

## Thermal Reactivity of Polynuclear Aromatic Hydrocarbons<sup>1</sup>

IRWIN C. LEWIS AND T. EDSTROM

Research Laboratory of National Carbon Company, Division of Union Carbide Corporation, Parma, Ohio

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Much recent interest has been directed toward understanding the reactivity characteristics of polynuclear aromatic systems. The major emphasis has pertained to simple radical substitution and oxidation-reduction reactions. Relatively little work has been applied to studies of self-condensation sequences, which are generally accomplished thermally and lead to the formation of complex carbonaceous residues from the typical polynuclear aromatic hydrocarbon. We report herein investigations of the thermal reactivity for eighty-four polynuclear aromatic hydrocarbons. Our approach has employed differential thermal analysis (d.t.a.) to categorize and delineate thermal reactivity. These results emphasize the importance of intermolecular thermal hydrogen transfer for the polynuclear aromatics. Thermal condensation reactivity is found to be dependent on molecular structure and correlates with other reactivity criteria but includes the additional parameter of molecular size.

Much recent chemical interest has been directed toward studies in the field of polynuclear aromatic hydrocarbons. Special emphasis has been placed on theoretical treatments of these materials<sup>2a,b</sup> and the relationship of theoretical parameters to spectroscopic,<sup>3</sup> reactivity,<sup>4-6</sup> and physiological<sup>8</sup> criteria. Chemical reactivity investigations for the polynuclear aromatics have been restricted largely in the past to radical substitution,<sup>4</sup> oxidation-reduction,<sup>5,6</sup> and electrophilic substitution.<sup>7</sup> The thermal reactivity characteristics of these compounds also have been the subject of recent studies.<sup>9</sup> Many of the aromatic hydrocarbons are known to be thermally reactive both individually and as constituents of complex mixtures. These thermal reactions are believed to involve condensation or polymerization sequences to produce complex carbonaceous products.<sup>10</sup>

Rapid developments in instrumental analytical techniques and in dynamic methods of measuring changes in materials during heating and cooling make a detailed study of carbonization reactions possible and practical at this time. This report is a survey of the thermal reactivity characteristics for a wide variety of aromatic hydrocarbons. Differential thermal analysis (d.t.a.) has been used to categorize the high temperature behavior of these hydrocarbons. This technique has been used extensively in investigations of polymers and inorganic solids.<sup>11</sup> It has found relatively little use, however, in the study of thermally reactive organic compounds.

D.t.a. gives a continuous thermal record of reactions occurring in a sample, although it does not indicate what these reactions are nor does it sort out simultaneously occurring reactions. By comparing the tem-

perature in a sample with the temperature in an inert reference material such as anhydrous alumina as both are heated at a uniform rate in a furnace, temperature regions where heat is absorbed (endothermic reactions) or evolved (exothermic reactions) by the sample can be observed.

Thermal reactivity behavior as derived from d.t.a. is interpreted in terms of reactivity parameters derived from electronic spectra and the adjunct of molecular size.

### Experimental

**D.t.a. Apparatus.**—Differential thermal analysis is the technique of measuring the difference in the temperature between a thermocouple embedded in a sample and a thermocouple in a standard inert material such as aluminum oxide while both are heated at a uniform rate. These temperature differences arise when phase transformations or chemical reactions in the sample evolve or absorb heat. Experimentally, it is desirable thermally to match and isolate the sample and reference holders and to maintain a uniform heating rate.

The basic design of the apparatus used in this study has been described in detail elsewhere.<sup>12</sup> A sketch of the sample holder and a block diagram of the controlling, detecting, amplifying, and recording systems are shown in Fig. 1A and 1B, respectively.

The d.t.a. thermocouple assembly shown in Fig. 1A consists of two matched chromel-alumel thermocouples supported in a porcelain tube, which is held in position in a furnace combustion tube. The sample and reference cups are Inconel cylinders with a thermocouple well extending into the center of the cup from the bottom. With this arrangement, the thermocouples are protected from the embrittling action of the hydrocarbons during carbonization and can be used repeatedly. This extended life justifies very careful matching of the thermocouples and Inconel cups. The sample and reference cups are also isolated from each other and independent of the thermocouples. This arrangement permits weighing before and after heating so that weight changes can be determined. In most cases, the quantity of sample and of reference anhydrous alumina was standardized at 100 mg. The heating rate was also arbitrarily standardized at 10° per minute. All experiments were run at atmospheric pressure in continuously flowing purified argon.

The argon and volatile products were swept into a potassium bromide-filled condensate trap<sup>13</sup> for collecting the condensable volatile reaction products and unchanged starting material. The noncondensable gases then pass through a sulfuric acid bubbler which seals the system. Samples were heated to 750° and the carbon yields reported were determined on the 750° residues.

Normally the d.t.a. experiments were carried out by heating continuously to 750° at which point the residue is essentially carbon. However, since the d.t.a. thermogram provides an excellent visual method of detecting reactions and determining end points, a number of runs were terminated at a temperature just preceding or following a reaction peak and the products were cooled

(1) Presented at "Symposium on Aromatic Hydrocarbons," Division of Petroleum Chemistry, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

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(12) I. C. Lewis and T. Edstrom, "Proceedings of the Fifth Carbon Conference," Pergamon Press, London, 1962.

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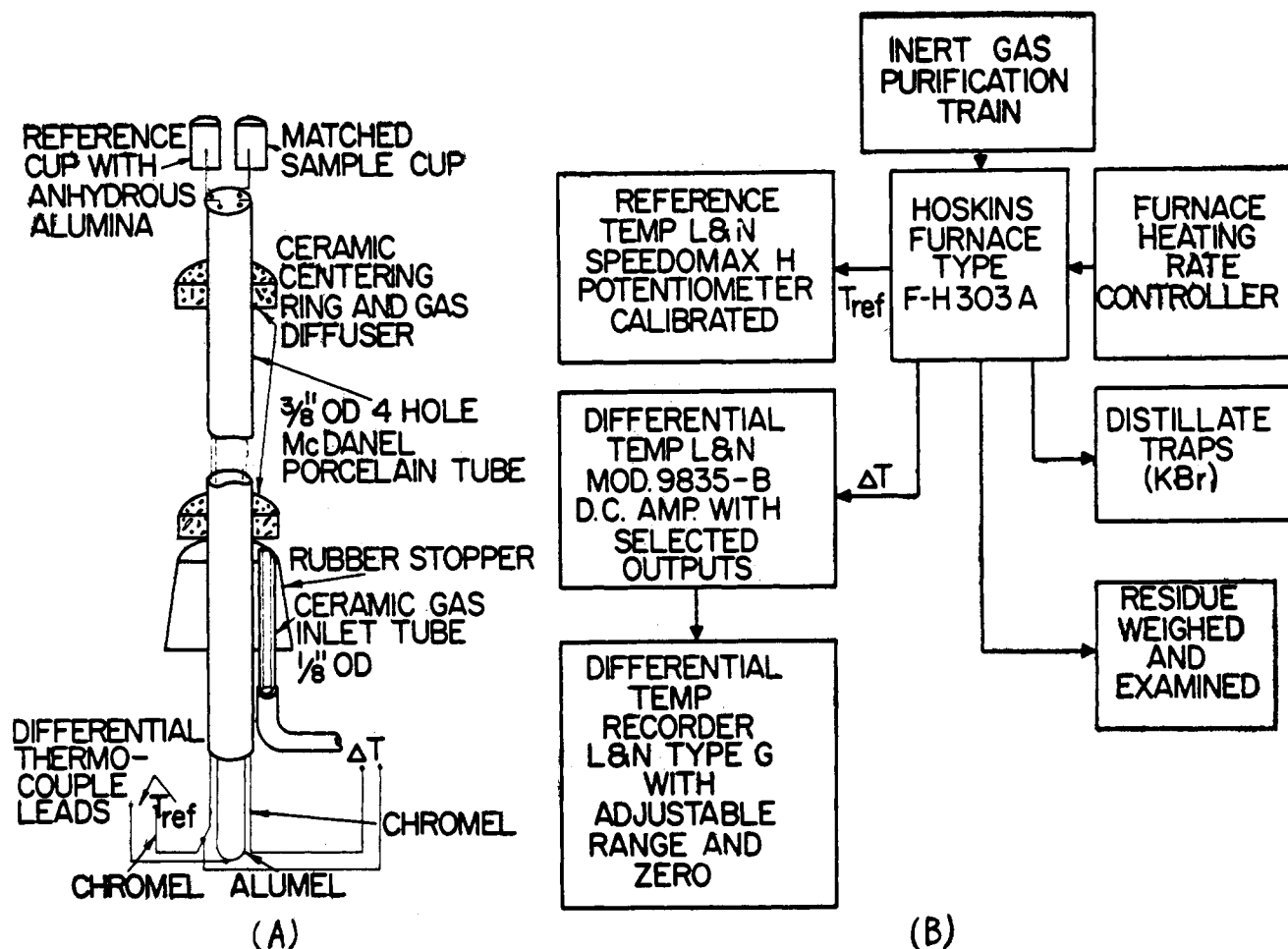


Fig. 1.—(A) D.t.a. thermocouple assembly; (B) block diagram of d.t.a. apparatus.

and analyzed. These experiments are discussed under the heading "Interrupted D.t.a. runs" in the following section.

**Analytical Techniques. Chromatography.**—Elution chromatography on alumina or silica gel columns has been extremely useful in the purification of reference compounds for this study, usually producing a much higher degree of purity than repeated recrystallization or sublimation and with less effort.

**Infrared Absorption Spectra.**—The infrared absorption spectra were measured on a Perkin-Elmer Model 21 or Model 221 double-beam spectrometer using conventional sampling techniques.

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

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

**Electron Spin Resonance.**—Electron spin resonance measurements were made on a number of the low temperature residues obtained in the d.t.a. apparatus. These measurements were made by L. S. Singer of this laboratory using methods and apparatus previously described.<sup>14</sup>

**Materials.**—The polynuclear aromatic compounds examined in this work were obtained through commercial supply houses and in many cases were used as received. Infrared and ultraviolet absorption spectra of each compound were compared with published spectra to ascertain purity. In those cases where thermally reactive compounds appeared to be contaminated, chromatographic purification was carried out and the purified material was re-examined in the d.t.a. apparatus. The impurity level after careful chromatographic purification is estimated to be in the parts per million range.

The solvents used in the chromatographic separations and for spectroscopic analysis were all Spectro-Grade solvents. The potassium bromide powder used in trapping the d.t.a. condensates and for infrared sampling was infrared quality powdered potas-

sium bromide. The anhydrous alumina used in chromatographic columns and as the d.t.a. reference material is chromatographic grade anhydrous alumina, 80 to 200 mesh. The alumina used for d.t.a. reference is specially treated by heating to 800°. It is stored in a sealed dispenser to avoid exposure of the bulk of the material to the atmosphere when transferring to the d.t.a. cup.

## Results

**D.t.a. Thermograms for Thermally "Unreactive" Aromatic Hydrocarbons.**—For the purposes of this study the aromatic hydrocarbons have been designated as either thermally "reactive" or thermally "unreactive." The thermally "reactive" species possess sufficient reactivity in an atmospheric pressure system to undergo a condensation sequence in the liquid phase and yield a measurable amount of polymerized carbonaceous residue at 750°.

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

Shown in Fig. 2 are the d.t.a. thermograms obtained for some representative aromatic hydrocarbon members of the thermally "unreactive" category. All of these thermograms exhibit common characteristic features. For solid compounds two major endothermic peaks corresponding to the melting and boiling processes are invariably obtained. For liquid compounds a simple major endotherm representative of the distillation process is always evident. Additionally no carbonace-

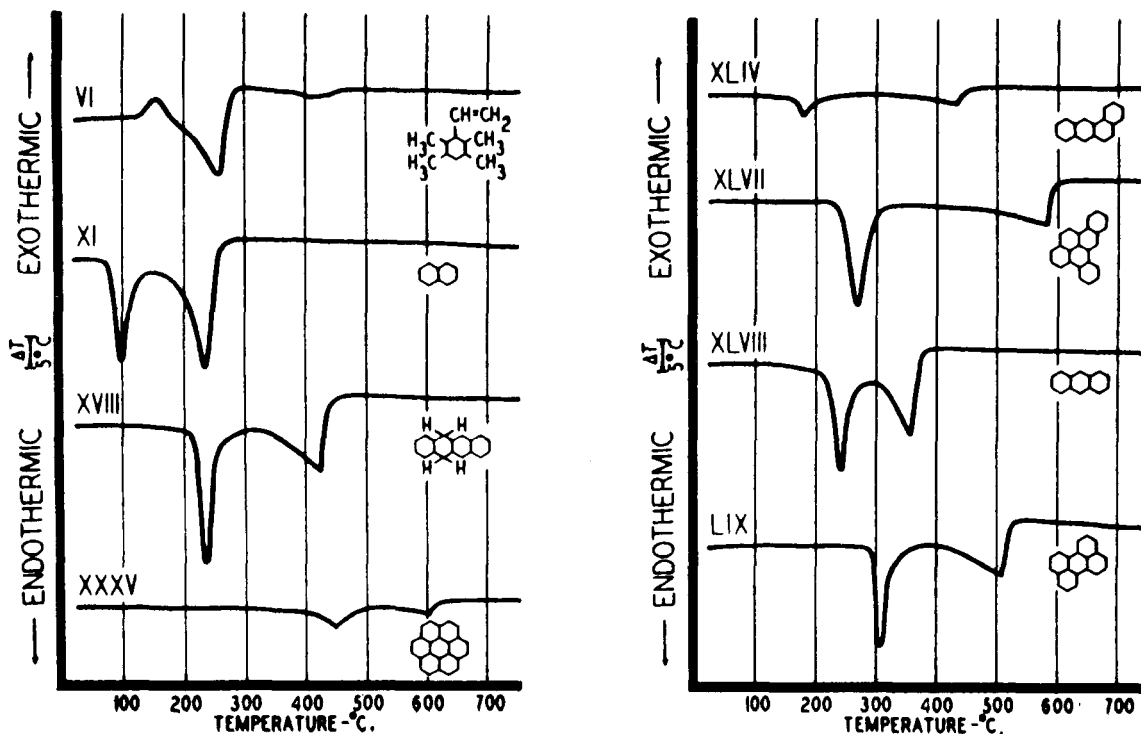


Fig. 2.—Typical d.t.a. thermograms of unreactive hydrocarbons.

ous residues are obtained in the d.t.a. sample cups at 750° and no products besides starting materials were observed in the condensed distillates.

For such materials d.t.a. offers a convenient if not precise method for measuring melting and boiling points. The initial inflection point of the melting endotherm has been found to be the most reliable method for ascertaining the melting points in our system. The melting points thus determined for the "unreactive" aromatic hydrocarbons are listed in Table I and compared with the appropriate literature values. In most cases the agreement is quite good.

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

Also listed in Table I are the frequencies of the long wave-length p-bands determined from the measured electronic spectra by the procedure of Clar.<sup>3</sup> These wave lengths can readily be determined within 1%. The Hückel relationship (equation 1) as employed by Matsen<sup>15</sup> has been utilized to calculate ionization parameters for the respective aromatic hydrocarbons from the p-band wave lengths.

$$i.p. = 4.39 + 0.857 \lambda p \quad (1)$$

i.p. = ionization potential in electron volts  
 $\lambda p$  = wave length of long wave-length p-band in electron volts

These values are given in the last column of Table I.

The compounds are listed in order of decreasing ionization potential.

In several instances the p-band definition from ultraviolet spectra was uncertain and the ionization potential data have been omitted. Such compounds have been placed in Table I in the approximate position based on a judicial estimate of the p-band.

**D.t.a. Thermograms for Thermally "Reactive" Aromatic Hydrocarbons.**—The thermograms for several representative aromatic hydrocarbons designated as thermally "reactive" are shown in Fig. 3. All of these compounds undergo thermal condensation and lead to carbonaceous residues at 750° in our d.t.a. system.

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

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

Further listed in Table II for the "reactive" aromatics are the per cent carbonaceous residues obtained at 750° and the temperatures of indicated d.t.a. reaction peaks. These latter may be exothermic or endothermic depending on the combination of physical and chemical changes proceeding at the reaction temperature. Also given in Table II are the  $\lambda$  of the long wave-length p-bands and the ionization potentials computed as described previously. Again the compounds have been listed in order of decreasing ionization potential.

TABLE I  
 THERMALLY STABLE AROMATIC HYDROCARBONS

Compound no.	Hydrocarbon, source no.	M.p., °C.		B.p., °C. d.t.a.	$\lambda$ p-band, m $\mu$	Calcd. i.p., e.v.
		lit.	d.t.a.			
I	Benzene	5.5	...	...	208	>10.0
II	Styrene	...	...	170	...	...
III	Biphenyl	70	64	268	247	8.69
IV	Allylbenzene	...	...	180	260	8.47
V	Vinylmesitylene	<25	<25	235	260	8.47
VI	Vinyldurene	...	...	255	...	...
VII	Fluorene	114	122	314	261	8.46
VIII	9,10-Dihydroanthracene	108	98	328	271	8.31
IX	2-Methylfluorene	104	113	332	278	8.21
X	Benzo[ <i>l</i> ]phenanthrene	198	197	450	284	8.14
XI	Naphthalene	80	77	245	285	8.12
XII	Vinylxylene	<25	<25	235	286	8.10
XIII	Phenanthrene	100	93	348	292	8.03
XIV	<i>p</i> -Quarterphenyl	320	317	495	292	8.03
XV	Vinyltoluene	<25	<25	200	298	7.96
XVI	4,5-Methylenephenanthrene	116	120	375	299	7.95
XVII	3-Methylphenanthrene	65	45	370	304	7.88
XVIII	5,12-Dihydronaphthacene	...	214	420	306	7.86
XIX	<i>m</i> -Quinquephenyl	...	110	545	308	7.84
XX	1,1'-Binaphthyl	156	140	418	313	7.78
XXI	Tetraphenylethylene	227	230	424	315	7.77
XXII	1-Allylnaphthalene	...	...	295	315	7.77
XXIII	Acenaphthene	95	91	280	319	7.72
XXIV	Chrysene	254	260	460	319	7.72
XXV	9-Benzylidene fluorene	76	80	440	325	7.66
XXVI	Picene	365	370	535	329	7.62
XXVII	Dibenzo[ <i>c,g</i> ]phenanthrene	178	145	490	329	7.62
XXVIII	Benzo[ <i>e</i> ]pyrene	179	179	496	331.5	7.60
XXIX	Pyrene	150	146	386	335	7.56
XXX	4,5,9,10-Tetrahydropyrene	138	142	383	300	7.94
XXXI	4-Methylpyrene	143	153	425	338	7.54
XXXII	Benzo[ <i>a</i> ]fluorene	187	200	420	340	7.52
XXXIII	Benzo[ <i>b</i> ]fluorene	209	220	420	340	7.52
XXXIV	Azulene	99	99	285	...	...
XXXV	Coronene	430	438	600	342	7.50
XXXVI	1,1,4,4-Tetraphenylbuta-1,3-diene	202	215	460	344	7.48
XXXVII	1-Methylpyrene	72	78	372	344	7.48
XXXVIII	Dibenz[ <i>a,c</i> ]anthracene	205	208	520	349	7.43
XXXIX	Benzo[ <i>b</i> ]fluoranthene	168	170	490	350	7.42
XL	Dibenz[ <i>a,h</i> ]anthracene	265	265	520	350	7.42
XLI	Tetrabenzonaphthalene	215	220	565	350	7.42
XLII	4,6,8-Trimethylazulene	...	85	344	...	...
XLIII	Fluoranthene	110	110	386	359	7.35
XLIV	Benzo[ <i>a</i> ]anthracene	159	166	430	359	7.35
XLV	Dibenzo[ <i>a,h</i> ]phenanthrene	294	308	537	362	7.32
XLVI	Benzo[ <i>a</i> ]pyrene	178	170	495	364	7.31
XLVII	Dibenzo[ <i>a,e</i> ]pyrene	225	237	580	375	7.23
XLVIII	Anthracene	217	215	350	376	7.22
XLIX	2-Phenylanthracene	207	221	465	383	7.17
L	9-Phenylanthracene	153	150	416	383	7.17
LI	Benzo[ <i>g,h,i</i> ]perylene	281	285	560	383	7.17
LII	9-Methylanthracene	80	77	370	386	7.14
LIII	1,10- <i>o</i> -Phenylene pyrene	...	160	538	386	7.14
LIV	9,9'-Bianthryl	320	322	520	389	7.12
LV	9,10-Diphenylanthracene	247	230	485	393	7.10
LVI	9,10-Dimethylanthracene	181	177	400	398	7.06
LVII	Benzo[ <i>j</i> ]fluoranthene	217	225	495	400	7.05
LVIII	Dibenzo[ <i>a,l</i> ]pyrene	227	225	522	400	7.05
LIX	Perylene	275	295	505	534	6.84

**Identification of Condensates Trapped from D.t.a. Runs.**—Spectrophotometric examination of the d.t.a. condensate traps showed that for nearly all the "unreactive" aromatic hydrocarbons only starting material could be identified.

In contrast, the majority of the "reactive" aromatic

hydrocarbons showed evidence of new volatile aromatic species in the condensate trap. In a number of cases these products have been identified by spectral and physical property comparison with known hydrocarbons.

Summarized in Table III are the results of examina-

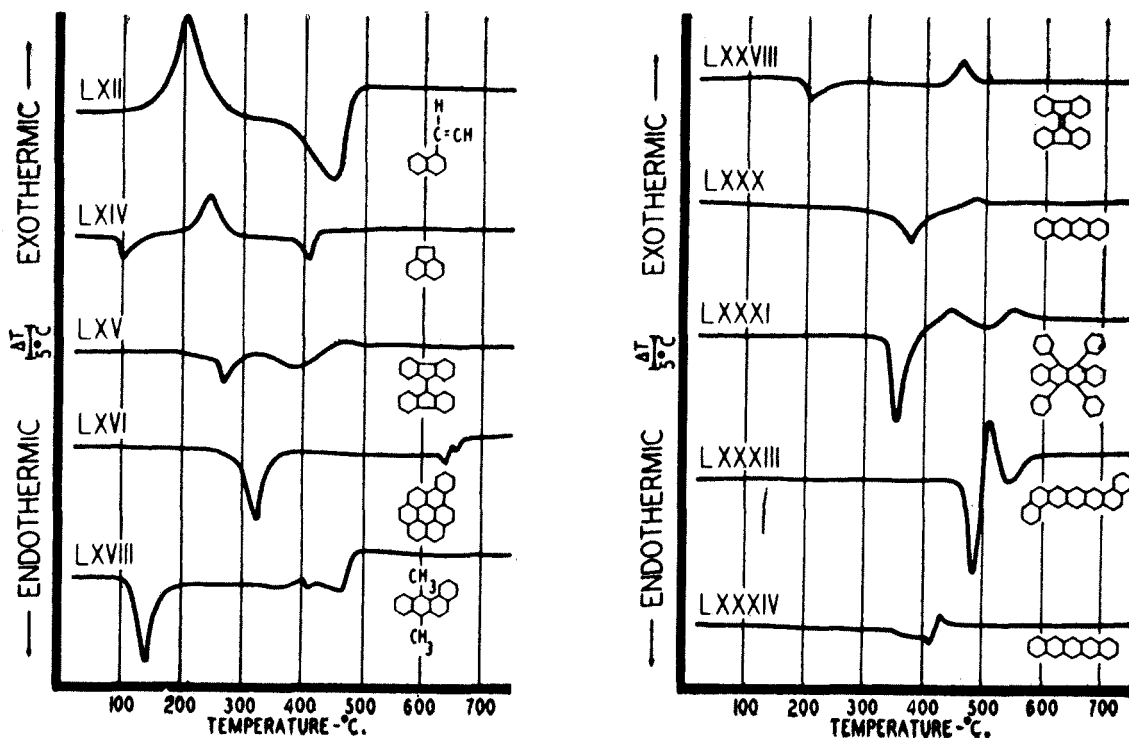


Fig. 3.—Typical d.t.a. thermograms of reactive hydrocarbons.

tion of the condensate traps for the "reactive" aromatic compounds.

**Interrupted D.t.a. Runs.**—The properties of residues obtained from the interrupted d.t.a. runs of acenaphthylene (LXIV) and 9,9'-bifluorenylidene (LXXVIII) are listed in Table IV. The temperatures at which heating was interrupted is given in the second column. Reference to the original thermograms in Fig. 3 shows the reaction stage at which these residues have been obtained. Also listed in Table IV are the general appearance of the residue, melting point, per cent yield, number average molecular weight, and the presence or absence of free radicals as measured by e.p.r.

### Discussion of Results

The thermal stability of the aromatic hydrocarbons shows a marked dependence on structure. In this investigation eighty-four aromatic hydrocarbons have been designated as either thermally "unreactive" or thermally "reactive." The d.t.a. method examines thermal behavior of materials in the solid and liquid phases. The reactivity classifications are, therefore, applicable to solid and liquid phase pyrolysis only. This classification, although internally consistent within our system, will be affected, as will also the actual reaction temperatures and residue yields, by the experimental conditions employed. For example, anthracene can be made to react by prolonged heat treatment in a confined pressure system.

The application of the d.t.a. method to these compounds is extremely useful in permitting the detection of thermal physical and chemical changes. For thermally unreactive entities it permits the measurement of atmospheric melting and boiling points. The presence of impurities in the sample in general can be readily determined from the d.t.a. thermogram by either observation of separate melting endotherms or general lowering of the melting endotherm of the major con-

stituent. Additionally, d.t.a. is effective in measuring crystal transformations, polymerizations, and degradations and hence provides an important tool for organic sample identification.

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

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

The second class of compounds listed in Table II have high i.p. values,  $>7.20$  e.v., which should normally situate them with the unreactive species of Table I. These compounds, however, have the extraneous structural feature of a readily polymerizable vinyl double bond in addition to an aromatic structure. These hydrocarbons may initially undergo a vinyl type polymerization to yield large polymer species. This thermal vinyl polymerization sequence differs in kind from the subsequent aromatic condensation sequence or carbonization. For these structural types of aromatics,

TABLE II  
THERMALLY REACTIVE AROMATIC HYDROCARBONS

Compound no.	M.p., °C.		Reaction <sup>a</sup> Temp., °C.	% Residue 750°	λ p-band, mμ	Calcd. i.p., e.v.	
	lit.	d.t.a.					
LX	4-Vinylbiphenyl	...	120	203 (430)	8.1	278	8.21
LXI	10,15-Dihydro-5 <i>H</i> -diindeno- [1,2- <i>a</i> :1'2'- <i>c</i> ]fluorene	370	375	(570)	32.9	298	7.96
LXII	1-Vinylnaphthalene	<25	...	200 (445)	4.2	299	7.94
LXIII	10,15-Dihydro-5 <i>H</i> -diindeno- [2,1- <i>α</i> :1',2'- <i>c</i> ]fluorene	...	175	(550)	13.5	336	7.55
LXIV	Acenaphthylene	92	89	245 (405)	20.9	339	7.53
LXV	9,9'-Bifluorenyl	247	250	(380)	5.8	364	7.31
LXVI	Benzo[ <i>a</i> ]coronene	...	291	(637) (652)	30.9	372	7.24
LXVII	9-Cinnamylidene fluorene	154	169	400 (435)	9.3	376	7.22
LXVIII	7,12-Dimethylbenz[ <i>a</i> ]anthracene	122	111	400 (405) (460)	4.7	381	7.18
LXIX	Tribenzo[ <i>a,e,i</i> ]pyrene	297	342	(525)	13.7	384	7.16
LXX	Dibenzo[ <i>a,i</i> ]pyrene	280	284	(560)	9.8	397	7.07
LXXI	9,10-Dibenzylanthracene	242	251	(445)	8.9	399	7.06
LXXII	Diacenaphtho[1,2- <i>j</i> :1',2'- <i>l</i> ]fluor- anthene	388	377	610	66.3	402	7.04
LXXIII	Dibenzo[ <i>b,k</i> ]chrysene	400	412	(571)	22.3	414	6.95
LXXIV	Dibenzo[ <i>def,mno</i> ]chrysene	257	272	(535)	18.5	430	6.86
LXXV	Benzo[1,2,3- <i>cd</i> :4,5,6- <i>c'd'</i> ]diperylene	...	295	(455) (680)	91.8	437	6.82
LXXVI	1-Methyl-dibenzo[ <i>b,i</i> ]pyrene	...	327	(548)	22.7	456	6.72
LXXVII	Pyranthrene	360	400	600 (606)	60.1	458	6.71
LXXVIII	9,9'-Bifluorenylidene	188	188	456	31.5	460	6.70
LXXIX	1,6-Dimethyl-dibenzo[ <i>b,i</i> ]pyrene	373	372	488 (525) (557)	33.6	464	6.68
LXXX	Naphthacene	343	340	480	13.9	471	6.64
LXXXI	5,6,11,12-Tetraphenylnaphthacene	333	333	442, 545	43.9	489	6.57
LXXXII	Rubicene	306	315	(551)	9.0	524	6.42
LXXXIII	Dibenzo[ <i>a,i</i> ]pentacene	440	460	505 (540)	53.2	529	6.40
LXXXIV	Pentacene	270	...	426 (411)	42.8	576	6.23

<sup>a</sup> Temperatures in parenthesis refer to endothermic reaction peaks. Unenclosed temperatures are those for exothermic peaks.

however, the former process is a prerequisite to the latter. Some vinyl derivatives may undergo a polymerization and depolymerization process to yield noncarbonizable products as exemplified by vinylidene, the thermogram of which is shown in Fig. 2. Several borderline compounds in Table II consist of aromatics with intermediate i.p., namely, benzo[*a*]coronene and tribenzo[*a,e,i*]pyrene. For such species one must take into account the added variable of molecular size in addition to general reactivity. The former parameter induces sufficient physical stability in the molecule to permit reaction before volatilization. General reactivity parameters such as i.p. values can, therefore, only serve as qualitative measures of thermal reactivity as defined here.

The activating effect of alkyl substituents on aromatic carbonization has been noted earlier by Madison and Roberts<sup>9</sup> and is evident in the reactivity of 7,12-dimethylbenz[*a*]anthracene, as contrasted to the non-reactivity of benz[*a*]anthracene.

Certain consistent features are apparent in the chemical thermal transformations for many of the "reactive" aromatic hydrocarbons. As shown in Table III, a large number of the volatile products obtained from the reacting aromatic hydrocarbons are hydrogenated derivatives of the parent material.

Carbonization of aromatics essentially involves a dehydrogenation and concomitant condensation process to produce complex hydrogen deficient aromatic species. At least initially, these dehydrogenations are accomplished internally in many instances and involve intermolecular hydrogen transfers between reacting molecules. Such a mechanism previously has been

proposed for catalytically induced carbonization reactions.<sup>15</sup> Our results indicate that this sequence is important in pure thermal uncatalyzed carbonization reactions.

Such hydrogen transfers could lead to the simultaneous formation of hydrogenated, less reactive (higher ionization potential) derivatives and more reactive aromatic derivatives or radicals, capable of undergoing further condensations. This pattern of thermal condensation may be discerned from the data for the interrupted d.t.a. residues of the reactive hydrocarbons, acenaphthylene, and 9,9'-bifluorenylidene as summarized in Table IV.

Acenaphthylene provides an example of an aromatic hydrocarbon of high ionization potential possessing an unusually reactive site in the form of a vinyl double bond. At 300° an extensive polymerization has proceeded as evidenced by the exotherm in the thermogram in Fig. 3. At 360° a thermal depolymerization has begun. Paramagnetism is observed for the residue. At higher temperatures rearrangement of aromatic structures to form larger species is indicated. Dehydrogenations are accomplished internally resulting in formation and distillation of the volatile derivative acenaphthene. Increased concentrations of aromatic radicals are observed in the residues with increasing temperatures.

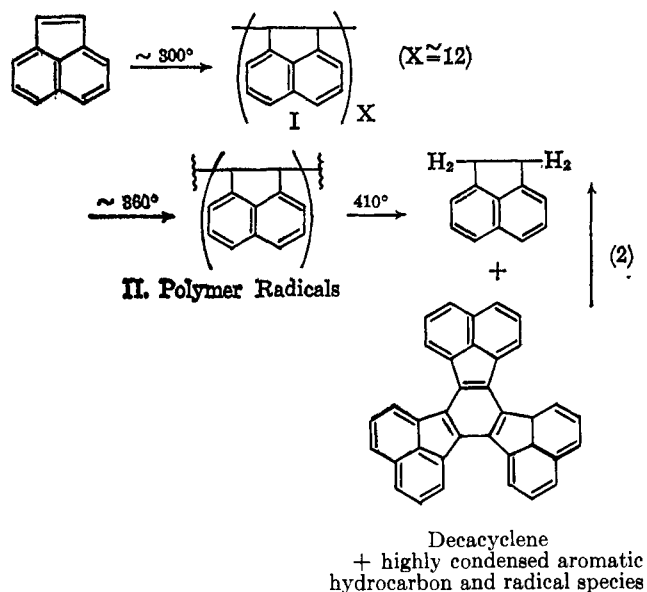
This reaction sequence may be generally summarized (see equation 2, p. 2056).

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TABLE III  
CONDENSED NEW PRODUCTS FROM D.T.A. RUNS OF "REACTIVE" AROMATIC HYDROCARBONS

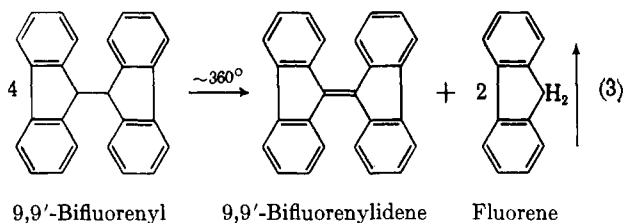
	Starting material	New product
LX	4-Vinylbiphenyl	Unknown aromatic hydrocarbons
LXI	10,15-Dihydro-5 <i>H</i> -diindeno[1,2- <i>a</i> :1',2'- <i>c</i> ]-fluorene	None
LXII	1-Vinylnaphthalene	1-Vinylnaphthalene (monomer)
LXIII	10,15-Dihydro-5 <i>H</i> -diindeno[2,1- <i>a</i> :1',2'- <i>c</i> ]-fluorene	None
LXIV	Acenaphthylene	Acenaphthene + unknown hydrocarbons
LXV	9,9-Bifluorenyl	Fluorene, 9,9'-bifluorenylidene, tetrabenzonaphthalene, and unknown hydrocarbon
LXVI	Benzo[ <i>a</i> ]coronene	Slight amount of hydrogenated derivative
LXVII	9-Cinnamylidene fluorene	Fluorene and major unknown hydrocarbon product
LXVIII	7,12-Dimethylbenz[ <i>a</i> ]anthracene	Slight amount of structurally similar hydrocarbon, (monomethyl?)
LXIX	Tribenzo[ <i>a,e,i</i> ]pyrene	Structurally similar hydrogenated derivative
LXX	Dibenzo[ <i>a,i</i> ]pyrene	Major amount of new products including large proportion of hydrogenated derivatives
LXXI	9,10-Dibenzylanthracene	Unknown hydrocarbon products
LXXII	Diacenaphtho[1,2- <i>j</i> :1',2'- <i>l</i> ]fluoranthene	Acenaphthylene + acenaphthene
LXXIII	Dibenzo[ <i>b,k</i> ]chrysene	None
LXXIV	Dibenzo[ <i>def,mno</i> ]chrysene	None
LXXV	Benzo[1,2,3- <i>cd</i> :4,5,6- <i>c'd'</i> ]diperylene	Unknown hydrogenated derivative
LXXVI	1-Methyldibenzo[ <i>b,i</i> ]pyrene	Major unknown but structurally similar product
LXXVII	Pyranthrene	None
LXXVIII	9,9'-Bifluorenylidene	Fluorene + major amount of unknown aromatic hydrocarbon
LXXIX	1,6-Dimethyldibenzo[ <i>b,i</i> ]pyrene	Identical product to that obtained for LXXXVI
LXXX	Naphthacene	5,12-Dihydronaphthacene
LXXXI	5,6,11,12-Tetraphenylnaphthacene	Unknown aromatic hydrocarbons
LXXXII	Rubicene	Slight amount of hydrogenated derivative
LXXXIII	Dibenzo[ <i>a,l</i> ]pentacene	Unknown hydrocarbons
LXXXIV	Pentacene	Isomeric dihydropentacenes



This reaction has been investigated previously by Dzewonski.<sup>17</sup> Identification of the trimer decacyclene as a product conforms to his early conclusions although the structural identification of the more complex products is still uncertain.

The hydrocarbon 9,9'-bifluorenylidene has been shown in this study to be formed as a thermal reaction product from the 9,9'-bifluorenyl by a hydrogen transfer disproportionation scheme as shown in equation 3.

The hydrocarbon fluorene is the volatile hydrogenated derivative produced.



The properties of progressive thermal condensation sequence products of 9,9'-bifluorenylidene are summarized in Table IV. Again with increasing temperature a continued increase in complexity of product and growth in size is apparent. At 750° an ultimate 31% infusible carbonaceous residue results. The concentration of free radicals also increases with heat-treatment temperature.

The initial thermal sequence for 9,9'-bifluorenylidene appears to involve a dehydrogenation and rearrangement to more condensed aromatic structures with concurrent formation of fluorene as a hydrogenated product. The hydrocarbon tetrabenzonaphthalene has been identified as one of the rearrangement products. This compound also has been reported to be a product of the pyrolysis of fluorene.<sup>18</sup> The generalized reaction scheme is shown in equation 4.

The pyrolysis of the reactive aromatic hydrocarbons are invariably accompanied by the formation of free radical species. It is felt that these radicals are transi-

(17) K. Dzewonski, *Chem. Ber.*, **53**, 142 (1920), and references cited therein.

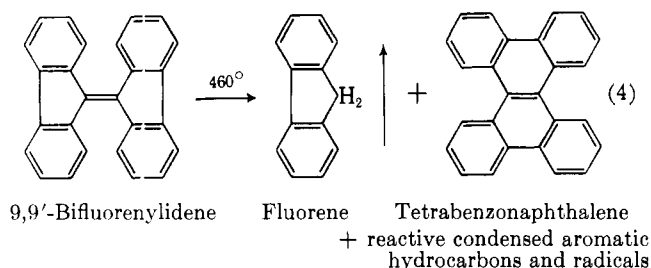
(18) K. Lang, H. Buffleb, and J. Kalowy, *ibid.*, **94**, 523 (1961).

TABLE IV

SUMMARY OF PROPERTIES OF RESIDUES FROM INTERRUPTED D.T.A. RUNS FOR ACENAPHTHYLENE AND 9,9'-BIFLUORENYLIDENE

Starting material	Temp., °C.	Nature of residue	M.p., °C. <sup>a</sup>	% Residue	Molecular weight	Free radicals
1. Acenaphthylene	25	Yellow solid	92	..	152	No
2. Acenaphthylene	300	Orange crystalline solid	315	92	1890	No
3. Acenaphthylene	360	Red crystalline solid	325-350	90	950	Yes
4. Acenaphthylene	410	Brown amorphous solid	210, 340	42	1360	Yes
5. Acenaphthylene	440	Brown amorphous solid	215, 325	37	2025 <sup>b</sup>	Yes
6. Acenaphthylene	750	Black carbonaceous solid	Infusible	21	..	Yes
7. 9,9'-Bifluorenylidene	25	Red solid	188	..	328	No
8. 9,9'-Bifluorenylidene	382	Red solid	110-115	94	396	Slight
9. 9,9'-Bifluorenylidene	400	Red solid	100, 170-184	88	565	Yes
10. 9,9'-Bifluorenylidene	450	Brown-red solid	115, 210-230	72	604	Yes
11. 9,9'-Bifluorenylidene	750	Black carbonaceous solid	Infusible	31	..	Yes

<sup>a</sup> In several residues, two melting points are reported as the material was heterogeneous. <sup>b</sup> Determined for benzene-soluble portion only.



tory aromatic radicals formed by thermal dissociations of hydrogens at reactive ring sites, by cleavage of substituent groups, or by rearrangement. The formation of such stable radicals as well as the internal rearrangements of hydrogens appears to be intrinsic to the thermal condensation or carbonization process for many of the "reactive" aromatic hydrocarbons.

In summary, the thermal reactivities of the aromatic hydrocarbons in our system show a marked dependence

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

Consistent patterns of hydrogen transfer and concurrent condensation to more reactive aromatic hydrocarbon molecules and radicals are found for many of the thermally "reactive" aromatics.

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## Hydrogen Peroxide-Vanadium Pentoxide Oxidation of Cyclohexenes<sup>1a</sup>

E. J. EISENBRAUN,<sup>1b</sup> A. R. BADER, J. W. POLACHECK, AND E. REIF<sup>1c</sup>

Research Laboratories of the Aldrich Chemical Company, Milwaukee 10, Wisconsin, and the Heidenheimer Chemisches Laboratorium, Heidenheim an der Brenz, Germany

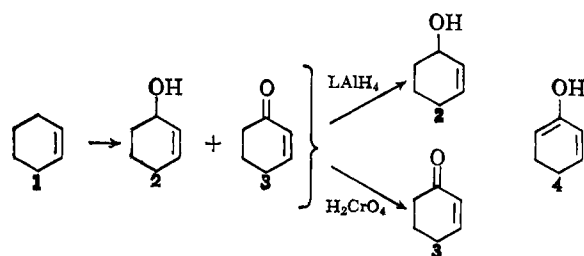
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A re-examination of the oxidation of cyclohexene (1) with hydrogen peroxide-vanadium pentoxide (HP-VP, peroxyvanadic acid) revealed 2-cyclohexen-1-ol (2) to be a major reaction product. This contradicts an earlier report<sup>2</sup> claiming exclusive formation of 2-cyclohexen-1-one (3) as the volatile product. Similar oxidative experiments with the isomeric methylcyclohexenes (7, 13, and 17) demonstrate the reaction to be essentially nonselective as to site of oxidation and that both alcohols and ketones appear in the volatile products, these being a mixture of direct oxidation products and products derived from allylic shifts.

Treibs<sup>2</sup> and co-workers claimed 2-cyclohexen-1-ol (2) to be absent from the products of the oxidation of cyclohexene (1) with HP-VP and 2-cyclohexen-1-one (3) was reported to be the exclusive low boiling product (40% yield). *trans*-1,2-Cyclohexanediol (6) and adipic acid were reported as higher boiling products (9% yield for both). These authors considered 2-cyclo-

hexen-1-one (3) to be present in part as the enol 4 to account for the formation of a borate ester.

We have demonstrated that 2-cyclohexen-1-ol (2)



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(2) W. Treibs, G. Franke, G. Leichsenring, and H. Roder, *Ber.*, **86**, 616 (1953).