

pentadiene.³⁷ Table I lists other examples of strained olefins that react with S₂ to give trithiolane products.³⁷ The trithiolane products obtained from these S₂ additions are in sharp contrast to the episulfide and thiophene products or no reaction that Ando and co-workers^{15b} report if reagent 57 (Scheme XIX) is used as the "S₂" source.

Conclusion

From our many S₂ experiments, S₂ additions to olefins give only disulfide or trisulfide products. The trisulfide products obtained can be explained, in all instances, in terms of addition of a second mole of S₂ followed by a rearrangement process that deposits atomic sulfur in its elemental octaatomic form. In none of our experiments did we find episulfide products, thiophenes, tetrasulfides, or polymeric material. Thus, we conclude that when these latter products are observed in the reaction mixture, the sulfuration was more likely a reaction of activated elemental sulfur and not S₂.

The recent widespread interest in S₂ chemistry is based on a fundamental point of view and also on possible applications to the synthesis of 1,2-dithiin compounds, many of which show antimicrobial activity, including anti-HIV activity.³⁸ Thus, we believe that this new area of organosulfur chemistry will be richly explored for many more years to come.

I thank the talented research students both past and present (many of whose names appear in the references) whom I have been privileged to work with on this project. I also thank Professors David N. Harpp and Alan G. Shaver (both of McGill University) and Dr. James P. Snyder (Searle R&D) for the many fruitful and stimulating discussions we have exchanged on S₂ chemistry. Finally, I am most grateful to the Natural Sciences and Engineering Research Council of Canada and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support.

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Thermal Reactions and Properties of Polycyclic Aromatic Hydrocarbons

STEPHEN E. STEIN

Chemical Kinetics Division, National Institute of Standards and Technology, U.S. Department of Commerce, Gaithersburg, Maryland 20899

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Introduction

Early studies of coal tar and the earliest applications of quantum theory have both dealt extensively with the varied, yet systematic behavior of polycyclic aromatic hydrocarbons (PAHs). They have remained at the center of soot, coal, and carbon chemistry for many years and, more recently, have gained notoriety (and attention) for their cancer-causing potential.¹ Intense and very recent interest in PAHs has developed in the study of diamond synthesis,² interstellar space,³ and carbon cages ("fullerenes").⁴

This Account reviews results of studies on the thermal chemistry and properties of PAHs. While most of this work has been motivated by practical concerns, especially in the areas of coal processing and soot formation, the results illuminate certain fundamental features of PAH chemistry.

Since facile routes are generally not available for building large hexagonal-ring systems characteristic of

PAHs, their ubiquity is largely a consequence of their high-temperature thermodynamic stability. Two separate factors are responsible for this stability. First, the delocalized orbitals in PAHs provide stable repositories for electrons. Second, and equally important, the low H/C ratios of PAHs tie up little hydrogen, serving to increase system entropy.

Some of the notable difficulties in the study of PAHs are low solubility, multisite reactivity, synthesis, and identification. Fortunately, several simplifying factors may also be cited. First, π -electron properties of PAHs are estimable. Moreover, the inherent thermodynamic stability of PAHs limits their energetically accessible reactions. In addition, well-developed predictive methods for free-radical reactions can be applied to PAH reactions.^{5,6}

The following discussion examines first properties and then reactions of PAHs and derived radicals. It

Stephen E. Stein was born in New York City in 1948 and educated in its public schools. He obtained a B.S. in chemistry from the University of Rochester in 1969 and a Ph.D. in physical chemistry under the direction of Prof. B. S. Rabinovitch at the University of Washington in 1974. This was followed by an appointment at SRI International in Menlo Park, CA, for two years in a group headed by Dr. S. W. Benson. In 1976 he joined the faculty of the Department of Chemistry at West Virginia University and was promoted to Associate Professor in 1981. He then joined the Division of Chemical Kinetics at NIST in 1981. His work has been equally divided between experiment and theory, and lately he has become interested in exploitation of personal computers as providers of data for chemists.

(1) See, for example: *The Proceedings of the Symposium on Polynuclear Aromatic Hydrocarbons*; Battelle Press: Columbus, OH, 1990.

(2) Badziag, P.; Verwoerd, W. S.; Ellis, W. P.; Greiner, N. R. *Nature* 1991, 343, 244-245.

(3) Frenklach, M.; Figelson, E. D. *Astrophys. J.* 1989, 341, 372.

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(5) Stein, S. E. A Fundamental Chemical Kinetics Approach to Coal Conversion. In *New Approaches to Coal Chemistry*; Blaustein, B. D., et al., Eds.; ACS Symposium Series 169; American Chemical Society: Washington, DC, 1981; pp 97-130.

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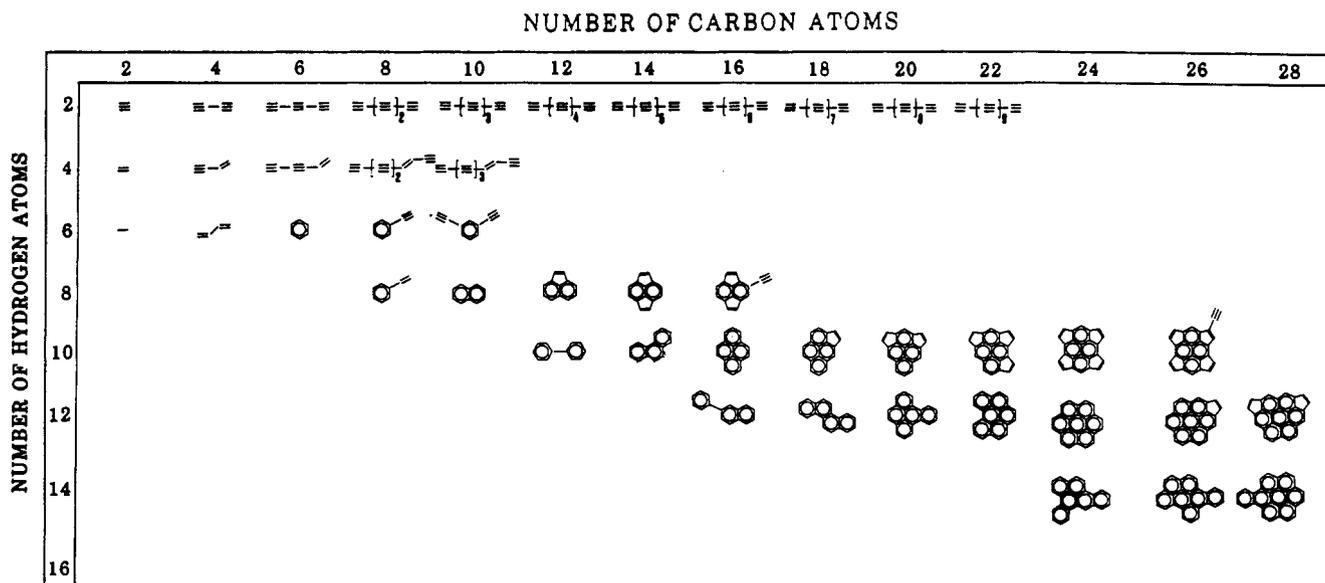


Figure 1. The most stable molecules at high temperatures.⁸

ends with a few words on the chemical transition "from benzene to graphite".

Properties

Thermodynamics. With the aid of estimation methods, we have examined relative thermodynamic stabilities of PAHs at high temperatures.^{7,8} For specific atomic formulas, by minimizing strain and triple bonds and maximizing aromaticity, we deduced the structural features of the most stable class of PAHs. In this manner, with corrections for isomers, relative thermodynamic stabilities of the most stable classes of PAHs were obtained up to $C_{42}H_{16}$.⁷ Reactions were balanced using acetylene and hydrogen, the most stable gaseous products of hydrocarbons at high temperatures. Figure 1 shows the most stable molecules for formulas up to $C_{28}H_{14}$ ("stabilomers"⁹). Figure 2 gives relative equilibrium concentrations for the classes represented by these molecules that are on the thermodynamically preferred path leading to graphite for three sets of conditions. Also shown are concentrations along paths composed solely of benzenoid (six-membered-ring only) PAHs. Minima on these paths represent a free energy barrier which, under some circumstances, can impede carbon "polymerization". They originate from the entropy loss associated with the hydrogen that must be added during PAH growth.

π -Electrons. Since most chemical properties of PAHs depend on their mobile networks of π -electrons, a reliable π -electron theory is essential for dealing with PAH chemistry. We examined the suitability of several π -electron theories for treating large PAHs.¹⁰⁻¹² A key requirement was that the method must extrapolate properly in the infinite-plane limit (single-layer graphite).

Of the methods tested, only Huckel theory passed. Conventional (SCF-MO) calculations predicted, even

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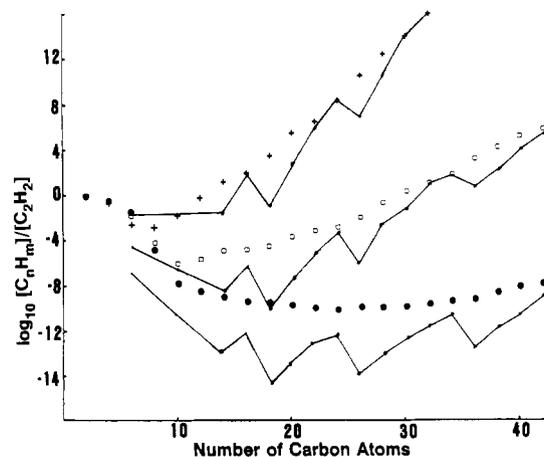


Figure 2. Equilibrium concentrations relative to acetylene along thermodynamically preferred growth paths.⁸ Calculations assumed 0.03 atm of acetylene and 0.1 atm of H_2 . Discrete points are for classes of compounds in Figure 1 with isomer corrections. $T/K = 1600$ (crosses), 1900 (filled circles), 2300 (filled circles). Solid lines are for paths through benzenoid PAHs.⁷

in the limit of infinite size, that energies of the highest occupied molecular orbitals (HOMOs) depend on the edge structure. Further, it predicted alternating bond lengths at this limit. On the contrary, single-layer graphite is accepted to have a single, characteristic HOMO level regardless of edge structure, and experiments show a single bond length. Related deficiencies of SCF-MO methods have been discussed in the literature.¹³ Treatments simpler than the Huckel theory^{14,15} also failed in their extrapolation to the infinite plane limit.

In order to separate size from edge-structure effects, four homologous series of hexagonally shaped PAHs (Figure 3) were examined by Huckel theory. One had "zigzag" edges (series 1) and another had "armchair" edges (series 3), representing the two distinct crystalline directions in a layer of graphite. The other edge types are hybrids of these. For each series the HOMO

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(15) Dewar, M. J. S.; Dougherty, R. C. *The PMO Method of Organic Chemistry*; Plenum: New York, 1975.

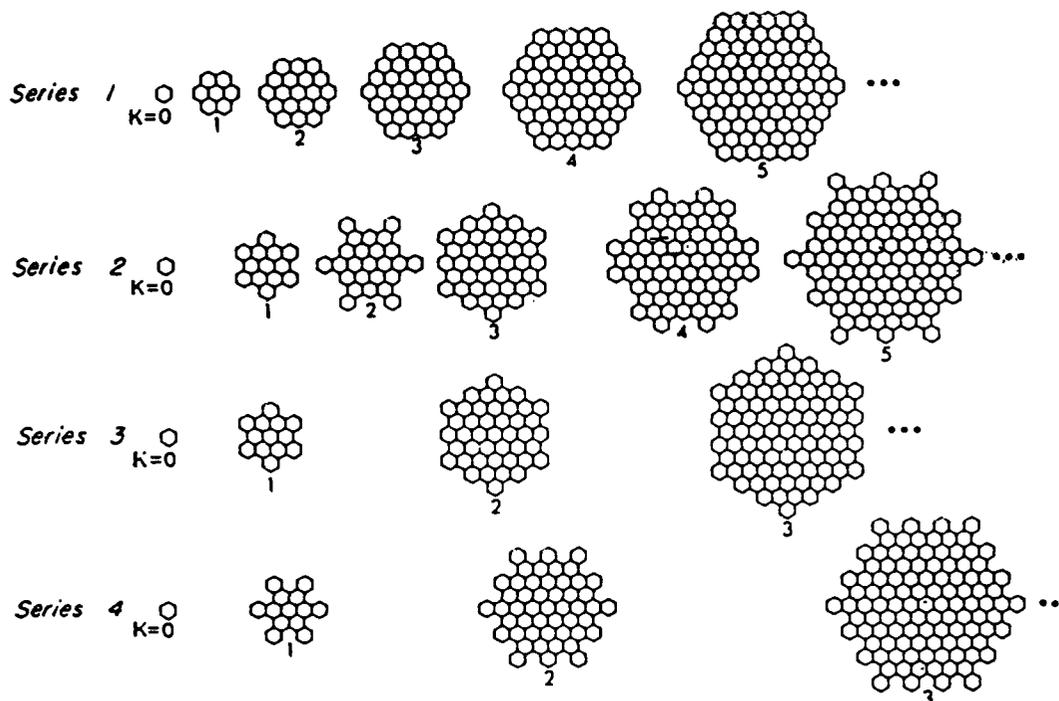


Figure 3. Four homologous series of hexagonal PAHs used for MO calculations. Series 1 and 3 have so-called "zigzag" and "armchair" edges, respectively.^{11,12} Reprinted with permission from ref 11. Copyright 1987 American Chemical Society.

properly approached the limiting zero value (Figure 4). The least stable, zigzag-edge series most rapidly approached the zero limit, while the most stable, armchair-edge series approached this limit most slowly.

These results are in accord with the qualitative "aromatic sextet" theory of Clar, where the most stable PAHs are those that can be depicted as networks of isolated aromatic rings.¹⁶ Series 2 and 3 can in fact be fully represented in this way (in Clar's terminology, they are "fully benzenoid") and have significantly lower HOMO energies than comparably sized members of the other series.

The properties of the higher energy orbitals depend strikingly on edge structure (Figure 5A,B). For the armchair-edge structure, electron densities are rather evenly distributed over the structure, while for the zigzag-edge series, densities are concentrated at the edges.

In sharp contrast to the behavior of molecular orbitals, site-specific free-radical reactivity depends almost exclusively on local structure (nearby bonds) (Figure 6).^{11,12} The most reactive position in phenanthrene, for instance, has virtually the same estimated reactivity as the corresponding position at the periphery of an infinite layer. In Figure 7 are shown H-atom affinity values for an assortment of edge sites.

These results demonstrate the lack of any intrinsic relationship between the reactivity of specific sites in a molecule and the molecular HOMO. A very large armchair-edge molecule, for instance, with a near-zero HOMO has no sites of high reactivity. Predictive schemes for reactivity of PAHs based on whole molecule properties such as the HOMO energy or ionization potential can fail badly for large PAHs.

Trends in proton affinities (PAs) of edge sites are predicted to exhibit still different behavior.¹² A simple thermodynamic cycle shows that PAs depend on both

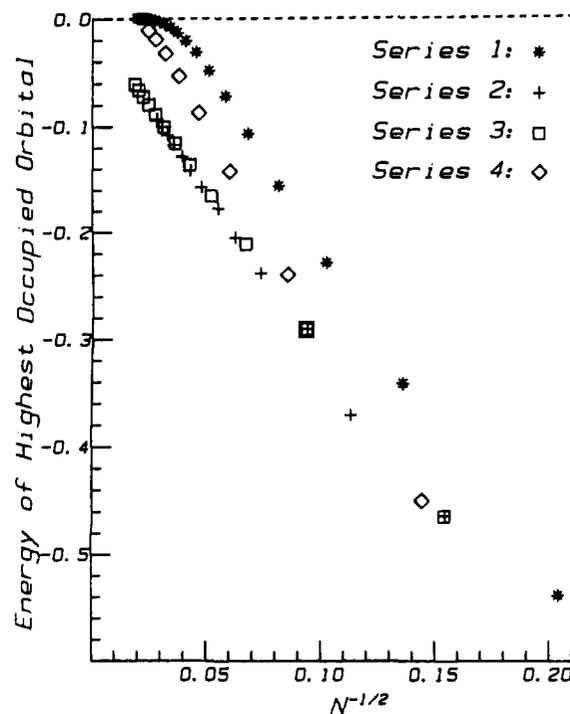


Figure 4. HOMO energy of molecules in Figure 3 versus inverse of molecular size ($1/(\text{number of C atoms})^{1/2}$).¹¹ Reprinted with permission from ref 11. Copyright 1987 American Chemical Society.

the H atom affinity (HA) of a site and the ionization potential (IP) of the derived radical [$\text{PA} = -\text{IP}(\text{H atom}) + \text{HA} + \text{IP}(\text{radical})$].

While the HA component depends little on molecular size, the IP is strongly size dependent (the IP of graphite is drastically lower than those of conventional PAH radicals). Hence, PAs for very large PAHs are expected to be very much greater than for conventional PAHs. For instance, while the difference in neutral H atom affinities of benzene and armchair-edge graphite

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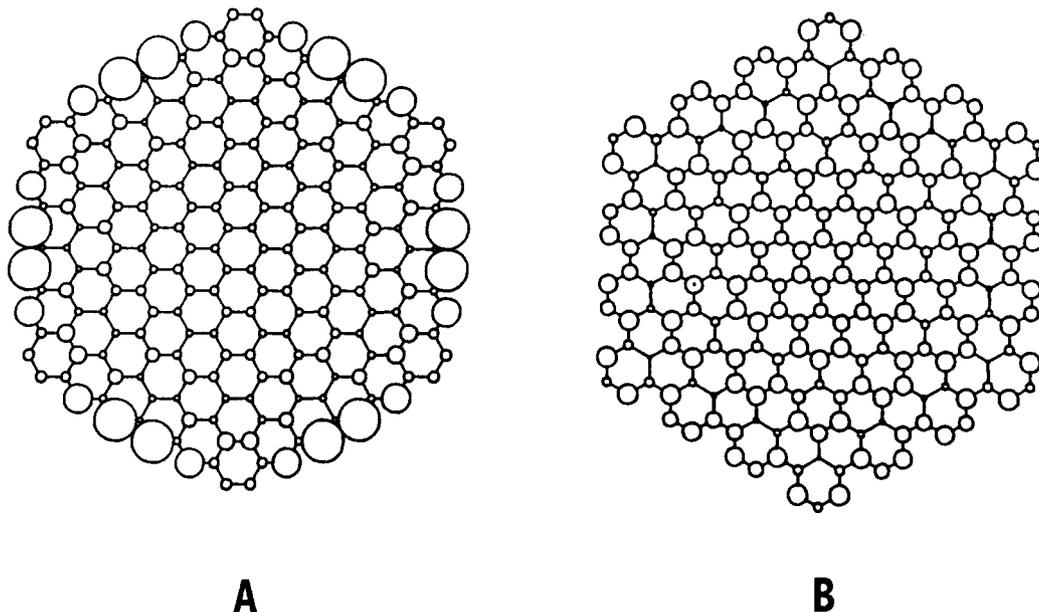


Figure 5. Huckel MO electron densities for members of series 1 (A) and 3 in Figure 3 (B).¹¹

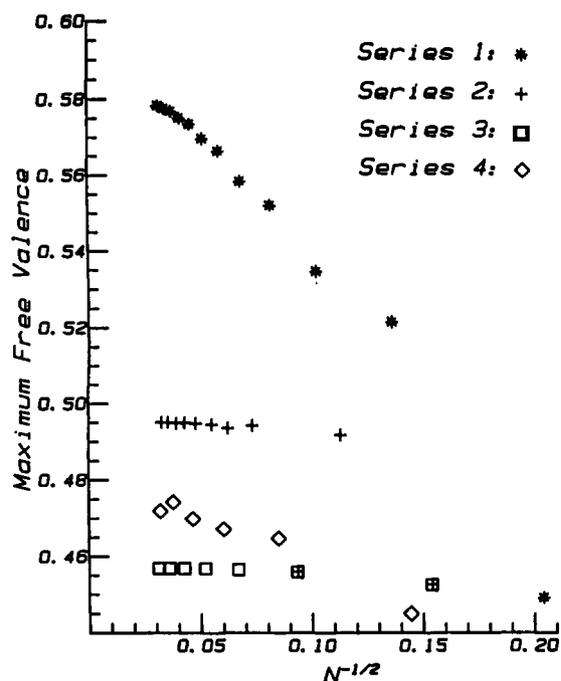


Figure 6. The maximum free valence for molecules of Figure 3 versus inverse of molecular size ($1/(\text{number of C atoms})^{1/2}$). Free valence is a measure of reactivity related to H atom addition energies.¹² Reprinted with permission from ref 11. Copyright 1987 American Chemical Society.

is only 15 kcal/mol, the corresponding difference in proton affinities is estimated as 60 kcal/mol.

σ -Electrons. While radical addition to PAHs generates delocalized π -radicals with considerable resonance stability, bond homolysis at the periphery generates localized, high-energy σ (aryl) radicals.

A relative lack of dependence of aryl radical energy and PAH structure was first shown by Swarc's finding that rates of aryl C-Br bond homolysis depended little on aryl structure.¹⁷ It was reinforced by a series of semiempirical calculations on PAHs.¹⁸

(17) Ladaki, M.; Swarc, M. *Proc. R. Soc. London, A* 1953, A219, 341; *J. Chem. Phys.* 1952, 20, 1814.

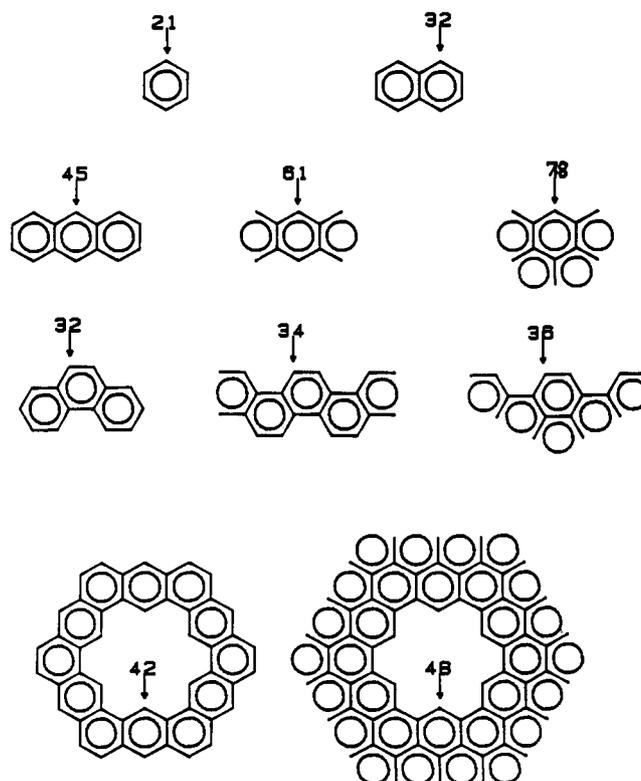


Figure 7. Enthalpies (kcal/mol) for H atom addition to conventional PAHs and their limiting values.¹²

We carried out a series of experimental studies on reactions of a series of aryl radicals, including phenyl, 1-naphthalenyl, 2-naphthalenyl, and 9-anthracenyl. Relative rates of H abstraction/arylation of toluene for these are 5.2, 4.1, 21, and 93.¹⁸ Qualitatively, differences can be explained by purely steric effects. However, since semiempirical calculations showed similar trends for the thermodynamic stabilities of these radicals, the precise origin of these differences is open to question.

Together with results of the π -electron calculations, these results strongly suggest that even at the periphery

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of very large PAHs, including graphite, except for steric differences, unsatisfied valences behave like those in conventional PAH-derived radicals. We have found no basis for unconventional radical sites involving stabilization by delocalization, a subject of occasional speculation in the older carbon literature.¹⁹

Kinetics

Two general factors are responsible for the complexity of PAH growth mechanisms. The first is the strict geometrical requirement for stable benzenoid PAHs. Most bond-forming pathways lead to strained, nonaromatic structures that need extensive rearrangement for continued growth. A second factor is the necessary involvement of slow hydrogen-transfer processes in the conversion of C-H to C-C bonds.

We now discuss the hydrogen-transfer and bond-formation reactions underlying these complex PAH transformations.

Hydrogen Transfer. Delineating hydrogen transfer between PAHs is perhaps the most difficult part of PAH mechanistic study. While substantial progress has been made in the past 10 years,²⁰ some of this work serves primarily to expose new areas of uncertainty.

The discussion of hydrogen transfer in PAH systems is divided into the following reaction types: (1) from a molecule to a radical (metathesis); (2) from a radical to a radical (radical disproportionation) and its reverse (molecular disproportionation); (3) from a radical to a molecule.

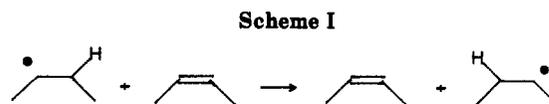
1. Metathesis. In PAH pyrolysis, simple abstraction readily scrambles H atoms on benzylic carbon atoms. These rates are comparable to the well-studied H-abstraction reactions of alkyl radicals²¹⁻²⁴ and are now relatively well understood.

The magnitude of the preexponential factor for metathesis rate constants in the condensed phase is a remaining uncertainty, with reported values for H transfer varying nearly 3 orders of magnitude^{21,23,24} although there are compensating differences in activation energy.

Predictive methods have their limits. Bockrath et al.²⁵ have found that rates were sensitive to various subtle (hard-to-estimate) steric factors.

2. Disproportionation. Because of the thermodynamic stability of the radicals dominating thermal PAH systems, the steps destroying these radicals, namely, recombination and disproportionation, are often reversible.^{5,6} This has a crucial impact on reaction mechanisms in high-temperature fluids, making it impossible, for instance, to control radical concentrations with conventional radical initiators and traps.

Disproportionation reactions are generally found to have minimal activation energies. In fact, trends in disproportionation rates for alkyl radical reactions have been interpreted by Benson solely in terms of entropy effects.²⁶ However, radicals stabilized by resonance



often disproportionate significantly more slowly than do alkyl radicals, an effect not readily explicable in terms of entropy effects. Disproportionation/recombination ratios for *tert*-butyl radicals, for example, are nearly 40 times greater than for cumyl radicals [$\text{PhC}^*(\text{CH}_3)_2$].^{27,28}

In a series of studies of resonance-stabilized radicals, we observed a wide variation in relative disproportionation/recombination rates.²⁹ For instance, self-disproportionation/recombination rates for the isomeric 9-hydrophenanthryl and 9-hydroanthryl radicals were 1.3 and 0.05, respectively. This 26-fold difference, we surmised, arose from the large differences in reaction enthalpy (-50 and -30 kcal, respectively). This idea is supported by a clear, more general correlation between these rates and exothermicity²⁹ and accounts for the difference in cumyl and *tert*-butyl radical disproportionation cited above.

While correlations between rates and thermodynamics are well-known for other types of radical reactions, they have not been reported for disproportionation. This must be at least partly due to high reaction exothermicity, resulting in a low sensitivity to thermodynamics. Moreover, the barrier for a hypothetical thermoneutral radical disproportionation reaction may be significantly lower than conventional H transfer. Using the reported linear relation between exothermicity and $\ln(k)$ (ref 29) and assuming no activation energy for recombination, the estimated "thermoneutral" activation energy for disproportionation is calculated as 8.5 kcal/mol, well below the 15 kcal/mol value typical for metathesis.

The reverse of radical disproportionation, "molecular disproportionation", is a key radical-forming step in many PAH pyrolysis systems.⁵ Since the rate of this reaction is very sensitive to reaction thermodynamics, it tends to generate only stable radicals. It appears to be largely responsible for the "background" concentrations of radicals in high-temperature PAH-containing systems.

In a study of H transfer from 9,10-dihydroanthracene to 2-ethylanthracene, we found an exceptional case³⁰ wherein molecular disproportionation becomes the rate-limiting step in a hydrogenation process. This reaction was strongly driven by the exceptional stability of the intermediate radicals. Other studies of H transfer from 9,10-dihydroanthracene to phenanthrene³¹ show a more typical situation, wherein a slow molecular disproportionation step serves as a means of generating radicals that in turn propagate a chain reaction. Such a mechanism was also proposed by Gavalas and co-workers³² in their studies of dihydronaphthalenes.

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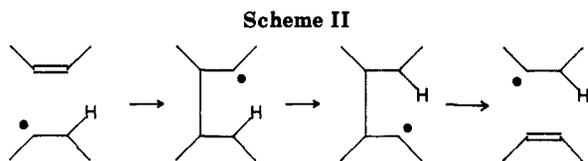
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3. Radical to Molecule H Transfer. When hydrogenated PAHs are heated above 300 °C, transfer of hydrogen from hydroaromatic to aromatic rings is commonly observed. This seemingly simple process cannot be rationalized by a conventional chain mechanism involving only bimolecular steps. A path involving a free H atom formed by unimolecular radical dissociation is the most obvious conventional process.

Nevertheless, hydrogen appears to migrate more selectively than expected if the hydrogenation agent were a free H atom. For instance, 9,10-dihydroanthracene is readily converted to other hydroanthracenes without the formation of significant amounts of H₂ (from H abstraction by H atoms).³⁰ Processes involving species of lower energy than free H atoms appear to be required. The simple but, until recently, unprecedented step depicted in Scheme I may serve as the propagation step in these reactions. This reaction has been called "radical hydrogen transfer" by McMillen and co-workers,³³ who suggest it to be of central importance in coal liquefaction chemistry.

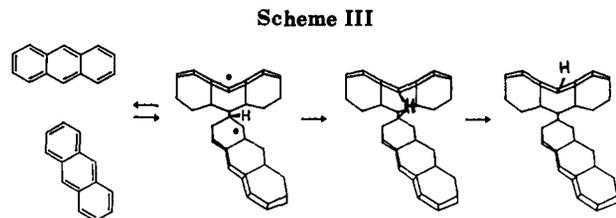
Rate constants for these reactions have been derived from two kinetic studies.^{30,31} In one, a rate constant for the near thermoneutral transfer of an H atom from one anthracene unit to another of 120 M⁻¹ s⁻¹ at 350 °C was derived, which is of the same order of magnitude as a conventional thermoneutral metathesis reaction. A rate constant of this magnitude would not be competitive with simple H atom dissociation under typical gas-phase conditions, perhaps explaining why such reactions have not been reported in the gas phase. Also, because of its high activation energy, this reaction is not competitive with radical-radical termination reactions at the lower temperatures of most previous liquid-phase free-radical studies. The "domain" of these reactions is confined to high-temperature, condensed-phase conditions.

Another determination of the rate constant for such a reaction comes from a kinetic model of the H transfer from 9,10-dihydrophenanthrene to anthracene.³¹ At 300 °C, the exothermic transfer of an H atom from the hydrophenanthryl radical to anthracene was found to be 60 times faster than for the above thermoneutral transfer between anthracene structures. Unlike paths involving the energetic H atom, this reaction is highly sensitive to thermodynamics.

While H transfer from a radical to a molecule does seem to occur, it is an open question whether this takes place in a single elementary step³³ or by a multistep process (Scheme II).

Bond Formation. 1. Intermolecular (Growth). Displacement of an H atom on an aromatic ring by an aryl radical provides a simple means of irreversibly joining aromatic units. The key factor limiting the role of aryl radicals in thermal reactions is their high energy (the C-H bond in benzene is over 20 kcal/mol stronger than the benzylic C-H bond in toluene). Also, when labile H atoms are available, aryl radicals abstract faster

(33) McMillen, D. F.; Malhotra, R.; Nigenda, S. E. *Fuel* 1989, 68, 380.



than they add.³⁴ Hence, arylation can dominate only after labile H atoms are consumed.

It is well established that at elevated temperatures aryl addition is reversible.³⁵ This leads to the curious result that net arylation rates are only indirectly related to initial addition rates. Instead they are the product of the overall equilibrium constant and reverse H atom addition step:

$$k_{\text{net}}(\text{arylation}) = K_{\text{eq}} \times k(\text{reverse})$$

Since most reported rates for arylation were obtained near room temperature, where addition is irreversible, results are not directly applicable to high-temperature arylation processes.

Any steric hindrance in the diaryl product reduces K_{eq} and hence reduces the net arylation rate. Since many of the diaryls most prone to cyclization are somewhat congested, this factor has the net effect of reducing the formation of regular benzenoid PAHs.

In some cases non-free-radical processes can also be significant. In the condensed-phase pyrolysis of anthracene over the range 400–450 °C, at low extents of reaction an unusual direct coupling process leads primarily to 2,9'-bianthracenyl.³⁶ The biradical mechanism depicted in Scheme III was proposed.

Phenanthrene pyrolysis, on the other hand, formed a nearly statistical mixture of diphenanthryls and followed kinetics as expected for a conventional aryl radical process. The difference in mechanism for phenanthrene and anthracene was attributed to the exceptional stability of π -radicals derived from anthracene in the direct coupling process.

However, in any hydrogen-starved system, direct coupling reactions can provide a relatively low energy means of generating labile hydrogen atoms which can then propagate free radical chain reactions. We suspect that such a process was significant in the condensed-phase pyrolysis of pure phenanthrene and naphthalene where alternative means of radical formation are not available. Hence, these coupling reactions may commonly serve as a means of radical initiation in hydrocarbon systems having no weak bonds.

2. Intramolecular (Condensation and Isomerization). Studies of the condensation and isomerization reactions of diaryls demonstrate that these reactions are rather slow, free-radical processes.³⁷ Even in cases with favorable geometry (1,1'-binaphthyl) and reaction conditions, these reactions were hardly faster than competing reactions leading to dissociation and growth.

A curious feature, first noted by Kline and co-workers,³⁸ is that addition of small amounts of hydrogen donors (up to ca. 5%) could increase condensation rates.

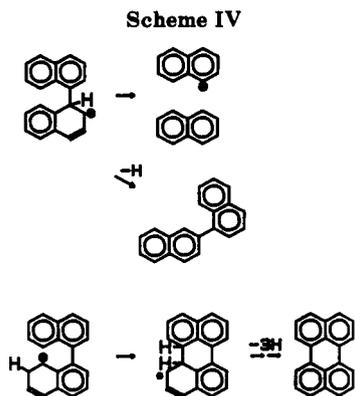
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(36) Stein, S. E.; Griffith, L. L.; Billmers, R.; Chen, R. H. *J. Org. Chem.* 1987, 52, 1582.

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That is, reducing agents (hydroaromatics) catalyzed oxidation processes (ring formation and hydrogen loss).

We carried out a series of mechanistic studies of condensation in which mechanisms were simplified by using single H atom donors (fluorene and xanthene) instead of more conventional hydroaromatic molecules.³⁷ The principal H-releasing process was simple H transfer from the donor to the diaryl (molecular disproportionation), and reactions were consistent with a mechanism starting from reduction (H addition) of the diaryl. In the case of condensation, this led ultimately to oxidation (loss of two H atoms).

The specific reaction undergone depended on the site of initial H atom attack (Scheme IV).

Summary

Our understanding of the fundamental properties of large and even macroscopic PAHs has reached a stage at which it is possible to begin to devise detailed thermal reaction mechanisms. An important simplification is the finding that the size and overall shape of a large PAH has little bearing on its free-radical chemistry. Free-radical reactivity depends on bonding in the proximity of the reaction site. Experiments on conventional PAHs can provide this information.

Of course, some very significant problems remain. A most serious one is the uncertain mechanism for transfer of an H atom from a molecule to a radical and the consequent inability to estimate rates. Also, no experimental studies of PAH growth have actually been modeled.

A major symposium entitled "From Benzene to Graphite" was held over 30 years ago.¹⁹ Driven largely by the desire to refine and apply their techniques, a number of distinguished quantum theoreticians applied their emerging methods to PAH properties and growth. Rather little similar work was done over the following 25 years. Then, driven by the desire to understand practical reacting systems, this area has reemerged as an area of fundamental study. It remains a fertile field in which the methods of quantum mechanics and experimental chemistry can work closely together to solve practical and difficult mechanistic problems.