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Thermodynamic Stability of Polycyclic Aromatic Hydrocarbons Detected in Our Environment

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Various polycyclic aromatic hydrocarbons (PAHs) are distributed widely in our environment. Diesel particulate extract contains many larger PAHs. All these PAHs have a percent resonance energy larger than 2.50. Dibenzo[def,mno]chrysene and anthracene constitute the most unstable PAHs among them. A couple of reaction paths to the formation of ovalene are discernible in flames by inspecting the combustion products. It seems likely that a similar type of reactions take place in the envelopes of carbon stars to give large compact PAHs and graphite.

Polycyclic aromatic hydrocarbons (PAHs) are formed abundantly by incomplete combustion of organic matter and fossil fuel.1,2) As a result, they are distributed virtually everywhere in our environment. Although reaction mechanisms in flames remain very elusive, formation of many PAHs has been confirmed by means of chromatographic and spectroscopic methods.1,2) Recently, Jinno et al. elaborately analyzed the Diesel particulate extract, and identified many very large PAHs.3–6) Most PAHs detectable both in our environment and in the Diesel particulate extract are devoid of side chains and substituents. PAHs can nowadays be detected in the interstellar medium.7,8) In this paper we attempt to find a rationale for the presence of such PHAs not only in our environment but also in the combustion products.

We previously defined the percent resonance energy (%RE) of a given molecule8–11) as 100 times the graph-theoretically defined resonance energy,9,12–15) divided by the total π-electron energy of the olefinic reference structure.8–11) Many examples indicate that the %RE is an excellent index for determining the thermodynamic stability of a cyclic conjugated system. We first estimate the degree of thermodynamic stability for widely detectable PAHs by evaluating the %REs. We then seek for the formation mechanisms of PAHs in incomplete combustion. Analysis of combustion processes might give an important clue to the question as to why there are large compact PAHs and graphite in the interstellar medium.7,8) Simple Hückel theory is used to calculate %REs.

Results and Discussion

The %REs of all PAHs investigated are listed in Table 1. The PAHs distributed widely in air, water, soil, and tissue are classified as group-A PAHs.1,2) They are usually formed by incomplete combustion of fossil fuel, organic matter, and plants, polluting our entire environment. It is noteworthy that all group-A PAHs have a %RE larger than 2.50 in the ground electronic state. Group-B PAHs are the ones identified in the Diesel Particulate extract by Jinno et al.5,6) These very large PAHs again have a %RE larger than 2.50. Most of the group-A PAHs are of course detectable in the Diesel Particulate extract.3,4) Thus, automobile exhaust is full

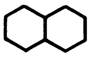
Table 1. Percent Resonance Energies of Polycyclic Aromatic Hydrocarbons

PAH	RE/β	%RE
Group A		
Naphthalene (**1**)	0.389	2.92
Anthracene (**2**)	0.475	2.52
Phenanthrene (**3**)	0.546	2.89
Pyrene (**4**)	0.598	2.73
Fluoranthene (**5**)	0.578	2.64
Benz[*a*]anthracene (**6**)	0.643	2.63
Chrysene (**7**)	0.688	2.81
Benzo[*a*]pyrene (**8**)	0.725	2.64
Benzo[*e*]pyrene (**9**)	0.791	2.87
Benzo[*b*]fluoranthene (**10**)	0.734	2.67
Benzo[*j*]fluoranthene (**11**)	0.700	2.54
Benzo[*k*]fluoranthene (**12**)	0.696	2.53
Perylene (**13**)	0.740	2.69
Dibenzo[*def,mno*]chrysene (**14**)	0.766	2.51
Benzo[*ghi*]perylene (**15**)	0.853	2.79
Indeno[1,2,3-*cd*]pyrene (**16**)	0.785	2.57
Coronene (**17**)	0.947	2.82
Group B		
Naphtho[1,2,3,4-*def*]chrysene (**18**)	0.925	2.79
Benzo[*rst*]pentaphene (**19**)	0.861	2.60
Dibenzo[*b,def*]chrysene (**20**)	0.844	2.55
Naphtho[8,1,2-*bcd*]perylene (**21**)	0.950	2.63
Naphtho[1,2,3,4-*ghi*]perylene (**22**)	1.015	2.81
Dibenzo[*cd,lm*]perylene (**23**)	0.942	2.61
Benzo[*a*]coronene (**24**)	1.118	2.85
Benzo[*pqr*]naphtho[8,1,2-*bcd*]-perylene (**25**)	1.095	2.79
Naphtho[8,1,2-*abc*]coronene (**26**)	1.162	2.75
Ovalene (**27**)	1.224	2.70
Others		
Naphtho[2,1-*a*]pyrene (**28**)	0.878	2.65
Triphenylene (**29**)	0.739	3.01
Dibenzo[*fg,op*]naphthacene (**30**)	0.983	2.96
Azulene (**31**)	0.151	1.14
Azupyrene (**32**)	0.217	0.99
Acenaphthylene (**33**)	0.354	2.18
Cyclopenta[*cd*]pyrene (**34**)	0.565	2.27
Pyracylene (**35**)	0.106	0.55

of PAHs. Dibenzo[*def,mno*]chrysene (**14**) and anthracene (**2**) constitute the most unstable PAHs among them.

Schmidt stressed that the thermodynamic stability of PAHs plays only a secondary role in determining the composition of combustion products.[16] This never means that the composition of the PAHs found in our environment are not governed by any thermodynamic factor. There are many PAHs which are less stable than dibenzo[*def,mno*]chrysene (**14**) and anthracene (**2**).[17,18] However, they have not been detected around us. Therefore, we might say that some thermodynamic factor indeed operates in the combustion process and in our environment.

Labile PAHs may be formed in substantial amounts in flames, but readily degrade thereafter. Therefore, the %REs of group-A and group-B PAHs give a good criterion for choosing PAHs which have a possibility of surviving in our environment. In other words, the %RE of 2.50 marks a borderline between stable and unstable PAHs. If a given PAH has a %RE larger than 2.50, it would not degrade readily. Such PAHs are being accumulated in our environment, polluting air, soil, water, and food.[1,2] In the polyacene series, the %REs of naphthacene and higher members are smaller than 2.50.[8] They are missing not only in the Diesel exhaust but also in our environment.[1–6]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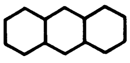
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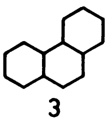
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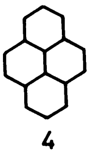
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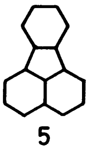
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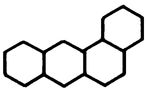
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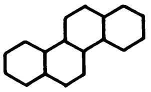
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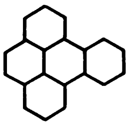
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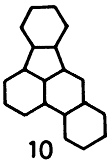
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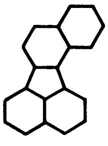
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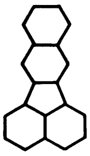
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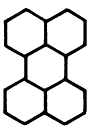
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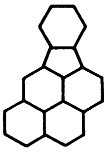
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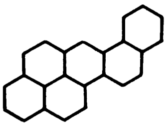
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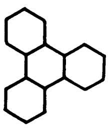
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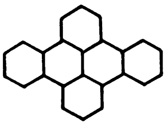
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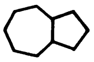
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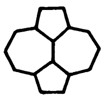
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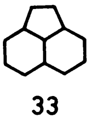
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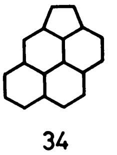
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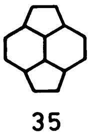
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Let us briefly review the formation mechanism of PAHs in incomplete combustion. Numerous intermediate species are involved whose sequential formation and destruction give a progression to decreasing amounts of larger species.[19–26] The largest amounts of species being produced and consumed in combustion are acetylene, 1,3-butadiyne (diacetylene), and 1-buten-3-yne (vinylacetylene).[20,21,25] These unsaturated aliphatics have been identified as important species for the growth of PAH and soot by addition reactions with aromatic radicals. Specifically, the combined presence of aromatic radicals and acetylene is particularly favorable to the growth of PAHs.[20,25]

In a hydrogen-deficient environment, rather compact PAHs with a low H/C ratio are produced preferentially. Non-compact PAHs provide active bonding sites for the attachment of smaller unsaturated species in Diels–Alder and cycloaddition reactions.[16] Compact PAHs must be less reactive in flames full of acetylenic species than non-compact ones. In this sense, the stability of compact PAHs are not only thermodynamic but also kinetic in nature. Compact PAHs, such as pyrene (**4**), dibenzo[*def,*

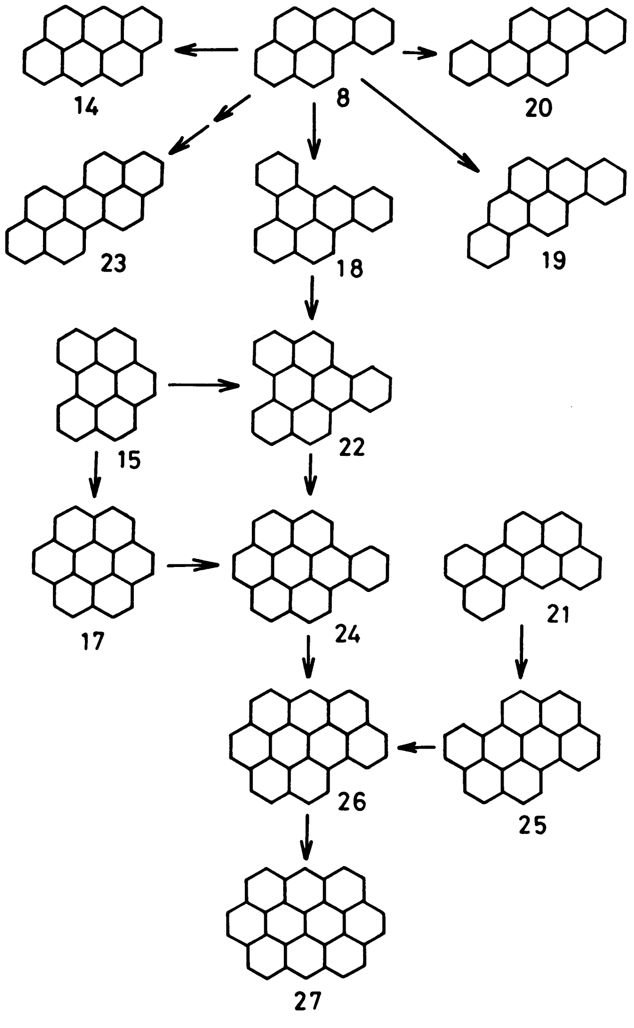

Fig. 1. Possible reaction paths in a Diesel engine.

mno]chrysene (**14**), coronene (**17**), and ovalene (**27**), are neither mutagenic nor carcinogenic.[1,27] Lack of carcinogenicity coincides with the non-existence of L and bay regions.

With such combustion chemistry in mind, possible reactions in a Diesel engine[3-6] can be inferred from the composition of combustion products. As shown in Fig. 1, most group-B PAHs can be arranged in such a manner that they constitute a couple of thermodynamically favored routes for building up ovalene (**27**), a typical large compact PAH. According to the reaction scheme of Stein[23] and Bockhorn et al.,[25] each PAH in this figure represents addition of one ring at a time. Starting with benzo[*a*]pyrene (**8**) and naphtho[8,1,2-*bcd*]perylene (**21**), individual rings are added by the formal addition of either C_4H_2 or C_2 units. Since most group-B PAHs can be arranged in this manner, it is highly probable that they are formed consecutively according to the analogous reaction scheme. Many other reaction pathways are in principle possible.

It is known that individual PAHs themselves serve to accelerate the formation of larger members of the group.[26] This further rationalizes the reaction scheme given in Fig. 1. Benzo[*ghi*]perylene (**15**) and coronene (**17**) coexist fairly abundantly in the automobile exhaust.[19] Therefore, air in Los Angeles is rich in **15** and **17**.[28] Such a comparative study supports the existence of a reaction route along which **17** is formed from **15**. There is a discontinuity between benzo[*a*]pyrene (**8**) and dibenzo[*cd,lm*]perylene (**23**) in Fig. 1. Naphtho[2,1-*a*]pyrene (**28**) must intervene between them. Although this PAH was not detected in the Diesel exhaust, it has been detected in the hard-coal combustion effluents.[16]

Various dimerization products are obtained by pyrolysis of naphthalene (**1**), among which are benzo[*j*]fluoranthene (**11**), benzo[*k*]fluoranthene (**12**), and perylene (**13**).[29] Thus, there are reaction paths along which small PAHs grow into larger ones through dimerization with elimination of hydrogen. By analogy, fluoranthenes (**5, 10, 11, 12**) and indeno[1,2,3-*cd*]pyrene (**16**) are presumably prepared by the condensation of two smaller aromatics.

Fully benzenoid hydrocarbons are the PAHs whose Clar structures consist of aromatic sextets only.[30] They are the PAHs of supreme thermodynamic stability.[8,17,18] Triphenylene (**29**) and dibenzo[*fg,op*]naphthacene (**30**) belong to the PAH family of this type. However, such PAHs are scarcely detected in the Diesel particulate extract and in our environment.[1-6] It was this fact that convinced Schmidt that thermodynamic factors are of secondary importance in combustion processes.[16] Fully benzenoid hydrocarbons have three or more bay regions, which are susceptible at high temperatures to reaction with acetylenic species.

In general, the carbon skeleton of a benzenoid PAH is stable towards isomerization and cleavage. Azulene (**31**) and azupyrene (dicyclopenta[*ef,kl*]heptalene) (**32**) thermally isomerize to naphthalene (**1**) and pyrene (**4**), respectively.[31,32] However, no reverse reaction occurs. This is why such nonbenzenoid PAHs are not found in our environment.[1-6] This is also why Fig. 1 consists of benzenoid PAHs alone. Semibenzenoid PAHs, such as fluoranthenes (**5, 10, 11,** and **12**) and indeno[1,2,3-*cd*]pyrene (**16**), seem to be free from this type of isomerization. Bay regions adjacent to a five-membered ring of a fluoranthene-type molecule appear to be much less reactive toward dienophiles.

Recently, infrared (IR) astronomy revealed that a set of discrete IR lines are emitted from many astronomical objects, such as reflection nebulae and active galaxies.[7] In 1984 Léger and Puget proposed that these IR bands can be assigned reasonably to fundamental vibrations of large compact PAHs in the interstellar medium.[33-36] These PAHs are presumably placed in the intense radiation field since they must be excited electronically in advance of IR emission. In a previous paper,[8] we supported the view of Léger and Puget by showing that many large compact PAHs have large %REs both in the ground and excited states.

Formation mechanisms of PAHs and graphite in the interstellar medium have not been clarified yet.[7] There is no evidence for the existence of small PAHs in the astronomical IR spectra. We showed that small PAHs are photochemically very unstable.[8] Then, the most plausible formation mechanism of PAHs in the intense radiation field is shattering of graphitic carbon grains in shocks.[34,37,38] However, if interstellar matter is rather dense, and if it is not exposed to hard UV radiation, the growth of PAHs and graphite from small molecular pieces is possible. This condition might be satisfied in such places as envelopes of carbon stars.[22,34]

In case PAHs are formed from smaller molecules in space, the combustion processes discussed above will give an important clue to the details of their formation mechanism. There are abundant acetylenic hydrocarbons not only in flames but also in the interstellar medium.[7] Reactions in flames must resemble those in the interstellar medium, in that large compact PAHs are formed preferentially. Thus, the formation of graphitic carbon grains and PAHs and their injection into the interstellar medium is explainable.[22,34]

Concluding Remarks

The PAHs which are formed in incomplete combustion and survive in our environment were found to be thermodynamically fairly stable. In general, the %REs of widely detectable PAHs are greater than 2.50. The PAHs with the %REs<2.50 presumably degrade rapidly in our environment. Some PAHs with the

%RE>2.50 are missing or very scanty in our environment, which may imply that they are scarcely formed in flames. For example, perylene (**13**) is very scanty in our environment for a very stable PAH.[1]

Acenaphthylene (**33**) has been detected in flames.[16,20] Cyclopenta[cd]pyrene (**34**) was isolated exceptionally from carbon black.[39] These PAHs have an olefinic C–C double bond, and their %REs are much less than 2.50. Since these PAHs are not very stable, it seems unlikely that they can survive long in our environment. Pyracylene (cyclopent[*fg*]acenaphthylene) (**35**) is essentially olefinic with a very small positive %RE. It has been reported that this compound is also formed in flames.[20,22] Synthetic pyracylene is stable only in solution, and far from isolable.[40,41]

Most of group-A and group-B PAHs are photochemically unstable with negative or small positive %REs in the electronically excited state.[8] This implies that the photochemical instability is not a crucial factor for determining the composition of combustion products. This is in marked contrast to the situation in the interstellar medium, where photochemically stable PAHs alone are probably abundant due to strong UV radiation.[8]

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