

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 "Refractory Inorganic Non-Metallic Materials: Graphitic"; Project No. 7381 "Materials Application", Task No. 738102 "Materials Process"; and Project No. 7-817 "Process Development for Graphite Materials". This work was administered under the direction of the Air Force Materials Laboratory, Research and Technology 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.

Other reports issued under USAF Contract AF 33(616)-6915 have included:

WADD Technical Notes 61-18 and 61-18, Part II, progress reports covering work from the start of the Contract on May 1, 1960, to October 15, 1961, and the following volumes of WADD Technical Report 61-72 covering various subject phases of the work:

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|-------------|--|
| Volume I | Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague. |
| Volume II | Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence. |
| Volume III | Decoration of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague. |
| Volume IV | Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch. |
| Volume V | Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper. |
| Volume VI | Creep of Carbons and Graphites in Flexure at High Temperatures, by E. J. Seldin. |
| Volume VII | High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar, and K. J. Zeitsch. |
| Volume VIII | Electron Spin Resonance in Polycrystalline Graphite, by L. S. Singer and G. Wagoner. |

Contrails

- Volume IX Fabrication and Properties of Carbonized Cloth
Composites, by W. C. Beasley and E. L. Piper.
- Volume X Thermal Reactivity of Aromatic Hydrocarbons,
by I. C. Lewis and T. Edstrom.

ABSTRACT

A survey of the thermal reactivity of 84 aromatic hydrocarbons was given in WADD 61-72, Volume X. This supplement presents the extension of this study to 26 new aromatic hydrocarbons, 25 heterocyclic compounds, 76 substituted aromatics, and 14 binary mixtures of aromatic compounds. Differential thermal analysis was employed to delineate the thermal behavior during pyrolysis to 750°C in an argon atmosphere. Emphasis has been placed on the role of heteroatoms and the effects of ring substituents on the thermal reactivity of aromatic hydrocarbon precursors to carbon and graphite.

This technical documentary report has been reviewed and is approved.



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TABLE OF CONTENTS

	PAGE
1. INTRODUCTION.	1
2. CONCLUSIONS CONCERNING THE THERMAL REACTIVITY AND CARBONIZATION OF AROMATIC COMPOUNDS	2
3. EXPERIMENTAL APPARATUS AND PROCEDURES	4
3.1. Differential Thermal Analysis (DTA) Apparatus	4
3.2. Analytical Procedures	4
3.2.1. Chromatography	4
3.2.2. Infrared Absorption Spectroscopy	4
3.2.3. Ultraviolet Absorption Spectroscopy	5
3.2.4. Hot Stage Microscope	5
3.3. Materials.	5
4. EXPERIMENTAL RESULTS	6
4.1. DTA Thermograms for Thermally "Unreactive" Aromatic Hydrocarbons	6
4.2. DTA Thermograms for Thermally "Reactive" Aromatic Hydrocarbons	9
4.3. DTA Thermograms of Thermally "Unreactive" Heterocyclic Compounds	9
4.4. DTA Thermograms of Thermally "Reactive" Heterocyclic Compounds	14
4.5. DTA Thermograms of Thermally "Unreactive" Substituted Aromatics	14
4.6. DTA Thermograms of Thermally "Reactive" Substituted Aromatics	14
4.7. DTA Thermograms for Mixtures of Aromatic Hydrocarbons	23
4.7.1. Thermally "Unreactive" Aromatic Mixtures	23
4.7.2. Thermally "Reactive" Aromatic Mixtures	26
5. DISCUSSION OF RESULTS	30
5.1. Structure and Reactivity	30
5.2. Thermally "Unreactive" Aromatic Hydrocarbons	31
5.3. Thermally "Reactive" Aromatic Hydrocarbons	31
5.3.1. Hexaphenylethane	32
5.3.2. 1,2-Di-9-fluorenylethane.	32

TABLE OF CONTENTS CONT'D.

	PAGE
5.3.3. 2-Vinylnaphthalene	33
5.3.4. Diphenylbutadiyne	33
5.3.5. Benzo[g, h, i] fluoranthene	33
5.3.6. Diphenylhexatriene	34
5.3.7. 9,10-Di-1-Naphthylanthracene	34
5.3.8. 1,8-Diphenyl-1,3,5,7-Octatetraene (trans) . .	34
5.3.9. 14H-Acenaph[1,2-j]indeno[1,2-f] fluoranthene- (peri-dinaphthylenefluorene).	35
5.4. Thermally "Unreactive" Heterocyclic Compounds . . .	35
5.5. Thermally "Reactive" Heterocyclic Compounds	36
5.5.1. 9-Vinylcarbazole	36
5.5.2. 5,7-Dimethylbenz[c] acridine	37
5.5.3. 6-Nitroindazole	37
5.5.4. 5H-Benzo[b] carbazole	37
5.5.5. 2-Hydroxydibenzofuran	38
5.6. Thermally "Unreactive" Substituted Aromatic Hydrocarbons	38
5.7. Thermally "Reactive" Substituted Aromatic Hydrocarbons	39
5.7.1. Halogen-Substituents	40
5.7.1.1. 9,10-Dibromoanthracene	40
5.7.1.2. 6,12-Dibromochrysene	40
5.7.1.3. 1-Bromopyrene	41
5.7.1.4. 3-Bromofluorene	41
5.7.1.5. 1-Chloroanthraquinone	41
5.7.2. Nitrogen-Containing Substituents	41
5.7.2.1. Amino-Compounds	41
5.7.2.1.1. 2-Fluorenamine	42
5.7.2.1.2. 2,3-Fluorenediamine	42
5.7.2.1.3. 1-Anthramine	42
5.7.2.1.4. 2-Anthramine	42
5.7.2.1.5. 9-Anthramine	42
5.7.2.2. Azo Compounds	44

TABLE OF CONTENTS CONT'D.

	PAGE
5.7.2.2.1. 9-Diazo fluorene	44
5.7.2.2.2. Diazodiphenylmethane	45
5.7.2.2.3. 2-Diazo-2- Phenylacetophenone	45
5.7.2.2.4. 2,2'-Azonaphthalene	45
5.7.2.3. Nitro Compounds	46
5.7.2.3.1. 1,4-Dinitronaphthalene	46
5.7.2.3.2. 2,7-Dinitrofluorene	46
5.7.2.3.3. 1-Nitropyrene	46
5.7.3. Oxygen-Containing Substituents	47
5.7.3.1. Quinones	47
5.7.3.1.1. 1,2-Naphthoquinone	48
5.7.3.1.2. 1,4-Naphthoquinone	48
5.7.3.1.3. Dichlone	48
5.7.3.1.4. Acenaphthenequinone	49
5.7.3.1.5. Phenanthrenequinone	49
5.7.3.1.6. 2-Ethylanthraquinone	49
5.7.3.1.7. 2,3-Dimethyl- anthraquinone	49
5.7.3.1.8. Benz[a]anthracene-7, 12-dione	50
5.7.3.1.9. 7H-Benz[de]anthra- cene-7-one	50
5.7.3.1.10. $\Delta^{10,10'}$ -Bianthrone	50
5.7.3.1.11. 4,4'-Dimethylbianthrone	51
5.7.3.1.12. Dibenzo[cd,jk]pyrene-6, 12-dione	51
5.7.3.2. Hydroxy Compounds	51
5.7.3.2.1. Naphthalenediols	52
5.7.3.2.2. 1,1'-Bi-2-Naphthol	53
5.7.3.2.3. Fluorenols	53
5.7.3.2.4. 4-Hydroxybenzophenone	53
5.7.3.2.5. Poly-hydroxy-derivatives of Anthracene	53

TABLE OF CONTENTS CONT'D.

	PAGE
5.7.3.3. Hydroxy-quinones.	54
5.7.3.3.1. 2,5-Dihydroxybenzoquinone	54
5.7.3.3.2. Juglone.	54
5.7.3.3.3. 1-Hydroxyanthraquinone	55
5.7.3.3.4. Tri- and Tetra-hydroxy- anthraquinone Compounds	55
5.7.3.4. Carboxylic Acids	56
5.7.4. Sulfur-Containing Substituents	56
5.8. Binary Mixtures of Aromatic Compounds.	57
5.8.1. "Unreactive" Mixtures	57
5.8.2. "Reactive" Mixtures.	58
5.8.2.1. 1:1 Mixture of Acenaphthene-p- Benzoquinone.	58
5.8.2.2. 1:1 Mixture of Acenaphthylene-p- Benzoquinone.	59
5.8.2.3. 1:1 Mixture of Fluorene-p- Benzoquinone.	59
5.8.2.4. 1:1 Mixture of Anthracene- Benzoquinone.	59
5.8.2.5. 1:1 Mixture of Naphthacene- Benzoquinone.	60
5.8.2.6. 1:1 Mixture of Benz[a]anthracene- p-Benzoquinone.	60
5.8.2.7. 1:1 Mixture of Acenaphthene- Chloranil	60
5.8.2.8. 1:1 Mixture of Anthracene-Chloranil	61
5.8.2.9. 100:16 Mixture of Chrysene-Sulfur .	61
6. REFERENCES.	62

LIST OF FIGURES

FIGURE		PAGE
1.	DTA Thermograms of Thermally "Unreactive" Aromatic Hydrocarbons.	7
2.	DTA Thermograms of Thermally "Reactive" Aromatic Hydrocarbons.	10
3.	DTA Thermograms of Thermally "Unreactive" Heterocyclic Compounds	12
4.	DTA Thermograms of Thermally "Unreactive" and "Reactive" Heterocyclic Compounds (a) "Unreactive" Compounds (b) "Reactive" Compounds	13
5.	DTA Thermograms of Thermally "Unreactive" Substituted Aromatic Hydrocarbons	18
6.	DTA Thermograms of Thermally "Reactive" Substituted Aromatic Hydrocarbons	19
7.	DTA Thermograms of Thermally "Reactive" Substituted Aromatic Hydrocarbons	20
8.	DTA Thermograms of Thermally "Reactive" Substituted Aromatic Hydrocarbons	21
9.	DTA Thermograms of Thermally "Reactive" Substituted Aromatic Hydrocarbons	22
10.	DTA Thermograms of Binary Mixtures of Aromatic Hydrocarbons.	27
11.	DTA Thermograms of Binary Mixtures of Aromatic Hydrocarbons.	28

LIST OF TABLES

TABLE		PAGE
1.	Thermally "Unreactive" Hydrocarbons.	8
2.	Thermally "Reactive" Hydrocarbons.	11
3.	Thermally "Unreactive" Heterocyclic Compounds . . .	15
4.	Thermally "Reactive" Heterocyclic Compounds. . . .	16
5.	Thermally "Unreactive" Substituted Aromatics	17
6.	Thermally "Reactive" Substituted Aromatics	24
7.	Thermally "Unreactive" Aromatic Mixtures	26
8.	Thermally "Reactive" Aromatic Mixtures	26
9.	Effect of 1-X-Substituents on Carbonization of Pyrene.	47

Contrails

1. INTRODUCTION

The first part of a general survey of the thermal reactivity of aromatic hydrocarbons known to be constituents of coal tar pitch and petroleum coking residues was reported in WADD TR 61-72, Volume X. ⁽¹⁾ Thermal reactivity behavior as derived from Differential Thermal Analysis (DTA) was interpreted in terms of reactivity parameters. Employing spectrally derived ionization potentials (IP) as a criterion of general reactivity, it was shown that aromatics of low IP were thermally reactive and those of high IP were usually thermally stable. Molecular size, through its effect on volatility, was also an important reactivity parameter. Substitution by alkyl and aryl groups increased reactivity, presumably by presenting a site of easy bond cleavage; while substitution by a vinyl group increased thermal reactivity through the conversion of less "reactive" monomer to "reactive" polymer species. Examination of simple aromatic mixtures also provided examples of both additive and nonadditive thermal behavior.

This supplement presents an extension of this study to additional aromatic, heterocyclic, and substituted aromatic compounds as well as binary mixtures. Specific emphasis has been placed on considering the effects of substituents on the thermal reactivity of aromatic hydrocarbons. DTA has been used as the primary tool to examine the thermal behavior of materials when they are subjected to increasing temperatures in a nonoxidizing environment and to categorize this behavior. Secondary examination of the reaction products has provided additional information respective to the reaction mechanisms involved in the thermal conversion of the hydrocarbon to essentially pure carbon.

This general survey serves as a basis for selection of model compounds for the more detailed thermochemical investigations necessary to delineate the specific pyrolytic reaction sequences. The preliminary results of these mechanistic studies have been reported in WADD TR 61-72, Volume XXVII. ⁽²⁾

Manuscript released by the authors July 1963 for publication as an ASD Technical Documentary Report.

2. CONCLUSIONS CONCERNING THE THERMAL REACTIVITY AND CARBONIZATION OF AROMATIC COMPOUNDS

The results described in this report have shown that the thermal reactivity of aromatic compounds is strongly dependent on chemical structure. The following general conclusions can be made relating to thermochemical reactivity and structure.

1. The conclusions reached earlier (Volume X) with respect to polycyclic aromatic hydrocarbons are further verified insofar as they apply to this greatly enlarged group of compounds; that is,

(a) The carbonization reactivity of polycyclic aromatic hydrocarbons at atmospheric pressures is dependent on a combination of physical and chemical reactivity criteria. The simple fused ring aromatics exhibit a close relationship between observed thermal reactivity and chemical reactivity parameters such as ionization potential.

(b) Additional structural features such as the presence of olefinic side chains or alkyl and aryl substituents lead to enhanced carbonization reactivity. Reactive olefinic groupings facilitate thermal polymerization to produce carbonizable polymer entities. Alkyl and aryl substituents present convenient sites of bond rupture for the formation of thermally reactive aromatic radicals.

(c) Physical size can ameliorate the chemical effects especially in border-line cases. Several highly volatile aromatic hydrocarbons present no carbon yield in spite of a high indicated chemical reactivity whereas several large molecular weight hydrocarbons do carbonize despite low chemical reactivity.

2. Heterocyclic compounds are more refractory than the analogous aromatic hydrocarbons. The heterocyclics generally distill out of the DTA system prior to reaction. Substituent alkyl and vinyl groups enhance the reactivity of the heterocyclics in much the same manner as in the hydrocarbons.

3. Substituent groups containing nitrogen, oxygen, sulfur, or halogens increase the reactivity of most polynuclear aromatics significantly. These effects may be the result of several factors:

(a) Alteration of the electron density of the aromatic ring to facilitate thermal disproportionation and radical formation.

(b) Introduction by an electronic or steric effect of a convenient site of bond rupture in the molecule.

(c) Presentation of a reactive site in the molecule for condensation and carbonization reactions.

4. The substituent effect is related to the nature of the substituent with NO_2 , NH_2 , OH and C=O groups being particularly effective. Multiple substitution increases the activating effect.
5. The position of reactivity can alter the extent of reactivity and can apparently affect the type of carbon product as well.
6. The pyrolysis of aromatic mixtures as investigated by DTA provide examples of both additive and nonadditive behavior of the following type:
 - (a) Noninteracting mixtures show pure physical effects leading to modified melting and boiling temperatures.
 - (b) Inert diluents can limit the thermal reactivity of thermally reactive compounds.
 - (c) Dehydrogenation and polymerization agents such as aromatic quinones and sulfur can markedly enhance the carbonization reactivity of aromatic hydrocarbons.
7. The DTA method permits a useful categorization of reactivity of organic compounds and an effective delineation of thermal reaction temperatures. Simultaneous spectroscopic investigation of the volatile products can provide an insight into possible mechanisms.

The DTA technique, however, is a prelude to the thorough chemical investigations of selected model organic systems which are ultimately necessary to provide an insight into the mechanisms of carbonization and a thorough understanding of the effects of structure on thermal reactivity.

3. EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus and procedures used in this study will be summarized briefly since a complete detailed description has already been reported in WADD TR 61-72, Volume X, ⁽¹⁾ pages 3 through 8.

3.1. Differential Thermal Analysis (DTA) Apparatus

Differential thermal analysis is a dynamic technique for determining the thermal changes occurring in a material as it is heated at a measured rate. The apparatus is so designed that the temperature of a reactive sample can be continuously compared to the temperature of an inert reference substance while the two materials are heated in the same manner. The reference substance is chosen so that its heat capacity and thermal conductivity approximate those of the reactive sample. When the reactive sample undergoes a physical or chemical transition in which heat is either absorbed or evolved, its temperature will change from that of the reference substance, and the differential thermocouple will register the temperature difference. The plot of temperature differential (ΔT) between the sample and reference as a function of the reference temperature (T_r) is reported as the DTA thermogram of the sample.

The DTA experiments reported here were carried out in a flowing argon atmosphere. Argon is introduced into the lower end of the combustion tube after passing through a heated copper wool purification tube to remove moisture and oxygen. A flow rate of 10 cc per minute is maintained. The argon is passed up the combustion tube through two diffuser rings and over the sample and reference cells and is exhausted from the top of the furnace into a KBr trap in which the condensable vapors from the sample are collected. The non-condensable gases pass through the trap and through a sulfuric acid bubbler which seals the system. A heating rate of 10°C per minute is maintained to 750°C when the sample has been converted essentially to carbon. The carbon residue is measured and reported herein.

3.2. Analytical Procedures

3.2.1. Chromatography

Elution chromatography on alumina or silica gel has been used extensively for purification of the compounds used in this study as well as for separation of some of the complex reaction products obtained as distillates in the DTA experiments.

3.2.2. Infrared Absorption Spectroscopy

The condensable reaction products collected in the KBr traps were all examined by infrared absorption spectroscopy using a Perkin-Elmer Model 21 or Model 221 double-beam spectrometer. The KBr pelleting technique was used most extensively because of the limited solubility of the materials studied.

3.2.3. Ultraviolet Absorption Spectroscopy

To further assist in identification of reaction products, the ultraviolet absorption spectra were also measured using a Beckman Model DK-1 double-beam recording spectrophotometer. The materials were usually measured in benzene solution using matched 10 mm silica cells.

3.2.4. Hot Stage Microscope

A Köfler Hot Stage and accessories with an American Optical Spencer binocular microscope were used to help interpret the low temperature transitions indicated in the DTA experiments.

3.3. Materials

The compounds examined in this study were obtained from commercial chemical suppliers and in many cases were used as received. Purity and identification were verified by comparing spectra of each compound with published spectra. If contamination was suspected, the material was chromatographically purified and the purified compound reexamined in the DTA apparatus.

The solvents used for chromatographic elution and for spectroscopic measurements were all Eastman Kodak Company, spectrograde solvents. The KBr powder used for collecting the DTA distillates and for IR sampling was IR quality powdered KBr purchased from the Harshaw Company. The anhydrous alumina used in chromatographic columns and as the DTA reference material was Fisher's Chromatographic grade anhydrous alumina, 80 to 200 mesh, Catalog No. A-540. The alumina used as a reference in DTA was specially treated by heating to 800°C and then stored in a sealed dispenser designed to avoid exposure of the bulk of the material to the atmosphere when transfer is made to the DTA cup.

4. EXPERIMENTAL RESULTS

The results of continued DTA investigations of pure compounds selected as prototype structures for the chemical constituents of graphite raw materials are presented in this section. The type of compounds investigated include: aromatic hydrocarbons, heterocyclics, substituted aromatic hydrocarbons and binary mixtures containing aromatics. For the purposes of discussion, the compounds have been classified on the basis of the structural features and have been designated as either thermally "reactive" or thermally "unreactive". The thermally "reactive" species are sufficiently reactive in the atmospheric DTA system to undergo a condensation sequence and yield a measurable amount of carbonaceous residue at 750°C. The thermally "unreactive" compounds have sufficient chemical stability so that such condensation reactions do not occur prior to complete volatilization and no carbonaceous residues are obtained at 750°C.

4.1. DTA Thermograms for Thermally "Unreactive" Aromatic Hydrocarbons

In continuing the survey of model compounds, DTA thermograms for 17 additional unreactive aromatic hydrocarbons are presented in Figure 1. The thermograms for the unreactive class of hydrocarbons exhibit discrete melting and boiling endotherms which are characteristic for each specific compound. The endothermic inflection temperatures on the whole correspond quite closely to melting and boiling points reported in the chemical literature.

DTA offers a convenient if not precise method for measuring melting and boiling temperatures for organic compounds. In the case of extremely high boiling materials such as the polynuclear aromatics, it is extremely difficult to determine boiling points by any more conventional method, so volatility data are thus rather sparse in the literature.

The DTA method also provides a sensitive method for determining the presence of impurities if the melting point differs appreciably from that of the major constituent. A number of the compounds shown in Figure 1 exhibit two melting endotherms. The minor endotherms are due to impurities, usually isomers, in the commercial chemicals used in these studies. The melting point is measured from the DTA endotherm by extrapolating the forward slope of the endothermic peak up to the baseline and recording the intercept.

The boiling endotherms have no readily defined inflection points. The slope of the endotherm is a function of the vapor pressure of the sample with increasing temperature. The normal gradual slope to the endothermic minimum indicates a slowly increasing vaporization rate. The reported boiling points are the endothermic minima where the vaporization rate is at a maximum.

Although several of the compounds included in this group show endothermic or exothermic activity after the boiling endotherm, indicating some thermal reactivity, no carbonaceous residues were obtained. All reaction products

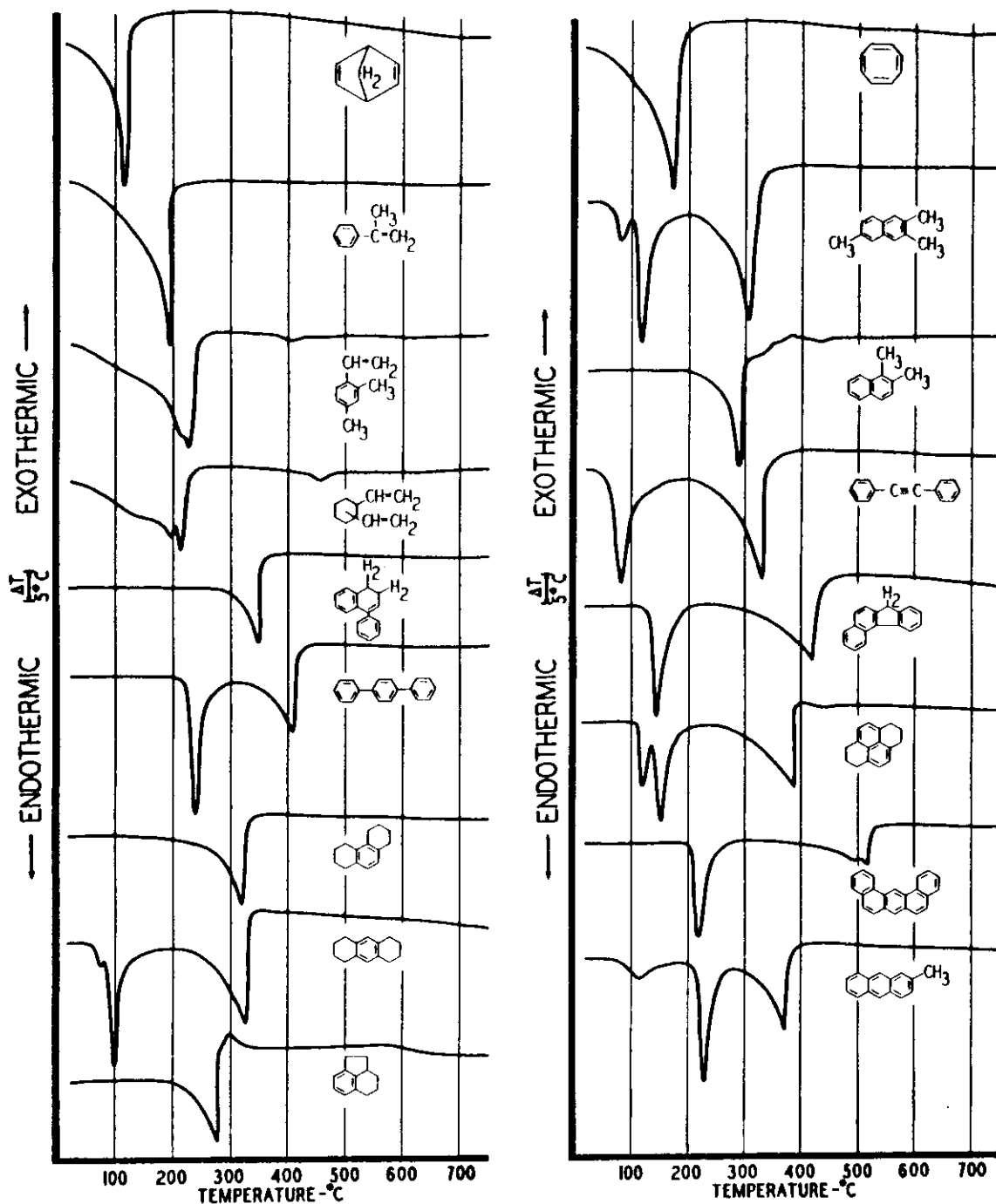



















Figure 1. DTA Thermograms of Thermally "Unreactive" Aromatic Hydrocarbons

formed were volatile and consequently, these hydrocarbons were listed as "unreactive".

The melting and boiling points for all of the compounds examined have been measured from the DTA thermograms and are listed in Table 1. Also listed are the best literature values for the melting points where available. The frequencies of the long wavelength p-bands, as defined by Clar⁽³⁾, and determined from the ultraviolet absorption spectra are given. These values have been used to calculate the ionization potentials for the respective aromatic hydrocarbons using the relationship developed by Matsen⁽⁴⁾ and which was discussed previously.⁽¹⁾

Table 1. Thermally "Unreactive" Hydrocarbons

Compound	Structure	DTA No.	M. P. - °C Lit.	M. P. - °C DTA	B. P. - °C DTA	U. V. λ_p m μ	I. P. Calc. e. v.
Bicyclo[2,2,1]hepta-2,5-diene		349	---	Liquid	115	---	----
α -Methylstyrene		272	---	Liquid	190	---	----
2,4-Dimethylstyrene		323	---	Liquid	220 400	250	8.64
Divinylbenzene (70 % m, ~ 30 % p)		273	---	Liquid	b. p. 212 & 455 exo. 203	---	----
4-Phenyl-1,2,-Dihydronaphthalene		354	---	Liquid	344	265	8.40
p-Terphenyl		282	213	220	407	280	8.18
1,2,3,4,5,6,7,8-Octahydrophenanthrene		369	16.7	Liquid	316	281	8.17
1,2,3,4,5,6,7,8-Octahydroanthracene		370	78	78	324	285	8.12
2a,3,4,5-Tetrahydroacenaphthene		350	12	Liquid	278	288	8.07
1,3,5,7-Cyclooctatetraene		324	-7	Liquid	170	---	----
2,3,6-Trimethylnaphthalene		275	95	98	310	290	8.06
1,2-Dimethylnaphthalene		351	-3.5	Liquid	290	293	8.01
Diphenylacetylene		312	63	65	325	297	7.97
7H-Benzo[c]fluorene		385	125	122	414	312	7.79
1,2,3,6,7,8-Hexahdropyrene		365	127	115 127	380	316	7.76
Dibenz[a,j]anthracene		329	196	205	515	351	7.42
2-Methylantracene		357	207	215	375	377	7.21

The ionization potentials thus calculated are given in the last column of Table 1. The compounds are listed in order of decreasing ionization potential. In several cases the p-band could not be defined from the UV spectra. Such compounds have been arbitrarily placed in the table.

4.2. DTA Thermograms for Thermally "Reactive" Aromatic Hydrocarbons

The thermograms for nine additional aromatic hydrocarbons classified as thermally "reactive" because carbonaceous residues were obtained at 750°C in our DTA experiments are shown in Figure 2. The thermograms of the thermally "reactive" compounds differ quite appreciably from those of the "unreactive" group. In most cases the boiling endotherms are either completely absent or are greatly diminished in area. In a majority of cases exothermic peaks indicative of polymerization reactions are observed.

In Table 2 the "reactive" hydrocarbons are listed in order of decreasing ionization potential as were the "unreactive" compounds described in the preceding section. In addition to the melting points, "p-bands", and ionization potentials, the reaction temperature indicated on the DTA thermograms and the percentage carbon residues obtained at 750°C are given in Table 2. Whereas the aromatic compounds discussed earlier in Volume X, WADD TR 61-72⁽¹⁾, consisted predominantly of conventional fused polycyclic hydrocarbons, a majority of the compounds reported herein possess unique structural features. These structural variations are apparently important in implementing thermal reactivity and hence the energetics of the aromatic system as represented by the ionization potential parameter are not as significant as for the conventional hydrocarbons.

Infrared absorption spectral examination of the condensable volatile products obtained during the DTA experiments showed that for nearly all the "unreactive" hydrocarbons, only starting material distilled off. In contrast, almost all of the "reactive" compounds indicated that new volatile products were present in the condensate. The results of spectroscopic examination of the condensate traps for the "reactive" aromatics are discussed in Section 5.

4.3. DTA Thermograms of Thermally "Unreactive" Heterocyclic Compounds

Numerous heterocyclic compounds have been identified in the compositional studies of coal tar pitches and other pyrogenous residues of interest in the manufacture of carbon and graphite. In order to further investigate the structural effects of heteroatoms on thermal reactivity, a number of heterocyclic analogues of aromatic hydrocarbons have been examined in our DTA apparatus.

The DTA thermograms of 20 thermally "unreactive" heterocyclic compounds are shown in Figures 3 and 4(a). Neither the thermograms nor the results of analysis of the volatile products indicate any thermal reactivity of these compounds with but four exceptions: 1-Azafluoranthene, 11 H-Benzo[a]-carbazole, benzacridine, and 3,4-dihydro-2H-pyran-2-methanol. These

10

Table 2. Thermally "Reactive" Hydrocarbons

Compound	Structure	DTA No.	M.P., °C Lit.	M.P., °C DTA	Reaction T-°C DTA	% Residue at 750°C DTA	U.V. λ_p m μ	I. P. Calc. ev.
Hexaphenylethane		136	95	95 to 150*	165 (exo) broad shallow endo. 200-350	8.5	248	8.67
1,2-Di-9-fluorenylethane		387	226	232	375 exo. (383)	5.1	270	8.35
2-Vinylnaphthalene		271	65	50	143 sharp strong exo.	9.9	296	7.98
Diphenylbutadiyne		313	88	85	235 very strong exo.	37.8	329	7.62
Benzo [g, h, i] fluoranthene		321	148	(1) 138 (2) 160 large	(443 endo.)	2.1	349	7.40
Diphenylhexatriene		311	194	210	305 (strong exo.)	0.8	371	7.25
9, 10-Di-1-naphthylanthracene		277	408	400	340 (exo) 483 (endo) 465 (endo) 514 (endo)	14.1	395	7.08
1,8-Diphenyl-1,3,5,7-Octatetraene (trans)		355	225	249	294 exo. (broad 460)	5.1	397	7.07
14H-Acenaph [1,2-j]indeno [1,2-f] fluoranthene		162	---	330	570 exo. (380) 582 exo.	50.1	403	7.04

*Reacting as it melts.

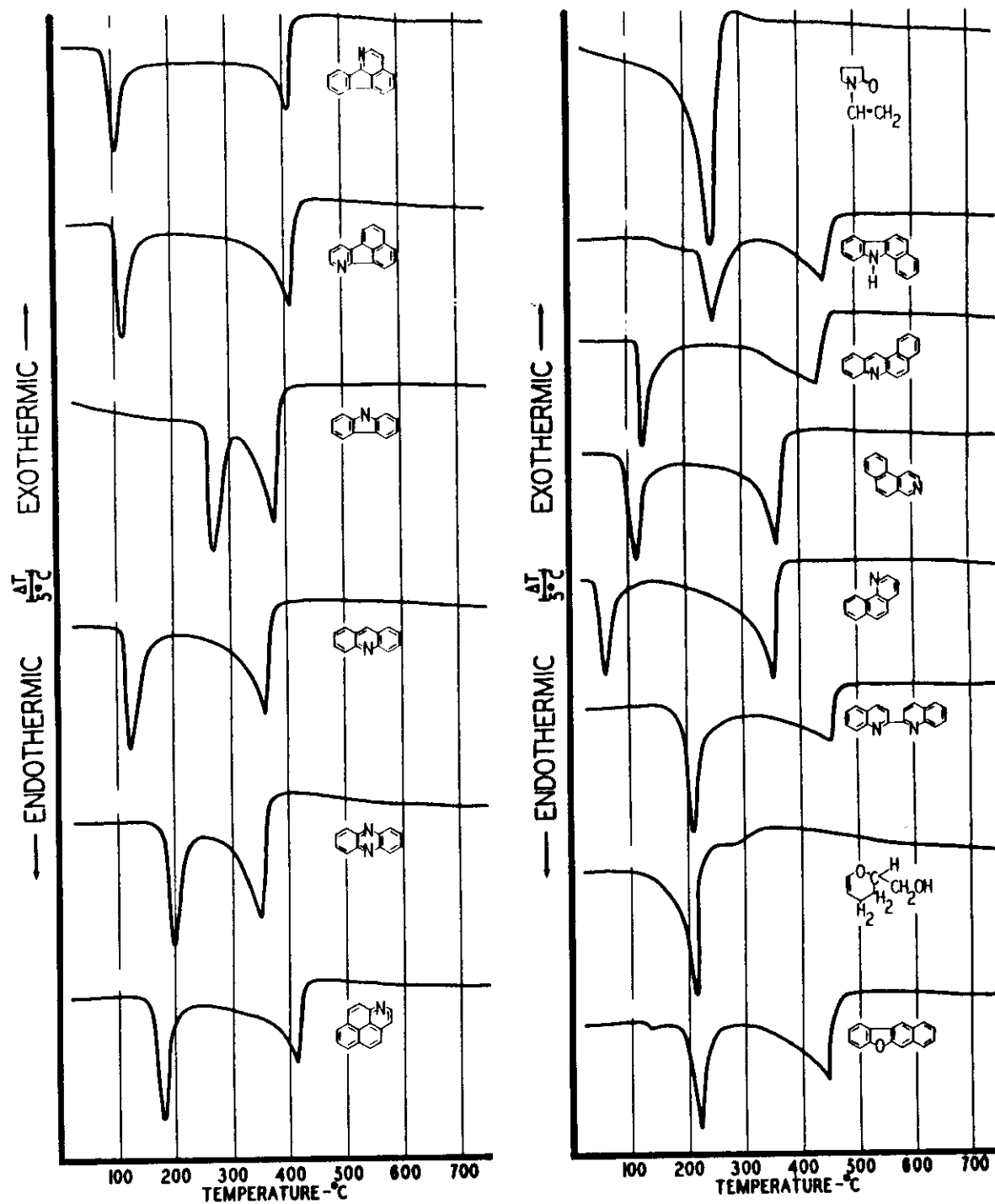
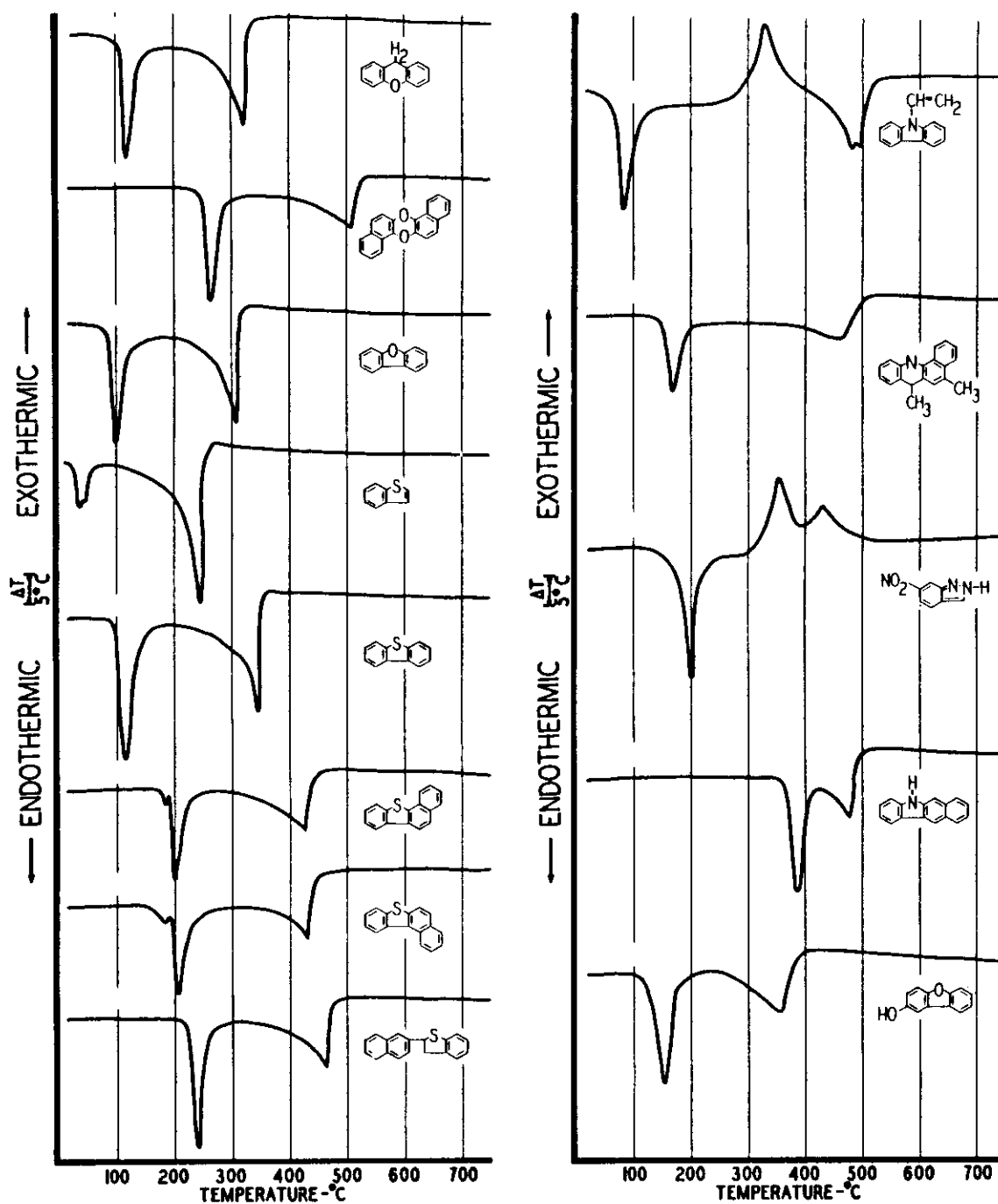


Figure 3. DTA Thermograms of Thermally "Unreactive" Heterocyclic Compounds



(a) "Unreactive" Compounds

(b) "Reactive" Compounds

Figure 4. DTA Thermograms of Thermally "Unreactive" and "Reactive" Heterocyclic Compounds

compounds do react slightly but produce only volatile products which yield no carbonaceous residue at 750°C. The thermograms are typical of nonreactive species. The melting and boiling points as measured on the thermograms are listed for these "unreactive" heterocyclics in Table 3.

4.4. DTA Thermograms of Thermally "Reactive" Heterocyclic Compounds

The DTA thermograms of five thermally "reactive" heterocyclic compounds are shown in Figure 4(b). With the exception of 5H-Benzo(b)-carbazole, these compounds all have substituents which enhance their thermal reactivity significantly. In three cases the thermograms show only the melting and boiling endotherms. In the other two instances, strong exothermic reactions are evident. The melting and boiling temperatures as well as the reaction temperatures and percentage of carbonaceous residue at 750°C are summarized in Table 4. The infrared absorption analysis of the condensates collected during each DTA run indicated that only starting material distilled over.

4.5. DTA Thermograms of Thermally "Unreactive" Substituted Aromatics

The activating effect of substituent groups on the benzene rings has been a subject of intensive study by many investigations for many years. Very little is known of the effects of substituents on polynuclear aromatics, especially in connection with their thermal reactivity.

Although the evidence favoring the existence of a variety of substituent types in the raw materials for graphite is not conclusive, these materials are of interest as additives to modify the physical and chemical properties of pitches and impregnants.

The substituted aromatic hydrocarbons which have been found to be thermally "unreactive" in our DTA experiments are listed in Table 5 with the melting and boiling points measured from the thermograms; literature values of melting points are also indicated.

The DTA thermograms of the 16 "unreactive" compounds are shown in Figure 5. These show the typical behavior described previously with melting and boiling endotherms only. The presence of impurities are noted in a couple of instances by melting point doublets or shoulders on the major endotherm. In most cases only the starting material was found in the condensate trapped in the exit KBr trap of the DTA apparatus.

4.6. DTA Thermograms of Thermally "Reactive" Substituted Aromatics

The thermograms for 60 substituted aromatic hydrocarbons designated as thermally "reactive" are given in Figures 6 through 9. All of these compounds undergo thermal condensation and yield carbonaceous residues at 750°C in the DTA apparatus.

Table 3. Thermally "Unreactive" Heterocyclic Compounds


































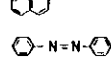
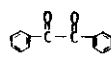


Compound	Structure	DTA No.	M.P., °C Lit.	M.P., °C DTA	B.P., °C DTA	Reaction Temp. °C DTA	% Residue at 750 °C
1-Azafluoranthene		199	97	93	406	---	0.0
7-Azafluoranthene		198	92	102	412	---	0.0
Carbazole		202	246	253	376	---	0.0
Acridine		210	108	111	361	---	0.0
Phenazine		216	171	183	350	---	0.0
Thebenidine		197	157	160	415	---	0.0
1-Vinyl-2-pyrrolidinone		209	25	Liquid	250	---	0.0
11 H-Benzo[a]carbazole		218	228	232	451	---	0.0
Benz[a]acridine		232	132	117	442	---	0.0
Benzo[f]quinoline		303	95	98	360	---	0.0
Benzo[h]quinoline		219	52	48	356	---	0.0
2,2'-Biquinoline		304	280	195	457	---	0.0
3,4-Dihydro-2H-pyran-2-methanol		360	---	Liquid	220	---	0.0
Benzo[b]naphtho[2,3-d]furan		263	210	208	401	---	0.0
Xanthene		352	1005	106	325	---	0.0
Dinaphtho[1,2-b,1',2'-e]-p-dioxin		264	---	250	515	---	0.0
Dibenzofuran		378	87	89	306	---	0.0
Thianaphthene		274	30	30	242	---	0.0
Dibenzothiophene		260	97	102	345	---	0.0
Naphtho[1,2-b]thianaphthene		331	184-5	195	436	---	0.0
2-(2-Naphthyl)-Benzo(b)thiophene		363	213-4	221	466	---	0.0

Table 4. Thermally "Reactive" Heterocyclic Compounds

Compound	Structure	DTA No.	M.P. °C Lit.	M.P. °C DTA	B.P. °C DTA	Reaction Temp. °C DTA	% Residue at 750 °C
9-Vinylcarbazole		201	66	69	475	335	1.9
5,7-Dimethylbenz[c]acridine		297	167	160	470	None	1.6
6-Nitroindazole		361	181	180	None	358 sharp exo. 432 exotherm	23.6
5H-Benzo[b]carbazole		384	332	365	475	None	1.0
2-Hydroxydibenzofuran		353		136	363	None	7.6

Table 5. Thermally "Unreactive" Substituted Aromatics

Compound	Structure	DTA No.	M. P. - °C Lit.	M. P. - °C DTA	B. P. - °C DTA
Hydroquinone		348	171	180	315
p-Benzoquinone		59	116	121	210
Anthraquinone		156	286	288	387
Chloranil		57	290	290 Sublimes	Sublimes
2-Chloroanthraquinone		382	211	213	412
9-Bromoanthracene		251	101	96	394
9,10-Dichloroanthracene		249	210	217	411
1-Chloropyrene		255	119	115	430
5-Bromoacenaphthene		317	52	48	344
Di-1-naphthylamine		302	115	117	469
p-Phenylenediamine		356	140	149	303
1-Pyrenamine		222	118	111	Broad ~ 475
Azobenzene		153	68	66	313
Benzil		152	95	94	350
Ferrocene		155	173	179	257
2-Naphthalenethiol		374	81	48 about 66 equal size	311

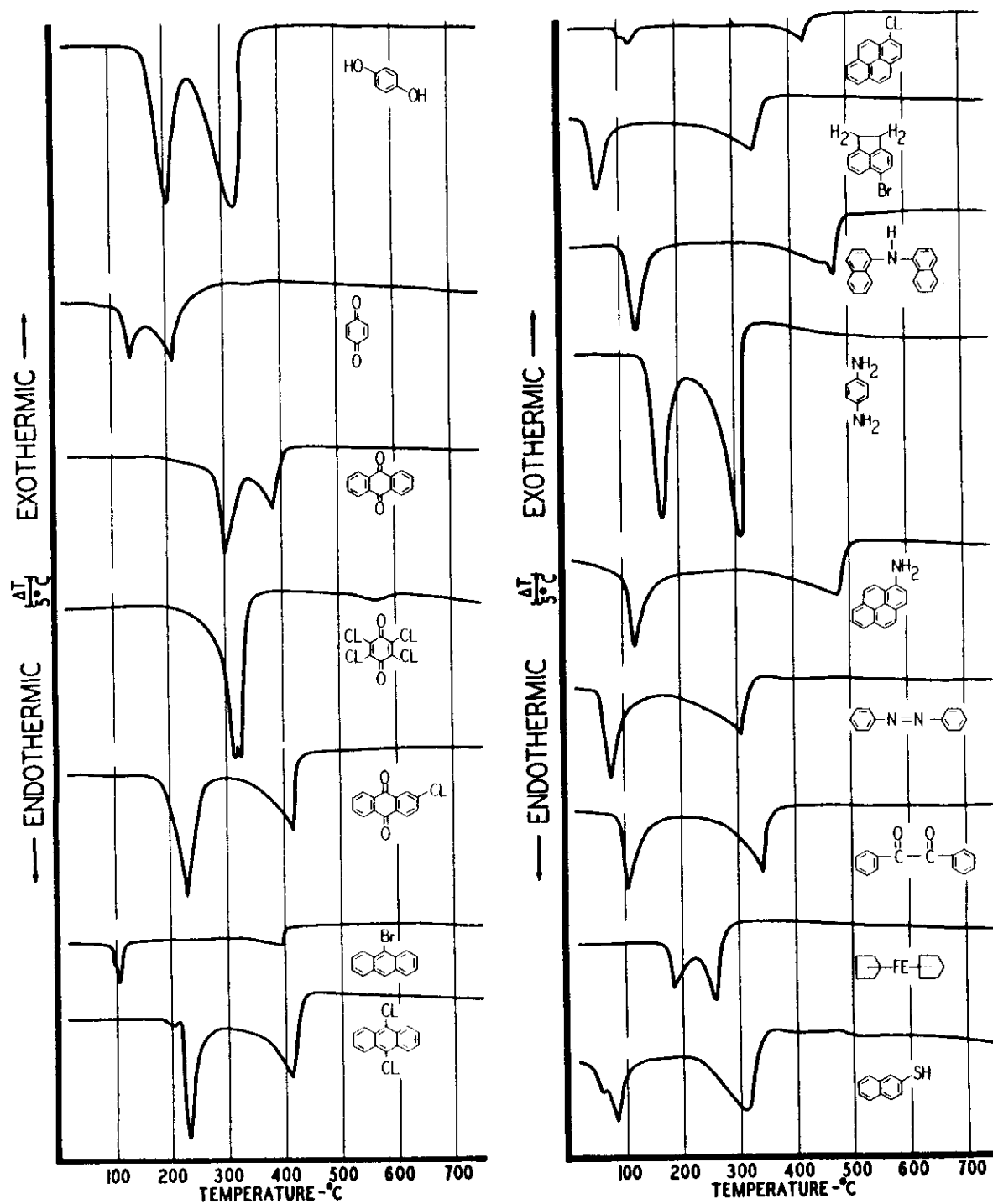


Figure 5. DTA Thermograms of Thermally "Unreactive" Substituted Aromatic Hydrocarbons

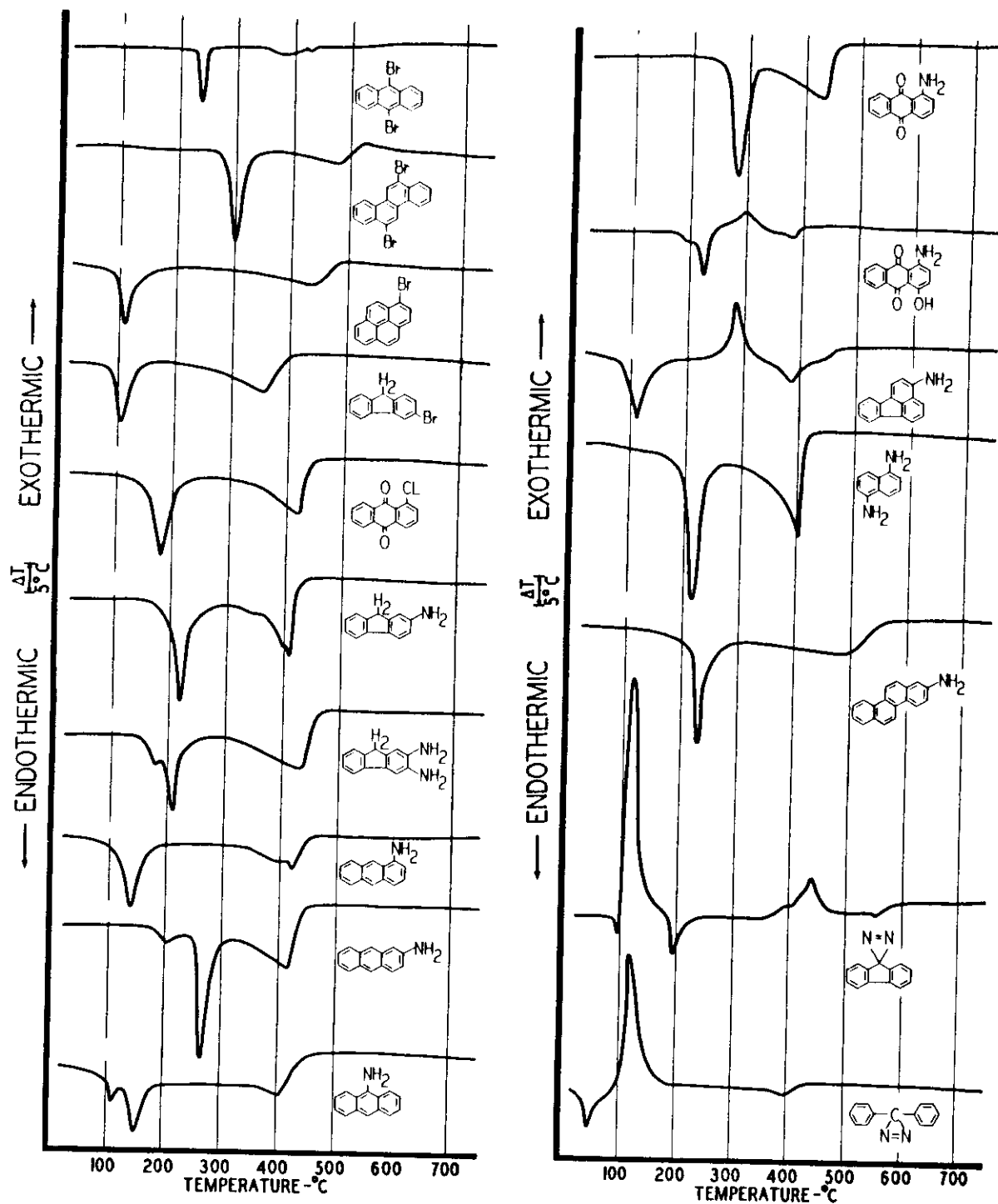


Figure 6. DTA Thermograms of Thermally "Reactive" Substituted Aromatic Hydrocarbons

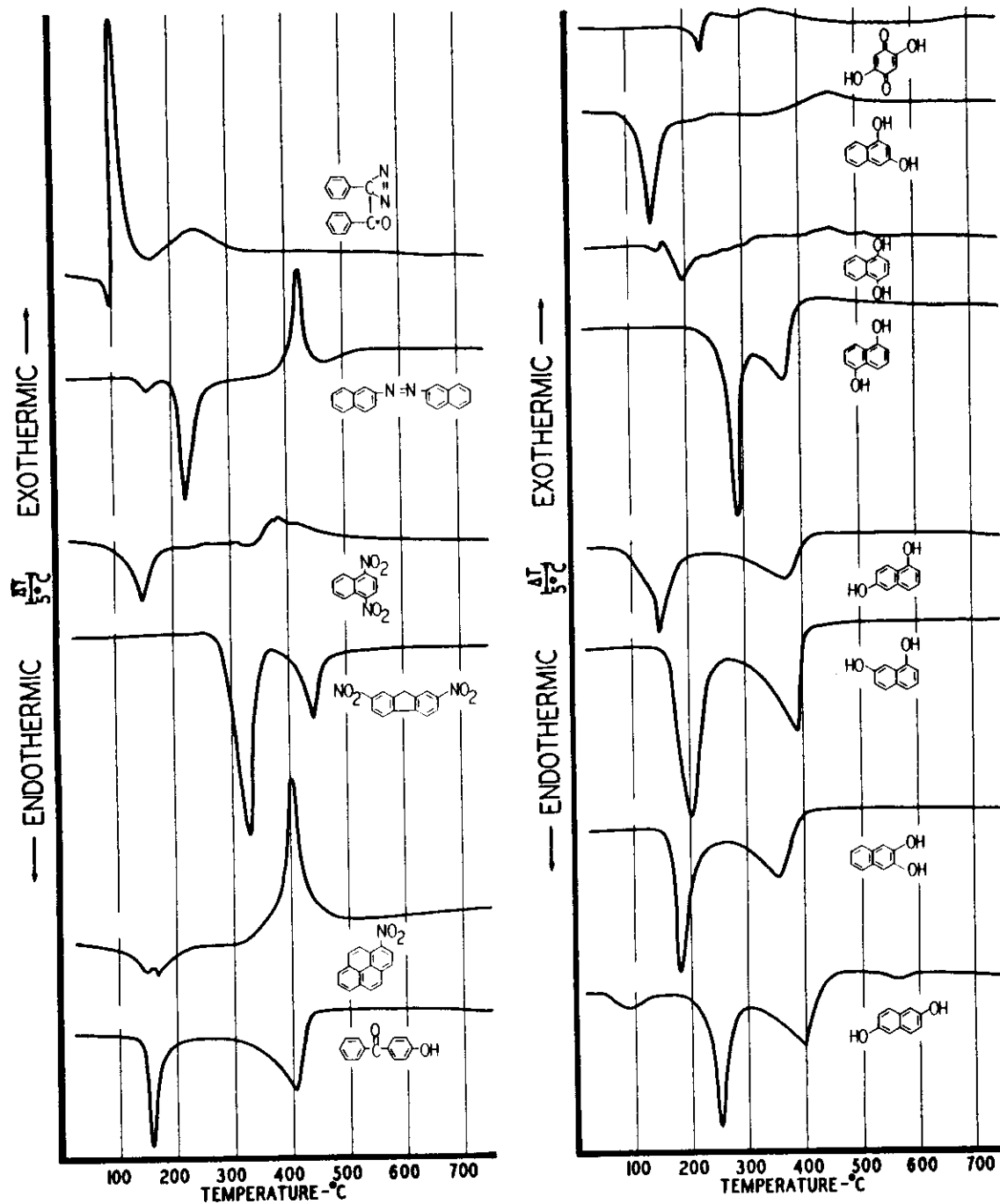


Figure 7. DTA Thermograms of Thermally "Reactive" Substituted Aromatic Hydrocarbons

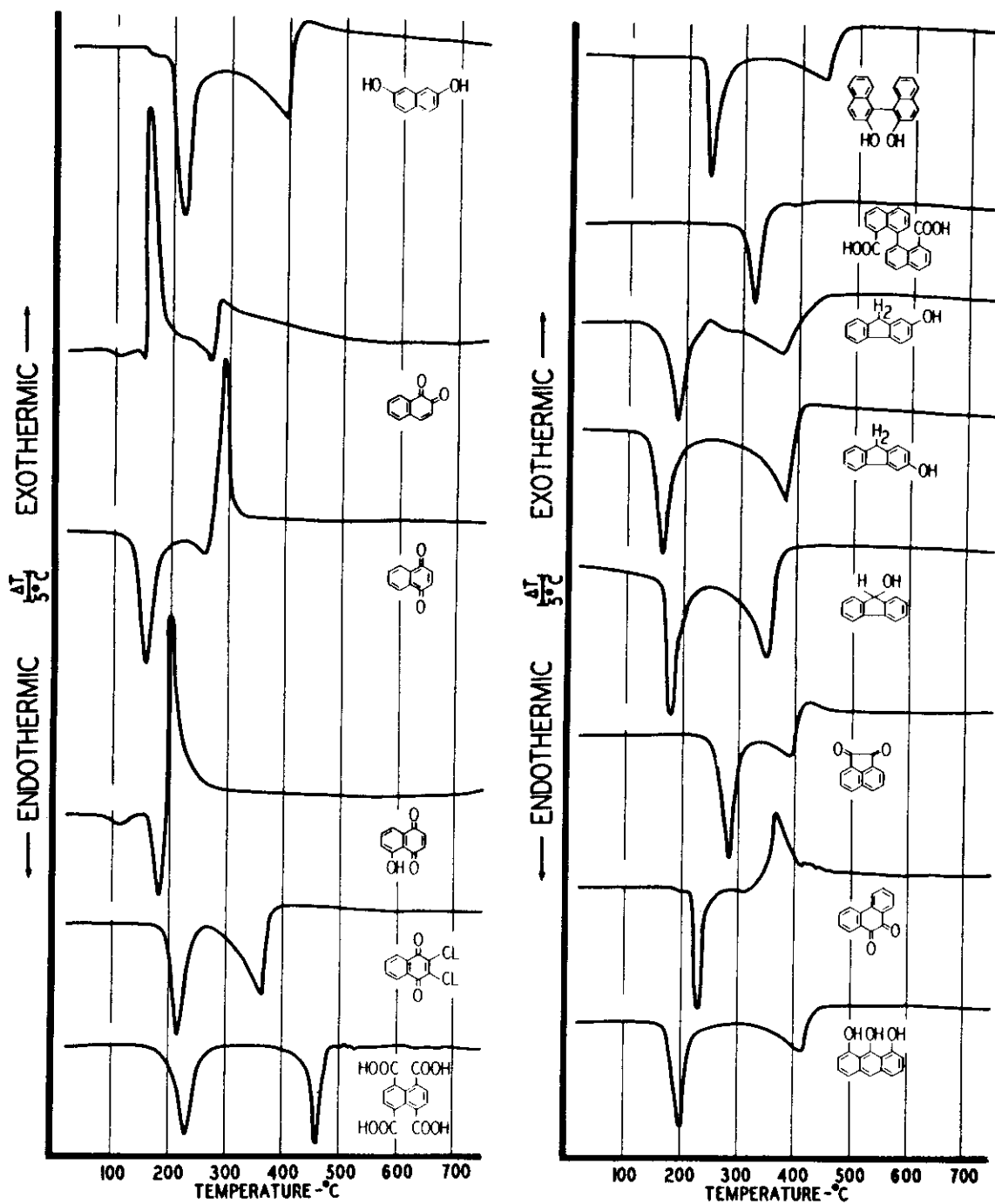


Figure 8. DTA Thermograms of Thermally "Reactive" Substituted Aromatic Hydrocarbons

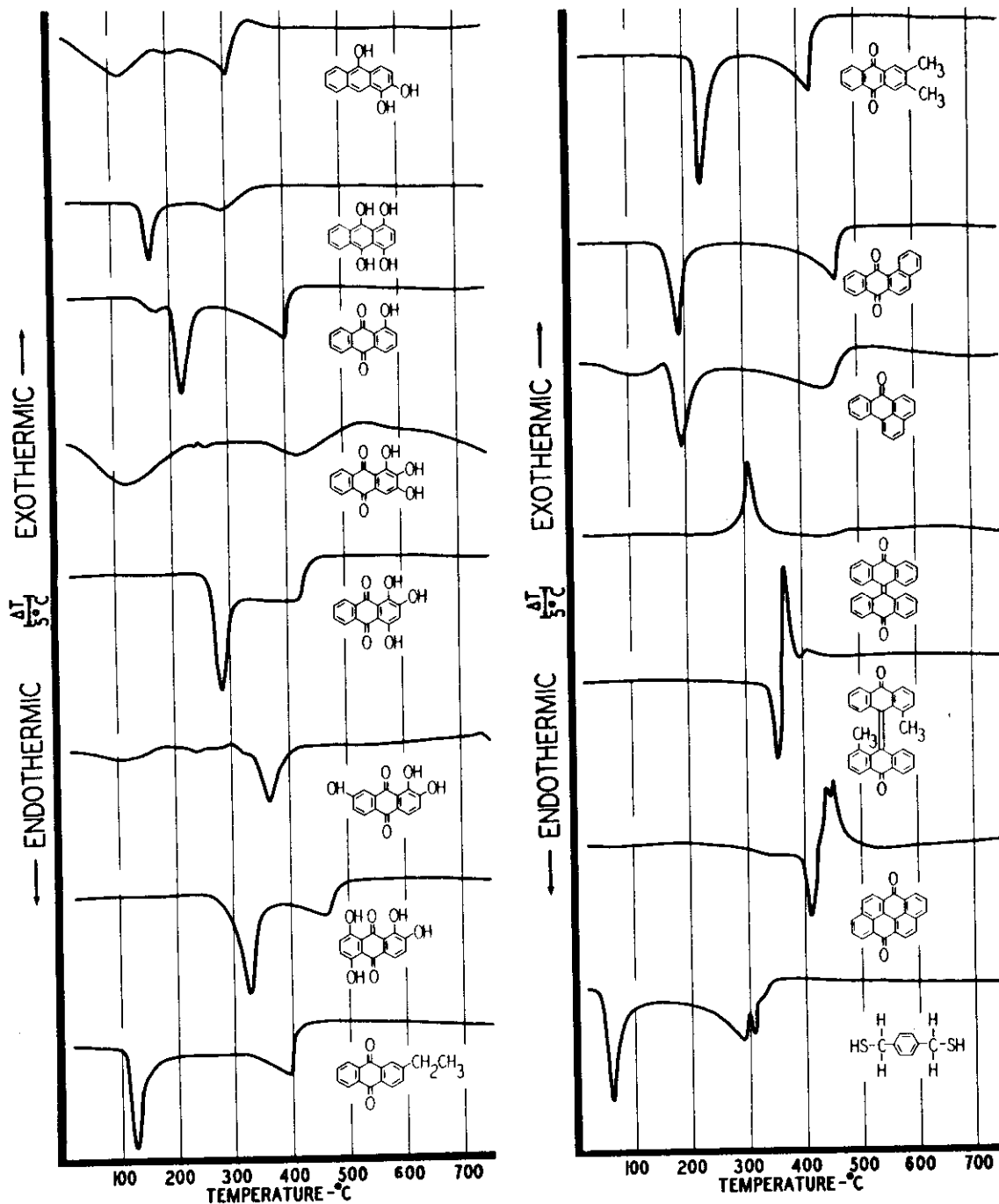


Figure 9. DTA Thermograms of Thermally "Reactive" Substituted Aromatic Hydrocarbons

The thermograms of the "reactive" substituted aromatics show exothermic reactions in many cases, and in most cases have the typically smaller vaporization endotherms previously described.⁽¹⁾ The major melting endotherms are evident as in the other categories of compounds. The DTA melting points have been determined from the inflection temperature and are compared to the literature values in Table 6. The boiling endotherms are either absent or substantially reduced in these thermograms. The DTA boiling point reported in Table 6 is the position of the endothermic band minimum. Further listed in Table 6 are the temperatures of the indicated DTA reaction peaks and the percentage of carbonaceous residue obtained at 750°C. The compounds are listed on the basis of type of substituent group insofar as possible. In a large number of cases new chemical species in addition to the starting materials were found in the condensed distillates.

4.7. DTA Thermograms for Mixtures of Aromatic Hydrocarbons

The pyrolysis of most organic compounds usually leads to the formation of a variety of structurally different products. At this initial stage the thermal behavior of a particular molecule may be influenced by the presence of a different species. The DTA method offers a convenient means of detecting such thermal interactions between different aromatic species.

DTA thermograms have been obtained on a number of binary mixtures. In most cases, the mixtures are composed of individually "unreactive" compounds. In two instances, however, a reactive hydrocarbon, acenaphthylene, was mixed with a large quantity of an unreactive compound to determine the effect of severe dilution. As in the case of the pure compounds, the mixtures have been arbitrarily classified as thermally "reactive" or "unreactive" depending on whether a significant carbonaceous residue was or was not obtained after heating to 750°C in the DTA experiment.

4.7.1. Thermally "Unreactive" Aromatic Mixtures

The five binary mixtures which were found to be chemically "unreactive" are listed in Table 7 with the DTA-determined melting and boiling temperatures tabulated. In two cases, exothermic reactions are also indicated and the approximate temperatures of these reaction maxima are given. The thermograms for these mixtures are shown in Figure 10 with the thermograms of the components also given for comparison.

The additivity of the individual thermograms is evident. The acenaphthylene-p-terphenyl mixture shows the normal melting point of acenaphthylene and a slightly lower melting temperature for the terphenyl. The boiling temperatures of the two components coincide around 400°C. No carbon residue is obtained. The acenaphthylene-m-quinquephenyl mixture physically interacts on melting as their melting points are fairly close together. The melting temperatures are significantly lowered but both are still evident. A slight exothermic reaction of acenaphthylene is seen around 280°C. The large dilution by quinquephenyl effectively inhibits the reaction. Only the boiling point of quinquephenyl is apparent in this thermogram. A coking value of 0.4 per cent from the

Table 6. Thermally "Reactive" Substituted Aromatics

Substituted Aromatic - Reactive	Structure	DTA No.	M. P., °C Lit.	M. P., °C DTA	B. P., °C DTA	Reaction Temp. °C DTA	% Residue DTA
9, 10-Dibromoanthracene		252	226	230	very broad and shallow ~ 390	418 sl. exo. 435 sl. exo.	19.9
6, 12-Dibromochrysene		368	273	283	480	None	15.0
1-Bromopyrene		386	93-4	95	442	None	9.2
3-Bromofluorene		225	90	92	365	None	5.1
1-Chloroanthraquinone		379	162	165	420	None	1.4
2-Fluorenamine		301	132	195	405	None - ragged line btn. 335 & 405	12.9
2, 3-Fluorenediamine		325	198	158 - small 196 - large	435	None	6.9
1-Anthramine		298	122	112	420	None	6.1
2-Anthramine		299	238	248	420	None	1.3
9-Anthramine		300	145	102 smaller 127	408	None	15.4
1-Amino Anthraquinone		359	252	255	436	456 small broad exo.	12.9
1-Amino-4-Hydroxyanthraquinone		358	215	213	382	296 exo.	42.9
3-Fluoranthenammine		326	115-16	95	385	284 exo.	36.2
1, 5-Naphthalenediamine		322	190	195	402	None	5.1
2-Chrysenamine		200	201-3	214	330 sl. endo. 490 broad	None	11.9
9-Diazo fluorene		332	95	93	555 small	110 very large exo. 440 exo.	35.7
Diazodiphenylmethane		376	29-32	33	398 small endo	125 very large sharp exo.	6.4
Z-Diazo-2-phenylacetophenone		377	79	78	None	100 very large sharp exo. 245 flat broad exo	2.7
2, 2'-Azonaphthalene		306	208	210	None	425 large exo.	12.1
1, 4-Dinitronaphthalene		345	131-2	130	None	368 exo. 430 exo. 380 exo. all broad	10.1
2, 7-Dinitrofluorene		320	295	318	448	None	25.8
1-Nitropyrene		254	150	127 larger 153 - smaller	None	405 very large exo.	39.5
4-Hydroxybenzophenone		362	135	138	408	None	2.2
2, 5-Dihydroxybenzoquinone		346	214-18	228	None	250 exo. both broad 340 exo.	29.8
1, 3-Naphthalenediol		371	124	124	None	264 exo. both low 450 exo. and broad	47.8
1, 4-Naphthalenediol		60	176	172	----	Many exo.	39.2
1, 5-Naphthalenediol		372	265	260	271	None	9.6
1, 6-Naphthalenediol		366	137-8	102 - small 135	375	None	21.9
1, 7-Naphthalenediol		364	178	178	388	None	1.5
2, 3-Naphthalenediol		307	160	167	355	None	3.1
2, 6-Naphthalenediol		373	218	224	395	None	4.3

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Table 6 Cont'd






























2, 7-Naphthalenediol		308	190	192	390	None	6.7
1, 2-Naphthoquinone		380	d 115-20	117 very shallow	264 small	155 very large sharp exo. 282 med. tails off	27.5
1, 4-Naphthoquinone		310	125	130	None	280 large exo.	42.6
Juglone		347	153-4	92 small endo 168 large endo	None	210 very large sharp exo.	64.7
Dichlone		214	196	193	364	None	1.5
1, 4, 5, 8-Naphthalenetetracarboxylic Acid		261	---	195	461	None	19.8
Bi-2-Naphthol		220	219	221	448	None	1.6
[1, 1'-Binaphthalene] di-carboxylic Acid		262	183	None	323	None	27.5
2-Fluorenlol		316	171	165	360	None	9.8
3-Fluorenlol		314	136-7	143	381	None	0.8
9-Fluorenlol		315	158	162	350	None	0.5
Acenaphthenequinone		305	261	265	390	419 flat exo.	14.6
Phenanthrenequinone		284	207	209	---	370 exo 420 small flat exo.	40.3
1, 8-Dihydroxyanthrone		319	178	181	415	None	13.1
Anthrarobin		340	282	broad 280-d	---	reacts between 60 & 175 endo.	60.5
1, 4, 10-Trihydroxyanthrone		318	156	156	300 Broad	None	45.4
1-Hydroxyanthraquinone		344	100	160 small 200 large	403	None	3.8
Anthragallol		388	310 d	----	415 broad	230 sl exo 550 exo 256 sl exo 790 endo	41.1
Purpurin		341	256	260	414	615 sl exo 440 sl exo	30.5
Anthrapurpurin		337	369	315 sl. 340	---	300 sl exo. 419 sl exo.	46.9
Quinalizarin		342	> 275	300	460	None	12.0
2-Ethylanthraquinone		339	105-7	116	398	None	6.9
2, 3-Dimethylanthraquinone		278	200	219	423	None	7.1
Benz[a]anthracene-7, 12-dione		375	169	172	469	None	0.6
7H-Benz[de]anthracene-7-one		335	170-1	175	445	None	15.9
Δ10, 10'-Bianthrone		367	316	None	None	310 st sharp exo	743.
4, 4'-Dimethyl-Δ10, 10'-Bianthrone		279	330-5d	347	391 sm end	369 large exo	48.8
Dibenzo[cd, jk]pyrene-6, 12-dione		248	340	400	None	440 exo 448 exo	70.0
Xylene-α, α'-dithiol		276	46-7	47	297	308 sharp endo. 315 small endo.	15.5

Table 7. Thermally "Unreactive" Aromatic Mixtures

Ratio	Mixture Composition	DTA mp °C	DTA bp °C	Reaction Temp. °C	C.V. at 750°C - %
1:10	Acenaphthylene-p-terphenyl	90 and 205	398	---	0
1:10	Acenaphthylene-m-quinquephenyl	60 and 92	545	280	0.4
1:1	Naphthalene-p-benzoquinone	60	220	---	0
1:1	Acenaphthene-9,10-anthraquinone	95	292 and 350	222	0
1:1	Anthracene-9,10-anthraquinone	225	370	---	0

reaction of the acenaphthylene was obtained but since there is no evidence of chemical interaction between these compounds the mixture is classed as "unreactive". The naphthalene-benzoquinone mixture exhibits a single broad melting point at a temperature lower than that of either component and a broad boiling endotherm encompassing the boiling temperatures of both compounds. No interaction is evident and no carbon residues were obtained.

In addition to the melting and boiling endotherms of the individual components, the acenaphthene-anthraquinone thermogram shows a reaction exotherm peaking at 222°C. This reaction exotherm is indicative of acenaphthylene polymerization and suggests that a hydrogen transfer occurred converting some acenaphthene to the more thermally reactive acenaphthylene. No carbon residue results, however, and the IR spectrum of the distillates showed only the presence of the two starting compounds. From the thermogram of the 1:1 mixture of anthracene and anthraquinone there is no indication of a reaction between these compounds. Only broad melting and boiling endotherms are observed and no carbon residue is obtained.

4.7.2. Thermally "Reactive" Aromatic Mixtures

Nine binary mixtures were found to be thermally "reactive" in the DTA apparatus. The pertinent physical properties, reaction temperatures and percent carbon residues obtained at 750°C in the DTA experiments are summarized in Table 8 for these systems. The thermograms obtained on these mixtures as well as those obtained on the individual compounds are illustrated in Figures 10 and 11.

Table 8. Thermally "Reactive" Aromatic Mixtures

Ratio	Mixture Composition	DTA mp °C	DTA bp °C	Reaction Temp. °C	CV at 750°C DTA - %
1:1	Acenaphthene-p-benzoquinone	82	265	218	13.1
1:1	Acenaphthylene-p-benzoquinone	58	230	260	9.5
1:1	Fluorene-p-benzoquinone	78	~255	198	17.7
1:1	Anthracene-p-benzoquinone	103	218	148, 255, 320	9.4
1:1	Naphthacene-p-benzoquinone	112	---	144, 210	36.1
1:1	Benz[a]anthracene-p-benzoquinone	95	210, 418	255	2.2
1:1	Acenaphthene-Chloranil	92	258	184, 324, 360	19.4
1:1	Anthracene-Chloranil	190	310	400 Broad	10.9
10:1.6	Chrysene-Sulfur	110, 255	385	270	15.0

Eight of these mixtures react exothermally, in most cases soon after the lower melting compound has melted. Undoubtedly the solubility of the higher melting component in the melt is a factor in the reaction both with respect to rate and temperature. For example, the anthracene-benzoquinone mixture

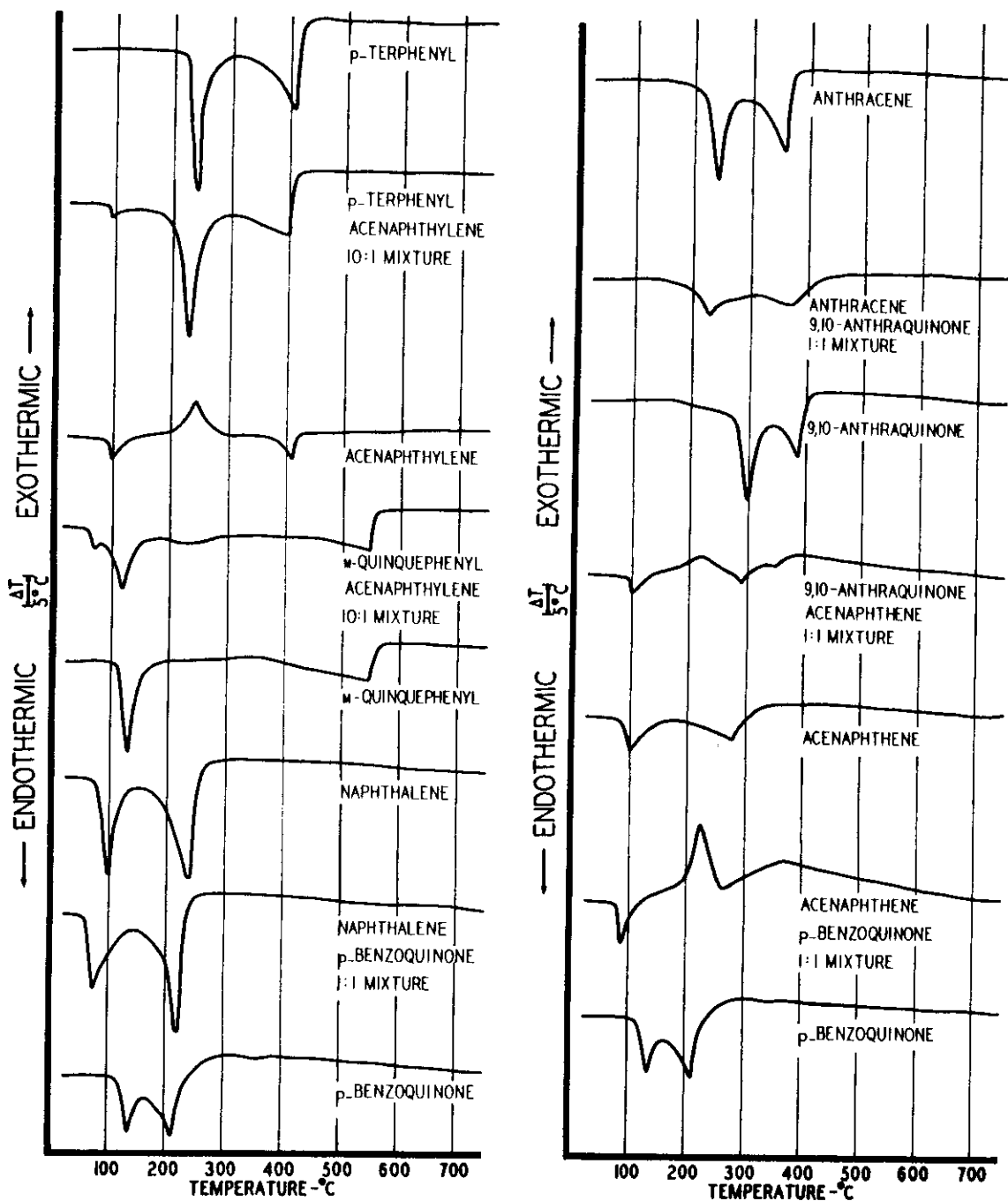


Figure 10. DTA Thermograms of Binary Mixtures of Aromatic Hydrocarbons

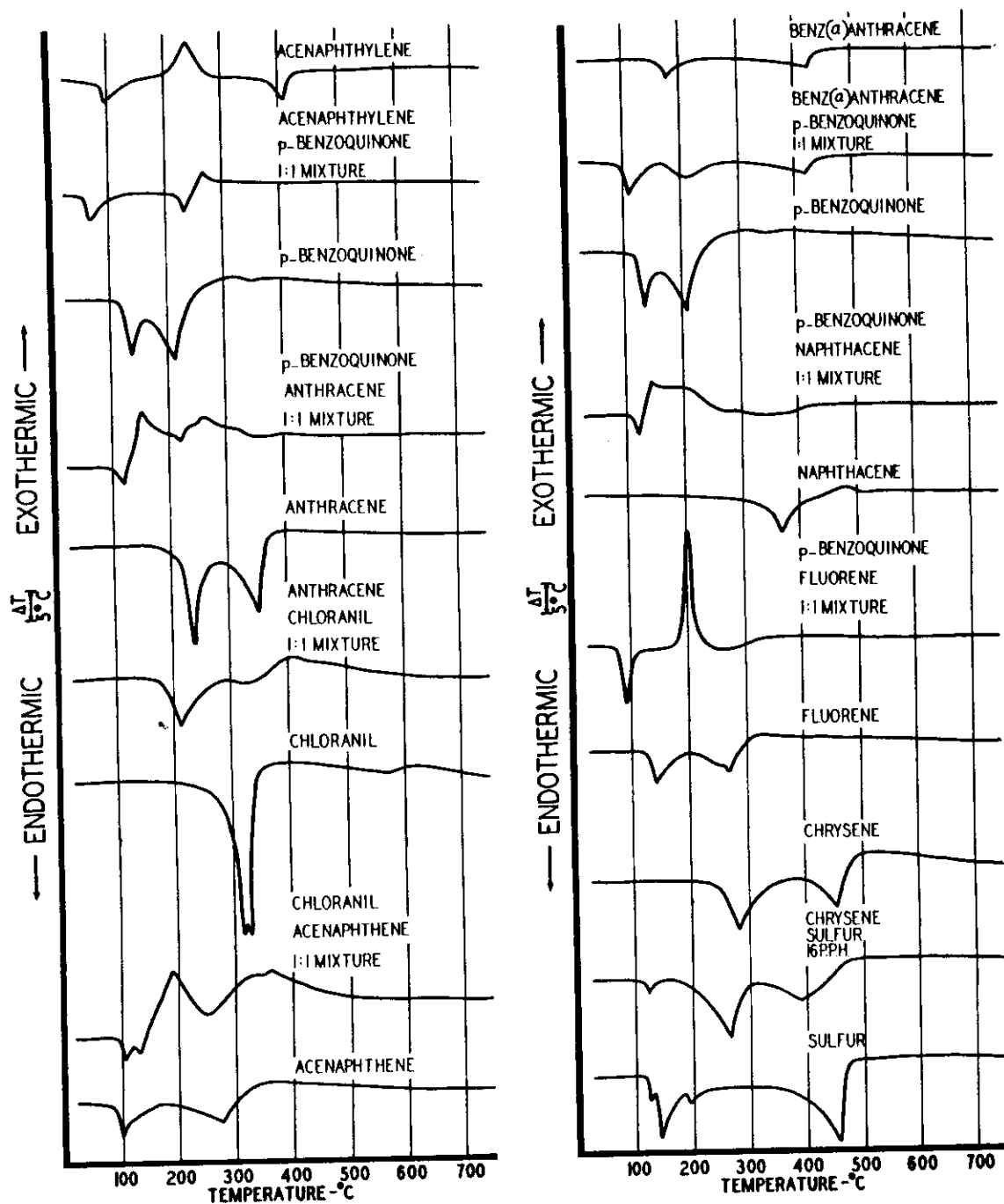


Figure 11. DTA Thermograms of Binary Mixtures of Aromatic Hydrocarbons

reacts immediately after the melting of benzoquinone, but the anthracene-chloranil mixture does not indicate any exothermic reactivity until both the anthracene and chloranil have melted. The solid chloranil is relatively insoluble in molten anthracene. The chrysene-sulfur mixture does not exhibit an exothermic region in its thermogram. Only the melting and boiling endotherms as affected by the presence of the other constituent are seen. All of these mixtures produced significant carbonaceous residues at 750°C. In every instance except for the reactions of benzoquinone with acenaphthene and acenaphthylene, the volatile fractions condensed in the exit KBr traps contained new products.

5. DISCUSSION OF RESULTS

5.1 Structure and Reactivity

The dependence of thermal reactivity of aromatic hydrocarbons on chemical structure has been discussed previously⁽¹⁾ in Volume X of WADD TR 61-72 in which 84 compounds were classified as thermally reactive or unreactive. In this supplement, the classification studies have been extended to 129 additional compounds of several different chemical types as well as to a number of binary mixtures of hydrogen donor-acceptor pairs.

Differential thermal analysis (DTA) has been extremely useful in providing significant information regarding the physical and chemical characteristics of model compounds at high temperatures. These studies have demonstrated the effectiveness of this technique in measuring melting and boiling points, crystal transformations, polymerization and degradation reactions, sample contamination, and even in sample identification. The DTA thermogram is an effective fingerprint that is sensitive to sample purity and crystallinity. The DTA results have again been utilized to classify the materials as thermally reactive, if a carbon residue was obtained, or thermally unreactive if no residue resulted. Reaction temperatures and residue yields are strongly dependent on the experimental conditions. Therefore this classification scheme is somewhat arbitrary inasmuch as both chemical reactivity and volatility have equally important roles in the classification.

As already discussed in detail in Volume X⁽¹⁾, the classification of the aromatic hydrocarbons within the respective "unreactive" and "reactive" categories by this DTA evaluation conformed fairly well with their classification based on reactivity parameters derived from electronic absorption spectra. No attempt has been made in this report to relate the determined reactivities of the substituted aromatics and the heterocyclics with other reactivity parameters. Since the mode and course of thermal reaction may vary with the nature of the substituent, it does not seem reasonable to consider the substituent effects as simple perturbation on the reactivity of the aromatic ring. The unsubstituted aromatic hydrocarbons listed in Tables 1 and 2 do not exhibit as close a correlation with reactivity and the derived ionization potentials as do the aromatics reported in Volume X. The reason is simply that the compounds included here cover a wide range of molecular structures diverging considerably from the simple fused polynuclear aromatics which were predominant in the first report. The thermal reactivity observed in the present DTA experiments for the majority of the reactive compounds in Table 2 can, in most cases, be related to the exocyclic structural features such as olefinic groups or a reactive linkage between two aromatic clusters.

The heterocyclic compounds listed in Tables 3 and 4 are found to be refractory compounds. Only 20 per cent of those examined gave a carbon residue in the DTA experiment and these "reactive" compounds all possessed substituents which have been found to increase reactivity of other fused ring compounds.

The activating effects of substituent groups on the thermal reactivity of aromatic systems is evident from the results of this survey for 76 substituted aromatics listed in Tables 5 and 6. Eighty per cent of the substituted aromatic compounds examined were found to give an appreciable carbon yield upon heating to 750°C. The majority of the compounds studied were two or three fused ring aromatics so that low volatility resulting from large molecular size is not a significant factor. The reactive compounds are discussed individually within each category in the remainder of this section.

5.2. Thermally "Unreactive" Aromatic Hydrocarbons

Thermograms have been run on an additional 27 aromatic hydrocarbons. Of this group, 18 have been classified as "unreactive" because no carbon residue was obtained. The thermograms for these materials in Figure 1 illustrate the thermal behavior. The majority of the thermograms show the melting and boiling endotherms only. Those compounds which are liquid at room temperature produce only the boiling endotherm. The presence of an impurity is shown in several of the thermograms by a melting point doublet or a shoulder on the major melting endotherm.

Physical property data on all of these unreactive aromatic hydrocarbons are given in Table 1. The majority of these materials boil at relatively low temperatures but many had interesting structural features, such as methyl or vinyl groups, which led to their examination. Several compounds show evidence of reactions in their thermograms but produced reaction products which were either volatile or unstable and did not yield a carbon residue. 2a, 3, 4, 5-Tetrahydroacenaphthene shows a small exotherm at 300°C, 1,2-dimethylnaphthalene gave a series of minor exothermic peaks around 350°-425°C and 1,2,3,6,7,8-hexahydropyrene also has a small exotherm at 400°C but in all cases no carbon product resulted. In a similar manner, both 2,4-dimethyl styrene and divinylbenzene have a small endothermic peak between 400° and 450°C, far above the major boiling endotherms of the monomers, indicating degradation and volatilization of polymeric product which had formed below 200°C. Several of the larger polynuclear aromatics in this group exhibit chemical thermal stability at temperatures approaching 500°C.

5.3. Thermally "Reactive" Aromatic Hydrocarbons

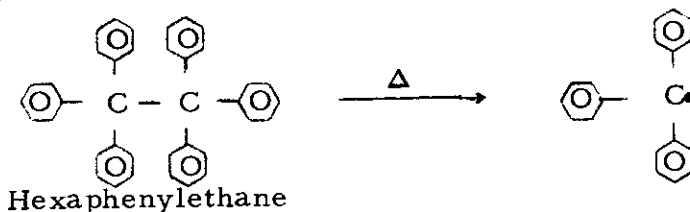
The thermal conversion of hydrocarbons to carbon and graphite results from a series of polymerization and dehydrogenation reactions. This reaction sequence produces a carbon-rich residue and a hydrogen-rich volatile product. The DTA examination of such a system gives information about the reaction temperatures as well as the extent of the reaction and, in some cases, considerable verification of the types of reaction. The individual thermograms of the reactive compounds are characteristically different than those of the unreactive species; in many cases exhibiting strong exothermic reaction maxima and in almost all instances the boiling endotherms are greatly reduced.

The thermally reactive polynuclear aromatics previously studied⁽¹⁾ have low ionization potentials, generally below 7.1 ev. However, in the somewhat

anomalous compounds reported here, where reactive substituents or extra-neous structures override the energy characteristics represented by ionization potentials, this relationship is obscured. A discussion of the thermal behavior for the nine aromatic hydrocarbons found to be thermally "reactive" follows:

5.3.1. Hexaphenylethane

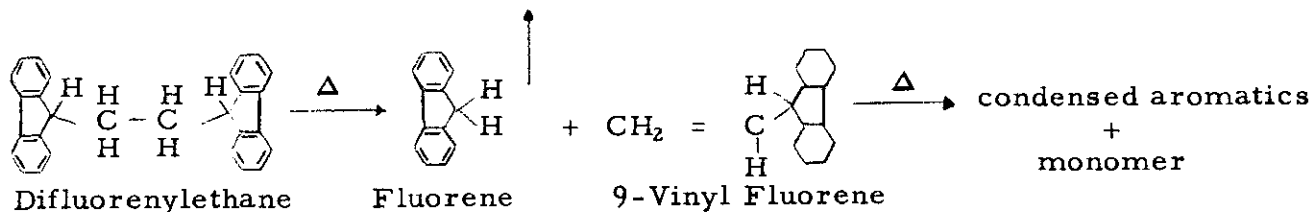
This interesting hydrocarbon is known to be readily dissociated into triphenylmethyl radicals. ⁽⁵⁾



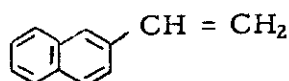
The thermogram (Figure 2) of hexaphenylethane exhibits a sharp melting endotherm followed by a gradual endothermic and subsequent exothermic rise. Presumably slow formation and reaction of these radical species occur over this wide temperature range. These reactions lead to the eventual formation of 8.5 per cent coke residue at 750°C and some volatile products unlike the starting material.

5.3.2. 1,2-Di-9-fluorenylethane

The thermogram of 1,2-Di-9-fluorenylethane seen in Figure 2, is characteristic of an unreactive material in that it consists of two sharply defined endotherms representing melting and boiling of the compound. To a large extent this represents the thermal behavior of this material as the condensate contained a major proportion of unreacted starting material. However, the large molecular size of this compound confers thermal stability and a surprisingly low volatility is exhibited to 335°C where a sharp boiling endotherm begins. The forward slope of this endotherm is modified at 370°C by some exothermic activity of short duration as the endothermic change again accelerates to a minimum at 392°C where vaporization is essentially complete. A carbon residue of 5 per cent was obtained. Fluorene and unidentified new products as well as 9-fluorenone and vinyl-fluorene were found in the condensate collected in the exit trap of the DTA apparatus. Thus, both disproportion and oxidation occurred with accompanying molecular growth and eventual carbonization of the higher molecular weight products. The alkyl bifluorene bridge presents a site of easy thermal bond cleavage in this molecule. Such a cleavage would be consistent with the volatile reaction products identified.



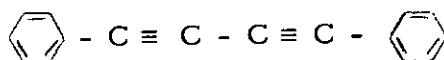
5.3.3. 2-Vinylnaphthalene



The typical vinyl polymerization-depolymerization behavior on thermal treatment is exhibited by 2-vinylnaphthalene. This compound leads to a 9.9 per cent carbon yield. The 2-vinylnaphthalene is more reactive than its 1-vinyl analog investigated earlier. The former undergoes its thermal transformation at appreciably lower temperatures and yields a larger carbonaceous residue.

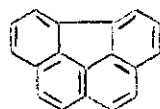
Similar to acenaphthylene and 1-vinylnaphthalene, major aliphatic products are formed on pyrolysis of this compound. Since acenaphthene and 1-ethylbenzene have been found as major products from the pyrolysis of acenaphthylene and 1-vinylnaphthalene, respectively, the role of the vinyl substituted aromatic grouping as an internal hydrogen acceptor during carbonization appears to be a general one.

5.3.4. Diphenylbutadiyne



Diphenylbutadiyne proved to be a very reactive material producing a 37.8 per cent carbon residue under our experimental conditions. The thermogram shown in Figure 2 exhibits a large exotherm peaking at 225°C indicating polymerization of the diacetylene chain. A complex highly cross-linked polymer is likely to result from this material since the reaction may produce several different isomers as well as the possibility of forming cumulenes. At higher temperatures, the thermogram exhibits a broad complex exotherm indicative of carbonization sequences. The condensates collected in the KBr trap differed from the starting compound but were not identified.

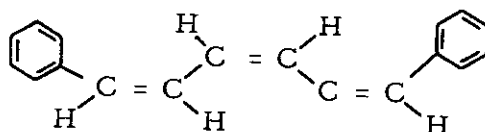
5.3.5. Benzo[g,h,i]fluoranthene



Benzo[g,h,i]fluoranthene is an interesting molecule because the strain introduced by the carbon-carbon bridge across the 5,1'-positions of the basic 3,4-benzophenanthrene structure should activate the 9,10-positions in the phenanthrene moiety. One would predict a higher reactivity for this compound than for 3,4-benzophenanthrene. Benzo[g,h,i]-fluoranthene gave a 2.1 per cent carbon residue in our DTA experiment. The DTA thermogram has a double melting endotherm, probably due to an impurity. Infrared analysis of the condensable volatiles showed some reaction products other than the starting compound, but the starting material is the major component of the distillate.

5.3.6. Diphenylhexatriene

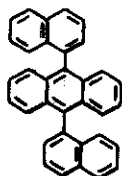
Diphenylhexatriene has a six-carbon bridge in which the double bonds are conjugated with the phenyl end groups.



The extent of resonance stabilization depends on the isomeric structure.

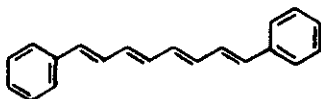
The DTA thermogram shows a strong polymerization exotherm with a maximum around 300°C followed by a broad unspecific exothermic trend at higher temperatures. A carbon residue of only one per cent was obtained at 750°C. The major portion of the trapped condensate exhibited an infrared spectrum similar to the starting material although several strong infrared absorption bands were missing. Additional more complex products were also obtained. The hexatriene bridge may undergo a Diels-Alder type condensation reaction to yield polymers which are, in general, readily depolymerized upon further heating.

5.3.7. 9,10-Di-1-Naphthylanthracene



The high reactivity (IP = 7.08 eV) and large size of this polynuclear aromatic hydrocarbon results in an ultimate 14.1 per cent carbon yield at 750°C. The DTA thermogram in Figure 2 is complex as a result of several simultaneously occurring exothermic and endothermic changes.

5.3.8. 1,8-Diphenyl-1,3,5,7-Octatetraene (trans)

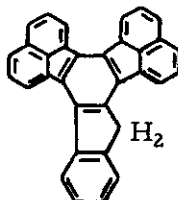


The DTA thermogram obtained when heating this compound shows a strong polymerization exotherm immediately following the melting endotherm. This is followed by a broad, shallow endotherm resulting from the gradual evolution of volatile products. A carbon residue of 5.1 per cent was obtained at 750°C. The volatile products which were condensed in the KBr trap proved to be entirely new materials which could not be identified. No starting compound was found in the condensate.

Conjugated polyenes, such as 1,8-diphenyl-1,3,5,7-octatetraene and diphenylhexatriene, are very reactive even when the terminal positions have been partially blocked by phenyl groups. These molecules can add to one another in a typical diene synthesis at moderate temperatures. The olefinic

functions can serve as good sites for polymerization as well as hydrogen addition. The products are usually complex as the reaction can proceed along several routes producing various cyclic systems. These are amenable to aromatization and subsequent carbonization at higher temperatures.

5.3.9. 14H-Acenaph[1,2-j] indeno[1,2-l]fluoranthene (peri-dinaphthylene-fluorene)



This interesting compound is actually a cyclic trimer formed from two molecules of acenaphthylene and one molecule of indene. The thermogram in Figure 2 somewhat resembles that previously obtained for decacyclene (acenaphthylene trimer). A double endothermic region is observed in the vicinity of 350°C. It is not yet known whether the apparent second endotherm actually results from exothermic reaction during melting or is a result of the melting of an admixed isomer or impurity. An interesting double exothermic region is observed in the temperature region between 550°C and 600°C. A carbon residue of 49.9 per cent is obtained at 750°C.

The condensate from the DTA treatment has been identified as the hydrocarbon decacyclene. It is not known whether decacyclene is formed as a reaction product from the disproportionation and recombination of acenaphthylene moieties or is largely admixed with the peri-dinaphthylene fluorene in the starting compound.

5.4. Thermally "Unreactive" Heterocyclic Compounds

Numerous heterocyclic compounds have been identified in the compositional analysis of coal tar pitches and other pyrogenous residues of interest in the manufacture of carbon and graphite.⁽⁶⁾ In order to investigate the structural effects of hetero atoms on thermal reactivity, a number of heterocyclic analogues of aromatic systems have been examined in our DTA apparatus.

The DTA thermograms shown in Figure 3 demonstrate the thermal behavior of some representative "unreactive" coal tar heterocyclics. These heterocyclics can be classed as "unreactive" since no carbon residue is obtained. All show sharp melting and boiling endotherms.

The DTA condensate from the majority of the heterocyclic compounds listed in Table 3 proved to be the pure starting materials. The condensate from 1-azafluoranthene shows some infrared structural differences from that of the starting material. 11H-Benzo[a]carbazole and benz[a]acridine underwent some thermal reaction as indicated by different species trapped in the distillates from the DTA runs. The infrared spectra of the **distillates showed**

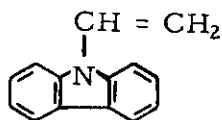
a large number of new bands in both cases. However, the reaction products as well as the starting materials are volatile and no carbon residues were obtained. 3,4-Dihydro-2-H-pyran-2-methanol also undergoes a thermal degradation to produce new volatile products that were collected in the KBr exit trap. The products could not be identified because of the complexity of the infrared spectrum but it is evident that the pyran ring opened at the oxygen atoms as the ether band at 8.1 microns was greatly diminished and the aliphatic C-H bands at 3.45 and 7.25 microns very much enhanced. The relative intensity of the alcohol OH band remained constant. It is interesting that the dibenzopyran, xanthene, was completely stable thermally and simply boiled out of the DTA apparatus at about 325°C. Compounds such as benzo[b]-naphtho[2,3-d]furan, xanthene, dinaphtho[1,2-b, 1',2'-e]-p-dioxin, and dibenzofuran may be regarded as aromatic ether in type. The thermal stability of the aromatic ether bonds is demonstrated by the complete nonreactivity of these oxygenated aromatics.

The thermal stability of the thiophene derivatives is attested by their formation in pyrolytic processes. Thiophene derivatives are found in coal tars and pitches and thianaphthene can be produced thermally by passing styrene and hydrogen sulfide over ferrous sulfide-alumina at 600°C.⁽⁷⁾ On the other hand, Badger⁽⁸⁾ states that in many ways the thiophene compounds resemble the corresponding benzene derivatives except that they are more reactive. They undergo substitution reactions with relative ease, and reactions by addition occur much more readily than with benzene homologs. The results of DTA examination indicate that in a noncatalytic thermal treatment the benzo-substituted thiophenes are "unreactive". The thermograms in Figure 4a show only melting and boiling endotherms and no carbon residues were obtained at 750°C. The condensates collected in the KBr condensate traps contained only starting material. It is apparent that the enhanced reactivity introduced by the heteroatom is insufficient to induce condensation reactions necessary to produce carbonization.

5.5. Thermally "Reactive" Heterocyclic Compounds

Only five of the 26 heterocyclic compounds examined in this study were found to yield carbon residue at 750°C. The substituent group activates the heterocyclic molecule in a manner similar to that observed with the aromatic hydrocarbons. The DTA thermograms of the reactive heterocyclics are given in Figure 4b and the properties and reaction data are summarized in Table 4.

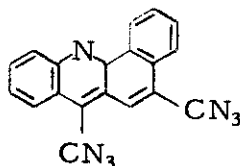
5.5.1. 9-Vinylcarbazole



This N-vinyl derivative of carbazole shows the same type of vinyl polymerization exotherm seen previously for vinyl naphthalene and acenaphthylene. An endotherm demonstrative of depolymerization and distillation follows. Only a minor portion of the polymer survives the depolymerization to undergo further condensation and rearrangements to carbon. A carbon yield of 1.9

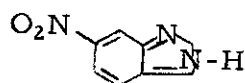
per cent was obtained. The thermally induced vinyl polymerization, therefore, introduces physical thermal stability of the carbazole moiety by increasing the molecular size. The carbazole structure appears to be more thermally stable than the naphthalene system in acenaphthylene or vinylnaphthalene, and resists the subsequent rearrangement sequences which lead to high carbon yields.

5.5.2. 5,7-Dimethylbenz[c]acridine



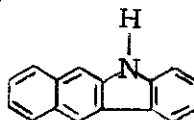
This compound gave a small carbon yield of 1.6 per cent in the DTA experiment. The thermogram shows no evidence of thermal reactivity other than the broad shallow vaporization endotherm which is found quite often with thermally reactive compounds. The activating effect of methyl substituents is again apparent in this instance since previously considered unmethylated benzacridines have been found to be unreactive.

5.5.3. 6-Nitroindazole



6-Nitroindazole is a reactive compound that produced a 23.6 per cent carbon yield in our DTA experiment. The thermogram shows a sharp well-defined melting endotherm in close agreement with the reported melting point. After melting, some evaporation occurs as the return to the baseline is gradual. At 300°C an exothermic reaction occurs that peaks at 355°C and is followed by a second exotherm peaking at 430°C. The nitro-group is known to increase the thermal reactivity of polynuclear aromatics by a very large factor. This compound is the only indazole examined to date and the thermal reactivity of indazole is not yet known. Since only the starting compound was found in the condensate there are no clues as to the thermal reactions taking place. This is an interesting system that warrants further study.

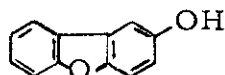
5.5.4. 5H-Benzo[b]carbazole



5H-Benzo[b]carbazole exhibits only the melting and boiling endotherms of a thermally stable compound. However, the relatively large molecular size has reduced the volatility of this compound to such an extent that its boiling temperature is around 475°C. This temperature is sufficient to induce dehydrogenation and free radical formation which results in molecular growth and finally carbonization at higher temperatures. A carbon residue of only

one per cent was obtained in the DTA experiment, attesting to the refractory nature of this compound. Only starting material was found in the KBr condensate trap.

5.5.5. 2-Hydroxydibenzofuran



The DTA thermogram of 2-hydroxydibenzofuran also shows only the melting and boiling endotherms with the reduction in the boiling endotherm often seen with reactive materials. The effect of the hydroxyl group is quite evident in comparing this thermogram with that of dibenzofuran in Figure 4a. The hydroxyl substituent has been shown to have a strong activating effect on aromatics such as naphthalene and fluorene although the effect is very dependent on the position of the substituent. Since the heterocyclic compounds, in general, have been found to be relatively unreactive, this activating effect of substituents is of interest and could be utilized to obtain carbon residues from heterocyclic ring systems. A carbon residue of 7.6 per cent was obtained from 2-hydroxydibenzofuran. No volatile new reaction products were found in the condensate collected in the exit KBr trap.

5.6. Thermally "Unreactive" Substituted Aromatic Hydrocarbons

The thermal behavior of a variety of aromatic and heterocyclic compounds characteristic of those found in the basic raw materials for carbon, i.e., coal tar and petroleum residues, have been discussed in the previous sections. Inferences have been drawn where possible relating thermal reactivity and chemical structure. In this and the following section, the discussion will continue on aromatic group compounds in which one or more of the periphery hydrogen atoms has been replaced by some other atom or group of atoms. Hydrocarbon groups such as methyl-, ethyl-, vinyl-, and phenyl- have already been discussed with aromatic hydrocarbons and are not included in these sections.

As in previous sections, the compounds have been classified as thermally "unreactive" if no carbon residue was obtained under the conditions of the DTA experiment and as "thermally reactive" if a residue was found. The compounds included in these two sections may be classified as follows: (1) Oxygenated aromatics; (2) Halogenated aromatics; (3) Aromatics with nitrogen substituents, and (4) Miscellaneous group with more than one type of substituent or with other atoms in the substituent group. This survey emphasizes the importance of substituent effects of carbonization reactivity and should provide a further basis for selection of raw materials for graphite.

Physical properties derived from the DTA thermograms of sixteen thermally "unreactive" substituted aromatics are summarized in Table 5 and the thermograms are given in Figure 5.

The substituents in these compounds represent most of the chemical elements found in the raw materials used in carbon manufacture: oxygen, halogen, nitrogen, iron and sulfur. All of these elements as substituents on an aromatic nucleus may greatly enhance the thermal reactivity toward carbonization. However, the compounds included in Table 5 are unreactive primarily because the substituents are incorporated in small unreactive ring systems. Again with the exception of 2-chloroanthraquinone, these compounds all distilled out of the DTA system without reaction as only starting material was found in the KBr traps. The 2-chloroanthraquinone did undergo reaction but forms only volatile products which were detected in the condensates along with unreacted starting material.

The DTA thermograms exhibit only melting and boiling endotherms typical of unreactive compounds. Small melting point doublets in the thermograms of 9,10-dichloroanthracene, 1-chloropyrene, and 2-naphthalenethiol indicate the presence of contaminants, probably isomers.

5.7. Thermally "Reactive" Substituted Aromatic Hydrocarbons

A systematized study of substituent effects of aromatic thermal reactivity in which all possible substituent orientations for several different chemical groups on any given aromatic nucleus were investigated, would be the most productive way to establish an experimental base for a sound theoretical solution. Unfortunately we have not been able to obtain many of the possible isomers for this complete approach so we must at the moment content ourselves with those compounds that are available and try to fill in the gaps later.

Substituent groups can greatly alter the reactivities of organic molecules. Considerable literature exists on the development of theories which describe the relationship between substituent effects and chemical reactivity.⁽⁹⁾ In the aromatics, good success has been achieved in correlating substituent effects with reactivity in benzene derivatives.⁽¹⁰⁾ Quantitative reactivity parameters, designated as σ values, have been determined for a wide variety of common substituent groups. These σ values represent the electronic effects of the substituent on reactivity.

It is expected that substituent groups would greatly modify the thermal reactivity of aromatic molecules. These substituents could significantly alter the electron density at various ring positions, alter the bond dissociation energies of the various bonds in the molecule and, stabilize reactive intermediates such as aromatic radicals. Perhaps most important, the substituents can themselves present reactive sites in the molecule at which various types of thermal condensation and degradation processes are possible.

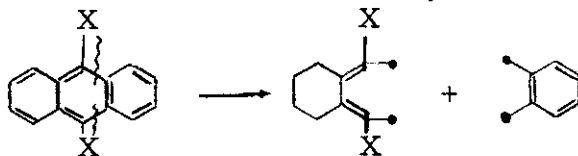
Substituents have been found to considerably influence thermal reactivity for the aromatics encompassed in these investigations. These results are discussed in this section. The sixty substituted aromatics found to be reactive from DTA examinations have been grouped by type of substituent insofar as possible to facilitate discussion. The physical property and reaction data derived from the DTA thermograms of all sixty compounds are summarized in Table 6 and the individual thermograms are shown in Figures 6 through 9 inclusive.

5.7.1 Halogen-Substituents

The five compounds included in this group are halogenated derivatives of thermally "unreactive" aromatic hydrocarbons and a quinone, anthraquinone, which is also "unreactive".

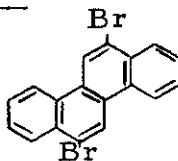
5.7.1.1. 9,10-Dibromoanthracene

The DTA thermogram of 9,10-dibromoanthracene shows evidence of reaction producing a broad endothermic region around 380°C followed by a small exothermic peak. Both the 9,10-dichloro- and 9,10-dibromoanthracenes exhibit the formation of new products in the trapped DTA distillate. The formation of new product was much more extensive for the dibromoanthracene, however, and a 19.9 per cent carbon residue was obtained. The 9,10-dichloroanthracene produced no carbon residue under the DTA conditions. Actually the dichloro-compound does give a carbon yield under normal coking conditions utilizing a slow heating rate. Unlike anthracene or any of the anthracene hydrocarbons, these two halogenated derivatives yield essentially non-graphitizable impervious type carbons. These carbons are obtained in the form of a shiny black film. These results suggest that the effect of the halogen substituents is to facilitate cleavage of the anthracene ring system to yield readily polymerizable radicals of the xylene or phenyl type.



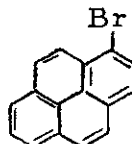
Such types of radicals could readily react to form highly cross-linked systems atypical of the anthracene hydrocarbons in general. Further studies of these systems are necessary before this mechanism can be regarded as more than speculative.

5.7.1.2. 6,12-Dibromochrysene



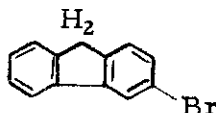
Dibromochrysene is seen to yield about 15 per cent carbon at 750°C. This carbon is very porous and disordered as if produced from a highly cross-linked organic material with extensive gas evolution occurring during the solidification stage. The volatile condensate from this material was not characterized. In the discussion of 9,10-dibromoanthracene ring cleavage facilitated by the halogen substituent was postulated as a possible reaction mechanism. The disordered carbon residue obtained from dibromochrysene is consistent with this postulate. The DTA thermogram shows a broad, shallow vaporization endotherm and a small reaction exotherm immediately following at about 520°C.

5.7.1.3. 1-Bromopyrene



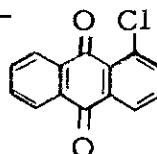
1-Bromopyrene was found to be reactive yielding 9.2 per cent carbon residue. The DTA curve is typical with a broad shallow vaporization endotherm followed by a slight exotherm at 485°C. The thermal reactions occur over a broad temperature range and include degradation reactions, possibly including ring cleavage as previously suggested. The condensate contained both starting material and new unidentified products.

5.7.1.4. 3-Bromofluorene



Although fluorene is unreactive and simply boils away, the bromo-substituent activates the fluorene nucleus thus effecting an ultimate debromination and condensation which gives rise to a carbon residue of 5.1 per cent in the DTA experiment. The thermogram does not provide much information on the reaction, however, as volatilization occurs over a broad temperature region and obscures any other phenomenological change. The distillate contained only the pure starting material.

5.7.1.5. 1-Chloroanthraquinone



1-Chloroanthraquinone, unlike 2-chloroanthraquinone and anthraquinone, produced a small carbon residue of about 1.5 per cent. The DTA curve gives no essential evidence of reaction and the condensed material found in the exit KBr trap was only starting 1-chloroanthraquinone.

5.7.2. Nitrogen-Containing Substituents

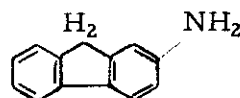
Three types of nitrogen substituents were included in this study: (1) amino compounds, (2) azo-compounds, and (3) nitro-compounds. All of these nitrogen groups were found to have a powerful influence on the thermal reactivity of aromatic hydrocarbons. Only about 15 per cent of the nitrogen substituted compounds examined were classed as unreactive. The activating effect of the group varies with the position of substitution and, of course, is sensitive to the presence of other substituent groups.

5.7.2.1. Amino-Compounds

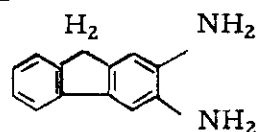
The amino-group has demonstrated a pronounced effect on the thermal reactivity of aromatic hydrocarbons. The substituent is readily oxidized and

also has a strong activating effect on the aromatic ring by contributing an electron pair to the π -electron system through resonance interaction. These effects are demonstrated by the thermal reactivity of the fluorene molecule substituted by amine groupings.

5.7.2.1.1. 2-Fluorenamine



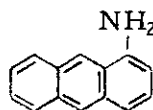
5.7.2.1.2. 2,3-Fluorenediamine



The thermograms of these two compounds show only the melting and boiling endotherms with the typical attenuation and broadening of the boiling curve seen in reactive compounds. The melting point doublet in the diamine thermogram indicates an impurity which may be responsible for the lower carbon yield of the latter amine. 2-Fluoreneamine gave a 12.9 per cent carbon residue and 2,3-fluorene-diamine yielded only 6.9 per cent carbon at 750°C.

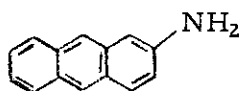
5.7.2.1.3. 1-Anthramine

(6.1 per cent residue)



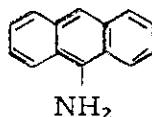
5.7.2.1.4. 2-Anthramine

(1.3 per cent residue)



5.7.2.1.5. 9-Anthramine

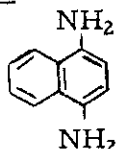
(15.4 per cent residue)



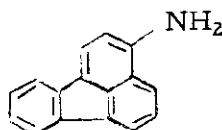
The amino group induces thermal reactivity in the **unreactive** anthracene ring system. The position of substitution by the amino group is seen to have an important effect on reactivity as measured by carbon residue. Hence the

9-anthramine with the $-NH_2$ group in the most reactive position of anthracene is more reactive than the corresponding 1- and 2-isomers. The thermograms of these compounds show only the melting and boiling endotherms. Melting point doublets, indicating impurities, are present in the 2-anthramine and 9-anthramine curves.

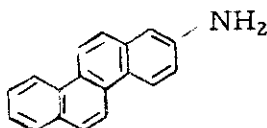
5.7.2.1.6. 1,5-Naphthalenediamine



5.7.2.1.7. 3-Fluorantheneamine



5.7.2.1.8. 2-Chryseneamine



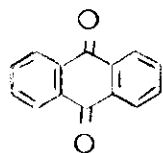
The aromatic hydrocarbons naphthalene, fluoranthene, and chrysene have been shown previously⁽¹⁾ to be unreactive in our DTA system. Introduction of the strongly electron releasing amino groups as a substituent activates the ring and presents a reactive site leading to carbon formation to the extent of 5.1, 36.2 and 11.9 per cent, respectively. The polar amino group seems to have an even larger effect on thermal activation than either the methyl group or the hydroxy group in these same ring systems.

Only the 3-fluorantheneamine exhibits a considerable reaction exotherm in its DTA thermogram. Any exothermic activity of the other compounds is masked by simultaneously occurring endothermic changes. The carbonization sequences apparently are gradually occurring processes. The DTA condensates provide no clues to the identity of reaction intermediates since only the volatile starting compound was found in each case.

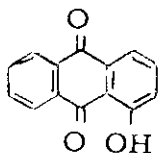
5.7.2.1.9. 1-Amino-anthraquinone

5.7.2.1.10. 1-Amino-4-Hydroxyanthraquinone

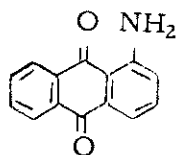
The activating effect of the amino group is further illustrated by the DTA results on 1-aminoanthraquinone and 1-amino-4-hydroxyanthraquinone which yielded 12.9 and 42.9 per cent carbon residues, respectively. The synergistic effect of an amino- and hydroxy-group in para-configuration is evident from the following comparison of carbonization behavior.



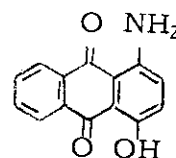
Anthraquinone
0% residue



1-Hydroxyanthra-
quinone
3.8% residue



1-Aminoanthra-
quinone
12.9% residue



1-Amino-4-hydroxy-
anthraquinone
42.9% residue

The thermogram of 1-aminoanthraquinone shows the melting and boiling endotherms with only a very small broad exothermic region above the boiling temperature probably associated with charring.

The thermogram of 1-amino-4-hydroxyanthraquinone has a melting endotherm followed by a fairly strong reaction exotherm peaking at 296°C. This exotherm is followed by a vaporization endotherm at 375°C and another broad and low exotherm beginning around 390°C.

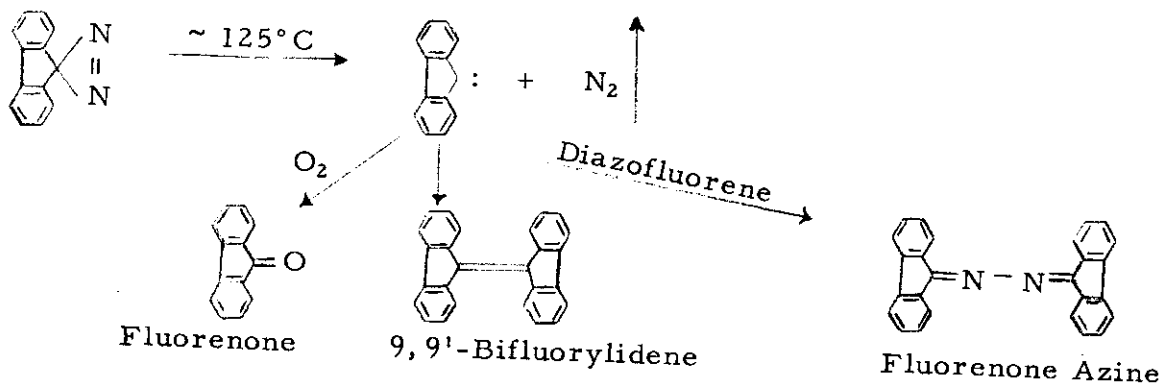
Only the starting compounds were found in the KBr condensate traps in both instances indicating that the reaction products were either not volatile or were noncondensable. It is probable that the reactions involved elimination of the amino and carboxyl groups in the form of noncondensable volatiles and molecular growth of the remaining aromatic moieties.

5.7.2.2. Azo Compounds

The azo compounds are interesting nitrogenated aromatics which can readily undergo carbon-nitrogen bond cleavage to yield reactive aromatic species.

5.7.2.2.1. 9-Diazofluorene

9-Diazofluorene reacts exothermically immediately after melting to form a readily carbonizable dimer, most probably 9,9'-bifluorylidene. A second exothermic peak around 440°C corresponds to the reaction temperature of 9,9'-bifluorylidene. From the condensable material examined in the KBr trap minor formation of fluorenone and fluorenone azine is indicated. All reactions are presumed to proceed via the carbene intermediate.⁽¹¹⁾

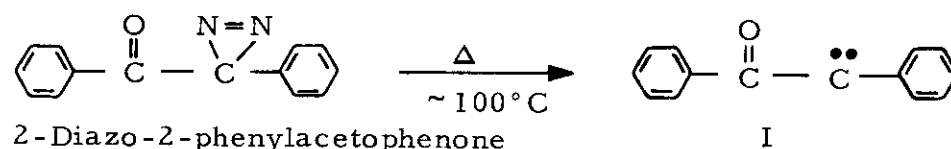


5.7.2.2.2. Diazodiphenylmethane

The thermogram of diazodiphenylmethane in Figure 6 shows the melting endotherm followed by a very large exotherm at about 125°C. The condensate in the KBr trap was found to contain mostly benzophenone. It is suspected that benzophenone formed as a result of oxidation of the thermal radical intermediate. Benzophenone azine was found to be the principal thermal product of diazodiphenylmethane heated to 136°C under vacuum in a separate experiment. The reaction is presumably initiated by formation of the carbene and rapid combination by the reactive species with the parent diazo-compound. (ii) Tetraphenylethylene and fluorene are also expected products but no evidence of their formation was found. A carbon yield of 6.4 per cent was obtained in the DTA run.

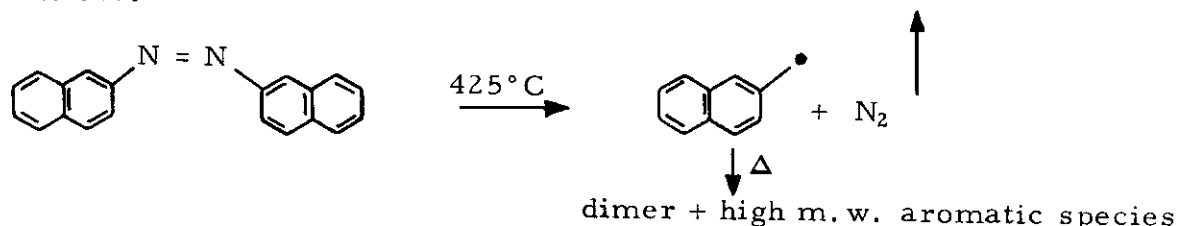
5.7.2.2.3. 2-Diazo-2-Phenylacetophenone

This compound undergoes an almost explosive exothermic reaction immediately after melting. This is followed by a second smaller and broader exotherm peaking around 245°C. At higher temperatures the thermogram is essentially flat. A residue of 2.7 per cent was obtained. The condensate contained no starting material. The products appear to be a rather complex mixture in which dicarbonyl compounds are an important fraction. The reaction is expected to proceed through the radical intermediate I.

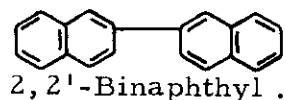


5.7.2.2.4. 2,2'-Azonaphthalene

The DTA thermogram and examination of the condensed volatile products indicate that 2,2'-azonaphthalene, similar to the diazo compounds, eliminates nitrogen to form reactive radical intermediates which can then undergo recombinations.



The major volatile product found in the KBr trap is the dimer:

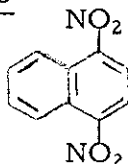


A carbon yield of 12.1 per cent was obtained at 750°C.

5.7.2.3. Nitro Compounds

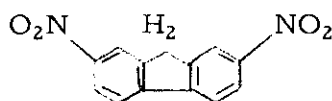
Nitro-groups strongly enhance thermal reactivity of aromatic hydrocarbons. The mechanism of this substituent effect is still unclear, although nitro compounds are well known to complex with aromatic rings and such types of self-complexing may be involved in these systems. Other possible reaction routes include thermal elimination of the substituent group, an activating effect of the group on other ring positions, and an oxidizing action of the nitro compound.

5.7.2.3.1. 1,4-Dinitronaphthalene



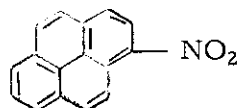
The DTA thermogram of 1,4-dinitronaphthalene, which gave a 10.1 per cent yield of carbon, indicates a somewhat complex series of exothermic reactions between 375° and 425°C. The condensate collected in the KBr trap contained only starting compound; no other condensable products were detected. From this information, no reaction mechanism can yet be postulated. The nitro-group is seen, however, to exert an extreme effect on the reactivity of the highly stable naphthalene moiety.

5.7.2.3.2. 2,7-Dinitrofluorene



The thermogram obtained from this compound shows no exothermic activity in spite of the high reactivity indicated by the carbon yield of 25.8 per cent. A large boiling endotherm is observed at 448°C. The condensate contained no starting compound. The infrared spectrum of the condensate had a strong carbonyl band indicating a probable oxidative effect of the nitro-groups on the aromatic portion of the molecule.

5.7.2.3.3. 1-Nitropyrene



A strong exothermic reaction at 400°C is seen in the thermogram of 1-nitropyrene. The products of the reaction were converted completely to carbon and noncondensable gases as the condensate collected in the KBr exit trap contained only starting material. The high initiation temperature of this reaction resulted in considerable volatile losses of the starting compound. The strong activating effect of the nitro-group on the pyrene system is illustrated in the following comparison of the carbon yields obtained from several different 1-substituted pyrenes.

Table 9
Effect of 1-X-Substituents on Carbonization
of Pyrene

Substituent in 1-Position	Carbon Yield at 750°C, Per Cent
-NO ₂	39.5
-NH ₂	0.3
-Cl	0.0
-CH ₃	0.0
-H	0.0

5.7.3. Oxygen-Containing Substituents


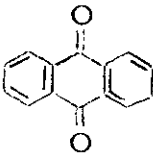
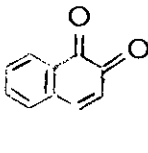
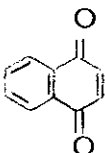
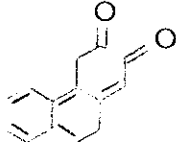
This is the largest group of reactive substituted aromatics which has been examined in this survey, encompassing a total of 37 compounds. For the purposes of this discussion, the oxygenated aromatics will be grouped by functional groups: (1) quinones, (2) hydroxy compounds, (3) hydroxy-quinones, and (4) carboxylic acids.

The reactivity introduced by hydroxy and quinone substitution on aromatic nuclei will be shown to be very dependent on the orientation of such placement. Both the quantity and quality of the coke obtained from these materials varies widely with the positioning of the substituents. It is not yet possible to suggest a uniform mechanism for the thermal changes leading to carbonization of these compounds.

5.7.3.1. Quinones

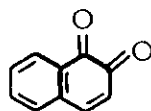
The quinones are an important class of compounds in carbonization since they are not only present in the raw materials for graphite but are undoubtedly formed from any oxidative treatment of these raw materials. The thermal interactions of quinone additives to aromatic hydrocarbon systems is also of great interest and will be discussed in a later section.

The DTA data summarized in Table 6 show that the thermal reactivity of the quinones is markedly dependent on structure and position of the quinone oxygen. The extent of carbon formation is not directly related to either molecular size or the oxidation potential of the quinone as evidenced from the following comparison:

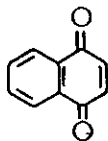
Quinone					
C. V. %	0.0	0.0	27.5	42.6	40.3
Oxid. Pot.	0.794	0.154	0.576	0.484	0.460

It is presently felt that structural features have a dominant influence on the reaction.

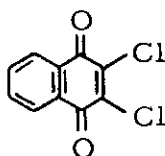
5.7.3.1.1. 1,2-Naphthoquinone



5.7.3.1.2. 1,4-Naphthoquinone

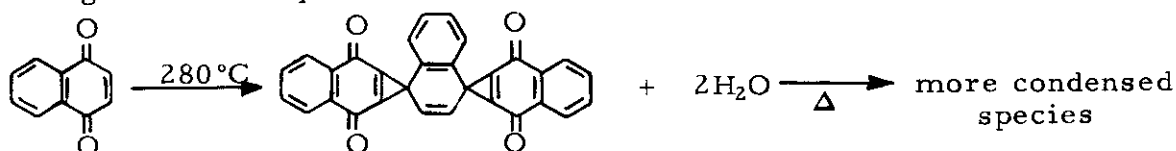


5.7.3.1.3. Dichlone



The thermogram of 1,2-naphthoquinone (Figure 8) is that of a very reactive material reported to decompose on melting. The thermogram shows that on melting, around 115°C, the material undergoes a violent exothermic reaction which reached a maximum at 155°C in this instance. Upon continued heating, vaporization ensues around 240°C but is abruptly interrupted by a second exothermic reaction at 275°C. The resultant products then carbonize to yield a residue of 27.5 per cent based on the starting sample. The condensate collected in the KBr trap contained no starting compound. Its infrared absorption spectrum had broad indistinct absorption bands indicative of a complex mixture. The spectrum included a strong OH band and a non-quinonoid carbonyl absorption indicating that hydrogen extraction and ring cleavage occur in the reaction sequence.

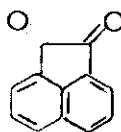
The thermogram of 1,4-naphthoquinone also exhibits a strong exothermic reaction but at a considerably higher temperature of about 280°C. Water was evolved during this polymerization reaction. A high yield of 42.6 per cent of poorly graphitizing carbon was finally obtained at 750°C. The tendency of quinones to readily undergo condensation reactions suggests the following reaction sequence.



Such polymeric aromatic structures would be quite disordered and nonplanar and yield an ultimately nongraphitizable carbon network.

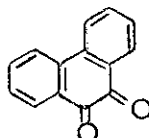
Substitution of the ortho-hydrogens in 1,4-naphthoquinone by chlorine, forming the compound dichlone, practically eliminates all tendency to polymerization and thermal treatment in the DTA apparatus leads to only a 1.5 per cent carbon residue. The thermogram for this compound (Figure 8) resembles those of the characteristic "unreactive" type. The major endothermic physical changes obscure any small polymerization exotherms. The condensate was largely the starting species but included a small amount of a new aromatic structure.

5.7.3.1.4. Acenaphthenequinone



The DTA thermogram of acenaphthenequinone indicates an exothermic reaction which interrupts the vaporization at about 400°C. A carbon residue of 14.6 per cent was obtained at 750°C. Examination of the condensate in the KBr trap indicates that actual carbon-carbon bond cleavage involving the C=O carbons may be initially involved.

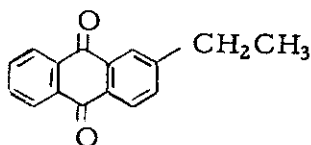
5.7.3.1.5. Phenanthrenequinone



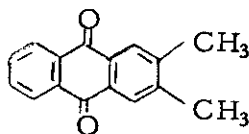
This ortho-quinone exhibits marked thermal reactivity as seen in its DTA thermogram in Figure 8. A large exothermic region occurs in the temperature range of 375°C to 450°C. A 40.3 per cent carbon yield which corresponds to about 60 per cent retention of the aromatic ring carbon is observed.

The nature of the condensable products which show the formation of non-ketonic carbonyl groups indicate that cleavage of the carbon-carbon bond between adjacent carbonyls may be important.

5.7.3.1.6. 2-Ethylanthraquinone



5.7.3.1.7. 2,3-Dimethylantraquinone

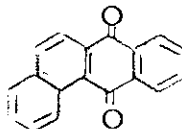


It is of interest to note that the activating effect of methyl and ethyl substituents demonstrated for the pure aromatic hydrocarbons is effective for the quinone system as well. Whereas the unsubstituted 9,10-anthraquinone is thermally stable, its ethyl and dimethyl derivatives proved to be reactive.

2-Ethylanthraquinone melts about 175°C lower and boils at about the same temperature as anthraquinone. Thus, this anthraquinone derivative has much more mobility over an extended temperature range in addition to having a substituent readily susceptible to bond cleavage or dehydrogenation. The thermogram shows no exothermic reactions but does exhibit the reduced boiling endotherm of a reactive material. A carbon residue of 6.9 per cent was obtained. The condensate collected in the exit trap contained only the starting compound.

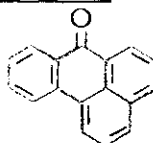
The dimethyl derivative also has a lower melting point and a higher boiling point than the parent anthraquinone. The thermogram of 2,3-dimethylantraquinone shows no exothermic reactivity. Only the characteristic melting and boiling endotherms are observed. A 7.1 per cent carbon residue is obtained in the DTA experiment. New products of an unidentified nature were observed in the volatile condensate. These indicates that carbon-carbon bond cleavage of the C=O carbon may be involved in the thermal reactions.

5.7.3.1.8. Benz[a]anthracene-7,12-dione



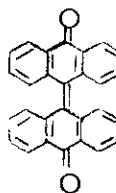
Benz[a]anthracene-7,12-dione, the 1,2-benzo-substituted anthraquinone was hardly more reactive than anthraquinone, yielding only 0.6 per cent carbon in the DTA run. It has a somewhat lower melting point and higher boiling point than anthraquinone and this slight increase in reactivity is due to its greater molecular size. The condensate contained a new quinone in low concentration. This product could not be identified.

5.7.3.1.9 7H-Benz[de]anthracene-7-one



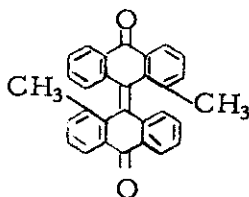
The DTA thermogram of this ketone derivative exhibits a broad endothermic band of unknown origin prior to a sharp melting endotherm at 175°C and a shallow broad vaporization endotherm between 325° and 475°C. Several of the trihydroxy-anthraquinones which will be discussed later also show an endothermic effect prior to melting. This behavior has not yet been explained. 7H-Benz[de]anthracene-7-one produced a 15.9 per cent carbon residue at 750°C.

5.7.3.1.10. $\Delta^{10,10'}$ -Bianthrone



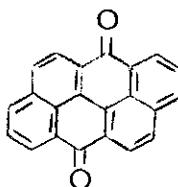
$\Delta^{10,10'}$ -Bianthrone is the quinonoid derivative of 9,9'-bianthryl, a dimer of anthracene. Its thermogram is singular in that it exhibits no melting or vaporization endothermic activity at all. The compound gives a strong sharp exothermic reaction peaking at 310°C which produced a 74.3 per cent ultimate carbon yield. The condensable volatiles collected in the KBr trap were completely new products which could not be identified from their IR spectra.

5.7.3.1.11. 4,4'-Dimethylbianthrone



This dimethyl derivative of $\Delta^{10,10'}$ -bianthrone demonstrates a high degree of thermal reactivity but is not as reactive as the nonmethylated parent compound. The thermogram (Figure 9) exhibits a large sharp exotherm at 375°C immediately following the melting endotherm, whereas the bianthrone reacted in the solid state at a temperature below 300°C . This reduced reactivity is unexpected in view of the normal activating effect of methyl substituents as well as the increased steric strains imposed on the molecule by the location of the methyl groups. It is possible that ring closure at the 4,4'-positions is important in the thermal reaction of the $\Delta^{10,10'}$ -bianthrone. Such closure would be hampered by the methyl substituents. However, this compound is still one of the more reactive of those studied, producing an ultimate carbon residue of 48.8 per cent in the DTA run. The condensate was found to contain new carbonyl compounds that could not be identified.

5.7.3.1.12. Dibenzo[cd,jk]pyrene-6,12-dione



The thermal reactivity introduced by the quinone function is demonstrated again by the DTA thermogram for dibenzo[cd,jk]pyrene-6,12-dione in Figure 9 which may be contrasted to that of the parent hydrocarbon, dibenzo[def,mno]chrysene.⁽¹⁾ The quinone undergoes a complex exothermic reaction sequence upon melting around $425^{\circ}\text{--}450^{\circ}\text{C}$. A very high carbon residue of 70.0 per cent is obtained. The absence of any condensable volatiles in the KBr trap, plus the large carbon residue, indicates that all of the carbon atoms exclusive of the carbonyl carbons are ultimately incorporated into the carbonaceous structures. The later group could simply be eliminated in the form of carbon monoxide.

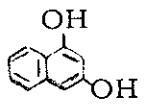
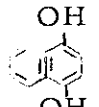
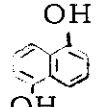
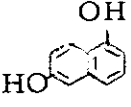
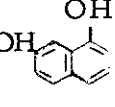
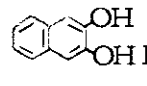
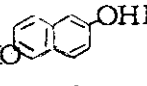
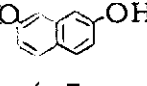
Quinone groupings are thus seen to invoke extreme enhancement of thermal reactivity of aromatic hydrocarbons. The mechanisms of these effects should be elucidated by further chemical study of selected compounds.

5.7.3.2. Hydroxy Compounds

The introduction of one or more hydroxyl groups on aromatic ring systems has increased the thermal reactivity in every case examined in this survey with the exception of hydroquinone and phenol, which distill out of the DTA system at relatively low temperatures.

5.7.3.2.1. Naphthalenediols

Eight of the ten possible structural isomers of dihydroxy naphthalene (naphthalenediols) have been examined by DTA. Their thermal reactivity was found to vary widely with structure, which differed in the positioning of the hydroxyl groups, as illustrated below. The carbon residue yield in the DTA apparatus is listed for each compound.

								
Per Cent Residue	47.8	39.2	9.6	21.9	1.5	3.1	4.3	6.7

Thermal reactions probably involve the OH group. The naphthalenediols are all readily oxidized and, in fact, oxidize in alkaline solution on standing at room temperature. In other reactions leading to the formation of additive intermediates, it is probable that at least one of the hydroxyl groups undergoes tautomeric change to the ketonic form.



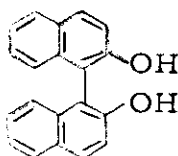
The thermogram for 1,3-Naphthalenediol in Figure 7 shows the melting point at 124°C followed by a small exotherm at 250°C and a larger exotherm at 450°C. A carbon residue of 47.8 per cent is obtained at 750°C. The condensate collected in the KBr trap contained no starting material. The new products were complex and had very little OH and no ketonic groups, indicating the elimination of the oxygen in the volatile products.

1,4-Naphthalenediol has been shown to have an extremely high coking value like its oxidation product 1,4-naphthoquinone. This latter material has been found to undergo a very rapid exothermic polymerization at 280°C and it was thought that the 1,4-naphthalenediol might react similarly.

As seen in the thermogram of Figure 7, 1,4-naphthalenediol exhibits a continued broad exotherm over the large temperature range above its melting point. The carbonization reactions for this material are undoubtedly much more gradual than for the corresponding quinone. No explanation is offered for the exotherm preceding the melting point. This curve is, however, completely reproducible and this system certainly warrants further study.

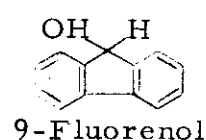
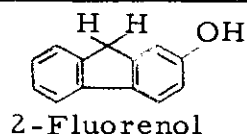
The thermograms for 1,5-, 1,6-, 1,7-, 2,3-, 2,6-, and 2,7-naphthalenediols which follow in Figures 7 and 8 show no exothermic regions although they exhibit the reduced vaporization endotherms typical of many reactive compounds. The condensates for the 1,6- and 1,7-isomers contained only the starting compound. The condensates for the 1,5- and 2,6-isomers contained new products of mixed composition.

5.7.3.2.2. 1,1'-Bi-2-Naphthol



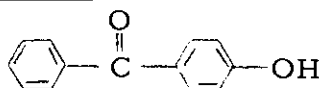
The thermogram obtained from this compound showed only the melting and attenuated boiling endotherms typical of a slightly reactive compound. The examination of the condensate by infrared absorption spectroscopy showed the presence of a new product with an ether band, indicating that a condensation reaction involving the hydroxyl groups had occurred. A 1.6 per cent carbon residue was obtained.

5.7.3.2.3. Fluorenols



These three hydroxy-isomers are all derivatives of the unreactive aromatic hydrocarbon, fluorene. In all cases, the -OH group induces thermal reactivity, although it is evident that the extent of activation is structure dependent. The DTA thermograms in Figure 8 indicate that only the 2-fluorenol isomer undergoes an exothermic polymerization. The other two compounds produced typically "unreactive" type thermograms. 2-Fluorenol gave a 9.8 per cent carbon yield as compared to 0.8 and 0.5 per cent for 3-fluorenol and 9-fluorenol, respectively. Of interest is the formation of fluorenone from 9-fluorenol indicating thermally induced oxidative reactions.

5.7.3.2.4. 4-Hydroxybenzophenone



4-Hydroxybenzophenone shows no indication of thermal reaction on heating to 750°C in the DTA apparatus. However, it did produce a carbon residue of 2.2 per cent. The thermogram shown in Figure 7 consists of a sharp melting endotherm which agrees with the reported melting temperature and a boiling endotherm peaking at 408°C. The volatiles collected in the KBr trap consisted entirely of the starting compound.

5.7.3.2.5. Poly-hydroxy-derivatives of Anthracene

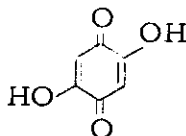
	1,8-Dihydroxyanthrone	Anthrarobin	1,4,10-Trihydroxyanthrone
Per Cent Carbon	13.1	60.5	45.4

These poly-hydroxy-derivatives of anthracene have all exhibited considerable thermal reactivity in the DTA examination although their thermograms show only endothermic reactivity. The thermograms of 1,8-dihydroxyanthrone and 1,4,10-trihydroxyanthrone consist only of a normal melting endotherm and a reduced broad boiling endotherm. On the other hand, the thermogram of anthrarobin (Figure 9) shows a rather complex series of endothermic bands between room temperature and 300°C. In an effort to understand the cause of the low temperature endotherm, this compound was examined in the hot stage microscope but no detectable change was observed below 190°C when sublimation began. Melting occurred only slightly at 280°C to produce a sintered appearance and above 300°C sublimation and vaporization stops. The material began to darken around 225°C and was black at 300°C. This compound is very reactive producing a carbon yield of over 60 per cent. No starting compound was found in the condensate collected in the exit KBr trap of the DTA apparatus. The condensate was a complex mixture containing hydroxyl and quinone oxygen groups. The formation of ether-like products from the 1,4,10-trihydroxyanthracene may be indicative of thermal polymerizations by dehydration. The broad endothermic regions found in these thermograms may indicate continual evolution of volatiles such as H₂O during the carbonization sequence.

5.7.3.3. Hydroxy-quinones

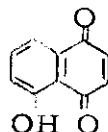
Seven compounds which contained both hydroxy- and quinone groups on the same aromatic nucleus have been included in this survey. As would be expected, these materials proved to be very reactive on thermal treatment producing in almost every case very high yields of carbon. In each instance the addition of the hydroxy substituents increased the carbon yield as compared to the unsubstituted quinone.

5.7.3.3.1. 2,5-Dihydroxybenzoquinone



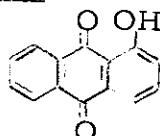
2,5-Dihydroxybenzoquinone is a relatively low molecular weight but high melting material which appears to react exothermally above its melting point at about 250°C and again at about 340°C. On heating to 750°C, a carbon residue of 29.8 per cent was obtained in the DTA run. No insight into the reactions involved was obtained on analysis of the condensates which yielded only starting 2,5-dihydroxybenzoquinone. The parent compound, p-benzoquinone, is unreactive, melts at 116°C, and boils out of the DTA apparatus at 210°C.

5.7.3.3.2. Juglone



The thermogram of juglone or 5-hydroxy-1,4-naphthoquinone shows this material to be another extremely reactive compound. The addition of the hydroxy group increases the reactivity of the parent quinone. 1,4-Naphthoquinone yielded 42.6 per cent carbon residue on heating to 750°C in a DTA run. Juglone yielded a 64.7 per cent carbon residue which is nearly the entire carbon composition of the molecule. Upon melting juglone reacts exothermally around 200°C producing a strong, sharp exotherm. The thermogram shows no further activity upon heating to 750°C. The condensate consisted almost entirely of starting compound. Only one new infrared band at 5.90 microns was observed in the spectrum of the condensate, indicating a small amount of a new quinone was formed during the reaction.

5.7.3.3.3. 1-Hydroxyanthraquinone



1-Hydroxyanthraquinone is the least reactive of a number of hydroxyanthraquinones examined giving only about 35 per cent residue in the DTA experiment. In addition, the DTA thermogram indicates the sample is not pure and there is no agreement between the literature reported melting point and the measured value. The thermogram consists of the melting and boiling endotherms only.

5.7.3.3.4. Tri- and Tetra-hydroxyanthraquinone Compounds

Anthragallol (1,2,3-trihydroxyanthraquinone)
 Purpurin (1,2,4-trihydroxyanthraquinone)
 Anthrapurpurin (1,2,7-trihydroxyanthraquinone)
 Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone)

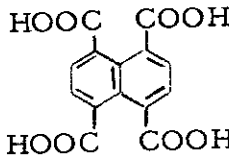
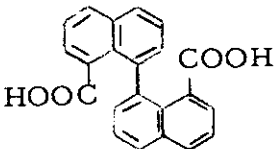
In Figure 7 are the thermograms for three trihydroxyanthraquinone isomers, and a tetrahydroxyanthraquinone. These compounds are used in dye-stuffs and are widely known under the trivial names used in this report. The thermograms show a diverse thermal behavior for these compounds which vary only in the position of the third (in the last case the third and fourth) hydroxyl group as follows:

3-Position I	4-Position II	7-Position III	5, 8-Positions IV
m. p. - (?) 310-d(Lit.)	260°C	340°C	300°C
b. p. - ~415°C	415°C	--	460°C
Residue 41 per cent	30 per cent	47 per cent	12 per cent

Anthragallol (I) and anthrapurpurin (III) exhibit endothermic activity between room temperature and 150°-200°C that does not entail melting or a color change detectable to the eye. Their thermograms are complex with a number of broad exothermic regions. Anthragallol has an endotherm of unknown origin at 790°C. Anthragallol produced a condensate that was aliphatic in nature, whereas anthrapurpurin produced no new condensable products as only starting material was found in the condensate.

Purpurin (II) and quinalizarin (IV) produced more normal thermograms which showed typical melting endotherms and reduced vaporization endotherms indicating considerable thermal reactivity. Both compounds gave less carbon residue than anthragallol and anthrapurpurin although the yields are appreciable. The condensates contained only starting material, although in the case of quinalizarin very little condensate was obtained.

5.7.3.4. Carboxylic Acids

		<u>Carbon Residue</u>
1)	1, 4, 5, 8-Naphthalene tetracarboxylic acid	
		19.8%
2)	1, 1'-Binaphthalene di-carboxylic acid	
		27.5%

The DTA thermograms for the above two polynuclear aromatic carboxylic acids examined in this survey are shown in Figure 8. Both compounds proved to be quite reactive on thermal treatment producing carbon yields at 750°C of 19.8 per cent and 27.5 per cent, respectively. The thermograms do not exhibit any pronounced exothermic reactivity and are quite unlike the DTA curves of other very reactive species.

Examination of the volatile products indicates that primary reactions occur by way of the functional -COOH groups. Evidence for considerable anhydride formation through dehydration is apparent from the trapped condensates. Additionally decarboxylation reactions can yield reactive species capable of undergoing further condensation.

5.7.4. Sulfur-containing Substituents

Sulfur is found in coal tar pitches and in petroleum coking residues in sufficient quantity to merit the examination of aromatic sulfur compounds. The availability of sulfur substituted aromatics is limited and, therefore, these compounds have not been extensively investigated by DTA.

p-Xylylene-dithiol gave a carbon residue of 15.5 per cent in the DTA run shown in Figure 9. The thermogram shows the melting endotherm at 47° followed by the vaporization endotherm which is interrupted at 295°C by an exothermic peak. This may be caused by the polymerization of di-p-xylylene, a probable product of the degradative condensation of the dithiol. The infrared spectrum of the volatile products shows only a slight hint of the presence of di-p-xylylene because all but two of its major bands coincide with those of p-xylylenedithiol.

In conclusion, this survey has demonstrated the considerable effect of ring substituents on aromatic carbonization reactivity. Besides providing a broader base for the selection of raw materials for graphite production, a basis for the choice of individual model compounds for further investigations for elucidating the mechanisms and reactions of carbonization is also provided.

5.8. Binary Mixtures of Aromatic Compounds

The DTA technique offers an excellent means of studying thermal interactions among components of aromatic mixtures. Such information is extremely pertinent since the usual raw material precursors of carbon and graphite are complex mixtures of aromatic species. Furthermore, the pyrolytic reactions of even simple aromatic compounds lead immediately to the formation of organic mixtures. The catalytic or synergistic effect of the presence of one aromatic compound on the thermal reactivity of another is, therefore, of practical interest. Our investigations of several two-component mixtures show that two kinds of interactions can generally occur, (1) a purely physical effect, and (2) a discrete thermochemical transformation leading to the formation of new chemical species and enhanced carbonization. Systems which typify the former case are designated as chemically "unreactive" and the latter as chemically "reactive".

5.8.1. "Unreactive" Mixtures

Five of the thermograms in Figure 10 illustrate the thermal behavior of the "unreactive" category of aromatic mixtures. The presence of a second component may produce an inhibiting effect on the reactivity of another or may simply act as the diluent if its principal effect is to reduce the concentration of reacting species and thus reduce the reaction rate or alter its course. The first two mixtures were studied to determine the effect of dilution of a reactive hydrocarbon, acenaphthylene, with compounds that were expected to be thermally inert at temperatures well above the reaction temperature of acenaphthylene. Our DTA investigations⁽¹⁾ showed the polyphenyl hydrocarbons to be extremely stable at high temperatures. The dilution experiments were therefore performed employing p-terphenyl and m-quinquephenyl, both of which exhibit high boiling temperatures and were readily obtained. Mixtures containing one part by weight of acenaphthylene to ten parts by weight of polyphenyl exhibited the melting endotherms of both components. In each case the minor component, acenaphthylene, melted first. The melting points are lowered as expected. The boiling endotherm of the inert solvent component occurs at the normal temperature. The acenaphthylene reaction exotherm at 250°C is not observed in either system, and on the basis of the carbon yields

it appears that the acenaphthylene polymerization is largely retarded by dilution. No interaction between the two components on a detectable level is observed. This situation proved to be very favorable for electron spin resonance studies of the acenaphthylene reaction. In this case the desired effect was to reduce the reaction rate of the initial radicals formed during the pyrolysis of acenaphthylene to permit the observation of their ESR spectrum in an inert liquid medium. ⁽¹¹⁾

The last three mixtures consist of 1:1 mixtures of aromatics previously shown to be individually thermally unreactive in DTA experiments. The melting and boiling points observed in these systems are listed in Table 7. In these mixtures only a single melting endotherm is observed as the higher melting component appears to dissolve in the first melting component. The naphthalene-p-benzoquinone and anthracene-anthraquinone mixtures show no indications of reacting. The acenaphthene-anthraquinone mixture gives an exothermic peak at about 220°C followed by two broad boiling endotherms, the first corresponding to the acenaphthene boiling point and the second to the anthraquinone boiling point. No carbon residue was obtained; so, the thermal interaction apparently produced a noncarbonizable product. No new products were observed in the condensate collected in the KBr trap. A reaction involving dehydrogenation of acenaphthene to the reactive acenaphthylene by the hydrogen acceptor anthraquinone would be expected.

5.8.2. Reactive Mixtures

The last set of thermograms in Figure 10 and all of the sets in Figure 11 demonstrate the thermal behavior of thermally "reactive" mixtures. In all of these examples except two, the individual compounds have been found to be thermally "unreactive". The mixture of acenaphthylene-p-benzoquinone produced a lower carbon yield than would be expected from the normal yield from acenaphthylene alone. The mixture of naphthacene-p-benzoquinone on the other hand produced about five times the normal yield expected from naphthacene. p-Benzoquinone appears to act as an inert diluent for acenaphthylene but reacts extensively with naphthacene.

The first eight mixtures all include an aromatic hydrocarbon in combination with a quinone. The chemistry of the quinone-hydrocarbon interactions is discussed in another report. ⁽²⁾ The DTA thermograms in Figures 10 and 11 show that these carbonization reactions are generally initiated by an exothermic transformation around 200°C. In the two instances where these low temperature exotherms are not observed, they are thought to be masked by simultaneously occurring endothermic physical transformation. The general appearance of exothermic peaks is evidence for a copolymerization interaction prior to carbonization. Finally, the last mixture in Figure 11 consists of an aromatic hydrocarbon, chrysene, and dehydrogenating agent, sulfur. Sulfur has found wide application as a dehydrogenating agent for carbon binders.

5.8.2.1. 1:1 Mixture of Acenaphthene-p-Benzoquinone

Both of these materials alone appear to be quite stable thermally and simply melt and distill or sublime to give essentially no carbon yield. This

is demonstrated in the two top thermograms in Figure 10 as well as in coking experiments. A mixture of acenaphthene and benzoquinone reacts exothermally between 200° and 260°C as shown in the lower thermogram of Figure 10. This product does not appear to melt or distill sharply as does the acenaphthylene polymer so acenaphthylene does not appear to be an intermediate product of the benzoquinone-acenaphthene reaction. A good carbon yield of 13.1 per cent was obtained in the DTA run. During the DTA run, the distillate fraction was collected. Infrared analysis proved it to be almost pure acenaphthene.

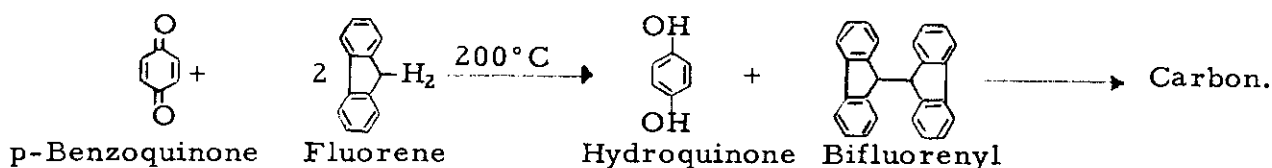
5.8.2.2. 1:1 Mixture of Acenaphthylene-p-Benzoquinone

The thermogram of this mixture as well as the thermograms of the two components alone is shown in Figure 11. In the thermogram of the mixture one observes a slightly shifted melting endotherm followed later by an endotherm attributable to distilling p-benzoquinone. The usual acenaphthylene exotherm is obtained but quite noticeable is the absence of the 410°C endotherm always observed for acenaphthylene. The thermal reaction sequence for acenaphthylene has, therefore, been modified by the quinone interaction. Only starting materials were observed in the KBr trap.

5.8.2.3. 1:1 Mixture of Fluorene-p-Benzoquinone

After an initial melting endotherm for the mixture, which reaches a maximum at 88°C, there is observed an extremely high reaction exotherm with maximum at 198°C. This exotherm is not present in either component thermogram (Figure 11), but is one of the largest exotherms observed in our studies of aromatics to date (about 20°C). This reaction leads to a 17.7 per cent coke residue, whereas none would be expected from either component separately.

The quinone-fluorene reaction likely involves dehydrogenation of fluorene by the oxidizing quinone:



Hydroquinone has been identified as a major reaction product. The presence of bifluorenyl cannot be ascertained from examination of the DTA condensate due to the masking effect of the distilled fluorene. Difluorenyl is the likeliest dehydrogenation product and has been shown previously to readily carbonize in the DTA experiment.

5.8.2.4. 1:1 Mixture of Anthracene-Benzoquinone

This is another mixture in which the components give essentially no coke on simple heating at atmospheric pressure. The thermogram in Figure 7

shows that anthracene reacts with benzoquinone just above the melting point of the benzoquinone. An exothermic reaction peaking at 150°C is observed. The second endotherm at 200°C corresponds to the melting of anthracene and the sublimation or boiling of benzoquinone. This is followed by a second smaller exothermic reaction at about 250°C which continues at a reduced rate to about 340°C. A coke yield of 9.4 per cent was obtained in this run. There was no anthracene in the material distilled from this mixture. The mechanism of this interaction has already been discussed and involves direct addition of the quinone to the anthracene ring.⁽²⁾

5.8.2.5. 1:1 Mixture of Naphthacene-Benzoquinone

Naphthacene is a high melting aromatic hydrocarbon that is considerably more reactive than anthracene and will give a substantial carbon yield on heating at atmospheric pressure in a standard coking run. The DTA curve of naphthacene indicates that an exothermic reaction occurs above 450°C in molten naphthacene. The thermogram of the mixture indicates that naphthacene reacts with molten benzoquinone just above the melting point of benzoquinone. The reaction is strongly exothermic and is sustained over a fairly large temperature range from 140°-210°C. The reaction product has a high coking value indicated by the 36.1 per cent yield obtained in this DTA run. The distillate was collected in a KBr trap and an infrared spectrum determined but the material could not be identified. There was no naphthacene, dihydronaphthacene, or hydroquinone in the distillate.

Continued efforts toward understanding the chemical nature of these interactions are warranted.

5.8.2.6. 1:1 Mixture of Benz[a]anthracene-p-Benzoquinone

The exothermic reaction peak observed in most of the interacting quinone-aromatic hydrocarbon mixtures is not evident in the thermogram for this system. Endothermic peaks indicative of the individual constituent melting and boiling endotherms are observed. A 2.2 per cent carbon residue was obtained, whereas no carbon formation occurred for either material separately. It is likely that the quinone-aromatic exotherm which usually occurs vicinal to 200°C is masked by the broad endotherm in this temperature region. The latter endotherm represents a combination of the boiling p-benzoquinone and melting benz[a]anthracene.

5.8.2.7. 1:1 Mixture of Acenaphthene-Chloranil

Chloranil, like benzoquinone, yields essentially no coke on thermal treatment. When mixed with acenaphthene, however, and heated in argon in the DTA apparatus, chloranil reacts exothermally with acenaphthene to give a product that carbonizes with a high yield of coke (Table 8). The thermogram obtained on this mixture (Figure 11) is quite complex and contains three exothermic peaks. This is an interesting system that will require closer study to elucidate the reactions leading to high coke yields. Infrared spectra were run on the materials distilled during the DTA run. Only acenaphthene could be identified in the distillate although the spectra contained a number of strong

bands of unidentified origin. The expected products chloranil, acenaphthylene, or tetrachlorohydroquinone were not found in the distillate.

5.8.2.8. 1:1 Mixture of Anthracene-Chloranil

The thermogram of the anthracene-chloranil mixture (Figure 11) indicates that quite a different situation exists here as compared to the previous mixtures discussed. The endotherm at 210°C for the melting of anthracene is not followed by a reaction exotherm indicating that chloranil is not very soluble in molten anthracene. The broad, shallow endotherm between 300° and 330°C corresponding to the melting point of chloranil and the boiling point of anthracene, is followed by an exotherm that is probably attenuated by the distillation and sublimation of unreacted anthracene and chloranil. Thus, it appears that the interaction between these two materials does not occur until both have melted. It is interesting to note, however, that the carbon yield was as high as with the benzoquinone-anthracene mixture (Table 8). The distillate was trapped in KBr and the infrared spectrum measured. Both anthracene and chloranil were identified in the distillate but there was no dianthranyl or tetrachlorohydroquinone which might be expected. A new as yet unidentified material was found in the distilled fraction.

5.8.2.9. 100:16 Mixture of Chrysene-Sulfur

The DTA thermogram of chrysene shows only the melting and boiling endotherms in good agreement with the literature values. No carbon residue is obtained on heating chrysene in an unpressurized open container. The effects of heating 100 parts of chrysene with 16 parts of sulfur are seen in the next to the last thermogram in Figure 11. The melting point of sulfur shows up as the first endotherm at 100°C and is followed by the melting endotherm of chrysene. The latter occurs at a lower temperature as a result of the presence of the molten sulfur. The third endotherm caused by the reaction of sulfur with the chrysene as well as the volatilization of both the reaction products and unreacted starting material occurs almost 100°C below the boiling range of chrysene. The sulfur-induced condensation products produced a carbon yield of 15 per cent of the starting mixture.

In conclusion, the general effects of physical and chemical interactions during heating between two compounds in a mixture have been demonstrated to fall into three categories.

1. Purely physical effects: which lead to a simple alteration of melting and boiling temperatures of the components of the mixture;
2. Inhibition: where one compound, either by dilution or by chemical interaction, alters the reaction course of the other constituent so as to reduce the carbon yield, and
3. Activation: where the combination of compounds undergo reactions such as hydrogen transfer or copolymerization which lead to enhanced carbon formation.

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