

# QUANTUM MECHANIC STUDY OF HIGH MOLECULAR MASS COMPOUNDS IN COMBUSTION CONDITIONS

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## Abstract

Experimental studies on soot formation show interesting trends that can only be explained by a polymerization pathway. These experimental findings are reviewed and ab initio calculations are used to evaluate possible mechanistic pathways. A sequence of chemical reactions between aromatic compounds and compounds containing conjugated double bonds was studied in detail.

The reactions analyzed represent a first possible propagation step of a sequence that can be easily repeated for the formation of high molecular mass compounds. The distinguishing features of the proposed model lie in the chemical specificity of the routes proposed. The aromatic radical attacks the double bond of five-membered ring PAH giving addition reactions. This is allowed by specific compounds that are exceptional monomers as they form resonantly stabilized radical intermediates, relieving part of the large strain in the five-membered rings by linear polymer formation.

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## Introduction

The generation by combustion processes of airborne species of current health concern such as polycyclic aromatic hydrocarbons (PAH) and soot particles necessitate a detailed understanding of chemical reaction pathways responsible for their formation. A significant research effort on PAH and soot formation has been undertaken during recent years<sup>1-3</sup>. Soot and the growth of hydrocarbons up to low molecular weight gas phase polycyclic aromatic hydrocarbons (PAH) have been well characterized in a variety of combustion conditions. However, the transformation from low molecular weight organic gas phase species to particulate matter is less understood since high molecular weight carbonaceous species formed during this process are difficult to analyze with certainty by conventional methods.

A large portion (75-90%) of organic material remains unresolved in analyses of power plants, diesel engines and other combustion exhausts as well as in atmospheric studies. These compounds are formed at a high rate in rich flames just downstream of the flame front and their concentration accounts for the total amount of soot formed in slightly-sooting conditions<sup>4,6</sup>. Light scattering measurements have shown that they build-up rapidly to nano-sized particles and their dimensions remain constant up to the inception of soot. At this point, coagulation starts, the scattering signal increases by orders of magnitude and larger particles are formed<sup>7-8,4</sup>.

In the inception region of slightly sooting flames, spectroscopic studies show that these compounds are transparent to the visible light, but absorb, scatter, and fluoresce in the ultraviolet region, suggesting the presence of nanometer-sized particles comprised typically of aliphatic and aromatic functionalities<sup>7</sup>. It has been observed that the total amount of carbonaceous material is formed by a very early inception of organic carbon nanoparticles and soot inception starts later on through a dehydrogenation and internal rearrangement of the organic carbon toward more aromatic graphitic structures without significant contribution of surface growth. These results have an important impact on the modeling of the formation of carbonaceous aerosols in flames. Other than the formation of soot, the formation of other classes of organic aerosol needs to be considered.

The experimental evidences described above brought to consider an alternative route for the formation of high molecular mass compounds faster than the classical HACA mechanism used to model PAH and soot formation<sup>9</sup>. A new kinetic mechanism for the formation of PAH and nanoparticles has been developed by D'Anna and Violi<sup>10-11</sup> where aromatic compounds are rapidly formed in the main flame region through the combination of resonantly stabilized radicals; they grow up to 2-, 3-rings attaining a concentration

level in flames comparable to the total concentration of soot, PAH and high molecular mass aromatics. As a consequence, the formation of high molecular mass aromatics and soot are considered just a rearrangement of PAH. High molecular mass aromatic compounds are postulated to form by the reactive polymerization of small PAH<sup>10-12</sup>. Soot inception consists in the progressive aromatization of the initially less aromatic structures through an H-atom abstraction process. The abstraction of H-atoms creates additional double bond and consequently fused aromatic rings in the cluster, with the increased extension of aromatic islands inside the structure.

This paper describes a new model developed to explain some of experimental results reported above and which is still in an evolutionary state. A molecular-level analysis of the relevant chemical reaction is used here to develop an understanding of the pathways for molecular weight growth. Particularly DFT was applied in order to obtain schematic energy profiles for the channel of reactions. Recent experimental results obtained by Prof. Homann in Darmstadt<sup>13</sup> and Prof. Pugmire<sup>14</sup> at the University of Utah provide support for the pathways being proposed.

### **Calculation procedure**

The geometries of reactants as well as intermediate, and products have been optimized by using the hybrid density functional B3LYP method (i.e. Becke's three-parameter non local exchange functional<sup>15</sup> with the non local correlation function of Lee, Yang and Parr<sup>16</sup>), with the 6-31G(d,p) basis set<sup>17</sup>. All the energies cited below include ZPE corrections in units of Kcal/mol. All the stationary points were identified by the number of imaginary frequencies (NIMF) with NIMF=0 for a stable species and NIMF=1 for a transition state. All the calculations have been performed by using the Gaussian 98 program<sup>18</sup>.

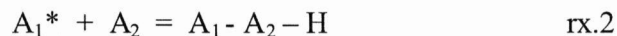
### **Results**

High molecular mass compounds can be formed in a sequence of chemical reactions between aromatic compounds with 6  $\pi$ -electron, i.e. benzene, naphthalene, and compounds containing conjugated double bonds i.e., acenaphthylene, cyclopentadiene, indene. The importance of cyclopentadienyl moieties in PAH growth and soot formation has been postulated because these radicals are neutral (stabilized by resonance) and ambident (reactive at different sites).

The sequence begins with the H-abstraction from aromatic compounds to produce the corresponding radical<sup>19</sup>.



The resulting radical furnishes higher aromatics through either a two-step reaction (radical-molecule reaction)

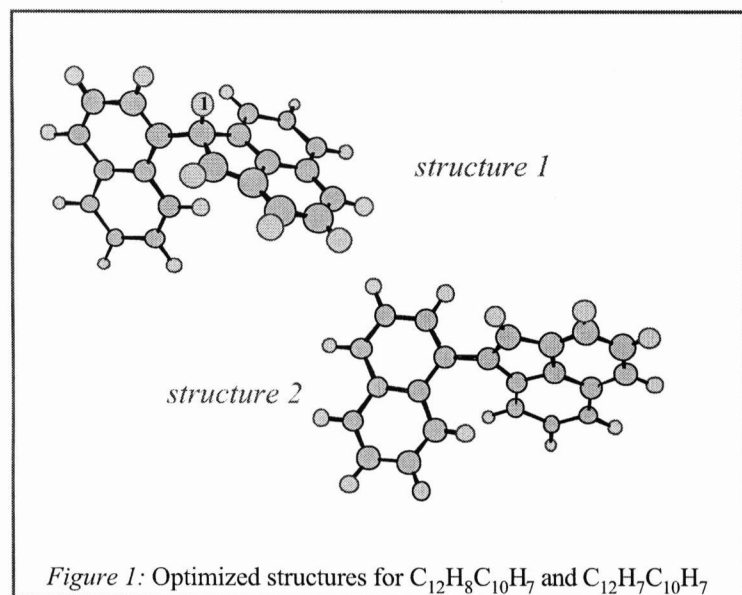


where  $A_1 - A_2 - H$  represents an intermediate formed through addition reaction, or a direct addition to another aromatic radical (radical-radical reaction):



Iteration of this mechanism followed by rearrangement of the carbon framework ultimately leads to high molecular mass compounds.

In this study the above described reaction pathways are analyzed in detail. The two reactants chosen are naphthyl ( $C_{10}H_7$ ) and acenaphthylene ( $C_{12}H_8$ ). The reaction of naphthyl and acenaphthylene begins with the formation of the intermediate  $C_{12}H_8C_{10}H_7$  ( $A_1 - A_2 - H$  in rx.2) species, reported as structure 1 in figure 1. This intermediate is produced by the addition of naphthyl to the double bond of acenaphthylene. A  $\pi$



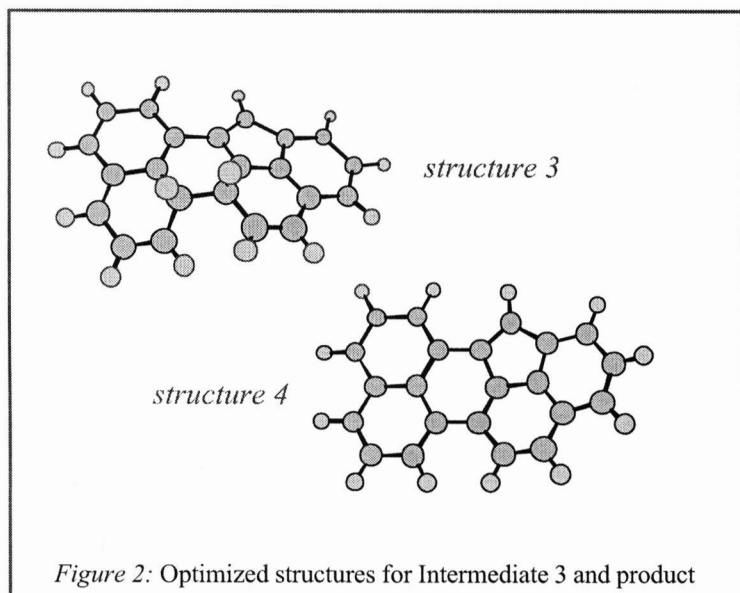
bond is broken and a  $\sigma$  bond is formed. The specific site in acenaphthylene structure (fig. 1) has been chosen in this study because of its aliphatic character and because it reacts with electrophilic reagents giving addition reactions. A deeper analysis of the different sites of acenaphthylene molecule is reported elsewhere<sup>19</sup>, together with the calculation of the reaction rates. Aromatic species are usually considered to give substitution reactions, but there are some compounds which have double bonds

that can be easily broken, giving addition reactions, i.e. 9,10 bond in phenanthrene<sup>20-21</sup> and the double bond in the five-membered ring such as acenaphthylene<sup>20</sup>. Due to the steric overcrowding also the H bonded to the  $sp^3$  C of the five member forms angles of  $108^\circ$  with the acenaphthylene plane. The new C-C bond is formed without encountering a barrier; the potential energy surface has an attractive character. The  $C_{12}H_8C_{10}H_7$  has energy about 40 Kcal/mol lower than that of the reactants, at our B3LYP level.

In a rich combustion environment high concentrations of H-atom are available, so intermediate 1 can undergo an abstraction reaction. In particular H1 can be abstracted by a H atom present in the gas bulk. Structure 2 in fig.1 reports the product ( $C_{12}H_7C_{10}H_7$ ) obtained after the H abstraction. The two electrons on the molecule arrange themselves, giving back a double bond in the five-membered ring. H-abstraction is exothermic because of the restoration of the resonance structures.

The product lies by 106 Kcal/mol lower in energy than the reactants. At the B3LYP level no transition state has been identified in the rx. 3 pathway from intermediate 1 ( $C_{12}H_8C_{10}H_7$ ) to intermediate 2 ( $C_{12}H_7C_{10}H_7$ ). This means that if the transition state exists, its energetic barrier is within the uncertainty of the level B3LYP (4-5 Kcal/mol). Since this value is very small, as the intermediate is formed, it rapidly forms the product. Reaction 2, specifically (naphthyl + acenaphthylene =  $C_{12}H_8C_{10}H_7$ ) can therefore be considered to be irreversible. Equilibrium is reached between reactants (naphthyl and acenaphthylene) and products<sup>19</sup>. The sequence analyzed above can be considered as the first propagation step of a sequence that can be easily repeated, i.e. starting from the product reported in fig.1 as structure 2, through further H-atom abstractions, it is possible to get compounds with higher molecular mass.

The energetic paths for following propagation steps (further addition of acenaphthylene) have the same trend as in the first sequence. The relative energetic barrier will be smaller due to the greater stability of

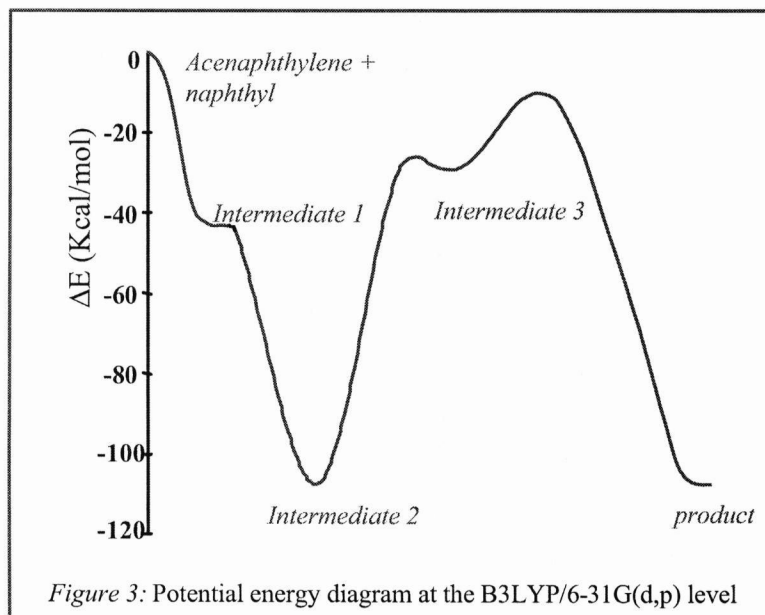


the higher molecular weight compounds.

Soot inception consists in the progressive aromatization of the initially less aromatic structures through an H-atom abstraction process. The abstraction of H-atoms creates additional double bond and consequently fused aromatic rings in the cluster, with the increased extension of aromatic islands inside the structure. To give an idea of this process another possible pathway is considered which includes the H-H elimination and ring closure of the

intermediate  $C_{12}H_7C_{10}H_7$ . Figure 2 reports the intermediate 3 and the product for this process starting from  $C_{12}H_7C_{10}H_7$ . Figure 2 shows the optimized structures for the intermediate 3 (structure 3) obtained after the ring closure, and the product  $C_{12}H_6C_{10}H_6$  (structure 4) after the H-H elimination.

The relative energy  $\Delta E$  (Kcal/mol) diagram for the pathway above described is reported in figure 3. The reference value considered for this graph is represented by the sum of the contribution of naphthyl, acenaphthylene and H atom, the latter being involved in the second part of the reaction sequence (rx.3).



### Supporting Experimental Findings

The concept of the linking of 2-, 3-aromatic rings in open structures that grow to yield nanoparticles that subsequently dehydrogenate to form soot provides an explanation for the following experimental observations:

1. Dobbins and co-workers<sup>22-23</sup> studied the chemical evolution of soot precursor particles on the centerline of the laminar ethane diffusion flame using laser microprobe mass spectrometry (LMMS). The analysis revealed the presence of the sequence 252, 276, 300 amu to be prominent masses in precursor particles sampled. LMMS analyses of young soots yield fragments with carbon numbers of 16 to 22 that correspond to 2-, 3-ring aromatic compounds or their dimers, which might be produced by laser microprobe breaking some of the cross-links.
2. Homann and co-workers<sup>13</sup> studied a benzene-oxygen flame for a large PAH molecules and radicals using molecular beam sampling combined with REMPI ionization and time-of-flight mass spectrometry. They reported in a C-H diagram the variety of molecular formulae and identified H-rich compounds as the compounds with H content higher than the corresponding peri-condensed ring structures. The authors showed that the growth of PAH does not follow a narrow path in a C-H diagram but a broad band in which H-rich PAH play an important role. The new model allows the formation of high molecular mass aromatics having H/C ratios higher than those of polybenzenoid structures of equal molecular weight with few condensed rings connected by aliphatic bonds. The presence of these compounds cannot be explained considering only a growth process of sequential addition of acetylene to aromatic rings.
3. Pugmire and co-workers<sup>14</sup> conducted <sup>13</sup>C NMR measurements of young soots and their precursors formed by the injection of anthracene and pyrene in flames. Their analyses showed that soot growth

consists of ring size growth and cluster cross linking which results in the formation of large cross linked structures. The large number of cross link sites per cluster suggests that a significant amount of cluster polymerization has occurred.

### **Conclusions**

In this work a possible reaction pathway is reported for the aromatic growth. The reactions analyzed here represent a sequence that can be easily repeated for the formation of high molecular mass compounds. The distinguishing features of the proposed model lie in the chemical specificity of the routes proposed. This is allowed by specific compounds which are exceptional monomers as they polymerize rapidly forming resonantly stabilized radical intermediates, relieving part of the large strain in the five-membered rings by linear polymer formation. The model proposed here add chemical specificity to the reactive coagulation process considering radical-molecule sequence of reactions involving gas-phase PAHs having conjugated double bond. The radical species attacks the  $\pi$  bond starting the propagation reaction. In particular, the chemical pathway proposed shows the importance of intermediate reactions that lead to thermodynamically stable intermediates during molecular weight growth.

Formation pathways for high molecular mass compound growth are presented, showing how specific reactions between aromatic moieties can be used to explain recent experimental findings. Previous studies have shown interesting experimental trends that can only be explained by the proposed pathway.

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## References

- <sup>1</sup> Lahaye J. Prado G, editors. Soot in combustion systems and its toxic properties, New York: Plenum Press, 1981.
- <sup>2</sup> Siegl DC, Smith GW, editors. Particulate carbon formation during combustion, New York: Plenum Press, 1981.
- <sup>3</sup> Bockhorn H, editors. Soot formation in combustion: mechanisms and models, Berlin: Springer, 1994.
- <sup>4</sup> Minutolo, P., Gambi, G., D'Alessio, A., *Proc. Combust. Inst.*, **27**:1461 (1998).
- <sup>5</sup> Ciajolo, A., D'Anna, A., Barbella R., Tregrossi, A., Violi, A., *Proc. Combust. Inst.*, **26**:2327 (1996).
- <sup>6</sup> D'Alessio, A., D'Anna, A., Minutolo, P., Sgro, L.A., Violi, A., *Proc. Combust. Inst.*, **28**: in press (2000).
- <sup>7</sup> D'Alessio A., D'Anna A., Gambi G., and Minutolo P., *J. Aerosol Sci.* **29**:397 (1998).
- <sup>8</sup> D'Alessio A., D'Anna A, D'Orsi A., Minutolo P., Barbella R. and Ciajolo A., *Proc. Combust. Inst.*, **24**:973 (1992).
- <sup>9</sup> Frenklach M., and Wang H., in Soot formation in Combustion, p. 165, H. Bockhorn (Ed.), Springer-Verlag, Heidelberg (1994).
- <sup>10</sup> D'Anna, A., Violi, A., *Proc. Combust. Inst.*, **27**: 425 (1998).
- <sup>11</sup> D'Anna A., Violi A., D'Alessio A., Sarofim A.F., *Comb. & Flame*, submitted, (2001).
- <sup>12</sup> Violi A., D'Anna A., and D'Alessio A., *Chem. Eng. Sci.* **54**:3433 (1999).
- <sup>13</sup> Keller A., Kovacs R., Homann K.-H., *Phys. Chem. Chem. Phys.* **2**:1667 (2000).
- <sup>14</sup> M.S. Solum, A.F. Sarofim, R.J. Pugmire, T. Fletcher, H. Zhang, *Energy & Fuels*, Submitted, (2001).
- <sup>15</sup> (a) Becke, A.D. *J. Chem. Phys.* 1992, **96**, 2155-2160. (b) 1992, **97**, 9173-9177. (c) 1993, **98**, 5648-5652.
- <sup>16</sup> Lee, C.; Yang, W. and Parr, R.G., *Phys. Rev. B.*, **37**:785, (1998).
- <sup>17</sup> Hehre W., Radom L., Schleyer P., R., Pople J. A., *Ab initio Molecular Orbital Theory*, Wiley, New York, 1986.
- <sup>18</sup> M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M.W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98, Revision A.7*, Gaussian, Inc., Pittsburgh PA, 1998.
- <sup>19</sup> Violi A., Truong T.N., Sarofim A. F., *Combustion and Flame*, Submitted (2001).
- <sup>20</sup> Badger, G.M., *Aromatic Character and Aromaticity*, Cambridge University Press, 1969.
- <sup>21</sup> Clar, E., *The Aromatic Sextet*, John Wiley & Sons, 1972.
- <sup>22</sup> Dobbins R.A. and Subramaniasivam, H., in Soot formation in Combustion, p. 290, H. Bockhorn (Ed.), Springer-Verlag, Heidelberg (1994). Dobbins, R.A., Fletcher, R.A., and Chang, H.-C., *Combust. Flame.* 115:285 (1998).
- <sup>23</sup> Dobbins, R.A., Fletcher, R.A., and Chang, H.-C., *Combust. Flame.* 115:285 (1998).