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CARBONIZATION OF ANTHRACENE IN A BATCH REACTOR

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Abstract—The coking of liquid anthracene in a batch tubular reactor was followed by measuring the formation of pyridine insolubles and the disappearance of anthracene as a function of time over the temperature range 465–525°C. Conditions, that can affect coking behavior and rates, like partition of the feed between liquid and vapor, agitation of the reactor, and whether the gas pressure in the reactor is autogeneous or imposed are considered. Carbonization primarily involves hydrogen-transfer reactions and condensation (polymerization) of free radicals into larger molecular weight species. Cleavage (cracking) of hydroaromatic species, giving smaller liquid and gas phase molecules, is at a minimum under the conditions used in this study.

Key Words—Carbonization, anthracene, batch reactor.

1. INTRODUCTION

A number of workers have recognized the importance of reactivity and coking rates while studying the carbonization of important petroleum and coal feedstocks. Mochida and co-workers note that the carbonization reaction proceeds through radical initiation, propagation, recombination (condensation), and termination[1]. They conclude that at too high a carbonization temperature, all of these processes take place too rapidly, and that there is little time for growth of an isochromatic area prior to fluidity of the medium decreasing to too low a level. Thus it is important to have information on coking rates of aromatic compounds that are major constituents of important commercial feedstocks. Further, it is important to understand the effects of structural indices, pendant functional groups, and heteroatoms on carbonization rates.

This paper concerns itself with the carbonization rates of anthracene, an important linear aromatic compound, which is found in coal-tar pitch feedstocks. Carbonization, as is frequently done commercially, is conducted in a batch reactor. Conditions that can affect coking behavior and rate, like partition of the feed between liquid and vapor, agitation of the reactor, and whether the gas pressure in the reactor is autogeneous or imposed, are considered.

2. EXPERIMENTAL

2.1 Reactants

Anthracene was supplied by Aldrich Chemical Company without further purification. The behavior of anthracene of >99% purity was compared to that of anthracene of >98% purity, and no significant differences in coking propensity were observed. Some of the properties of anthracene are summarized in Table 1.

The N_2 used to apply an inert pressure contained <1 ppm O_2 and <10 ppm water.
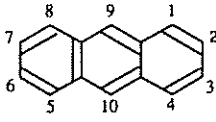
2.2 Carbonization

2.2.1 *Equipment.* The coking experiments were performed in batch tubing reactors similar to those used previously in coal liquefaction studies[2,3]. The reactors were constructed from 1.27-cm diameter stainless steel tubing (type 316) and threaded Swagelok end fittings. Their capacities were 15 cc. For the majority of runs, 4 g of anthracene were charged to each of two reactors and duplicate runs performed simultaneously. The rationale behind the selection of this standard weight is presented later. Nitrogen, used as the inert pressurizing gas, was provided from a standard gas cylinder to an operating pressure of 6.9 MPa at reaction temperature. The reactors were evacuated to <30 Pa prior to pressurization with N_2. The pressurizing gas was introduced through a 0.6-cm diameter stainless steel sidearm containing a plug valve and a quick-connect stem.

Rapid and uniform heating of the reactors and their contents was accomplished by plunging them into a preheated fluidized-bed sandbath (Model SBL–2, Techne Inc., Princeton, New Jersey). The maximum operating temperature that would permit constant temperature control was 575°C. Thermocouples, which were located internally and on the exterior of the reactors, indicated that by careful manipulation of the sandbath temperature controller, the requirements of acceptable temperature-time histories were met. The operating temperature was reached in less than 3 min, while quenching to room temperature was considerably more rapid.

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Table 1. Properties of anthracene

Structural formula and numbering scheme	(anthracene structure with numbering 8, 9, 1 on top; 7, 2; 6, 3; 5, 10, 4 on bottom) Anthracene
Empirical formula	$C_{14}H_{10}$
Molecular wt, g/mol	178.2
Melting point, °C	218
Normal boiling point, °C	342
Origin	Coal tar contains ~1.1%
Family	Polynuclear aromatic fused-ring hydrocarbon
Geometry	Flat

The reactors, which were oriented horizontally within the sandbath, were agitated by a pneumatically driven rocking mechanism. The maximum agitation rate that was commensurate with acceptable temperature control was 120 cycles/min. As discussed later, 60 cycles/min was normally employed, and this was sufficient to minimize mass-transfer effects within the reactors.

2.2.2 *Procedure*. Typical coking runs were performed as follows. Two identical reactors were charged with pre-weighted samples of anthracene and the Swagelok end caps attached. The reactors were attached to the manifold via the quick connects and evacuated to <30 Pa. They were then pressurized with N_2, removed from the manifold and placed into the rocking mechanism above the fluidized-bed sandbath. Simultaneously, the reactors were plunged into the preheated sandbath, the rocking mechanism was activated, and a timer was started. After the reaction time had elapsed, the rocking was stopped and the rocking mechanism, still containing the reactors, raised from the sandbath. The bath was then replaced by a stainless steel water bath. The reactions were quenched by lowering the bombs into the water bath.

Following cooling, the pressure in the reactors was relieved through the valved sidearm, either into a pre-evacuated sampling bottle or to atmosphere. The Swagelok ends were then removed and the contents of the reactors recovered separately. Typically, recovery efficiencies were about 90 wt%.

2.3 *Product analyses*

2.3.1 *Coke formation*. For the purposes of this investigation, coke was defined arbitrarily as pyridine insoluble (PI) material. The term coke, therefore, is used as a generic term rather than indicating a minimum carbon-to-hydrogen ratio or even a range of carbon-to-hydrogen ratios. This definition has been adopted conventionally in the petroleum industry[4,5], as has insolubility in quinoline. While it has been customary to monitor the extent of mesophase formation by measuring changes in such solubilities[6–8], it must be recognized that these cannot be used universally as criteria for the amount of mesophase[9]. Quinoline and pyridine have been shown to dissolve appreciable amounts of anisotropic phases, in addition to isotropic phases, as defined microscopically using polarized light.

Insolubility in pyridine at its boiling point (115°C) was determined using conventional Soxhlet extractors. Extractions were performed under 0.1 MPa N_2 to minimize oxidation of the samples. The solubility of model aromatic compounds, pitches, and mesophases has been studied theoretically and experimentally[10]. Solubility has been linked to the theory of solubility for non-electrolytes[11], which considers three basic parameters: the system temperature, the melting point of the solute, and the respective cohesive energy densities of the solvent and solute. The solubility parameter, defined as (cohesive energy density)$^{0.5}$, is a measure of the attractive energy a molecule possesses for another molecule of the same type. Solubility is maximized when the solubility parameter of the solvent and solute is identical. For aromatic hydrocarbons, solubility parameters increase linearly with increase in C/H ratio, reaching a value equivalent to that of pyridine for a C/H ratio of 1.5. For anthracene with a C/H ratio of 1.4, the solubility parameters were matched sufficiently for complete dissolution in pyridine. The C/H ratio increased as coking proceeded, causing divergence in solubility parameters of the solute and solvent, thereby inducing insolubility.

Procedures used to determine PI have been considered in detail elsewhere[12]. Essentially complete extraction corresponded to when the extract became clear.

2.3.2 *Molecular weight distributions*. The technique of gel permeation chromatography (GPC) using quinoline as an eluent was applied to measure molecular weight distributions in PI fractions. This technique has been applied previously to petroleum-pitch mesophases and semicokes with quinoline-insoluble contents approaching 100%[13]. Ideal elution behavior was achieved for these molecules after reductive hydrogenation to render them soluble in the quinoline eluent. The technique of reductive hydrogenation with lithium in anhydrous ethylene diamine, to convert aromatic ring structures to cyclo-olefins and cyclo-paraffins, has been applied previously to coals, cokes, and chars[14,15]. The principal objective of the GPC work was to measure the lowest molecular weight species that was insoluble to pyridine. This, at least, was required before attempting to relate the formation of PI material to the disappearance of anthracene.

2.3.3 *Disappearance of anthracene*. The technique of Fourier Transform Infrared Spectroscopy (FTIR) was used to monitor the disappearance of anthracene. Specifically, the absorbance of the C-H

out-of-plane bending mode, associated particularly with the reactive 9 and 10 positions, was measured quantitatively. The cumulative absorbance from 950 to 835 wavenumbers (cm^{-1}) was monitored as a function of time at reaction temperature. If polymerization occurs preferentially at the 9 and 10 positions, then the decrease in absorbance would be related conceptually to the disappearance of anthracene.

The operating and data-collecting techniques associated with the FTIR equipment have been presented in detail[16]. Pellets were prepared by grinding samples in KBr in a Wig-L-Bug and pressing in a vacuum die to 138 MPa. This produced a relatively optically clear sample. Concentrations varied upwards of 0.35 mg/300 mg KBr for that of the least-carbonized sample containing no PI. Spectra were recorded by a Digilab model FTS 15B FTIR spectrometer.

2.3.4 *Gas formation.* The composition of the product gases from the coking of anthracene was measured quantitatively by gas chromatography (GC). Data were obtained on a Carle 111 gas chromatograph coupled to a Hewlett Packard 3380 integrator. Detection of the following gases was possible to levels of 0.1 mol% or higher: H_2, O_2, N_2, methane, ethane, ethylene, C_3 + C_4 hydrocarbons, CO, CO_2, H_2O, SO_2, and H_2S. A quantitative measure of the total gas production was necessary to complete material balances associated with the coking process.

3. RESULTS AND DISCUSSIONS

3.1 *Mass transfer effects*

A basic requirement for obtaining meaningful kinetic data for any conversion process is the elimination of mass transfer effects. For batch systems, this is achieved commonly by agitating the reactor to enhance mixing of the contents and by operating with a minimum of sample weight. In such cases, mass transfer effects are manifested as an increase in conversion with increase in agitation rate or decrease in sample weight.

In the case of anthracene in the tubing reactors, the situation is more complex. Anthracene has been classified as a thermally unreactive hydrocarbon with respect to its stability in the liquid phase[17]. Upon heating to 750°C at atmospheric pressure in a differential thermal analyzer, anthracene does not produce a polymerized carbonaceous residue prior to complete volatilization[17]. The implication is that upon heating to reaction temperature, anthracene will distribute itself between the liquid and vapor phases according to the vapor pressure. Reducing the sample weight in a batch reactor, therefore, will alter the distribution until, for sufficiently small weights, complete volatilization of the sample will be required to achieve, or partially achieve, the vapor pressure.

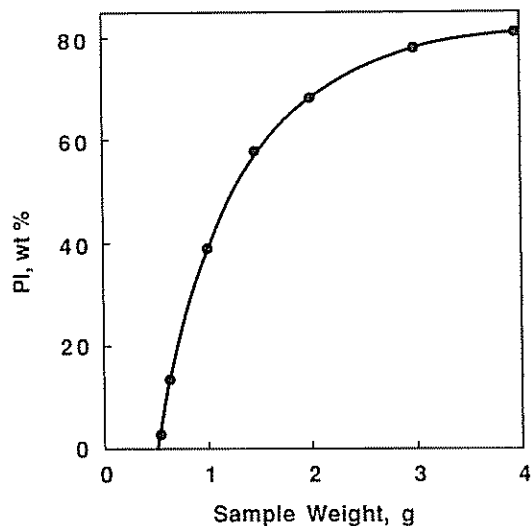Vapor pressure data for anthracene have been measured experimentally up to 350°C[18,19]. For the

Fig. 1. Effect of sample weight on the conversion of anthracene into PI: 525°C, 1 h, 6.9 MPa N_2.

higher temperatures used in this investigation, it was necessary to employ an extrapolating technique to predict anthracene vapor pressures. The semi-empirical equation attributed to van der Waals and presented in standard textbooks[20] was used. The vapor pressure data can be used to calculate the partitioning of anthracene between liquid and vapor in the reactor, as will be seen shortly.

The effect of sample weight on the conversion of anthracene into PI is given in Fig. 1 for reaction at 525°C for 1 h under 6.9 MPa N_2. There is a monotonic increase in conversion with increase in sample weight. This is in contrast to expected behavior in the presence of mass transfer effects.

The distribution of anthracene between the liquid and vapor phases at 525°C is given in Fig. 2 as a function of sample weight. It has been shown pre-
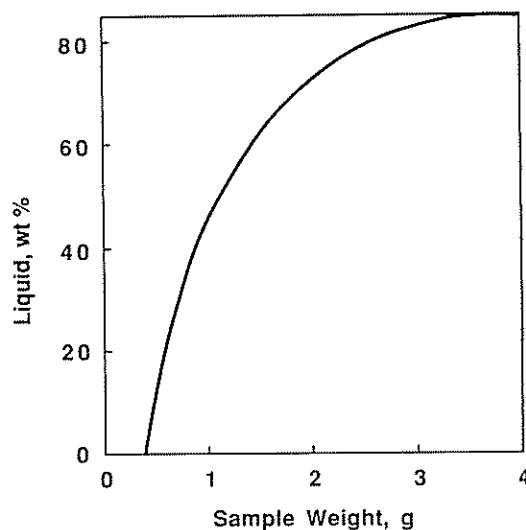

Fig. 2. Vapor-liquid equilibria at 525°C for anthracene in the tubing reactors as a function of sample weight.
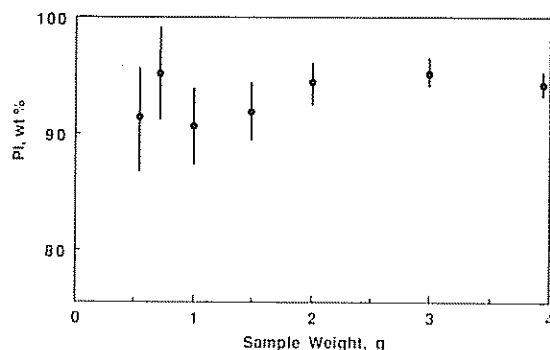
Fig. 3. Effect of sample weight on the conversion of liquid anthracene into PI: 525°C, 1 h, 6.9 MPa N₂.

viously that anthracene vapor is virtually unaffected under similar carbonizing conditions, whereas the liquid produces a considerable yield of heavy residue[21]. The data of Fig. 1 were therefore expressed on the basis of conversion of liquid anthracene into pyridine insolubles. As shown in Fig. 3, the data then displayed independency of sample weight. This is consistent with, but not proof of, the absence of significant mass transfer effects. Large errors in the data for low sample weights can be attributed to the increased significance of errors associated with the vapor pressure predictions. For this reason 4 g was selected as the standard sample weight for coking experiments. The distribution of anthracene between the liquid and vapor phases for this sample weight can be calculated for the range of operating temperatures between 465 and 525°C. Between 80 and 90 wt% of the sample was initially in the liquid phase.

The data of Fig. 1 were obtained experimentally using a reactor rocking frequency of 60 cycles/min. This is sufficient to ensure that the conversion to PI was independent of the rocking frequency, as shown in Fig. 4. The yield was lower in the absence of agitation for both 2 and 4 g samples of anthracene,
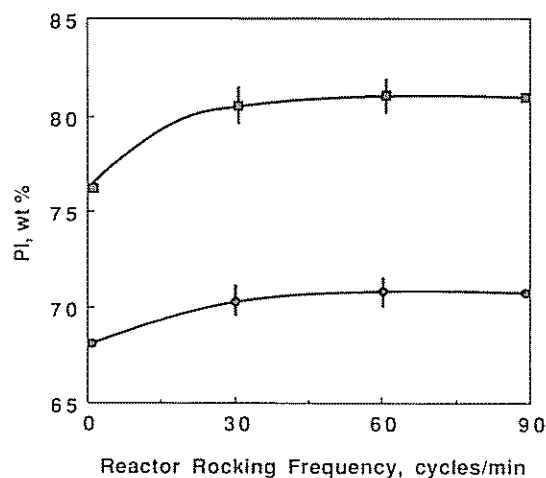
but reached a constant value once rocking was provided.

Based on the above discussion, it was concluded that kinetic data not limited by mass transfer could be obtained for the conversion of liquid anthracene into PI material. The adjustable parameters were set at 4 g sample weight and 60 cycles/min rocking frequency.

3.2 Pressure effects

In view of previously demonstrated pressure effects on the initial carbonization reactions of anthracene[22], the effect of 6.9 MPa N₂ pressure at reaction temperature was investigated. This is considerably less than pressures applied previously, which ranged from 34 to 207 MPa. A comparison of data obtained for coking runs at 510°C with and without the applied N₂ pressure is given in Fig. 5. No detectable difference was observed between the two cases with respect to the formation of PI.

It has been established theoretically that using an inert gas to compress a liquid causes an increase in its vapor pressure[23]. An approximate relationship for calculating purposes is:

$$RT \ln(P/P_o) = V_1 \, \Delta P \qquad (1)$$

where T = temperature
P_o = vapor pressure of liquid
P = vapor pressure under the applied inert pressure
ΔP = applied inert pressure
V_1 = molar volume of the liquid
R = universal gas constant

The technique of Yen and Woods[24] was used to calculate liquid densities, hence molar volumes, of

Fig. 4. Effect of agitation rate on the conversion of anthracene into PI: 525°C, 1 h, 6.9 MPa N₂; ● 2 g; ■ 4 g.
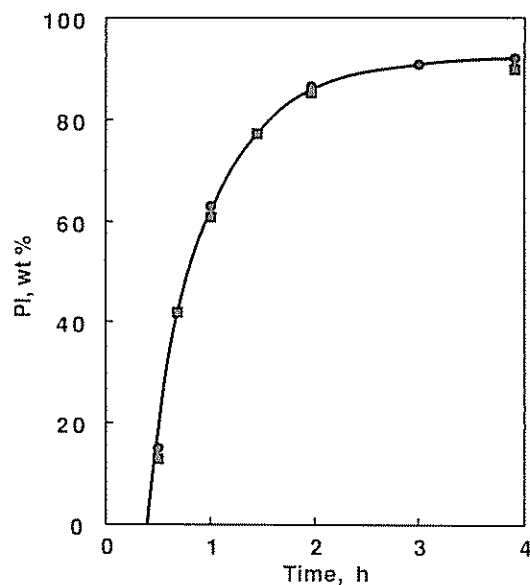

Fig. 5. Effect of pressure on the conversion of anthracene into PI at 510°C: ■ vapor pressure only, ● 6.9 MPa N₂.

anthracene as required in eq. (1). The calculation reveals that an applied pressure of 6.9 MPa would raise the vapor pressure of anthracene by approximately 30% for the range of operating temperatures used. However, at 500°C for example, the amount of anthracene in the liquid phase would be reduced by only 3 to 4% by the presence of the applied inert pressure. Even if this were not offset to an extent by a higher reactivity of anthracene in the liquid phase, large differences in the yield of PI would not be expected.

3.3 Kinetic data

Data for the conversion of anthracene into PI are given in Fig. 6 as a function of isothermal reaction time and temperature. Conversion increases monotonically with increase in time at reaction temperature. In addition, for a specified reaction time, conversion increases with reaction temperature over the range 465 to 525°C.

There is an apparent induction time, t_i, before the formation of measurable quantities of PI. This apparent induction time is temperature-dependent as shown in Fig. 7. The value of t_i increases with decrease in the reaction temperature from 525 to 445°C. One interpretation of the apparent induction time is that it is the time required to reduce the concentration of anthracene to a fraction, N, of its initial value. A similar interpretation has been applied to the elapsed time before the detection of a sharp exotherm, which is observed to accompany the transition from a liquid mixture to a solid polymer at the reaction condition[25]. Accordingly, the value of N can be related to a rate constant, k, for first-order kinetics by:

$$N = \exp(-kt_i) \qquad (2)$$

$$\ln N = -kt_i \qquad (3)$$
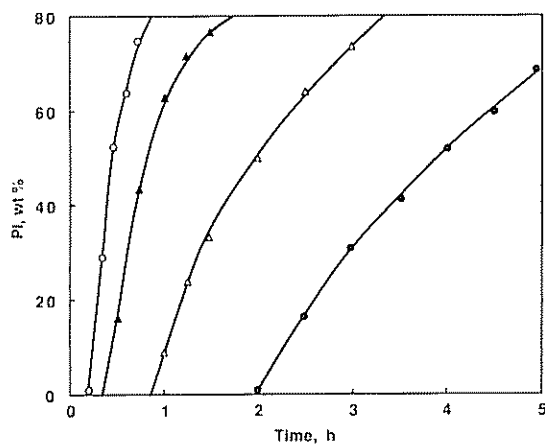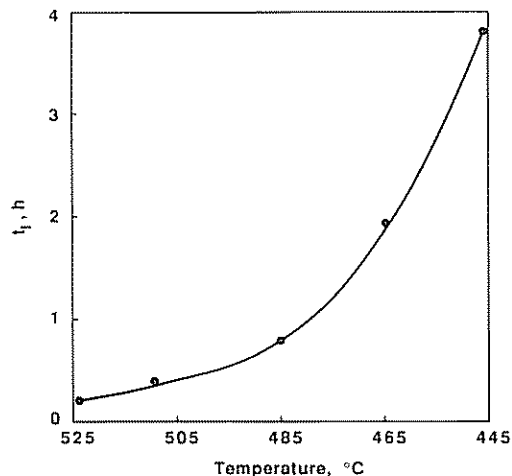
$$k = -t_i^{-1} \ln N \qquad (4)$$

Fig. 7. Apparent induction time associated with the formation of PI from anthracene under 6.9 MPa N_2.

Equation 4 is valid only if the value of N at t_i is independent of temperature. That is, the initial detection of PI occurs at a specific value of N for all temperatures. The validity of this assumption has not yet been established.

If the value of k, as determined from eq. 4, follows the Arrhenius expression, then a plot of $\ln t_i$ against $1/T$ should produce a straight line, the slope of which would be independent of the value of N and would be equal to E/R. Hence, an apparent activation energy, E, can be determined without prior knowledge of the value of N. A plot of $\ln t_i$ against $1/T$ for the coking of anthracene in the liquid phase under 6.9 MPa N_2 is given in Fig. 8. The correlation coefficient associated with a least-squares analysis is 0.999, indicating a good fit of the data by a straight line. The apparent activation energy was determined to be 40 kcal/mole with a standard deviation of 1 kcal/mole.

According to the analysis presented above, the apparent activation energy for the reduction in con-
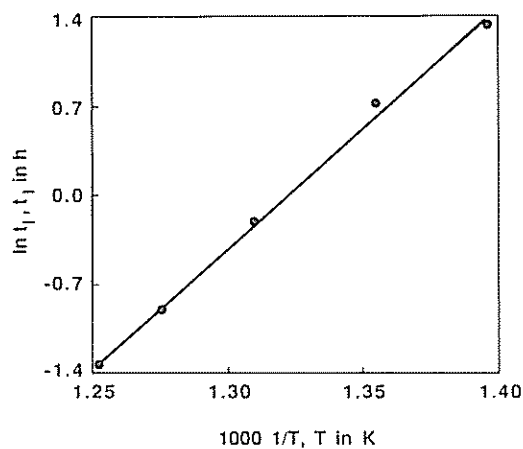

Fig. 6. Effect of time and temperature on the conversion of anthracene into PI: 4 g Sample, 6.9 MPa N_2, °C ○ 525, ▲ 510, △ 485, ◉ 465.

Fig. 8. Arrhenius relationship between apparent induction time and temperature for the formation of PI from anthracene under 6.9 MPa N_2.
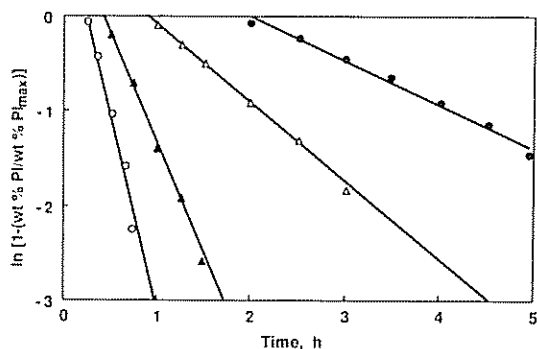
Fig. 9. First-order plots for the formation of PI from anthracene: 4 g sample, 6.9 MPa N_2; °C ○ 525, ▲ 510, △ 485, ● 465.

centration of the reactant, that is, the disappearance of anthracene, is 40 kcal/mole. This can be compared to the apparent activation energy for the formation of PI from anthracene, as determined according to the following analysis. The data can be tested for first-order kinetics with respect to the formation of PI, according to the eqn:

$$1-(\text{wt}\% \ PI/\text{wt}\% \ PI_{max}) = \exp(-kt) \qquad (5)$$

where wt% PI_{max} represents the wt% anthracene initially in the liquid phase. Equation 5 is based on the assumption that the yield of gaseous products, on a weight basis, is negligible. It will be shown later that this is the case for the liquid phase coking of anthracene. For example, for coking at 510°C for 1 h under 6.9 MPa N_2, the yield of gaseous products represents less than 0.2 wt% of the anthracene initially in the liquid phase.

According to eqn 5, a plot of ln [1-(wt% PI/wt% PI_{max})] against time for a specified temperature should produce a straight line of slope, -k. A test plot for the first-order kinetics for the conversion of anthracene into PI under 6.9 MPa N_2 in the liquid phase is given in Fig. 9 for temperatures between 465 and 525°C. Correlation coefficients associated with a least-squares analysis are given in Table 2. The reasonably high values indicate good fitting of the data by straight lines. First-order rate constants, calculated from the slopes in Fig. 9, are also given in Table 2.

Conceptually, first-order behavior indicates that, once the formation of PI has been initiated, the rate

of formation of additional PI is proportional to the concentration of material not yet converted to PI. Unconverted material could include intermediate products, as well as unreacted anthracene. If the reaction mechanism does not involve intermediate products which are soluble in pyridine, then the rate of disappearence of anthracene should equal the rate of appearance of PI. An Arrhenius plot, based on the data of Table 2, is given in Fig. 10. The apparent activation energy for the formation of PI was calculated to be 46 kcal/mole. The pre-exponential factor was $4 \times 10^9 \ s^{-1}$. The correlation coefficient for the regression analysis in 0.991.

Kinetic parameters for the coking of a range of organic feedstocks have been assembled from the literature and are presented in Table 3. In all cases involving the monitoring of insolubility in pyridine or quinoline, the data were fitted by a single first-order reaction equation. In addition, first-order rate constants were related to reciprocal absolute temperature by the Arrhenius expression in all cases. The kinetic equation obtained in this investigation for the appearance of PI, $k = 4 \times 10^9 \ s^{-1} \exp(-46 \ \text{kcal/mole}/RT)$, is in excellent agreement with that obtained for the disappearance of anthracene, $k = 3 \times 10^{-9} \ s^{-1} \exp(-46 \ \text{kcal/mole}/RT)$, as monitored by ultraviolet spectrophotometry[22]. A valid comparison, however, requires the inclusion of apparent induction times. For the disappearance of anthracene by UV spectrophotometry, the values of the apparent induction times before significant disappearance of reactant were 22 and 28 min for reaction at 509 and 490°C, respectively. For the appearance of PI, however, the equivalent values of t_i were 28 and 42 min. That is, induction times associated with the formation of PI were considerably longer than those associated with the disappearance of anthracene. Similar results are presented later in this study when the disappearance of anthracene is monitored by FTIR.

3.4 Gaseous products

It has long been recognized that, under severe thermal conditions, organic compounds can undergo a disproportionation; there can be breakdown to simple compounds and the elements, and a polymerization/condensation to polynuclear aromatic hydrocarbons[30]. Both processes produce carbon, since simple compounds degrade to carbon and hydrogen and, in the limit, polymerization/condensa-

Table 2. First-order rate constants for the conversion of anthracene into PI in the liquid phase under 6.9 MPa N_2

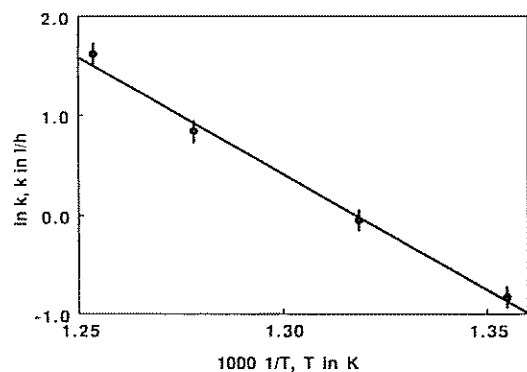| T, °C	k, h^{-1}	Correlation Coefficient
525	5.18	0.958
510	2.26	0.999
485	0.88	0.995
465	0.48	0.995

Fig. 10. Arrhenius plot for the formation of PI from anthracene under 6.9 MPa N_2.

tion reactions can produce a carbon of high C/H ratio. During the thermal treatment of coal tars, gaseous product analyses have been used to determine the preponderance of ring openings[31]. No increase in the yield of low-molecular-weight hydrocarbons accompanying a decrease in the yield of tars, was interpreted to indicate that polymerization/condensation reactions dominated thermal cracking reactions.

A typical analysis of the gaseous contents of a reactor is given in Table 4 for the coking of anthracene at 510°C for 1 h under 6.9 MPa N_2. A list of the gases capable of being detected was given previously. For the coking conditions given in Table 4, the yield of PI was 63 wt%. The N_2 introduced to the reactors as an inert pressurizing gas was used as a tracer to determine the percentage conversion of anthracene into gaseous products. For the conditions given in Table 4, less than 0.1 wt% of the anthracene charged to the reactor was converted into gaseous products. This small gas production, when expressed on a weight basis, provided justification for using the total weight of anthracene in the liquid phase as the maximum possible yield of PI in the previous kinetic analysis.

The total yield of gaseous products can be expressed alternatively as 0.03 moles of gas/mole of

anthracene converted to PI. The production of H_2 gas, therefore, represents less than 0.02 moles of H_2 (or 0.04 moles of H atoms) per mole of anthracene converted to PI. It will be shown later that a substantial increase in the C/H ratio of the PI accompanies an increase in their quantity. At a conversion level of 63 wt%, the same level applicable to the gas analysis given in Table 4, the change in the C/H ratio of the PI indicated that 3.6 moles of H atoms/ mole of anthracene converted to PI had been liberated. It is apparent that the liberated hydrogen was not converted to H_2 gas. The implication is that hydrogen has been transferred to the pyridine-soluble liquid fraction. This implies a high degree of hydrogen transfer between hydrocarbon molecules. This is in agreement with the recent findings of Sasaki, et al.[32].

It has been proposed the coking of anthracene proceed initially by the formation of free radicals via biomolecular disproportionation reactions[22]. Two of the reactions proposed are:
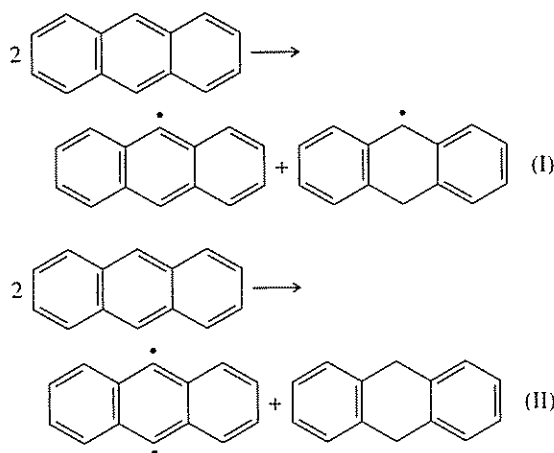
No H_2 gas is produced in either reaction. Such reactions would be consistent, therefore, with low production of H_2 gas. In addition, the lack of production of significant quantities of low-molecular-weight hydrocarbon gases (on a mole of gas per mole of an-

Table 3. Literature values of kinetic parameters for coking reaction in the liquid phase

Precursor	Measurement	E, kcal/mole	Reference
Anthracene	disappearance of reactant	46	22
Phenanthrene	wt% PI	75	26
Petroleum Pitch	wt% PI	53	6
Petroleum Residue	wt% PI	61	7
Ethylene Tar Pitch	wt% PI	36	6
Coal Tar Pitch	wt% PI	33	8
Coal Tar Pitch	wt% PI	39	27
Acenaphthylene Pitch	wt% PI	44	28
Solvent Refined Coal	wt% PI	35	29

Gas	Total, mole %	Product, mole %
N_2	99.0	--
H_2	0.6	60
CH_4	0.3	30
C_2H_6	0.1	10

thracene converted basis) is consistent with an absence of thermal cracking reactions. The implication is that polymerization/condensation reactions dominate thermal cracking reactions during the coking of anthracene in the liquid phase.

Thermochemical kinetic calculations have been performed for the coking of anthracene in the liquid phase near 500°C[33]. The calculations predict that self-disproportionation between anthracene molecules to produce free radicals is extremely slow. At 500°C, for example, the half-life of anthracene with respect to Reaction I is estimated to be in excess of 10^9 years. The calculations predict, however, that disproportionation reactions between anthracene and adventitious impurities in the anthracene (9,10 dihydroanthracene, for example) are more likely to initiate the coking process via the production of free radicals. The disproportionation reaction of anthracene with 9,10 dihydroanthracene is illustrated by Reaction III.

2   (III)
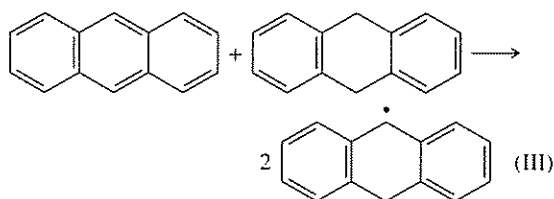
For Reaction III, the half-life of 9,10 dihydroanthracene in an anthracene solution is calculated to be about 4 s at 500°C[33]. For the rate of formation of free radicals via Reaction III to be in excess of that via Reactions I and II, the concentration of 9,10 dihydroanthracene would only need be of the order of 5×10^{-12} molar. This concentration is below the purity level of anthracene used (99.9 + % Gold Label), although phenanthrene is most likely the main impurity.

The thermochemical kinetic calculations of Stein predict further that hydrogen released during carbonization of anthracene would be held in hydrogenated anthracene structures rather than be liberated as H_2 gas[33]. The hydrogen would be held primarily in 9,10 dihydroanthracene molecules and 9,10 dihydroanthryl radicals. At 500°C, the mole ratio of hydrogen held in hydrogenated anthracene structures to hydrogen released as H_2 gas is predicted to be eighty-five[33]. Experimentally, the mole ratio was found to be ninety following the production of 63 wt% PI at 510°C. The experimental data from this investigation, therefore, are in good agreement with Stein's theoretical predictions.

The production of H_2 gas is predicted to increase, however, at high extents of reaction, particularly when all 9,10 anthryl sites have been depleted. It is possible, therefore, that for conversions to PI in excess of 63 wt% (the level of conversion corresponding to the data of Table 4) considerably higher concentrations of H_2 gas will be produced. This has not yet been determined experimentally.

In summary, the analysis of gases produced during the coking of anthracene is consistent with the theoretical predictions. The data support the dominance of polymerization sequences over cracking reactions. In addition, the polymerization sequences are probably initiated and propagated primarily by molecular disproportionation reactions involving hydrogen transfer between anthracene and hydrogenated anthracene molecules.

3.5 Pyridine insolubles

The yield of PI from the coking of anthracene at 485°C for 4 h under 6.9 MPa N_2 was 90 wt%. Reductive hydrogenation of the PI with lithium in ethylene diamine, to convert aromatics to hydroaromatics, rendered 40 wt% of the PI soluble in quinoline. The molecular weight distribution within the fraction made soluble in quinoline was measured by GPC. The GPC calibration between 450 and 2500 molecular weight units was achieved by fractioning a polymerized petroleum pitch on the GPC, and subjecting the fractions to vapor-phase osmometry to determine number average molecular weights. Calibration for molecular weights below 450 was achieved by using a series of polynuclear aromatic hydrocarbon model compounds. Details of the procedure are given elsewhere[13].

The distribution of molecular weights within the fraction made soluble in the quinoline eluent is given in Fig. 11 on a number basis. The lowest molecular weight detected in measurable quantities, about 350, corresponded approximately to the molecular weight of an anthracene dimer. Molecular weights of up to 2500 were detected. Species with higher molecular weights may have existed in the original PI however, given that only 40 wt% of the PI was made soluble in quinoline. Although not representative of the entire PI fractions, the number average molecular
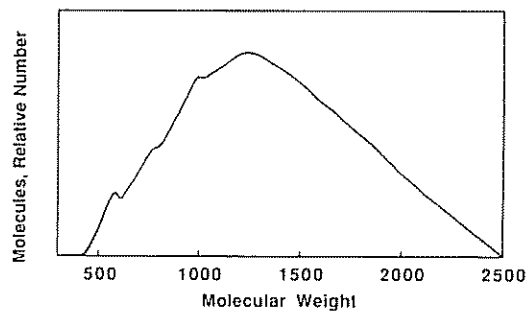

Fig. 11. Differential GPC curve for molecular weight distribution in the hydrogenated PI from anthracene coking: 485°C, 4 h, 6 MPa N_2.
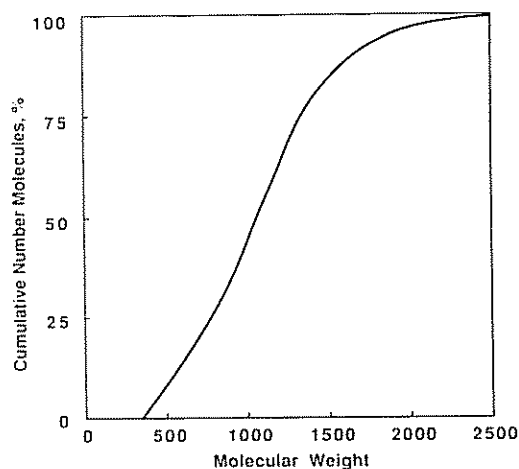
Fig. 12. Integral GPC curve for data of Fig. 11.

weight was approximately 1100. The cumulative number percentage of molecules as a function of molecular weight is given in Fig. 12. In a previous investigation, distinctive peaks were found corresponding to each oligimer of anthracene following coking at 440 and 500°C[34]. Similar peaks were not as apparent in this investigation. The data were not inconsistent though, with a predominance of molecular weight increases by polymerization/condensation reactions.

A qualitative indication of the level of hydrogenation of the PI by treatment with lithium in ethylene diamine was obtained from a proton NMR spectrum of the hydrogenated PI. An NMR spectrum, obtained using CDCl₃ as a solvent, is illustrated in Fig. 13. The reference point from which chemical shifts were measured is for that of tetramethylsilane, $(CH_3)_4Si$. The spectrum contained two dominant peaks, the largest at 1.2 ppm and a smaller peak at 7.2 ppm. The former is characteristic of secondary hydrogens, R_2CH_2; the latter is characteristic of aromatic hydrogens, Ar—H[35]. The detection of a peak at 7.2 ppm indicates that complete hydrogenation of aromatics has not been achieved. The dominant peak at 1.2 ppm, however, indicates qualitatively that extensive hydrogenation has occurred. The fact that 60 wt% of the PI remained insoluble in quinoline, following the hydrogenation treatment, is attributed to both incomplete hydrogenation and insolubility associated with hydrogenated molecules of high molecular weight.

As previously indicated, molecular weights as low as those corresponding to dimers of anthracene were detected by GPC in the PI. The dimer of anthracene formed initially, 9.9' bianthryl, and the initial products of coking in the liquid phase have been shown to have appreciable solubility in benzene[36]. Dimers formed from anthracene, therefore, should have even greater solubility in pyridine, which is a more polar solvent than benzene. The fact that molecular weights corresponding to dimers of anthracene were detected in the PI is not necessarily inconsistent, however, with their having appreciable solubility in pyridine, as discussed below.

Mesophase formation results primarily from the alignment of high molecular weight, planar molecules, which increase in concentration as coking proceeds[37]. This ordering into lamella is induced mainly by van der Waals forces, which increase as
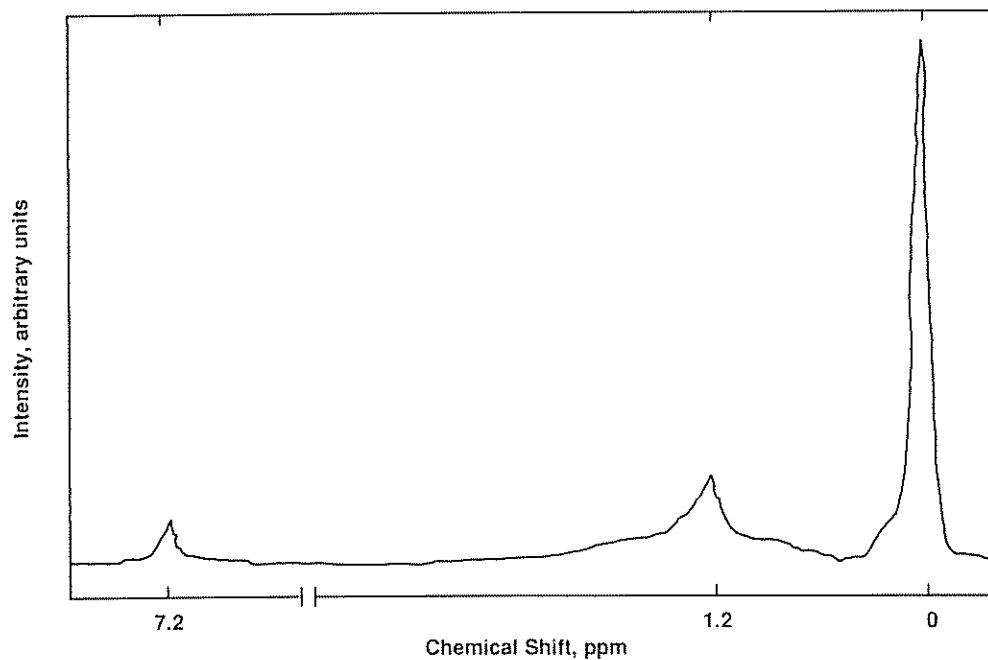

Fig. 13. Proton NMR spectrum of CHCl₃ soluble, hydrogenated anthracene coke: coking conditions, 485°C, 4 h, 6.9 MPa N₂.

Table 5. Carbon/hydrogen ratios of PI anthracene cokes as a function of time at 485°C
under 6.9 MPa N_2

Reaction Time, h	Wt% PI	C/H
0	0	1.40
1	0	1.53
2	52	2.15
4	86	2.21
4.5	89	2.26

the planar size of molecules increases. These partly ordered assemblages separate from the pitch as the mesophase. It is not unreasonable to expect that the attractive forces between large planar molecules and dimers of anthracene would be sufficiently high to induce alignment. Association of dimers of anthracene in the mesophase could render them insoluble in pyridine, in that the mesophase, to a large extent, is insoluble in pyridine. Reductive hydrogenation of the PI material with lithium in ethylene diamine would be expected to include disassociation of molecules that had aligned preferentially. This would include the disassociation of hydrogenated dimers of anthracene from larger-molecular-weight units. The dimers would then dissolve in pyridine or quinoline and be detected by gel-permeation chromatography as having been in the original PI fraction. Incorporation of dimers of anthracene in mesophase, therefore, is considered to render them insoluble in pyridine.

For the coking of anthracene at 485°C under 6.9 MPa N_2, the change in carbon/hydrogen ratio of the PI was monitored as a function of reaction time. This is shown in Table 5, with zero reaction time corresponding to pure anthracene, which is completely soluble in pyridine. The C/H ratio increases monotonically with reaction time from 1.40 for anthracene in 2.26 for the PI from a coking run of 4.5 h duration. This, together with the molecular weight data, indicates that the PI material changed in nature, as well as quantity, with the progress of coking. This emphasizes one of the restricting aspects of using solubility as a parameter for the basis of a kinetic analysis.

The PI produced at a level of 52 wt% were characterized with respect to surface area and He density. Their surface area was measured by Kr adsorption at –196°C. The adsorption data were analyzed according to the BET equation[38], and a cross-sectional area of 0.195 nm^2 was assumed for an adsorbed Kr atom[39]. The samples were produced from the coking of anthracene at 485°C for 2 h under 6.9 MPa N_2. Their measured surface area, employing a mean particle size of 500 μm, was 0.28 m^2/g; and the He density was 1.50 g/cc. For nonporous spherical particles of this diameter and density, the external surface area is calculated to be 0.008 m^2/g. The measured surface area of 0.28 m^2/g is a factor of thirty-five in excess of the calculated surface area, indicating some internal porosity. The low measured surface area of less than 1 m^2/g, how-

ever, is consistent with an absence of extensive microporosity.

3.6 Initial reactions

The reactivity of the different positions in the anthracene molecule has been predicted theoretically, based primarily on the calculations of electronic properties by molecular orbital theory[40]. The theoretical predictions have been confirmed experimentally by reactivity studies with benzyl[41] and phenyl[42,43] radicals. There is consensus that reactivity decreases in the order of positions 9 > 1 > 2 for anthracene.

The disappearance of anthracene during coking can be monitored by using FTIR. A vibrational assignment in the infrared spectrum of anthracene is the C—H out-of-plane bending at 886 cm^{-1} for the 9 and 10 positions[44]. Furthermore, partial replacement of the hydrogens in these positions with any substituent or removal of the hydrogens to form free radicals causes a decrease in the intensity of the band at 886 cm^{-1}. The disappearance of anthracene, therefore, can be followed as a function of time at reaction temperature, by following the decrease in the intensity of the band at 886 cm^{-1}. To obtain quantitative data, it is necessary to integrate under the peak at 886 cm^{-1}.

Data are shown in Table 6 for coking of anthracene at 465°C for times up to 2 h under 6.9 MPa N_2. The data are normalized against the absorbance of anthracene, per mg of sample. For reaction times up to 0.75 h, there was no change in the relative intensity within the experimental error. This implies no appreciable disappearance of anthracene. A further implication is that there is an apparent induction time prior to the disappearance of measurable quantities of anthracene. At 465°C under 6.9 MPa N_2, the induction time is about 0.75 h. For times greater than 0.75 h at 465°C, there is appreciable decay in

Table 6. FTIR data for the disappearance of anthracene: relative intensity of band at 886 cm^{-1} as a function of time at 465°C under 6.9 MPa N_2

| Time, h	A/A$_0$
0	1
0.25	1.01
0.75	1.03
1.00	0.88
1.50	0.90
2.00	0.78

the anthracene concentration. After 2 h at 465°C, the concentration of anthracene has decayed to 78% of its initial value. While there is some scatter in the data, the trend of a reduction in the concentration of anthracene with increase in reaction time is clear. Qualitatively, the data are in agreement with that obtained elsewhere[22] by monitoring the disappearance of anthracene by ultraviolet spectrophotometry. A temperature-dependent induction time was observed prior to the first-order decay in the concentration of anthracene.

The existence of an apparent induction time prior to the disappearance of measurable quantities of anthracene indicates that initially the rate of formation of free radicals is slow. Mechanistically, this involves the formation of free radicals via molecular disproportionation reactions with no net evolution of hydrogen. Comparison between the induction times at 465°C for the disappearance of anthracene and the appearance of PI, however, indicates that the former is considerably shorter, 0.75 compared to 2 h. Specifically, 22 wt% of the anthracene had disappeared prior to the onset of PI formation.

According to thermochemical calculations[33], the most rapid reaction of 9,10 dihydroanthryl radicals (the predominant radicals formed according to Reactions I and III) will be addition to the 9 position of anthracene, as shown in Reaction IV.

(IV)
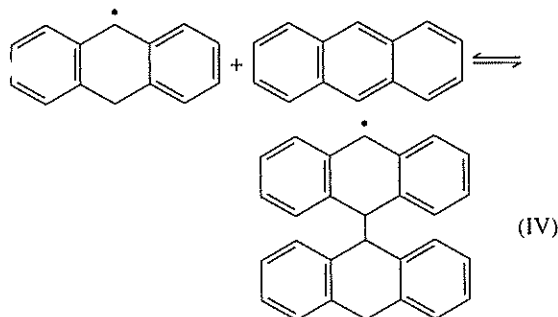
Reaction IV is predicted to be reversible, however, so that for a net consumption of anthracene by Reaction IV, the reaction product must undergo an irreversible reaction. The reaction predicted most likely to occur is Reaction V[33].

(V)
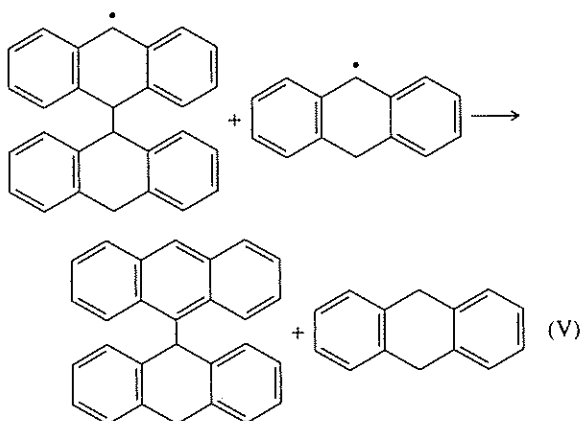
Both products of Reaction V are predicted to be quite reactive with respect to further free radical production and subsequently further polymerization[33]. The dimer is expected to act as a hydrogen donor since loss of a H atom from its tertiary carbon atom will produce a highly delocalized radical[33], as illustrated below.

+ H· (VI)
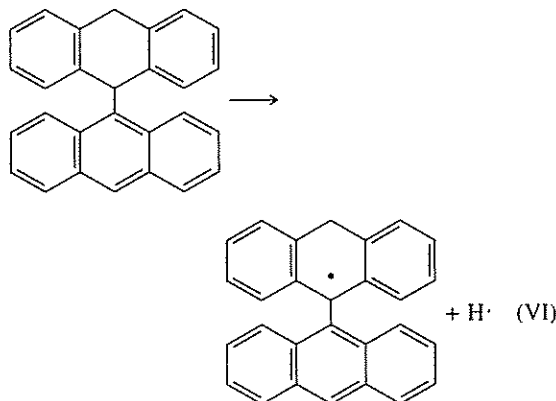
The 9,10 dihydroanthracene will form radicals via Reaction III.

The initial products, therefore, are predicted to effectively catalyze the coking process once a small amount of reaction has taken place[33]. This is in agreement with the experimental data. During the apparent induction time, the rate of disappearance of anthracene is presumably too small to be detected. Following the production of measurable quantities of products, or following the disappearance of measurable quantities of anthracene, the reaction proceeds at a rate which then follows a simple kinetic law. The slow initial rate of formation of free radicals, as previously inferred from the FTIR data, may also result from the existence of free radical inhibitors in the anthracene. The apparent induction time can then be ascribed as the time required to generate sufficient free radicals to consume the inhibitors.

ADDENDUM

Recently, Stein et al.[45] reported that the predominant initial products in the thermal chemistry of anthracene are 2,9'–bianthryl and 9,10–dihydroanthracene. Following pyrolysis at 500°C for 20 min, the ratio of 9,9' bianthryl to 2,9'–bianthryl recovered was 0.052. Stein notes, however, that 9,9'–bianthryl is expected to be the most reactive dimer of anthracene[33]; therefore, 9,9'-bianthryl could still be a more important precursor to the formation of coke than 2,9'–bianthryl. It has been shown that the carbonization of 9,9'–bianthryl leads to the ultimate production of highly graphitic carbon, similar to that produced with anthracene is carbonized[36]. To the authors' knowledge, the character of carbon produced from 2,9'–bianthryl has not been studied.

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