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Odd Electrons in Polymer Molecules

BY F. H. WINSLOW, W. O. BAKER AND W. A. YAGER

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Two series of pyrolytic derivatives, from polyvinylidene chloride and pre-oxidized polydivinylbenzene, exhibited paramagnetic resonance absorption. Close correlations were observed among composition, semiconductivity and odd electron concentration of these residues, and also of pure dihydrogen phthalocyanine. Their properties presumably result from extensive conjugation in a dense, rigid carbon–carbon primary valence bond mesh. The low energies seemingly involved in providing conduction carriers lead to suggestions about electron movement in aromatic compounds.

Although unpaired electrons were discovered in organic compounds (triphenylmethyl) over a half century ago,[1] their fundamental importance in reactions and significance in structure are just now being realized.[2] They generally approach maximum stability in rigid configurations of high resonance energy. Studies of these electrons are complicated in small molecules by intermolecular gaps. Thus, electrodes cannot be put "on the bonds," as they might if macroscopic chunks of continuous bonds were available. Such structures could occur in pyrolyzed polymers which exhibit dense cross-linkage and extensive unsaturation.

Fairly dense networks of carbon bonds can now be made by polymerizing polyfunctional hydrocarbons like multi-vinyl benzenes and acetylenes. Recourse to oxidation and pyrolysis was necessary to vary unsaturation widely. Recent studies of pre-oxidized polydivinylbenzene and polytrivinylbenzene have shown that enough (~50%) of the carbon network remains intact throughout pyrolysis to retain, in detail, the original gross form in the final "polymer carbon."[3] During the course of decomposition of these polymers, much of the aliphatic part of their structure is lost. There is nearly complete reshuffling of the original carbon network accompanied by a large increase in unsaturation. Some of the unsaturation presumably develops, during dehydrogenation, into sites of unpaired electrons, stabilized by resonance energy.

Evidence for Radicals.—Microwave resonance absorption techniques provide a sensitive means of detecting the presence of such unpaired electrons.[4-6] All measurements were made at ~25° with a conventional Zeeman Modulation spectrometer operating at a frequency of 24,000 mc./sec. The equipment consisted of an Arthur D. Little electromagnet and a spectrometer which utilized a rectangular transmission-type cavity, 280 cycle magnetic field modulation, heterodyne detection at r.f. level, narrow band detection at audio level, and a recorder. When the static magnetic field was swept slowly through an absorption line, the derivative of the line appeared on the recorder. The spectrometer was capable of detecting the presence of approximately $4 \times 10^{13} (\Delta H)^2$ spins in the test specimen. ΔH represents the line width in oersteds between points of maximum slope of the absorption curve. The sample in the form of particles (70–80 μ in diameter) was packed in a thin wall glass tube $^3/_{32}$″ i.d. to an apparent density of ~0.8. The sample tube was then inserted through holes at the center of the broad faces of the rectangular cavity a half wave length from the end of the cavity, and the static magnetic field applied perpendicular to the r.f. magnetic field was measured with a nuclear fluxmeter.

The paramagnetic resonance absorption data are expressed in arbitrary units in the tables and figures that follow. The correspondence between arbitrary units and spins/cm.^{3} was not established for the results given in Fig. 1. For all other data, one arbitrary unit corresponds roughly to $3 \times 10^{15} (\Delta H)^2$ spins/cm.^{3} as deduced from the data in footnote *a*, Table II.

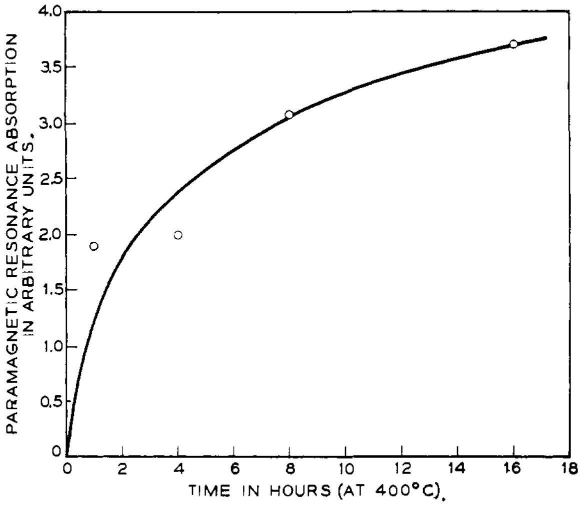

Fig. 1.—Paramagnetic resonance absorption at 24,000 mc./sec. due to "odd electrons" in polydivinylbenzene heated at 400° after oxidation at 250°.

The evolution of radical states, as oxidized polydivinylbenzene is heated at 400° *in vacuo*, is shown in Fig. 1. The line width between points of maximum slope was 10–15 oersteds in these samples. In the expression $\nu = \Delta E/h = g\mu H/h$, where μ = Bohr magneton, H = external magnetic field strength, and h = Planck's constant, the polymers have a Landé g-factor close to the free spin value, as found also in more familiar organic "radical compounds."[4]

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(1) M. Gomberg, *Ber.*, **33**, 3150 (1900).

(2) See, for instance, D. H. Hey, Chapt. 7, in "Progress in Organic Chemistry," v. 1, Butterworth's Scientific Publications, London, 1952; E. Müller, *Fortschr. Chem. Forsch.*, **1**, 325 (1949); D. Voigt, *Bull. soc. chim. France*, 679 (1949).

(3) W. O. Baker and F. H. Winslow, p. 126, Abstracts XIIth Intl. Cong. Pure and Applied Chem., N. Y., 1951; F. H. Winslow, W. O. Baker, N. R. Pape and W. Matreyek, *J. Poly. Sci.*, **16**, 101 (1955).

(4) A. N. Holden, C. Kittel, F. R. Merrett and W. A. Yager, *Phys. Rev.*, **77**, 147 (1950).

(5) C. A. Hutchison, A. Kowalsky, R. C. Pastor and G. W. Wheland, *J. Chem. Phys.*, **20**, 1485 (1952).

(6) B. Commoner, J. Townsend and G. E. Pake, *Nature*, **174**, 689 (1954).

Conductivity Associated with Radical States.—The d.c. resistivities of pre-oxidized divinylbenzene polymers heated below 700° were characteristic of typical insulators. But they were rapidly converting to a semiconductor level of $<10^7$ ohm cm. when pyrolyzed to 700°, as shown in Table I and Fig. 2. Both sets of data summarize the change in specific resistivity at 25° with pyrolysis temperature (hence composition).

TABLE I

THE D.C. RESISTIVITIES OF PYROLYSIS PRODUCTS FROM PRE-OXIDIZED POLYDIVINYLBENZENE

Pyrolysis temp., °C.	Empirical formula of residues	Resistivity, ohm cm. 25°
500	$C_{26}H_{17}O$	10^{15}
600	$C_{34}H_{13}O$	10^{12}
700	$C_{45}H_{16}O$	10^6
1000	~0.6% H	10^{-2}

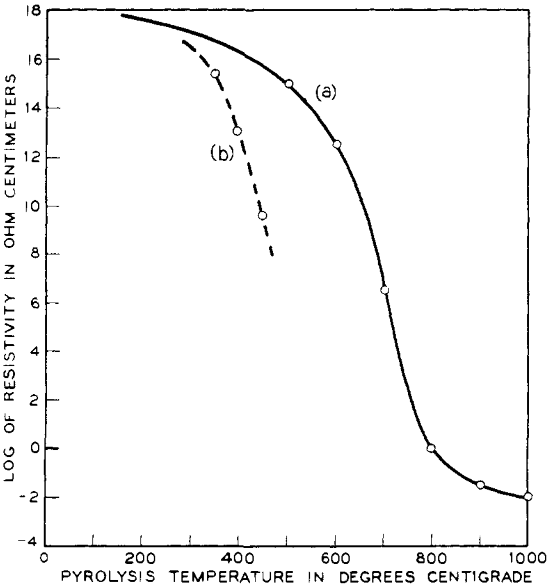

Fig. 2.—Specific resistivity of (a) pre-oxidized polydivinylbenzene pyrolysates and (b) polyvinylidene chloride pyrolysates at about 25°.

Striking changes in microwave resonance absorption that occur over this range are presented in Table II and Fig. 3.

TABLE II

THE EFFECT OF TREATMENT TEMPERATURE ON THE PARAMAGNETIC RESONANCE ABSORPTION OF PRE-OXIDIZED DIVINYLBENZENE POLYMER PYROLYSATES AS MEASURED AT 25°

Treatment temp., °C.	Absorption (arbitrary units)	ΔH (oe) (points of max. slope)	Treatment temp., °C.	Absorption (arbitrary units)	ΔH (oe) (points of max. slope)
250	4.4	12	600[a]	64	12
300	19	10	650	34	15
450	75	12	700[b]	7	..
500	110	10	725	(No detectable absorption—high loss)	
550	77	11			

[a] Relative to this sample, an equivalent volume of hydrazyl (2,2-diphenyl-1-picrylhydrazyl) has 420 times greater absorption and 55 times more spins per cm.³. Consequently, one arbitrary unit corresponds roughly to 3×10^{15} $(\Delta H)^2$ spins/cm.³. This relation applies also to the data in Table III and Figs. 3, 6 and 8. [b] No appreciable change in resonance absorption occurred after air exposure over a two-year period.

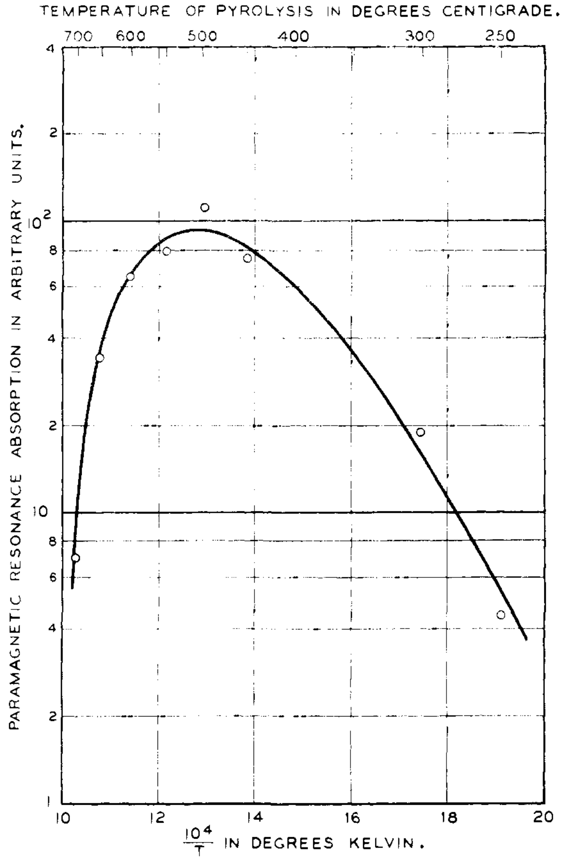

Fig. 3.—Paramagnetic resonance absorption in pre-oxidized polydivinylbenzene as a function of progressively higher temperatures of pyrolysis. [Reprinted with permission of the Editor, *J. Polymer Sci.*, **16**, 101 (1955).]

The low temperature branch of the curve thus represents the regular increase in concentration of unpaired electrons before there is appreciable conduction through the network.[7] But as pyrolysis continues, additional circulation of all current carriers (*i.e.*, change in valence bond structure with unsaturation) reverses the situation sharply[8] at a composition of about $(C_{34}H_{13}O_1)_n$. (In all samples, O content was by difference, and hence is a maximum content.) From peak absorption to the onset of semiconductivity, the paramagnetic resonance absorption falls off dramatically with increasing temperature.[9]

An Alternate Approach to Conjugated Structures.—A similar study was made of polyvinylidene chloride. This polymer, though linear,[10] pyrolyzes

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(7) H. Honda, K. Ouchi and K. Nagata, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **74**, 720 (1953). Magnetic susceptibilities of glucose and cellulose were reported to have decreased in samples that had been heated at successively higher temperatures. A minimum value was reached in samples pyrolyzed at 700°. Beyond 700°, a gradual increase was observed up to 1100°. Above 1400° the increase became rapid; V. A. Garten and D. E. Weiss, *Aust. J. Chem.*, **8**, 68 (1955).

(8) D. J. E. Ingram and J. G. Tapley, *Nature*, **174**, 797 (1954); J. E. Bennett, D. J. E. Ingram and J. G. Tapley, *J. Chem. Phys.*, **23**, 215 (1955).

(9) NOTE: No detectable resonance absorption was observed in polymers heated above 700°. However, Castle reported (J. G. Castle, Jr., *Bull. Amer. Phys. Soc.*, **29**, No. 3, 12 (1954); *Phys. Rev.*, **95**, 846 (1954)) paramagnetic resonance absorption in cokes after heat treatment at 1400° or above.

(10) R. C. Reinhardt, *Ind. Eng. Chem.*, **35**, 422 (1943).

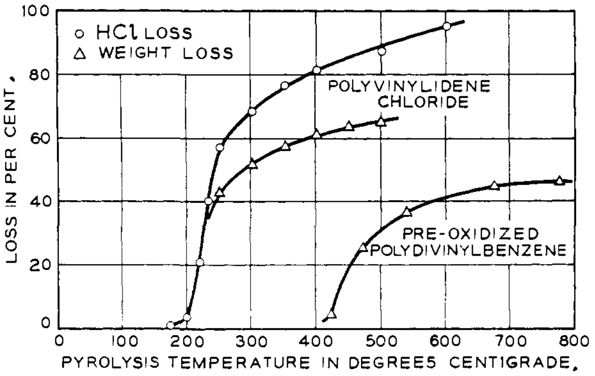

Fig. 4.—Weight loss characteristics of polyvinylidene chloride and pre-oxidized polydivinylbenzene pyrolyzed by increasing temperature at the constant rate of 100° per hour.

without significant loss of carbon.[11–13] The rate of HCl loss at 160, 175 and 200° are plotted in Fig. 4. Below 200° the reaction is essentially first order with a rate that becomes negligible at 50% total HCl loss. This would seem to indicate a chain reaction mechanism releasing HCl from allylic configurations to form chain molecules of conjugated unsaturation, without appreciable cross-linking or cyclization.[14] Above 200°, the polyene molecules cyclize, within themselves or in conjunction with adjacent molecules, to form aromatic structures that exhibit paramagnetic resonance absorption and eventually become semiconducting. Polyvinylidene chloride pyrolyzes at a lower temperature than oxidized polydivinylbenzene. Summaries of the pyrolytic behavior of both polymers heated at a constant temperature increase of 100° per hour are compared in Fig. 5. The relationship between total weight loss and residual composition is shown by the two curves representing polyvinylidene chloride pyrolysis. A similar relationship applies to oxidized polydivinylbenzene. Over-all differences in pyrolysis temperature (composition) are reflected in d.c. resistivities and paramagnetic resonance absorption patterns in Figs. 2, 3 and 6. The resistivity and absorption patterns and their related data listed in Tables II and III were obtained from samples corresponding to the series of points forming the curves in Fig. 5. Measured g-factors presented in Fig. 7 show a definite trend toward the free spin value of an unpaired electron in samples prepared at successively higher temperatures. Near the transition from radical-like to

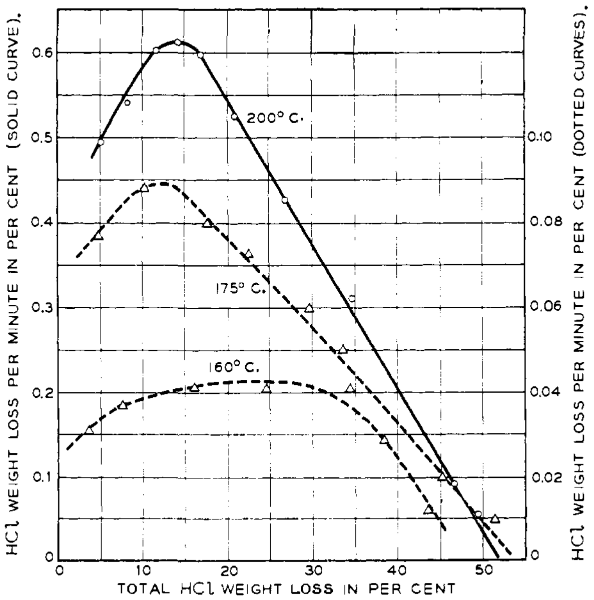

Fig. 5.—Pyrolysis of polyvinylidene chloride.

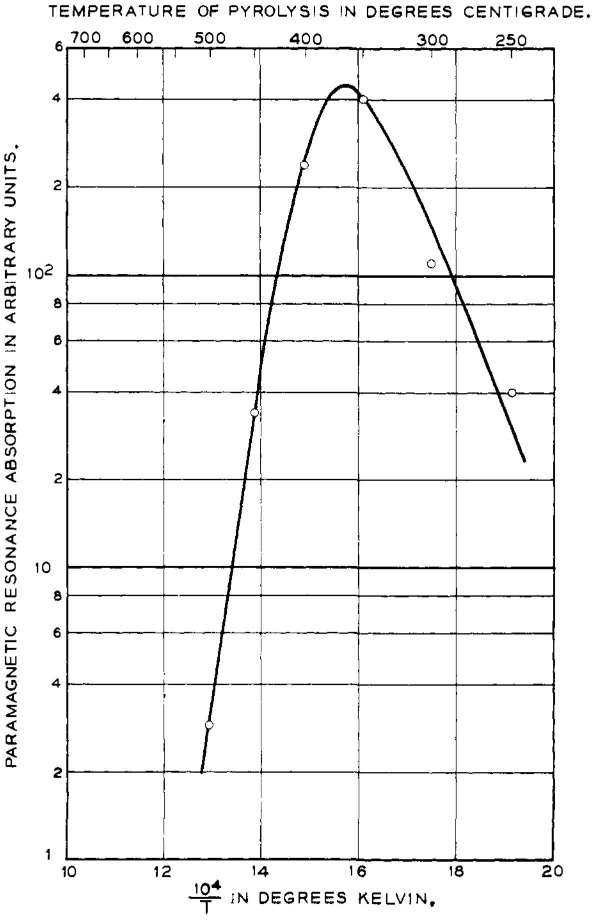

Fig. 6.—Variation in paramagnetic resonance absorption with treatment temperature for polyvinylidene chloride residues.

TABLE III

RELATION BETWEEN PARAMAGNETIC RESONANCE ABSORPTION AND PREPARATION TEMPERATURE OF POLYVINYLIDENE CHLORIDE PYROLYSIS INTERMEDIATES

Pyrolysis temp., °C.	Absorption (arbitrary units)	ΔH (oe.) (points of max. slope)	Pyrolysis temp., °C.	Absorption (arbitrary units)	ΔH (oe.) (points of max. slope)
200	40	16	450	32	19
300	110	13	500	2.9	. .
350	405	13	600	No detectable resonance—high loss	
400	242	11			

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[11] C. Pierce, J. W. Wiley and R. N. Smith, *J. Phys. Colloid. Chem.*, **53**, 669 (1949).

[12] C. Pierce, R. N. Smith, J. W. Wiley and H. Cordes, THIS JOURNAL, **73**, 4551 (1951).

[13] R. E. Franklin, *Proc. Roy. Soc. (London)*, **A209**, 196 (1951).

[14] R. F. Boyer, *J. Phys. Colloid. Chem.*, **51**, 80 (1947).

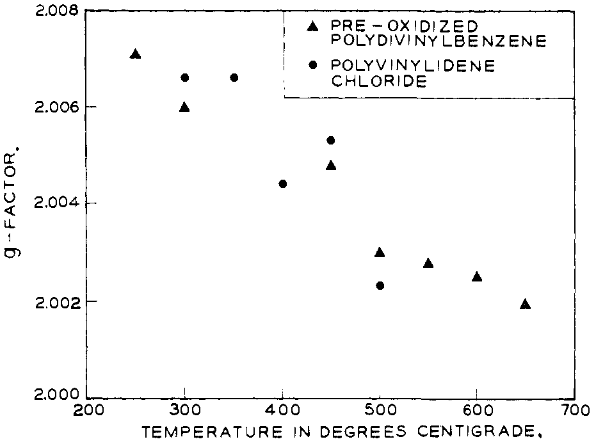


Fig. 7.—g-Factor of pre-oxidized polydivinylbenzene and polyvinylidene chloride residues as a function of preparation temperature.

semiconducting states, only small composition changes cause a sharp drop in resonance absorption as shown in Fig. 8.

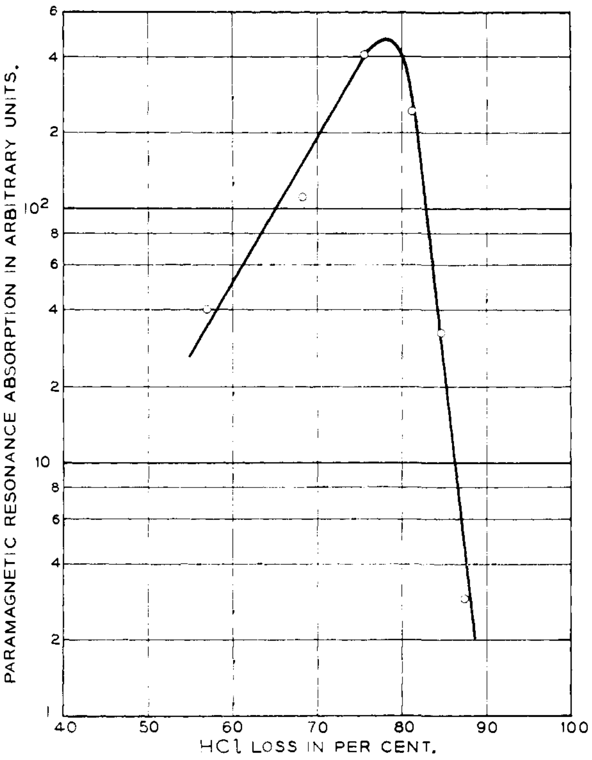


Fig. 8.—Dependence of paramagnetic resonance absorption on composition of polyvinylidene chloride pyrolysates.

Comparison with Phthalocyanine.—At peak absorption, the compositions of both polymer pyrolysates indicate approximately the same degree of unsaturation as exists in phthalocyanine. For example, the ratio of skeletal (atoms in the ring network, itself) to non-skeletal atoms (H in phthalocyanine) in these structures is nearly five to two, respectively. This suggested examination of pure, metal-free phthalocyanine, in which Eley[15,16] and simultaneous experiments of our own, found considerable d.c. electrical conduction at elevated temperatures. Surprisingly, highly purified microcrystalline phthalocyanine, which acts diamagnetic,[17] showed relatively intense and sharp paramagnetic resonance absorption[18] under the same measurement conditions as the polymers, and further purification increased the effect. Apparently, enough thermal energy is absorbed at room temperature to produce unpaired electrons (see Fig. 9) in crystals of this highly conjugated structure.[19-21] Stable radical (triplet) states, like those alleged for Chichibabin's hydrocarbon,[5] p,p'-biphenylene-bis-(diphenylmethyl), could originate from homolytic scission of a π-electron bond. In that event, the presence of numerous excited electronic configurations, related to the two shown in Fig. 9, could contribute to a large resonance stabilization of the lowest triplet in phthalocyanine. Another of the same type of electronic states has been postulated by Clar[22] to account for the peculiar properties of zethrene, a curious condensed-ring hydrocarbon

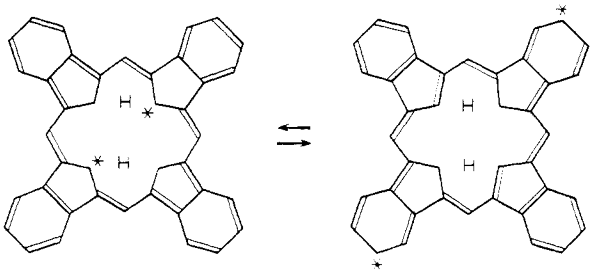
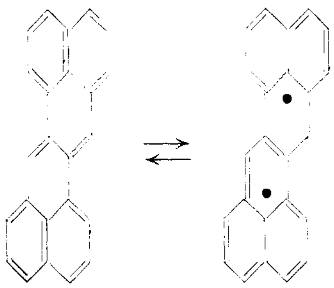


Fig. 9.—Two of many possible excited states illustrating observed behavior of phthalocyanine. (*) Represents an unpaired electron.



Polynuclear compounds like zethrene occupy a structural position intermediate between saturated hydrocarbon polymers, on the one hand, and graphite crystallites, on the other. The possibility of their formation in pyrolyzed polymers[6,23] through continuous changes in conjugation provides the basis for the following hypothetical ex-

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[15] D. D. Eley, *Nature*, **162**, 819 (1948).

[16] D. D. Eley, G. D. Parfitt, M. J. Perry and D. H. Taysum, *Trans. Faraday Soc.*, **49**, 79 (1953).

[17] K. Lonsdale, *Proc. Roy. Soc. (London)*, **A159**, 149 (1937).

[18] D. J. E. Ingram and J. E. Bennett, *J. Chem. Phys.*, **22**, 1136 (1954); W. O. Baker and F. H. Winslow, "Entrapped Polymer Radicals," Lecture Series at Polytechnic Inst. of Brooklyn, Jan. 19, 1953.

[19] N. S. Bayliss, *J. Chem. Phys.*, **16**, 287 (1948).

[20] W. T. Simpson, *ibid.*, **16**, 1124 (1948).

[21] J. S. Griffith, *Trans. Faraday Soc.*, **49**, 345 (1953).

[22] E. Clar, p. 174, Abstracts, XIIIth Intl. Cong. Pure and Applied Chem., Stockholm, 1953.

[23] J. Uebersfeld, A. Etienne and J. Combrisson, *Nature*, **174**, 614 (1954).

planation of observed paramagnetic resonance absorption phenomena: During pyrolysis there is a progressive increase in unsaturation, part of which becomes localized in aromatic configurations that are gradually linked together, by a network of carbon valence bonds. As aromatic regions grow in size and number, unpaired electrons progressively develop in configurations resembling those in triphenyl-methyl (doublet) or zethrene[22] (triplet). Eventually the unpaired electrons reach a concentration beyond which their combination to form graphitic systems exceeds their rate of formation and a reduction in paramagnetic resonance absorption is observed. Yet, the rapid merging of condensed-ring regions continually adds to the over-all resonance energy and results in reduction of the energy required for thermal excitation. At this stage in pyrolysis only small changes in composition quickly complete continuous paths of conjugation throughout the entire mesh of carbon atoms. D.c. conduction in such a structure then occurs through mere shifts in double bonds (mobile electrons in overlapping orbitals). Radical loci, created by thermal excitation, are also capable of drifting along conjugated chains and participating in conduction. If these same radical loci, or atoms with incomplete valence shells, behave like electron deficiencies or "holes," they could account for electrical conductivity of carbon,[24] anthracene[25] and phthalocyanine.[26]

Semiconductivity and Composition.—D.c. resistivity measurements were obtained from discs (1″ dia. × $^1/_{16}$″ thick) of pyrolyzed polymer pressed at elevated temperatures in a graphite mold. Pre-oxidized polydivinylbenzene pelletizes below 600°,[3] or about 200° above the similar upper limit for polyvinylidene chloride. A silver acryloid paste, applied to the sample and then preheated at 150° for 48 hr. in dry nitrogen, was suitable contact material below 300°. Resistivities were measured in a dry nitrogen atmosphere with temperature regulation to 0.5°. High resistance samples were measured at 80 volts in a conventional shielded but unguarded electrode assembly with a Leeds and Northrup Type 9836A Amplifier. At higher temperatures or where contact resistance was appreciable, resistivities were determined by the potential probe method using a Leeds and Northrup Type K potentiometer. Seebeck voltage and potential probe voltage were measured by a procedure similar to that described by Morin.[27] Resistance measurements on any one sample were reproducible to within 1–2% providing pyrolysis temperature exceeded the maximum temperature of measurement by 150°.

Following a study of various unsaturated organic compounds, Eley, *et al.*,[16] concluded that d.c. conductivity was primarily associated with the π-electrons in polynuclear systems while those in linear polyenes were much less effective. The changes in semiconductivity during pyrolysis of polyvinylidene chloride tend to substantiate their results. For example, the polymer in Fig. 10 that was made by pyrolysis at 394° has an empirical formula, $(C_5HCl)_n$ (composition of maximum unpaired electron concentration). If a completely conjugated structure is assumed, it could consist, on the average, of fused aromatic rings, the size of phthalocyanine molecules, bound together by primary valence bonds into an enormous compact network of conjugated double bonds. Yet such a model is inadequate if continuous conjugated chains are actually electrical conductors, because the polymer residue has a d.c. resistivity of 10^{13} ohm cm. at ~25°. Its activation energy (13.1 kcal.) is only slightly lower than the values[16] calculated for anthracene (~19 kcal.) and phthalocyanine (16–19 kcal. or for compressed samples, 9–13 kcal.). In fact, further HCl loss to a composition of $(C_{10}HCl)_n$ is required before a semiconductor state of less than 10^7 ohm cm. is reached.

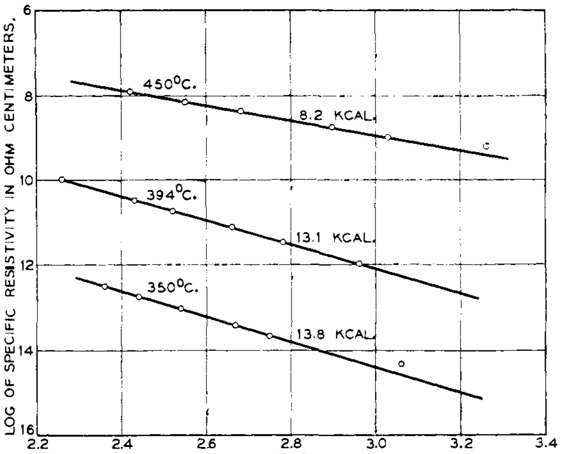

Fig. 10.—Temperature dependence of resistivity of polyvinylidene chloride pyrolyzed at 350, 394 and 450°.

It would appear from X-ray[28] and microwave resonance absorption studies that aromatic condensed-ring systems form in the early stages of pyrolysis. But any polynuclear regions in the composition $(C_5HCl)_n$ are still sufficiently isolated to preclude appreciable interaction of odd electrons. However, the changes in resistivity, odd electron concentration and viscous flow between compositions $(C_5HCl)_n$ and $(C_{10}HCl)_n$ indicate a considerable condensation of aromatic regions.

Studies involving photoconductivity,[25] thermoelectric effect,[29] and Hall effect,[30] all indicate that holes are the principal current carriers in aromatic compounds and cokes pyrolyzed below 700–800°. The *g*-factor values in Fig. 7, which exceed the free spin value of an unpaired electron, are also consistent with "hole" conduction that possibly converts to *n*-type above 700°. Rough calculations from conductivity and thermoelectric data like those in Figs. 11 and 12 give a large carrier concentration (>10^{19}/cc.) and a low mean free path (~1 Å.). Nearly equal numbers of n- and p-type carriers could explain the small Hall effect.

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(24) S. Mrozowski, *Phys. Rev.*, **86**, 1056 (1952).

(25) A. G. Chynoweth and W. G. Schneider, *J. Chem. Phys.*, **22**, 1021 (1954).

(26) F. H. Winslow and F. J. Morin (unpublished results).

(27) F. J. Morin, *Phys. Rev.*, **83**, 1005 (1951).

(28) H. L. Riley, *Quart. Rev. Chem. Soc.*, **1**, 59 (1947).

(29) E. E. Loebner, *Phys. Rev.*, **84**, 153 (1951); and Errata, reference 24.

(30) E. A. Kmetko, *J. Chem. Phys.*, **21**, 2152 (1953).

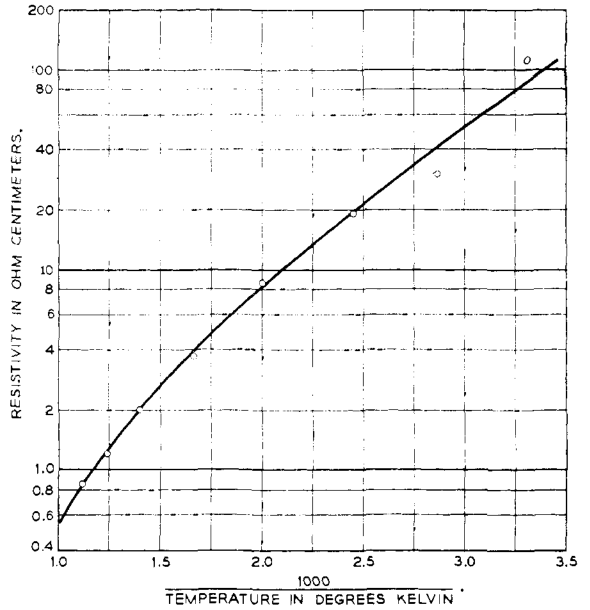

Fig. 11.—Resistivity as a function of reciprocal absolute temperature of pre-oxidized polydivinylbenzene pyrolyzed at 750°.

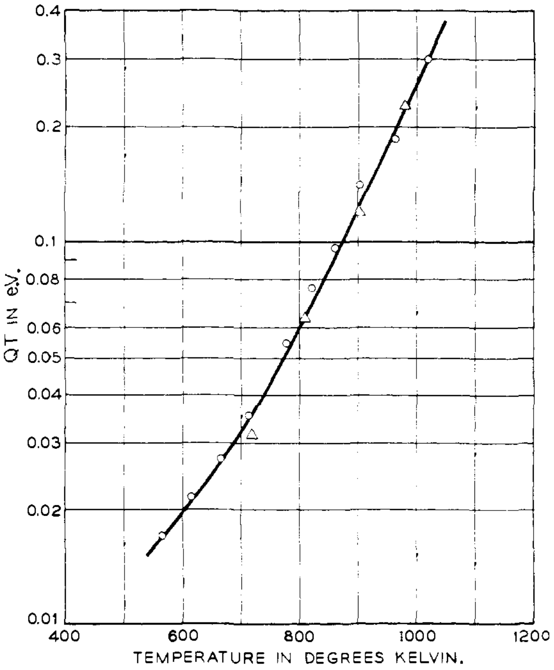

Fig. 12.—Temperature dependence of Seebeck voltage × temperature of pre-oxidized polydivinylbenzene pyrolyzed at 750°.

While there is general agreement that conduction electrons are derived from π (P_z) electrons in conjugated systems, the nature of conducting holes is less certain. The existence of organic ions[31] could probably be discounted in a neutral system of carbon chains. But there is ample evidence for radicals. Mrozowski[24] suggested that holes could be peripheral free valences, in unusual hybridized states on crystallite surfaces, and could originate from loss of hydrogen and other volatile products during carbonization. Entrapped radicals from broken σ-bonds are undoubtedly produced during pyrolysis and could conceivably be quite numerous during the rearrangement process of graphitization[13] found in some carbons above about 1400°. But a supplementary source of holes could still supply most of the huge number of current carriers in carbons. Another mechanism, based on excitation of π-electrons, was proposed[25] in connection with photo-induced "hole" conduction in anthracene, that was enhanced by the presence of oxygen.[32] This second mechanism is applicable to all conjugated systems including carbon, and is much like the one already outlined in regard to odd electrons in pyrolyzed polymers. Its relationship with d.c. conductivity and unpaired electrons can perhaps be best expressed as a sequence of electronic shifts in valence structures of high resonance energy. When a π-bond is broken symmetrically, both electrons remain tightly bound to carbon atoms that need one electron each to complete their valence shells. Each of these atoms can regain an octet and share in a double bond by acquiring an electron from an adjacent double bond, thereby shifting the odd electron site by two carbon atoms. Thus, radical sites can drift (*ad infinitum*) through a conjugated network in successive steps resembling hole movement in semiconductor crystals. This process differs from the one involving pure (intrinsic) semiconductors with diamond-type lattices in that excited electrons in an aromatic system are not always free to drift under the influence of an external electric field. In compounds with activation energies of conduction near 20 kcal., ordinary thermal excitation is not sufficient to free electrons for conduction, but does yield radical sites which behave like impurity acceptors whose concentration varies reversibly with temperature. In structures with higher resonance energy, more electrons participate in conduction and the numerical difference between electron and "hole" carriers is reduced.

Available evidence seems to fit the observation[16] that resonance energy is required to establish overlapping orbitals between conjugated molecules. Yet confirmation awaits quantitative semiconductivity data from single crystals of pure, highly stable organic compounds of known structure like phthalocyanine.[33,34] As others have already mentioned,[25,35] the vital functions of related compounds in sight, growth and respiration processes impart added significance to this complicated problem.

Acknowledgment.—The authors are indebted to W. P. Slichter and W. Matreyek for resistivity measurements and F. R. Merritt for paramagnetic resonance absorption measurements.

Murray Hill, N. J.

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(31) D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).

(32) A. G. Chynoweth, *J. Chem. Phys.*, **22**, 1029 (1954).

(33) G. T. Byrne, R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, 1017 (1934).

(34) J. M. Robertson, *ibid.*, 1195 (1936).

(35) A. Szent-Gyorgyi, *Nature*, **148**, 157 (1941).