.28	0.00	231.13
110.	457.	7.11	0.00	9.11	0.00	933.39
115.	473.	8.69	234.37	9.93	0.00	4632.84
120.	490.	11.22	249.74	18.22	0.00	933.39
125.	507.	12.64	268.95	57.98	19.57	115.56
130.	523.	14.22	365.01	165.66	62.63	28.89
135.	532.	16.12	403.43	387.65	138.96	0.00
140.	547.	18.65	461.06	670.94	205.50	0.00
145.	562.	18.81	547.51	728.92	176.15	0.00
150.	574.	18.96	499.48	563.26	93.94	0.00
155.	586.	19.28	422.64	430.72	35.23	0.00

Table VII. Results of Reaction 1,8-DQ IV.

ATMOSPHERIC PRESSURE IS 625.20 MM.HG.
 CHROMATOGRAPH COLUMN TEMP IS 119.00 DEGREES C
 CARRIER GAS FLOW RATE IS 65.00 CC.PER MIN.
 SWEEP GAS FLOW RATE IS 65.000 CC.PER MIN.
 INITIAL WT. OF 1,8-DINAPHTHYLENETHIOPHENE IS 1.0025 GRAMS

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	RATE OF GAS EVOLUTION MULTIPLIED BY (10**8)			
			MOLES/(MIN)(GM. STARTING MATERIAL)			
			HYDROGEN	METHANE	ETHANE	HYDROGEN SULFIDE
.	30.	0.00	0.00	0.00	0.00	0.00
5.	35.	0.00	0.00	0.00	0.00	0.00
10.	45.	0.00	0.00	0.00	0.00	0.00
15.	57.	0.00	0.00	0.00	0.00	0.00
20.	73.	0.00	0.00	0.00	0.00	0.00
25.	92.	0.00	0.00	0.00	0.00	0.00
30.	113.	0.00	0.00	0.00	0.00	0.00
35.	135.	0.00	0.00	0.00	0.00	0.00
40.	157.	0.00	0.00	0.00	0.00	0.00
45.	182.	0.00	0.00	0.00	0.00	0.00
50.	206.	0.00	0.00	0.00	0.00	0.00
55.	229.	0.00	0.00	0.00	0.00	0.00
60.	253.	.55	0.00	0.00	0.00	0.00
65.	277.	.77	0.00	0.00	0.00	0.00
70.	303.	.88	0.00	0.00	0.00	0.00
75.	320.	1.76	0.00	0.00	0.00	0.00
80.	342.	2.31	6.67	0.00	0.00	0.00
85.	362.	2.42	9.34	0.00	0.00	0.00
90.	380.	3.30	20.02	1.15	0.00	60.24
95.	402.	3.96	42.72	1.72	0.00	84.34
100.	418.	7.16	80.11	2.87	0.00	120.48
105.	436.	8.15	133.52	3.45	0.00	298.98
110.	456.	9.80	176.24	5.75	0.00	3787.36
115.	473.	12.45	213.63	11.51	2.72	5717.89
120.	490.	15.43	293.74	40.29	13.60	3219.94
125.	508.	16.75	373.86	109.38	48.97	298.98
130.	522.	17.85	527.41	287.85	122.42	80.32
135.	537.	18.29	574.14	460.56	176.84	24.09
140.	550.	18.73	667.61	662.06	186.36	0.00

Table VIII. Results of Reaction 1,8-DQ V.

ATMOSPHERIC PRESSURE IS 625.70 MM.HG.
 CHROMATOGRAPH COLUMN TEMP IS 119.00 DEGREES C
 CARRIER GAS FLOW RATE IS 65.00 CC.PER MIN.
 SWEEP GAS FLOW RATE IS 65.000 CC.PER MIN.
 INITIAL WT. OF 1,8-DINAPHTHYLENETHIOPHENE IS .7046 GRAMS

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	RATE OF GAS EVOLUTION MULTIPLIED BY (10**8)			
			MOLES/(MIN)(GM. STARTING MATERIAL)	HYDROGEN	METHANE	ETHANE
						HYDROGEN SULFIDE
0.	50.	0.00	0.00	0.00	0.00	0.00
5.	54.	0.00	0.00	0.00	0.00	0.00
10.	63.	0.00	0.00	0.00	0.00	0.00
15.	77.	0.00	0.00	0.00	0.00	0.00
20.	93.	0.00	0.00	0.00	0.00	0.00
25.	114.	0.00	0.00	0.00	0.00	0.00
30.	134.	0.00	0.00	0.00	0.00	0.00
35.	157.	0.00	0.00	0.00	0.00	0.00
40.	177.	0.00	0.00	0.00	0.00	0.00
45.	203.	0.00	0.00	0.00	0.00	0.00
50.	226.	0.00	0.00	0.00	0.00	0.00
55.	250.	.31	0.00	0.00	0.00	0.00
60.	270.	.73	0.00	0.00	0.00	0.00
65.	297.	.94	0.00	0.00	0.00	0.00
70.	317.	1.25	3.79	0.00	0.00	0.00
75.	336.	1.56	9.49	0.00	0.00	0.00
80.	360.	2.19	20.88	0.00	0.00	0.00
85.	375.	2.50	30.37	0.00	0.00	0.00
90.	390.	3.13	37.96	0.00	0.00	28.54
95.	414.	3.45	47.45	0.00	0.00	45.67
100.	431.	4.23	58.84	0.00	0.00	114.19
105.	450.	5.48	119.58	5.72	0.00	667.29
110.	467.	8.62	0.00	20.46	0.00	4220.85
115.	483.	11.60	205.00	24.55	0.00	4577.65
120.	500.	13.95	212.60	26.19	9.66	228.38

Table IX. Results of Reaction 1,8-DQ VI.

ATMOSPHERIC PRESSURE IS 625.00 MM.HG.
 CHROMATOGRAPH COLUMN TEMP IS 119.00 DEGREES C
 CARRIER GAS FLOW RATE IS 65.00 CC.PER MIN.
 SWEEP GAS FLOW RATE IS 65.000 CC.PER MIN.
 INITIAL WT. OF 1,8-DINAPHTHYLENETHIOPHENE IS .8933 GRAMS

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	RATE OF GAS EVOLUTION MULTIPLIED BY (10**8) MOLES/(MIN)(GM. STARTING MATERIAL)			
			HYDROGEN	METHANE	ETHANE	HYDROGEN SULFIDE
.	50.	0.00	0.00	0.00	0.00	0.00
5.	54.	0.00	0.00	0.00	0.00	0.00
10.	64.	0.00	0.00	0.00	0.00	0.00
15.	76.	0.00	0.00	0.00	0.00	0.00
20.	82.	0.00	0.00	0.00	0.00	0.00
25.	110.	0.00	0.00	0.00	0.00	0.00
30.	127.	0.00	0.00	0.00	0.00	0.00
35.	150.	0.00	0.00	0.00	0.00	0.00
40.	172.	0.00	0.00	0.00	0.00	0.00
45.	193.	0.00	0.00	0.00	0.00	0.00
50.	215.	0.00	0.00	0.00	0.00	0.00
55.	237.	0.00	0.00	0.00	0.00	0.00
60.	258.	.24	0.00	0.00	0.00	0.00
65.	285.	.37	0.00	0.00	0.00	0.00
70.	309.	.61	0.00	0.00	0.00	0.00
75.	327.	.98	0.00	0.00	0.00	0.00
80.	345.	1.23	2.99	0.00	0.00	0.00
85.	365.	1.48	5.99	0.00	0.00	0.00
90.	382.	1.73	10.49	0.00	0.00	9.01
95.	403.	2.10	16.78	0.00	0.00	13.52
100.	424.	2.96	35.97	1.29	0.00	45.08
105.	445.	4.45	77.94	3.23	0.00	261.62
108.	462.	5.69	118.41	3.87	0.00	3614.72

Table X. Results of Reaction 1,8-DQ VII.

ATMOSPHERIC PRESSURE IS 623.60 MM.HG.
 CHROMATOGRAPH COLUMN TEMP IS 119.00 DEGREES C
 CARRIER GAS FLOW RATE IS 65.00 CC.PER MIN.
 SWEEP GAS FLOW RATE IS 65.000 CC.PER MIN.
 INITIAL WT. OF 1,8-DINAPHTHYLENETHIOPHENE IS .9944 GRAMS

RATE OF GAS EVOLUTION MULTIPLIED BY (10**8)						
TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	MOLES/(MIN)(GM. STARTING MATERIAL)			
			HYDROGEN	METHANE	ETHANE	HYDROGEN SULFIDE
.	51.	0.00	0.00	0.00	0.00	0.00
5.	54.	0.00	0.00	0.00	0.00	0.00
10.	63.	0.00	0.00	0.00	0.00	0.00
15.	76.	0.00	0.00	0.00	0.00	0.00
20.	92.	0.00	0.00	0.00	0.00	0.00
25.	110.	0.00	0.00	0.00	0.00	0.00
30.	130.	0.00	0.00	0.00	0.00	0.00
35.	150.	0.00	0.00	0.00	0.00	0.00
40.	173.	0.00	0.00	0.00	0.00	0.00
45.	197.	0.00	0.00	0.00	0.00	0.00
50.	220.	0.00	0.00	0.00	0.00	0.00
55.	244.	.22	0.00	0.00	0.00	0.00
60.	263.	.66	0.00	0.00	0.00	0.00
65.	289.	.77	0.00	0.00	0.00	0.00
70.	314.	.88	0.00	0.00	0.00	0.00
75.	332.	1.11	0.00	0.00	0.00	0.00
80.	352.	1.33	2.69	0.00	0.00	0.00
85.	370.	1.55	5.39	0.00	0.00	0.00
90.	386.	2.00	8.09	0.00	0.00	0.00
95.	405.	2.55	12.14	0.00	0.00	20.29

Table XI. Results of Reaction 1,8-DQ VIII.

ATMOSPHERIC PRESSURE IS 621.30 MM.HG.
 CHROMATOGRAPH COLUMN TEMP IS 119.00 DEGREES C
 CARRIER GAS FLOW RATE IS 65.00 CC.PER MIN.
 SWEEP GAS FLOW RATE IS 65.000 CC.PER MIN.
 INITIAL WT. OF 1,8-DINAPHTHYLENETHIOPHENE IS .7290 GRAMS

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	RATE OF GAS EVOLUTION MULTIPLIED BY (10**8)			
			MOLES/(MIN)(GM. STARTING MATERIAL)			
			HYDROGEN	METHANE	ETHANE	HYDROGEN SULFIDE
.	49.	0.00	0.00	0.00	0.00	0.00
5.	52.	0.00	0.00	0.00	0.00	0.00
10.	63.	0.00	0.00	0.00	0.00	0.00
15.	78.	0.00	0.00	0.00	0.00	0.00
20.	94.	0.00	0.00	0.00	0.00	0.00
25.	113.	0.00	0.00	0.00	0.00	0.00
30.	133.	0.00	0.00	0.00	0.00	0.00
35.	153.	0.00	0.00	0.00	0.00	0.00
40.	175.	0.00	0.00	0.00	0.00	0.00
45.	200.	0.00	0.00	0.00	0.00	0.00
50.	223.	0.00	0.00	0.00	0.00	0.00
55.	242.	.15	0.00	0.00	0.00	0.00
60.	267.	1.06	0.00	0.00	0.00	0.00
65.	295.	1.97	0.00	0.00	0.00	0.00
70.	317.	2.27	0.00	0.00	0.00	0.00
75.	336.	2.27	0.00	0.00	0.00	0.00
80.	357.	2.57	3.69	0.00	0.00	0.00
85.	375.	2.87	5.54	0.00	0.00	27.78
90.	390.	3.63	9.23	0.00	0.00	50.01
95.	412.	4.85	18.47	0.00	0.00	66.69
100.	430.	6.82	39.72	0.00	0.00	166.72
105.	448.	7.73	81.29	4.78	0.00	3187.68
110.	465.	10.45	115.48	7.96	0.00	5857.46

Table XII. Results of Reaction 1,8-DQ XII.

ATMOSPHERIC PRESSURE IS 625.60 MM.HG.
 CHROMATOGRAPH COLUMN TEMP IS 119.00 DEGREES C
 CARRIER GAS FLOW RATE IS 65.00 CC.PER MIN.
 SWEEP GAS FLOW RATE IS 65.000 CC.PER MIN.
 INITIAL WT. OF 1,8-DINAPHTHYLENETHIOPHENE IS .7686 GRAMS

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	RATE OF GAS EVOLUTION MULTIPLIED BY (10**8)			
			MOLES/(MIN)(GM. STARTING MATERIAL)			
			HYDROGEN	METHANE	ETHANE	HYDROGEN SULFIDE
.	40.	0.00	0.00	0.00	0.00	0.00
5.	43.	0.00	0.00	0.00	0.00	0.00
10.	52.	0.00	0.00	0.00	0.00	0.00
15.	65.	0.00	0.00	0.00	0.00	0.00
20.	83.	0.00	0.00	0.00	0.00	0.00
25.	102.	0.00	0.00	0.00	0.00	0.00
30.	124.	0.00	0.00	0.00	0.00	0.00
35.	146.	0.00	0.00	0.00	0.00	0.00
40.	174.	0.00	0.00	0.00	0.00	0.00
45.	192.	0.00	0.00	0.00	0.00	0.00
50.	215.	0.00	0.00	0.00	0.00	0.00
55.	237.	0.00	0.00	0.00	0.00	0.00
60.	262.	0.00	0.00	0.00	0.00	0.00
65.	290.	.28	0.00	0.00	0.00	0.00
70.	313.	1.29	0.00	0.00	0.00	0.00
75.	337.	1.43	0.00	0.00	0.00	0.00
80.	352.	1.72	0.00	0.00	0.00	0.00
85.	373.	2.30	0.00	0.00	0.00	0.00
90.	393.	2.58	0.00	0.00	0.00	0.00
95.	412.	3.01	3.48	0.00	0.00	0.00
100.	470.	4.60	3.48	0.00	0.00	57.58
105.	450.	5.60	48.73	0.00	0.00	477.27
110.	470.	8.91	99.20	0.00	0.00	5323.91
115.	487.	11.64	0.00	15.00	0.00	5904.62
120.	505.	13.94	226.25	41.27	8.86	4197.15
125.	521.	14.52	330.68	150.08	56.74	845.61
130.	535.	15.52	0.00	337.69	124.12	157.05
135.	552.	15.81	496.02	585.33	177.31	104.70
140.	566.	16.10	469.91	600.34	159.58	41.88
145.	579.	16.53	386.37	450.25	74.47	26.17
150.	590.	16.96	306.31	300.17	26.59	20.94
155.	605.	17.25	0.00	345.19	8.86	5.23
160.	619.	17.25	311.53	382.71	0.00	0.00

Table XIII. Total Moles of H_2 , CH_4 , C_2H_6 , and H_2S Liberated per gram of Starting Material During Interrupted Pyrolysis Reactions of 1,8-Dinaphthylenethiophene.

Final Temperature	Run Number	Total Moles H_2 per gram 1,8-D.	Total Moles CH_4 per gram 1,8-D.	Total Moles C_2H_6 per gram 1,8-D.	Total Moles H_2S per gram 1,8-D.
405	1,8-DQ VII	163×10^{-8}	000	000	000
462	1,8-DQ VI	976×10^{-8}	000	000	$9,140 \times 10^{-8}$
465	1,8-DQ VIII	895×10^{-8}	81×10^{-8}	000	$32,600 \times 10^{-8}$
505	1,8-DQ V	$3,740 \times 10^{-8}$	326×10^{-8}	41×10^{-8}	$45,000 \times 10^{-8}$
550	1,8-DQ IV	$11,710 \times 10^{-8}$	$5,200 \times 10^{-8}$	$1,630 \times 10^{-8}$	$63,900 \times 10^{-8}$
600	1,8-DQ III	$14,300 \times 10^{-8}$	$5,540 \times 10^{-8}$	$2,850 \times 10^{-8}$	$50,200 \times 10^{-8}$
628	1,8-DQ XII	$13,500 \times 10^{-8}$	$11,630 \times 10^{-8}$	$2,690 \times 10^{-8}$	$74,300 \times 10^{-8}$

Table XIV. Percent of Each Material Present in Condensate of Reaction 1,8-DQ XIII. (Chromatographic Analysis.)

<u>Material Number</u>	<u>Material Name</u>	<u>Percent of Total Condensate</u>
2	Naphthalene	4.74
3		.40
4		3.95
5		1.99
6		2.37
7		24.53
8	Acenaphthylene Acenaphthene	21.74
9		.80
10	1,8-Dinaphthylenethiophene	39.50

Table IXV. Total Moles of H_2 , CH_4 , C_2H_6 , and H_2S Liberated per Mole of Starting Material During Interrupted Pyrolysis Reactions of 1,8-Dinaphthylenethiophene.

Final Temp. °C	Run Number	Total Moles H_2 per Mole 1,8-D.	Total Moles CH_4 per Mole 1,8-D.	Total Moles C_2H_6 per Mole 1,8-D.	Total Moles H_2S per Mole 1,8-D.
405	1,8-DQ VII	.0005	.0000	.0000	.0000
462	1,8-DQ VI	.0033	.0000	.0000	.0300
465	1,8-DQ VIII	.0029	.0003	.0000	.1068
505	1,8-DQ V	.0125	.0009	.0002	.1500
550	1,8-DQ IV	.0389	.0174	.0054	.2130 *
600	1,8-DQ III	.0475	.0185	.0095	.1673 *
628	1,8-DQ XII	.0450	.0387	.0090	.2469 *

* Errors introduced in measuring area under curves.

Table XVI. Analysis of Condensable Products of the Pyrolysis Reaction of 1,8-Dinaphthylenethiophene, Not Including Starting Material.

Final Temp. °C	Run Number	Amount of Material Produced (%)					
		Material Number					
		2	4	5	6	7	8
405	1,8-DQ VII	10.4	35.1	10.0	18.4	8.6	17.5
465	1,8-DQ VIII	20.1	24.1	4.9	8.1	20.1	23.7
505	1,8-DQ V	10.7	13.0	2.6	2.9	35.2	35.6
550	1,8-DQ IV	13.6	10.4	1.6	1.7	29.6	43.1
626	1,8-DQ XII	10.9	8.8	1.3	1.5	46.7	30.8

Table XVII. Materials Present in Carbonaceous Residue Extract and Condensables of Interrupted Pyrolysis Reactions of 1,8-Dinaphthylenethiophene. (Starting Material Not Included.)

Final Temp. °C	Run Number	Melting Point, Residue	Condensate	Residue Extract
405	1,8-DQ VII	260°C	7, 5, 2, 8, 6, 4	2, 4
462	1,8-DQ VI	300°C	No Results	(Traces 7, 8)
465	1,8-DQ VIII	No Results	5, 6, (2, 7), 8, 4	No Results
505	1,8-DQ V	375°C	5, 6, 2, 4, 7, 8	(Traces 2, 4)
550	1,8-DQ IV	550°C	5, 6, 4, 2, 7, 8	(Traces 2, 4)
600	1,8-DQ III	550°C	No Results	(Traces 2, 4)
628	1,8-DQ XII	550°C	5, 6, 4, 2, 8, 7	No Results

(Note: Materials present are listed in increasing order of magnitude.)

Table XVIII Analysis of Carbonaceous Residues Produced During Interrupted Pyrolysis Reactions of 1,8-Dinaphthylenethiophene

Final Temp. °C	Run Number	Wt. % S in Residue	<u>Residue Composition</u>	
			Percent Carbonaceous Material	Percent CS ₂ Extractable Material
405	1,8-DQ VII	7.01	7.9	92.1
462	1,8-DQ VI	3.66	50.2	49.8
505	1,8-DQ V	1.87	71.3	28.7
550	1,8-DQ IV	1.30	91.7	8.3
600	1,8-DQ III	1.42	98.9	1.1

Table XIX. Summary of Qualitative Pyrolysis Reactions Conducted on 1,8-Dinaphthylene-thiophene.

Run Number	Sample Size (gms)	Final Temp. °C	% Carbonaceous Residue	Remarks
1,8-D I	.341	615	80.1	Collected condensate for analysis; Replaced reactor thermocouple.
1,8-D II	.745	622	81.2	Collected condensate for analysis; identified gaseous products of reaction.
1,8-D III	.474	---	80.1	Collected Condensate for analysis; rebuilt nitrogen preheater.
1,8-D IV	.667	---	---	No data; water problem.
1,8-D V	.942	626	82.1	Collected condensate for analysis; confirmed identification of gaseous products.
1,8-D VI	1.697	628	83.8	Sample too large. Boil-up problems.
1,8-D VII	.686	620	82.0	Used helium for inert atmosphere; same condensable products of reaction.
1,8-D VIII	---	626	---	No data taken;
1,8-D IX	---	608	---	Runs made for condensable
1,8-D X	---	620	---	product collection.

Table XX.. Summary of Quantitative and Interrupted Pyrolysis Reactions Conducted on 1,8-Dinaphthylenethiophene.

<u>Run Number</u>	<u>Sample Size (gms)</u>	<u>Final Temp. °C</u>	<u>Usable Results</u>	<u>Remarks</u>
1,8-DQ I	.8237	---	No	Thermocouple problem.
1,8-DQ II	.8843	---	No	Heating rate too fast.
1,8-DQ III	.6690	600	Yes	Heating rate: 3.69C°/min.
1,8-DQ IV	1.0025	550	Yes	
1,8-DQ V	.7046	505	Yes	
1,8-DQ VI	.8933	465	Yes	
1,8-DQ VII	.9944	405	Yes	
1,8-DQ VIII	.7290	462	Yes	
1,8-DQ IX	.5262	---	No	Nitrogen sweep line plugged.
1,8-DQ X	.6499	550	Yes	Reactions to
1,8-DQ XI	.8944	505	Yes	collect condensate
1,8-DQ XII	.7686	626	Yes	for analysis.

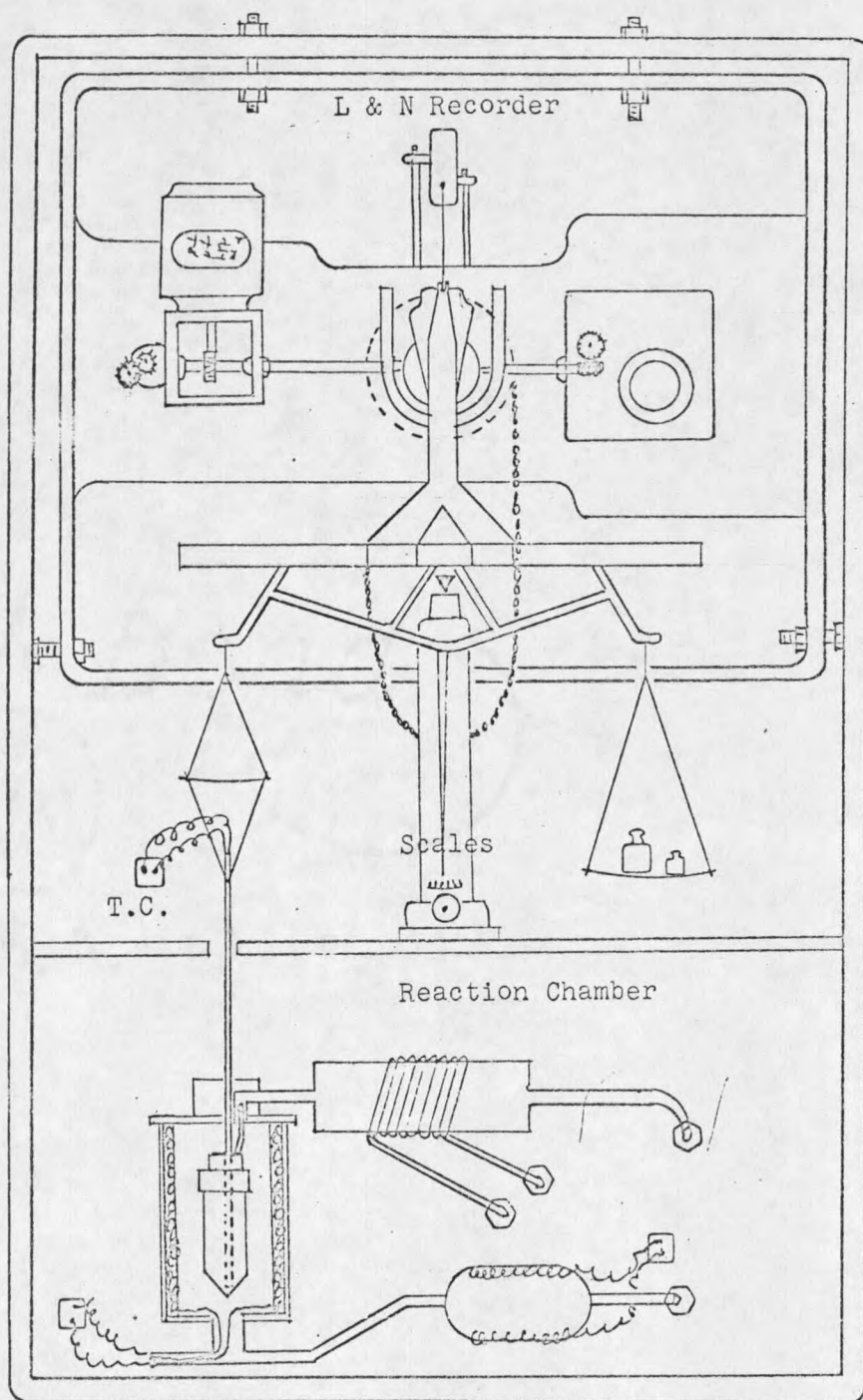


Figure 1. Modifications to a Leeds and Northrup Recorder for use as an Automatic Recording Balance.

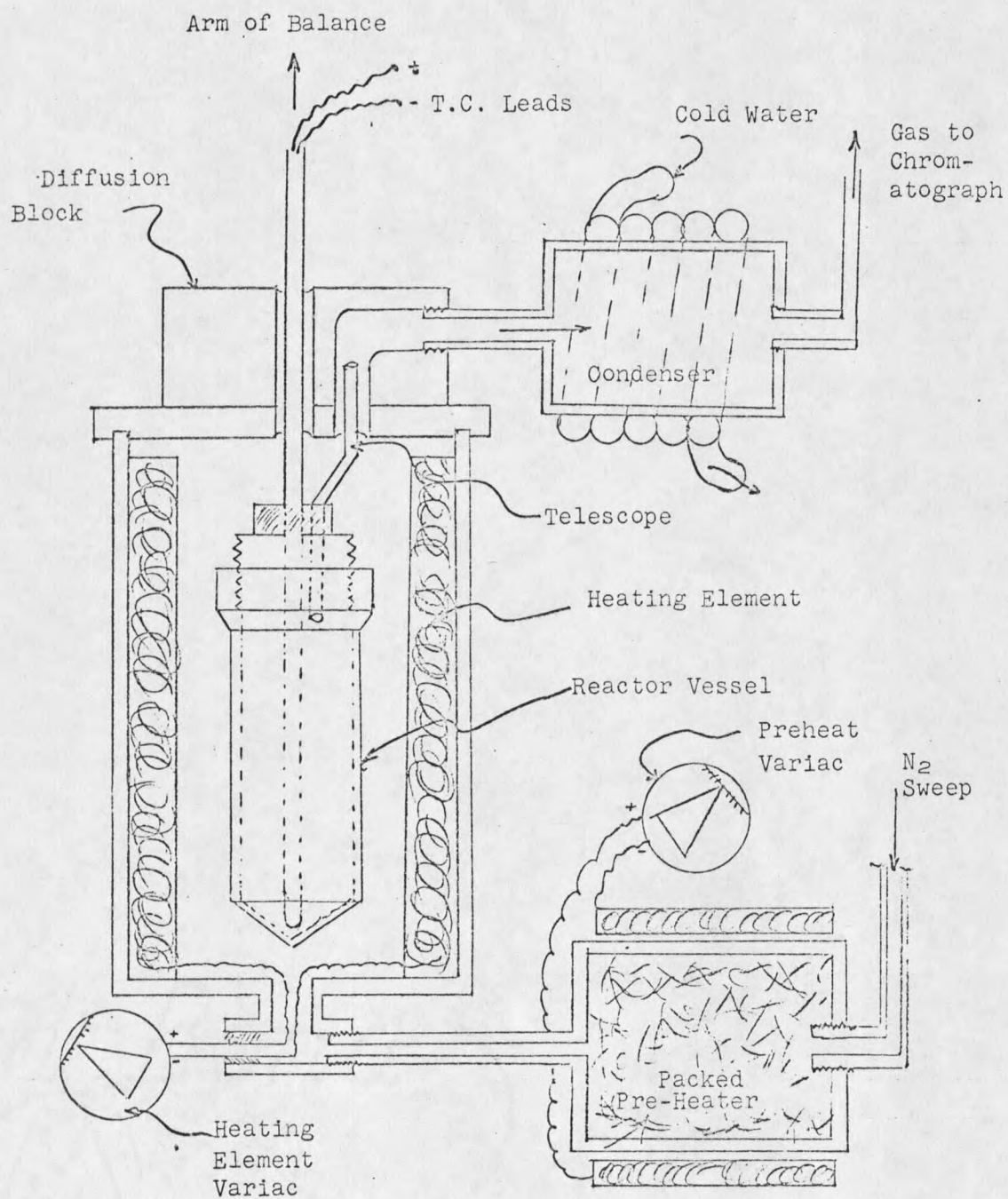


Figure 2. Design and Assembly of the TGA Pyrolysis Reaction Chamber.

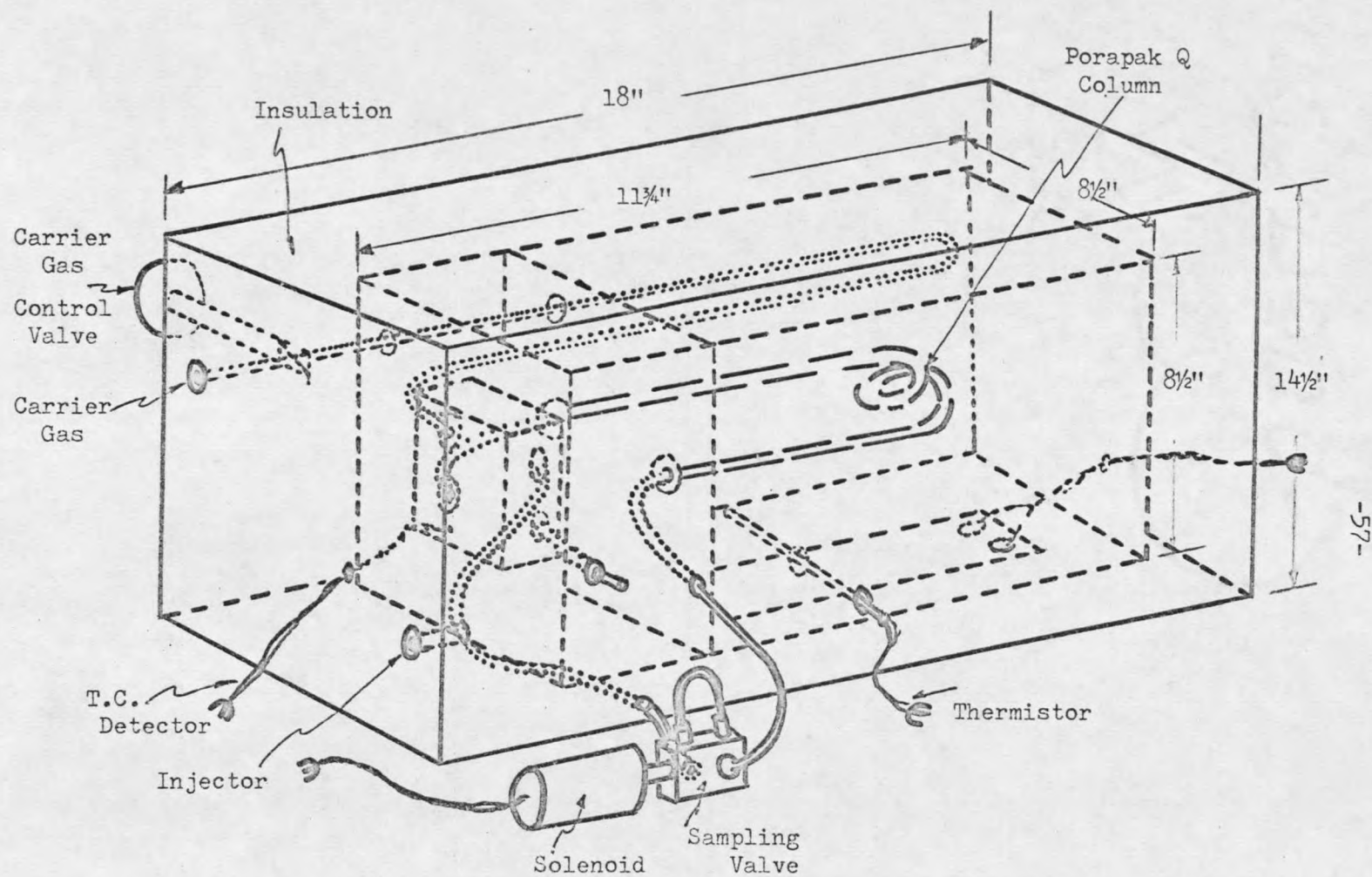


Figure 3. Design of Chromatograph Oven Used in the Study of Pyrolysis of 1,8-Dinaphthylenethiophene.

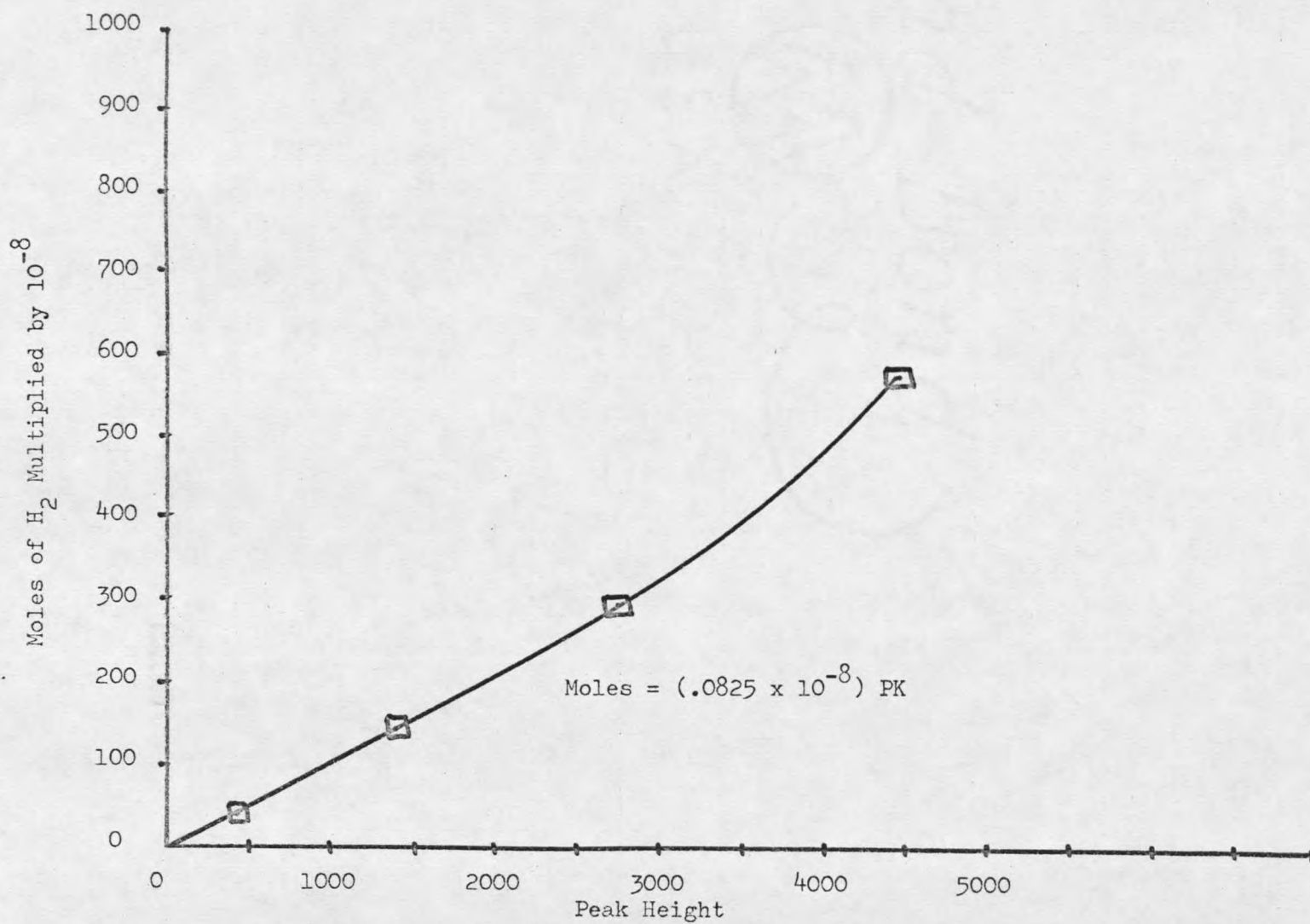


Figure 4. Calibration Curve for H₂ Used in the Pyrolysis Study of 1,8-Dinaphthylene-thiophene.

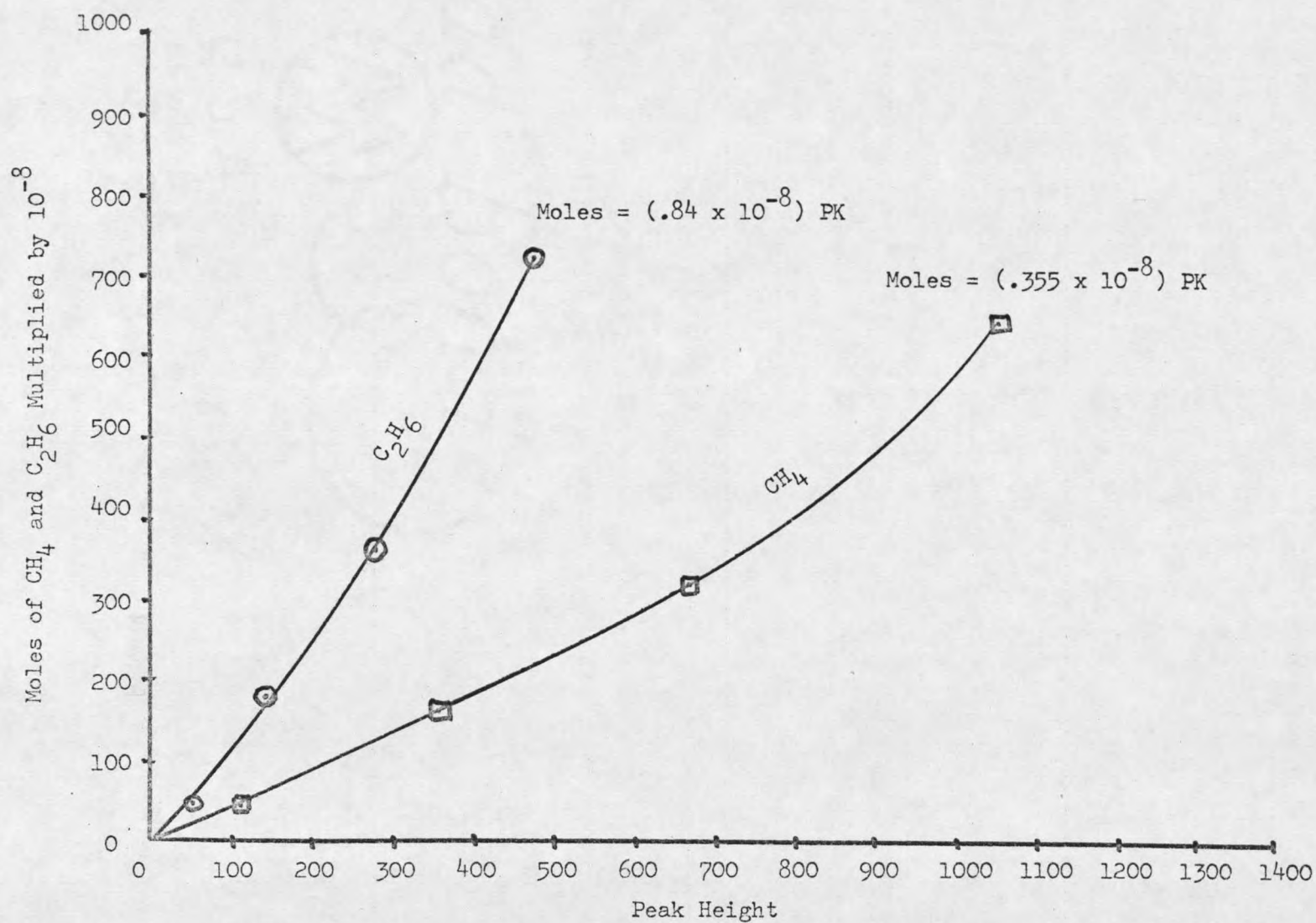


Figure 5. Calibration Curve for CH_4 and C_2H_6 Used in the Pyrolysis Study of 1,8-Dinaphthylenethiophene.

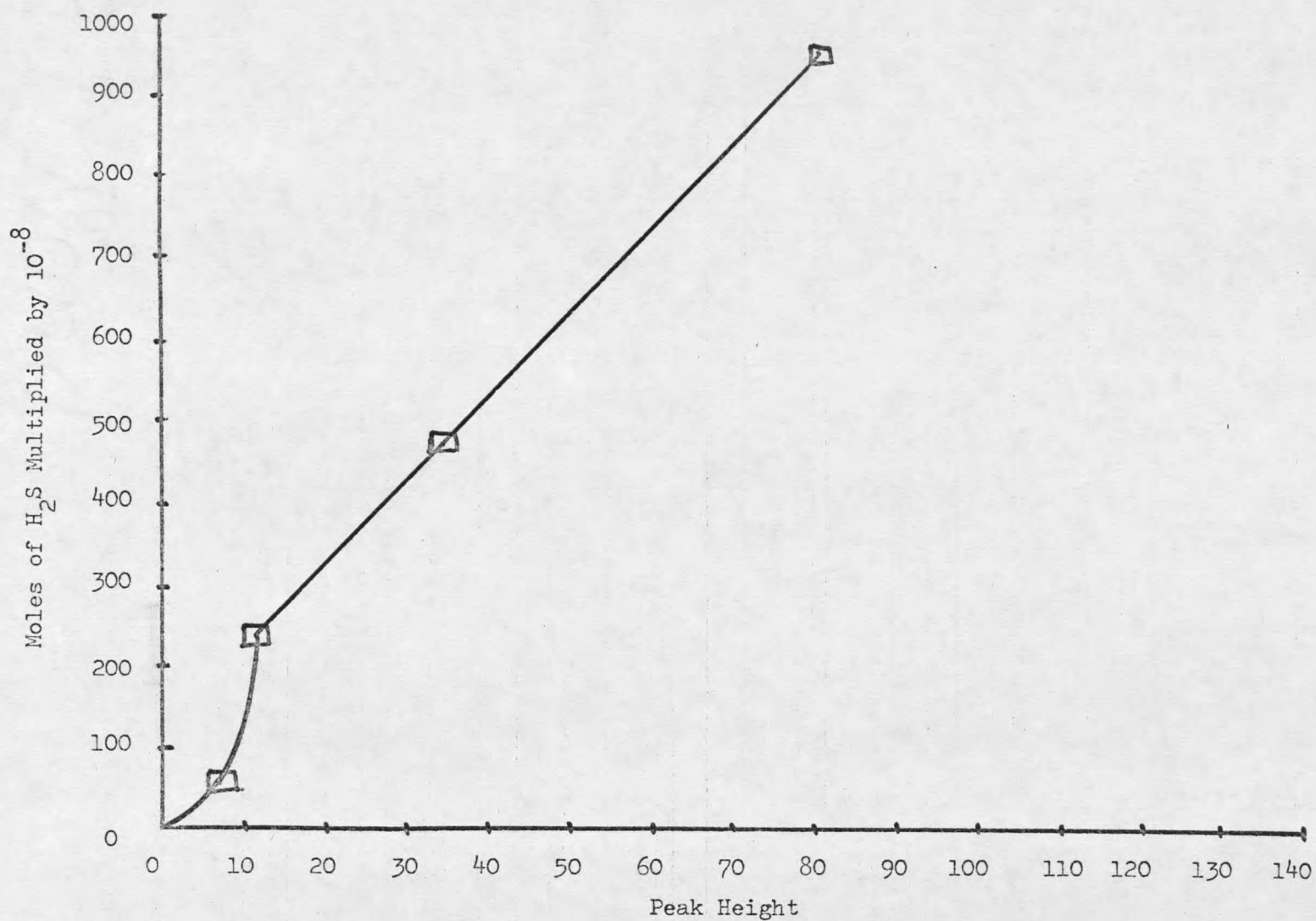


Figure 6. Calibration Curve for H_2S Used in the Pyrolysis Study of 1,8-Dinaphthylene-thiophene.

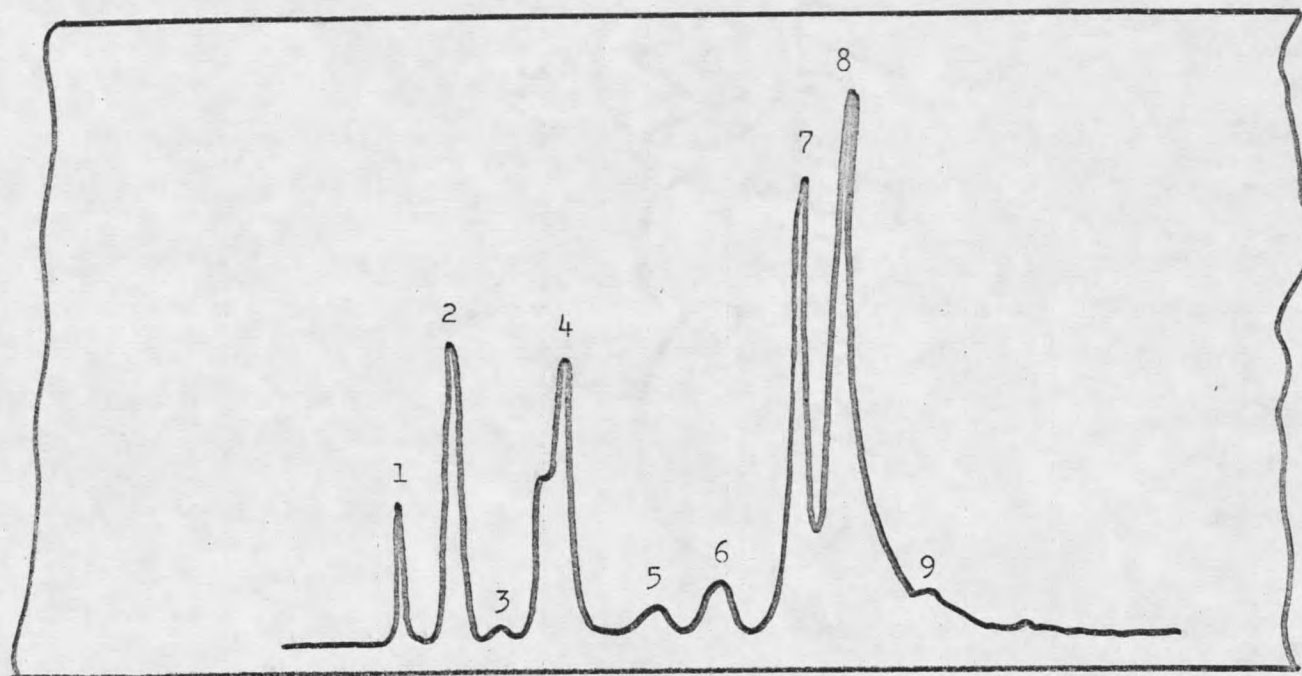


Figure 7. A Typical Chromatogram of Condensate Produced in the Pyrolysis Reaction of 1,8-Dinaphthylenethiophene.

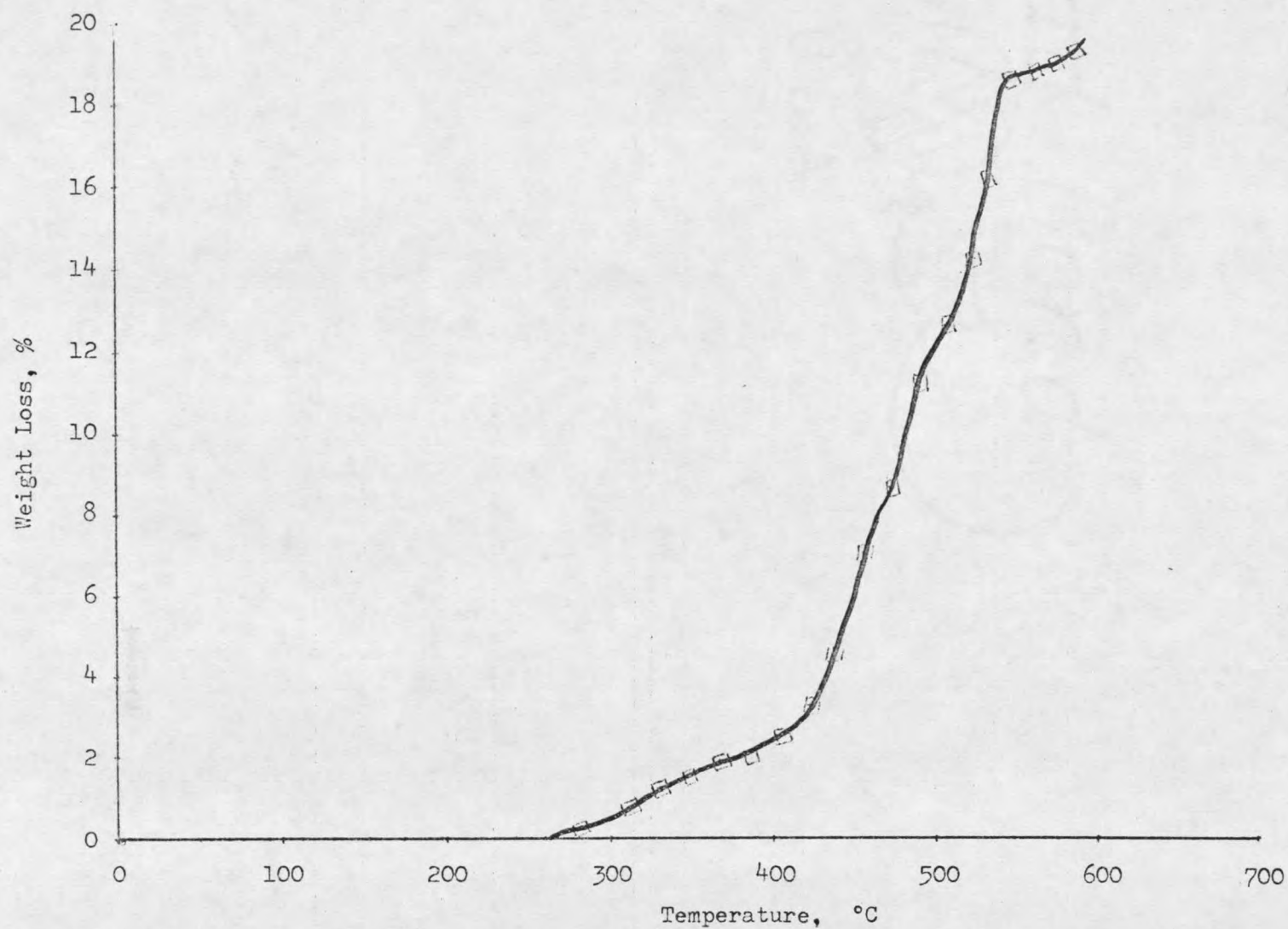


Figure 8. Typical Weight Loss Curve During the Pyrolysis of 1,8-Dinaphthylene-thiophene.

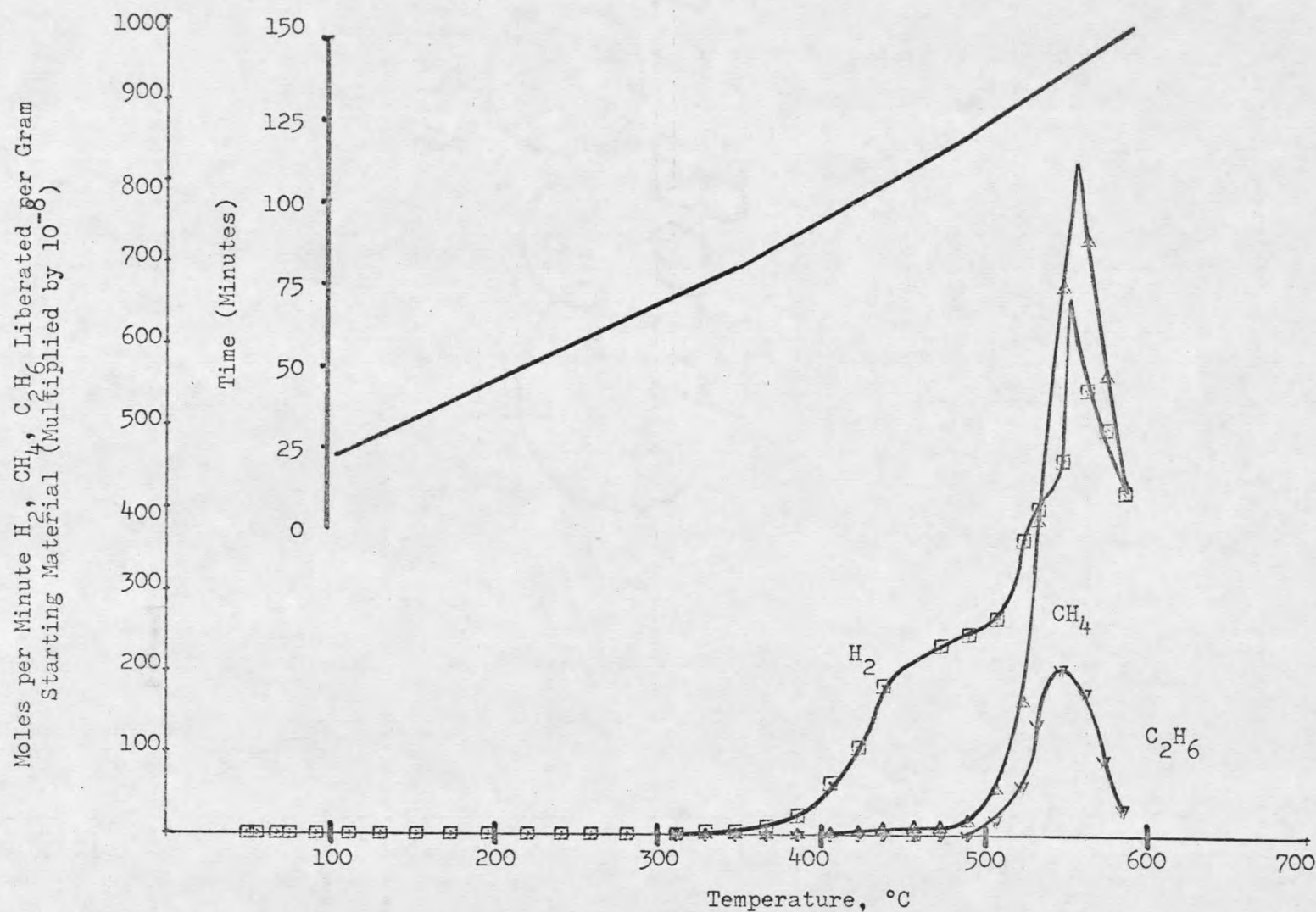


Figure 9. Moles per Minute H_2 , CH_4 , C_2H_6 Liberated per Gram of Starting Material in a Typical Pyrolysis of 1,8-Dinaphthylenethiophene, (1,8-DQ III)..

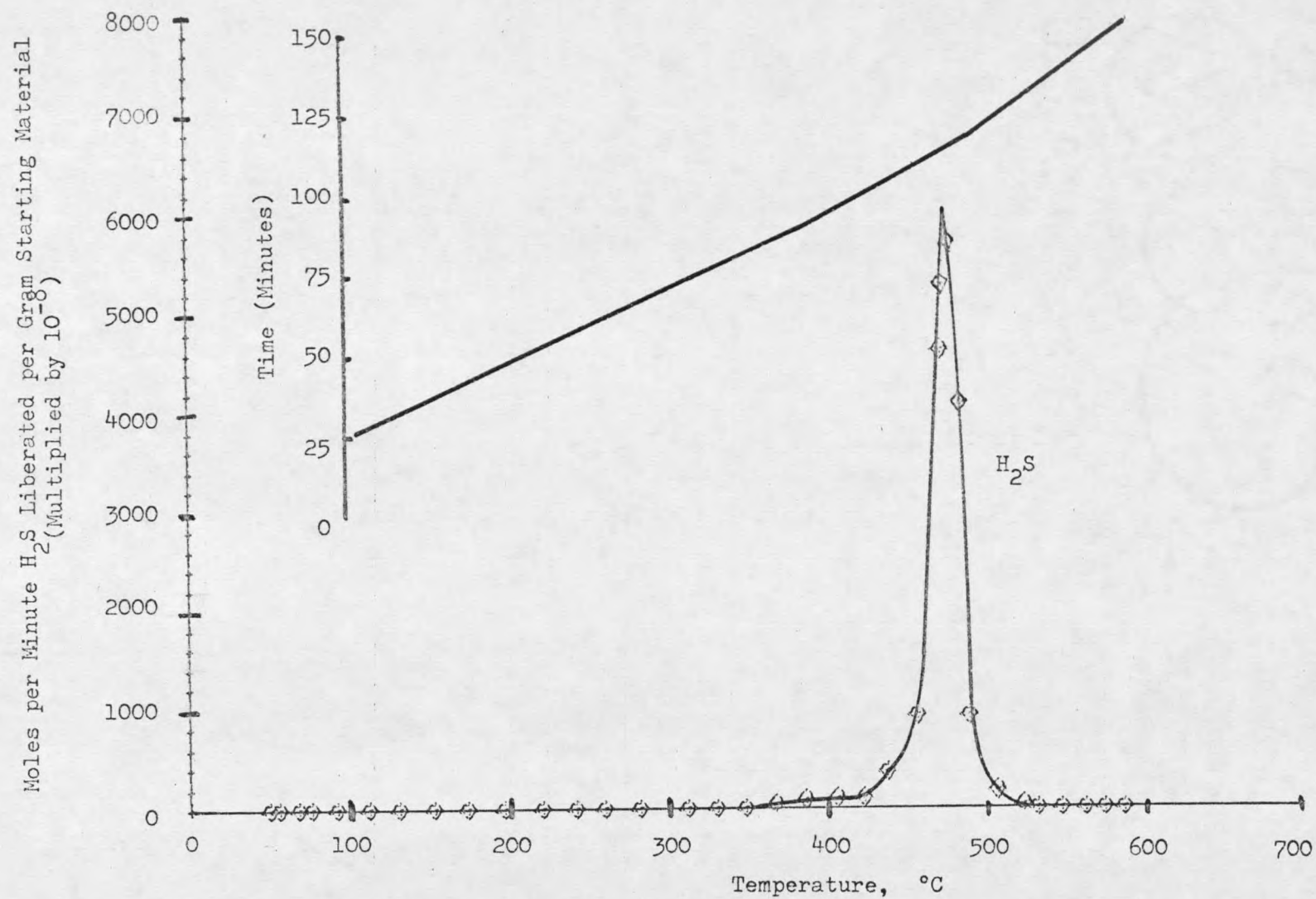


Figure 10. Moles per Minute H_2S Liberated per Gram of Starting Material in a Typical Pyrolysis of 1,8-Dinaphthylenethiophene, (1,8-DQ III).

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