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CARBON: AN OLD BUT NEW MATERIAL -- THE CONTINUING STORY

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There have been many advances in carbon science and technology in the past thirty years. I had the opportunity of reviewing advances in both the decades of the 1950s and 1960s. These advances are again briefly reviewed, followed by a review of advances in the 1970s. This is followed by consideration of some recent studies on carbonization from our laboratory and an updated look at carbon active sites from the viewpoint of gas-carbon interaction.

INTRODUCTION

I have been asked to update what I see as our advances in carbon science and technology for this Sixth London International Carbon and Graphite Conference. First, I had the opportunity of reviewing recent advances in my Sigma Xi national lecture in 1961.¹ This was followed by a second review in 1971 in the form of my Skakel Lecture.² As I contemplated the preparation of this lecture, my ultimate reaction was -- what a material carbon is and what a period to review its progress! Maybe I am prejudiced,^d but I would contend that no element leads to materials exhibiting more desirable and diverse properties in the solid state than does carbon. Diamond, with its cubic lattice and tetrahedral bonding, is the hardest material known, is an electrical insulator, and in large sizes is the most valued gem. Its properties are essentially isotropic. Graphite, with its hexagonal lattice and trigonal bonding, exhibits an extreme diversity of properties in different crystallographic directions. It is this diversity, coupled with the ability to prepare artifacts based on trigonally bonded carbon crystallites having alignments ranging from essentially completely random to perfectly aligned, which results in being able

to impart to the end product a wide range of properties. It is the understanding of how to effect controlled degrees of crystallite alignment in carbons produced from different organic precursors as they undergo liquid and gas phase thermal processing which forms the base of carbon science and technology as we know it today.

I will first give my impressions of some of the highlights of where we were in carbon science in 1961 and 1971. I will then consider some of the highlights of where we are in 1982. I then want to consider in somewhat more detail two areas which continue to interest me very much and in which we have made some recent progress -- carbonization and active sites.

By 1961

In the 1950s Franklin³ and Bacon⁴ laid the foundation for the use of x-ray diffraction to quantitatively characterize the crystalline ^{structure} (character) of carbons. They showed that ideal hexagonal graphite, that is material having infinite crystallite size and no stacking faults in its c-direction, has a spacing between basal planes of 0.33538 nm at 288 K. As crystallite size decreases and the fraction of stacking faults between basal planes increases, interlayer spacing increases. At a spacing of 0.344 nm the fraction of stacking faults goes to one (termed turbostratic carbon by Warren⁵), and the average crystallite diameter decreases to about 10 nm. Carbons of smaller crystallite sizes, which frequently contain significant concentrations of heteroatoms and carbon interstitials, have still larger interlayer spacings.

By 1961, stimulated by the enormous growth potentials in the use of the electric furnace for steel production and gas-cooled nuclear

reactors for power production, there was great interest in the production of highly graphitic carbons from organic precursors via liquid phase carbonization. The key fact was that the graphitizability of cokes exhibiting flow patterns within their particles, as shown in Figure 1, was found to be high. It was suggested that large, platelike aromatic molecules are aligned parallel to the flow as a result of shear stresses produced as volatiles evolve during carbonization. We showed that calcined cokes, exhibiting an extensive flow pattern, had superior crystallite alignment and that this alignment was preserved during the graphitization process.⁶ We showed that the extent of crystallite alignment in the cokes determines the asymmetry of particle shape upon grinding,⁷ a high degree of crystallite alignment leading to cokes of high asymmetry of needle-like character.

The potential of carbon for nose cones on missiles and as encapsulating layers for fission products generated in nuclear fuels prompted the search for ways to produce carbons of crystallite alignments superior to that which could be produced via liquid phase carbonization. By 1961 it was possible to produce massive artifacts of pyrolytic carbon exhibiting very high crystallite alignment as a result of cracking of gas phase hydrocarbons. The morphology of pyrolytic carbon was shown to be entirely different (Figure 2) than that of the conventional graphite artifact on which it was usually deposited.⁸ To attain excellent crystallite alignment, it was thought necessary to operate at low pressures of hydrocarbon in order to minimize formation of large aromatic (liquid) species in the gas phase which would then condense on the surface. Rather one wants, ideally, individual molecules chemisorbing on the surface, losing their hydrogen, yielding

carbon atoms of high mobility which diffuse to positions of low potential energy on the surface. Pyrolytic carbons of high carrier mobility, high anisotropy of thermal and electrical conductivity, and low permeability to gases could be produced.^{9,10} Subsequent heat treatment of artifacts up to 3500 K resulted in further crystallite growth, enhanced crystallite alignment, and a concurrent change in properties to approach more closely those of a graphitic single crystal.¹¹

In 1955, Bundy and co-workers announced their successful production of synthetic diamonds.¹² Workers knew under what conditions of temperature and pressure diamond was the stable phase relative to graphite, but the rate of conversion was too slow, even at temperatures as high as 1800 K. In addition to developing equipment to withstand high pressures at high temperatures, the ultimate solution was to add a catalyst (solvent) like nickel. The trigonal bonds of carbon in graphite are broken as atoms go into solution; atoms come back out of solution forming the equilibrium phase, diamond, with tetrahedral bonding.¹³

By 1971

The decade of the 1960s was probably the most exciting period ever for carbon science and technology. Shindo¹⁴ and Watt and co-workers¹⁵ produced carbon fibers exhibiting very high crystallite alignment, Brooks and Taylor discovered the mesophase,¹⁶ Ubbelohde and co-workers produced highly oriented pyrolytic graphite,¹⁷ Walker, among others, showed that thermosetting resins could be used to produce carbon molecular sieves,¹⁸ and Hennig identified the carbon active site.¹⁹ Let us look at each achievement briefly.

In spite of the success in improving the asymmetry of carbon particles produced from the delayed coking of petroleum feedstocks, it was clear that, if the anisotropy of properties exhibited by the graphite crystallite was going to be better realized in carbon artifacts, a filler exhibiting a much higher asymmetry of shape with accompanying improved crystallite alignment had to be developed. In retrospect, the solution is obvious; use polymer fibers as precursors. They already have a high degree of structure as a result of their processing. Polyacrylonitrile (PAN) fibers proved to be the prime precursor.¹⁵ Heating at relatively low temperatures, about 500 K, involves cyclization to an imine structure, which tautomerizes to an enamine structure, followed by mild oxidation in air to yield a pyridone structure.²⁰ This 'ladder' structure imparts rigidity along the chain, which, along with hydrogen bonding between the polymer chains through the C=O and N-H groups, maintains the structure of the degraded material as it is subsequently pyrolyzed to carbon fibers.

Even though workers had been using the light microscope to study the coking of coals since the 1920s, it was really Brooks and Taylor, in their studies on the carbonization of coal tar pitches, who revolutionized carbon science.²¹ Using reflected polarized light, they showed that pitch first melts to form an isotropic liquid. With increasing temperature and time, spheres, exhibiting optical anisotropy appear in the isotropic medium. They grow in size and number at the expense of the isotropic phase. Ultimately, these spheres coalesce into mosaic regions, followed by the formation of low temperature coke. The spheres were named mesophase by Brooks and Taylor, or the intermediate phase between the organic precursor and coke. As

it was understood that the propensity to form mesophase spheres, to grow in size, and to agglomerate to form large mosaics from organic precursors determined ultimate crystallite alignment in cokes and graphites, research in this area rapidly expanded.

One of the things which slowed up progress in carbon science was the inability to obtain large natural graphite crystals on which meaningful physical measurements could be made. Even though from a monetary standpoint, the production of highly oriented pyrolytic graphite by Ubbelohde and co-workers is unimportant compared to developments just discussed, its contributions to carbon science were enormous. Although carbons deposited by the cracking of hydrocarbons at around 2300 K show marked preferred orientation with consequent anisotropy of properties, they still contain numerous structural defects. Recrystallization under uniaxial pressures of about 40 MPa at 3300 K, followed by annealing under a small pressure at around 3700 K, produced blocks of graphite whose properties are comparable to those in small natural graphite crystals.²²

Much of the emphasis so far has been on advances to achieve enhanced crystallite alignment in the carbon. Walker and co-workers, among others, achieved just the opposite -- negligible crystallite alignment. In so doing this they produced highly microporous carbons exhibiting interesting properties as molecular sieves^{23,24} and selective catalyst supports.^{25,26} They showed that molecular sieves could be prepared from a range of thermosetting precursors. Their sieve properties can be altered by the selection of heat treatment temperature and by the addition of second phases like activated carbons. Molecular sieve carbons are, in fact, low temperature forms of "glassy carbons."

They are thought to be aperture-cavity materials, which have not been heated to sufficiently high temperatures to close the apertures to all molecules. Glassy carbons, developed in the 1960s by taking thermosetting resin systems ultimately to 3300 K, have large surface areas in their cavities and low densities despite their imperviousness to helium.²⁷

Whereas the basal plane of graphite is one of the lowest energy surfaces of any solid, the prismatic surfaces (at right angles) have a reasonably high surface energy. Thus the extent and rate of interaction of all atmospheres with carbon are highly dependent upon the fraction of the total surface area which consists of prismatic surfaces or active sites. Hennig used this anisotropy of reactivity to enlarge vacancies in the basal plane of graphite crystals by exposure to oxygen.¹⁹ This enlargement was followed by decorating the defects with evaporated gold, as seen by transmission electron microscopy in Figure 3. This advance formed the basis for continuing electron microscopy studies to elucidate the fundamentals of carbon gasification. Walker and co-workers used physical and chemical adsorption techniques to measure active site concentrations in carbons.^{28,29}

By 1982

The decade of the 1970s again marked a period of significant progress in carbon science and technology; it could be characterized primarily, though, as a period of consolidation based on some of the seminal discoveries of the past two decades.

Spurred on by the incentive of producing high modulus carbon fibers from a cheaper precursor than PAN, Singer and co-workers at

Union Carbide developed a process based on pitch.³⁰ Taking pitches from which solids had been removed, they heated them in N_2 to about 650 K to convert them, in part, to mesophase. They found that the use of agitation during heating reduced the average molecular weight of the mesophase formed and permitted the subsequent spinning of a product having a high mesophase content. Following spinning in N_2 , the fibers can be made infusible by heating in oxygen at about 570 K for several minutes. Subsequent graphitization yields fibers of excellent crystallite alignment, which usually exhibit a higher modulus but lower tensile strength than PAN fibers. Much effort was expended during the decade at identifying defects in PAN fibers by TEM and X-ray diffraction,³¹⁻³³ improving processing to reduce defect concentration, and enhancing the bond between the fibers and matrix in composites by etching fiber surfaces and adding coupling agents to the surface.^{34,35}

A voluminous amount of work was published during the past decade on mesophase concerned with its quantitative measurement,³⁶ factors affecting its size and perfection,³⁷⁻³⁹ its rate of formation,⁴⁰ and the effect of its formation on viscosity of the liquid.⁴¹ Mesophase solubility depends on the precursor from which it is formed; the amount of mesophase formed is not necessarily the same as amount of insolubles formed. It is necessary to use direct optical observations to determine mesophase formed.³⁶ We now know that the propensity of mesophase formation and its size depends dramatically upon the specific precursor selected -- reactivity of different positions in the molecule to form free radicals and then whether condensation of

free radical molecules leads to the formation of larger and larger planar species.

Particularly fruitful have been the studies of the French school in showing striking analogies between disc-like molecules and mesophase⁴² and in using high resolution TEM to study microtexture.³⁸ Gasparoux⁴² recognized the clear need for a well defined chemically stable system which could serve as a model for carbonaceous mesophase, that is a disc-like nematic liquid crystal. He achieved this by adding substituents to the triphenylene core which exhibit a high degree of steric hindrance. A. Oberlin and co-workers³⁸ confirmed by TEM studies, using selected area electron diffraction and dark field images, the microtexture of mesophase spheres originally suggested by Brooks and Taylor.²¹ In this model, polyaromatic molecules are both approximately parallel to one another and perpendicular to the surface of the sphere. The microtexture, Figure 4, was confirmed in the case of a coal tar pitch precursor by comparing the predicted structure of sections to the experimental ones obtained by their sectioning. Lattice imaging of their sections shows disc-like polyaromatic planar structures about five to ten rings in diameter, piled up in highly distorted close packed columns. It is suggested that the spheres are discotic mesomorphs which turn into a nematic arrangement upon their coalescence.

There had been some interest in graphite intercalates for years as potential polymerization catalysts,⁴³ molecular sieves,⁴⁴ lubricants,⁴⁵ and a means of producing exfoliated graphite;⁴⁶ but great interest in these materials only developed during the past decade, based on the high electrical conductivity of some new intercalates. In particular,

Vogel produced a composite wire consisting of an SbF_5 intercalated graphite powder core with a copper sheath.⁴⁷ This composite was shown to have a greater electrical conductivity in a 1 mm diameter by 10 cm length than did a control sample of copper. This finding and later apparent confirmation by Vogel and co-workers⁴⁸ have led to a plethora of studies on the synthesis of new intercalates,⁴⁹ the extent of charge transfer between the intercalate and the graphite,⁵⁰ and the effect of intercalation on carrier density and mobility.⁵⁰ It is thought that graphite intercalates offer great potential in batteries.⁵¹

Hardly has anyone dominated a field such as Bokros who developed much of the science of producing isotropic pyrolytic carbon and then developed and tested material particularly for biomedical applications.⁵² Such material is being marketed widely today as prosthetic heart valves. Pyrolytic carbon is thought to also have great potential in orthopedics. Its success is a combination of excellent compatibility with tissue and blood and superior resistance to wear and fatigue. Because of the work of Bokros⁵³ and others, we now know what conditions of temperature, pressure, and substrate bed area to use for the cracking of methane to produce pyrolytic carbons ranging from highly anisotropic to isotropic in character. Interestingly, Bokros showed that carbon density and anisotropy do not necessarily need to decrease with increasing methane concentration. It depends upon the level of methane concentration and deposition temperature as seen in Figure 5. If organic particles are semifluid when they deposit on the surface, they can spread out, resulting in alignment of planar molecules parallel to the surface. Gas phase reactions do not necessarily need to be minimized to produce anisotropic pyrolytic carbons.

I discussed at the last London Carbon Conference the renewed interest in carbon as a catalyst support.⁵⁴ Expanded interest continues, since there is demand for supports which are conductors, have low cracking activity for hydrocarbons, and can withstand corrosive environments. Precious metals supported on carbon have been important liquid phase hydrogenation catalysts for years. Recent studies have shown the utility of cobalt-molybdenum supported on carbon as hydrodesulfurization catalysts.^{55,56} More recently we have shown, in this laboratory, that iron supported on carbon can have activities for CO hydrogenation up to four times higher than Fe/Al₂O₃ catalysts.⁵⁷ Further the olefin/paraffin ratios in the product were enhanced more than ten-fold by the use of carbon supports.⁵⁷ It is felt that the ability to produce glassy carbon molecular sieve catalyst supports, containing feeder pores of the desired macro size and well dispersed metals,⁵⁸ has much potential for future exploitation.

Juntgen and co-workers have successfully developed carbon molecular sieves, starting with bituminous coal as a precursor, which are now being used commercially to obtain nitrogen-rich gases from air.⁵⁹ It is the opinion of the author that if carbon sieves can be made to separate N₂ from O₂, whose minimum kinetic diameters differ by roughly 0.01 nm, they can be tailor-made to separate ^{at} most any two compounds. They are made by the judicious selection of the right precursor, with adjustments in aperture size being effected by a possible combination of heat treatment temperature, carbon gasification, carbon deposition, and/or carbon filler addition.

CARBONIZATION

For years we have been interested, in this laboratory, in the conversion of individual organic compounds to carbonaceous solids via liquid phase carbonization. Kinney was one of the first to show that there are major differences in the graphitizability of cokes produced from different organic compounds.⁶⁰ In recent years we have been particularly interested in the carbonization of three compounds -- anthracene, phenanthrene, and biphenyl.⁶¹⁻⁶⁴ Selected properties of these compounds are summarized in Table 1. Because of the relatively high vapor pressure of these compounds, it is necessary to carry out carbonizations in closed reactors. We showed at the Third Industrial Carbon and Graphite Conference that anthracene and phenanthrene carbons are highly graphitizable, whereas biphenyl carbons are not.⁶² In this study, initial carbonization was conducted at 823 K. Of particular interest to me were results from carbonizing various mixtures of the precursors. Carbonization of anthracene-biphenyl mixtures led to cokes and carbons exhibiting multiple phases, as identified by microscopy and x-ray diffraction. Carbonization of phenanthrene-biphenyl mixtures led to cokes and carbons exhibiting only one phase, but this one phase showed a progressive change in important properties as the composition of the original mixture was varied (see Figures 6 and 7). We attributed these differences in behavior to anthracene having a much higher reactivity at the 9 and 10 positions than any position in phenanthrene or biphenyl and, hence, carbonizing at a much more rapid rate than the two latter molecules. In this laboratory,^{65,66} we have recently confirmed major differences in reactivity of anthracene and phenanthrene for the first appearance

of pyridine insolubles (Figure 8) and the subsequent rate of increase in pyridine insolubles (Figure 9).

In addition to our recent studies on the kinetics of carbonization of phenanthrene we have also studied properties of calcined cokes (1473 K) and graphites (2773 K) subsequently produced following initial carbonization at five temperatures between 783 and 903 K to pyridine insoluble yields greater than 90%. Consider briefly the phenomenon of carbonization in a closed system. The critical temperature (T_c) of phenanthrene is 878 K. Below the critical temperature, phenanthrene partitions into a liquid and vapor phase. The amount in each phase depends upon the temperature, amount of phenanthrene in the reactor, and the reactor volume. From data on vapor pressure, fugacity coefficients, and liquid densities for phenanthrene, partitioning can be estimated. At least up to 823 K, carbonization rates in the vapor phase are found to be negligible compared to rates in the liquid phase for starting weights of phenanthrene ranging from 1-5 g in a total reactor volume of 15 cc. The reason for this is that the concentration of phenanthrene in the liquid is much greater than the concentration in the vapor at temperatures substantially below T_c .

When starting with 5 g of phenanthrene, we found that as carbonization temperature increased below T_c , the average size of mesophase spheres formed decreased; carbonization above T_c produced no detectable mesophase spheres. Domain size and asymmetry in particle shape in the graphites produced decreased as initial carbonization temperature increased. Further, from the (002) peak in x-ray diffraction, it was seen that crystallite alignment and average crystallite size

decreased and interlayer spacing increased (Figure 10) in the graphitized samples as the previous carbonization temperature was increased. Carbonization at 783 K subsequently yielded a high temperature carbon of substantial graphitic character ($d = 0.3363$ nm); carbonization above the critical temperature (903 K) yielded a high temperature turbostratic carbon ($d = 0.345$ nm).

The fundamental question raised is why does initial carbonization temperature affect so strongly the ability of products from the carbonization of phenanthrene to form large spheres of mesophase and, thence, large mosaic domains upon mesophase coalescence. We are not sure, but we propose that it is related to differences in reactivity in the different positions in phenanthrene. The order of reactivity, around the plane of symmetry in the molecule, is $9 > 1 > 3 > 2$. Initial loss of hydrogen at the 9 (or 10) position to form free radicals, followed by condensation of two radicals at this position can lead ultimately to larger planar molecules (Figure 11) and concurrent formation of mesophase. By contrast, initial loss of hydrogen at the 2 or 3 positions, followed by condensation of two radicals at these positions, cannot lead ultimately to larger planar molecules (Figure 12). It is suggested that because of the higher expected activation energy to form free radicals at the 2 and 3 positions compared to the 9 position the relative concentration of the former radicals increases with increasing carbonization temperature. The presence of these free radicals is expected to have the same effect on the graphitizability of phenanthrene derived cokes as the deliberate addition of biphenyl to phenanthrene has -- it will sharply reduce it. Indeed, workers who conducted the gas phase pyrolysis of phenanthrene

at 973 K identified extensive formation of biphenanthryls bonded at the 2 and 3 positions.^{67,68}

A physical explanation for the effect of carbonization temperature on tendency to form mesophase could also possibly apply. As temperature is increased the rotational and vibrational energies in the planar molecules increase, perhaps making it more difficult to form liquid crystals (mesophase) upon carbonization, due to van der Waals attraction between molecules.

In any case, it seems that our concept of what is a graphitizable precursor has to be reexamined. Phenanthrene is a very graphitizable precursor provided it is carbonized in the liquid phase considerably below its critical temperature. If it is carbonized, even only slightly above its critical temperature, the vapor phase carbon formed cannot be graphitized, at least at 2773 K.

ACTIVE SITES

If one is to understand the interaction of gases and liquids with carbon surfaces, it is necessary to be able to measure active site concentrations. These sites exhibit higher heats of physical adsorption and the ability to chemisorb species -- some dissociatively, others non-dissociatively. Active sites are thought to be located at the edges of basal planes of carbon crystallites and defects within basal planes. For those carbons containing a large fraction of basal plane area, active surface area (ASA) can be measured by physical adsorption using at least two approaches. In one approach, isotherms at low relative pressures (around 10^{-5}) exhibit linearity or Henry's law behavior for adsorption on the basal plane. If active sites are present, extrapolation of the isotherm to zero relative pressure yields

a positive intercept on the ordinate, which is the volume adsorbed on strong sites.⁶⁹ In a second approach, steps in the isotherms appear at relative pressures where complete adsorption layers are laid down on the basal plane surface.^{70,71} The volume adsorbed in the steps is subtracted from the total volume adsorbed in the monolayer to give volume adsorbed on strong sites.

Walker and co-workers pioneered the use of dissociative chemisorption of oxygen to measure active sites. If one assumes that oxygen dissociates to form carbonyl groups on the surface, with each oxygen atom occupying about 0.08 nm^2 of area on the (100) or (110) surfaces, ASA can be calculated. We have shown for a graphitized carbon black²⁹ how markedly different changes in total surface area (TSA) and ASA can be upon carbon gasification (Figure 13). In this example, the ASA increased from about 0.3% of the TSA for the original black to 3% following gasification to 35% burn-off. More recently, we have shown, in this laboratory, that hydrocarbons also chemisorb on carbon active sites and thus can be used to measure ASA.⁷² At 573 K, for example, propylene non-dissociatively chemisorbs.

So far we have considered chemical interaction of molecules with carbon active sites in the essential absence of carbon gasification. In the presence of gasification, the number and/or activity of active sites appears to increase dramatically. For example, we found that the reactivity of carbon to CO_2 , during heating up at a linear rate to 1223 K, is significantly enhanced if oxygen was previously chemisorbed on the carbon and then comes off as CO and CO_2 complex during the heating up.⁷³ Desorption of the complex in the presence of CO_2 supplies a high concentration of "nascent" active sites for reaction.

More recently, Taylor studied the reactivity of Saran char to 0.1 MPa of dry air at 648 K.⁷⁴ Following different levels of burn-off, the sample remaining was heated to 1223 K to recover the oxygen complex formed as CO and CO₂. As seen from Table 2, as burn-off proceeds very large amounts of oxygen are added to the char. If one assumes that the oxygen complex consists of one oxygen atom chemisorbed on a carbon site occupying about 0.08 nm², the area occupied by oxygen exceeds the area occupied by physically adsorbed N₂ (77 K) at high carbon burn-offs. Further, if following desorption at 1223 K, the samples are exposed to 0.1 MPa of air at 373 K for 24 h to allow equilibrium to be reached in oxygen chemisorption, areas now covered by oxygen are much reduced. For example, for the 71.6% burn-off sample, oxygen coverage achieved during gasification is some sixteen times that achieved by chemisorption in the absence of gasification.

We suggest that the "nascent" active sites produced during gasification are free radical sites. At some rate most of them rehy^bridize to less active sites by forming in-plane σ pairs with π electrons.⁷⁵ However, if a collision event between the nascent sites and oxygen occurs prior to rehybridization, the probability of chemical interaction is markedly enhanced. We attribute the fact that "inert" gases can, at low reaction pressures, enhance carbon gasification rates in CO₂ to be due to their physical interaction with nascent sites, thus decreasing rates of their rehybridization.⁷⁶

Indeed, recently Yang and Wong, in order to explain their results showing enlargement of vacancies in the basal plane of graphite crystals to continue after O₂ was replaced by Ar at 923 K, concluded that oxygen had even chemisorbed on the basal plane.⁷⁷ They suggest that this

oxygen diffused across the basal plane to vacancy edges and reacted, thus continuing gasification.

Hennig's development of the etch decoration technique to follow the enlargement of vacancies in the basal plane of graphite finally gave us a visual quantitative technique to follow gasification rates at carbon active sites.¹⁹ It offered a direct check to previous kinetic studies in our laboratory on the C-O₂ reaction, where ASA was measured by oxygen chemisorption.²⁹ Hennig's microscopy studies on reaction of highly purified Ticonderoga natural graphite with O₂ was followed by a number of other light and electron microscopy studies, also using Ticonderoga natural graphite. It finally enables us to have a good picture of the fundamental rate of the C-O₂ reaction. Conditions under which the experiments were conducted are summarized in Table 3, and rates, in different units, are given on an Arrhenius plot, Figure 14, at an O₂ pressure of 1.3 kPa. From microscopy studies, rates can be measured in units of cm/sec, that is the recession rate of a vacancy, a pit, or a channel. Rates can be converted to atoms C per cm² of total ASA (TASA) per sec, using the true density of graphite (2.268 g/cc). Rates can be given as "turn-over" numbers by assuming that the area occupied by an active carbon site is 0.08 nm².

Let us consider the results and their possible limitations. It should first be understood that specific rates are being given in Figure 14 and not specific rate constants. That is, Laine et al., who measured the kinetics of the C-O₂ reaction on graphitized carbon black using a combination of mass spectroscopy and oxygen chemisorption, showed clearly that gasification rates depend upon the fraction of ASA uncovered by a stable oxygen complex.²⁹ It is only when the amount

of this complex is known that a specific rate constant, based on the uncovered ASA, can be determined. To place the Laine et al., result on Figure 14, their specific rate constant has been converted to a specific reaction rate by converting to a basis of TASA. Unfortunately, investigators using microscopy have not all worked at the same pressure and have failed to clearly establish the order of reaction. Hennig suggests 0.5 order;¹⁹ this order is assumed in giving all specific rates at an O₂ pressure of 1.3 kPa in Figure 14. It is noted, as previously pointed out by Thomas et al.,⁸³ that recession rates from multilayer steps (followed by light microscopy) are nearly a factor of 100 greater than recession rates from monolayer steps (followed by TEM). The reason for this difference is not understood at this time, but it obviously has a fundamental bearing on our understanding of carbon gasification.

Leaving out the light microscopy results of Thomas and Hughes, best fit equations for rates of gasification are given in Table 4, with activation energy in units of kJ/g mole.

Recently it has been shown in this laboratory that the rate of cracking of hydrocarbons over carbon surfaces is also dependent upon the concentration of active sites.⁷² Specific rate constants for carbon deposition onto graphitized carbon blacks from the cracking of propylene are given in the Arrhenius plot, Figure 15. Sample 1 was the original black which had a TSA of 76 m²/g and an ASA (from propylene chemisorption at 573 K) of 0.056 m²/g. With increasing extents of carbon burn-off up to 24.5 wt% for sample 4, the TSA increased to 124 m²/g and the ASA to 1.89 m²/g. The rate constant, in cm/sec, equals $7.88 \times 10^9 \exp(-241/RT)$. It is interesting that the

activation energy of 241 kJ/mole agrees well with the value for gas phase cracking of propylene,⁸⁴ meaning that the much enhanced rate of cracking over carbon active sites can be attributed to a larger preexponential term.

CONCLUSIONS

Carbon is, indeed, an old but new material. It becomes a more important material with time, because it is reasonably cheap and very versatile. Advances continue to be based on our gaining an increasingly better fundamental understanding of its preparation, its bulk and surface structure, and its resulting properties.

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Table I
Properties of Organic Precursors

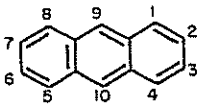
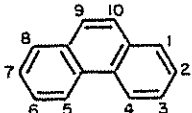
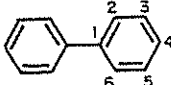
Structural formula and numbering scheme	 <p style="text-align: center;">Anthracene</p>	 <p style="text-align: center;">Phenanthrene</p>	 <p style="text-align: center;">Biphenyl</p>
Empirical formula	C ₁₄ H ₁₀	C ₁₄ H ₁₀	C ₁₂ H ₁₀
Molecular wt, g/mol	178.2	178.2	154.2
Melting point, K	491	373	343
Normal boiling point, K	615	613	528
Critical temp, K	873	878	801

TABLE 2
 OXYGEN CONTENTS AND SURFACE AREAS OF SARAN CHARs
 GASIFIED IN 0.1 MPa AIR AT 648 K

Sample Burn-off, %	Oxygen Content, wt%	Surface Area, m ² /g		
		From CO and CO ₂ Following Rxn.	Oxygen Chemisorption at 373 K	N ₂ at 77 K
As-received	4.1	124	50.4	1,123
16.5	8.4	262	48.0	1,175
35.2	16.0	500	43.2	1,183
50.4	18.7	576	43.7	976
71.6	21.9	686	42.6	459
89.1	21.6	675	39.7	249

TABLE 3
STUDIES ON RATES OF CARBON GASIFICATION
BY OXYGEN

<u>Worker(s)</u>	<u>Reference</u>	<u>Exptl. Pressure, kPa</u>	<u>Method</u>
Laine, et al.	29	5.2×10^{-3}	Mass spectroscopy and oxygen chemisorption
Hennig	19	1.3	TEM with vacancy decoration
Thomas & Hughes	78	1.3	Light microscopy with enlargement of hexagonal pits
Baker	81	6.6	TEM with vacancy decoration
Evans & Thomas	79	1.3	TEM with vacancy decoration
Baker & Harris	80	2.6	CAEM with channel enlargement
Yang & Wong	77	20.0	TEM with vacancy decoration
Baker & Chludzinski	82	0.66	CAEM with channel enlargement

TABLE 4
SPECIFIC REACTION RATES FOR THE C-O₂
REACTION AT 1.3 kPa PRESSURE

$$\text{Rate (cm/sec)} = 9.35 \times 10^3 \exp(-239/RT)$$

$$\text{Rate (atoms C/cm}^2 \text{ TASA-sec)} = 1.06 \times 10^{27} \exp(-239/RT)$$

$$\text{Rate (l/sec)} = 8.82 \times 10^{11} \exp(-239/RT)$$

FIGURE CAPTIONS

1. Texture of a calcined, needle coke, 75X.
2. Pyrolytic carbon deposited on bulk graphite, 250X.
3. Vacancy loops in the basal plane of natural graphite etched by O_2 and decorated by gold, 28,000X (19).
4. Microtexture of mesophase spheres as originally suggested by Brooks and Taylor (21).
5. Density as a function of methane concentration for carbons deposited at 1573 K (53).
6. Change in average crystallite height of the 3073 K carbon with starting composition of the phenanthrene-biphenyl system. Initial carbonization temperature, 823 K.
7. Change in helium density of 1223 K coke and 3073 K carbon with starting composition of the phenanthrene-biphenyl system. Initial carbonization temperature, 823 K (62).
8. Arrhenius plots of induction periods for the first appearance of pyridine insolubles during carbonization of (Δ) anthracene (65) and (o) phenanthrene (66).
9. Arrhenius plot of first order rate constant for formation of pyridine insolubles from (Δ) anthracene (65) and (o) phenanthrene (66).
10. Effect of carbonization temperature of phenanthrene on the inter-layer spacing and average crystallite height of 2773 K carbon ultimately produced (66).
11. Formation of planar dibenzoperylenes from the condensation of phenanthryl radicals.
12. Formation of non-planar biphenanthryls from condensation of phenanthryl radicals.
13. Change in TSA (Δ) and ASA (o) with burn-off of graphitized carbon black at 898 K in 66 Pa of O_2 (29).
14. Arrhenius plot of rate constants for the $C-O_2$ reaction at 1.3 kPa pressure.
15. Arrhenius plot of rate constant for carbon deposition from the cracking of propylene over carbon active sites (72).

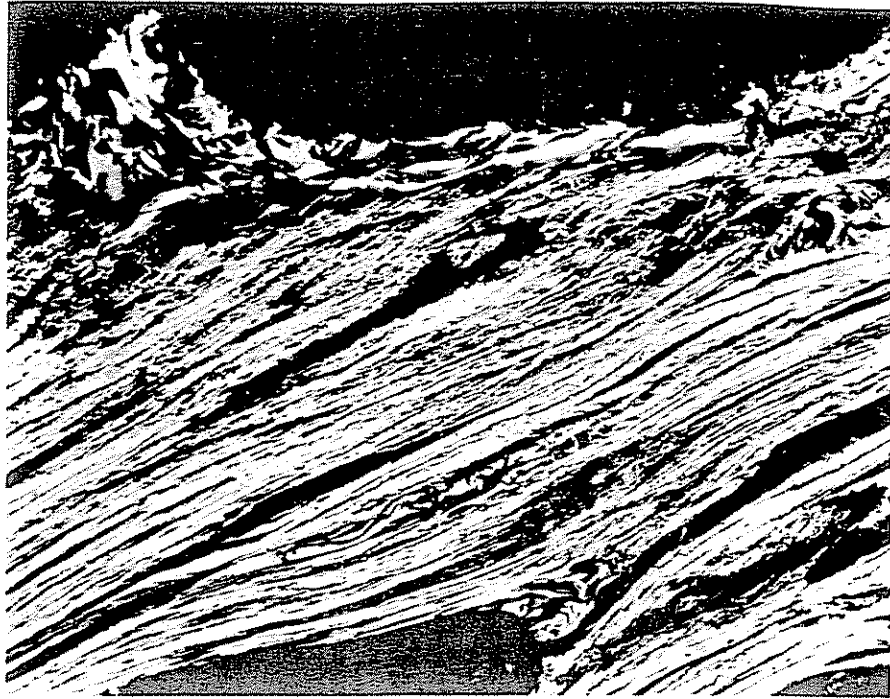


Figure 1

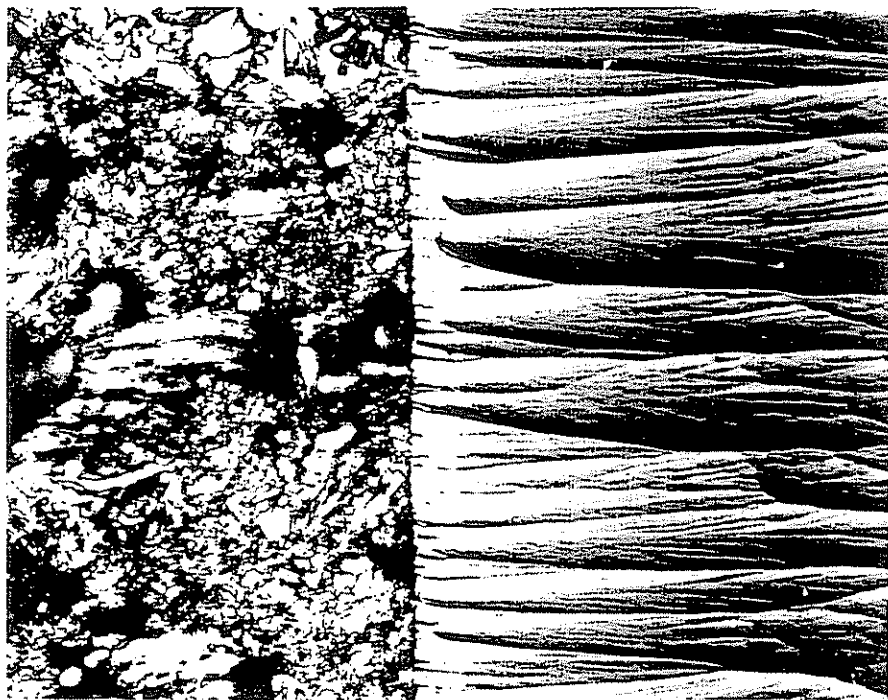


Figure 2

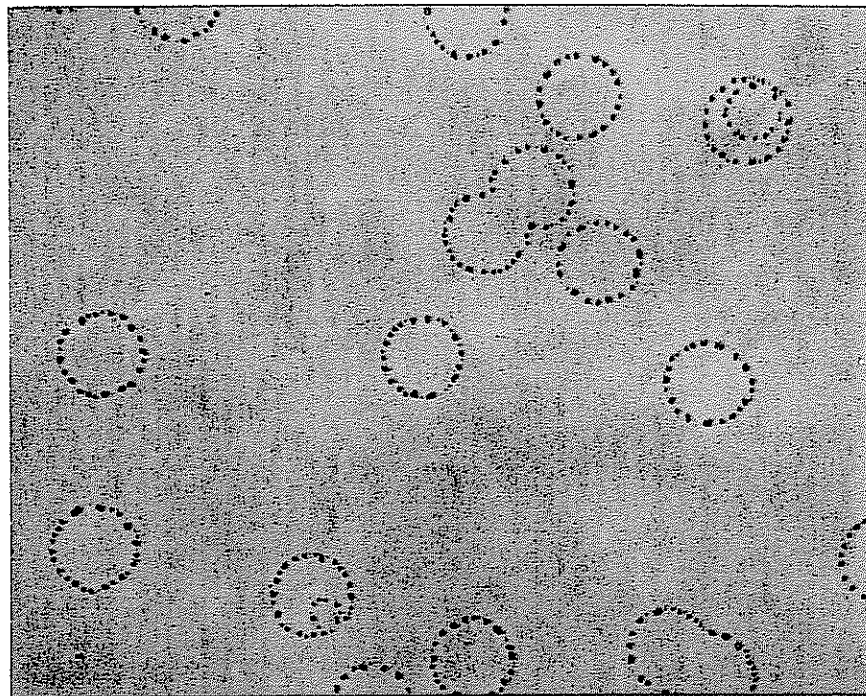


Figure 3

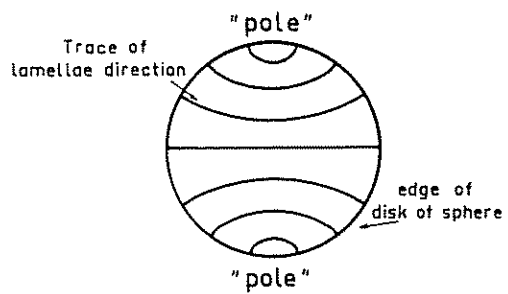


Figure 4

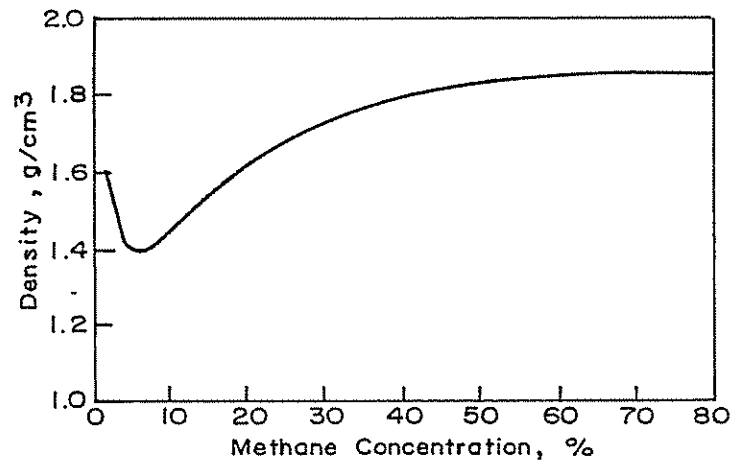


FIGURE 5

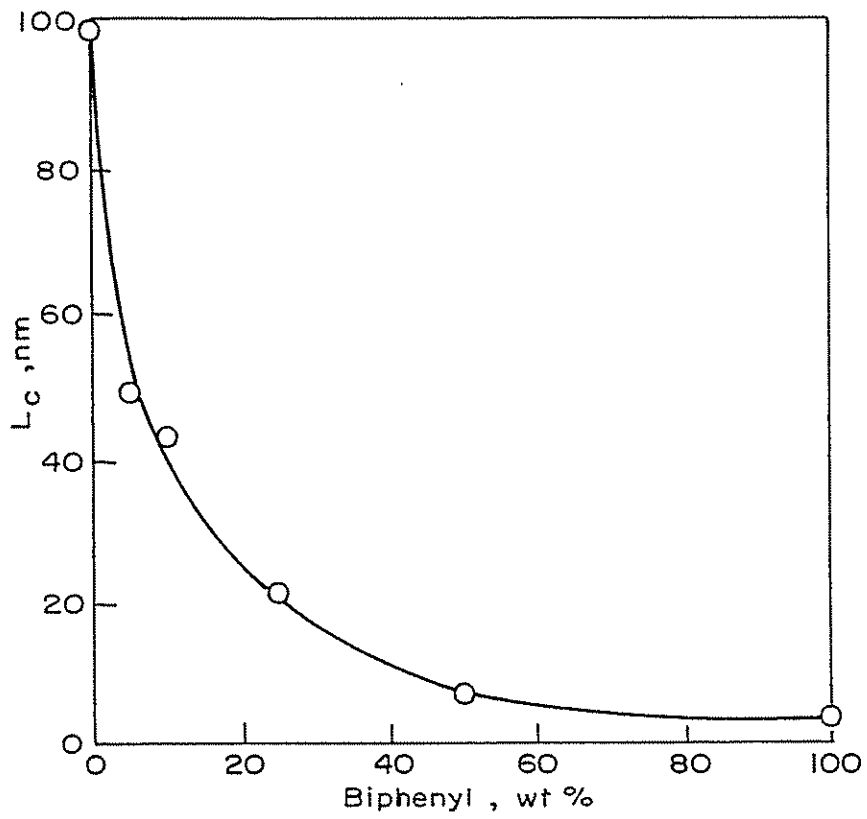


FIGURE 6

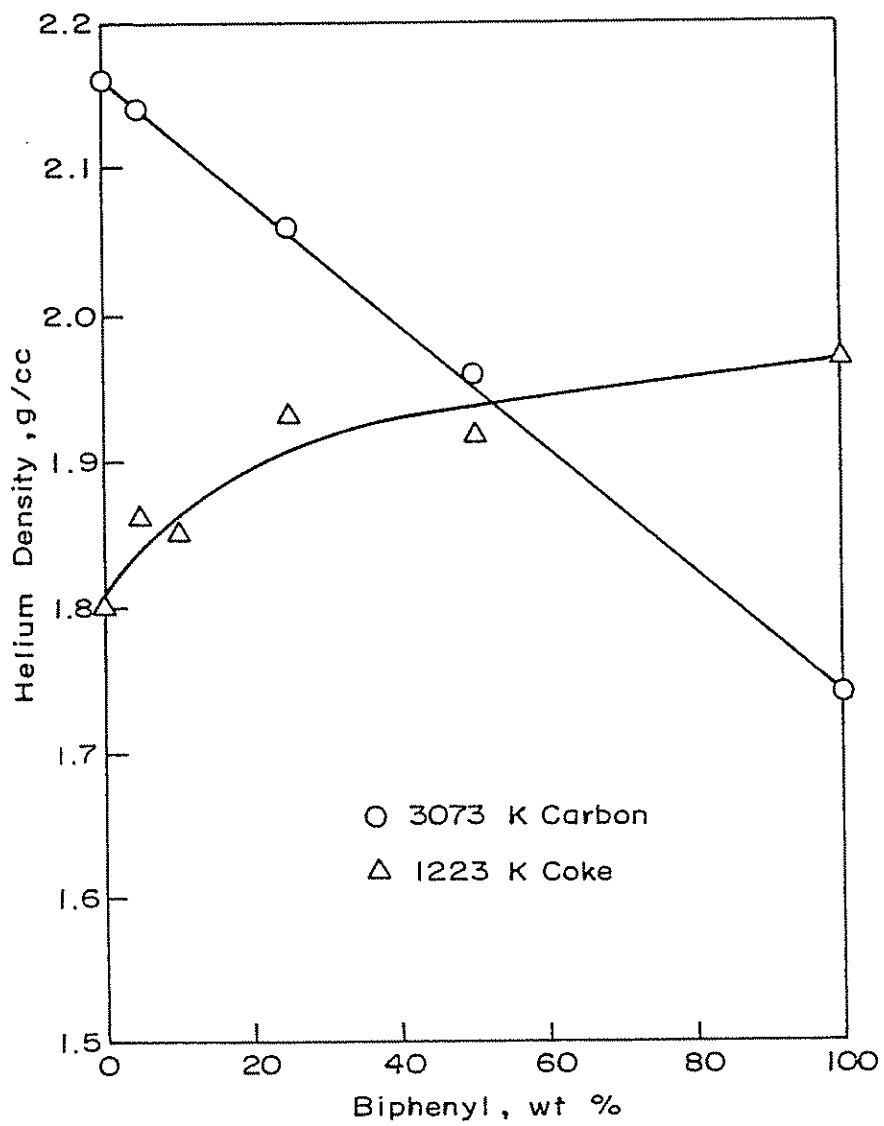


FIGURE 7

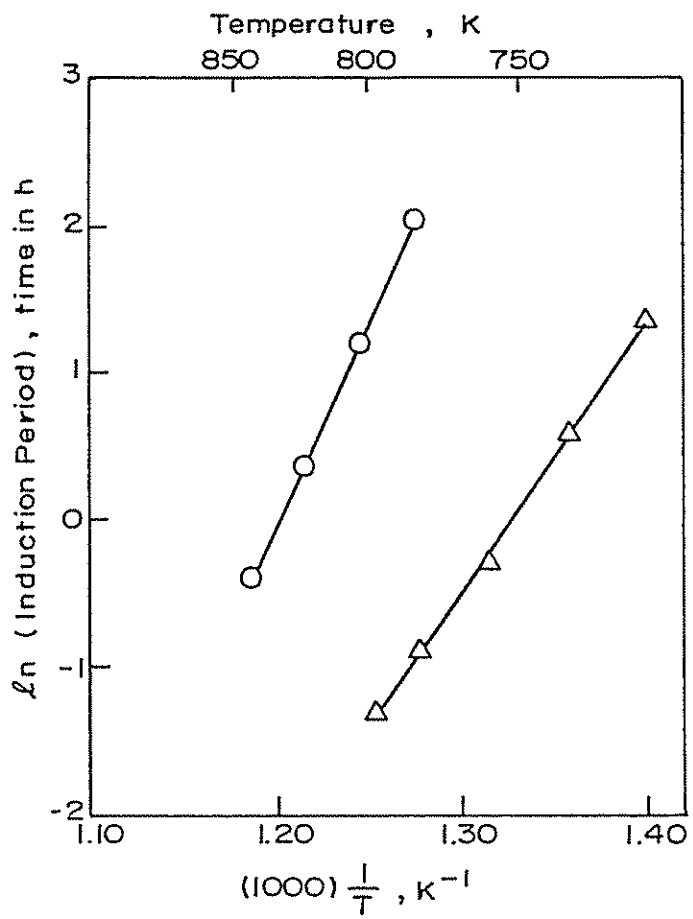


FIGURE 8

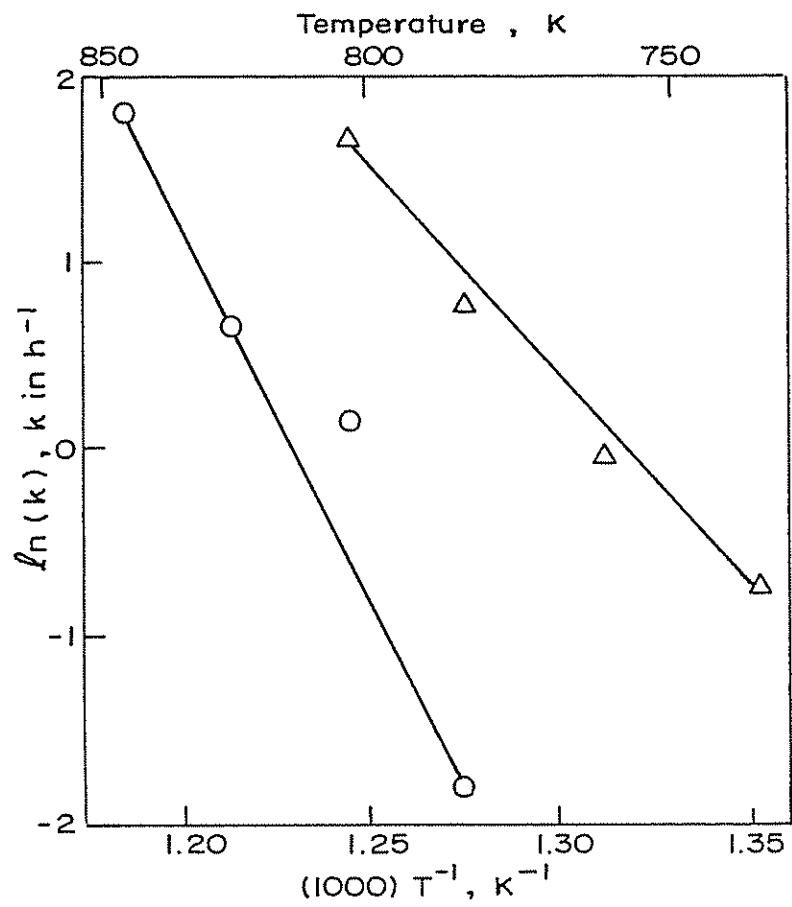


FIGURE 9

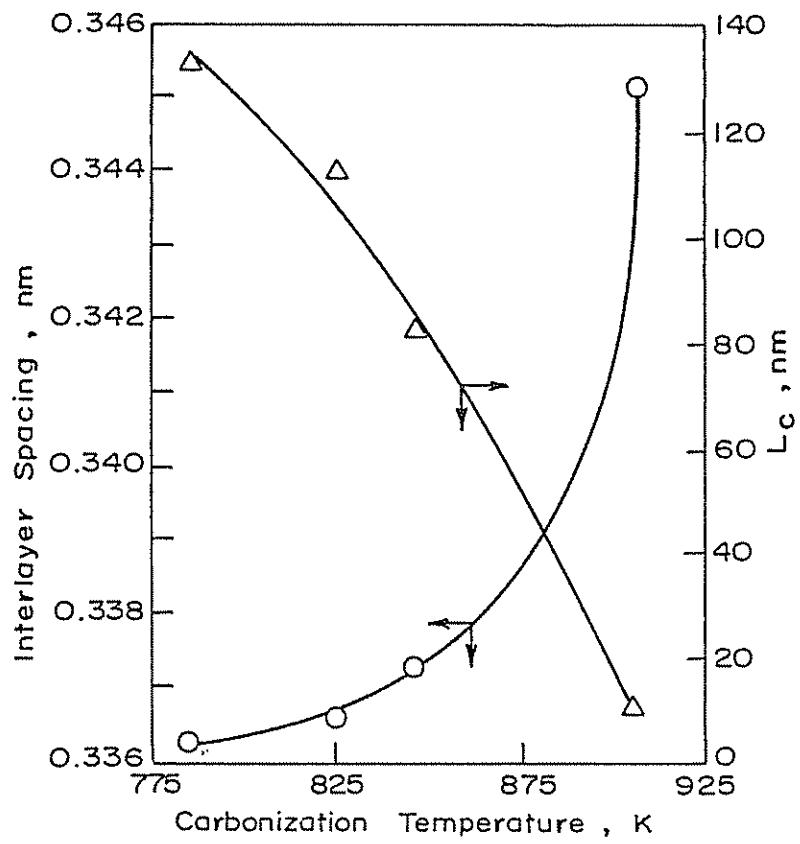


FIGURE 10

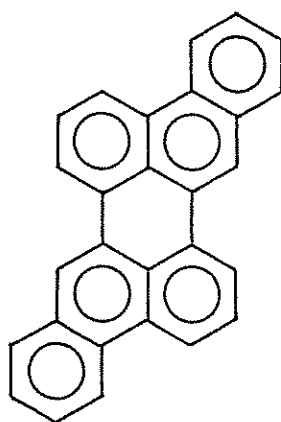
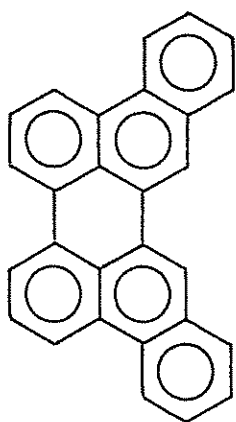


FIGURE 11

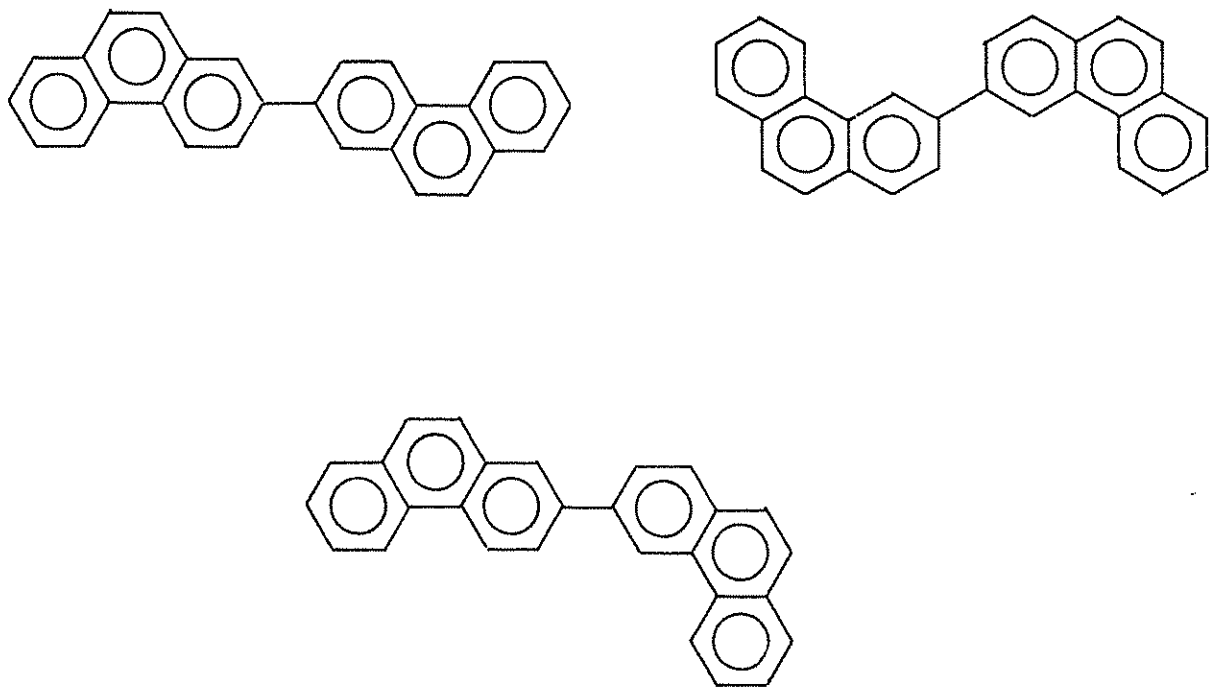


FIGURE 12

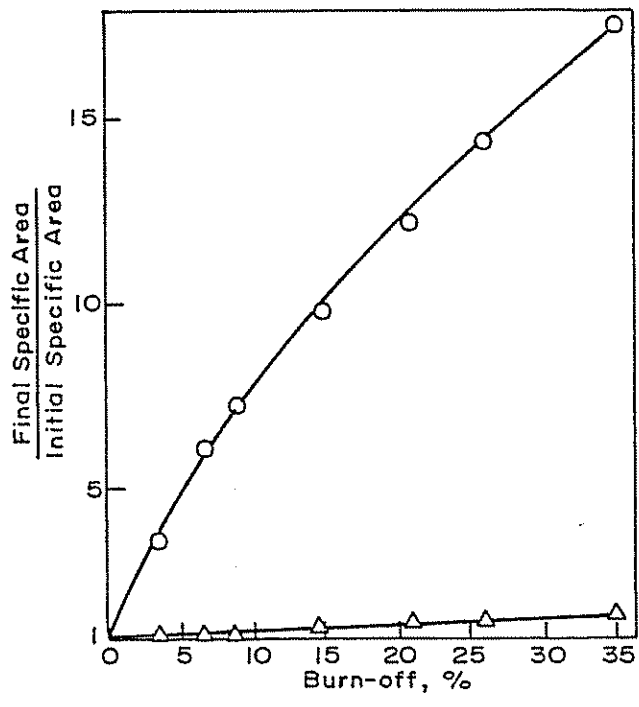


FIGURE 13

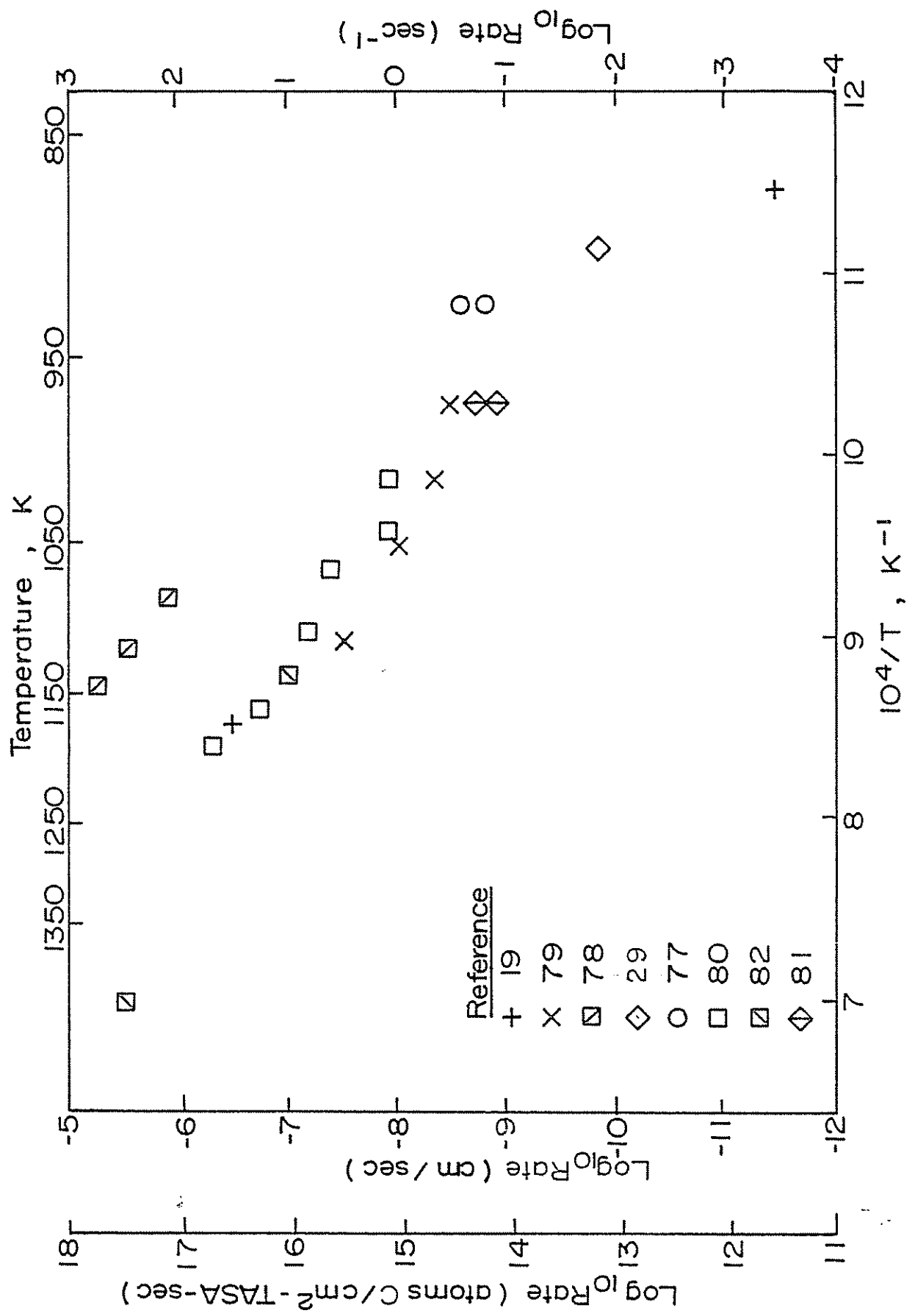


FIGURE 14

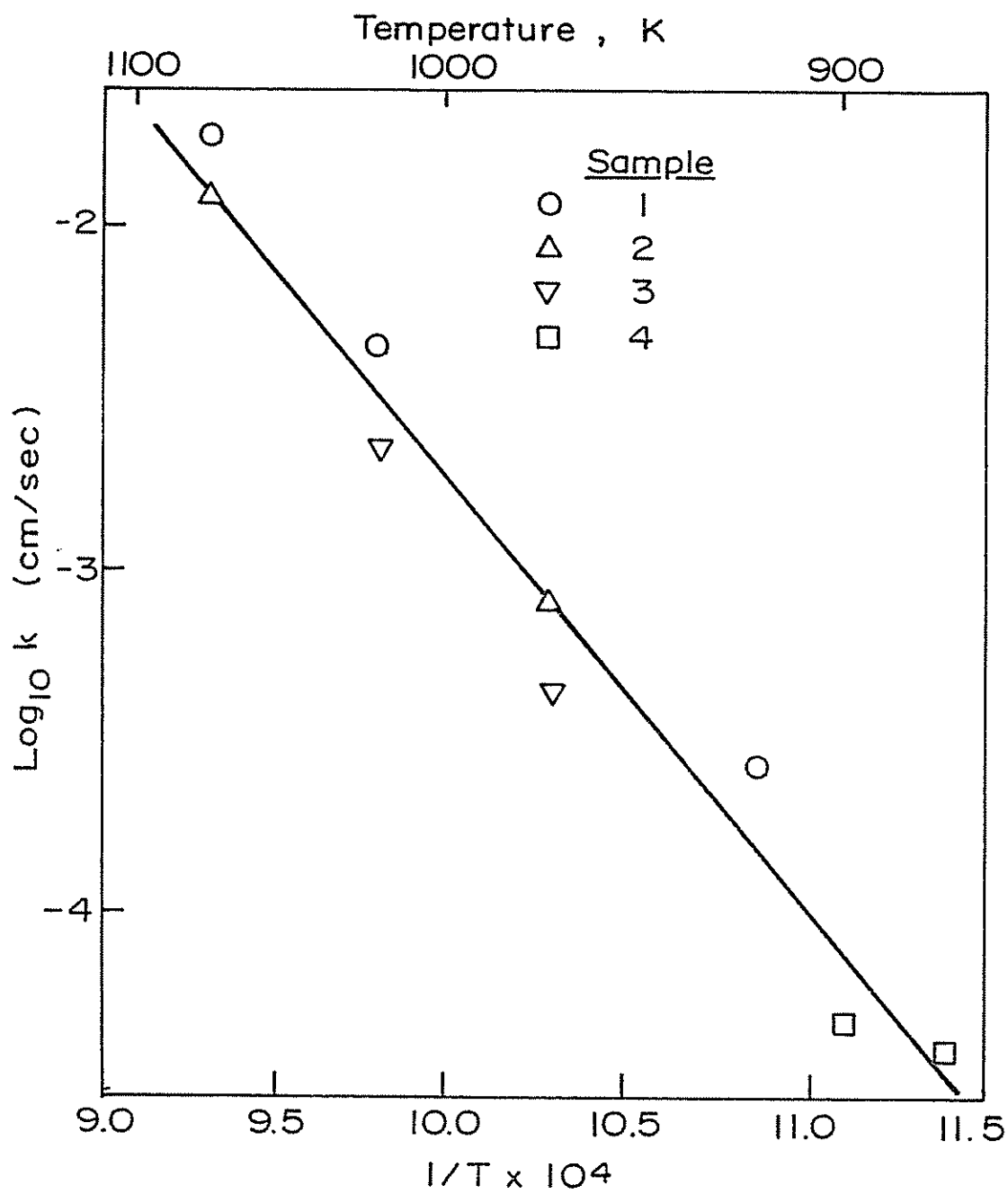


FIGURE 15