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On the High Temperature Chemical Equilibria of Polycyclic Aromatic Hydrocarbons

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Concentrations of selected benzenoid polycyclic aromatic hydrocarbons in equilibrium with acetylene and hydrogen over the range 1400–3000 K are estimated by extension and application of existing predictive methods. Implications of these results concerning chemical equilibria and reaction kinetics of high temperature hydrocarbon systems are explored. Of special interest is the finding that in idealized homogeneous equilibrium systems above 1700 K, there exists a "critical" highly condensed polycyclic aromatic species whose concentration is at a minimum relative to other highly condensed aromatics. Equilibrium concentration and size of this critical species depend on temperature and partial pressures of light gases (chiefly acetylene and hydrogen) and this species may constitute a natural thermodynamic barrier for homogeneous high temperature carbon particle formation. Also, concentrations of polyaromatic members of the most thermodynamically stable "benzene polymerization" pathway are examined in selective equilibrium with benzene and hydrogen. For this series, over a wide range of conditions, *o*-terphenyl is found to have the lowest equilibrium concentration.

Introduction

Incomplete combustion of hydrocarbon fuels not only wastes energy but also creates serious environmental problems resulting from the release of soot and carcinogenic polycylic aromatic hydrocarbons (PCAHs) into the atmosphere. These problems may become more acute as coal-derived fuels with higher carbon-to-hydrogen ratios than conventional petroleum derived fuels increase in use, since the former substances are more prone to incomplete combustion. Bituminous coal itself, when burned, can produce copious quantities of smoke, since the highly aromatic tars evolved upon heating rapidly degrade to soot.

Soot and PCAHs are also formed in many industrial processes involving high temperature hydrocarbon reactions, as in carbon black manufacture, pure pyrolysis of hydrocarbons, and coal pyrolysis.

The ubiquitous nature and importance of such hydrocarbon "polymerization" processes is reflected by the enormous number of studies reported in this area.[1] However, due to the intrinsic complexity and experimental difficulties inherent to this area of study few details concerning chemical mechanisms in even rather well-controlled chemical systems are known with certainty.

Studies of species concentration in premixed hydrocarbon–oxygen flames,[2] and pyrolysis studies in shock tubes[3] and flow reactors,[4] have provided fundamental information regarding soot and PCAH formation. Flame studies are exemplified by the elegant work of Homann and Wagner[2] who studied concentration profiles of a number of species in soot formation zones of premixed flames, and deduced that under their conditions polyacetylenes are the primary soot precursors. However, these experiments could not answer mechanistic questions with certainty. Moreover, other soot and PCAH forming systems may involve different mechanisms in formation, growth, and agglomeration of soot particles and it is not straightforward to apply results of one system to another.

Shock tube experiments have clarified conditions and rates of soot formation under isothermal homogeneous conditions, however, little unambiguous chemical mechanistic insight has resulted from such studies. High temperature flow studies have been severly hindered by undesired heterogeneous reactions on reactor walls.

The chemical steps leading to a nascent soot particle are particularly difficult to study experimentally since precursor species need be present in only trace concentrations. Observation of major species profiles in soot forming zones cannot, in themselves, reveal these chemical steps. Clearly, to elucidate soot formation, thermochemistry and kinetics of all reactive species present in soot forming regions must be well understood.

A fundamental area of uncertainty in these systems concerns the thermodynamic and kinetic behavior of PCAHs. The influence of temperature, size, degree of ring condensation, etc. on individual PCAH stability has never been quantitatively analyzed primarily due to the lack of

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TABLE I: Group Values for $C_p{}^\circ{}_T$/cal mol^{-1} K^{-1} and $\Delta G_f{}^\circ{}_T$/kcal mol^{-1}

	$[C_B-(H)]$		$[C_{BF}-(C_B)_2-(C_{BF})]^a$		$[C_{BF}-(C_{BF})_3]^b$
T/K	$C_P{}^\circ{}_T$	$\Delta G_f{}^\circ{}_T$	$C_P{}^\circ{}_T$	$\Delta G_f{}^\circ{}_T$	$\Delta G_f{}^\circ{}_T$
300	3.24	4.94	2.99	6.71	1.50
400	4.44	5.48	3.66	7.33	1.50
500	5.46	6.08	4.22	7.92	1.50
600	6.30	6.74	4.64	8.51	1.50
800	7.54	8.11	5.23	9.66	1.50
1000	8.41	9.48	5.55	10.78	1.50
1200	9.01	10.89	5.92	11.88	1.50
1500	9.73	13.07	6.16	13.51	1.50
2000	10.24	16.56	6.36	16.14	1.50
2500	10.57	20.02	6.45	18.71	1.50
3000	10.77	23.48	6.51	21.26	1.50

[a] $C_p{}^\circ{}_T$ values for the group $[C_{BF}-(C_B)(C_{BF})_2]$ are assumed to be equal to these values, $\Delta G_f{}^\circ{}_T$ for this group is greater than those given here by 1.50 kcal mol^{-1}. [b] $C_p{}^\circ{}_T$ values are identical with $C_p{}^\circ{}_T$ for graphite,[8] and are not given here.

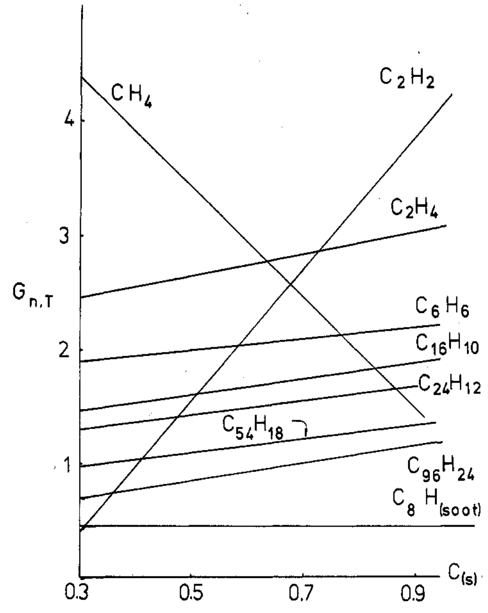


Figure 1. $G_{n,T}$/kcal mol^{-1} ($\equiv \Delta G_f{}^\circ{}_T(C_nH_m)/4.58nT$) values for a series of highly condensed PCAHs, CH_4, C_2H_2, and C_8H (soot). Note that $C_{16}H_{10}$ is pyrene, $C_{24}H_{12}$ is coronene, $C_{54}H_{18}$ is circumcoronene, and $C_{96}H_{24}$ is "circumcircumcoronene".

requisite thermochemical properties of PCAHs. To remedy this situation, the present work uses a recently reported scheme for estimating thermochemical properties of PCAHs[5] to explore the equilibrium behavior of PCAHs in hydrocarbon systems at high temperatures.

An important finding of these studies in that above 1700 K, concentrations for members of a series of highly condensed PCAHs in equilibrium with acetylene and hydrogen pass through a minimum. The nature and concentration of the PCAH having the lowest equilibrium concentration depends on the concentration of acetylene and hydrogen as well as the temperature. The fact that at these high temperatures the only large, thermodynamically stable molecules capable of extensive growth are highly condensed PCAHs indicates that this minimum concentration may constitute an effective thermodynamic barrier to soot particle formation ("nucleation") at high temperatures.

Concentrations of selected PCAHs in equilibrium with solid carbon and with benzene have also been considered. PCAH concentrations in equilibrium with solid carbon decline monotonically and are always exceedingly small. Over a wide range of conditions, concentrations of PCAHs that compose a "benzene-polymerization" series achieve a minimum concentration at *o*-terphenyl.

Calculational Method

The method of group additivity for estimation of standard enthalpies of formation, entropies, and heat capacities has recently been extended to include gaseous benzenoid PCAHs.[5] This scheme simply breaks down a given PCAH into four types of atomic groups; the contributions of these groups toward a specific thermochemical property are then summed to obtain the corresponding thermodynamic value for the PCAH. The value obtained for entropy must then be corrected for rotational and optical symmetry. This procedure is easily applied to substituted PCAHs using available groups derived from substituted benzenes and biphenyls.[6] The four groups for PCAHs are represented as, $[C_B-(H)]$,[7] $[C_{BF}-(C_B)_2(C_{BF})]$, $[C_{BF}-(C_B)(C_{BF})_2]$, and $[C_{BF}-(C_{BF})_3]$ where C_B is a carbon atom that is a member of only one aromatic ring (a benzene-like carbon atom) and C_{BF} is a carbon atom at the junction of two or three fused benzenoid rings. The first atom in each of these group representations is the central atom and atoms in parentheses are covalently bonded to this central atom. The subscript outside a parentheses indicates the total number of such bonded atoms (no subscript implies one atom of that type). In Table I group values taken from ref 5 are given along with values determined in the present work (see later). Values for the first group are simply those for benzene (corrected for rotational symmetry); the next two groups were derived from known thermochemical properties of fused aromatics; the last group is based on estimated properties of a carbon atom in a hypothetical "gaseous" layer of graphite. To illustrate the use of these groups, benzo(*a*)pyrene is composed of the following groups: $12[C_B-(H)]$, $2[C_{BF}-(C_B)_2(C_{BF})]$, $4[C_{BF}-(C_B)(C_{BF})_2]$, $2[C_{BF}-(C_{BF})_3]$.

For equilibrium calculations it is convenient to derive group contributions to the Gibbs energy of formation of PCAHs over the range of temperatures of interest using group values for PCAHs and thermochemical data for elemental carbon (graphite) and hydrogen.[8] These group $C_P{}^\circ{}_T$ values have been derived from published vibrational frequencies for benzene,[9] naphthalene,[10] and from tabulated $C_P{}^\circ{}_T$ for graphite and hydrogen.[8] These group values, along with resulting $\Delta G_f{}^\circ{}_T$ group values are given in Table I for temperatures up to 3000 K.

Using the values given in Table I, $G_{n,T} \equiv \Delta G_f{}^\circ{}_T/4.58nT$ values have been derived and are plotted in Figure 1 as a function of T^{-1}, where n is the number of carbon atoms, for selected PCAHs. For comparison, $G_{n,T}$ values for methane, ethylene, and acetylene are also shown. The thermodynamic quantity, $G_{n,T}$, is used since the equilibrium constant, $K_{eq,T}$, for system 1 is simply evaluated

$$\frac{1}{n}C_nH_m \rightleftarrows \frac{1}{n^1}C_{n^1}H_{m^1} + \frac{1}{2}\left(\frac{m}{n} - \frac{m^1}{n^1}\right)H_2 \qquad (1)$$

as

$$\log K_{eq,T} = G_{n,T} - G_{n^1,T}$$

As acute lack of accurate thermochemical data for large PCAHs in conjunction with the ostensibly nonlocal nature of resonance energy result in less satisfactory predictive ability of additive methods for PCAHs than for numerous classes of acyclic compounds. However, the focus of this work is on relative equilibrium concentrations and for this purpose group additive methods are entirely satisfactory since convergence to graphite is assured and errors in $G_{n,T}$ are very small even for substantial errors in the absolute magnitude of $\Delta G_f°$.

An uncertainty in extrapolation of group values of heat capacity to high temperatures arises from the neglect of electronic and anharmonic contributions of all groups except the graphite group $[C_{BF}-(C_{BF})_3]$, in which such contributions are intrinsically included. Such errors are expected to be small and, in any case, will cancel to a large degree when comparing equilibrium concentrations of one PCAH to another.

High Temperature Homogeneous PCAH Equilibrium

Upon complete equilibration in the temperature range 1500–3500 K, hydrocarbon mixtures generally degrade to the elements and contain very low concentrations of gaseous hydrocarbons. Since elemental carbon is primarily present as a solid under these conditions, such systems involve gas–solid "heterogeneous" equilibrium. However, in many systems equilibration of gases is much faster than such heterogeneous equilibration, and therefore, a metastable form of "homogeneous" equilibrium may develop.

This work focuses on relative equilibrium concentrations in an idealized region in between heterogeneous and homogeneous equilibrium, where sufficient time is available for equilibration of large molecules, yet carbon formation is kinetically limited. Although the extent to which such equilibria occur in actual systems is unclear, these considerations will allow an examination of PCAH thermodynamic stability and of the detailed thermodynamics of a possible mode of soot formation.

Even though acetylene is known to be the major hydrocarbon component of homogeneous hydrocarbon equilibrium systems in the range 1500–3500 K, there exists large PCAH molecules that, if in equilibrium with acetylene, would actually attain a higher concentration than acetylene. For instance, at any temperature T_e, if G_{n,T_e} for any PCAH is lower than $G_{n,T_e}(C_2H_2)$, then if $P_{H_2} = P_{C_2H_2}$ = 1 atm (P_x denotes the partial pressure of x), the equilibrium concentration of this PCAH would be greater than the concentration of acetylene. As an illustration, refer to Figure 1 where, at temperatures below ~2500 K for $P_{H_2} = P_{C_2H_2}$ = 1 atm, the gaseous PCAH $C_{96}H_{24}$ (circumcircumcoronene) has a higher equilibrium concentration than acetylene, while above 2500 K the reverse is true. Even rather large errors in $\Delta G_f°_T$ will have relatively little effect on this "crossover" temperature. For instance, if $\Delta G_f°_T$ for $C_{24}H_{12}$ is in error by 10 kcal mol^{-1}, this intersection temperature changes by <50 °C. The forced convergence of large highly condensed PCAHs to "gaseous" graphite, and the accurate Gibbs energies available for small PCAHs ensure relatively small errors for large PCAHs. Note that for large highly condensed PCAHs, $G_{n,T}$ values are lower than for smaller PCAHs, therefore these larger PCAHs persist as thermodynamically favored species up to higher temperatures than smaller PCAHs. This idealized behavior is expected since large, highly condensed PCAHs tend to have lower H/C atomic ratios and resemble graphite more closely than smaller or less highly condensed PCAHs.

Since acetylene is the primary light hydrocarbon in high temperature hydrocarbon equilibria, to assess the role of PCAHs in these systems it is useful to consider equilibrium concentrations of individual PCAHs relative to fixed acetylene concentrations. In Figure 2 is shown the logarithm of the concentrations (or partial pressures) of selected PCAHs relative to C_2H_2 as a function of T^{-1} in equilibrium with 0.1 atm of C_2H_2 and 1.0 atm of H_2 over the range 1700–3000 K. This figure clearly shows that with increasing PCAH size the temperature at which individual PCAH equilibrium concentrations becomes equal to the C_2H_2 concentration increases. The increasing slope of the curves with molecular size is also prominent. Under the above conditions, concentrations of *all* PCAHs become negligible above ~2500 K. At 2000 K, only highly condensed PCAHs larger than circumcoronene have equilibrium concentrations comparable to or greater than acetylene concentrations.

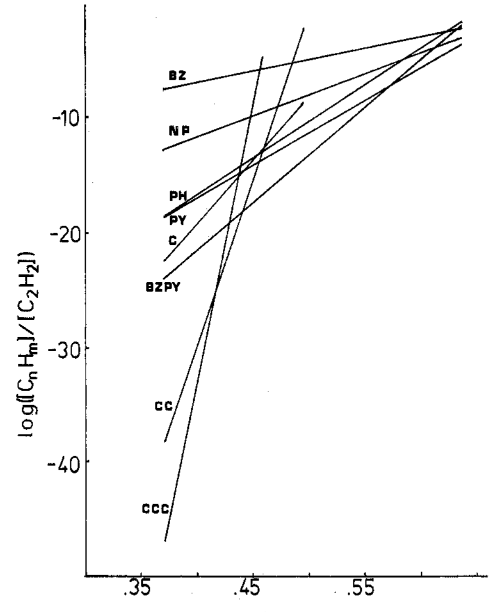


Figure 2. Concentrations of selected PCAHs with 0.1 atm of C_2H_2, 1 atm of H_2; Bz, benzene; Np, naphthalene; Ph, phenanthrene, Py, pyrene, BzPy, benzopyrene, C, coronene; CC, circumcoronene, CCC, "circumcircumcoronene".

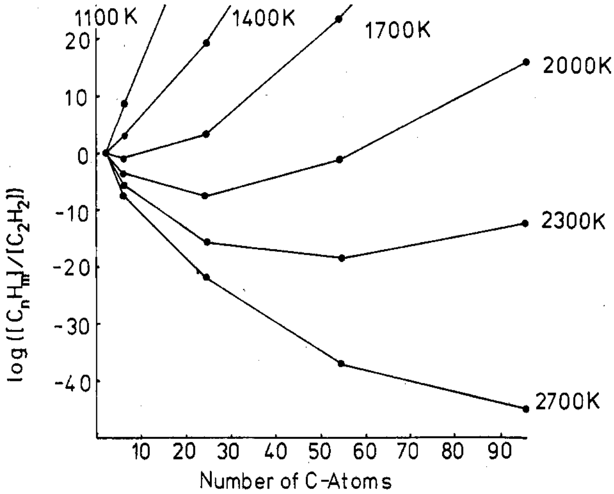


Figure 3. Equilibrium concentrations of circularly symmetric PCAH over a range of temperatures for $P_{C_2H_2}$ = 0.1 atm, P_{H_2} = 1 atm. Points are connected for clarity only.

Since, in general, high temperature thermodynamic stability increases with decreasing H/C, for a given carbon number the most stable PCAH will have the most condensed configuration possible. Therefore, the most thermodynamically stable homologous series of PCAHs consists of circularly symmetric (hexagonal overall shape) molecules, i.e., benzene, coronene, circumcoronene,.... Equilibrium concentrations of the first six members of this series relative to acetylene are shown in Figure 3 as a function of temperature for $P_{C_2H_2}$ = 0.1 atm, and in Figure 4 as a function of acetylene partial pressure at 2000 K. A

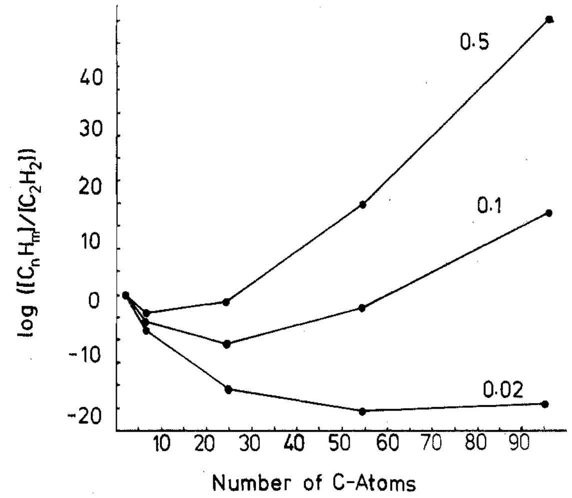


Figure 4. Equilibrium concentrations of circularly symmetric PCAHs over a range of acetylene concentrations (number on figure refer to $P_{C_2H_2}$/atm) for H_2 = 1 atm, T = 2000 K.

characteristic feature of most of these series is the existence of a PCAH whose concentration attains a minimum value relative to the other members of the series (the "critical" PCAH) whose size and concentration depend on temperature and concentrations of acetylene and hydrogen. The equilibrium concentration of such a critical species increases and its size decreases with decreasing temperature, with increasing acetylene concentration and with decreasing hydrogen concentration. This critical species can be regarded as a natural thermodynamic barrier to the formation of larger PCAHs and soot. However, at low temperatures, sufficiently great acetylene concentration and sufficiently low H_2 concentration no such barrier exists since equilibrium concentrations do not achieve an overall minimum under these conditions (see low temperature curves in Figure 3, for example). Also, at high enough temperatures the critical PCAHs becomes so large and attains such a low concentration as to lose any practical significance.

Consider now a more detailed carbon polymerization route. There exists a unique series of PCAHs that constitute the most thermodynamically favored route for building up large highly condensed PCAHs by addition of one ring at a time. Starting with benzene, individual rings are added by the addition of either C_4H_2 or C_2 units. In building up this series, when possible a C_2 unit is added in preference to a C_4H_2 unit since the former results in a greater decrease in the H/C ratio. Also, to assure maximum stability such a series must contain the previously discussed hexagonal PCAHs as members. Differences in resonance energy of different structural isomers are only several kilocalories per mole[8] and, therefore, do not influence the choice of members in this series. The first eight members of the series constructed in accord with these criteria are shown in Figure 5. Concentrations of the first 20 members of this series at 1700, 1900, and 2100 K in equilibrium with 0.1 atm of C_2H_2 and 1.0 atm of H_2 are given in Figure 6. Note that there exists a different critical species in the series for each different temperature. At 1700 K this species is phenanthrene whose partial pressure is 10^{-5} atm, at 1900 K benzopyrene is the critical species with a partial pressure of 10^{-9} atm, and at 2100 K benzocoronene is the critical species with a partial pressure of 10^{-15} atm. Generally, local minima occur for PCAH formed by addition of a C_4H_2 group to the preceding member of the series, since such an addition results in a decrease in entropy and a concomittant increase in the Gibbs energy of the system at these high temperatures.

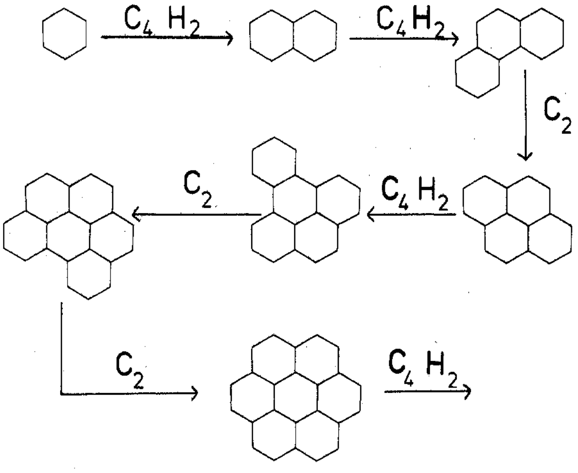


Figure 5. First six members of the most thermodynamically favorable high temperature PCAH polymerization route. Note that C_2 and C_4H_2 refer only to the number and type of atoms added in each step and do not refer to specific chemical species or mechanism.

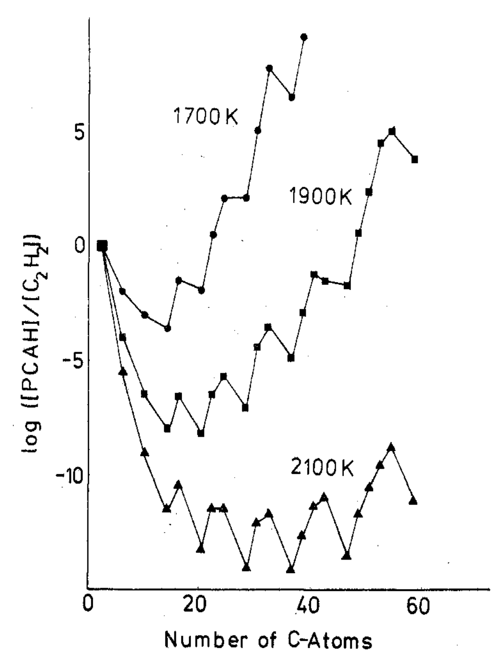
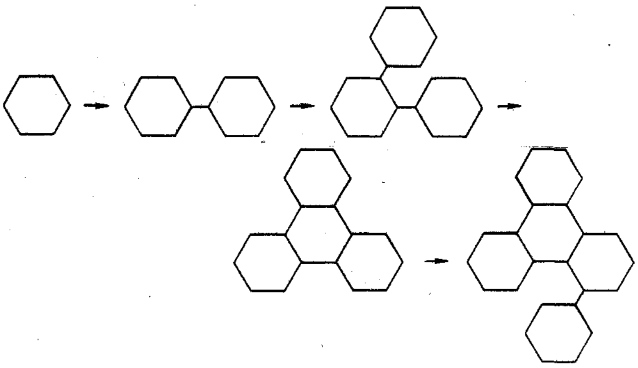


Figure 6. Equilibrium concentrations of PCAHs obtained by sequence given in Figure 5 for 1700, 1900, and 2100 K with $P_{C_2H_2}$ = 0.1 atm and P_{H_2} = 1 atm.

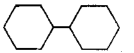
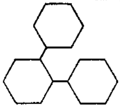
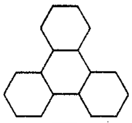
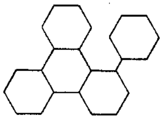
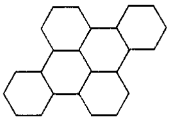
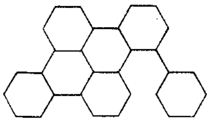
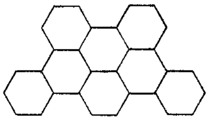
Benzene-PCAH Partial Equilibrium

In pyrolytic aromatic systems a commonly proposed route for soot and PCAH formation is through direct aromatic condensation in which aromatic units remain intact. Such a pathway is given in (2) for the first few



benzene polymerization steps. Equilibrium constants for equilibration with benzene (PhH) and H_2 for the first seven

TABLE II: Equilibrium Constants for Intermediates in Direct Aromatic Polymerization[a]

	PCAH	$\log K_e$	$\log K_e$ ($T =$ 1000 K)
A.		$-0.8 - 850/T$	-1.7
B.		$-1.8 - 1600/T$	-3.4
C.		$+1.0 - 500/T$	$+0.5$
D.		$+0.7 - 1200/T$	-0.5
E.		$+4.6 + 130/T$	$+4.7$
F.		$+2.5 - 900/T$	$+1.6$
G.		$+8.1 + 770/T$	$+8.9$

[a] Equilibrium constant for PhH = PCAH + nH$_2$ equilibrium in atmosphere units; evaluated using heats of formation and entropies at 298 K; PCAH thermochemical properties are evaluated using estimation methods described in ref 5 and S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, N.Y., 1976.

intermediates in this sequence are given in Table II. The equilibrium constants, as defined in footnote *a* in Table II, at 1000 K clearly show that *o*-terphenyl is the least thermodynamically stable of these intermediates over a wide variety of conditions. Straightforward manipulation of the various equilibrium expressions in Table II show that if $P_{H_2} < 10^{2.8+1100/T}$ atm then $P_B < P_C$, if $P_{PhH} < P_{H_2 10}{}^{1.0+800/T}$ atm then $P_B < P_A$, and if $P_{PhH} < P_{H_2 10}{}^{-2.5+800/T}$ atm then $P_B < P_D$. Thus, except at very high H_2 pressures or P_{PhH}/P_{H2} ratios, *o*-terphenyl is at a minimum equilibrium concentration relative to both larger and smaller molecular intermediates in this polymerization pathway.

Implications for Kinetics of PCAH Reactions

A substantial portion of soot formation in premixed flames takes place in relatively cool regions (≤1500 K) where the thermodynamic stability of PCAHs in homogeneous hydrocarbon equilibrium systems monotonically increases with increasing size. Also, at these temperatures other pathways involving more highly hydrogenated intermediates become thermodynamically feasible. It is unclear, at present, whether in this region there is any fundamental distinction other than size between a soot particle and a gas molecule.

Under conditions where carbon formation takes place above 1500 K in a homogeneously equilibrated mixture (predominant components are C_2H_2 and H_2) initial carbon polymerization must proceed by through a series of steps in which small hydrocarbon units are added sequentially. Therefore, since PCAHs are the only species both thermodynamically stable and capable of further growth at high temperatures (the thermodynamic stability, for instance, of polyacetylenes decreases uniformly with increasing size) the critical species discussed in the preceding section on the basis of purely thermochemical grounds may actually have kinetic significance. That is, since at high temperatures homogeneous carbon polymerization is expected to proceed through the most thermodynamically favorable pathway, the species present at the lowest concentration in the pathway is expected to be involved in the rate-limiting step. For instance, if each elementary addition step is of the form

$$C_2H + PCAH \xrightarrow{k_{add}} adduct$$

the rate of each addition is $k_{add}[C_2H][PCAH]$; the slowest addition step is the step involving the PCAH at lowest concentration. As a result, all PCAH smaller than the critical size are close to mutual equilibrium.

A useful generalization derived from these considerations is that highly condensed PCAHs smaller than the critical species will tend to degrade while highly condensed PCAHs larger than the critical size will tend to polymerize to solid carbon. Also, nonhighly condensed species (chrysene is an example) are generally unstable relative to more highly condensed structures of comparable carbon number.

In these systems, soot particle formation is expected to decrease with increasing temperatures due to an increase in size and a diminishing steady-state concentration of the soot nuclei with increasing temperatures. In this region also one expects a very strong dependence of soot formation rate on acetylene concentration. Both of these effects have, in fact, been observed[3] in shock tube pyrolyses of aromatics at 1600–2300 K. However, the actual mechanism may be more complex due to possible competition of direct benzene polymerization with homogeneous equilibration at the lower temperatures of these studies.

In high temperature systems which contain aromatic species not in equilibrium with acetylene, polymerization kinetics are expected to be considerably different. The critical species for benzene polymerization is *o*-terphenyl whose equilibrium concentration is $10^{-1.8-1600/T} P_{PhH}{}^3 P_{H_2}{}^{-2}$ (Table II). The concentration of *o*-terphenyl is far less sensitive to temperature and partial pressures of hydrocarbons and hydrogen than is the critical species in acetylene polymerization systems. On the basis, a decrease in soot formation rate at higher temperatures is not expected as long as the rate of direct polymerization is faster than the rate of degradation to acetylene.

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Effects of Alkyl Group Size and Counterion Type on the Behavior of Copolymers of Maleic Anhydride and Alkyl Vinyl Ethers. 1. Potentiometric Titrations[1]

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The acid–base properties of a series of hydrolyzed 1–1 copolymers of maleic anhydride and alkyl vinyl ethers were studied in the presence of tetramethylammonium (TMA), lithium, and sodium ions in order to assess the effects of both the size of the alkyl groups and the nature of the counterion. A certain critical minimum value of α, the degree of neutralization, had to be attained before counterion specificities set in. This critical value of α was substantially smaller for the hexyl copolymer which has a compact conformation at low charge than for the ethyl copolymer which exists only in the random coil form. Values of the standard free energy of the conformational transition at zero charge obtained for the butyl, hexyl, and octyl copolymers lead to a value of 370 cal/mol for the contribution of one methylene group to the hydrophobic stabilization of the compact form. However, in going from the butyl to the pentyl and from the pentyl to the hexyl copolymer, the values of this quantity are 600 and 100 cal/mol, respectively, indicating a deviation in the effect of the pentyl group from the effects of the even-numbered alkyl groups.

Introduction

The alternating copolymers of maleic anhydride and alkyl vinyl ethers combine a number of properties valuable for elucidating phenomena characteristic of biological macromolecules. One of these properties is the ability of those members of this copolymer family with intermediate alkyl group size to undergo, upon ionization, transitions from a compact to a random-coil conformation.[3] These conformational transitions resemble, both in cause and effect, the denaturation of proteins whose native conformations are stabilized by hydrophobic forces.[4] Another property of these copolymers is their capacity to interact specifically with metal ions. In particular, it has been shown that the dicarboxylate group and the ether oxygen act as cooperating ligands in binding alkali and alkaline earth metal ions, whereas the ether oxygen seems to play no role in the strong binding of silver ion.[5]

The study of these copolymers can take advantage of a wide range of possible chemical variations. The size and type of the alkyl group of the alkyl vinyl ether moiety may be changed systematically, while the high reactivity of the anhydride group of the maleic anhydride moiety may be utilized for the chemical attachment of useful groups, such as spectroscopic probes or ligands specific to desired substrates.[6]

It may be expected that a change in the size of the pendant alkyl groups will affect the stability of the compact conformation as well as the interactions of the macromolecules with their counterions. We have commenced a number of studies of the effects of variation in the alkyl group size utilizing a variety of experimental methods which monitor the behavior of the macromolecules, the counterions, and the solvent. The methods used include potentiometric titration, dilatometry, calorimetry, and absorption and fluorescence spectroscopy.

Since the acid–base behavior of these copolymers is fundamental to the understanding of their other properties, we start out by presenting in this paper a study involving potentiometric titrations of the ethyl, butyl, pentyl, hexyl, and octyl copolymers. The bases used were tetramethylammonium (TMA), lithium, and sodium hydroxides. All titrations were carried out in an excess of supporting electrolyte having in common the cation of the base.

Experimental Section

Materials. The butyl, hexyl, and octyl copolymers (samples B-II, C, and D, respectively) have been described previously.[3,7,8] The ethyl and pentyl copolymers (samples A-VII and P, respectively) were prepared in this laboratory by P. Dubin and B. Barbieri, respectively, by the method used for the above samples.

All acids, bases, and electrolytes used were Reagent Grade. Water was deionized, distilled over potassium permanganate, and redistilled.

Preparation of Copolymer Stock Solutions. The copolymers were weighed out to give approximately 5×10^{-3} monomolar solutions. While the ethyl and butyl copolymers could be simply dissolved in water with some agitation, the pentyl, hexyl, and octyl copolymers had to be dissolved in dilute base which was neutralized with an exactly equivalent amount of acid after dissolution of the

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