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This is a collaborative study between AeroChem Research Laboratories and the Pennsylvania State University. The ultimate objective of this program is to develop a quantitative physical/chemical model of the mechanism of soot formation that is consistent with available experimental data. During the twelve-month period the chemical reaction mechanism of ionic growth developed by the AeroChem parallel efforts was tested with shock tube and laminar premixed stationary flame codes for acetylene-oxygen-argon mixtures. The results of these computations indicate that the formation of polycyclic aromatic hydrocarbons via the ionic reaction pathway is much more slower than that via the pathway involving neutral radicals under the conditions tested. Further analysis is in progress.

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**COMPUTER MODELING OF SOOT FORMATION
COMPARING FREE RADICAL AND IONIC MECHANISMS**

(A Collaborative Project between AeroChem and Penn State
Principal Investigators: H. F. Calcote and M. Frenklach)

Annual Technical Report

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

Covering the period from December 1, 1987 to November 30, 1988

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.....	4
WORK PROPOSED.....	4
RESULTS.....	5
Shock-Tube Simulations.....	5
Flame Simulations.....	11
FUTURE WORK.....	16
PROFESSIONAL PERSONNEL.....	18
REFERENCES.....	18

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INTRODUCTION

This is a 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 is 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 are: 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.

WORK PROPOSED

To achieve the stated objectives, the following three phases were proposed:

Phase I: Delineate the relative importance of radical and ionic mechanisms on soot nucleation.

1. Organize and interpret the available rate and thermochemical data on ion-molecule (AeroChem) and neutral (Penn State) reactions
2. Incorporate the data from task (1) above into computer codes (Penn State)
3. Measure H atom concentration in flames (AeroChem)
4. Simulate the "well-studied" flame (Penn State)
5. Analyze the results of computer simulations from task (4) above (AeroChem & Penn State)

Phase II: Extent the computer model to include all the important steps in the formation of coagulated soot

1. Organize and interpret the available rate and thermochemical data on soot particle growth (AeroChem)
2. Incorporate the data from task (1) above into computer codes (Penn State)
3. Simulate the "well-studied" flame with the the more complete mechanism (Penn State)
4. Analyze the results of computer simulations from task (3) above (AeroChem & Penn State)

Phase III: Confirm the generality of the model by comparing it with experimental data from other flame systems

RESULTS

During the twelve-months period since the beginning of the project the program is nearing completion of Phase I and entering into Phase II. Only the Penn State results will be reported here, those of AeroChem are reported in their (parallel) annual report.

Shock-Tube Simulations

Although our objective is to simulate a "well-studied" acetylene-oxygen flame, the computations for the shock-tube conditions were aimed at providing initial computer tests of the ionic mechanism as well as sensitivity analysis providing guidelines for mechanism modification and reduction necessary for flame simulations. A similar strategy was successfully utilized in our previous flame simulation of PAH formation and growth from neutrals.¹

A set of reactions for ionic and odd-carbon-atom species and the corresponding rate coefficient and thermodynamic data provided to us by the AeroChem were reviewed and transformed into the form comparable with the Penn State kinetic codes for soot formation. Among other things it involved development of a computer-suitable nomenclature for ionic species, similar to one developed for neutral species,² and incorporation of thermodynamic and rate data for ions, an electron, and additional odd-numbered hydrocarbons into our data bases. The initial mechanism, composed by combining this set of reactions with our most recent mechanism for acetylene oxidation,¹⁻³ was numerically integrated under the conditions of shock-tube experiments on soot formation in acetylene-oxygen-argon mixtures.⁴ The reaction mechanism and the rate and thermochemical data associated with it are reported and discussed in the (parallel) AeroChem Annual Report.

Selected results obtained in these shock-tube simulations are depicted in Figures 1 through 4. Figure 1 presents "soot yields" versus initial reaction temperature at a number of reaction times computed for a 1.09 % C₂H₂ - 0.3 % O₂ - Ar mixture at total density $\rho = 1.38 \times 10^{-5}$ mol/cm³ (conditions "B" in Reference 2). The "soot yield" in these simulations is defined as a fraction of carbon atoms accumulated in six- and seven-ring aromatic species. The numerical results depicted in Figure 2 show that the computed soot yields exhibit a maximum as a function of temperature at about 1600 K. This prediction is in a better agreement with the experimental data⁴ than the results computed with the radical mechanism.² However, the absolute values of the soot yield computed

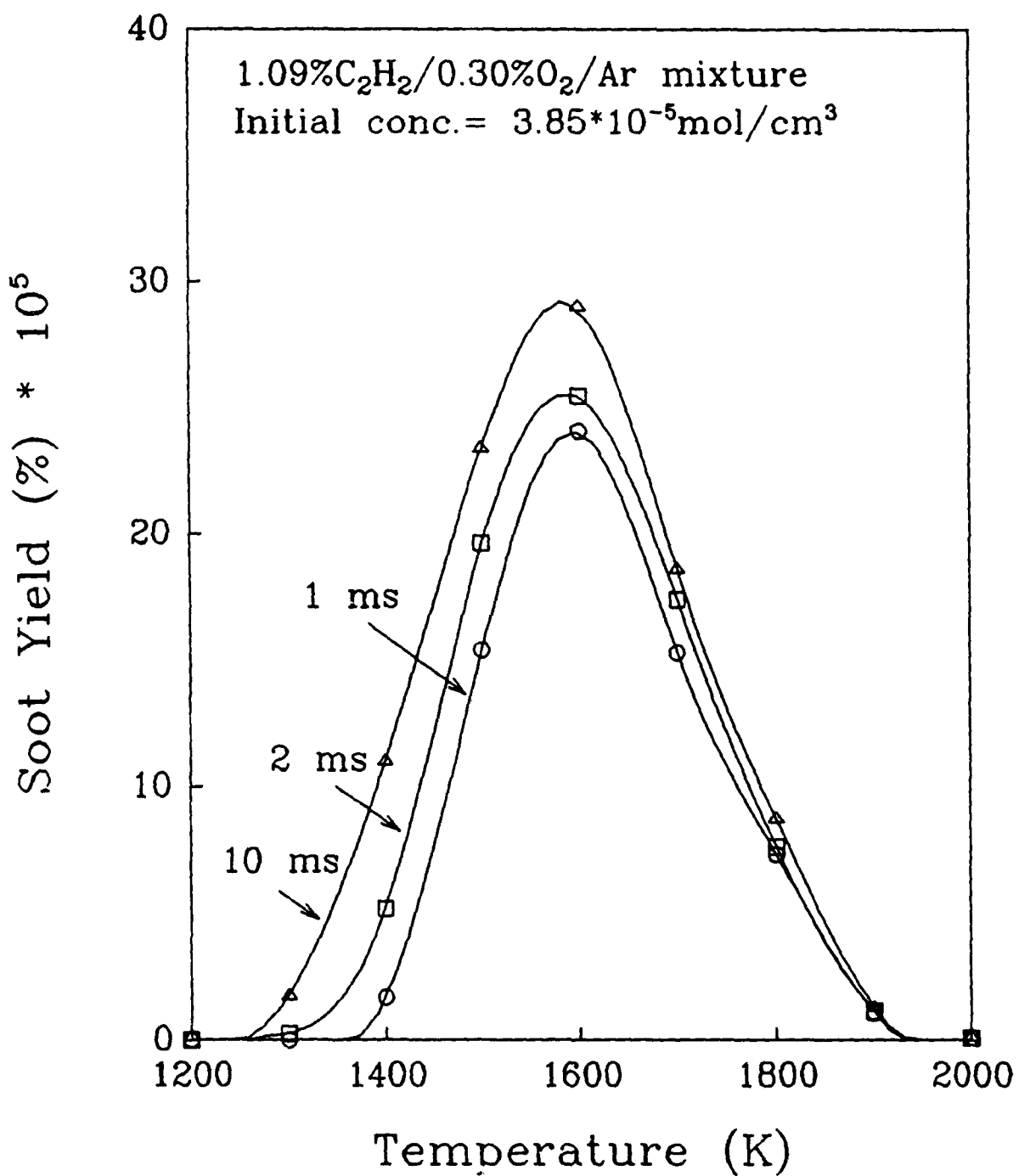
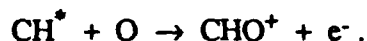


Figure 1. Soot yield versus initial temperature at three reaction times computed for the shock-tube conditions

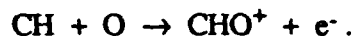
with the ionic mechanism (Figure 1) are much lower than the corresponding values computed with the radical mechanism (Figure 1 of Reference 2). The difference is one order of magnitude, and this is under the conditions when the oxidation reaction, removing substantially the aromatic flux in the radical mechanism, are not included in the computations with the ionic mechanism. Another feature which is not reproduced by the ionic mechanism is the dependence of the soot yield on the reaction time (cf the results at the three reaction times in Figure 1 with the experimental data⁵).

Figure 2 presents the dependence of the soot yield on the equivalence ratio of the mixture (ϕ) computed for the case of $T_0 = 1600$ K and 3 % argon. As can be seen from the results in this figure, the computed soot yield peaks at about $\phi = 2.8$ with the maximum value which is still significantly lower than the soot yield computed with the radical mechanism.

The above comparisons indicate that at shock-tube conditions the ionic mechanism produces polycyclic aromatic hydrocarbons (PAHs) at significantly lower rate than does the mechanism composed of only reactions of radical species. An extensive sensitivity and rate analysis found no conceivable adjustments in the parameter values that would affect this conclusion. The reaction pathway that dominates the formation of PAHs, as identified by the sensitivity and rate analysis, is depicted in Figure 3. There are two basic factors identified in the present 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 reaction initiating the formation of primary ions was identified to be



The rate of this reaction is given in Figure 4, where it is compared to the rate of the competing reaction



The second factor limiting the rate of PAH production via the ionic mechanism is the reversibility of some of the principal reaction steps. A close inspection of Figure 3 indicates that a number of steps in the principal reaction sequence are reversible. The computer simulations indicated that the forward and reverse reactions of these steps are tightly balanced, i.e. are in partial equilibrium, as is the case for the neutrals.² This reduces dramatically the net mass flux and thus limits the rate of PAH production.

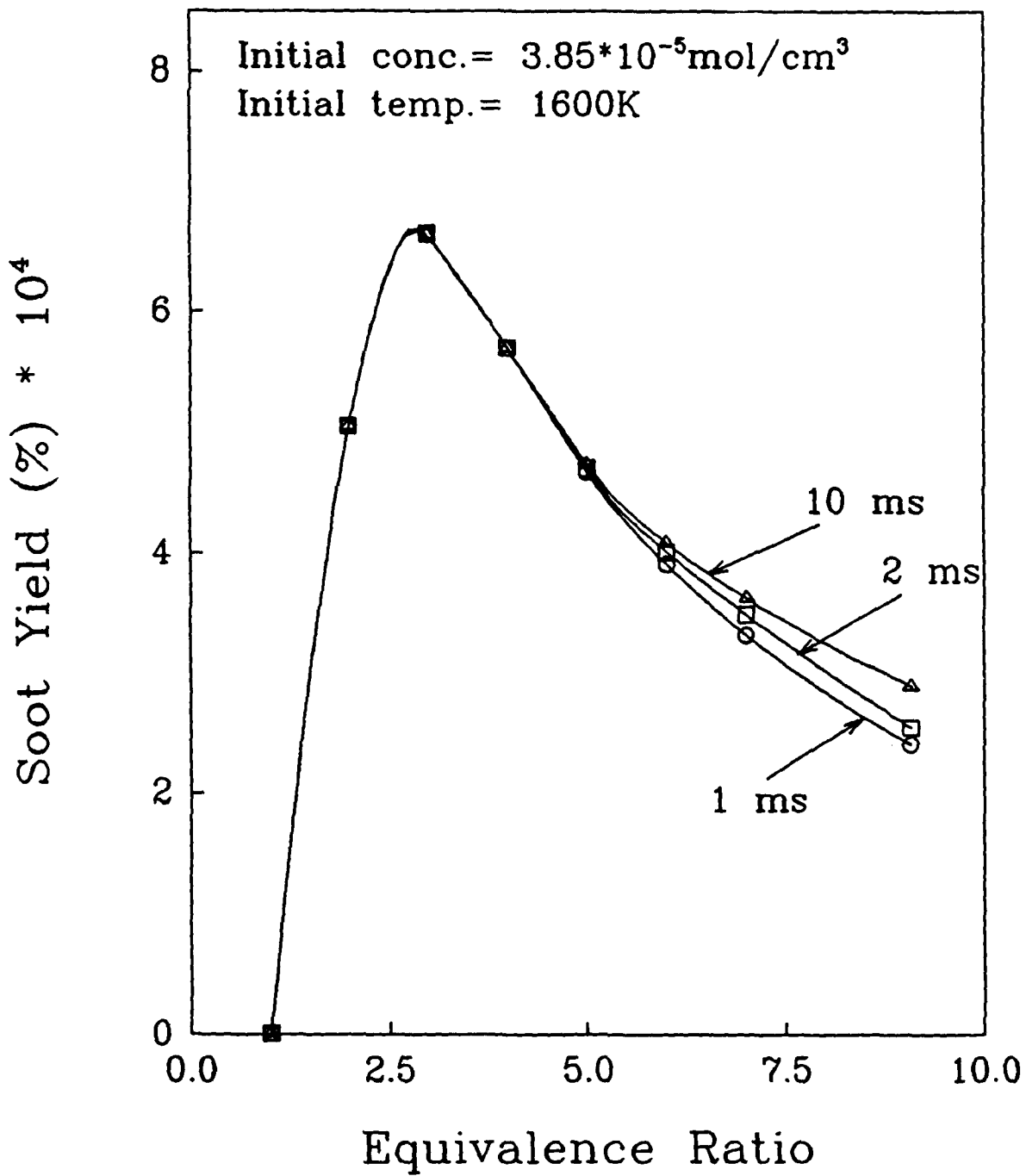


Figure 2. Soot yield versus equivalence ratio at three reaction times computed for the shock-tube conditions

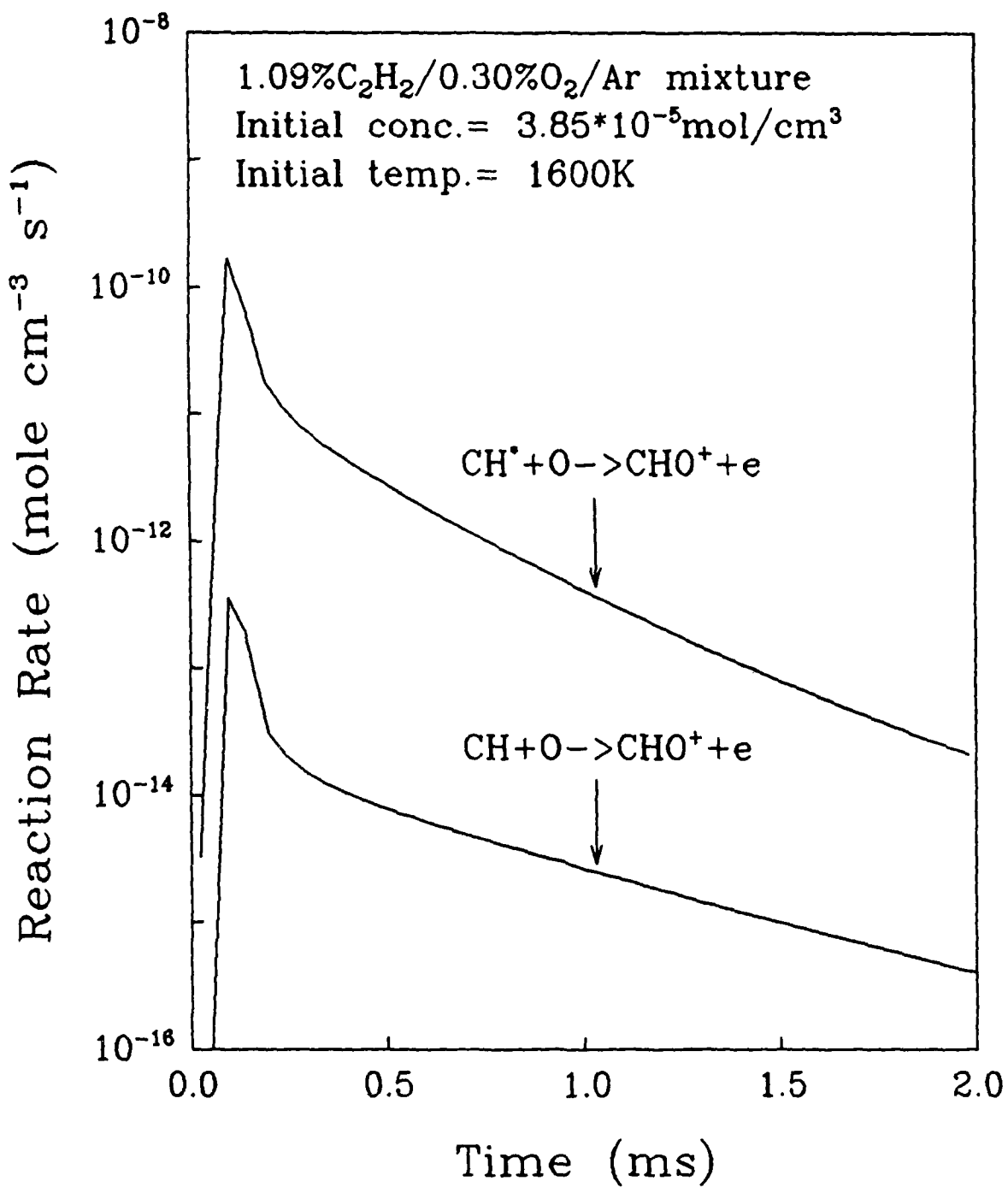


Figure 4. Rate of reactions responsible for the formation of primary ions

Flame Simulations

Prior to making any final conclusions on the competition between the ionic and radical mechanisms for PAH production, we must examine this question at the flame conditions, for which the experimental data on ionic species concentrations are available. Thus, using the reaction mechanism described above, a "well-studied" laminar premixed flame was simulated. The computations were performed using the Sandia burner code⁶ installed at the National Center for Supercomputing Applications at Urbana, Illinois.

As there is no single flame reported for which there are measurements available of all the chemical species, two 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 1 — is the flame for which ion concentration profiles were measured by Calcote and co-workers:⁷ 52.9 % C₂H₂ – 44.1 % O₂ – 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 Vovelle⁸ — referred to as Flame 2 — 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 1. 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 1 and 2 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 results of the flame simulations are presented in Figures 5 through 8. Examination of Figure 5 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 thermochemistry, 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 6 and 7. The agreement is worse for these species compared to the agreement seen for the major species in Figure 5. 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 radical mechanism.¹ The reasons for this are discussed in the cited work. 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 the order of magnitude of the experimental numbers.

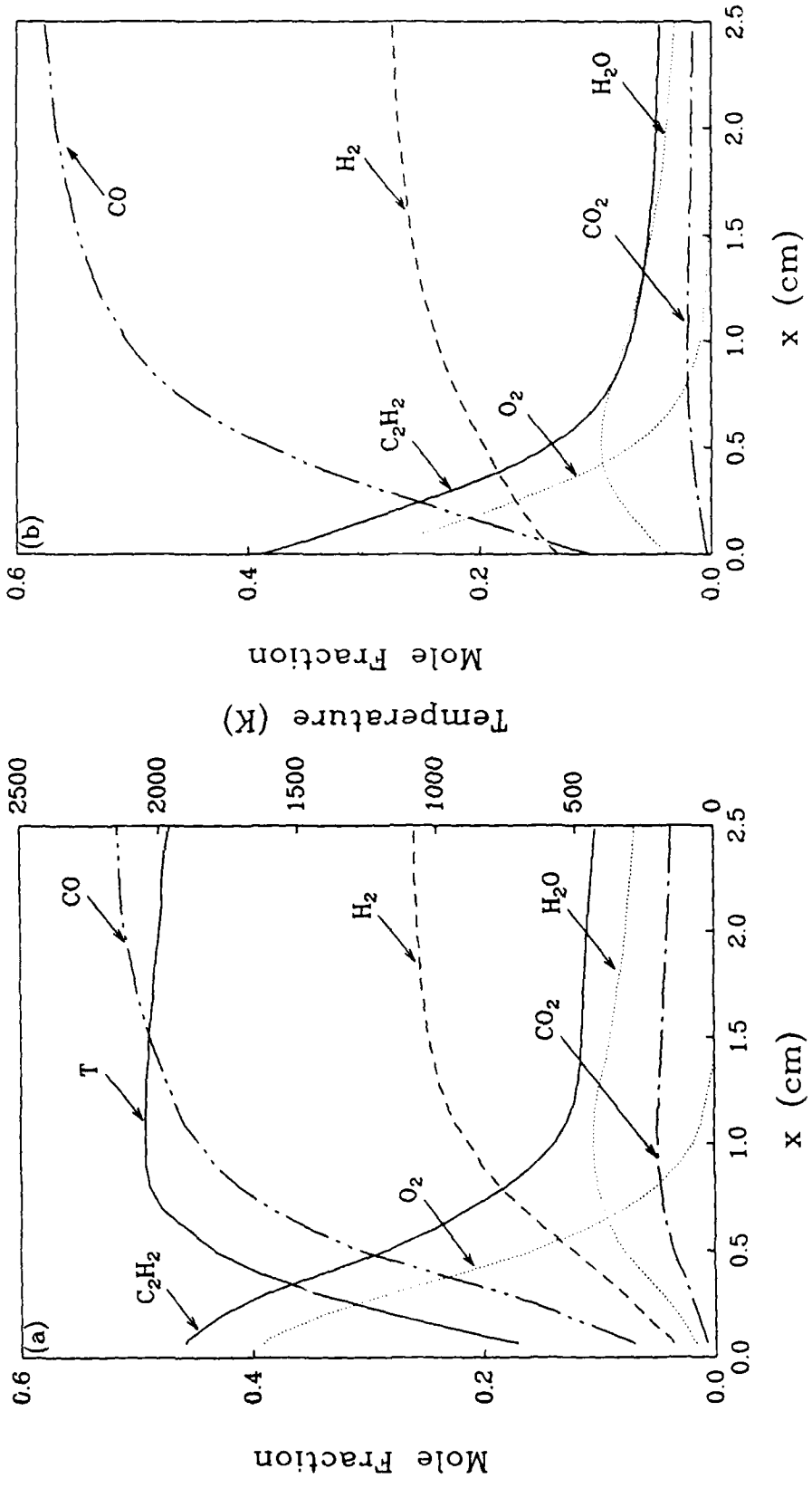


Figure 5. Concentration profiles of reactants and major products in Flame 2 (see test):
 a) experimental measurements; b) present computations using the temperature profile given in (a)

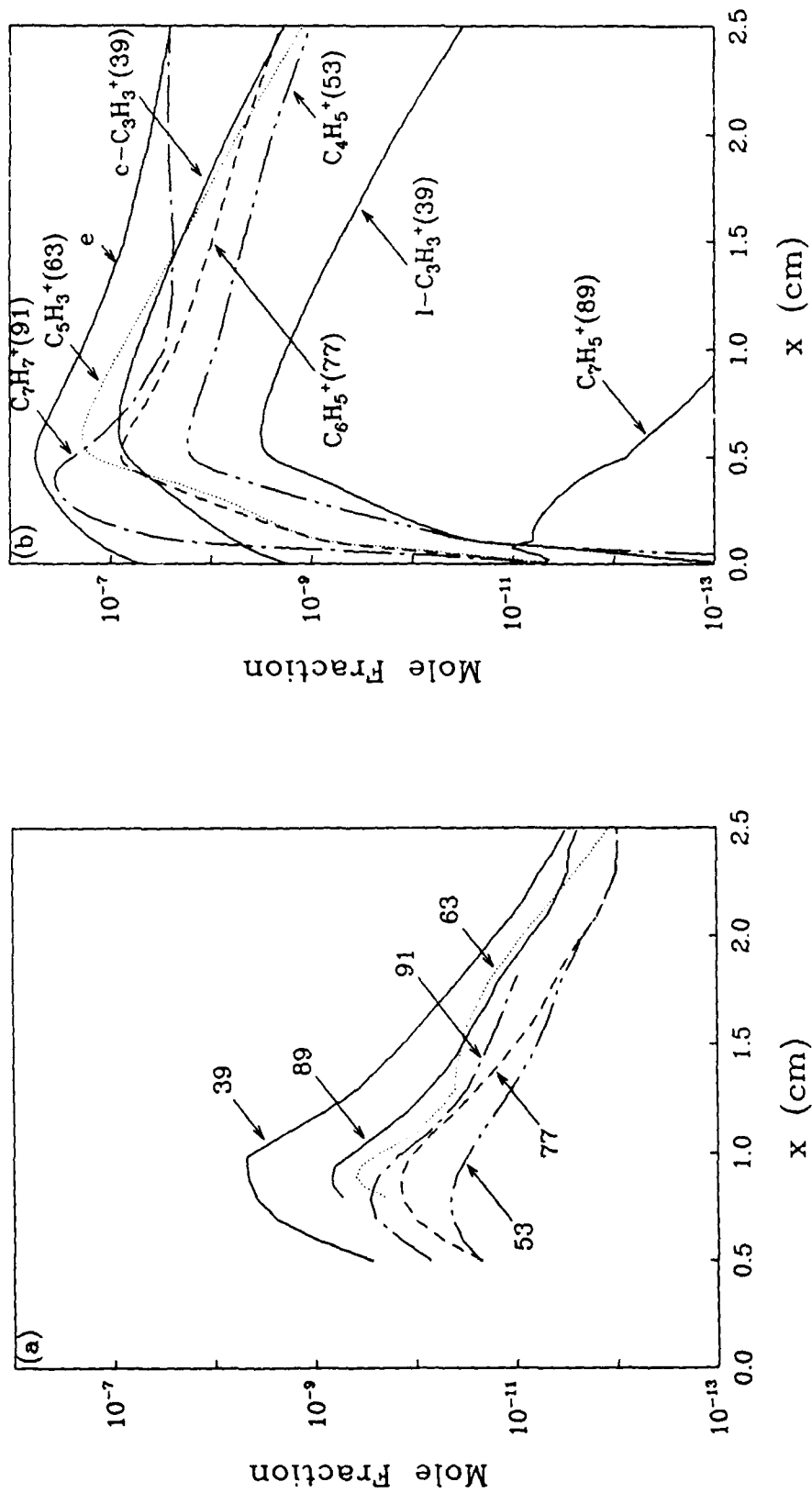


Figure 6. Concentration profiles of small ions in Flame 1 (see text): a) experimental measurements⁷; b) present computations using the temperature profile of Ref. 7

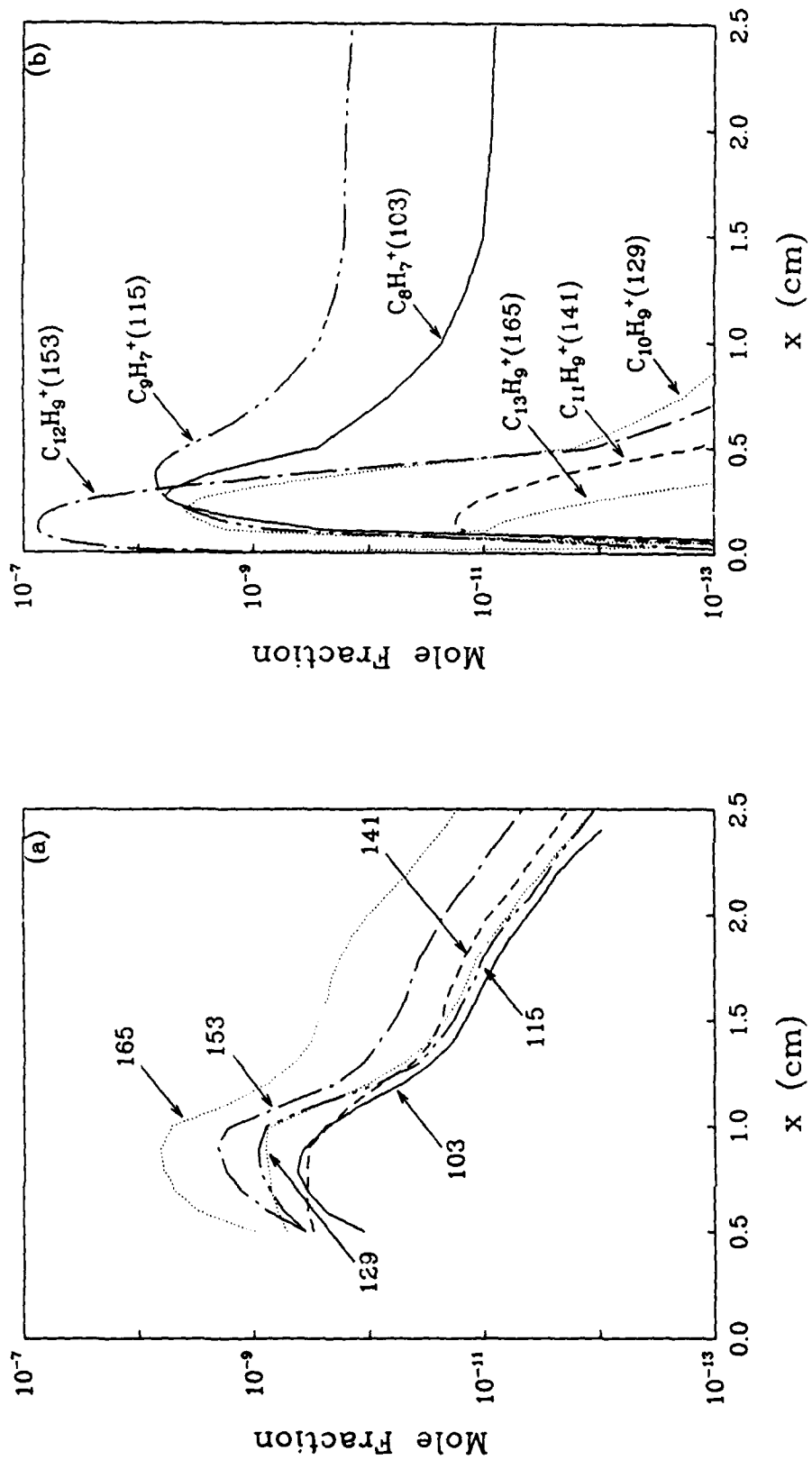


Figure 7. Concentration profiles of selected large ions in Flame 1 (see text): a) experimental measurements; b) present computations using the temperature profile of Ref. 7

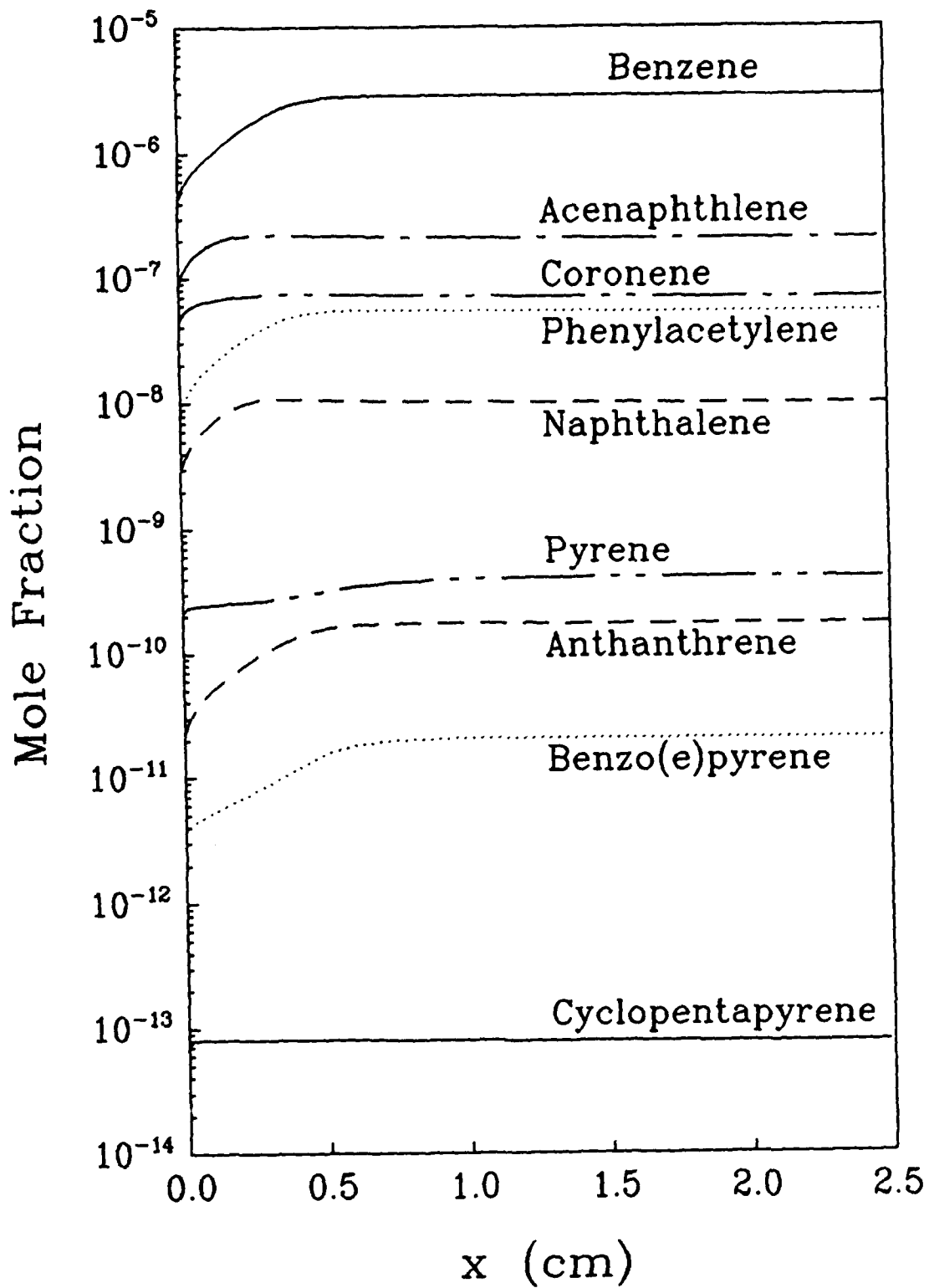


Figure 8. Computed concentration profiles of aromatic species in Flame 1

The computed concentrations of neutral aromatic molecules are shown in Figure 8. It should be stressed again that the current ionic mechanism does not contain oxidation reactions of aromatic species. The omission of the oxidation reactions is probably responsible for the absence of the decay in the concentration profiles. Thus, the results in Figure 8 are the computational upper limit for the corresponding experimental concentration peaks. The experimental measurements,⁹ however, are higher by about an order of magnitude compared to these predicted upper limits. The analysis of the results obtained in the flame simulations are in progress.

FUTURE WORK

The objective for the next year is to complete Phase I and to proceed with Phase II of the program. The specific tasks are the following:

1. To undertake and complete the analysis of the flame simulations with the current mechanism. This will involve a sensitivity and rate analysis. A number of additional flames, with different initial conditions, will be simulated. These results will be compared to those computed for the same flame conditions but with the "neutral" mechanism. (Penn State & AeroChem).
2. To complete the overall analysis of the competition of the PAH formation between the "ionic" and radical mechanisms and report the results in a full-length manuscript. (Penn State & AeroChem). This will conclude Phase I of the program.
3. To review the reactions and the associated rate and thermochemical data for the production of larger species and soot particles developed by that time by the AeroChem. (Penn State)
4. To develop a computer code for modeling of the formation and growth of large-sized species and soot particles. This task is two-fold. First, the present capabilities of the state-of-the-art premixed laminar flame codes that take transport properties into account correctly are limited, by physically realistic constraints on computer time and memory, to about 50 or so chemical species and a couple of hundreds of chemical reactions. In dealing with PAH and soot formation, one needs to consider a significantly larger mechanisms, since it is unclear at present which part of the reaction set will be dominant at flame conditions. The second difficulty is that there are no flame codes available that incorporate or are suitable for an implementation of chemical lumping.¹⁰ The latter (being developed under the Penn State program supported by the NASA-Lewis Research Center, Grant No. NAG 3-688) is required to model properly PAH growth and soot formation. To resolve these problems the following steps will be taken. First, the reaction mechanism will be reduced in size in such a way that it

still describes faithfully the flame structure. To accomplish this in a systematic way, a procedure will be developed which is an extension of the principles proposed previously and successfully applied to ignition phenomena.¹¹ Then, the formation of PAHs and soot will be computed with the full reaction mechanism using a simple kinetic code however with the imposed flame environment (temperature and critical species profiles) that were computed with the reduced mechanism. This strategy will be tested initially with a simpler, e.g. methane combustion, case. (Penn State).

5. After the numerical algorithm and computer codes in part (4) above are developed and tested, the lumping algorithm will be added to the kinetic code. The latter will be further developed to include the ionic reactions developed in part (3) above. A series of computer runs with the complete mechanism are expected to be completed by the end of the next twelve-month period. (Penn State).

PROFESSIONAL PERSONNEL

Dr. Michael Frenklach — Principal investigator

Mr. Hai Wang — Graduate student

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