September, 1992] *Bull. Chem. Soc. Jpn.*, ***65***, *2427—2431 (1992)*

Estimation of the Mechanism of Fused Aromatic Hydrocarbon Formation in Sooting Flames by Molecular Orbital Method

Keizo SAKAGUCHI and Seishiro FUKUTANI
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University,
Yoshida-honmachi, Sakyo-ku, Kyoto 606
(Received March 16, 1992)

Formation mechanism of fused aromatic hydrocarbons in a methane–air diffusion flame was investigated theoretically and experimentally. The reactivity of hydrocarbons taking part in the formation route was evaluated by means of the *ab initio* calculation of the molecular orbitals. The reactions of the formation route are classified into two groups: Reactions increasing the number of carbon atoms of hydrocarbon molecules and aromatic ring formation. The former reactions further consist of three steps: An attack of a hydrogen atom at a certain position of a hydrocarbon molecule, addition of an acetylene molecule at that position, and dehydrogenation. The position of the large frontier electron density is chosen as the reacting point of the first step. The formation of an aromatic ring can take place when the HOMO of the hydrocarbon and the LUMO of acetylene overlap each other. The above estimation gives the following reaction route of fused aromatic hydrocarbons in methane flames: acetylene→1-buten-3-yne→benzene→ethynylbenzene→naphthalene→acenaphthylene, or naphthalene→1-ethynylnaphthalene→phenanthrene. The predicted route was also supported by experimental results.

Soot, which is formed in rich hydrocarbon flames, increases the emissivity of the flames and promotes radiational heat transfer; it causes, on the other hand, reduction of combustion efficiency if emitted from the flames in the unburned state. It is, therefore, of great importance to control the production and oxidation processes of soot, and hence to understand, in particular, its production mechanisms.

It has been accepted for the soot production mechanism in hydrocarbon flames that polyfused aromatic hydrocarbons (PAH) are first formed as soot precursors, grow up to molecules of soot, which still maintain polyaromatic structures, and finally aggregate to soot particles.[1)] The soot formation, therefore, consists of two processes: The chemical process where PAH are formed and the physical process where soot particles grow due to aggregation. Most of the studies on the soot formation have been performed on the physical processes,[2,3)] but some of them have proposed models for the chemical reactions in soot formation.[4,5)] In these papers, the formation of benzene was explained such that unsaturated chain-hydrocarbon radicals like C_6H_5 and C_6H_7 are formed and then they produce benzene molecules after cyclization into phenyl radicals. The formation of naphthalene, on the other hand, was assumed to be produced as follows: Ethynylbenzene is formed by the reaction between phenyl radicals and acetylene and is dehydrogenated at the ortho-position, acetylene is added there forming *o*-ethynylstyryl radicals, and then the two side-chains close producing naphthyl radicals. The experimental results were also analyzed by using the above chemical reaction models for soot formation. The occurrence probabilities of the above reactions have not yet been discussed in detail.

This investigation aims to recognize the most probable reaction routes of the initial processes of soot formation based on the *ab initio* evaluation of the reactivities of species which possibly participate in those processes.

Creation and extinction of chemical bonds result from the changes in the states of the participating electrons. It can, therefore, be predicted theoretically which part of a molecule is open to reactions, what structure the reaction products should possess and so on, if the states of the electrons can be described by using, for example, the frontier orbital theory proposed by Fukui et al.[6—8)] The frontier orbital theory describes a chemical reaction as a phenomenon characterized by electron transfer occurring selectively from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of reactants when both orbitals have large frontier electron densities.

Experimental

A methane–air diffusion flame was stabilized on a coaxial burner; methane issued with the average flow velocity of 15 cm s^{-1} from the inner nozzle and air flowed with 30 cm s^{-1} from the outer nozzle. The diameters of the inner and the outer nozzles were 10 mm and 50 mm, respectively. The PAH in the flame were analyzed qualitatively by gaschromatography–mass spectrometry after dissolving the condensed samples in dichloromethane and condensing, and the concentrations of gaseous species were determined by gaschromatography. A silicone OV-17 capillary column was used to separate the isomeric aromatics such as biphenylene and acenaphthylene, phenanthrene and anthracene, and unknown species were identified by comparing the obtained peaks with those of standard samples.

Estimation of Frontier Electron Density

Various programs have been developed for the *ab initio* calculation in the molecular orbital theory. The GAUSSIAN 82 code, which was devised by Pople et al.[9)] and is one of the most well-known programs, was used here; this program was adapted to the Kyoto University Data

Processing Center by Tachibana et al.[10] and registered there as a library program.

The *ab initio* calculation gives the energy levels and the wave functions of individual molecular orbitals in a ground state molecule. In flames the temperature reaches about 2000 K, but it is validly assumed that most of molecules are in their ground energy levels since the energy difference between the HOMO and LUMO of benzene, for instance, is 1.287 MJ mol^{-1}. The frontier electron density[6] at the r-th atom, f_r, which is defined as the quota of the total electron density of a frontier orbital to that atom, is evaluated by the following expression:

$$f_r = 2\sum_i \left(C_i^2 + \sum_{j \neq i} C_i \cdot C_j \cdot S_{ij}\right)$$

where C_i is the coefficient for the i-th atomic orbital of the r-th atom in the linear combination expression of the frontier orbital, and S_{ij} is the overlap integral between the i-th and the j-th orbitals and the summation for j is taken for all the atomic orbitals of that molecule except the i-th orbial. The above equation is derived on the basis of Mulliken's population analysis,[11] where the electron population of a certain molecular orbital is given by the summation of those of the atomic orbitals which are constituents of that molecular orbital. Since for radicals the HOMO and the LUMO have equal contribution,[7] the frontier electron density of a radical is assumed here to be given as:

$$f_r = (f_r^{\mathrm{HOMO}} + f_r^{\mathrm{LUMO}})/2$$

When the HOMO and/or the LUMO are degenerated such as those of acetylene and benzene, the frontier electron density was averaged among the individual orbitals.

We applied the 3-21G basis function system[12] and optimized the calculated structure of molecules. However, for hydrocarbons containing twelve or more carbon atoms we expanded the molecular orbitals with the simpler STO-3G system[13] since the application of the 3-21G system was too time-consuming.

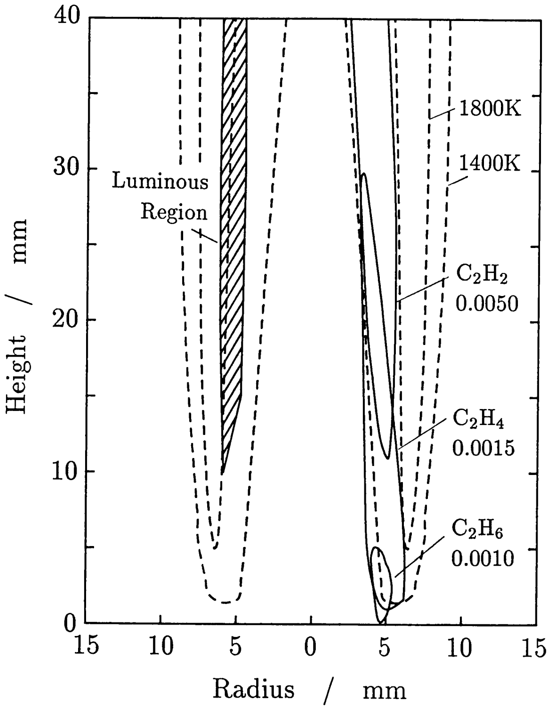


Fig. 1. Temperature, mole fractions of C_2 species and the luminous region in the methane–air diffusion flame.

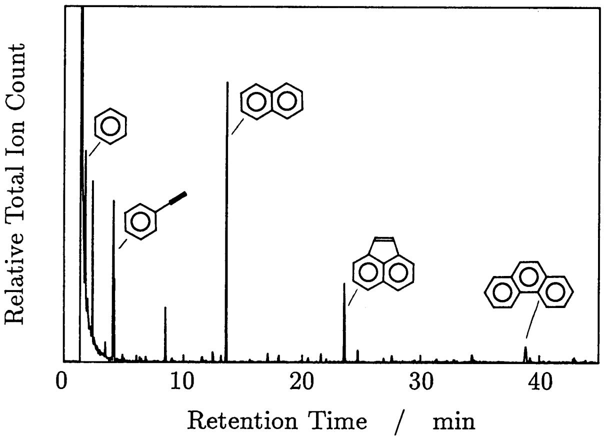


Fig. 2. Aromatic hydrocarbons detected at the lowest position of the luminous region.

Results and Discussion

The hydrocarbons experimentally detected in the methane–air diffusion flame are shown in Figs. 1 and 2. Figure 1 shows the luminous flame region and the distributions of C_2 species with the contour lines corresponding to 80% of the respective maximum concentrations. Figure 2 shows the total ion intensities of various PAH measured by GC-MS at the lowest position of the luminous zone. The PAH species detected in the methane flame were the same as those which have been reported for propane flames.[14] This figure indicates that (1) all PAH contain even number of carbon atoms suggesting that they have grown with units of C_2, (2) acenaphthylene is present in an amount larger than phenanthrene though the former is thermodynamically less stable due to its five-membered ring, and (3) phenanthrene concentration is about ten times as large as that of anthracene. According to Fig. 1, in the regions of the presence of PAH, that is, in the luminous zone and the zone a little toward the centerline, acetylene is present in the largest amount among the C_2 species, and therefore, the PAH are expected to grow through reactions with acetylene.

In the following we will discuss the ring formation mechanism by complementary use of the experimental results and the molecular orbital theory.

The investigation on the soot formation mechanism should pursue, step by step, the pathways from the starting species. The formation route of PAH in flames is divided into two stages; the increase in the number of carbon atoms and the formation of a new aromatic ring.

We have analyzed the reaction mechanisms of combustion and the first few steps toward soot formation in a methane diffusion flame;[15,16] in these studies we measured the temperature and the concentrations of stable species from C_1 up to C_4 hydrocarbons, and then calculated the distributions of active species and the reaction rates using a chemical reaction model. Those investigations have elucidated, in addition to the importance of acetylene shown in Fig. 1, that hydrogen atoms play a decisive role as active species particularly in dehydrogenation in the soot formation. These results are in good agreement with those presented in the literature.[4,5]

We accordingly assumed the following sequential reactions for the increase in the number of carbon atoms in the methane diffusion flame: (1) a hydrogen atom attacks a hydrocarbon molecule on a certain position, which is predicted by the estimation of the frontier electron density, and dehydrogenates the molecule there, and (2) an acetylene molecule is added to that point in forming the hydrocarbon with two more carbon atoms.

One of the most famous reactions forming rings is the Diels–Alder reaction. This reaction proceeds in the formation of new bonds at overlapping points of the HOMO of dienes and the LUMO of dienophile according to the theory on the interactions between the HOMO and LUMO proposed by Fukui et al.[8] The following two conditions must be satisfied for the occurrence of this reaction; the HOMO of one molecule and the LUMO of the other one overlap closely at two reacting points, and the phases of the corresponding wave functions match each other.

The Diels–Alder reaction itself does not directly yield aromatic rings. If the ring products of that reaction can be stabilized successively by dehydrogenation and hence by the delocalization of the π electrons, the Diels–Alder reaction should work as the first step of aromatic ring formation. Therefore, as for the formation of aromatic rings in the flame we will apply the mechanism composed of the Diels–Alder reaction and the dehydrogenation; this type of mechanism has not yet been applied to soot formation processes.

Bach et al. described in their theoretical study on the mechanism of benzene formation from acetylene that the HOMO's of three acetylene molecules overlap simultaneously one another.[17] But here we assumed that a benzene molecule is formed through reactions where two acetylene molecules yield 1-buten-3-yne and then this C_4 species reacts again with another acetylene molecule since the acetylene concentration is not large enough to support the termolecular reaction in the flame and the presence of 1-buten-3-yne is experimentally verified.

The initial step of the first aromatic ring formation is, as described above, assumed here to be the dehydrogenation of acetylene by an attack of a hydrogen atom forming an ethynyl radical. Another attack of an acetylene molecule on the ethynyl radical yields 1-buten-3-yne via a C_4H_3 radical. The 1-buten-3-yne further reacts with acetylene. Figure 3 illustrates the reaction producing phenyl radicals from 1-buten-3-yne and acetylene; the HOMO of 1-buten-3-yne and the LUMO of acetylene are also drawn. According to the figure the HOMO has the same phases with the LUMO of acetylene and, in addition, the LUMO of acetylene spreads outside due to its anti-bonding characteristic to overlap with the HOMO of 1-buten-3-yne. These two species, therefore, can make new bonds between the four terminal carbon atoms respectively and form a phenyl radical.

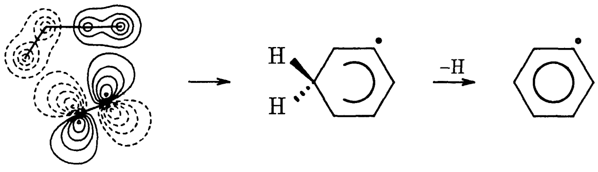


Fig. 3. HOMO of 1-buten-3-yne and LUMO of acetylene, and the reaction routes forming phenyl radicals.

Two other possible unsaturated C_4 species, 1,3-butadiene and 1,3-butadiyne, are also observed experimentally in almost the same quantities as that of 1-buten-3-yne in the methane diffusion flame. However, the first species does not participate in the main route of the soot formation since it cannot react further but is decomposed into vinyl radicals again.[16] The second species has a linear structure with larger distance between the terminal carbon atoms and its HOMO can overlap only in a small extent with the LUMO of acetylene, and therefore it cannot contribute to the benzene formation.

The paths to the second ring formation, which starts from phenyl radicals, are shown in Fig. 4. There are two possible routes from styryl radicals, which are produced by phenyl radicals and acetylene: the formation of ethynylbenzene and that of styrene. The amount of the latter species in the flame, however, is negligibly small indicating that the dehydrogenation occurs intensively, just like the promotion of acetylene formation from ethylene through vinyl radicals in the same area of the methane diffusion flame.

The previously devised models[4,5] have proposed two routes for the acetylene addition to ethynylbenzene; that at the ortho position of ethynylbenzene and that at the

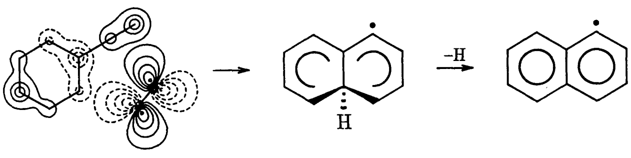
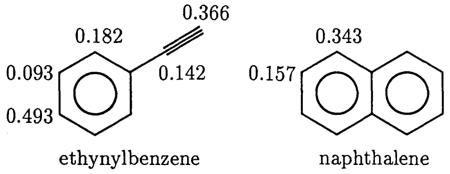


Fig. 4. HOMO of ethynylbenzene and LUMO of acetylene, and the reaction routes forming 1-naphthyl radicals.

end of the ethynyl side chain. However, according to the f_r estimation of ethynylbenzene shown in Fig. 5, *p*-diethynylbenzene should be produced in an amount larger than those of the above two species, and, in addition, according to the experimental data shown in Fig. 2, *p*-diethynylbenzene and its further products could not be found in considerable amounts. Consequently the routes proposed in the literature need to be revised.

We propose again the Diels–Alder type reaction for naphthalene formation from ethynylbenzene. As shown in Fig. 4, the phase of the HOMO of ethynylbenzene matches that of the LUMO of acetylene, and furthermore the two MO's can overlap to form the bonds to naphthalene.

The two possible routes of the third ring formation are illustrated in Figs. 6 and 7; one is the formation of acenaphthylene due to the reaction of naphthalene with one acetylene molecule and the other is that of phenanthrene due to the sequential reactions starting from 1-ethynylnaphthalene, which can be validly predicted according to the f_r estimation of naphthalene shown in Fig. 5, and acetylene.



ethynylbenzene naphthalene

Fig. 5. The frontier electron densities of ethynylbenzene and naphthalene.

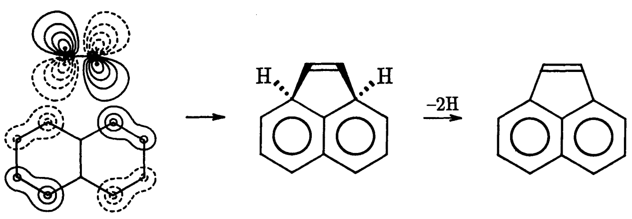


Fig. 6. HOMO of naphthalene and LUMO of acetylene, and the reaction routes forming acenaphthylene.

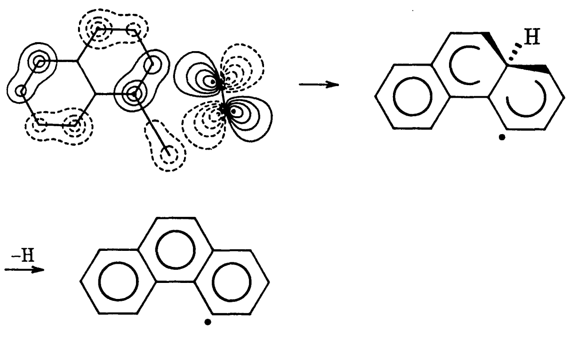


Fig. 7. HOMO of 1-ethynylnaphthalene and LUMO of acetylene, and the reaction routes forming 4-phenanthryl radicals.

As for the first route, the electron density of the HOMO of naphthalene is large at the α positions and the phases of the wave function agree with those of the LUMO of acetylene at the 4 and 5 positions of carbon atoms as shown in Fig. 6, and therefore, the bonds to acenaphthylene can be formed there according to the similar mechanism to those of benzene and naphthalene formation. Another possible route for the acenaphthylene would be that 1-ethynylnaphthalene is once produced and the C_2H side chain reacts with the ring. This is improbable because of the excessive distortion of the C_2H bond.

From the 1-ethynylnaphthalene, on the other hand, phenanthrene is produced according to the HOMO–LUMO interactions as shown in Fig. 7. This mechanism for the third aromatic ring formation cannot yield anthracene and this agrees with the experimental result shown in Fig. 2.

Conclusions

Polyfused aromatic hydrocarbons containing rings up to three are produced in methane-air diffusion flames in sequence as acetylene→1-buten-3-yne→benzene→ethynylbenzene→naphthalene→acenaphthylene, or naphthalene→1-ethynylnaphthalene→phenanthrene. These pathways were determined by estimation of the reactivities of the participating molecules and obtained as (1) the attack of a hydrogen atom on the position of the large f_r and the acetylene addition to form hydrocarbons with two more carbon atoms, and (2) the aromatic ring formation due to the interaction of the HOMO of the produced hydrocarbons and the LUMO of acetylene.

This approach would also apply to the analyses of the further reaction routes of PAH with larger molecular weights.

The authors wish to express their thanks to the Tanikawa Fund Promotion of Thermal Technology for its financial support.

References

1) A. Thomas, *Combust. Flame,* **6**, 46 (1962).

2) B. S. Haynes and H. Gg. Wagner, *Prog. Energy Combust. Sci.,* **7**, 229 (1981).

3) I. Glassman, "Twenty-Second Symposium (International) on Combustion," The Combustion Institute, Pittsburgh (1989), p. 295.

4) M. Frenklach, D. W. Clary, W. C. Gardiner, Jr., and S. E. Stein, "Twentieth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh (1985), p. 887.

5) S. J. Harris, A. M. Weiner, and R. J. Blint, *Combust. Flame,* **72**, 91 (1988).

6) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.,* **20**, 722 (1952).

7) K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.,* **22**, 1433 (1954).

8) K. Fukui, "Molecular Orbitals in Chemistry, Physics,

and Biology," ed by P. O. Löwdin and B. Pullman, Academic Press, New York (1964), p. 513.

9) J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople, "GAUSSIAN82 Release A," Carnegie-Mellon University, Pittsburgh (1982).

10) Y. Asai, A. Tachibana, H. Teramae, and M. Koizumi, *Koho, Data Processing Center, Kyoto University,* **19**, 389 (1986).

11) R. S. Mulliken, *J. Chem. Phys.,* **23**, 1833 (1955).

12) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.,* **102**, 939 (1980).

13) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.,* **51**, 2657 (1969).

14) H. Bockhorn, F. Fetting, and H. W. Wenz, *Ber. Bunsen-Ges. Phys. Chem.,* **87**, 1067 (1983).

15) K. Sakaguchi, S. Fukutani, and H. Jinno, *Nippon Kagaku Kaishi,* **1988**, 2037 (1988).

16) K. Sakaguchi, S. Fukutani, and H. Jinno, "Joint International Conference Australia/New Zealand and Japanese Sections," The Combustion Institute (1989), p. 79.

17) R. D. Bach, G. J. Wolber, and H. B. Schlegel, *J. Am. Chem. Soc.,* **107**, 2837 (1985).