DTIC FILE COPY

(2)

AD-A232 32

COMPUTER MODELING OF SOOT FORMATION COMPARING FREE RADICAL AND IONIC MECHANISMS

(A Collaborative Project between AeroChem and Penn State)

AFOSR-TR- 91 0169

Final Technical Report

of the Penn State Efforts (Grant No. AFOSR 88-0072)

Covering the period from December 1, 1987 to November 30, 1990

prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Bolling AFB

by

Michael Frenklach and Hai Wang
Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

DTIC
ELECTE
MAR 13 1991
S B D

January 22, 1991

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

91 3 11 141

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Pennsylvania State University	6b. OFFICE SYMBOL *(If applicable)*
7a. NAME OF MONITORING ORGANIZATION AFOSR/NA	
6c. ADDRESS *(City, State, and ZIP Code)* University Park, PA 16802	7b. ADDRESS *(City, State, and ZIP Code)* Building 410, Bolling AFB DC 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR/NA	8b. OFFICE SYMBOL *(If applicable)* NA
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR 88-0072	
8c. ADDRESS *(City, State, and ZIP Code)* Building 410, Bolling AFB DC 20332-6448	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2308	A2	

11. TITLE *(Include Security Classification)*
(U) Computer Modeling of Soot Formation Comparing Free Radical and Ionic Mechanisms

12. PERSONAL AUTHOR(S) Michael Frenklach

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT *(Year, Month, Day)*	15. PAGE COUNT
Final Technical	FROM 12-1-87 TO 11-30-90	January 22, 1991	23

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
FIELD	GROUP	SUB-GROUP	Soot Formation, Computer Modeling, Ionic Mechanism

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

This is a final report on collaborative study between AeroChem and Penn State, aimed at development of a quantitative physicochemical model of soot formation. The Penn State accomplishments during the past three-year period are: The AeroChem ion-reaction mechanism was run with a flame code, and the computational results indicate that the formation of polycyclic aromatic hydrocarbons, the precursors to soot, via the ionic reaction pathway is slower than via the pathway involving neutral species; A computer code for modeling large species and soot particle formation and growth was developed; Our neutral reaction mechanism was updated and tested; and A detailed computer simulation of soot particle nucleation and growth in laminar premixed flames was successfully performed using our updated neutral reaction mechanism -- for the first time soot particle inception could be modeled from first principles, starting with fuel decomposition and going all the way to predicting, in quantitative agreement with experiment, soot particle properties.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☑ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Julian M Tishkoff	22b. TELEPHONE *(Include Area Code)* (202) 767-0465	22c. OFFICE SYMBOL AFOSR/NA

DD Form 1473, JUN 86 *Previous editions are obsolete.* SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

TABLE OF CONTENTS

INTRODUCTION

This is a final report on collaborative study between AeroChem Research Laboratories (principal investigator — Dr. H. F. Calcote) and the Pennsylvania State University (principal investigator — Dr. M. Frenklach). The ultimate objective of this program was to develop a quantitative physical/chemical model of the mechanism of soot formation that is consistent with available experimental data. The specific objectives of the proposed 3-year study were: 1) to delineate the relative importance of radical and ionic mechanisms of soot nucleation in flames, and 2) to determine the optimum chemical and physical model of the total soot formation process. Only the work performed at Penn State is reported here, that of AeroChem is reported in their parallel final technical report.

WORK PROPOSED

The general objectives proposed for the Penn State efforts were:

1. To undertake flame simulation and reaction-path analysis using the ion-reaction mechanism provided to us by AeroChem.

2. To analyze the competition for the formation of soot and soot precursors between the ionic and neutral reaction mechanisms.

3. To update the Penn State neutral-reaction mechanism for the formation of polycyclic aromatic hydrocarbons (PAH).

4. To develop a numerical algorithm and a computer code for modeling the formation and growth of large-sized species and soot particles.

5. To perform computer simulation of soot particle formation in flames with the code developed.

RESULTS

During the three-year period of the project, we completed most of the planned work: several ion reaction mechanisms provided to us by AeroChem were "cleaned-up" and run with a flame code, the computational results were analyzed, a computer code for modeling large species and soot particle formation and growth was developed, our neutral reaction mechanism was updated and tested, and a detailed computer simulation of soot particle nucleation and growth in laminar premixed flames was successfully performed using our updated neutral reaction mechanism. The latter part is a particularly significant accomplishment, as it is for the first time soot particle inception could be modeled from first principles, starting with fuel decomposition and going all the way to predicting, in quantitative agreement with experiment, soot particle properties. The following is a detailed account for the work performed and the results abtained.

Ion Reaction Mechanism

We began our work by testing the general performance of an ion-molecule reaction mechanism under shock-tube conditions. The premise of such testing is founded on our previous result that the major neutral-reaction pathways for PAH formation under shock-tube oxidation[1] and laminar premixed flame[2] conditions are very similar to each other. The initial ionic mechanism provided to us by AeroChem has been reported and discussed in the AeroChem reports.[3,4] The detailed account of the shock-tube calculations is given in our first annual report.[5]

The basic results of the shock-tube simulations indicated that the ionic mechanism produces polycyclic aromatic hydrocarbons at significantly lower rate than does the mechanism composed of only reactions of neutral species. An extensive sensitivity and rate analysis found no conceivable adjustments in the parameter values that would affect this conclusion. There are two basic factors identified by the sensitivity and rate analysis to be responsible for the low rate of PAH production via the ionic mechanism tested. First is the relatively low rate of ion production. The second factor limiting the rate of PAH production via the ionic mechanism is the reversibility of some of the principal reaction steps, and a significant number of steps in the principal reaction sequence was found to be reversible. The computer simulations indicated that the forward and reverse reactions of these steps are tightly balanced, *i.e.*, these reactions are in partial equilibrium, similarly to the case for the neutral-reaction mechanism.[2,6] This reduces dramatically the net mass flux and thus limits the rate of PAH production. Among other things, it implies that an oversimplified analysis presented recently,[7] ignoring the kinetic-thermodynamic coupling controlling the rate of the principal reaction pathway, cannot possibly be valid.

We next examined the competition between the ionic and neutral mechanisms for PAH production at flame conditions. For this purpose, a "well-studied" laminar premixed flame, for which the experimental data on ionic species concentrations are available, had to be chosen for the computer simulations. As there is no single flame reported for which there are measurements available of *all* the pertinent chemical species, two close flames were chosen to represent a "well-studied" flame. As the primary focus of this study is on the ionic species, the main flame — referred to as Flame I1 — is the flame for which ion concentration profiles were measured by Calcote and co-workers:[8] 52.9 % $C_2H_2 - 44.1$ % $O_2 - Ar$ ($\phi = 3.0$), pressure 20 torr, cold gas velocity 50 cm/s. Since, however, Calcote and co-workers did not measure the concentrations of neutral species in this flame, a second flame, that of Delfau and Vovelle[9] — referred to as Flame I2 — was chosen to test the predictions of the present simulations for the major neutral species. The stoichiometry, pressure and cold gas velocity of this flame are exactly the same as those of Flame I1. The mixture used by Delfau and Vovelle did not contain any argon, whereas that of Calcote and Keil had 3 % argon. Also, the reported temperature profiles of Flames I1 and I2 are slightly different from each other. Temperature profile is a critical input parameter for the flame simulations and even small differences in the given profile data cause significant changes in computed profiles of minor (*e.g.*, PAHs) species.

The flame computations were performed using the Sandia burner code.[10] Several reaction mechanisms provided to us by AeroChem have been tested and analyzed during the course of the study. Some of the results of these flame simulations, thsoe obtained with the most recent version of the AeroChem mechanism, are presented in Figures 1 through 4. Examination of Figure 1 indicates that the concentrations of major species are predicted well — as good as the present state of the art in the knowledge of chemical reactions, their rates and thermochemistr , the accuracy of numerical techniques, and quality of experimental measurements allow. The comparison between the computed and experimental concentrations of ions is given in Figures 2 and 3. The agreement is worse for these species compared to the agreement seen for the major species in Figure 1. In the computer simulation as opposed to the experiment, the positions of the concentration peaks are shifted towards the burner and the decay in the concentration profiles is much steeper. Similar behavior was seen in computer simulations of an acetylene flame with the neutral-reaction mechanism.[2] The reasons for this are discussed in the work cited. It is important to notice, however, that the peak values of the ion concentrations are predicted reasonably well, taking into account the uncertainty in the input reaction data and in the experimental measurements — most of them are computed within an order of magnitude of the experimental numbers. In this sense, the results obtained with different versions of the AeroChem ionic mechanism, as far as the ions-vs-neutrals competition is concerned, are very similar to each other (compare, for example, the data in present Figures 1 through 4 with the data reported in Figures 5 through 8 in our first annual report[5]).

Although the analysis of the results obtained in the flame simulations is not entirely completed, the following conclusion, similar to to those reached based on the shock-tube

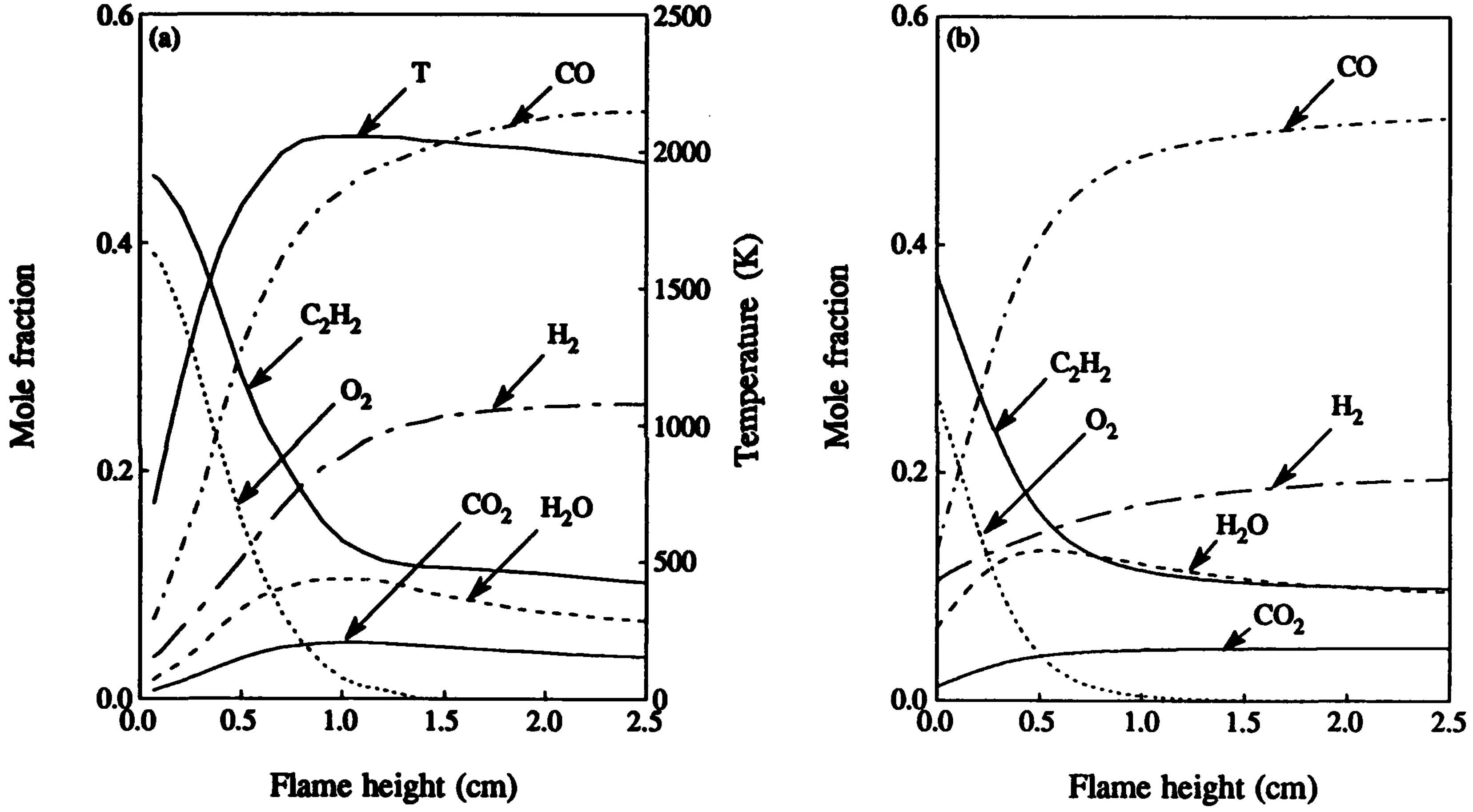

Figure 1. Concentration profiles of reactants and major products in Flame I2: a) experimental measurements;[9] b) present computations using the temperature profile given in (a).

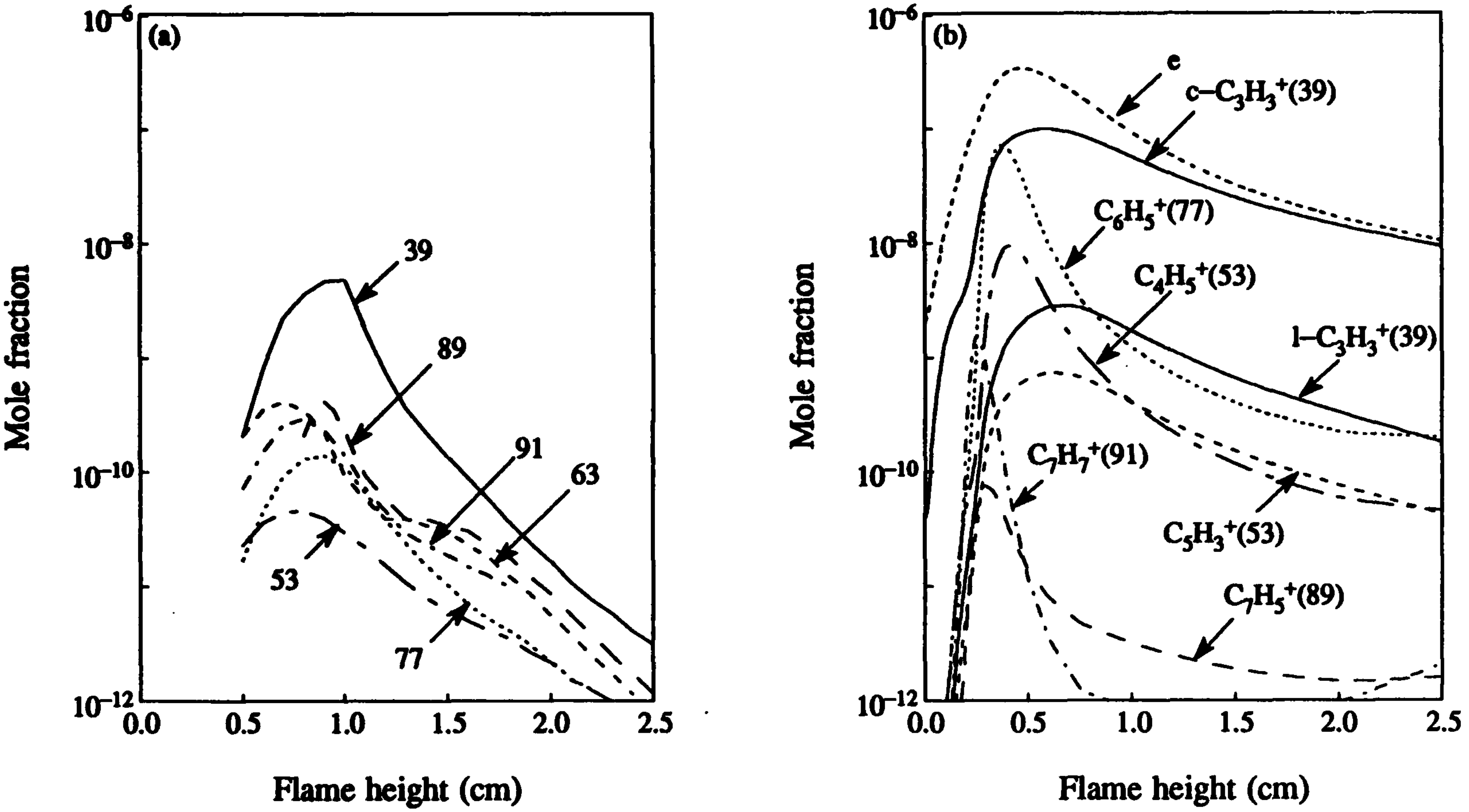

Figure 2. Concentration profiles of small ions in Flame I1: a) experimental measurements;[8] (b) present computations using the temperature profile of Ref. 8.

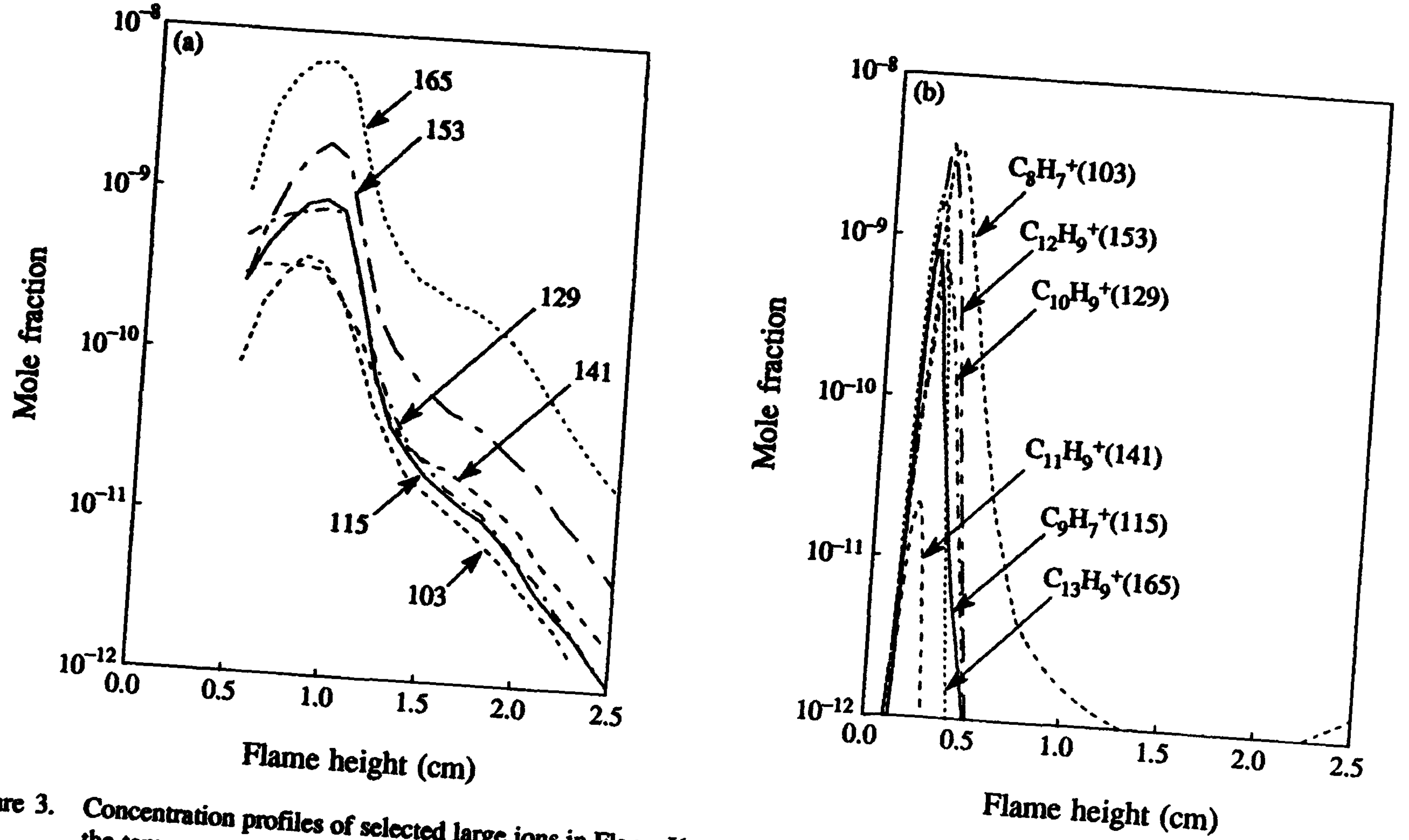

Figure 3. Concentration profiles of selected large ions in Flame I1: a) experimental measurements;[8] (b) present computations using the temperature profile of Ref. 8.

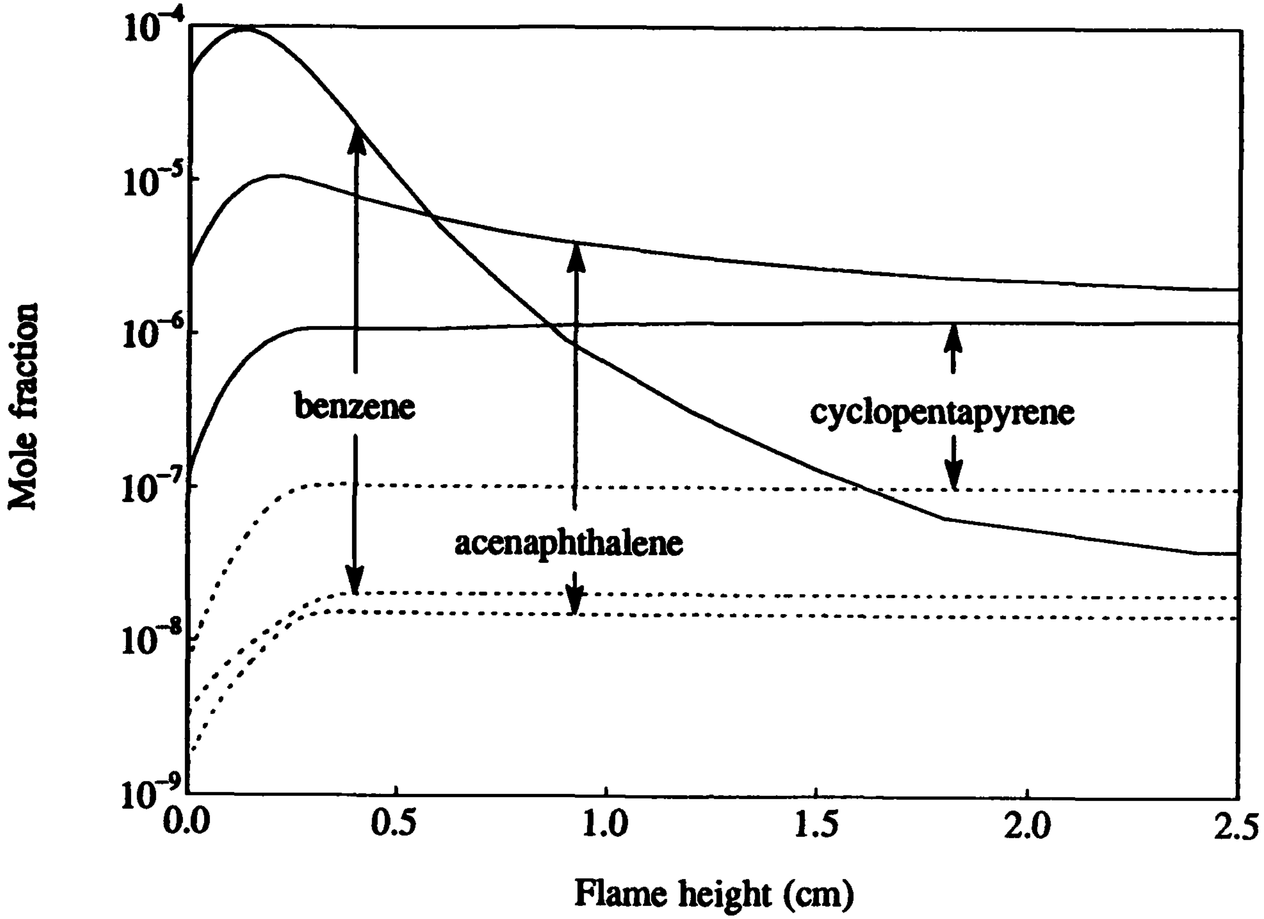

Figure 4. Profiles of selected aromatic hydrocarbons computed with radical (solid lines) and ionic (dotted lines) mechanism.

simulation results, has emerged: the ionic mechanism produces polycyclic aromatic hydrocarbons at significantly lower rates than does the neutral-reaction mechanism. This result is illustrated in Fig.4, where the concentrations of selected aromatics computed with the ionic mechanism are compared to those computed with the neutral-reaction mechanism at the same flame conditions. As can be seen from this comparison, the production of aromatics via the neutrals is much faster than that via ions (the difference between the two cases increases with the switching off oxidation reactions in computer simulations with the neutral-reaction mechanism; also note that the computed concentrations of ions are significantly larger than the experimental counterparts). A sensitivity and rate analysis performed so far found no conceivable adjustments in the parameter values that would change this principal conclusion. The factors responsible for this are the same as those identified in the analysis of the shock-tube results: a relatively low rate of chemi-ionization as compared to that of radical production at the same conditions, and reversibility of the reaction steps responsible for the formation of high-molecular weight species.

Another shortcoming of the present ionic mechanism is the lack of knowledge on the microscopic mechanism of many ion-molecule reaction in the AeroChem scheme. In fact, it is unlikely that many individual reaction steps will proceed as written and with the rate coefficient values assigned to them. Most of these ion reactions are written on the premises[11] that ion-molecule reactions have no potential-energy barriers and that ionic species isomerize fast. However, some available (although limited) information indicates to the opposite. For instance, we performed quantum-chemical calculations on a key ion-molecule step. It appears that even a more conceivable reaction step of the AeroChem mechanism has a measurable potential energy barrier. This means, that the rate coefficients and, more importantly, reaction channels of the present ionic mechanism are most likely to greatly overestimate the growth rate of polycyclic aromatic species in flame environments.

Neutral Reaction Mechanism

Accurate prediction of polycyclic aromatic hydrocarbons in flames is critical for modeling of soot formation in hydrocarbon combustion. In our initial efforts, the objective was a proof-of-a-concept computer simulation of PAH production in high-temperature hydrocarbon pyrolysis,[6] and later, in a low-pressure laminar premixed acetylene flame.[2] Now, when the acetylene-addition mechanism we have advocated for the last seven years is well tested under various experimental conditions and by different research groups, the objective is to improve the mechanism to a point that it is capable of *quantitative* predictions. Initial results of such efforts are reported below.

We chose to model the PAH profiles in three well-studied laminar premixed flames, whose conditions are summarized in the following table:

Table 1. Flame conditions for modeling with neutral-species mechanism

No.	Composition in Argon	P (torr)	Cold gas velocity (cm/s)	Reference
N1	46.5% C_2H_2 – 48.5% O_2	20	50	MIT group[12]
N2	23.6% C_2H_2 – 21.4% O_2	90	20	Bockhorn *et al.* [13]
N3	16.5% C_2H_4 – 17.9% O_2	760	7.8	Harris *et al.*[14]

These flames were computed using the Sandia burner code.[10] The Lennard-Jones parameters of PAH molecules were calculated using empirical correlations and available physical properties.[15] The transport coefficients obtained in this manner agreed well with experimental data available for several compounds. The thermodynamic data were taken from Stein and Fahr,[16] except for the C_t–H group additivity which was based on the recent results of Green *et al.*[17]

The reaction mechanism is composed of two parts: the small molecule reactions, responsible for the main flame structures; and reactions describing the formation and growth of PAHs. The reaction mechanism for the former part was composed of data taken primarily from several sources: (a) our recently optimized methane oxidation mechanism,[18] (b) revised mechanism of Frenklach and Warnatz,[2] and (c) revised acetylene oxidation mechanism of Hwang *et al.*[19] The main revisions included: the rate coefficients of acetylene-hydroxyl, and acetylene-oxygen atom reactions

$$C_2H_2 + OH \rightarrow \text{products}$$

$$C_2H_2 + O \rightarrow \text{products}$$

were taken from Miller and Melius,[20] and Mahmud and Fontijn,[21] respectively. The rate coefficient for reaction

$$C_2H_2 + C_2H_3 \rightarrow C_4H_4 + H$$

was taken from Fahr and Stein.[22]

The formation of the first aromatic ring followed the basic reaction scheme of Frenklach and Warnatz,[2]

$$\text{n-}C_4H_3 + C_2H_2 \rightarrow \text{phenyl}$$

$$\text{n-}C_4H_5 + C_2H_2 \rightarrow \text{benzene} + H$$

however with the rate coefficients taken from the work of Westmoreland *et al.*,[23] who used a QRRK methodology of estimating chemical activation processes involved in these reactions. The assignment of the rate coefficients for the main reaction classes responsible for PAH growth are summarized in Table 2.

Table 2. Revision of rate coefficients for main reaction classes of PAH growth

Reaction	Prototype reaction	Reference
aryl–H + H → aryl + H_2	benzene + H → phenyl + H_2	Kiefer *et al.*[24]
aryl + C_2H_2 → aryl–C_2H + H	phenyl + C_2H_2 → phenyl–acetylene + H	Fahr and Stein[22]
aryl + O_2 → products	phenyl + O_2 → products	Lin and Lin[25]

The computational results for the three flames are presented in Figures 5 to 10. These results were obtained with the rate coefficients for several small-molecule reactions adjusted by a factor of 2 to 3, still within their experimental uncertainties. As can be seen in these figures, the agreement between the modeling predictions and experimental data is good for major species. The agreement for PAHs is not exactly quantitative, but certainly much closer — in both shape and absolute values — than reported by us previously.[2] The important result here is that the near-quantitative accuracy was obtained for PAHs with a single reaction mechanism for all the three flames simultaneously. The major reaction pathways, their roles in PAH growth, and the sensitivity information are essentially the same as reported and discussed in the previous work.[2]

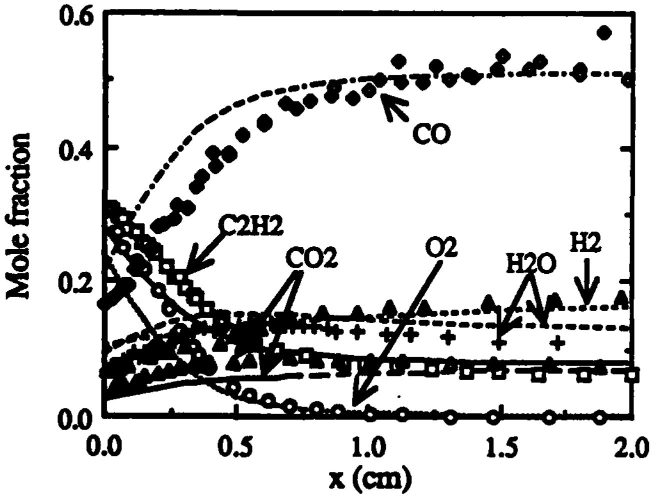

Figure 5. Computed vs. experimental major species concentrations of Flame N1.

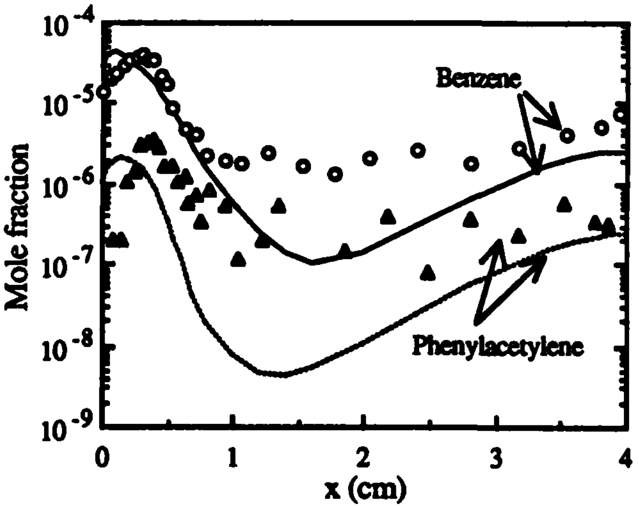

Figure 6. Computed vs. experimental major aromatic species concentrations of Flame N1.

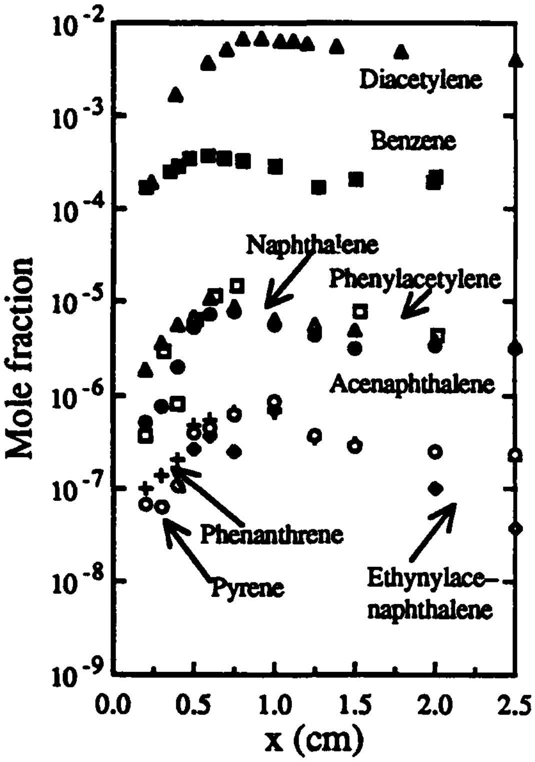

Figure 7. Measured mole fractions of diacetylene and selected PAHs of Flame N2.

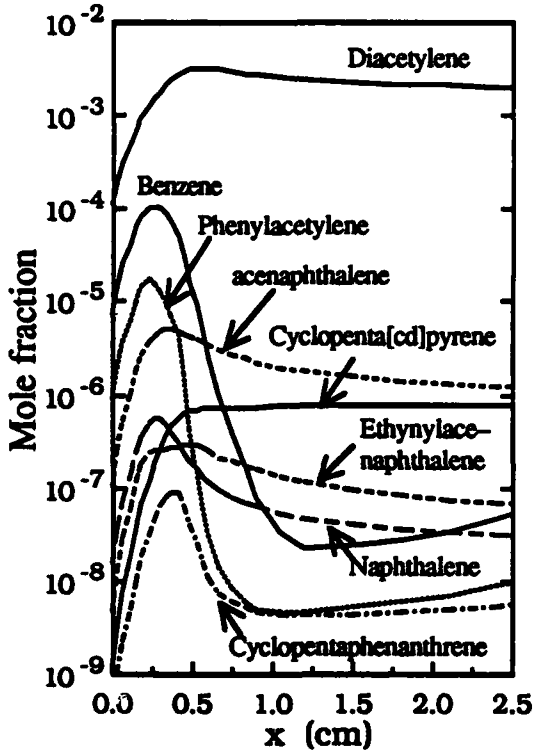

Figure 8. Computed mole fractions of diacetylene and PAHs of Flame N2.

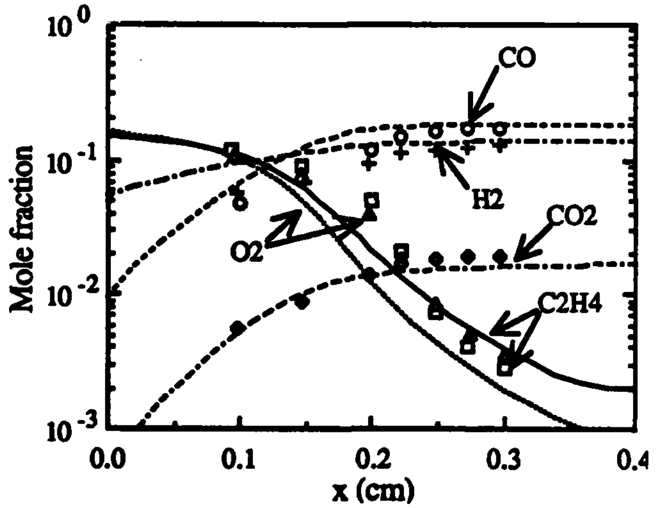

Figure 9. Computed vs. experimental major species concentrations of Flame N3.

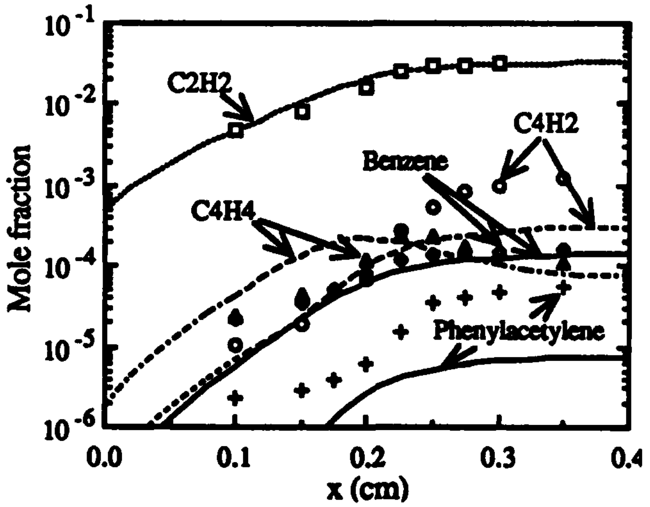

Figure 10. Computed vs. experimental minor species concentration of Flame N3.

Flame Simulation of Soot Particle Nucleation and Growth

Using the neutral reaction mechanism described in the previous section, we performed detailed modeling of soot particle nucleation and growth in several laminar premixed flames. The computational model consists of three logical parts: (I) *initial PAH formation*, which includes a detailed chemical kinetic description of acetylene pyrolysis and oxidation, formation of the first aromatic ring, and its subsequent growth to a prescribed size; (II) *planar PAH growth*, comprised of replicating-type growth of PAHs beyond the prescribed size; and (III) *spherical particle formation and growth*, consisting of coagulation of PAHs formed in part (II) followed by the growth of the resulting particles by coagulation and surface reactions.

The initial part of the particle dynamics model, *nucleation*, describes the planar growth of PAHs via the H-abstraction/C_2H_2-addition reaction sequence[2,6] using the technique of chemical lumping.[26,27] This method provides a mathematically rigorous description of the growth process to an infinite size PAH, which can be schematically represented as

$$A_l \rightarrow A_{l+1} \rightarrow A_{l+2} \rightarrow \cdots \rightarrow A_\infty , \tag{1}$$

where A_l represents an aromatic species containing l fused rings. The PAH species formed in (1) are then allowed to *coagulate*, that is, all the A_i's ($i = l, l+1, \ldots, \infty$) collide with each other forming dimers; the dimers, in turn, collide with A_i forming trimers or with other dimers forming tetramers; and so on. The coalescence reactions were treated as irreversible having sticking coefficients of unity. As the focus of this work was on very young, small particles, it was assumed that the coagulation dynamics is in the free-molecular regime. A size-independent enhancement factor of 2.2, based on the results of Harris and Kennedy,[28] was used in calculations of collision frequencies.

Beginning with the dimers, the forming clusters were assumed to be "solid phase" and allowed to add and lose mass by surface reactions

$$C_{soot}\text{–}H + H \rightleftharpoons C_{soot}\bullet + H_2 \tag{2}$$

$$C_{soot}\bullet + H \rightarrow C_{soot}\text{–}H \tag{3}$$

$$C_{soot}\bullet + C_2H_2 \rightarrow C_{soot}\text{–}H + H \tag{4}$$

$$C_{soot}\bullet + O_2 \rightarrow \text{products} \tag{5}$$

$$C_{soot}\text{–}H + OH \rightarrow \text{products} , \tag{6}$$

where C_{soot}–H represents an arm-chair site on the soot particle surface and $C_{soot}\bullet$ the corresponding radical. This mechanism is adopted based on the postulate[29–31] that the

H-abstraction/C_2H_2-addition (HACA) reaction sequence[6] is responsible for high-temperature growth of all forms of carbonaceous materials. Wieschnowsky *et al.*[32] also suggested that the HACA reactions[2,6] "offer a key to the understanding of a number of phenomena" observed in their flame study.

Estimation of the rate coefficients of the heterogeneous reactions was based on analogous gas-phase reactions of one-ring aromatics, benzene and phenyl. The reference gaseous reactions for heterogeneous reactions (2)–(5) were the corresponding gas-phase reactions in Table (2). Oxidation by OH, reaction (6), was assumed to proceed with the collision efficiency of 0.13, based on the results of Neoh *et al.*[33] The particle dynamics — the evolution of soot particles undergoing simultaneous nucleation, coagulation and surface reactions described above — was modeled by a method of moments (Method II of Ref. 34). This method does not require the assumption of a particle size distribution function (PSDF). The closure of the differential equations for the PSDF moments is accomplished by interpolation between the moments.[26,34] The numerical integration of the moment equations is extremely economical; for instance, one computer run took from 20 to 50 s on an IBM 3090/600S main-frame computer.

Figures 11 and 12 present the results computed using the model discussed above for two of the chosen flames: Flame B — flame No. 1 of Bockhorn and co-workers[32] — 25.4 % C_2H_2 – 19.6 % O_2 – Argon, pressure 90 torr; and Flame H — an atmospheric 16.5 % C_2H_4 – 17.9 % O_2 – Argon, of Harris and co-workers.[35] Both flames were computed with the same kinetic model, assuming A_4 (pyrene or acepyrene) to be the A_l species which initiates the planar growth of PAHs and the formation of particles, parts (II) and (III) of our model, respectively. Changing A_l affects strongly the rate of particle nucleation.

It can be seen in Figs. 11 and 12 that the model predictions are in relatively close agreement with experiment for the initial, particle inception part of the flames; however, the computed and experimental results begin to deviate from one another with increasing flame height. One factor identified as a cause of this disagreement is the shape of the PAH profiles. This is demonstrated in Fig. 11, where it is shown that using a narrower (experimental-like[13]) profile for A_4 improves the agreement between the model and experiment for Flame B. It was also computed that PAH condensation on the particle surface is sufficiently fast to significantly affect the PAH profiles in the post-flame zone.

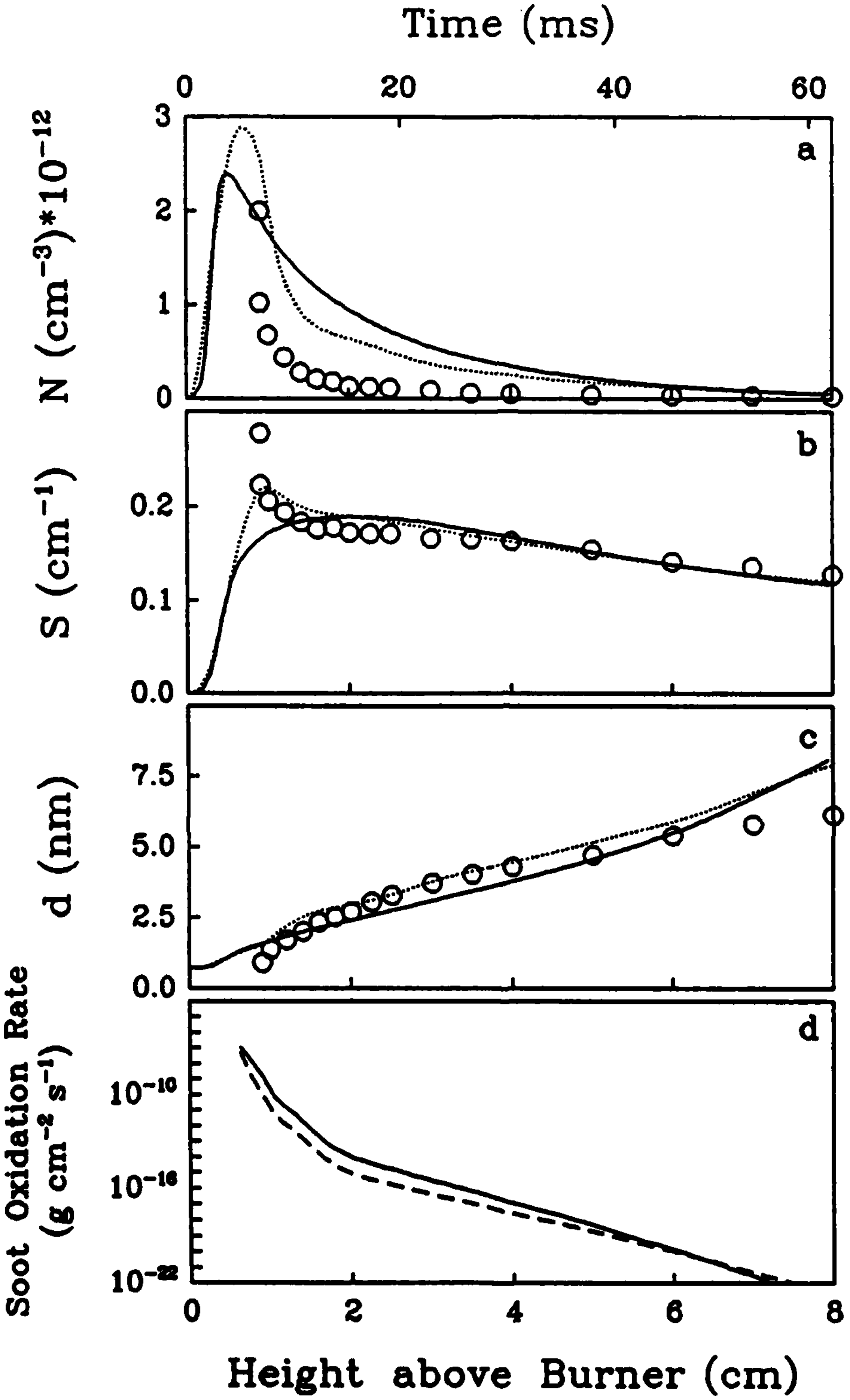

Fig. 11. Comparison of model predictions and experimental data for Flame B: (a) particle number density; (b) particle surface area; (c) average particle diameter [circles – experimental results,[32] solid lines – model prediction, dotted lines – model prediction using an experimental-like profile for A4]; (d) specific rate of soot particle oxidation by O_2 [solid line – model prediction, dashed line – from the expression of Nagle and Strickland-Constable.[36]

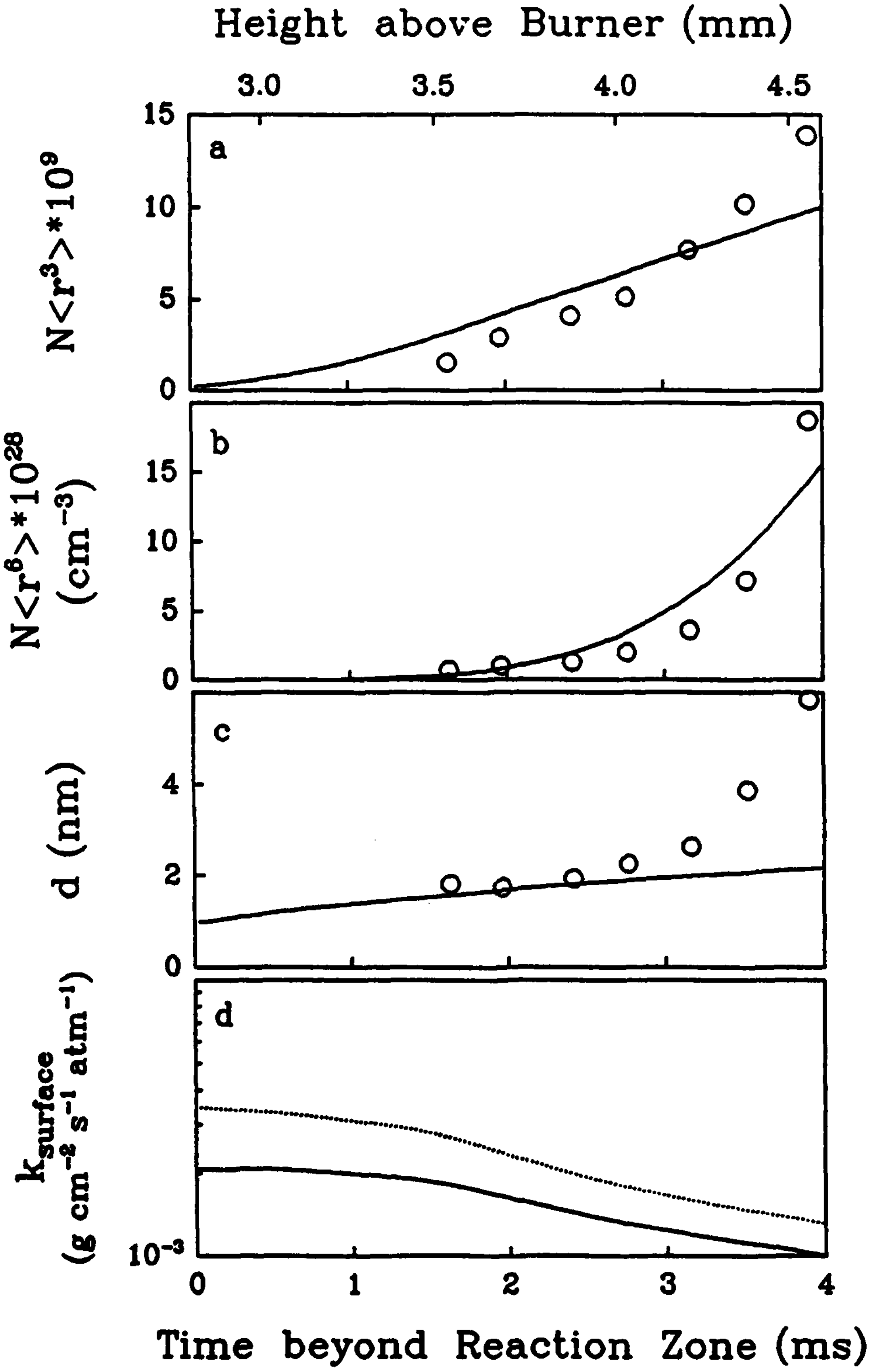

Fig. 12. Comparison of model predictions and experimental data for Flame H: (a)–(c) N – particle number density, r – particle radius, $<r^p>$ – average r^p, d – average particle diameter, circles – experimental results,[35] solid lines – model prediction; (d) specific surface growth rate coefficient.

As expected from the dynamics of Smoluchowski coagulation, the computed rate of nucleation is balanced by the rate of coagulation throughout the particle inception zone. Particle inception is primarily determined by PAH coagulation, initiated and controlled by PAH coalescence into dimers. Our model describes the surface processes in terms of elementary reactions of active sites. The density of active sites is determined by the gas-phase environment — by the competition among reactions (2)– (6). Hence, the dissimilarity in surface growth behavior can be explained by the difference in the dynamics of active sites. Our model resolves the controversy brought up recently by Bockhorn and co-workers,[32] who observed that the surface growth rate is independent of the surface area of soot particles, contrary to Harris and Weiner,[37] who postulated that the rate of surface growth is first order in particle surface area. Also, the computed net surface growth rate is computed to be in close agreement with that determined by Harris and Weiner[32] (Fig. 12d) and the predicted rate of soot oxidation by O_2 agrees well with the expression of Nagle and Strickland-Constable[36] (Fig. 11d).

Our model predicts what is essentially the classical picture of soot particle inception:[38] formation of PAHs, their coagulation into clusters and cluster coagulation, and surface growth due to chemical and physical processes. The model also predicts the classical structure of soot particles:[39] a less dense particle core, composed of randomly oriented PAH oligomers, and a more dense concentrically-arranged particle shell.

PRINCIPAL CONCLUSIONS AND RESULTS

The principal conclusion of this study is that the formation of polycyclic aromatic precursors to soot in hydrocarbon flames is dominated by the reactions of neutral species and not ionic ones. Whether ions play role in other soot-forming processes, like PAH coagulation is yet to be investigated.

A computer code for modeling large species and soot particle formation and growth was developed.

A detailed computer simulation of soot particle nucleation and growth in laminar premixed flames was successfully performed using our updated neutral reaction mechanism — for the first time soot particle inception could be modeled from first principles, starting with fuel decomposition and going all the way to predicting, in quantitative agreement with experiment, soot particle properties.

FUTURE WORK DIRECTION

Following the successful accomplishments in soot formation model development, culminated in quantitative prediction of soot particle properties in several laminar premixed flames, the direction for the future research, under the new AFOSR-sponsored project entitled "Development of Predictive Reaction Models of Soot Formation," is to extend the modeling efforts to computer simulation of soot particle phenomena in other flames of hydrocarbon fuels along with further refinement of the underlying reaction mechanism of soot formation.

PRESENTATIONS AND PUBLICATIONS

1. "Detailed Modeling of Soot Particles Nucleation and Growth," Frenklach, M., Poster presentation at the Twenty-Second International Symposium on Combustion, Seattle, Washington, August 14–19, 1988.
2. "Particulate Formation in Hydrocarbon Combustion," Frenklach, M., Invited seminar at the University of Cincinnati, Department of Chemical and Nuclear Engineering, February 2, 1989.
3. "Formation of PCA," Frenklach, M., Prepared statement at the workshop on "Current Problems in Soot Formation during Combustion, Especially the Mechanism of Soot Formation," the Commission on Condensation, Academy of Sciences Göttingen, FRG, March 29–30, 1989.
4. "Surface Growth," Frenklach, M., Prepared comment at the workshop on "Current Problems in Soot Formation during Combustion, Especially the Mechanism of Soot Formation," the Commission on Condensation, Academy of Sciences Göttingen, FRG, March 29–30, 1989.
5. "Modeling of PAH Profiles in Premixed Flames," Wang, H. and Frenklach, M., Paper presented at the Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Albany, New York, October 1989, Paper 12.
6. "Detailed Mechanism and Modeling of Soot Formation," Frenklach, M., in Extended Abstracts of the Conference on *Mechanism of Non-Uniform Combustion*, Tokyo Institute of Technology, Japan, 1990, p. 115.
7. "Kinetics and Mechanism of Formation of Carbonaceous Materials," Frenklach, M., Invited seminar at the University of Tokyo, Japan, September 13, 1990.
8. "Understanding Carbon: From Soot in Flames to Synthetic Diamond to Interstellar Dust," Frenklach, M., Invited seminar at SUNY at Binghamton, Department of Chemistry, New York, October 12, 1990.

9. "Detailed Modeling of Soot Particle Nucleation and Growth." Frenklach, M. and Wang, H., *Twenty-Third Symposium International on Combustion*, The Combustion Institute, in press.

10. "Reduction of Chemical Reaction Models," Frenklach, M., in *Numerical Approaches to Combustion Modeling* (E. S. Oran and J. P. Boris, Eds.), Am. Inst. Aeronautics Astronautics Prog. Ser., Washington, D.C., 1991, in press.

11. "Development of Chemical Reaction Models," Frenklach, M., in *Mobil Workshop on Chemical Reactions in Complex Systems*, Reinhold, 1991, in press.

12. "A New Mechanism for the Formation of Meteoritic Kerogen-Like Material," Morgan, W. A., Feigelson, E. D., Wang, H., and Frenklach, M., *Science*, submitted.

PROFESSIONAL PERSONNEL

Dr. Michael Frenklach — Principal investigator

Mr. Hai Wang — Graduate student

INVENTIONS

None.

REFERENCES

1. Frenklach, M., Clary, D. W., Yuan, T., Gardiner, W. C., Jr., and Stein, S. E., *Combust. Sci. Technol.* 50, 79 (1986).
2. Frenklach, M. and Warnatz, J., *Combust. Sci. Technol.* 51, 265 (1987).
3. Calcote, H. F. and Gill, R. J., Annual Report, AeroChem TP–486, November 1989.
4. Calcote, H. F. and Gill, R. J., Annual Report, AeroChem TP–482, March 1989.
5. Frenklach, M., Annual Report, AFOSR 88–0072, December 1988.
6. Frenklach, M., Clary, D. W., Gardiner, W. C., Jr., and Stein, S. E., *Twentieth Symposium (International) on Combustion*, The Combustion Institute, 1985, p. 887.
7. Calcote, H. F. and Gill, R. J., "Formation of Large Species in Sooting Flames by the Free Radical and Ionic Mechanisms," Twenty-Third Fall Technical Meeting of the Eastern Section of the Combustion Institute, 1990, Paper 124.
8. Calcote, H. F. and Keil, D. G., *Combust. Flame* 74, 131 (1988).
9. Delfau, J.-L., Vovelle, C., *Combust. Sci. Technol.* 41, 1 (1984).
10. Kee, R. J., Grcar, J. F., Smooke, M. D., and Miller, J. A., "A Fortran Program for Modeling Steady Laminar One-Dimensional Premixed Flames," Sandia Report No. SAND85–8240, December 1985.
11. Calcote, H. F., *Combust. Flame* 42, 215 (1981).
12. Westmoreland, P. R., "Experimental and Theoretical Analysis of the Oxidation and Growth Chemistry in a Fuel-Rich Acetylene Flame," Ph.D. thesis, MIT, 1986.
13. Bockhorn, H., Fetting, F., and Wenz, H. W., *Ber. Bunsenges. Phys. Chem.* 87, 1067 (1983); Bockhorn, H., Fetting, F., Heddrich, A. and Reh, CH., "Formation of High Molecular Hydrocarbons in Sooting Premixed Hydrocarbon-Oxygen Flames." Paper presented at the Twenty-First Symposium (International) on Combustion, Munich, FRG, August 1986, Poster 1.
14. Harris, S. J., Weiner, A. M., Blint, R. J., and Goldsmith, J. E. M., *Twenty-First Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1988, p. 1033.
15. Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., *The properties of Gases and Liquids*, McGraw–Hill, New York, 1975, p. 678.
16. Stein, S. E. and Fahr, A., *J. Phys. Chem.* 94, 3714 (1985).
17. Green, P. G., Kinsey, J. L., and Field, R. W., *J. Chem. Phys.* 91, 5160 (1989).
18. Frenklach, M, Wang, H., and Rabinowitz, M. J., "Optimization and Analysis of Large Chemical Kinetic Mechanisms Using the Solution Mapping Method — Combustion of Methane," submitted for publication.

19. Hwang, S. M., Gardiner, W. C., Jr., Frenklach, M., and Hidaka, Y., *Combust. Flame* 67, 65 (1987).

20. Miller, J. A. and Melius, C. F., *Twenty-Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1989, p.1031.

21. Mahmud, K. and Fontijn, A., *J. Phys. Chem.* 91, 1918 (1987).

22. Fahr, A. and Stein, S. E., *Twenty-Second Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1989, p.1023.

23. Westmoreland, P. R., Dean, A. M., Howard, J. B., and Longwell, J. P., *J. Phys. Chem.* 93, 8171 (1990).

24. Kiefer, J. H., Mizerka, L. J., Patel, M. R., and Wei, H. C., *J. Phys. Chem.* 89, 2013 (1985).

25. Lin, C.-Y. and Lin, M. C., Twentieth Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Geithersburg, MD, November 2–5, 1987, Paper 7–1.

26. Frenklach, M., in *Complex Chemical Reaction Systems, Mathematical Modelling and Simulation* (J. Warnatz and W. Jäger, Eds.), Springer-Verlag: Berlin, 1987, p. 2.

27. Frenklach, M., *Chem. Eng. Sci.* 10, 1843 (1985).

28. Harris, S. J. and Kennedy, I. M., *Combust. Sci. Technol.* 59, 443 (1988).

29. Frenklach, M., "A Unifying Picture of Gas-Phase Formation and Growth of PAH, Soot, Diamond and Graphite," in *Carbon in the Galaxy: Studies From Earth and Space* (J. C. Tarter, S. Chang and D. J. DeFrees, Eds.), NASA Conference Publication 3061, 1990, p. 259.

30. Frenklach, M. and Spear, K. E., *J. Mater. Res.* 3, 133 (1988).

31. Frenklach, M., *J. Appl. Phys.* 65, 5142 (1989).

32. Wieschnowsky, U., Bockhorn, H., and Fetting, F., *Twenty-Second Symposium (International) on Combustion*, p. 343, The Combustion Institute, 1989.

33. Neoh, K. G., Howard, J. B., and Sarofim, A. F., in *Particulate Carbon: Formation During Combustion* (D.C. Siegla and G.W. Smith, Eds.), p. 261, Plenum, New York, 1981.

34. Frenklach, M. and Harris, S. J., *J. Colloid Interface Sci.* 118, 252 (1987).

35. Harris, S. J., Weiner, A. M. and Ashcraft, C. C., *Combust. Flame* 64, 65 (1986).

36. Nagle, J. and Strickland-Constable, R. F., *Proceedings of the Fifth Conference on Carbon*, p. 154, Pergamon, London, 1962.

37. Harris, S. J. and Weiner, A. M., *Combust. Sci. Technol.* 32, 267 (1983).

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

39. Donnet, J. B., *Carbon* 20, 266 (1982).