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. 7381002, "Materials Process"; and Project No. 7-817, "Process Development for Graphite Materials." The work was administrated under the direction of the AF Materials Laboratory, Deputy Commander/Research and Engineering, Aeronautical Systems Division, with Captain R. H. Wilson, L. J. Conlon, and W. P. Conrardy acting as Project Engineers.

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

Prior 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:

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.
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.
Volume XI	Characterization of Binders Used in the Fabrication of Graphite Bodies, by E. de Ruiter, A. Halleux, V. Sandor, H. Tschamler.
Volume XII	Development of an Improved Large Diameter Fine Grain Graphite for Aerospace Applications, by C. W. Waters and E. L. Piper.
Volume XIII	Development of a Fine-Grain Isotropic Graphite for Structural and Substrate Applications, by R. A. Howard and E. L. Piper.
Volume XIV	Study of High Temperature Tensile Properties of ZTA Grade Graphite, by R. M. Hale and W. M. Fassell, Jr.
Volume XV	Alumina-Condensed Furfuryl Alcohol Resins, by C. W. Boquist, E. R. Nielsen, H. J. O'Neil, and R. E. Putcher - Armour Research Foundation.
Volume XVI	An Electron Spin Resonance Study of Thermal Reactions of Organic Compounds, by L. S. Singer and I. C. Lewis.
Volume XVII	Radiography of Carbon and Graphite, by T. C. Furnas, Jr., and M. R. Rosumny.
Volume XVIII	High Temperature Tensile Creep of Graphite, by E. J. Seldin.
Volume XIX	Thermal Stresses in Anisotropic Hollow Cylinders, by Tu-Lung Weng.
Volume XX	The Electric and Magnetic Properties of Pyrolytic Graphite, by G. Wagoner and B. H. Eckstein.
Volume XXI	Arc Image Furnace Studies of Graphite, by M. R. Null and W. W. Lozier.
Volume XXII	Photomicrographic Techniques for Carbon and Graphite, by G. L. Peters and H. D. Shade.
Volume XXIII	A Method for Determining Young's Modulus of Graphite at Elevated Temperatures, by S. O. Johnson and R. B. Dull.

Volume XXIV	The Thermal Expansion of Graphite in the c-Direction, by C. E. Lowell.
Volume XXV	Lamellar Compounds of Nongraphitized Petroleum Cokes, by H. F. Volk.
Volume XXIV	Physical Properties of Some Newly Developed Graphite Grades, by R. B. Dull.
Volume XXVII	Carbonization Studies of Aromatic Hydrocarbons, by I. C. Lewis and T. Edstrom.

ABSTRACT

Polarographic reduction potentials ($E_{1/2}$) have been measured for polynuclear aromatic hydrocarbons. The $E_{1/2}$ parameters for structurally similar hydrocarbons have been related to the positions of the respective long wavelength "p" bands. Polarographic reduction potentials have also been determined for a series of substituted pyrenes and anthracenes. $E_{1/2}$ is shown to relate to the electronic effect of the substituent group. The application of polarography to the characterization of aromatics in complex pyrolytic residues is discussed.

This technical documentary report has been reviewed and is approved.

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Division
AF Materials Laboratory

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

Polarography, which is essentially an electrolytic process, has become an important technique in organic chemistry. The greatest application has been in the determination of polarographic reduction potentials of organic compounds.

Polarographic reductions are usually performed with the use of a dropping mercury electrode as the cathode and an appropriate standard half cell or a mercury pool as the anode. The organic substance, in solution with an added electrolyte, is reduced at the surface of the mercury drop, provided a sufficient potential exists for reaction. In a typical polarographic experiment, the potential is gradually increased and a current-voltage curve is recorded. At a certain potential the substance is reduced at a rate dependent only on the diffusion of the molecules to the mercury drop. The current flowing at this point is the diffusion current and is represented by the rising portion of the typical s-shaped polarographic curve. The potential at the mid-point of the diffusion current is the half-wave potential, $E_{1/2}$. The $E_{1/2}$ potential is a specific parameter for the organic material being reduced.

Polynuclear aromatic hydrocarbons readily undergo polarographic reduction generally with the reversible addition of one or two electrons. The $E_{1/2}$ potential can thus be easily obtained and represents a direct increase of the reactivity of the aromatic ring to electron addition. Polarographic half-wave reduction potentials are therefore the most extensively studied reactivity parameter for the polynuclear aromatic hydrocarbons. Specifically, the work of Wawzonek,[1] Hoijtink,[2] and Bergman[3] and their co-workers has led to a thorough compilation of $E_{1/2}$ values for the polycyclic aromatic hydrocarbons.[4] These parameters are a measure of the energies needed to place one or more electrons into the lowest vacant molecular orbital of the hydrocarbon[5] and therefore show a specific dependence on aromatic structure. Linear relationships have been obtained for plots of $E_{1/2}$ values of polynuclear aromatics in aqueous dioxane and in 2-methoxyethanol versus the Hückel molecular orbital (HMO) energy of the lowest vacant molecular orbital of the respective hydrocarbons.[4] The $E_{1/2}$ parameters have also been directly related to ionization potentials and to the frequencies of the long wavelength spectral p-bands.[3,6] Given and Peover[7] have extended the application of polarographic reduction potentials to the characterization of the polynuclear aromatics in coal extracts.

The normal mechanism for the reduction of polynuclear aromatics in neutral environments has been shown with a few exceptions to involve discrete one electron additions:[8]

$$(1) \quad R + e \rightarrow R^{\cdot -}$$

$$(2) \quad R^{\cdot -} + e \rightarrow R^{=}$$

$$(3) \quad R^{=} + 2H^{+} \rightarrow RH_2$$

Manuscript released by the authors June, 1963 for publication as an ASD Technical Report.

Separate one-electron polarographic waves are usually observed for each reduction step, although several hydrocarbons are known to undergo direct two-electron reductions.

$E_{1/2}$ values, as well as relating to the reactivity of the ground state aromatic molecule, measure the stability of the free radical intermediate formed by the addition of an electron to the aromatic nucleus. Polarography has therefore been combined with electron spin resonance spectroscopy for studying stable organic free radicals.[9]

The recognized importance of both polynuclear aromatic hydrocarbons and aromatic radicals in carbonization and in carbon raw materials,[10, 11] led to a study of the polarographic technique and its application to polynuclear aromatic systems. This report presents some results for polarographic reduction of aromatics in dimethylformamide solvent. The sensitivity of $E_{1/2}$ values to both aromatic structure and to substituents on the aromatic ring is discussed. Some initial applications of the results of the characterization of complex organic pyrolysis products are considered.

2. EXPERIMENTAL

2.1 Polarographic Measurements

Polarograms were obtained with a Leeds and Northrup Electrochemograph Type E polarograph in conjunction with a modified Lingane H cell.[12] Potentials were applied against a saturated calomel electrode. Half-wave potentials, $E_{1/2}$, and diffusion currents, i_d, were generally measured using approximately 0.001 molar solutions of aromatic in dimethylformamide solvent. This solvent has been found highly suitable for many aromatics.[7, 8] The reductions of the aromatic hydrocarbons, acenaphthene and acenaphthylene, were performed in 85 per cent aqueous ethanol.

The solutions contained 0.1M tetrabutyl ammonium iodide as a supporting electrolyte and 0.01 per cent ethyl cellulose as a maximum suppressor. Cell temperature was thermostated at 25.0°C ± 0.2°C. The solvent mixture was deaerated by prior treatment with bubbling nitrogen gas.

Half-wave potentials and diffusion currents were determined from the polarographic curves by standard methods.[13] The drop-weight (m) and the drop-time (t) were measured at various potentials. Typical values of $(m^{2/3} t^{1/6})$ as a function of potential were: 0.64 at -1.0 volt, 0.67 at -1.5 volts, and 0.66 at -2.0 volts.

2.2 Chemical Materials

Dimethylformamide was spectroscopic grade obtained from Olin Mathieson Company. Ethyl cellulose was obtained from Fisher Scientific Co. The majority of the polynuclear aromatics and substituted aromatics were obtained from commercial chemical supply houses. They were purified by recrystallization or elution chromatography prior to use. 9-Aminoanthracene was synthesized by the reduction of 9-nitroanthracene with $SnCl_2$.[14] 9-Acetaminoanthracene and 3-acetaminopyrene were prepared by acetylation of 9-aminoanthracene and 3-aminopyrene respectively.

Pyrolytic products of acenaphthylene were prepared by heating acenaphthylene samples in quartz containers to the desired temperatures. Heat treatments were conducted under an argon atmosphere in a standard tube furnace.

3. EXPERIMENTAL RESULTS

The experimental data are summarized in Tables 1-4. Compiled in Table 1 are the polarographic data obtained for a variety of polynuclear

Table 1. Polarographic Data for Polynuclear Aromatic Hydrocarbons in Dimethylformamide Solvent

	$-E_{1/2}$, Volts	i_d, μa	$i_d/m^{2/3} t^{1/6} c$
Acenaphthene	2.62	22.0	33.3
Naphthalene	2.57	----	----
Pyrene	2.15	2.6	5.6
Anthracene	2.04	4.3	6.5
Acenaphthylene	1.95	14.5	22.0
	2.62	22.0	33.3
Bianthryl	1.91	----	----
Perylene	1.72	3.8	5.8
Naphthacene	1.57	4.1	6.1
	2.26	4.0	6.0
	2.75	4.2	6.3
Pentacene	1.01	---	---

aromatic hydrocarbons in dimethylformamide. The half-wave potentials of the first observed reduction waves are listed in the second column. For acenaphthylene and naphthacene, the potentials of additional recorded waves are also given. The individual diffusion currents and diffusion current constants are shown in the third and fourth columns.

In Table 2 are listed $E_{1/2}$ values for a series of meso-substituted anthracenes. Substituents of widely varying electronic character are included. In the last column are computed the $\Delta E_{1/2}$ values which represent the difference between the reduction potential of the substituted anthracene and anthracene itself.

The reduction potentials for a limited group of 3-substituted pyrenes are compiled in Table 3. The $\Delta E_{1/2}$ parameters in the last column are the differences in $E_{1/2}$ between the substituted pyrenes and unsubstituted pyrene.

Table 2. $E_{1/2}$ Values of Substituted Anthracenes

Substituent	$-E_{1/2}$, Volts	$\Delta E_{1/2}$
9-NH_2	2.24	-0.20
9-C_6H_5	2.06	-0.02
9-CH_3	2.05	-0.01
9, 10-di-CH_3	2.04	0.00
None	2.04	0.00
9, 10-di-$C_6H_5CH_2$	1.94	+0.10
9, 10-di-C_6H_5	1.94	+0.10
9-$NHCOCH_3$	1.92	+0.12
9-$C_{14}H_9$	1.91	+0.13
9, 10-di-$C_{10}H_7$	1.88	+0.16
9-Br	1.65	+0.39
9, 10-di-Cl	1.51	+0.53
9, 10-di-Br	1.38	+0.66
9-NO_2	0.76	+1.28

Table 3. $E_{1/2}$ Values of 3-Substituted Pyrenes

Substituent	$-E_{1/2}$, Volts	$\Delta E_{1/2}$
NH_2	2.38	-0.23
CH_3	2.17	-0.02
None	2.15	0.00
$NHCOCH_3$	2.14	+0.01
Cl	1.88	+0.27
NO_2	0.95	+1.20

In Table 4 are given the $E_{1/2}$ values for a series of pyrolytic products prepared from the aromatic hydrocarbon acenaphthylene. The heat-treatment temperatures are shown in the first column while the $E_{1/2}$ values of the first and additional measured waves are summarized in the last two columns.

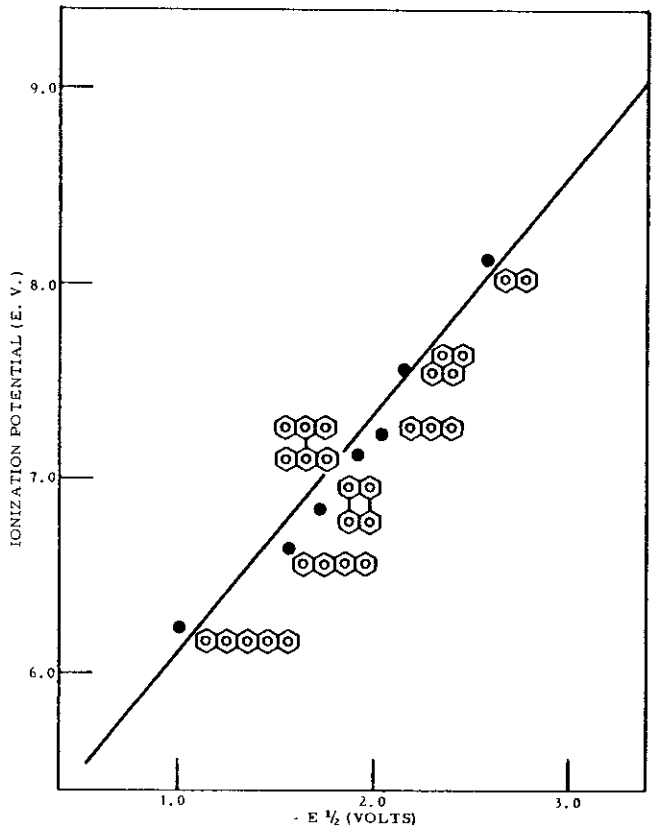
Table 4. $E_{1/2}$ Values of Acenaphthylene Pyrolysis Products

Pyrolysis Temperature °C	$-E_{1/2}$, Volts, 1st Wave	$-E_{1/2}$, Volts, Additional Waves
275	2.33	--
310	1.98	--
335	1.56	2.11, 2.56
350	1.54	2.03, 2.55
400	1.55	2.12, 2.61
450	1.57	2.15, 2.77

4. DISCUSSION OF RESULTS

4.1 Polynuclear Aromatic Hydrocarbons

The hydrocarbons included in Table 1 encompass an extensive range of aromatic reactivities. A variation in structure from the relatively stable naphthalene to highly reactive pentacene is seen to result in a change in reduction potential of 1.5 volts. Shown in Figure 1 is a plot of $E_{1/2}$ values for the series of alternant polynuclear aromatic hydrocarbons versus ionization potentials determined from the wavelengths of the spectral p-bands.[12]



N-3994

Figure 1. Plot of Ionization Potential Versus $E_{1/2}$ for Polynuclear Aromatic Hydrocarbons

A linear plot is observed which is concordant with the results of previous investigations relating $E_{1/2}$ to aromatic structure.[2-6] Our present results further illustrate the general applicability of $E_{1/2}$ constants obtained in dimethylformamide for categorizing the reactivities of polynuclear aromatic hydrocarbons.

4.2 Substituted Aromatics

The data presented in Tables 2 and 3 show that $E_{1/2}$ parameters, in addition to exhibiting a gross dependence on polynuclear aromatic structure, are significantly influenced by substituents in the aromatic ring. Substituents of widely varying electronic properties, ranging from the strongly electron withdrawing NO_2 group to the electron donating NH_2 group have been included in this study.

Plotted in Figure 2 are the $E_{1/2}$ values for some 3-substituted pyrenes versus those of anthracenes similarly substituted in the 9-position. A precise linear relationship is observed indicating comparable substituent effects

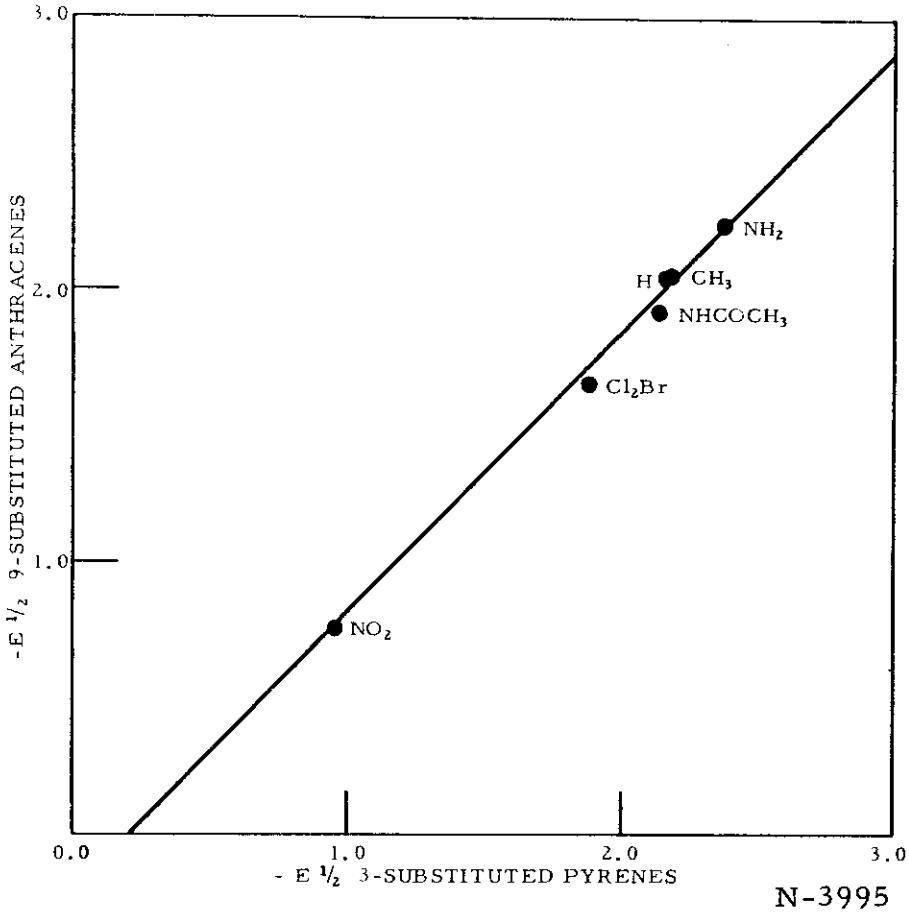


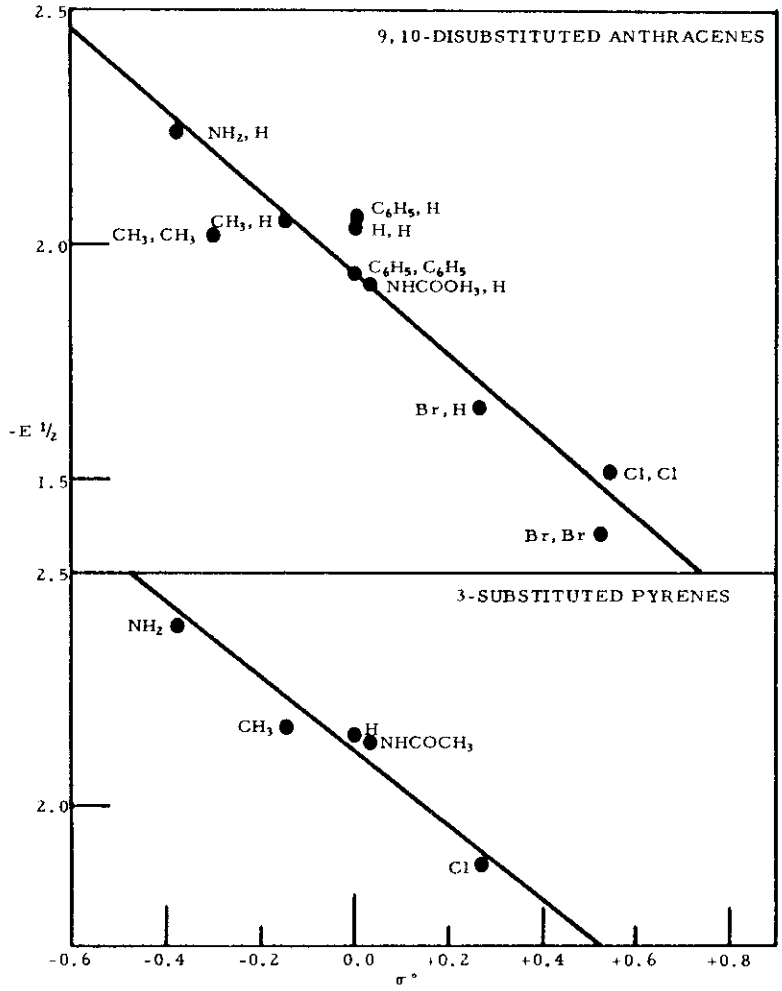
Figure 2. Plot of $E_{1/2}$ for 9-Substituted Anthracenes Versus $E_{1/2}$ for 3-Substituted Pyrenes

in both ring systems. The extremely high (less negative) reduction potentials of the nitro compounds are not believed attributable to substituent effects. In these cases actual chemical reduction of the nitro group is felt to be involved. Ring substitution, however, is seen to appreciably alter $E_{1/2}$.

The total change encompassed in $E_{1/2}$ in progressing from NH_2 to Cl substitution is 0.5 to 0.6 volts.

The substituent effects on $E_{1/2}$ seem related to the electronic nature of the substituent group. Electron withdrawing groups generally increase $E_{1/2}$ while electron releasing groups tend to decrease $E_{1/2}$. Both resonance and inductive effects appear important.

Shown in Figure 3 are plots of the $E_{1/2}$ values of substituted pyrenes and anthracenes versus the aromatic substituent, σ°. The constant is purported



N-3996

Figure 3. Plots of $E_{1/2}$ for Substituted Pyrenes and Anthracenes Versus Substituent Constant, σ°

to represent the direct electronic effects of substituent groups on the aromatic ring system of benzenes.[15] These constants have been utilized in correlation with nuclear magnetic resonance chemical shifts of substituted benzenes and of fluorobenzenes and for polarographic reduction potentials of substituted nitrobenzenes.[9] A fair linear relationship is observed in Figure 3 although several significant deviations are apparent. It is possible that to some extent the substituent effects operative between the ground state hydrocarbon and the radical ion are nonuniform. Such effects generally lead to specific breakdowns in correlations with substituent constants.

In conclusion, it has been shown that $E_{1/2}$ constants in dimethylformamide provide sensitive reactivity parameters for the polynuclear aromatics. Additionally these reduction potentials are influenced by substituents on the aromatic ring. The sensitivity of $E_{1/2}$ values to changes in aromatic structure and aromatic substitution could lead to their use in characterizing the aromatics in complex organic pyrolysis products since aromatic pyrolysis is known to induce changes in ring structure and substitution. A preliminary study of this application is discussed in the following section.

4.3 Pyrolytic Products

Organic pyrolysis generally leads to the formation of complex aromatic residues.[16] Characterization of these residues is essential toward understanding the pyrolytic mechanism. The polarographic technique offers a method for ascertaining the aromatic nature of such residues. In this connection a series of thermal reaction products have been prepared from the pure aromatic hydrocarbon acenaphthylene. The $E_{1/2}$ values have been measured for each material and followed as a function of temperature. Although the actual $E_{1/2}$ measurement is difficult for such complex and highly insoluble products, distinct reduction waves could be discerned. These data are presented in Table 4.

The $E_{1/2}$ values as listed in Table 4 are seen to change in the expected manner with temperature. As the temperature of heat-treatment is increased, more aromatic and easily reducible species are formed. The residues obtained above 335°C possess a reactivity comparable to naphthacene, ($E_{1/2}$ = -1.56 v.). These data are consistent with the thermal reaction sequence presented elsewhere for this hydrocarbon.[16]

5. REFERENCES

1. S. Wawzonek and H. A. Laitinen, J. Am. Chem. Soc. 64, 1765, 2365 (1942).

2. G. J. Hoijtink, Chem. Weekblad 56, 54 (1960).

3. I. Bergman, Trans. Far. Soc. 50, 829 (1954).

4. A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," J. Wiley & Sons, New York, N.Y. (1961).

5. A. Maccoll, Nature 163, 178 (1949).

6. A. T. Watson and F. A. Matsen, J. Chem. Phys. 18, 1305 (1950).

7. P. H. Given and M. E. Peover, Fuel 39, 463 (1960).

8. G. J. Hoijtink, J. Van Schooten, E. DeBoer and W.I.J. Aalbersberg, Rec. Trav. Chim. 73, 355 (1954).

9. A. H. Maki and D. H. Geski, J. Am. Chem. Soc. 83, 1852 (1961).

10. WADD Technical Report 61-72, Vol. X, "Thermal Reactivity of Aromatic Hydrocarbons," by I. C. Lewis and T. Edstrom.

11. WADD Technical Report 61-72, Vol. XVI, "An Electron Spin Resonance Study of Thermal Reactions of Organic Compounds," by L. S. Singer and I. C. Lewis.

12. J. J. Lingane and H. A. Laitinen, Ind. Eng. Chem. Anal. Ed. 11, 504 (1939).

13. L. Meites,"Polarographic Techniques," Interscience Publishers, Inc., New York, New York (1955).

14. P. D. Bartlett and S. G. Cohen, J. Am. Chem. Soc. 62, 1187 (1940).

15. R. W. Taft, S. Ehrenson, I. C. Lewis and R. E. Glick, J. Am. Chem. Soc. 81, 5352 (1959).

16. WADD Technical Report 61-72, Vol. XXVII, "Carbonization Studies of Aromatic Hydrocarbons," by I. C. Lewis and T. Edstrom.