FOREWORD

This work was conducted by the National Carbon Company, a Division of Union Carbide Corporation under USAF Contract AF 33(616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials," Task No. 735002 "Graphite Materials Development"; Project No. 7381 "Materials Application," Task No. 738102 "Materials Preproduction Process Development"; and Project No. 7-817 "Process Development for Graphite Materials." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Captain R. H. Wilson, L. J. Conlon and W. P. Conrardy acting as Project Engineers.

Work under this contract has been in progress since May 1, 1960. The work covered in this report was conducted at the Research Laboratory of the National Carbon Company located at Parma 30, Ohio, under the direction of J. C. Bowman, Director of Research, and W. P. Eatherly, Assistant Director of Research.

This is the tenth of a series of volumes of WADD Technical Report 61-72 prepared to describe various phases of the work. The preceding volumes of this series are:

ABSTRACT

A general survey is given of the thermal reactivity of aromatic hydrocarbons to provide information basic to the understanding of the conversion of organic materials to carbon. Differential thermal analysis was employed on 84 aromatic hydrocarbons to delineate the thermal sequences during pyrolysis to 750°C. Absorption spectra, electron spin resonance, chromatography, and molecular weight determinations have been used to determine the mechanisms and structural changes which occur.

This report has been reviewed and is approved.

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iii

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION

The mechanisms involved in the thermal conversion of organic materials to carbon are of fundamental importance to the continuing efforts to improve present carbon products and to produce new, uniquely different artificial carbon and graphite materials.

The only practical precursors to artificial carbon have been derived from petroleum refining and coal carbonization. A thorough understanding of the mechanisms by which these materials are converted to carbon is essential. It is commonly inferred that the quality of a petroleum coke derived carbon is essentially determined during the early stages in its thermal history. It is important to know when this quality factor is irrevocably established. In the case of the coal tar derived binder materials, the properties of the binder both before and after carbonization are important in determining the quality of the carbon produced. Unfortunately, the best forming characteristics are not completely compatible with the best baking characteristics. A judicious compromise must be made to obtain the best possible bond carbon and still maintain proper forming conditions.

Much work has been done on petroleum cokes, on the forming, and baking processes, and on the chemical and thermochemical means of altering the carbonization characteristics of binders to improve their carbon yield and reduce the quantities of volatile materials produced during pyrolysis. Pitches have been modified with polymerizing resins, treated with acidic and basic catalysts, free radical catalysts and dehydrogenating agents with varying degrees of success.

The chemical composition of petroleum residues and coal tar pitches is complex and is known to include to a large extent a wide variety of polynuclear aromatic hydrocarbon species. These raw materials are therefore unsuitable for studies of reaction mechanisms. A more fruitful approach is to examine the thermal behavior of representative compounds and simple mixtures. Much recent chemical interest has been directed toward studies in the field of polynuclear aromatic hydrocarbons. Special emphasis has been placed on theoretical treatments of these materials[1,2] and the relationship of theoretical parameters to spectroscopic,[3] reactivity,[4,5,6] and physiological[7] criteria. Chemical reactivity investigations for the polynuclear aromatics have been restricted largely in the past to radical substitution[4] and oxidation-reduction.[5,6] The thermal reactivity characteristics of these compounds have also been the subject of recent studies.[8] Many of the aromatic hydrocarbons are known to be thermally reactive both individually and as constituents of complex mixtures. These thermal reactions are believed to involve condensation or polymerization sequences to produce complex carbonaceous products.[9]

1

Rapid developments in instrumental analytical techniques and in dynamic methods of measuring changes in materials during heating and cooling make a detailed study of carbonization reactions possible and practical at this time. This report is a survey of the thermal reactivity characteristics for a wide variety of aromatic hydrocarbons. Differential Thermal Analysis (DTA) has been used to categorize the high temperature behavior of these hydrocarbons. This technique has been used extensively in investigations of polymers and inorganic solids.[10] It has found relatively little use, however, in the study of thermally reactive organic compounds.

DTA gives a continuous thermal record of reactions occurring in a sample although it does not indicate what these reactions are nor does it sort out simultaneously occurring reactions. By comparing the temperature in a sample with the temperature in an inert reference material such as anhydrous alumina as both are heated at a uniform rate in a furnace, temperature regions where heat is absorbed (endothermic reactions) or evolved (exothermic reactions) by the sample can be observed. This gives information both as to the type of reaction occurring and the temperature where the reaction takes place. Variations in peak areas and shapes provide information on heats and rates of reactions.

DTA permits delineation of the hydrocarbons into thermally stable and thermally reactive categories in an atmospheric pressure system. It allows the simple evaluation of melting and boiling points for the thermally stable compounds and melting and reaction temperatures for the thermally reactive species. Quantitative thermodynamic data for unambiguous thermal transformations are additionally determinable. Isolation of volatile products and reaction residues at various stages of reaction provide clues to the pyrolytic sequences.

Thermal reactivity behavior as derived from DTA may be interpreted in terms of reactivity parameters derived from electronic spectra and the adjunct of molecular size. Examination of simple aromatic mixtures further provide examples of both additive and nonadditive thermal behavior.

2. SUMMARY AND CONCLUSIONS

This report presents a general survey of the thermal reactivity characteristics of aromatic hydrocarbons. These hydrocarbons as important constituents of coal tar and petroleum refining residues, the major raw materials for the carbon industry, are the chemical precursors to graphite.

Our approach has employed Differential Thermal Analysis (DTA) to delineate the thermal sequences for 84 representative aromatic hydrocarbons and some hydrocarbon mixtures. The aromatics may thus be subdivided into thermally "reactive" and "nonreactive" categories. The "reactive" aromatics produce a carbon yield at 750°C at atmospheric pressure. The nonreactive entities undergo complete volatilization prior to reaction. The DTA method additionally permits the determination of melting and boiling points and the reaction temperatures at which carbonization reactions occur.

Reactivity parameters have been derived for the aromatic hydrocarbons from measured electronic spectra. Several conclusions have been derived pertaining to aromatic structure and reactivity and to the chemical nature of the early thermal carbonization reactions.

These conclusions may be summarized as:

1.   Thermal reactivity of aromatic hydrocarbons depends on both molecular size and energetic character.

2.   Employing spectrally derived ionization potential data (IP) as a criterion of general reactivity, it is seen that aromatics of low IP are thermally reactive while those of high IP are usually thermally stable.

3.   Molecular size, by increasing or reducing physical stability, is an adjunctive reactivity parameter. Several volatile aromatics of low IP are found to be "unreactive" whereas several large physically stable aromatics of higher IP have been found to be thermally "reactive."

4.   Substitution by exocyclic vinyl double bonds increases thermal reactivity through the thermal conversion of less "reactive" monomer entities to "reactive" polymer species.

5.   Alkyl and aryl substituents increase "reactivity" presumably by presenting a site of easy bond cleavage in the molecule.

6.   Thermal hydrogen transfers appear to be important in the early carbonization reactions for many of the aromatics. These hydrogen transfers can result in the simultaneous formation of less "reactive" and more "reactive" aromatic species. The latter may to an extent consist of aromatic free radicals which can undergo further condensations in the carbonization and graphitization sequence.

3. EXPERIMENTAL APPARATUS AND PROCEDURES

3.1. DTA Apparatus

Differential thermal analysis is the technique of measuring the difference in the temperature between a thermocouple embedded in a sample and a thermocouple in a standard inert material such as aluminum oxide while both are heated at a uniform rate. These temperature differences arise when phase transformations or chemical reactions in the sample evolve or absorb heat. Theoretically, the magnitude of the temperature difference integrated with respect to time can be equated to the heat of reaction. The two effects that require treatment are: (1) the differential flow of heat to the thermocouple in the center of the sample,

3

and (2) the heat of the reaction. Experimentally, it is desirable to thermally match and isolate the sample and reference holders and to maintain a uniform heating rate.

The basic design of the apparatus used in this study was that developed by R. V. Sara[11] in this Laboratory. A sketch of the sample holder and a block diagram of the controlling, detecting, amplifying, and recording systems are shown in Figure 1. The furnace is a Hoskins, Type F-H 303A, 15-volt a.c. electric
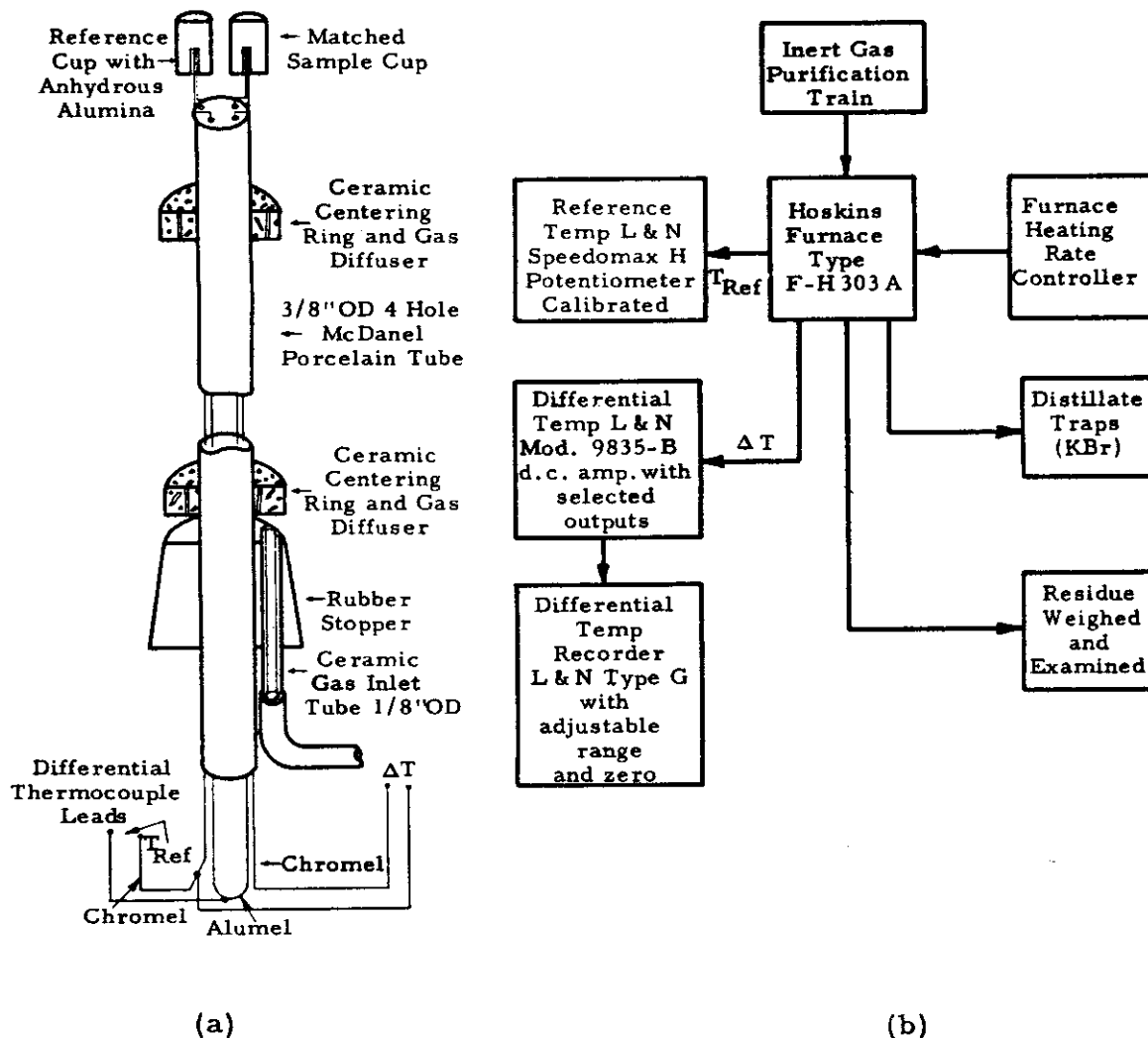

Figure 1. (a) DTA Thermocouple Assembly; (b) Block Diagram of DTA Apparatus.

furnace mounted vertically and fitted with a McDanel zircon combustion tube 1-inch ID by 18 inches in length. A Sorgel (Type INS) step-down transformer

4

supplies up to 32 amperes at 17 volts to the furnace. The rate of heating of the DTA furnace is controlled by the initial setting on a Superior Electric Company Powerstat, Type 2 PF 136, and on the rate at which the Powerstat setting is changed. The Powerstat driver is a Bodine speed reducer motor, Type NSI-12 RG, coupled to a Zero-Max variable speed torque converter, Model 14-R, with reverse. Heating rates between 1°C to 20°C per minute can be maintained with excellent reproducibility.

The signal voltage from the differential thermocouple circuit is amplified by a Leeds & Northrup Model 9835-B stabilized d.c. microvolt amplifier which has an output range from 5 to 20,000 microvolts. The amplifier output is recorded on a Leeds & Northrup Type G recorder supplemented with a d.c. millivolt recorder with adjustable range and zero position. A continuous record of the reference temperature with time is obtained with a Leeds & Northrup Speedomax H temperature potentiometer calibrated for a Chromel-Alumel couple.

The DTA thermocouple assembly shown in Figure 1(a) consists of two matched thermocouples supported in a McDanel four-hole, 3/8-inch OD porcelain tube of 10-inch length. The thermocouples are 24-gauge Chromel-Alumel butt-welded with a microspot welder to minimize the mass of the junction. Two centering rings which also act as gas diffusers are cemented to the support tube to give positive centering in the furnace. The thermocouple assembly is fitted with a rubber stopper and a gas inlet tube. The rubber stopper serves to hold the vertical assembly in position in the furnace combustion tube. Care must be taken to locate the thermocouple junctions in exactly the same position with respect to the furnace axis for each experimental trial in order to assure a reproducible, flat baseline. The sample and reference cups are Inconel cylinders 0.250-inch in diameter by 0.375-inch high with a wall thickness of 0.010-inch and a weight of about 0.950 gram. A thermocouple well extends 0.187-inch into the center of the cup from the bottom. It is drilled with a 1-1/2° taper to match the tapered thermocouple tips. This assures maximum thermal contact between the thermocouple and the cup and reduces the problem of poor fit as the cups and thermocouples wear with use. With this arrangement, the thermocouples are protected from the embrittling action of the hydrocarbons during carbonization and can be used for 25 to 50 runs. This extended life justifies very careful matching of the thermocouples and Inconel cups. The sample and reference cups are isolated from each other and independent of the thermocouples. This permits weighing before and after heating so that weight changes can be determined. The loss of sensitivity caused by the use of thermocouple wells is partly offset by the thermal isolation and the reduced mass and heat capacity of the cups. In most cases, the quantity of sample and of reference anhydrous alumina was standardized at 100 milligrams. The heating rate was also arbitrarily standardized at 10°C per minute. All experiments were run at atmospheric pressure in purified argon. Baselines were checked frequently as wear from cleaning and erosion from thermal cycling tends to change the sample and reference cups at different rates.

Electrical shielding of the thermocouples is not necessary since the microvolt amplifier has an a.c. current filter which is adequate for eliminating any stray periodic alternating signals.

A nonoxidizing furnace atmosphere is maintained by purging with purified argon. Argon is introduced into the combustion tube at the lower end after passing through a heated copper wool purification train to remove oxygen and moisture. The argon passes through two diffuser rings and upward past the sample and reference cups and is exhausted from the top into a condensate trap for collecting the condensable volatile products. The noncondensable gases then pass through a sulfuric acid bubbler which seals the system. Samples were heated to 750°C and the carbon yields reported were determined on the 750°C residues. A schematic diagram of the DTA assembly is shown in Figure 1(b).

The condensable volatile products were collected in a KBr filled trap placed at the exhaust end of the combustion tube. This trapping method devised by H. Leggon[12] for gas chromatography is convenient for infrared analysis of the condensates.

Normally, the DTA experiments were carried out by heating continuously to 750°C at which point the residue is essentially carbon. However, since the DTA thermogram provides an excellent visual method of detecting reactions and determining end-points, a number of runs were terminated at a temperature just preceding or following a reaction peak and the products were cooled and analyzed. These experiments are discussed under the heading "Interrupted DTA" in the following sections.

3.2. Analytical Techniques

3.2.1. Chromatography

Thermal reaction products are usually complex mixtures that require some separation before effective analysis can be accomplished. Elution chromatography on alumina or silica gel columns has proved to be particularly applicable to these materials. A simple 12 mm ID x 300 mm long Pyrex tube with a washed Pyrex wool plug is used to contain the column. Twenty grams of chromatographic grade alumina (Fisher Scientific Co.) produce a column 200 mm long that is sufficient to handle between 10 and 100 milligrams of sample. Elution is started with n-heptane followed by benzene, chloroform, ethyl alcohol and sometimes terminated with water. Elution is continued with each solvent until no further change is observed on the column and in the eluate. Separations are followed by observing the color, the UV fluorescence on the column and eluate, and the infrared spectra of the fractions. The columns are protected from light and solvent is removed from fractions by room temperature evaporation. Elution chromatography has also been extremely useful in the purification of reference compounds for this study, usually producing a much higher degree of purity than repeated recrystallization or sublimation and with less effort.

3.2.2. Infrared Absorption Spectra

The infrared absorption spectra were measured on a Perkin-Elmer Model 21 or Model 221 double-beam spectrometer using conventional sampling techniques. The KBr pellet technique was used extensively because of the limited solubility of the compounds studied.

3.2.3. Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were measured on a Beckman DK-1 double-beam spectrometer using solution methods with 10 mm matched silica cells, exclusively.

3.2.4. Molecular Weight

A Mechrolab Osmometer, Model 301, was used to determine number average molecular weights of those compounds and fractions soluble in benzene.

3.2.5. Hot Stage Microscope

A Kofler Hot Stage and accessories with an American Optical Spencer binocular microscope was used to observe melting points, phase transformations, color changes, polymerizations, and other visual changes that occurred during heating.

3.2.6. Electron Spin Resonance

Electron Spin Resonance measurements were made on a number of the low temperature residues obtained in the DTA apparatus. These measurements were made by L. S. Singer of this Laboratory using methods and apparatus previously described.[13]

3.3. Materials

The polynuclear aromatic compounds examined in this work were obtained through commercial chemical supply houses and in many cases were used as received. Spectra of each compound were compared with published spectra to ascertain purity. In those cases where thermally reactive compounds appeared to be contaminated, chromatographic purification was carried out and the purified material was re-examined in the DTA apparatus. The sources of the compounds listed in Tables 2 and 3 are given below in Table 1. The key number before

Table 1. Sources of Polynuclear Aromatic
Hydrocarbons Used in This DTA Study

Key Number	Supplier
(1)	Eastman Kodak Company, Distillation Products Industries
(2)	Aldrich Chemical Co., Inc.
(3)	Terra Chemicals, Inc.
(4)	L. Light & Co., Ltd.
(5)	Bios Laboratories, Inc.
(6)	Union Carbide Olefins Company

7

each supply house is used in these tables in parentheses after the compound name to indicate the source of each compound.

The solvents used in the chromatographic separations and for spectroscopic analysis were all Eastman Kodak Company, Spectro-Grade solvents. The KBr powder used in trapping the DTA condensates and for IR sampling was Harshaw Chemical Company, IR Quality powdered KBr. The anhydrous alumina used in chromatographic columns and as the DTA reference material is Fisher's Chromatographic Grade Anhydrous Alumina, 80 to 200 mesh, Catalog No. A-540. The alumina used for DTA reference is specially treated by heating to 800°C. It is stored in a sealed dispenser to avoid exposure of the bulk of the material to the atmosphere when transferring to the DTA cup.

4. EXPERIMENTAL RESULTS

4.1. DTA Thermograms for Thermally "Unreactive" Aromatic Hydrocarbons

For the purposes of this study the aromatic hydrocarbons have been designated as either thermally "reactive" or thermally "unreactive." The thermally "reactive" species possess sufficient reactivity in our atmospheric system to undergo a condensation sequence and yield a measurable amount of polymerized carbonaceous residue at 750°C.

The thermally "unreactive" entities have sufficient chemical stability so that such condensation reactions do not occur prior to complete volatilization. Hence, no carbonaceous residues are observed at 750°C for these compounds.

Shown in Figures 2(a) - 2(d) are the DTA thermograms obtained for 58 aromatic hydrocarbon members of the thermally "unreactive" category. All of these thermograms exhibit common characteristic features. For solid compounds, two major endothermic peaks corresponding to the melting and boiling processes are invariably obtained. For liquid compounds, a simple major endotherm representative of the distillation process is always evident. Additionally, no carbonaceous residues are obtained in the DTA sample cups at 750°C and with two exceptions, no products besides starting materials were observed in the condensed distillates.

DTA offers a convenient if not precise method for measuring melting and boiling points for such materials. Depending on the physical characteristics of the apparatus, either the initial inflection point of the endotherm, the endothermic minimum or the endothermic minimum minus the temperature difference between the reference and sample couples may give the more reliable result. The former method has been found to be the most reliable method for ascertaining the melting points in our system. The melting points thus determined for the "unreactive" aromatic hydrocarbons are listed in Table 2 and compared with the appropriate literature values. In most cases the agreement is quite good.

The DTA method also provides a sensitive method for determining the presence of impurities possessing a different melting point from that of the major constituent. The thermograms for a number of the hydrocarbons, namely,

8

Table 2. Thermally "Unreactive" Aromatic Hydrocarbons

Compound No.	Hydrocarbon and (Source No.)	M.P. Lit. °C	M.P. DTA °C	B.P. DTA °C	λ p-band mμ	Calc. I.P. e.v.
I	Benzene	5.5	--	--	208	>10.0
II	Styrene (1)	--	--	170	--	--
III	Biphenyl (1)	70	64	268	247	8.69
IV	Allybenzene (2)	--	--	180	260	8.47
V	Vinylmesitylene (4)	<25	<25	235	260	8.47
VI	Vinyldurene (2)	--	--	255	--	--
VII	Fluorene (3)	114	122	314	261	8.46
VIII	9,10-Dihydroanthracene (3)	108	98	328	271	8.31
IX	2-Methylfluorene (4)	104	113	332	278	8.21
X	Benzo(*l*)phenanthrene (5)	198	197	450	284	8.14
XI	Naphthalene (1)	80	77	245	285	8.12
XII	Vinylxylene (4)	<25	<25	235	286	8.10
XIII	Phenanthrene (1)	100	93	348	292	8.03
XIV	p-Quarterphenyl (1)	320	317	495	292	8.03
XV	Vinyltoluene (4)	<25	<25	200	298	7.96
XVI	4,5-Methylenephenanthrene (2)	116	120	375	299	7.95
XVII	3-Methylphenanthrene (2)	65	45	370	304	7.88
XVIII	5,12-Dihydronaphthacene (2)	--	214	420	306	7.86
XIX	m-Quinquephenyl (2)	--	110	545	308	7.84
XX	1,1'-Binaphthyl (1)	156	140	418	313	7.78
XXI	Tetraphenylethylene (5)	227	230	424	315	7.77
XXII	1-Allylnaphthalene (2)	--	--	295	315	7.77
XXIII	Acenaphthene (3)	95	91	280	319	7.72
XXIV	Chrysene (3)	254	260	460	319	7.72
XXV	9-Benzylidenefluorene (4)	76	80	440	325	7.66
XXVI	Picene (3)	365	370	535	329	7.62
XXVII	Dibenzo(c, g)phenanthrene (2)	178	145	490	329	7.62
XXVIII	Benzo(e)pyrene (2)	179	179	496	331.5	7.60
XXIX	Pyrene (3)	150	146	386	335	7.56
XXX	4,5,9,10-Tetrahydropyrene (4)	138	142	383	300	7.94
XXXI	4-Methylpyrene (2)	143	153	425	338	7.54
XXXII	Benzo(a)fluorene (4)	187	200	420	340	7.52
XXXIII	Benzo(b)fluorene (4)	209	220	420	340	7.52
XXXIV	Azulene (2)	99	99	285	--	--
XXXV	Coronene (6)	430	438	600	342	7.50
XXXVI	1,1,4,4-Tetraphenylbuta-1,3-diene (2)	202	215	460	344	7.48
XXXVII	1-Methylpyrene (2)	72	78	372	344	7.48
XXXVIII	Dibenz(a,c)anthracene (2)	205	208	520	349	7.43
XXXIX	Benzo(b)fluoranthene (4)	168	170	490	350	7.42
XL	Dibenz(a,h)anthracene (1)	265	265	520	350	7.42
XLI	Tetrabenzonaphthalene (4)	215	220	565	350	7.42
XLII	4,6,8-Trimethylazulene (3)	--	85	344	--	--
XLIII	Fluoranthene (3)	110	110	386	359	7.35
XLIV	Benz(a)anthracene (3)	159	166	430	359	7.35
XLV	Dibenzo(a,h)phenanthrene (1)	294	308	537	362	7.32
XLVI	Benzo(a)pyrene (1)	178	170	495	364	7.31
XLVII	Dibenzo(a,e)pyrene (3)	225	237	580	375	7.23
XLVIII	Anthracene (3)	217	215	350	376	7.22
XLIX	2-Phenylanthracene (4)	207	221	465	383	7.17
L	9-Phenylanthracene (2)	153	150	416	383	7.17
LI	Benzo(g,h,i)perylene (4)	281	285	560	383	7.17
LII	9-Methylanthracene (1)	80	77	370	386	7.14
LIII	1,10-o-phenylenepyrene (4)	--	160	538	386	7.14
LIV	9,9'-Bianthryl (3)	320	322	520	389	7.12
LV	9,10-Diphenylanthracene (4)	247	230	485	393	7.10
LVI	9,10-Dimethylanthracene (4)	181	177	400	398	7.06
LVII	Benzo(j)fluoranthene (4)	217	225	495	400	7.05
LVIII	Dibenzo(a,*l*)pyrene (3)	227	225	522	400	7.05
LIX	Perylene (3)	275	295	505	434	6.84

M.P. - Melting point; B.P. - Boiling point; Lit. - Literature; I.P. - Ionization potential.
See Table 1 for Hydrocarbon Source No.

pyrene, benzo(a) fluorene, benzo(b)fluorene, 9, 10-diphenylanthracene, and dibenzo(a, h) phenanthrene exhibit second minor melting endotherms in addition to the major one. These endotherms are due to minor impurities in the commercial materials which can be removed by chromatographic separation. The tendency toward sublimation can also be discerned from the DTA thermogram by a steadily depressing baseline prior to melting. This feature is evident in a number of the thermograms in Figure 2.

The boiling endotherms are generally broad and have no specifically defined inflection temperature. The shape of the endotherm reflects the increasing vapor pressure of the sample with increasing temperature. The gradual approach to the boiling endothermic minimum indicates slow but increasing vaporization. The calculated values of the boiling points listed in Table 2 are the endothermic minima. Very few literature values are available for direct comparison although in cases where such comparisons are possible the agreement appears to be quite good. DTA offers a suitable method of determining atmospheric boiling temperature of extremely high boiling organic materials, such as the aromatic hydrocarbons.

Two of the included materials, vinyl toluene and vinyl xylene exhibit minor endotherms after the major distillation endotherm. The second endotherms result from depolymerization of small amounts of polymer formed in the temperature range of distillation. The large distillation endotherm masks any polymerization exotherm peak. Since the final depolymerization sequence does not lead to any condensed carbonaceous residue, these hydrocarbons have been classed as "unreactive."

Also listed in Table 2 are the frequencies of the long wavelength p-bands determined from the measured electronic spectra by the procedure of Clar.[3] The Hückel relationship (Eq. 1) as employed by Matsen[14] has been utilized to calculate ionization potential parameters for the respective aromatic hydrocarbons from the p-band wavelength. These values are given in the last column of Table 2. The compounds are listed in order of decreasing ionization potential.

$$I.P. = 4.39 + 0.857 \, \lambda_p \qquad \qquad \text{Eq. (1)}$$

$I.P.$ = ionization potential in electron volts

λ_p = wavelength of long wavelength p-band in electron volts

In several instances the p-band definition from UV spectra was uncertain and the ionization potential data have been omitted. Such compounds have been arbitrarily placed in Table 2.

4.2. DTA Thermograms for Thermally "Reactive" Aromatic Hydrocarbons

The thermograms for 25 aromatic hydrocarbons designated as thermally "reactive" are shown in Figures 3(a) and 3(b). All of these compounds undergo thermal condensation and lead to carbonaceous residues at 750 °C in our DTA system.

10

Figure 2(a). DTA Thermograms of Thermally "Unreactive" Aromatic Hydrocarbons, II through XVI.

11

Figure 2(b). DTA Thermograms of Thermally "Unreactive" Aromatic Hydrocarbons, XVII through XXXIII.

12

Figure 2(c). DTA Thermograms of Thermally "Unreactive"
Aromatic Hydrocarbons, XXXIV through XLVI.

13

Figure 2(d). DTA Thermograms of Thermally "Unreactive"
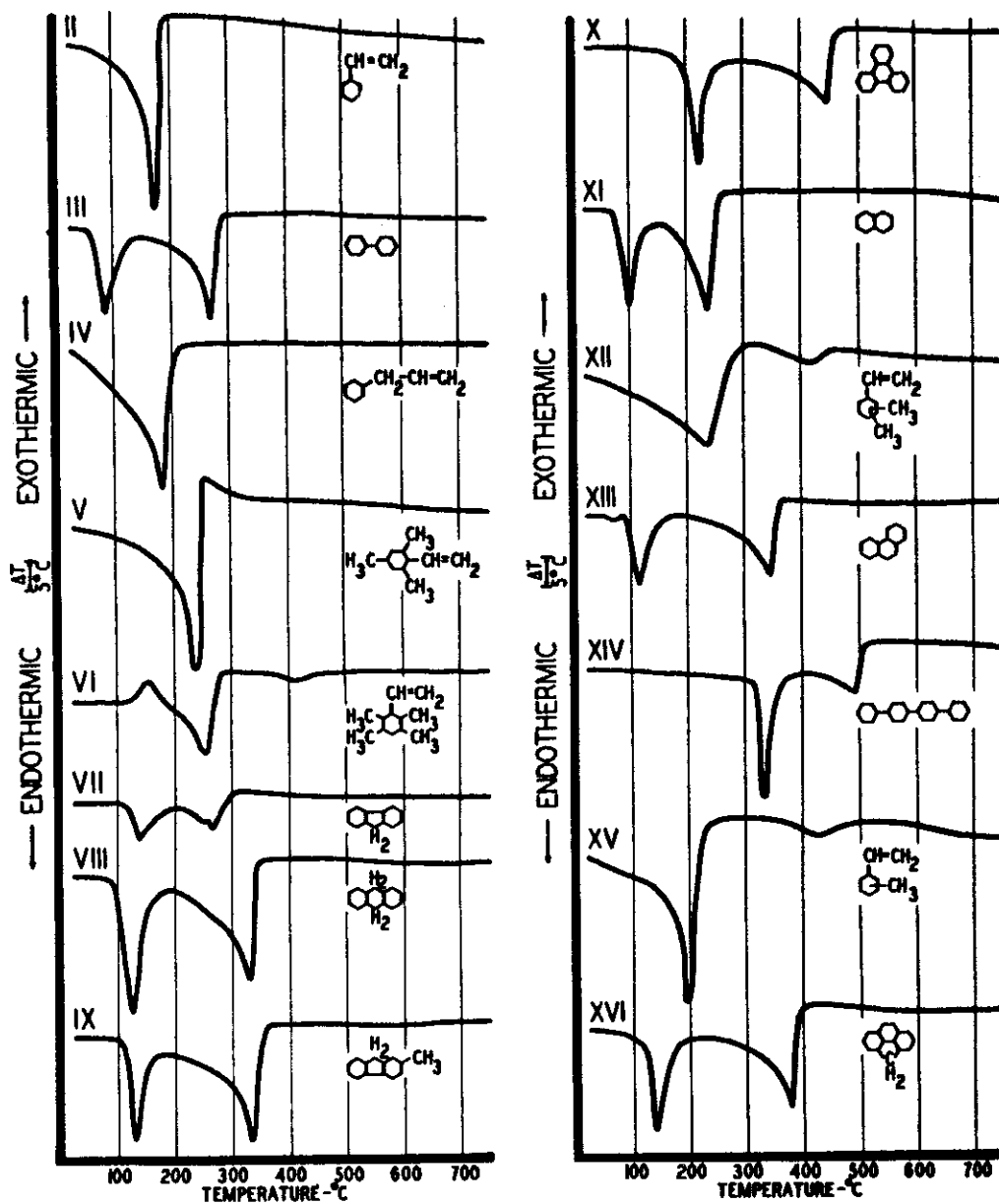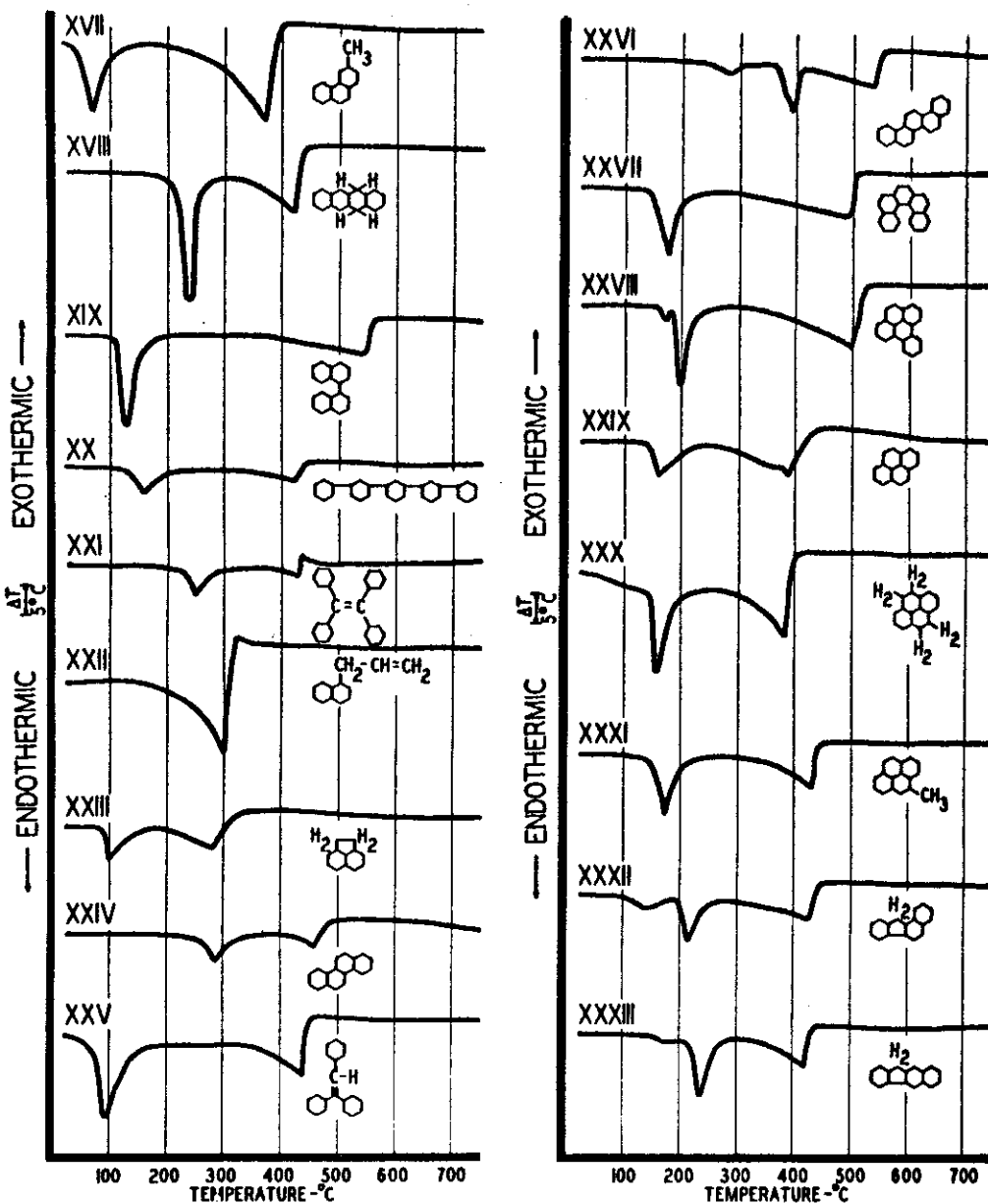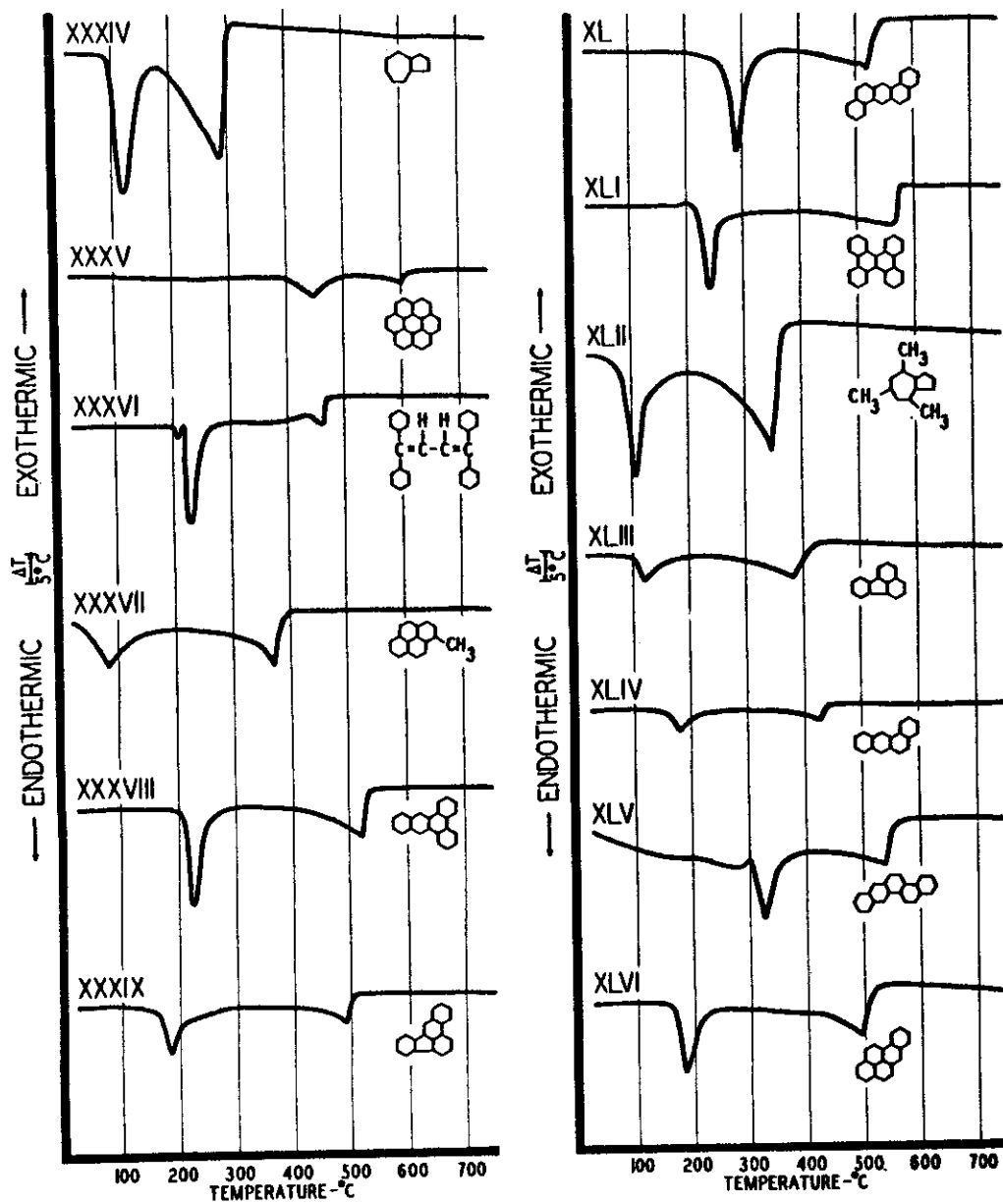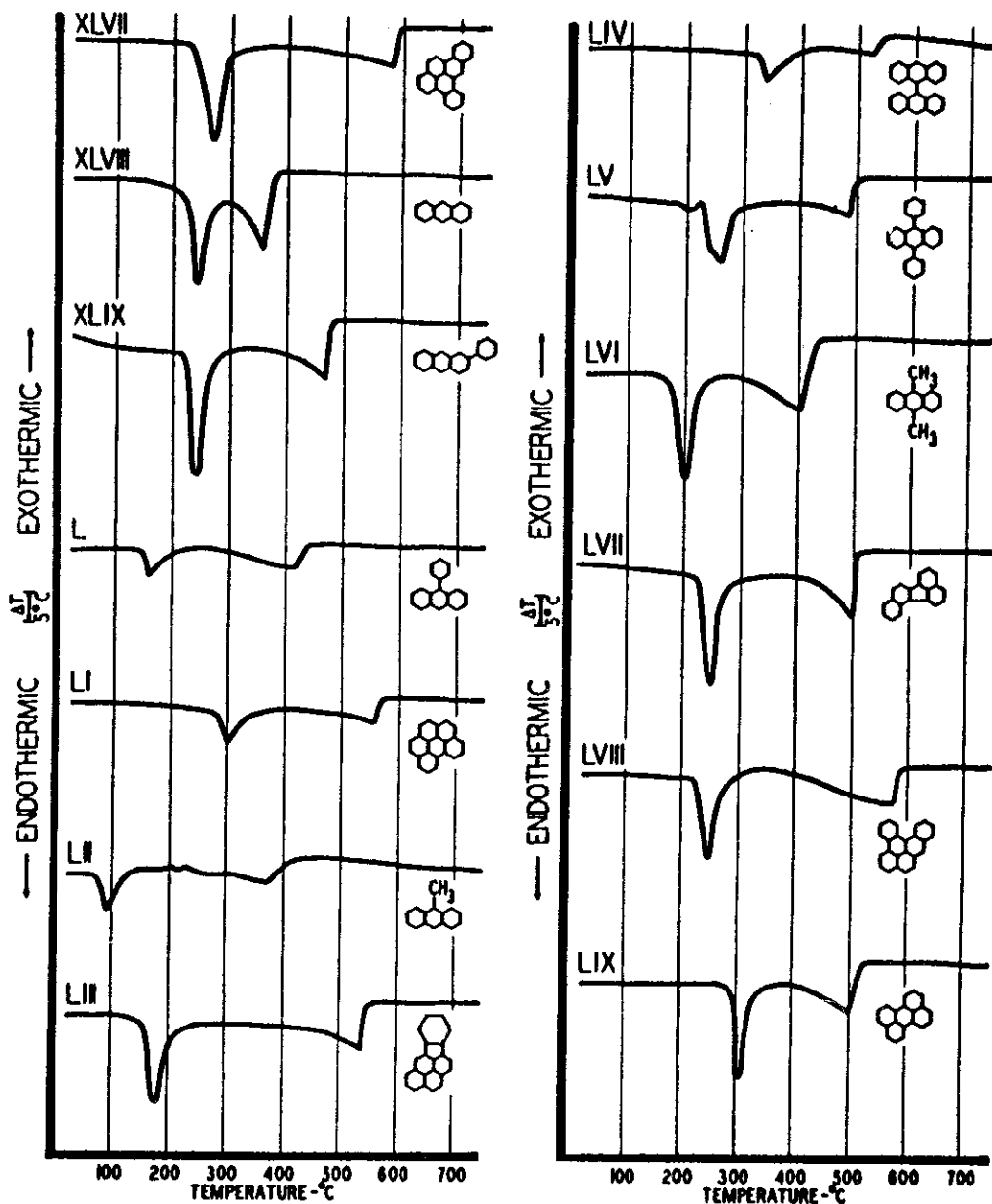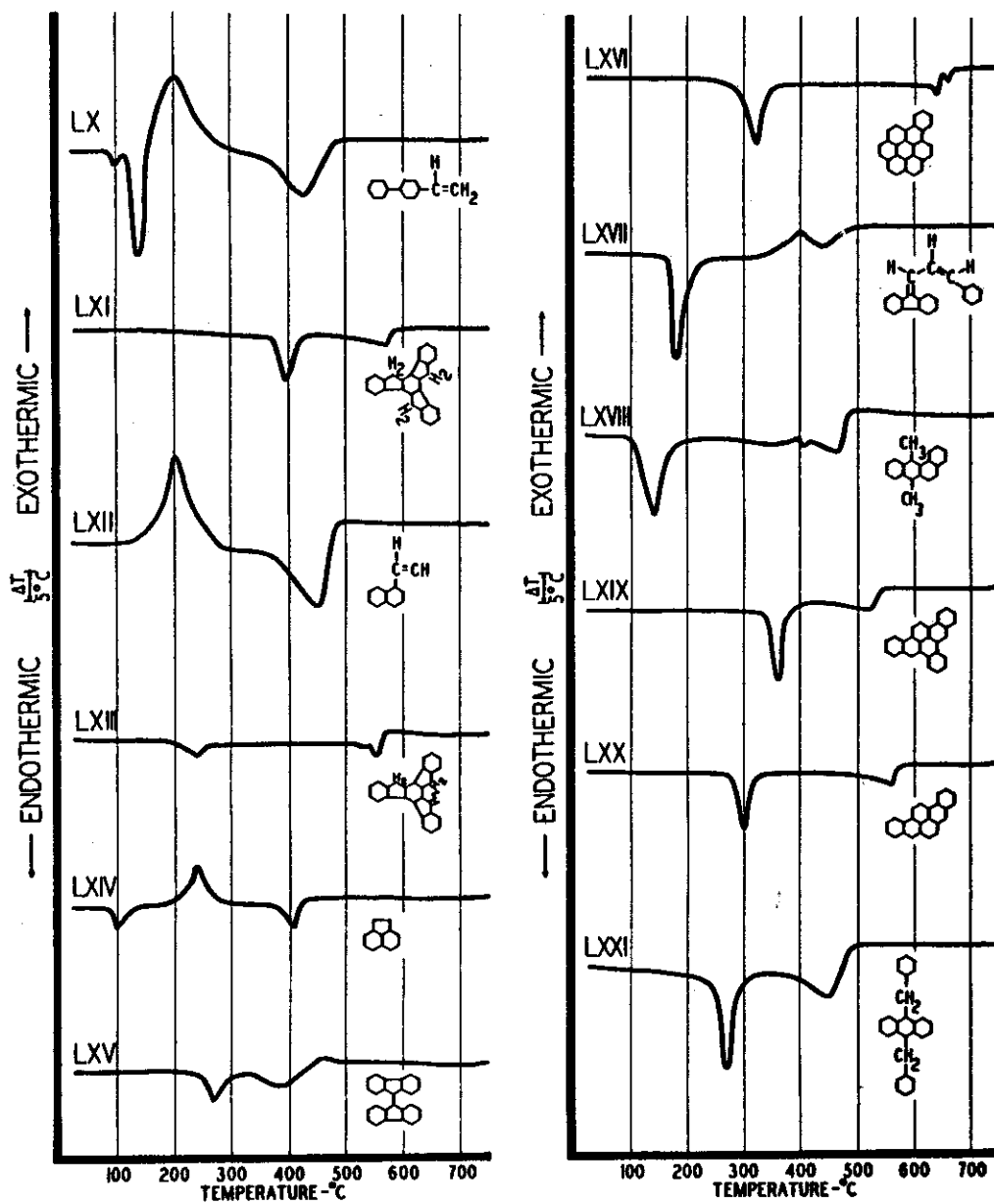Aromatic Hydrocarbons, XLVII through LIX.

14

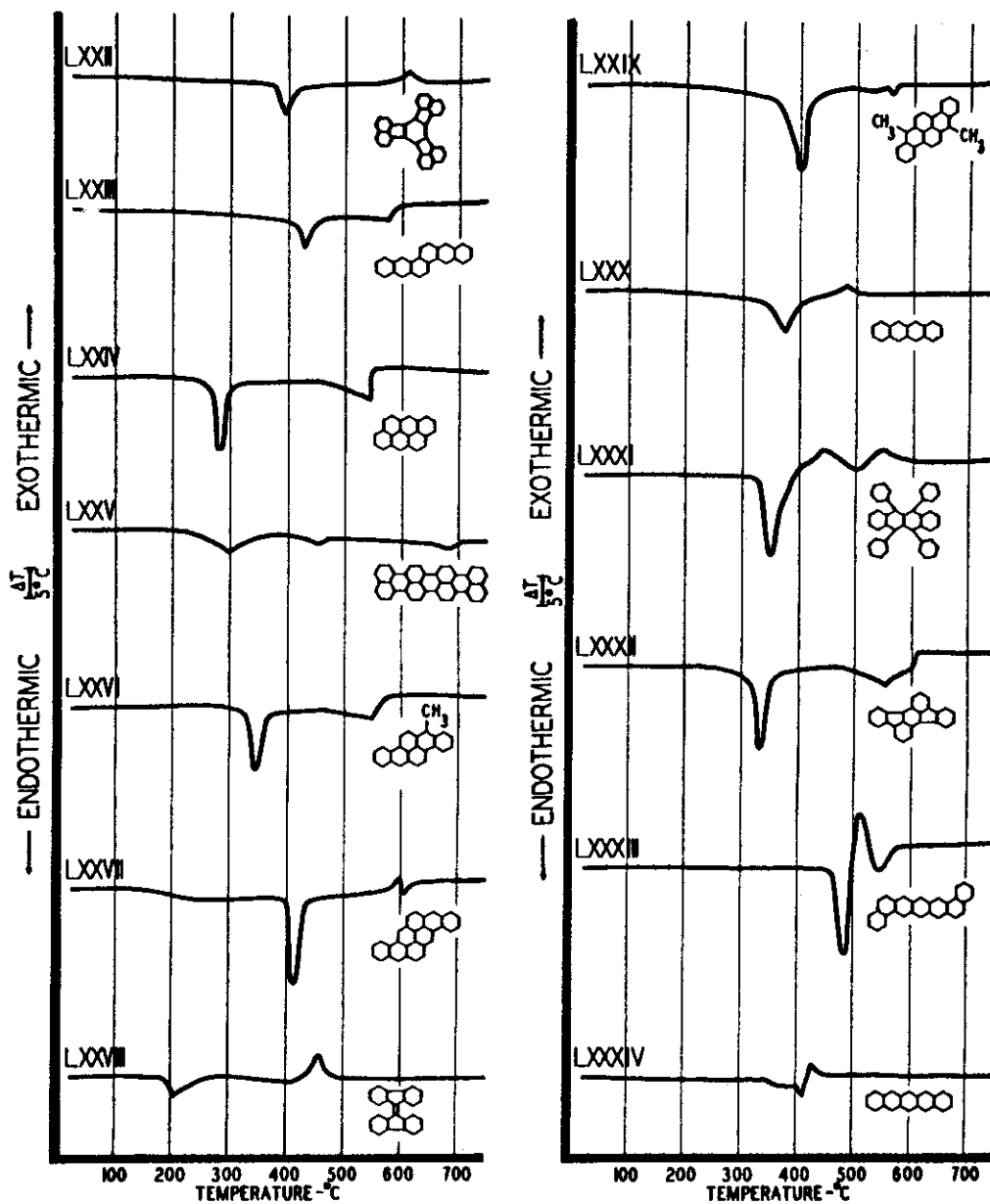Figure 3(a). DTA Thermograms of Thermally "Reactive" Aromatic Hydrocarbons, LX through LXXI.

15

Figure 3(b). DTA Thermograms of Thermally "Reactive"
Aromatic Hydrocarbons, LXXII through LXXXIV.

16

The thermograms for these "reactive" aromatics differ appreciably from those of the previous category. The major melting endotherms are, however, still evident. The DTA melting points have again been calculated from the inflection temperatures and are compared with the literature values in Table 3.

The boiling endotherms are observed to be either completely absent or largely diminished in these thermograms. In a large number of cases, an exothermic peak indicative of polymerization or condensation is found. In nearly every instance new chemical species in addition to starting material were obtained in the condensed distillate. These have been examined by infrared spectrophotometry.

Further listed in Table 3 for the "reactive" aromatics are the percentage carbonaceous residue obtained at 750°C and the temperature of indicated DTA reaction peaks. These latter may be exothermic or endothermic, depending on the combination of physical and chemical changes proceeding at the reaction temperature. Also given in Table 3 are the λ of the long wavelength p-bands and the ionization potentials computed as described in Section 4.1. Again, the compounds have been listed in order of decreasing ionization potential.

4.3. Identification of Condensates Trapped From DTA Runs

Spectrophotometric examination of the DTA condensate traps showed that for nearly all the "unreactive" aromatic hydrocarbons only starting material could be identified. The only exceptions were (XXXVII), 1-methylpyrene, and (LV), 9, 10-diphenylanthracene where slight amounts of new product indicated that some rearrangements may have taken place which yielded non-carbonizable products.

In contrast, the majority of the "reactive" aromatic hydrocarbons showed evidence of new volatile aromatic species in the condensate trap. In a number of cases, these products have been identified by spectral and physical property comparison with known hydrocarbons. In other instances, such identification has not yet been possible.

Summarized in Table 4 are the results of examination of the condensate traps for the "reactive" aromatic compounds.

4.4. DTA Thermograms for Mixtures of Polynuclear Aromatic Hydrocarbons

A major interest in the thermal reaction of aromatic hydrocarbons pertains to their behavior as constituents in petroleum and coal tar fractions in which they are present as complex mixtures. Investigations have been included herein of the thermal behavior of several aromatic hydrocarbon mixtures.

The thermograms for four 1:1 two-component mixtures of aromatic hydrocarbons of the "unreactive" category are shown in Figure 4(a). The mixtures are: fluoranthene-pyrene, phenanthrene-anthracene, fluorene-anthracene, and benz(a)anthracene-anthracene. Reference to the individual component thermograms in Figure 2 will demonstrate the completely additive thermal behavior of these systems. The phenanthrene-anthracene and fluoranthene-pyrene mixtures show single melting and boiling endotherms. In both cases the mixed melting

17

Table 3. Thermally "Reactive" Aromatic Hydrocarbons

Compound No.	Hydrocarbon and (Source No.)	M.P. Lit. °C	M.P. DTA °C	Reaction Temp.* °C	% Residue 750°C	λ p-Band mμ	Calc. I.P. e.v.
LX	4-Vinylbiphenyl (3)	--	120	203(430)	8.1	278	8.21
LXI	10,15-Dihydro-5H-diindeno-[1,2-a:1',2'-c]fluorene (4)	370	375	(570)	32.9	298	7.96
LXII	1-Vinylnaphthalene (4)	<25	--	200(445)	4.2	299	7.94
LXIII	10,15-Dihydro-5H-diindeno-[2,1-a:1',2'-c]fluorene (4)	--		(550)	13.5	336	7.55
LXIV	Acenaphthylene (3)	92	175	245(405)	20.9	339	7.53
LXV	9,9'-Bifluorenyl (3)	247	89	(380)	5.8	364	7.31
LXVI	Benzo(a)coronene (3)	--	250	(637)(652)	30.9	372	7.24
LXVII	9-Cinnamylidene fluorene (2)	154	291	400(435)	9.3	376	7.22
LXVIII	7,12-Dimethylbenz(a)anthracene (1)	122	169	400(405)(460)	4.7	381	7.18
LXIX	Tribenzo(a,e,i)pyrene (3)	297	342	(525)	13.7	384	7.16
LXX	Dibenzo(a,i)pyrene (4)	280	284	(560)	9.8	397	7.07
LXXI	9,10-Dibenzylanthracene (2)	242	251	(445)	8.9	399	7.06
LXXII	Diacenaphtho[1,2-j:1',2'-l]fluoranthene (3)	388	377	610	66.3	402	7.04
LXXIII	Dibenzo[b,k]chrysene (4)	400	412	(571)	22.3	414	6.95
LXXIV	Dibenzol[def,mno]chrysene(4)	257	272	(535)	18.5	430	6.86
LXXV	Benzol[1,2,3-cd:4,5,6-c'd']diperylene (3)	--	295	(455)(680)	91.8	437	6.82
LXXVI	1-Methyl-dibenzo(b,i)pyrene (4)	--	327	(548)	22.7	456	6.72
LXXVII	Pyranthrene (4)	360	400	600(606)	60.1	458	6.71
LXXVIII	9,9'-Bifluorenylidene (6)	188	188	456	31.5	460	6.70
LXXIX	1,6-Dimethyl-dibenzo(b,i)pyrene (4)	373	372	488(525)(557)	33.6	464	6.68
LXXX	Naphthacene (3)	343	340	480	13.9	471	6.64
LXXXI	5,6,11,12-Tetraphenylnaphthacene(1)	333	333	442, 545	43.9	489	6.57
LXXXII	Rubicene (3)	306	315	(551)	9.0	524	6.42
LXXXIII	Dibenzo(a,l)pentacene (4)	440	460	505(540)	53.2	529	6.40
LXXXIV	Pentacene (3)	270	--	(411)426	42.8	576	6.23

*Temperatures in parentheses refer to endothermic reaction peaks. Unclosed temperatures are those for exothermic peaks.

See Table 2 for definition of abbreviations.

18

Table 4. Condensed New Products from DTA Runs
of "Reactive" Aromatic Hydrocarbons

| Compound No.	Starting Material	New Product
LX	4-Vinylbiphenyl	Unknown Aromatic Hydrocarbons
LXI	10,15-Dihydro-5H-diindeno-[1,2-a:1',2'-c]-fluorene	None
LXII	1-Vinylnaphthalene	1-Vinylnaphthalene (Monomer)
LXIII	10,15-Dihydro-5H-diindeno-[2,1-a:1',2'-c]-fluorene	None
LXIV	Acenaphthylene	Acenaphthene + Unknown Hydrocarbons
LXV	9,9-Bifluorenyl	Fluorene, 9,9'-Bifluorenylidene, Tetrabenzo-naphthalene, and Unknown Hydrocarbon
LXVI	Benzo(a)coronene	Slight Amount of Hydrogenated Derivative
LXVII	9-Cinnamylidene fluorene	Fluorene and Major Unknown Hydrocarbon Product
LXVIII	7,12-Dimethylbenz(a)anthracene	Slight Amount of Structurally Similar Hydrocarbon (Monomethyl?)
LXIX	Tribenzo(a,e,i)pyrene	Structurally Similar Hydrogenated Derivative
LXX	Dibenzo(a,i)pyrene	Major Amount of New Products Including Large Proportion of Hydrogenated Derivatives
LXXI	9,10-Dibenzylanthracene	Unknown Hydrocarbon Products
LXXII	Diacenaphtho[1,2-j:1',2'-l] fluoranthene	Acenaphthylene + Acenaphthene
LXXIII	Dibenzo[b,k] chrysene	None
LXXIV	Dibenzo[def,mno] chrysene	None
LXXV	Benzo[1,2,3-cd:4,5,6-c'd'] diperylene	Unknown Hydrogenated Derivative
LXXVI	1-Methyldibenzo(b,i)pyrene	Major Unknown but Structurally Similar Product
LXXVII	Pyranthrene	None
LXXVIII	9,9'-Bifluorenylidene	Fluorene + Major Amount of Unknown Aromatic Hydrocarbon
LXXIX	1,6-Dimethyl-dibenzo(b,i)pyrene	Identical Product to that Obtained for LXXVI
LXXX	Naphthacene	5,12-Dihydronaphthacene
LXXXI	5,6,11,12-Tetraphenylnaphthacene	Unknown Aromatic Hydrocarbons
LXXXII	Rubicene	Slight Amount of Hydrogenated Derivative
LXXXIII	Dibenzo(a,l)pentacene	Unknown Hydrocarbons
LXXXIV	Pentacene	Isomeric Dihydropentacenes

19
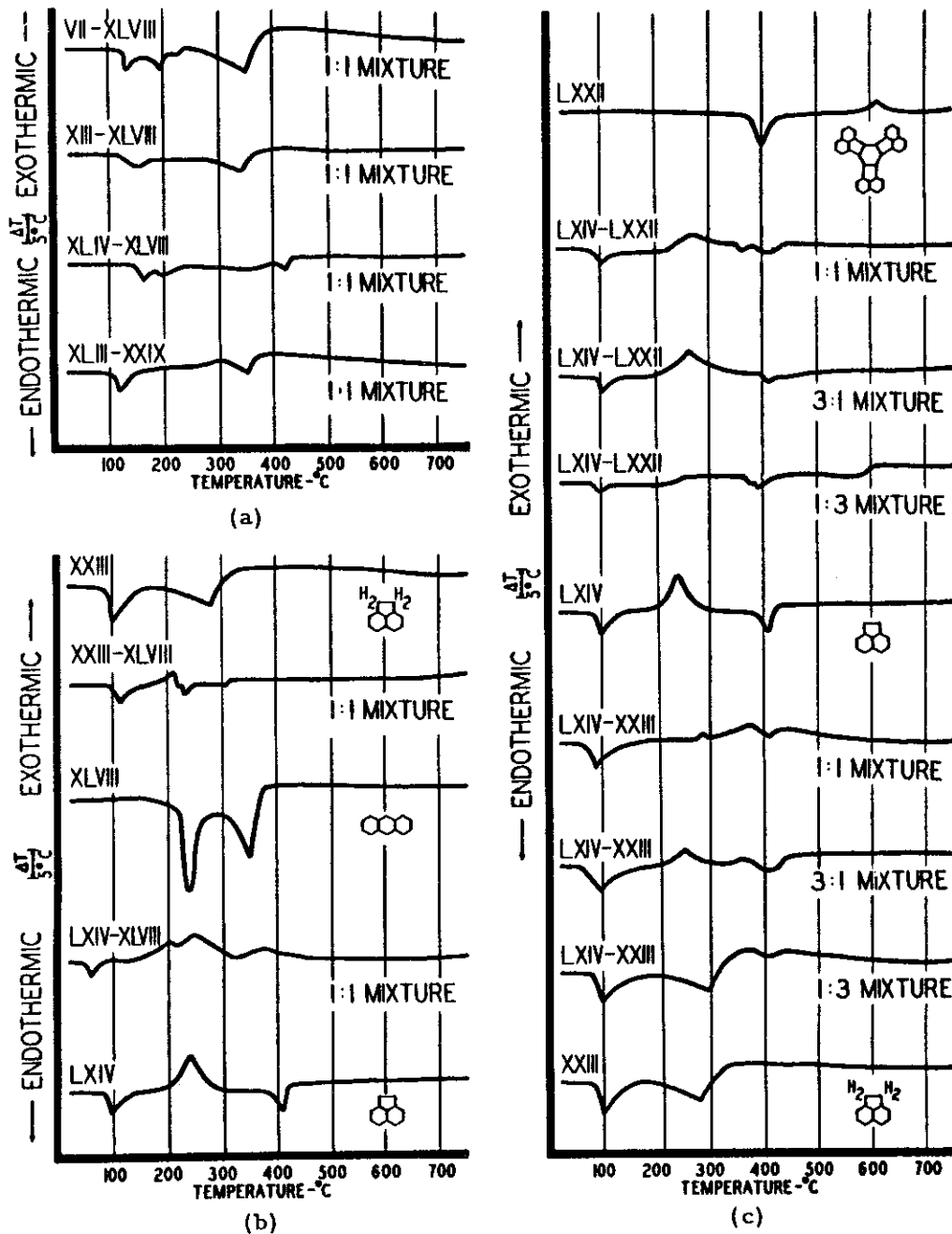
Figure 4. DTA Thermograms of Aromatic
Hydrocarbon Mixtures

20

point indicates a slight depression from that of either of the constituents. This behavior is typical of mixtures in which the higher melting component is soluble in the melt of the lower melting component.

The fluorene-anthracene and benz(a)anthracene-anthracene mixtures exhibit distinctive melting endotherms for each of the components. The boiling endothermic behavior is in all cases additive.

Shown in Figure 4(b) are the DTA thermograms for various percentage mixtures of the "reactive" hydrocarbon acenaphthylene with the "unreactive" hydrocarbon acenaphthene and with the "reactive" aromatic hydrocarbon diacenaphtho-(1, 2-j:1', 2'-1) fluoranthene--(LXXII) [decacyclene]. The individual component curves are included for comparison.

In the acenaphthene-acenaphthylene mixtures, the former compound acts as a diluent for the acenaphthylene reactive thermal sequences. One melting endotherm is observed for the 1:1, 1:3, and 3:1 mixtures. The acenaphthylene exotherm at 245°C is continually diminished by the increased dilution of acenaphthene. In the 1:3 acenaphthylene-acenaphthene mixture, this exotherm is completely obscured by the distillation endotherm of acenaphthene. A continual decrease in the size of the acenaphthylene endotherm at 407°C is also observed with dilution.

The acenaphthylene-decacyclene mixtures again show the effects of dilution on the acenaphthylene exotherm. In the 1:1 mixture, the decacyclene melting endotherm is observed prior to the acenaphthylene reaction endotherm. In the nonequal mixtures, only one broad endotherm is seen encompassing both processes.

The DTA thermograms for 1:1 mixtures of acenaphthylene-anthracene and acenaphthene-anthracene are shown in Figure 4(c). Again the pure component curves are included for comparison. In the acenaphthylene-anthracene system an exothermic doublet is observed. An additional depolymerization peak at 200°C is thus superimposed on the acenaphthylene polymerization peak. The rest of the thermogram also demonstrates nonadditive behavior.

The acenaphthene-anthracene mixture exhibits a thermal reaction exotherm at 200°C. No exotherm is discerned in either of the pure compound thermograms. Following this exotherm, one observes the melting endotherm of the acenaphthene and the distillation endotherm of anthracene. No residue is obtained at 750°C.

4.5. Interrupted DTA Runs

The properties of residues obtained from the interrupted DTA runs of acenaphthylene (LXIV), decacyclene (LXXII), and 9, 9'-bifluorenylidene (LXXVIII) are listed in Table 5. The temperatures at which heating was interrupted are given in the second column. Reference to the original thermograms in Figure 3 shows the reaction stage at which these residues have been obtained. Also listed in Table 5 are the general appearance of the residue, melting point, UV fluorescence color, percentage yield, number average molecular weight, and the presence or absence of free radicals as measured by EPR.

21

Table 5. Summary of Properties of Residues from Interrupted DTA Runs

	Starting Material	Heating Temperature °C	Nature of Residue	Melting Point	UV Fluorescence Color in Solution	% Residue	Molecular Weight	Free Radicals
1.	Acenaphthylene	300	Orange Crystalline Solid	Reddens-315°C Softens 335-350°C	Blue	92.0	1890	No
2.	Acenaphthylene	360	Red Crystalline Solid	325-350°C	Blue	90.0	950	Yes
3.	Acenaphthylene	410	Brown Amorphous Solid	Part at 210°C Rest at 340°C	Green	42.0	1360	Yes
4.	Acenaphthylene	440	Brown Amorphous Solid	Part at 215°C Rest at 325°C	Green	37.0	2025*	Yes
5.	Decacyclene	560	Brown-Green Amorphous Solid	Decomp. 330°C	Green	86.0	----	Yes
6.	Decacyclene	615	Black Carbonaceous Solid	Infusible	Insol.	58.0	----	Yes
7.	9,9'-Bifluorenylidine	382	Red Solid	110-115°C	None	94.5	396	Slight
8.	9,9'-Bifluorenylidine	400	Red Solid	Part 100°C Rest 170-184°C	Blue	88.5	565	Yes
9.	9,9'-Bifluorenylidine	450	Brown-Red Solid	Part 115°C Rest 210-230°C	Blue	72.0	604	Yes
10.	9,9'-Bifluorenylidine	700	Black Carbonaceous Solid	Infusible	Insol.	31.5	----	Yes

*Determined for benzene soluble portion only.

22

5. DISCUSSION OF RESULTS

5.1. Structure and Reactivity

The thermal stability of the aromatic hydrocarbons show a marked dependence on structure. In this investigation 84 aromatic hydrocarbons have been designated as either thermally "unreactive" or thermally "reactive." This classification, although internally consistent within our system, will be affected, as will also the actual reaction temperatures and residue yields, by the experimental conditions employed.

The application of the DTA method to these compounds is extremely useful in permitting the detection of thermal physical and chemical changes. For thermally "unreactive" entities it permits the measurement of atmospheric melting and boiling points. The presence of impurities in the sample can in general be readily determined from the DTA thermogram by observation either of separate melting endotherms or general lowering of the melting endotherm of the major constituent. Additionally, DTA is effective in measuring crystal transformations, polymerizations, and degradations and hence provides an important tool for organic sample identification.

The extension of quantitative procedures to the DTA thermograms presents a means of evaluating such thermodynamic parameters as heats of fusion, heats of vaporization, and heats of reaction for organic compounds. Endothermic and exothermic peaks can thus be equated with calorimetric quantities. It should be emphasized however that the observed peak represents the cumulative thermal changes occurring at the particular temperature range. For the aromatic hydrocarbons, thermal condensation sequences are in many instances concomitant with physical and structural changes of the chemical components. An observed chemical reaction exotherm or endotherm may thus be the additive result of a variety of simultaneous chemical and physical processes.

The categorization of the aromatic hydrocarbons within the respective "unreactive" and "reactive" categories conforms fairly well with their respective classification with regard to general reactivity characteristics. The ionization potential parameters as empirically determined from the measured electronic spectra appear to offer a convenient and readily obtainable reactivity parameter for these materials. The hydrocarbons of high ionization potential generally fall in the "unreactive" class of Table 2. These aromatics on the whole possess I.P. values > 7.10 e.v. The few compounds which are listed in Table 2 and have I.P. ≤ than 7.10 e.v. are borderline cases and can be made to undergo some thermal condensation sequences by slightly modifying the reaction conditions.

The aromatic hydrocarbons listed in Table 3 as thermally "unreactive" fall into two categories. The major class contains species which possess I.P. less than about 7.10 e.v. These materials would be classed as highly "reactive" on almost any chemical scale and are shown in this study to contain sufficient energetic character to readily undergo thermal condensation sequences prior to volatilization.

23

The second class of compounds listed in Table 3 have high I. P. values, > 7.20 e.v., which should normally situate them with the "unreactive" species of Table 2. These compounds, however, have the extraneous structural feature of a readily polymerizable vinyl double bond in addition to an aromatic structure. These hydrocarbons may initially undergo a vinyl-type polymerization to yield large polymer species. This thermal vinyl polymerization sequence differs in kind from the subsequent aromatic condensation sequence or carbonization. For these structural types of aromatics, however, the former process is a prerequisite to the latter. Several borderline compounds in Table 3 consist of aromatics with intermediate I. P., namely benzo(a)coronone and tribenzo(a, e, i)pyrene. For such species one must take into account the added variable of molecular size in addition to general reactivity. The former parameter induces sufficient physical stability in the molecule to permit reaction before volatilization.

The activating effect of alkyl substituents on aromatic carbonization has been noted earlier by Madison and Roberts[8] and is evident in the reactivity of 7, 12-dimethylbenz(a)anthracene.

In summary, the thermal reactivities of the aromatic hydrocarbons in our system show a marked dependence on structure. Employing the spectral p-band measurement and the empirically derived ionization potential as a criterion of reactivity, it is evident that the aromatic hydrocarbons of high ionization potential are thermally "unreactive" whereas those of low ionization potential are thermally "reactive." Molecular size and concomitant physical stability criteria are seen to influence borderline cases in both categories. Additionally, hydrocarbons capable of undergoing vinyl-type polymerizations can produce thermal polymers which represent more reactive molecular entities capable of carbonizing.

5.2. Thermally "Unreactive" Aromatic Hydrocarbons

A majority of the aromatic hydrocarbons reported herein are found to be thermally "unreactive." The thermograms for these materials in Figure 1 illustrate the physical behavior of these compounds as discussed in Section 4.

The individual members of this category possess quite varying structural and reactivity characteristics. The I. P. values for these compounds range from 8.69 e.v. to 6.84 e.v. (although nearly all fall above 7.10) and the ring size from 1 to 7. Yet none of these aromatic molecular entities possess a proper combination of both structural features to permit the initiation of thermal condensation or carbonization sequences prior to volatilization. A large number of the aromatics exhibit chemical thermal stability at temperatures as high as 500 to 600°C.

Included among the aromatic hydrocarbons in Table 2 are four vinyl substituted methyl benzenes. Three of these actually appear to undergo some thermal vinyl polymerization prior to monomer distillation. This polymerization is followed by a depolymerization process as described in Section 4, and leads to non-carbonizing entities.

5.3. Thermally "Reactive" Aromatic Hydrocarbons

Carbonization of aromatic hydrocarbons is essentially a thermal dehydrogen-
ation and condensation sequence with the ultimate product yielding a graphite or
graphite-like material. The thermograms for the "reactive" aromatics in
Figure 3 give some indications of the early thermal reaction steps in carboniza-
tion of the aromatic hydrocarbons. The individual thermograms in general possess
unique characteristics demonstrating that the actual thermal reaction sequences
and temperatures are quite dependent on structure. Although specific types of
rearrangements and polymerizations are indicated for the aromatic hydrocarbon
included in this survey, certain general characteristic features may be discerned
for carbonization reactions in general which are independent of structure. A dis-
cussion of the thermal behavior for the 25 individual "reactive" hydrocarbons which
follows should illustrate these points.

1.   4-Vinylbiphenyl (LX)

The thermogram for this hydrocarbon is similar to that obtained for a num-
ber of the vinyl substituted aromatics included in this study. After the melting
endotherm, a large polymerization exotherm is apparent. This exotherm corres-
ponds to the formation of a vinyl polymer. At about 400°C, thermal depolymeriza-
tion ensues to produce discrete monomer entities which can then revert to the
original vinylbiphenyl or rearrange to form more condensed aromatic hydrocarbons.
The reaction scheme is summarized in Eq. (2).
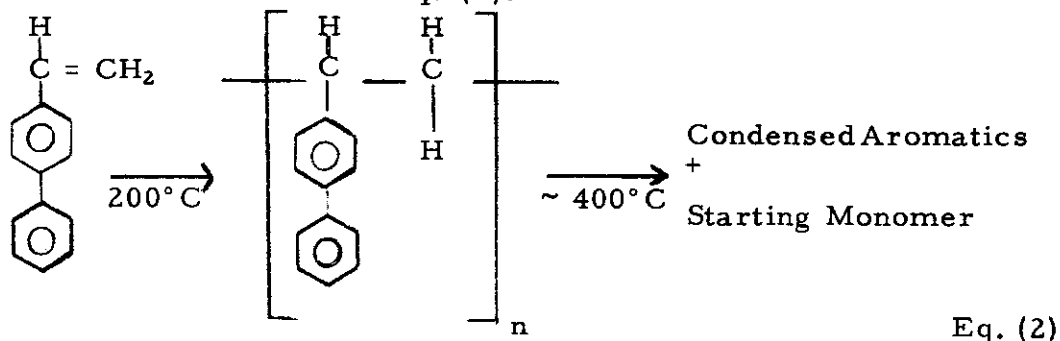
Recombination of the monomer entities into various types of aromatic hydro-
carbon species is possible. Our results are as yet inconclusive regarding the
identity of these products. It is clear, however, that this recombination does lead
to larger condensed aromatic hydrocarbon derivatives which would be classed in
the thermally reactive category. These in turn undergo rapid condensation to
larger aromatic carbonaceous products.

2.   10, 15-Dihydro-5H-diindeno[1, 2-a:1', 2'-c] fluorene (LXI)-a-truxene) and 10, 15-Dihydro-5H-diindeno [2, 1-a:1', 2'-c] fluorene (LXIII)-(β-truxene)

The existence of two isomeric cyclic trimers of indene has recently been
reported.[15]   These isomers have been designated as a- and β-truxene and the

assigned formulas are shown below:
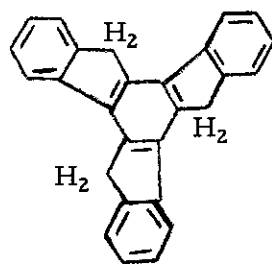
α-truxene   β-truxene

The thermograms for both materials are rather similar, exhibiting melting endotherms and relatively small distillation endotherms at 560°C to 580°C. Both isomers are quite thermally reactive with the α-truxene leading to a 33 per cent carbonaceous residue at 750°C and the β-isomer to a 13.5 per cent yield.

Little is known with regard to the chemistry of these compounds although all indications are that both may be considered as nonplanar m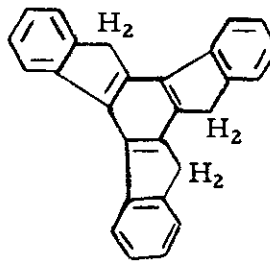oderately strained ring systems. The large size introduces a high degree of physical stability for these molecules, although on an energy scale their ionization potentials are quite high. It is likely that at high temperatures, thermal disproportionation of both ring structures occurs and then leads to a recombination in the form of reactive carbonizing aromatic species. Like the "reactive" hydrocarbons already discussed, these molecules possess reactive polymerizable bonds exocyclic to the benzenoid ring system.

3.   1-Vinylnaphthalene (LXII)

The thermogram for 1-vinylnaphthalene exhibits the characteristic features of the vinyl "reactive" aromatics. Comparable to 4-vinylbiphenyl, this hydrocarbon exhibits a large polymerization exotherm at 200°C and a depolymerization endotherm at 460°C. A 4.2 per cent carbonaceous residue is obtained and again a thermal polymerization, depolymerization, and recombination sequence is indicated.

Eq. (3)

26
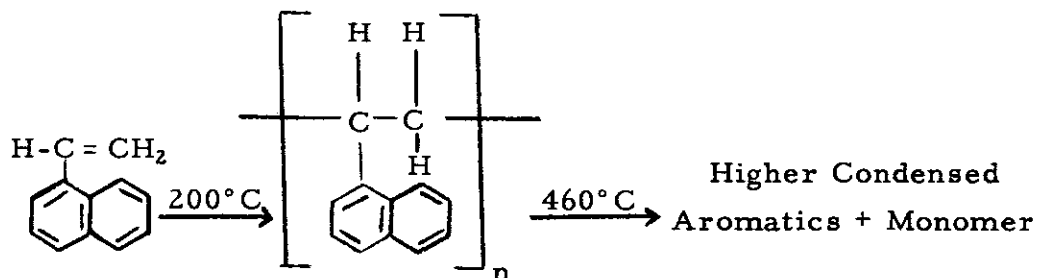
The higher condensed aromatics formed from the thermal depolymerization of polyvinylnaphthalene are apparently "reactive" entities and undergo a rapid carbonization sequence. These species may be similar to those formed from acenaphthylene.

4.   Acenaphthylene (LXIV)

Acenaphthylene is a further example of a vinyl substituted aromatic hydrocarbon of high ionization potential which is quite reactive thermally. The pyrolysis of this compound has been studied by Dziewonski.[16]
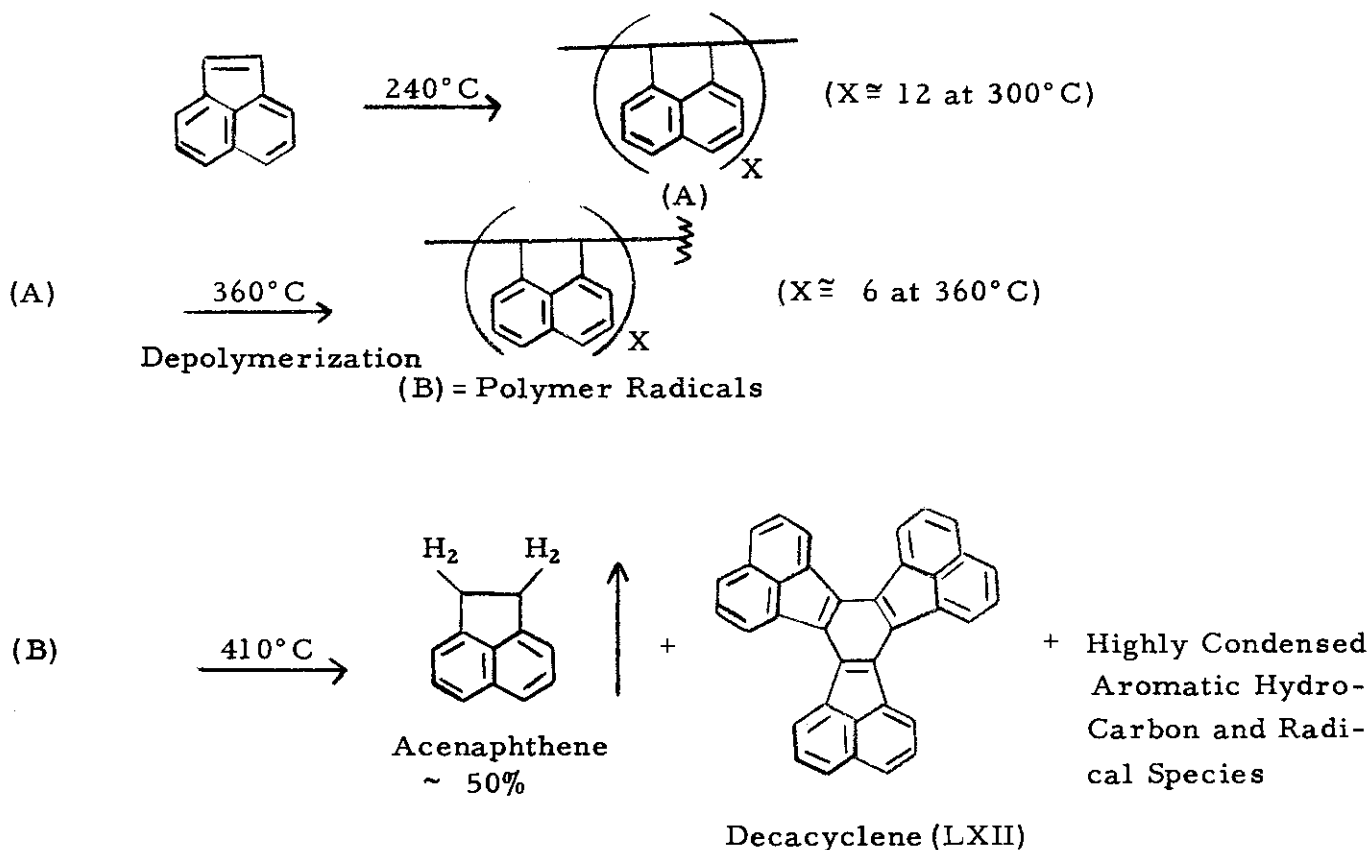
As seen from the thermogram in Figure 3(a), acenaphthylene shows the characteristic vinyl polymerization exotherm at about 240 °C. Polymer degradation and rearrangement reactions give rise to the endotherm at 400 °C. This endotherm like that for the previous "reactive" vinyl aromatics encompasses both chemical depolymerization and rearrangement processes as well as pure physical transformations of melting and boiling.

The major volatile product obtained from the polyacenaphthylene depolymerization sequence is the hydrogenated hydrocarbon acenaphthene. The extensive formation of this hydrocarbon demonstrates the importance of thermal hydrogen transfers in this reaction. This will be discussed further in the following section.

Application of the interrupted DTA technique to acenaphthylene as summarized in Table 5 shows that the formation of the stable derivative acenaphthene at 400 °C is accompanied by extensive rearrangement of acenaphthylene-like moieties to a variety of complex hydrocarbon products. This process occurs between samples 1 and 2 in Table 5. The transformed hydrocarbons as found in the thermal residue are highly reactive toward further condensation as evidenced by the growth in molecular size between samples 3 and 4. Additionally, these materials exhibit significant paramagnetism suggesting that these thermal products may be composed of aromatic hydrocarbon free radical species. A thorough discussion of the paramagnetism of organic thermal chars has been presented by L. S. Singer.[17]

Although Dziewonski, as well as others, has postulated various products from the pyrolysis of acenaphthylene, the structural verification of these remains uncertain. We have separated a variety of large complex aromatic materials from the acenaphthylene thermal residue but will refrain from any structural assignments until after obtaining further proof. One of the minor products which has been verified, is the dehydrogenated trimer diacenaphtho[1, 2-j: 1', 2'-𝑙] - fluoranthene (LXXII) or decacyclene.

27

The generalized reaction scheme for acenaphthylene may be represented by Eq. (4).

(X ≅ 12 at 300°C)

(A)

(X ≅ 6 at 360°C)

(A) → 360°C
Depolymerization

(B) = Polymer Radicals

(B) → 410°C

Acenaphthene
~ 50%

+

Decacyclene (LXII)

+ Highly Condensed
Aromatic Hydro-
Carbon and Radi-
cal Species

Eq. (4)

Investigations of these reactions are being continued with the purpose of elucidating the nature of the condensed aromatic species and radicals.

5.   9,9'-Bifluorenyl (LXV)

The thermogram for 9,9'-bifluorenyl shows a typical melting endotherm which is followed by a very broad endothermic region at about 380°C and then a slight exotherm at 460°C. Our results indicate that at 380°C a disproportionation reaction is occurring in the manner shown in Eq. (5)

9,9'-bifluorenyl   9,9'-bifluorenylidine   fluorene
                                   (LXXVIII)   (VII)
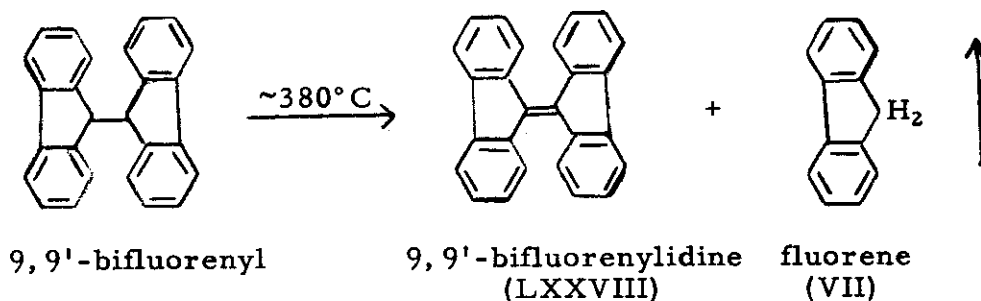
Eq. (5)

The ~380°C endotherm represents predominantly the gradual distillation of the stable hydrocarbon fluorene which is forming continuously at this temperature range. The reaction exotherm is the same as that seen for 9,9'-bifluorenylidine (LXXVIII) in Figure 3(b). This sequence provides another example of a pure thermal hydrogen transfer disproportionation sequence for an aromatic hydrocarbon.

The 5.8 per cent carbon yield obtained from 9,9'-bifluorenyl is derived from the thermal reactions of the 9,9'-bifluorenylidine entity. The reactions of this latter hydrocarbon will be discussed later.

6.   Benzo(a)coronene (LXVI)

On an energy scale benzo(a)coronene is a fairly unreactive aromatic hydrocarbon, I.P. = 7.24 e.v. Its large size induces extreme physical stability so that no distillation occurs prior to the reaction temperature of 640°C. As seen in the thermogram in Figure 3(a) endothermic and exothermic peaks are observed in this temperature range. A high degree of reactivity leading to a 31 per cent carbonaceous residue is evident. Indications are that the reactive sequence at 640°C involves thermal hydrogen transfers between molecular species to produce volatile hydrogenated derivatives of benzo(a)coronene.

The higher condensed species are too complex to be chemically identified.

7.   9-Cinnamylidene Fluorene (LXVII)

This hydrocarbon possesses polymerizable double bonds exocyclic to the aromatic ring structure. The thermogram in Figure 3(a) does show a polymerization exotherm at 400°C and a subsequent endotherm at 440°C. A 9.3 per cent carbonaceous residue is obtained.

It is not clear whether this sequence represents a polymerization, depolymerization, and recombination sequence as has been found for some of the previous aromatic olefinic compounds. Possibilities exist in this hydrocarbon for direct rearrangement to more highly condensed aromatic ring systems. The identify of the reaction products has not yet been established. The formation of fluorene as a minor product may be indicative of some cinnamyl-fluorene bond cleavage.

29

8. 7, 12-Dimethylbenz(a)anthracene (LXVIII)

Whereas benz(a)anthracene (XLIV) has been classed as thermally unreactive, introduction of 2 methyl groups into the 7, 12-positions induces reactivity and leads to a 4.7 per cent carbon residue. On an energy scale, the methyl substitution lowers the ionization potential of the molecule from 7.35 to 7.18 e.v.

Madison and Roberts[8] have reported a general effect of alkyl substitution on increasing the thermal reactivity of aromatic hydrocarbons. These authors postulated the ease of formation of benzyl-type radicals by hydrogen dissociation and subsequent cleavage of the aryl-alkyl bonds as a prime factor in this effect.

The thermogram for this hydrocarbon demonstrates a complex thermal sequence at 400°C to 475°C. A slight exothermic region at about 400°C may indicate some chain process such as proposed by Madison and Roberts. A large endothermic peak resulting from distillation, however, largely masks this change. Slight amounts of volatile structurally similar products which may be monomethyl derivatives have been obtained although this structural designation is not conclusive.

9. Tribenzo(a, e, i)pyrene (LXIX)

The I.P. for tribenzo(a, e, i)pyrene is fairly high (7.16 e.v.) for a condensed aromatic of its size. Probably both factors enter into its reactivity and resultant 13.7 per cent carbon yield. The thermogram in Figure 3(a) shows the usual melting endotherm but very little indication of a distillation endotherm. It is likely that exothermic condensation sequences may be combining with physical distillation to provide a relatively flat curve in the reactive temperature region between 450°C and 520°C.

The volatile products obtained in this temperature region appear to be hydrogenated derivatives of the starting material. Thermal hydrogen transfer sequences are therefore involved in carbonization of this compound.

10. Dibenzo(a, i)pyrene (LXX)

Several dibenzopyrenes (XLVII) and (LVIII) have been classed as thermally "unreactive." The low I.P. for the a, i-isomer compared to (XLVII) and its increased physical stability as compared to (LVIII) leads to an eventual 9.8 per cent carbon residue.

The thermogram in Figure 3(a) is very uncharacteristic and exhibits the melting endotherm plus a diminished volatilization endotherm at 560°C. This latter small endotherm may again be a cumulative representation of a variety of concurrent processes. Extensive hydrogen transfers are occurring in this temperature region as evidenced by the large proportion of hydrogenated derivative in the condensate.

11.   9, 10-Dibenzylanthracene (LXXI)

9, 10-Dibenzylanthracene has about the same I.P. (7.06 e.v.) as the 9, 10-dimethyl derivative (7.05 e.v.) and the 9, 10-diphenyl derivative (7.10 e.v.). The former compound is the only one to demonstrate reactivity, however, leading to an 8.9 per cent carbon residue. This effect is probably not due to size induced physical stability since the reaction of the 9, 10-dibenzyl compound occurs at a temperature intermediate between the boiling points of the other two cited derivatives.

Reactivity may be interpreted in terms of ease of formation of phenyl-methyl type radicals by hydrogen dissociation analogous to the reaction discussed for (LXVIII). The thermogram for dibenzylanthracene exhibits a very broad endothermic region at about 450°C. This endotherm encompasses a variety of complex changes and leads to the formation of new condensed aromatic species.

12.   Diacenaphtho(1, 2-j:1'2'-*l*)fluoranthene(LXXII)(decacyclene)

The formation of this hydrocarbon as a product of the thermal condensation of acenaphthylene (LXIV) has been mentioned previously. The thermogram in Figure 3(b) shows a high temperature exotherm at 610°C for this hydrocarbon. Interrupted DTA studies show that this exothermic region represents the disproportionation of decacyclene into acenaphthylene like moieties and recombination of these to yield condensed aromatic species identical to those found for the reacting acenaphthylene entities discussed earlier.

The formation of acenaphthylene and acenaphthene as volatile products results again from thermal hydrogen transfer between thermally reacting aromatic hydrocarbon entities. This reaction may be summarized in Eq. (6).

decacyclene

+ Highly Condensed Aromatic Hydrocarbon and Radical Species
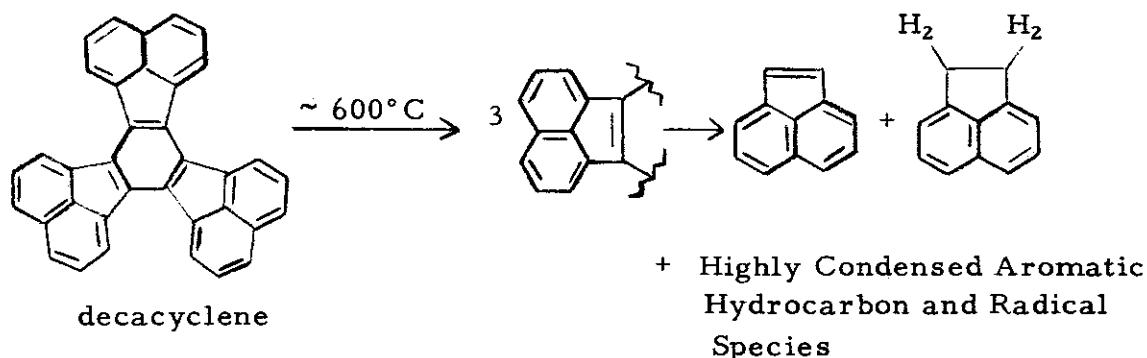
Eq. (6)

13.   Dibenzo[b, k] chrysene (LXXIII)

This large hydrocarbon is quite reactive (I.P. = 6.95 e.v.) and as would be expected leads to a high carbon residue of 22.3 per cent. The DTA thermogram is unspecific and this compound, after melting at 420°C, appears to undergo continual volatilization and reaction up to a final temperature of 570°C at which point a residual carbonaceous product is left. No new volatile products have been identified.

14. Dibenzo[def, mno] chrysene (LXXIV)

The thermogram for (LXXIV) is nonspecific showing a melting endotherm and a distillation endotherm at 535°C. High thermal reactivity would be expected from this hydrocarbon from its low I.P. of 6.86 e.v. This is confirmed by a high carbon yield of 18.5 per cent.

Further condensations of (LXXIV) would be expected to produce large and complex aromatic entities. No discrete chemical compounds have been isolated from this pyrolysis.

15. Benzo[1, 2, 3-cd:4, 5, 6-c'd'] diperylene (LXXV)

The hydrocarbon (LXXV) commonly known as quaterrylene is an 11-ring condensed aromatic with I.P. = 6.82 e.v. Its thermogram shows 2 small endotherms at 445°C and 680°C following the initial melting endotherm. The latter endotherm is the highest temperature transformation for an aromatic hydrocarbon observed in our studies. An extremely high carbonaceous residue of 91.8 per cent is obtained at 750°C.

The two high temperature endotherms may likely encompass thermal hydrogen transfer type disproportionations and condensations since hydrogenated quaterrylene derivatives are observed to distill at these temperature regions.

16. 1-Methyl-dibenzo(b, i)pyrene (LXXVI)

This methyl-dibenzopyrene derivative is far more reactive than any of the previously considered dibenzopyrenes. A carbon residue of 22.7 per cent is obtained again demonstrating the efficacy of alkyl substituents towards increasing thermal reactivity.

The thermogram in Figure 3(b) shows a small but protracted endothermic region from 470°C to 540°C. Gradual condensation reactions and formation and distillation of new, more stable hydrocarbon products are occurring in this temperature region. These hydrocarbon products appear to be either rearranged methyl derivatives or hydrogenated starting species.

17. Pyranthrene (LXXVII)

Pyranthrene is a large hydrocarbon (8 condensed rings) of very low I.P. (6.71 e.v.). Its extreme thermal reactivity leading to a 60.1 per cent carbon residue is therefore not surprising. Its thermogram demonstrates a consecutive exothermic and endothermic region at 600°C. This thermal feature at carbonizing temperatures has been seen for a number of the reactive aromatic hydrocarbons. No new reaction products have been identified from the carbonization process for pyranthrene.

18. 9, 9'-Bifluorenylidine (LXXVIII)

The formation of bifluorenylidine from the thermal disproportionation of 9, 9'-bifluorenyl has been cited earlier. Bifluorenylidine is more thermally reactive than the latter material leading to a carbon residue of 31.5 per cent. A large polymerization exotherm is seen to occur at 456°C in the thermogram in Figure 3(b). Investigation of the distillates and residues (Table 5) indicates the formation of fluorene and tetrabenzonaphthalene as reaction products. Additional aromatic hydrocarbons and radical species are also formed.

The formation of fluorene results from a disproportionation and hydrogen transfer sequence. The formation of tetrabenzonaphthalene results from a bond rearrangement. Lang, Buffleb and Kalowy [18] have studied the pyrolysis of fluorene at 700°C and reported the formation of tetrabenzonaphthalene along with rubicene and a rubicene isomer as products. We have not observed rubicene (LXXXII) as a reaction product of bifluorenylidine or bifluorenyl. A generalized thermal reaction scheme for 9, 9'-bifluorenylidine may be written as in Eq. (7).

9, 9'-bifluorenylidine   fluorene   tetrabenzonaphthalene
                                (VII)   (XLI)

+   Reactive Condensed
    Aromatic Hydrocarbons
    and Radicals
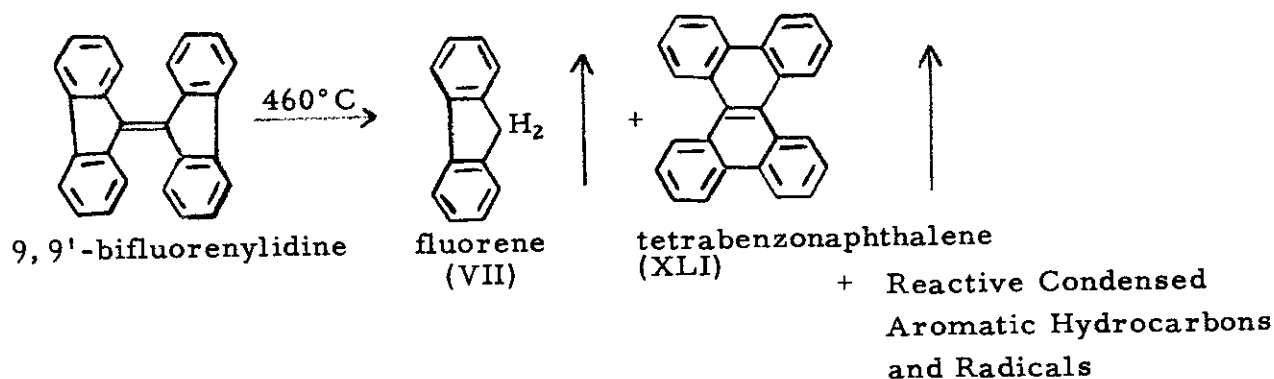
Eq. (7)

Both fluorene and tetrabenzonaphthalene are thermally stable and readily distill at the exothermic temperature region. The residual aromatic product is, however, highly reactive and contributes to the ultimate carbonization condensation process.

19. 1, 6-Dimethyl-dibenzo (b, i) pyrene (LXXIX)

Introduction of a second methyl substituent on the dibenzo (b, i) pyrene nucleus increases thermal reactivity over that of the monomethyl derivative (LXXVI). A carbonaceous residue of 33.6 per cent is obtained for this reactive hydrocarbon, (I.P. = 6.68 e.v.). The thermogram shows a small exotherm at 488°C followed by a small broad endotherm at 525°C and a minor sharp endotherm at 557°C. The trapped condensate showed the formation of a new hydrocarbon entity which is identical to that obtained from the monomethyl compound, (LXXVI).

These results are consistent with the scheme cited earlier for alkyl activation of thermal reactivity via cleavage of aryl-alkyl bonds to create readily carbonizable entities since identical products are obtained from the monomethyl

33

and dimethyl derivatives. Further investigations of these systems to elucidate the nature of these effects are in progress.

20. Naphthacene (LXXX)

High thermal reactivity would be expected for naphthacene based on its low I.P. (6.64 e.v.). The thermogram produces a reaction exotherm subsequent to the melting endotherm. An ultimate carbon residue of 13.9 per cent is formed. The formation of the stable 5,12-dihydro-derivative (XVIII) at this temperature region has been confirmed. It is likely that the initial thermal condensations as well as the hydrogen transfers occur at these reactive 5,12-positions.

21. 5,6,11,12-Tetraphenylnaphthacene (LXXXI)

Substitution by phenyl groups in the naphthacene nucleus greatly increases thermal reactivity as shown by the large 43.9 per cent carbon residue for the 5,6,11,12-tetraphenyl derivative. Reaction occurs at a much lower temperature for this derivative (442°C) as compared to naphthacene (480 °C).

The thermogram for LXXXI actually shows a double exothermic region with peak maxima at 442°C and 545°C. The nature of these reactions is not yet known and they result in production of unidentified complex aromatic hydrocarbons species. The thermal reactions of this interesting hydrocarbon are being subjected to further study.

22. Rubicene (LXXXII)

The low I.P. for rubicene (6.42 e.v.) would predict significant thermal reactivity. The rubicene thermogram shows a broad complex endothermic region at 550°C following the melting endotherm. A carbon yield of 9 per cent is observed.

Again hydrogenated derivatives are produced and distilled in this temperature region.

23. Dibenzo (a, *l*) pentacene (LXXXIII)

A high carbon residue of 53.2 per cent is obtained for this extremely reactive aromatic, (I.P. = 6.40 e.v.). A very significant condensation exotherm at 505°C is seen to follow the melting endotherm in the thermogram of dibenzopentacene. This exotherm then leads to a sharp endotherm at 540°C. The hydrocarbon products formed at this temperature have not yet been identified.

24. Pentacene (LXXXIV)

The thermogram for pentacene illustrates a complex endothermic region from 350°C to 410°C, followed by a reaction exotherm at 425°C. Distillation of isomeric dihydropentacenes resulting from thermal hydrogen transfer reactions occur in this temperature interval. A large carbon residue of 42.8 per cent is observed.

5.4. Binary Mixtures of Polynuclear Aromatic Hydrocarbons

The petroleum and coal tar products which comprise the major source of raw materials for the production of carbon are mixtures of many molecular species. The catalytic or synergistic effect of the presence of one aromatic hydrocarbon on the thermal reactivity of another is of practical interest. All of the previously discussed results emphasize the importance of thermal hydrogen transfer between aromatic molecules in the precarbonization sequence. Under the proper circumstances it should be possible to demonstrate the interaction between two different and known molecular aromatic species. The DTA technique offers a useful means of detecting such possible thermal interactions. The results of examinations of several unreactive mixtures as well as several reactive mixtures are discussed.

1. Unreactive Mixtures

The thermograms in Figure 4(a) demonstrate the additive thermal behavior of two types of mixtures of refractory hydrocarbons which also do not interact. The case of two immiscible or only slightly miscible hydrocarbons is illustrated in the first and third thermograms in Figure 4(a). The endothermic peaks observed correspond to the melting and boiling points of the individual compounds. Small temperature shifts indicate some solubility of components. The second and fourth thermograms in Figure 4(a) illustrate the case for mixtures of miscible materials. The melting endotherm of the higher melting component does not appear and a common boiling endotherm displaced to lower temperatures is observed.

The effects of dilution of a thermally reactive hydrocarbon, acenaphthylene (LXIV), with a refractory hydrocarbon are shown in Figure 4(b). These mixtures were examined because diacenaphtho[1,2-j:1',2'-*l*] fluoranthene (LXXII), also known as decacyclene, and acenaphthene (XXIII) are logical products of the reaction of acenaphthylene. By polymerization and hydrogen transfer reactions, six molecules of acenaphthylene can form one molecule of decacyclene and three molecules of acenaphthene.
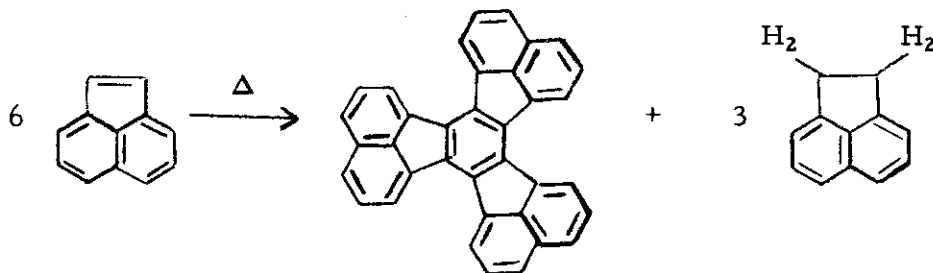
The presence of the 407°C endotherm in the acenaphthylene thermogram (LXIV) appeared to corroborate this hypothesis. However, from the thermograms of the mixtures in Figure 4(b), curves 2, 3, and 4, the 407°C endotherm does not appear to result from the presence of decacyclene. Instead a double endotherm is observed. The first endotherm, at about 365°C in the 1:1 mixture, is believed to be the decacyclene melting point lowered by the presence of polyacenaphthylenes. The

second at 407°C is the polyacenaphthylene decomposition and distillation endotherm. The presence of the decacyclene reduces the extent of acenaphthylene reaction and shifts it to higher temperatures. The reactions of decacyclene discussed earlier also appear to be attenuated by the presence of the acenaphthylene products.

Under the thermal conditions of the DTA experiments, there is no chemical interaction between acenaphthylene (LXIV) and its saturated homolog, acenaphthene (XXIII). There is a very evident dilution effect on the polymerization of acenaphthylene in the presence of acenaphthene. The thermograms of these mixtures, curves 6 through 8 in Figure 4(b), show a shift in the reaction exotherm to higher temperatures with increased dilution and a large reduction in the carbon yield obtained at 750°C.

Heat-treatment experiments with acenaphthylene-acenaphthene mixtures under reflux conditions for long periods indicate that acenaphthene does react slowly with the complex acenaphthylene polymerization products. The experiments have shown that continued heating of acenaphthylene polymer above its melting point of 250°C to 275°C results in a depolymerization reaction that produces about equal quantities by weight of acenaphthene and a heterogeneous pitch-like product. Continued heating under reflux at the boiling temperature of this solution (approximately 295°C) slowly reduces the concentration of acenaphthene. It is postulated that the acenaphthene is converted to acenaphthylene through hydrogen transfer reactions to activated polymer molecules or free radicals. The overall rate of this conversion is low under the conditions of the experiments conducted to date.

2. Reactive Mixtures

The thermograms in Figure 4(c) presenttwo examples of thermal interactions between unsubstituted polynuclear aromatic hydrocarbons. In both cases the thermograms show exothermic reactions in the mixtures that are not shown by the pure materials alone.

Andersen and Norrish[19] have recently reported a reaction between photosensitized anthracene and styrene at 70°C. These authors postulated a hydrogen transfer from styrene to photoexcited triplet-state anthracene molecules. Such an interaction facilitated the polymerization of styrene and led to incorporation of 9,10-dihydroanthracene in the polymer.

A similar reaction is observed on heating a 1:1 mixture of acenaphthylene (LXIV) and anthracene (XLVIII) in the DTA apparatus. The anthracene is moderately soluble in molten acenaphthylene. The solution undergoes polymerization and solidifies between 150° and 200°C. It then melts, changes color, and recrystallizes again into fern-like needles. These transformations are shown in the two exotherms at 200° and 235°C in curve 4 in Figure 4(c) and have been observed in the hot stage microscope. It is believed that acenaphthylene reacts in a hydrogen transfer process with excited anthracene leading to the formation of 9,10-dihydroanthracene as one of the products.

36
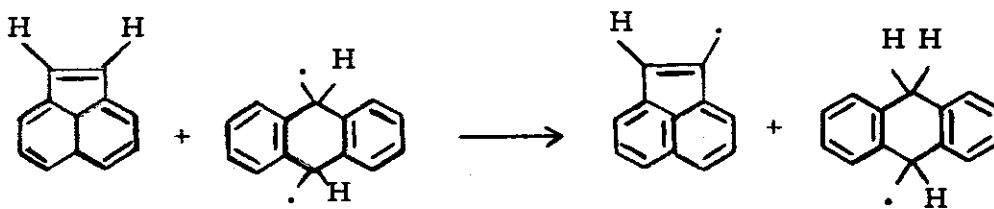
It appears that the polymerization of acenaphthylene proceeds to a lesser extent. The concentration of activated anthracene molecules is very low and the normal anthracene molecules act as a diluent resulting in a reduced carbon residue at 750°C.

The mixture of acenaphthene and anthracene provides an interesting example of the thermal interaction of two unreactive compounds. The thermogram of a 1:1 mixture is shown in Figure 4(c), curve 2, flanked by the thermograms of the individual compounds. Anthracene is much less soluble in molten acenaphthene than in acenaphthylene. Notwithstanding this low solubility, a reaction exotherm between 150° and 200°C occurs followed by two endotherms that result from melting and distillation of the product. Direct observation of this mixture in the hot stage microscope indicates a reaction between liquid acenaphthene and solid anthracene in the exothermic temperature region. Heat-treatment of this mixture under reflux conditions provides further evidence of this reaction. 9,10-Dihydroanthracene as well as some of the lower melting products separated from acenaphthylene pitch are among the products isolated. The interaction could involve initially a hydrogen transfer from acenaphthene to excited anthracene, leading to dihydroanthracene and acenaphthylene, or directly to the copolymerization product of the anthracene - acenaphthylene reaction.
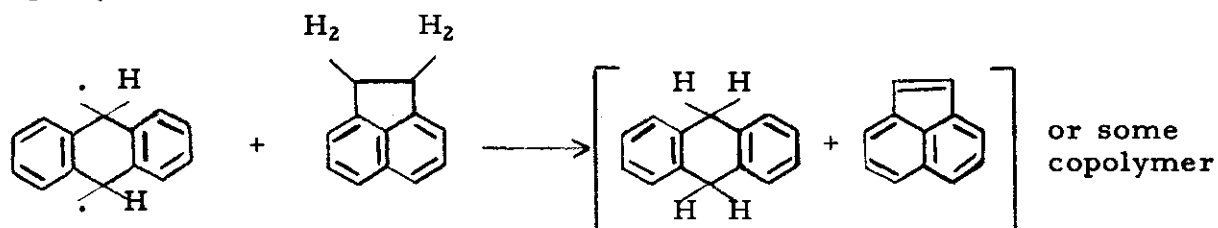
Apparently there is sufficient dilution of the acenaphthylene to prevent polymerization into a high molecular weight nonvolatile polyacenaphthylene, since no carbon residue is obtained in the DTA experiment.

These results do conform to those reported by Andersen and Norrish[19]. Such interactions should be highly significant in the thermal reactions of polynuclear aromatic hydrocarbons since thermal hydrogen transfers may occur between structurally dissimilar as well as structurally identical aromatic species.

Additionally, consistent patterns appear to develop for the general thermal conversion of simple aromatic hydrocarbons to large dehydorgenated aromatic molecular species designated as carbon. Initially these dehydrogenations appear, in many instances, to be accomplished internally by intermolecular hydrogen

transfers between aromatic hydrocarbon molecules. With pure compounds, identical molecular types may act as both hydrogen donors and acceptors. In some instances with mixtures of hydrocarbons, it appears that these individual functions may be assumed by different materials. Such a hydrogen transfer scheme has been proposed recently for catalytic thermal condensation reactions of aromatics[20]. Our results indicate that this sequence is important in pure thermal uncatalyzed carbonization reactions.

The hydrogenated aromatic molecule should in all instances be more stable than the parent aromatic and may thus be often identified as a volatile distillable product. The dehydrogenated aromatic molecule may exist as a free radical entity or may condense or rearrange to new more highly condensed aromatic systems. The pyrolysis of the reactive aromatic hydrocarbons are invariably accompanied by the formation of stable free radical species. It is felt that these radicals are aromatic radicals or radical ions formed by thermal dissociations of hydrogens at reactive ring sites or by cleavage of substituent groups in the case of alkylated aromatics. The stability of aromatic free radicals is well known and has been the subject of many recent investigations[6,24].

These generalized conclusions, although useful, leave unanswered many significant questions relating to the thermal reactions of aromatic hydrocarbons. Little is yet known regarding the specific progressive condensation and rearrangement sequences of the individual reactive hydrocarbons with continuing thermal treatment. The nature and role of the thermally generated free radicals in carbonization is still uncertain. Finally the interactions and synergistic effects between dissimilar aromatic hydrocarbon molecules in mixtures is little understood.

5.5. General Conclusions for the Thermal Carbonization Reactivity of Aromatic Hydrocarbons

The results of this investigation may be summarized in terms of the following general conclusions pertaining to the thermal reactivities of aromatic hydrocarbons.

(1)   The carbonization reactivity of polycyclic aromatic hydrocarbons at atmospheric pressures is dependent on a combination of physical and chemical reactivity criteria.

    (a)   Chemically unreactive aromatics resist thermal treatment and volatilize before reactions can occur.

    (b)   Highly volatile aromatics distill prior to reaction in spite of high indicated chemical reactivity.

    (c)   Physically stable aromatics with moderate indicated chemical reactivities will carbonize on attaining extremely high temperatures.

    (d)   Aromatics of high chemical reactivity will carbonize at atmospheric pressure. The extent of carbonization appears related to the degree of reactivity. No thermally stable aromatic hydrocarbon with an ionization potential lower than perylene, 6.84 e.v., has been found to date.

(2)   The DTA method provides a convenient means of determining the melting and boiling constants for the thermally stable compounds and the reaction temperatures for the reactive aromatics.

(3)   Spectral measurements and "p-band" determinations provide a useful means of categorizing aromatic reactivity in terms of ionization potentials.

(4)   Extra structural features which permit thermal stabilization through vinyl-type polymerization enhance carbonization reactivity. In such instances, one must consider the polymer rather than the monomer as the carbonizing entity.

(5)   Alkyl and aryl substituents on the aromatic rings enhance carbonization reactivity, presumably by providing a convenient site of bond rupture. This effect is manifested by both increased carbon yields and lower reaction temperatures.

It is hoped that this broad survey of the thermal characteristics of aromatic hydrocarbons may serve as a guide and impetus towards resolving some of these scientific questions and towards gaining an improved insight into the complex chemical process designated as carbonization.

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