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DEVELOPMENT OF PREDICTIVE REACTION MODELS OF SOOT FORMATION

Annual Technical Report

Grant No. AFOSR 91-0129

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INTRODUCTION

This is a second-year annual report on the project. The ultimate objective of this program is to develop a predictive reaction model for soot formation in hydrocarbon flames. The specific objectives of the proposed 3-year study are: 1) To extend the modeling efforts to computer simulation and analysis of more complex sooting phenomena, such as sooting limits in laminar premixed flames, soot formation in premixed flames of aromatic fuels, and soot formation in laminar diffusion flames, and 2) Further refinement of the underlying reaction mechanism of soot formation.

WORK PROPOSED

The specific objectives for the past year were:

1. To complete simulations of the sooting limits in a series of laminar premixed flames and examine the results.
2. To complete the revision and testing of the neutral reaction mechanism of PAH formation and growth.
3. To revise the computer code for soot particle nucleation and growth, i.e., to insert the optical model developed into our main soot-kinetics code.
4. To perform quantum-chemical calculations on additional ion-molecule reactions of interest to the ionic mechanism of soot formation and perform the associated rate-coefficient calculations.
5. To initiate a computational study of pressure effect on soot formation since this subject is of interest due to growing concern over controlling soot emission from practical combustion devices.
6. To prepare manuscripts reporting the results of (1) – (4) above.

ACCOMPLISHMENTS

During the second twelve-months period of the project, progress has been made in all the areas, (1)-(5) above. The principal accomplishments of the past year are the following: (1) The computational study of sooting limits in laminar premixed flames was completed. It was found that the critical equivalence ratios for soot appearance, both the absolute values and temperature dependencies, can be predicted fairly close to the experimental observations. Sensitivity and reaction-path analyses were performed to examine the factors responsible for the computed behavior. (2) New estimation techniques were developed and applied for calculations of standard-state enthalpies of formation and binary gaseous diffusion coefficients of polycyclic aromatic hydrocarbons (PAHs) and their radicals, thus providing critical information for accurate modeling of soot formation in flames. (3) Theoretical studies of a bench-mark ion-molecule reaction were completed. (4) Computer simulations of the effect of pressure on soot formation were initiated. (5) Several manuscripts summarizing the results obtained have been completed and submitted for publication. The results obtained are detailed below.

RESULTS

Sooting Limits in Laminar Premixed Flames

The critical equivalence ratios were determined for several atmospheric laminar premixed flames of C_2-fuels: ethane, ethylene and acetylene. The value of the critical equivalence ratio, ϕ_c, for a given fuel and a given maximum flame temperature, T_m, was determined by computing flames with different equivalence ratios. The maximum flame temperature in these runs was maintained approximately the same by adjusting, similarly to the experiment, the amount of N_2 in the mixture. For each of the fuels, at least two series of flames were simulated, each at a different maximum flame temperature, in order to test the temperature dependence predicted for ϕ_c.

The numerical simulation of soot particle formation was performed in two stages: first, the production of the initial PAH species; and second, PAH further growth and nucleation and growth of soot particles. In the first stage, PAH formation up to coronene was simulated in a burner-stabilized flame configuration with a specified temperature profile and flow rate. The temperature profile and the flow rate were those computed from an equivalent free adiabatic flame, with only small-hydrocarbon chemistry included (primarily C_1 to C_4, 32 species, 139 reactions). In other words, the free-flame simulation with the reduced chemistry was used to determine the initial conditions, temperature profile and gas velocity for the subsequent burner-stabilized flame simulation with the "full" chemistry that included the desired PAH formation and growth reactions. Such two-step "free flame" simulations were almost identical, with respect to the predicted concentrations of the principal radicals and molecular products, to equivalent free flames computed with the "full" reaction mechanism. Yet, splitting the calculations in this fashion saved substantial amounts of computational time.

The maximum temperature reached in the free-flame simulation, with a given ϕ, was matched to the corresponding experimental value measured by Harris et al.[1]. The adjustment of the maximum flame temperature was accomplished, similarly to the experiment, by varying the amount of N_2 present in the mixture, but not necessarily equal to the experimental level of dilution, and being typically 5% higher in N_2 mole fraction.

All the calculations in the first stage were carried out with the Sandia burner code,[2] using forward differencing on the convective terms with a mesh consisting of 160–210 grid points. The runs were performed without considering thermal diffusion. The effect of thermal diffusion is not significant at the conditions of interest to the present study, as was found out in test runs.

In the second stage, the profiles of H, H_2, C_2H_2, O_2, OH, H_2O and acepyrene (A4R5) obtained in the flame simulation were used as input for the simulation of the growth of PAHs beyond acepyrene by the technique of chemical lumping and the soot particle nucleation and growth by a method of moments. The calculations were performed using an in-house kinetic code. The mathematical and computational details of this part of the model can be found in Ref. 3.

The gas phase and surface reaction mechanisms used in both stages of the calculations were essentially the same as the ones developed earlier.[3,4] Briefly, the reaction mechanism used in the first stage consisted of 337 reactions and 70 chemical species and included a detailed description of fuel pyrolysis and oxidation and the formation and growth of aromatics up to coronene. The chemical model used in the second stage describes the growth of PAHs beyond acepyrene, the coagulation of the planar PAHs into spherical particles and the growth of the resulting particles by coagulation and surface growth via PAH condensation and heterogeneous reactions with C_2H_2. The surface processes were described in terms of elementary chemical reactions of active surface sites. The oxidation of the soot particles was described by the reactions of active surface sites with O_2 and of soot particles with OH. The rates of the surface reactions were expressed as previously,[3]

$$k_{g,s}\, C_g\, \alpha\, \chi_s\, S$$

where $k_{g,s}$ is the per site rate coefficient, C_g the concentration of the colliding gaseous species g, α the fraction of surface sites available for a given reaction, χ_s the number density of surface sites, and S the total particle surface area. The steric factor α was introduced[4] to account for the fraction of surface carbon sites capable of undergoing growth reactions with C_2H_2 and oxidation with O_2. In the present work, this steric property was represented as a function of the maximum flame temperature in the form

$$\alpha = \frac{1}{2}\left[\tanh\left(\frac{12180}{T_m} - 7.19\right) + 1\right]$$

Such representation warrants that α approaches unity at the low temperature limit, implying that in this limit the outer carbon atoms of the soot particle comprise a locally open structure such that every carbon site is available for further reaction, and becomes zero at an infinitely high temperature, when the annealing covers the particle with the unreactive basel planes of the aromatic rings. The above expression was obtained by fitting the values of α determined in the previous study,[4] i.e., $\alpha = 0.1$ at 2000 K and $\alpha = 0.7$ at 1600 K.

In the experiments of Harris et al.,[1] the critical equivalence ratio for the appearance of soot was determined by observing the onset of yellow light emission in a flame. To be consistent with this, the critical equivalence ratio ϕ_c in our simulations was determined from the computed luminous intensity flux emitted by soot particles.[3] We assumed that the critical equivalence ratio is reached when the luminous intensity flux undergoes a sudden rise, i.e., the critical ϕ is defined at the point of maximum curvature in the normalized luminous flux plotted against the equivalence ratio, or in practical terms, by the intercept on the ϕ-axis made by the line tangential to this curve. Associated with some uncertainty, this procedure was found to provide a most consistent way of obtaining ϕ_c in the present modeling study, in light of the lack of quantitative information for the onset of soot appearance in the comparable experimental studies. Such determination procedure was found to be also consistent with the spectral sensitivity of the human eye: assuming a circular burner with a diameter of 6 cm and an observer's eye located at a distance of 50 cm from the soot inception zone, the absolute value of the radiant flux calculated at the critical equivalence ratio determined in the manner described above is of the same order of magnitude with the absolute threshold of human vision (the latter data are taken from Wald[5]).

The critical equivalence ratios determined in this manner for the three fuels are displayed in Fig. 1, where they are compared with the experimental data of Harris et al.[1] As can be seen in this figure, the computed critical equivalence ratios follow the correct temperature dependence for each fuel, i.e., the critical equivalence ratio increases as the flame temperature increases, and the correct dependence on fuel type, for a constant flame temperature T_m, i.e., acetylene soots earlier than ethylene which soots earlier than ethane. The quantitative agreement between the computed and experimental values of ϕ_c is also reasonable, considering the lack of the precise experimental data for model input and boundary conditions, uncertainties in the model parameters, and the fact that the reaction mechanism was adopted from the previous study[4] without any adjustments.

The analysis of the computational results strongly suggested that the appearance of soot and hence the sooting limits in these flames is controlled by two factors: concentration of acetylene and the growth of PAHs. The second factor—the PAH build-up—is limited by the rise in flame temperature towards the end of the main reaction zone. The oxidation of PAHs, the molecular precursors to soot particles, was not found to be a controlling factor. This does not mean, however, that hydrocarbon oxidation does not play a role in soot formation. On the contrary, oxidation of pre-aromatic-ring species, like C_2H_3 by O_2, determines to a great degree the concentration level of phenyl, the first aromatic ring. Also, the oxidation of PAHs by OH begins to be more pronounced in locations away from the main flame zone, where OH becomes the dominant oxidant.

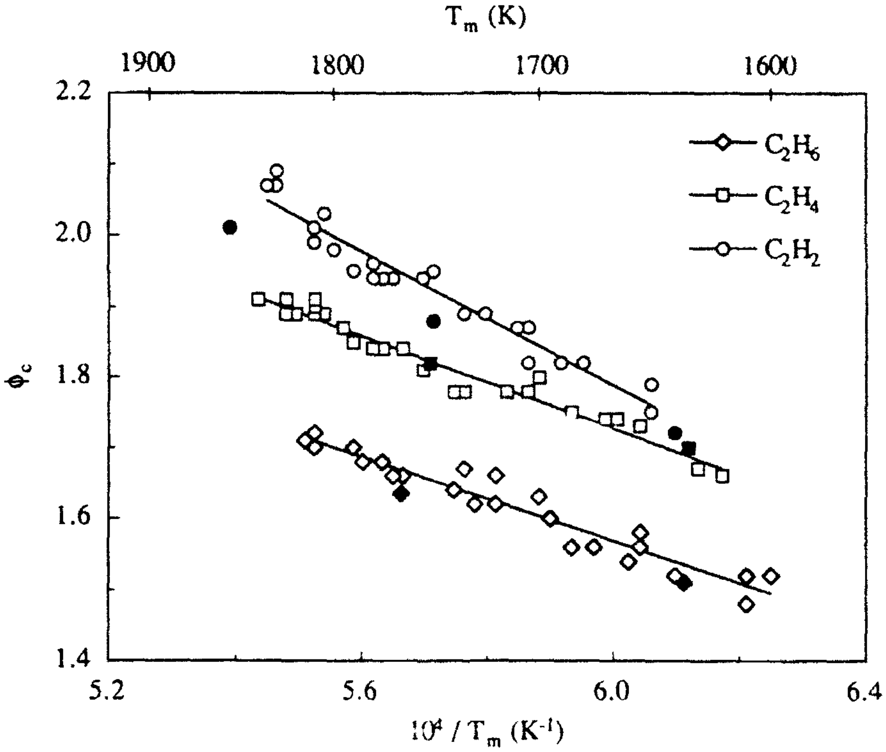


Figure 1. Comparison of the computed and experimentally determined critical equivalence ratios ϕ_c for ethane, ethylene and acetylene flames, as a function of the maximum flame temperature T_m. The open symbols represent the experimental data of Harris et al.,[1] solid lines—linear fits to the experimental points, and solid symbols—the present computational predictions.

As part of the ongoing efforts on soot formation model development and refinement, the enthalpies of formation of polycyclic aromatic hydrocarbon (PAH) molecules, radicals and substituted aromatics were investigated. The enthalpy data used in previous and current modeling efforts have been mainly derived from Benson's group additivity method.[6] Recent results from ab initio quantum mechanical calculations have shown that for large peri-condensed PAHs, the enthalpies of formation predicted by the group additivity method could be off by as much as 10 kcal/mol.[7] The objective of the present work was to determine accurately the enthalpies of formation for the major aromatic species involved in the growth of PAHs and soot in high-temperature environments. These species include PAH molecules up to 3-circumcoronene, PAH radicals up to coronyl, and some substituted aromatics.

A method for accurate and economical estimation of the enthalpies of formation for benzenoid aromatic species was developed which combines semiempirical quantum-mechanical calculations with group corrections. In this method, the deviation between experimental and calculated enthalpies of formation is partitioned into structural groups. The general idea is to use a calculation method which is computationally less demanding than quantum ab initio but physically more realistic than group-additivity calculations, and then to correct the results using a group-additivity scheme for the numerical inaccuracy of the semiempirical quantum-chemical method. The advantage of this approach is that it can be applied consistently to both molecules and radicals. The results of the present study demonstrate that the suggested approach is capable of accurate estimation of $\Delta_f H^\circ_{298}$ for benzenoid aromatics.

The AM1 method of the AMPAC and MOPAC computer packages was used for the calculations. The AM1-group correction (AM1-GC) method developed here assumes that the deviation between the experimental and calculated enthalpies of formation can be partitioned into structural groups that comprise the chemical species. It is further assumed that the group correction of a given structural group is independent of the overall molecular structure. If we denote the contribution of the ith structural group to the overall deviation by a group correction property, GC_i, the enthalpy of formation ($\Delta_f H^\circ_{298}$) can be expressed by

$$\Delta_f H^\circ_{298} = \Delta_f H^\circ_{298}\,(\mathrm{AM1}) - \sum_{i=1}^{N} \mathrm{GC}_i \qquad (1)$$

where $\Delta_f H^\circ_{298}$ (AM1) is the AM1 enthalpy of formation and N the total number of the structural groups. The group assignment was the same as that of Benson's group-additivity method, i.e., one perimeter C–H group, $[\mathrm{C_B}\text{–}(\mathrm{H})]$, and three fused-carbon groups, $[\mathrm{C_F}\text{–}(\mathrm{C_B})_2(\mathrm{C_F})]$, $[\mathrm{C_F}\text{–}(\mathrm{C_B})(\mathrm{C_F})_2]$ and $[\mathrm{C_F}\text{–}(\mathrm{C_F})_3]$.

The GC values for the aromatic groups described above were derived by weighted least-squares minimization of

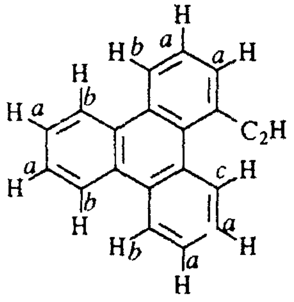
$$\sum_{k=1}^{K} w_k \left[\Delta_f H^\circ_{298,k}(\mathrm{expt}) - \Delta_f H^\circ_{298,k}(\mathrm{AM1}) + \sum_{i=1}^{N_k} \mathrm{GC}_i \right]^2 , \qquad (2)$$

where $\Delta_f H^\circ_{298,k}$(expt) is the experimental enthalpy of formation of the kth compound, w_k the weight factor, N_k the total number of groups in the kth compound, and K the total number of compounds considered for the least-squares fitting of GC values. The experimental enthalpies of formation were taken from the most recent compilation available in the literature.[8] w_k was set inversely proportional to the squared uncertainty in the experimental $\Delta_f H^\circ_{298,k}$. With this choice, the experimental data with smaller uncertainty are given more weight during least-squares minimization.

The best set of the GC values were derived as follows: GC[C_B-$(C_B)_3$] = 0.331 kcal/mol, GC[C_F-$(C_B)_2(C_F)$] = 1.083 kcal/mol, GC[C_F-$(C_B)(C_F)_2$] = 1.162 kcal/mol and GC[C_F-$(C_F)_3$] = 2.879 kcal/mol. The AM1-GC enthalpies of formation are close to experimental values, with an average deviation of 1.4 kcal/mol per molecule for unsubstituted benzenoid aromatic compounds. Calculations for large peri-condensed aromatic compounds to 3-circumcoronene ($C_{150}H_{96}$) indicated that the enthalpies of formation predicted by the AM1-GC method extend smoothly to that of the limit of a graphite monolayer.

The GC values were also derived for the substituents and radical groups including C_B–CH_3, $>C_B$–C_2H_5, $>C_B$–C_2H_3, $>C_B$–C_2H, cyclopentenyl ring group, $>C_B$-$C_B<$, $>C_B\bullet$ and $>C_B$–CH=CH. The enthalpies of formation for several families of structural isomers, namely a series of closely related methyl- and ethyl-substituted aromatics were examined. The results indicate that the present GC-AM1 method is capable of accurately predicting not only the absolute values of $\Delta_f H^\circ_{298}$ (to a few tenths of kcal/mol), but also the relative stability of these structural isomers. The same accuracy was not obtained when the similar MNDO-GC method was used.

We also examined the stability of aryl radicals as functions of molecular size and radical position. The bond dissociation energies were obtained from the AM1-GC enthalpies of formation. Examination of these BDE values indicates that the strength of aryl–H bond is essentially independent of molecular size, but dependent on the neighboring geometry of the C–H bonds. The calculated BDE values can be placed into three groups according to type of the aryl–H bonds, i.e., group *a*, *b* and *c* depicted in the following diagram:



The aryl–H bonds of group *b* are weaker than those of group *a* by 1–2 kcal/mol. The optimized AM1 geometries of the molecules having aryl–H bonds of group *b* appear to have either a twisted plane or deformed six-member rings, which is apparently a result of steric repulsion between the two H atoms on the edge of the bay area. Lower strength of aryl–H bonds of group *b* is thus the result of this larger steric repulsion. The steric repulsion is further increased by about 3 kcal/mol in group *c*.

A summary of the calculated enthalpies of formation of PAH molecules and radicals pertinent to PAH formation in flames are summarized in the following table.

molecules	$\Delta_f H^\circ_{298}$ (kcal/mol)		radicals	$\Delta_f H^\circ_{298}$ (kcal/mol)		BDE
	AM1	AM1-GC		AM1	AM1-GC	(kcal/mol)
benzene	22.0	20.0	phenyl	79.5	78.6	110.7
naphthalene	40.6	35.8	1-naphthyl	98.4	94.7	111.0
			2-naphthyl	98.0	94.3	110.6
biphenyl	47.6	43.4	2-biphenyl radical	105.1	102.0	110.7
			3-biphenyl radical	105.3	102.2	110.9
			4-biphenyl radical	105.2	102.1	110.8
phenanthrene	57.4	49.6	1-phenanthryl	115.2	108.5	111.0
			2-phenanthryl	115.2	108.5	111.0
			3-phenanthryl	114.8	108.1	110.6
			4-phenanthryl	114.2	107.5	110.0
			9-phenanthryl	114.9	108.2	110.7
anthracene	62.9	55.3	1-anthryl	120.4	113.9	110.7
			2-anthryl	120.2	113.7	110.5
			9-anthryl	121.2	114.7	111.5
pyrene	67.3	53.9	1-pyrenyl	125.3	113.0	111.2
			2-pyrenyl	124.7	112.4	110.6
			4-pyrenyl	124.7	112.4	110.6
benzo[*e*]pyrene	84.0	67.5	benzo[*e*]pyren-1-yl	140.3	124.8	109.4
			benzo[*e*]pyren-5-yl	140.2	124.7	109.3
benzo[*ghi*]perylene	91.3	69.2	benzo[*ghi*]perylen-1-yl	148.0	126.9	109.8
coronene	96.2	68.5	coronyl	153.9	127.2	110.8
acenaphthylene	80.7	62.1	3-acenaphthyl	139.2	121.3	111.7
			4-acenaphthyl	139.2	119.7	111.7
			5-acenaphthyl	138.7	121.9	111.4
acephenanthrylene	95.9	74.3				
acepyrenylene	109.5	82.3				
ethynylbenzene	76.5	73.8	2-ethynylphenyl	134.8	133.2	111.5
			3-ethynylphenyl	134.3	132.7	111.0
			4-ethynylphenyl	134.0	132.4	110.7
1,2-diethynylbenzene	132.4	129.0				
1-ethynylnaphthalene	96.1	90.6	8-ethynylnaphth-1-yl	154.1	149.3	110.8
4-ethynylphenanthrene	117.6	109.1	5-ethynylphenanthr-4-yl	171.3	163.9	106.9
4-ethynylpyrene	123.1	109.0	4-ethynylpyren-5-yl	180.9	167.9	111.0
4-ethynylacenaphthylene	135.4	116.1				
5-ethynylacenaphthylene	135.7	116.4				
styrene (ethenylbenzene)	38.7	35.4	styryl	88.5	94.6	

Transport Properties of Polycyclic Aromatic Hydrocarbons

The transport properties of aromatic compounds, especially the gaseous binary diffusion coefficients, are key components in modeling PAH formation in hydrocarbon flames. As part of the ongoing project, the Lennard-Jones self-collision diameters and well depths of 29 polycyclic aromatic hydrocarbons were derived using a group contribution technique for the estimation of critical temperatures and pressures and the Tee-Gotoh-Stewart correlations of corresponding states.

The estimation of gaseous binary diffusion coefficients of PAH compounds involves the determination of LJ self-collision diameters σ and well depths ε. Values of σ and ε are often derived from viscosity measurements. However, only a limited number of such measurements are available for PAHs. A review of the available physical property data of aromatic compounds indicated that at present the most complete set of data is for the normal boiling point. Based on this consideration, we employed a group contribution technique which correlates the critical temperature of a substance with its normal boiling point and critical pressure with molecular weight. The critical temperature and pressure obtained in this manner were then used to estimate the LJ self-collision diameter and well depth using the correlations of corresponding states developed by Tee, Gotoh and Stewart:[9]

$$\sigma\left(\frac{1.013P_c}{T_c}\right)^{1/3} = 2.3551 - 0.0874\omega \tag{3}$$

and

$$\frac{\varepsilon}{k_B T_c} = 0.7915 + 0.1693\omega \tag{4}$$

where P_c and T_c are critical pressure and temperature in bar and K, respectively, and k_B the Boltzmann constant. The acentric factor, ω. is a macroscopic measure of the extent to which the force field around a molecule deviates from spherical geometry. The empirical constants in Eqs. (3) and (4) were obtained from the viscosity and second virial coefficient data of 14 substances ranging from inert gases to benzene and normal heptane. The correlations were shown to provide accurate estimations of viscosity with an average deviation of 2.57%. In this study, we applied Eqs. (3) and (4) to PAH compounds.

The critical temperature T_c and pressure P_c were estimated following a group contribution technique. This technique was recently re-examined and updated by Somayajulu,[10] who suggested the following relations:

$$\frac{T_b}{T_c - T_b} = 1.242 + 0.138N_t \tag{5}$$

and

$$\left(\frac{10^3 M_w}{P_c}\right)^{1/2} = 0.339 + 0.226N_p\ , \tag{6}$$

where T_b is the boiling temperature in K, M_w the molecular weight in kg/mol, and N_t and N_p are the temperature and pressure indices of a molecule, respectively, and are calculated as the sums of the molecular structural group indices, i.e., $N_t = \sum n_t$ and $N_p = \sum n_p$. The values of n_t and n_p were obtained by Somayajulu[10] through evaluation of the experimental T_c and P_c data of hydrocarbons from small alkanes to aromatics of the size of anthracene and phenanthrene. The acentric factor ω in Eqs. (3) and (4) was evaluated using the Lee-Kesler vapor-pressure relations[11] which give

$$\omega = \frac{-\ln(1.013P_c) - 5.927 + 6.096\theta^{-1} + 1.289\ln\theta - 0.169\theta^6}{15.252 - 15.688\theta^{-1} - 13.472\ln\theta + 0.436\theta^6} \tag{7}$$

where $\theta = T_b/T_c$.

The normal boiling points (at 1 atm) of 29 selected PAH compounds were taken from the most recent compilation of CRC Handbook.[12] The LJ parameters were then evaluated using Eqs. (3)–(7). The obtained σ and ε values are plotted against molecular weight in Fig. 2. Also included in this figure are the data for molecular hydrogen and selected small hydrocarbon compounds reported by Svehla.[13] As can be seen, the LJ parameters of PAHs correlate strongly with molecular weight. These correlations can be expressed by

$$\sigma = 1.234\ (10^3 M_W)^{0.33}\quad (\text{Å}) \tag{8}$$

and

$$\varepsilon/k_B = 37.15\ (10^3 M_W)^{0.58}\quad (\text{K}), \tag{9}$$

where M_w is in kg/mol.

Given the LJ collision diameters and well depths, the gaseous binary diffusion coefficients were evaluated with the Chapman-Enskog equation

$$D_{ij} = \frac{3}{16}\frac{\sqrt{2\pi(k_B T)^3/\mu_{ij}}}{P\pi\sigma_{ij}^2\Omega} f_D, \tag{10}$$

where P is the pressure, T the temperature, Ω the collisional integral, μ_{ij} the reduced mass of species i and j, f_D is a correction term ($1.0 < f_D < 1.1$) and was assumed here to be equal to unity. Eq. (10) is valid at low pressures when the ideal gas law is applicable. The calculation of D_{ij} was facilitated by a computer code developed by Kee et al.[14] In addition, a second approach based on the Fuller approximation[15] was taken for the analysis of the diffusion coefficients,

$$D_{ij} = \frac{0.3162\ T^{1.75}\sqrt{\dfrac{1}{M_{W,i}} + \dfrac{1}{M_{W,j}}}}{1.013P\left[(\sum \upsilon)_i^{1/3} + (\sum \upsilon)_j^{1/3}\right]^2} \tag{11}$$

where T is in K, P in bar, $M_{w,i}$ and $M_{w,j}$ the molecular weights of binary components i and j in kg/mol, respectively, and υ the atomic diffusion volume.

In Fig. 3, the binary diffusion coefficients calculated using the estimated LJ parameters are compared with those obtained with the Fuller approximation[15] for naphthalene-, pyrene-, and ovalene-N_2 binary mixtures at a pressure of 1 atm. The LJ parameters of ovalene were obtained with Eqs. (8) and (9). As seen in Fig. 3, the agreement between the two methods for the estimated binary diffusion coefficients of naphthalene in N_2 is very good. For pyrene and ovalene, the Fuller approximation[15] gave estimates that are about 10 and 15 % higher, respectively, than those derived with the estimated LJ parameters. Considering the fact that both approaches have not been tested for molecules of sizes as large as ovalene, the agreement should be considered as good. The good agreement between the results obtained with Eq. (11) and with the derived LJ parameters provide a cross check for the developed LJ-parameter method. The LJ parameters derived in this study can be added to the existing transport database, such as that available with the Sandia burner codes.

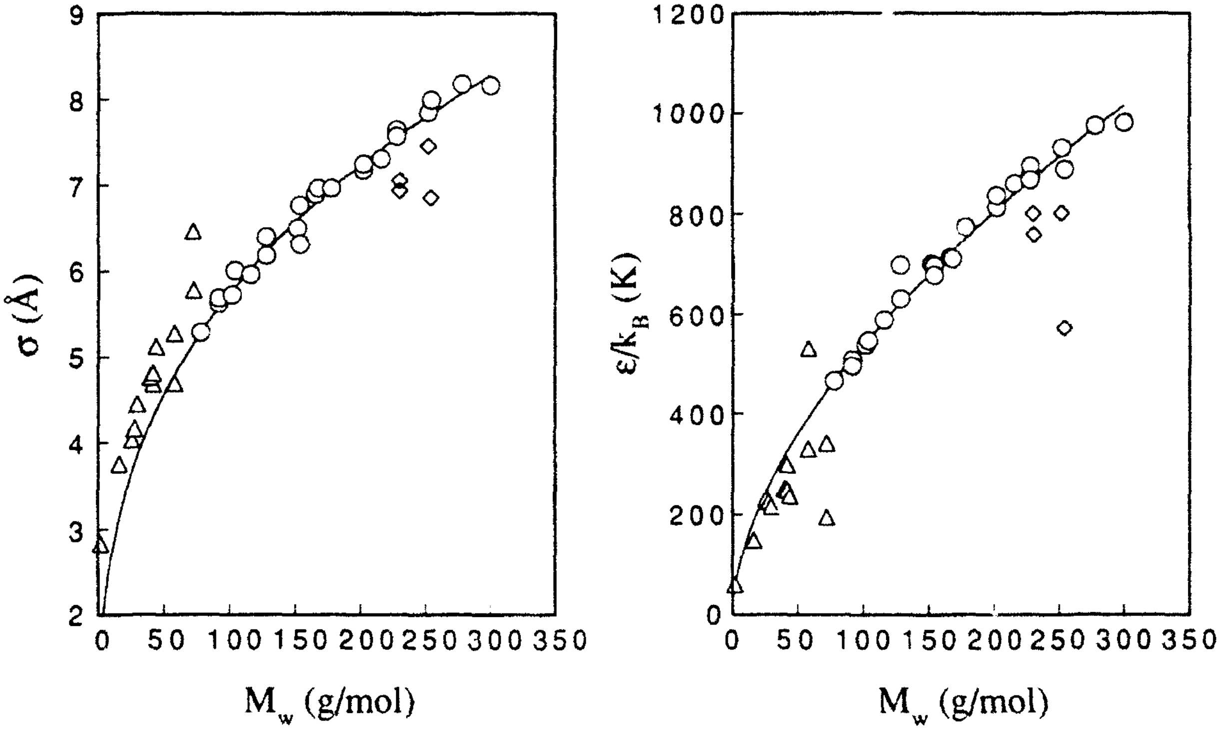


Figure 2. Lennard-Jones collision diameter (left) and well depth (right) plotted as a function of molecular weight. Circles and diamonds: PAH molecules of this study, triangles: small linear hydrocarbon molecules and H_2, solid lines: Eqs (8) and (9), fitted to the data given by the circles.

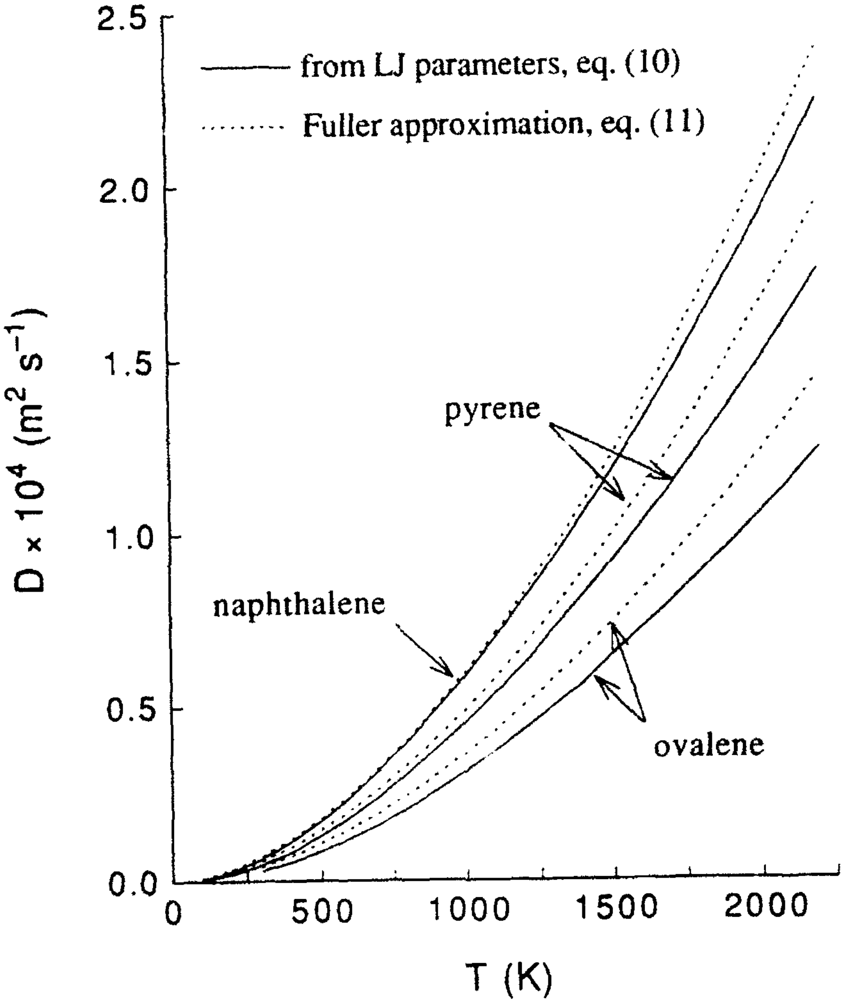
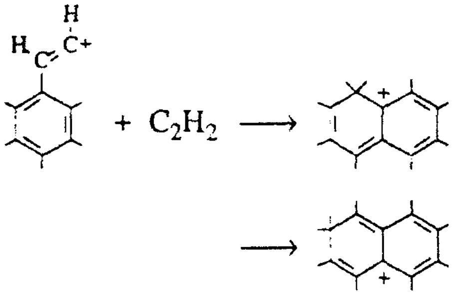


Figure 3. Comparison of gaseous binary diffusion coefficients obtained from the LJ collision diameters and well depths and from the Fuller approximation[15] for naphthalene-, pyrene-, and ovalene-N_2 mixtures at a pressure of 1 atm.

Semiempirical Quantum-Mechanical and RRKM Studies of Reaction $C_8H_7^+ + C_2H_2 \rightarrow C_{10}H_9^+$

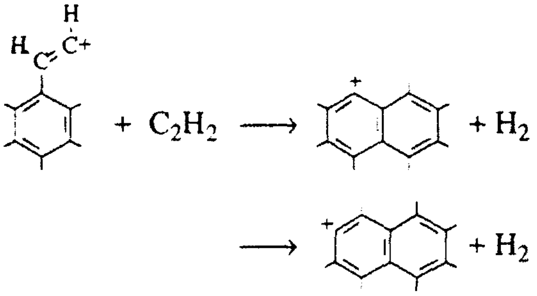
We have completed our theoretical study on the title ion-molecule reaction. This reaction is one of the key steps in the mechanism proposed by Calcote and coworkers.[16] Seven major isomers for the $C_{10}H_9^+$ adduct and 11 possible product channels were identified in our study, indicating the complexity of the reaction. The energetics and molecular parameters of the reactants, intermediate species, products, and transition states were evaluated using the semiempirical quantum-mechanical AM1 method. The rate coefficients and their pressure and temperature dependence were then calculated based on the RRKM theory with a full consideration of angular momentum conservation. The microscopic rate coefficients for the reaction channels involving the dissociation of the energized complexes were determined with the microcanonical variational transition state theory. RRKM calculations were performed for temperatures from 300 to 2000 K and at a pressure of 20 torr. These conditions are the same as our previous kinetic modeling study of ion formation in flames. The major results of this study can be summarized as follows: (1) at temperatures lower than 1000 K, the major reaction channels are to form the two most stable $C_{10}H_9^+$ isomers



(12a)

(12b)

The overall rate coefficient of the above two reactions at T < 1000 K is equal to that of the Langevin limit, 6×10^{14} $cm^3mol^{-1}s^{-1}$; (2) at flame temperatures (1500K < T < 2000K), the overall rate coefficients are more than an order of magnitude lower than the Langevin limit. The major products are those from the addition/dissociation channels, i.e.,



(12c)

(12d)

The computed rate coefficients of (12c) and (12d) in the 1500 to 2000 K temperature window are about 1×10^{13} and 3×10^{13} $cm^3mol^{-1}s^{-1}$, respectively. The latter result suggests that the rate coefficients used in the reaction model of ion formation proposed by Calcote and coworkers[16] may be an order of magnitude too high.

FUTURE WORK

The objectives for the next year are the following:

1. To complete the revision and testing of the neutral reaction mechanism of PAH formation and growth, and to prepare a manuscript summarizing the results.

2. To continue a computational study of pressure effect on soot formation.

3. To perform computer simulation of soot formation in benzene flames. This is a part of the overall proposed work, in the context of developing and testing models of soot formation in more complex environments. The ability to predict soot formation in flames of aromatics, consistently with the predictions for soot formation from non-aromatic hydrocarbons, is the next important milestone towards simulation of soot formation from fuel blends of practical importance.

4. To investigate the details of the surface growth kinetics of soot particles. This is one of the key factors affecting the accuracy of soot model predictions in realistic combustion environments. A detailed study of the processes involved will be studied using our newly developed theoretical techniques for gas-surface reaction kinetics.

5. To prepare a manuscript reporting the results obtained in the theoretical study on a bench-mark ion-molecule reaction, $C_8H_7^+ + C_2H_2 \rightarrow C_{10}H_9^+$.

6. To initiate computer simulation of soot formation in more practical environments, like diffusion flames and/or diesel engines.

PRESENTATIONS AND PUBLICATIONS

1. M. Frenklach, "Chemistry of Particle Forming Systems," Engineering Foundation Conference on Vapor Phase Manufacture of Ceramics," Kona, Hawaii, January 12–17, 1992 (Invited).

2. M. Frenklach, "Development of Predictive Reaction Models of Soot Formation," AFOSR Contractors Meeting on Propulsion, La Jolla, CA, June 15–19, 1992.

3. M. Frenklach, "Mechanism of Soot Particle Formation," Scientific Conference on Obscuration and Aerosol Research, Aberdeen Proving Ground, MD, June 22–25, 1992 (Invited).

4. M. Frenklach, "The Chemistry and Modeling of Soot Formation," Caterpillar Inc., Engine Division Engineering, July 8, 1992.

5. H. Wang and M. Frenklach, "Enthalpies of Formation of PAH Molecules and Radicals," To be presented at the Joint Technical Meeting of the Central and Eastern States Sections of the Combustion Institute on *Combustion Fundamentals and Applications*, New Orleans, March 15-17, 1993.

6. M. Frenklach and H. Wang, "Detailed Mechanism and Modeling of Soot Particle Formation," in *Mechanisms and Models of Soot Formation* (H. Bockhorn, Ed.), Springer-Verlag, Heidelberg, in press.

7. M. Frenklach and H. Wang, "Detailed Mechanism and Modeling of Soot Formation," in *Advanced Combustion Science* (T. Someya, Ed.), Springer-Verlag, in press.

8. H. Wang and M. Frenklach, "Enthalpies of Formation of Benzenoid Aromatic Molecules and Radicals," *J. Phys. Chem.*, in press.

9. P. Markatou, H. Wang and M. Frenklach, "A Computational Study of Sooting Limits in Laminar Premixed Flames of Ethane, Ethylene and Acetylene," *Combust. Flame*, submitted.

10. H. Wang and M. Frenklach, "Lennard-Jones Parameters and Gaseous Diffusion Coefficients of PAHs in He, Ar, H_2, N_2 and Air at Low Pressures," *J. Phys. Chem. Ref. Data*, submitted.

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INVENTIONS

None.

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