

AeroChem TP-486

APOSR. TR. 89-1809

AD-A216 533

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

(A Collaborative Effort between AeroChem, Penn State and Iowa State)

H. F. Calcote and Robert J. Gill

AEROCHEM RESEARCH LABORATORIES, INC.

P.O. Box 12

Princeton, New Jersey 08542

November 1989

Annual Report for Period 1 October 1988 to 30 September 1989

Approved for Public Release
Distribution Unlimited

Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Bolling Air Force Base

Washington, DC 20332

DTIC
ELECTE
JAN 05 1990
S E D

90 01 01 028

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) TP-486			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR. 89-1809		
6a. NAME OF PERFORMING ORGANIZATION AeroChem Research Laboratories, Inc.		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NA		
6c. ADDRESS (City, State, and ZIP Code) P.O. Box 12 Princeton, New Jersey 08542			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 F49620-88-C-0007		
8c. ADDRESS (City, State, and ZIP Code) Building 410, Bolling AFB DC 20332-6448			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2308	TASK NO. A2
11. TITLE (Include Security Classification) (U) Computer Modeling of Soot Formation Comparing Free Radical and Ionic Mechanisms					
12. PERSONAL AUTHOR(S) H.F. Calcote and R.J. Gill					
13a. TYPE OF REPORT Annual		13b. TIME COVERED FROM 10/1/88 TO 9/30/89		14. DATE OF REPORT (Year, Month, Day) 1989 November 29	
15. PAGE COUNT 25					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Soot Formation; Ionic Mechanism; Thermodynamics; Ion-Molecule Reactions; Ion Electron Recombination		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This is the second annual report on a collaborative effort between AeroChem, Penn State, and Iowa State to compare the relative importance of the free radical mechanism of Frenk-lach and associates and the ionic mechanism of Calcote and associates by use of computer programs run at Penn State and Iowa State. The thermodynamic and reaction kinetics coefficients for the detailed ionic reaction mechanism are being developed by correlating data in the literature and performing theoretical calculations. Comparison of the computer model, using the present set of rate coefficients, with experimental ion concentrations in the standard acetylene-oxygen flame at 1.67 kPa demonstrates a number of problems with the present set of rate coefficients. These are being corrected. A comparison of the time it takes for the neutral and ionic mechanisms, using experimental species concentrations and typical rate coefficients used in the two respective mechanisms, demonstrates that the time to add ten carbon atoms, from C ₁₀ to C ₂₀ , by the two mechanisms is comparable. The (over)					
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

BLOCK 19 (continued)

higher concentration of neutral species is balanced by the greater reaction rate coefficients for ion-molecule reactions, and the fewer number of steps involved in adding a specific number of carbon atoms to the growing species for the ionic mechanism than for the neutral mechanism. This analysis demonstrates the need to go to larger species than C₂₀ to determine the relative rates of the two mechanisms in producing large carbon species.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



TABLE OF CONTENTS

	<u>Page</u>
I INTRODUCTION	1
II STATEMENT OF WORK	2
III THERMODYNAMICS	3
IV REACTION MECHANISM AND REACTION COEFFICIENTS	3
A. Excited State/Chemiiionization	3
B. Ion-Molecule Reactions	4
C. Ion-Electron Recombination	5
V COMPARISON OF THE RATE OF CARBON SPECIES GROWTH FOR NEUTRAL AND IONIC MECHANISMS	6
VI PUBLICATIONS	9
VII PROFESSIONAL PARTICIPATION	9
VIII TECHNICAL INTERACTIONS	9
IX INVENTIONS	9
X REFERENCES	10

LIST OF TABLES

	<u>Page</u>
I EXCITED STATE/CHEMIIONIZATION REACTIONS	13
II ION-MOLECULE REACTIONS	14
III ION-ELECTRON RECOMBINATION REACTIONS	18
IV TO ADD TEN CARBON ATOMS BY THE FREE RADICAL MECHANISM	20
V TO ADD TEN CARBON ATOMS BY THE IONIC MECHANISM	21

I. INTRODUCTION

This is the second annual report on this program which is a collaborative effort between AeroChem (Principal Investigator: H. F. Calcote), Penn State (Principal Investigator: M. Frenklach) and Iowa State (Principal Investigator: Robert C. Brown). The ultimate objective is to develop a quantitative model of soot formation in flames that is consistent with experimental data. The specific objectives of this collaborative three-year study are: (1) to delineate the relative importance of the neutral free radical and ionic mechanisms of soot formation in flames; (2) to determine the optimum model of the total soot formation process based upon what is currently known; and (3) to recommend what is required to improve the model and what additional experiments are necessary to clarify any discrepancies.

Professor Robert Brown, Iowa State University, has just been added as a collaborator to this program via a subcontract from AeroChem with funds which were added to this program for that purpose. He brings to the program previous experience in developing a code for modeling ionic reactions in flames^{1,2} involving the solution of the stiff equations involved in such reactions. He also plans to include ambipolar diffusion in his model; experimentally this has been demonstrated to be very important.³ The method Brown plans to employ will solve the Poisson equation for electric field strength as a function of one-dimensional charge distribution in the flame. His computer program should allow us to go to larger species than is now possible which appears to be important, see Section V below.

In this report, the AeroChem effort is reviewed; the Penn State effort will be covered in their companion report⁴; it is premature to report on the Iowa State results. AeroChem is responsible for development of the thermodynamics, diffusion coefficients, reaction mechanism, and reaction rate coefficients for the ionic mechanism. There were no previous sets of data on the ionic mechanism to draw upon when we initiated this program; two papers were subsequently published by Brown and Eraslan,^{1,2} in which they calculated the concentrations of ions in both stoichiometric and fuel rich flames and compared the calculations with experiments. For the sooting flames we wished to model in this program, it has been necessary not only to construct the ionic mechanism and identify the rate coefficients but also to develop neutral mechanisms and to organize data for odd number neutral carbon compounds. Such species are not generally utilized in the free radical mechanisms of soot formation. Odd carbon neutral species, however, play a significant role in the ionic mechanism and are observed in relatively large concentrations in sooting flames.

The computer modeling results are being compared with the well-documented acetylene/oxygen flame (the "standard flame") burning on a flat flame burner at a pressure of 1.67 kPa (20 Torr) and a linear flow rate of 50 cm/s in the unburned gases. In our previous AFOSR contract work,^{3,5,6} we duplicated the burner Bittner and Howard⁷ used to obtain neutral species concentrations and we measured ion concentration profiles with this burner so that the ion profiles and the neutral profiles would be from the same system. We also compared the data

obtained by a number of other researchers on very nearly the same flame; we previously presented the results of this comparison³ which showed amazing agreement among several laboratories. This data base forms an excellent experimental standard with which to compare the computer modeling results.

II. STATEMENT OF WORK

- A. Organize relevant data on ion-molecule reactions, thermochemistry, electron attachment, ion recombination, and ion and electron diffusion to be used in the computer codes.
- B. Determine the hydrogen atom concentration in the "well-studied" C_2H_2/O_2 flame and determine if this concentration exceeds the thermal equilibrium concentration.
- C. Analyze the computer simulation data obtained by Penn State and Iowa State and compare the results with available experimental data to determine the major chemical pathways to incipient soot and to simplify the computer model.
- D. Organize relevant data on the elementary steps involved in the growth of incipient soot to soot particles, including growth by molecular addition, coagulation, and oxidation.
- E. Analyze the computer simulation data obtained by Penn State and Iowa State using the extended model and compare the results with available experimental data to determine the major pathways to particulate soot and to determine how to alter the model to make it more in conformity with experimental results.
- F. Review the literature and choose flame experiments with which to compare the model developed above.
- G. Analyze the computer simulation data obtained by Penn State and Iowa State and compare the results with the experimental data to determine the general applicability of the model and to recommend what is required to improve the model and what additional experiments are necessary to clarify any discrepancies.

The statement of work for the subcontract with Brown at Iowa State is:

- A. Incorporate reaction mechanism and thermochemical data developed at AeroChem Research Laboratories in the TRANSEQL computer code.
- B. Assess the utility of determining ambipolar diffusion by numerical solution of the Poisson equation using a sample ion model.

- C. Perform baseline simulations of a test flame.
- D. Perform numerical simulations of the standard acetylene/oxygen flame.

III. THERMODYNAMICS

The thermodynamic work was reported on in detail in the last report⁸ and will not be elaborated on here. The inaccuracy of thermodynamic data continues to contribute a major question in any reaction kinetics scheme. During this report period we have added a few new species to our data base and have reevaluated some of the data. We plan to publish, probably with Steve Stein at NIST, a compilation of the data we have both generated on large ions. Where the ions overlapped, the agreement has been good except for the perinaphthalene ion, $C_{13}H_9^+$. These estimates are $\Delta H_f(298) = 1115$ kJ/mol (298) and 917 kJ/mol, depending upon whether the ion is anti-aromatic or not, respectively. Since $C_{13}H_9^+$ is a very dominant ion in flames and shows up repeatedly in ion spectra,⁹ the lower value is probably correct.

IV. REACTION MECHANISM AND REACTION COEFFICIENTS

The present mechanism has recently been run by M. Frenklach and H. Wang at Penn State and has not been completely analyzed so only qualitative interpretations will be given. It is certainly premature to make any judgment from the computer runs made to date. They have mostly been concerned with matching the computer program and the ionic mechanism. The basic problems appear to have been solved so that, in the near future, effort can be made to match the ionic mechanism to experimental data as has been done for the neutral mechanism.⁴

Our emphasis in this report will be on the limitations in the ionic mechanism and what specific work is being done. The neutral part of the mechanism which furnishes the reactants important in the ion-molecule reaction steps are the same as in the neutral mechanism except for the steps added last year to account for the odd number of carbon neutral species which are observed in flames and were added to the neutral mechanism.⁸ Thus, we will not discuss this part of the mechanism.

A. EXCITED STATE/CHEMIIONIZATION

Those specific reactions which produce excited CH , (CH^*) , important in the chemiionization process, and the chemiionization steps are presented in Table I. Probably the two most important reactions in this set (a sensitivity analysis has yet to be analyzed), are Reactions (3) and (9). The rate coefficient for Reaction (3) was estimated by W. Gardiner¹⁰ and the rate coefficient for Reaction (9) was measured by Cool relative to the rate coefficient for Reaction

(7).¹¹ The reaction coefficients for Reactions (7) and (8) are from a bimolecular quantum RRR theory calculation by Westmoreland and are in agreement with experiment.^{12,13}

B. ION-MOLECULE REACTIONS

The present set of ion-molecule reactions, chosen from a set of about 250 reactions, is presented in Table II. There were two criteria for the choice: (1) only neutral reactants: C_2H_2 , C_4H_2 , C_3H_2 , C_3H_4 and H_2O were used; (2) only reactions with a negative free energy over the temperature range from the initial temperature to the observed maximum flame temperature were used. The second criterion was employed to avoid difficulties which were experienced with previous sets of data; the reverse reactions turned out to be unrealistically fast. While this device avoided the problem, it probably led to smaller forward rates than are realistic--see Section V. The concentration of acetylene is so much greater than any other potential neutral reactant, that anything other than acetylene as a growth species can probably be ignored, as in soot growth, without a great loss in ion growth rate. Considering acetylene as the only reactant will involve reducing some of the rate coefficients to avoid excessive reverse reaction rates at high temperatures. In general, in the way we have chosen to write the reactions, always toward increasing molecular size, the free energy of reaction becomes more positive as the temperature is increased.

When available, experimental rate coefficients were used, but these are available only for small ions. In general, experimental rates are very close to the rate calculated by the average dipole orientation, ADO, theory¹⁴

$$k = \frac{2\pi e}{\mu^{1/2}} \left[\alpha^{1/2} + C\mu_D \left(\frac{2}{\pi kT} \right)^{1/2} \right] \quad (1)$$

where, μ is the reduced mass, α is the polarizability of the neutral reactant, C is a locking constant determined from experimental data, and μ_D is the dipole moment of the neutral reactant. For nonpolar species such as the neutral growth species in our ionic model, except for propyne, Eq. (1) reduces to the Langevin equation which does not have a temperature coefficient.

There have been several theoretical analyses with the objective of defining the temperature effect on ion-molecule reactions but these have all concentrated on the situation when the neutral reactant has a dipole moment.¹⁵⁻²⁰ In the Langevin theory,²¹ which forms the basis for these analyses, the ion is treated as a point charge. This is certainly not true for many of the large ions; even when the charge is localized it would be shielded from the approaching reactant by the rest of the molecule. Intuitively the larger ions should have a smaller rate coefficient and a negative temperature coefficient; the theoretical basis has to be developed.

Equation (1) accounts only for the number of collisions (it does not include collision efficiency) and fits most room temperature experimental rate coefficient data. There is considerable evidence that the rate of ion-molecule reactions is directly dependent upon the exothermicity of the reaction, ΔH_r , and we hope to use such correlations to estimate the collision efficiency for this set of reactions but have not yet devised a logical means.

One of the major problems in working with large ions is their identification; mass spectrometry gives mass only. The number of carbon and hydrogen atoms has been determined by use of isotopes.³ Thus for a given molecular formula there can be several isomeric structures. We thus include several isomers for some ions when their free energies of formation are close; we seek a rational means of reducing this to "one isomer" per ion, probably by weighting the thermodynamic quantities, ΔH_f and C_p appropriately and by mechanistic considerations.

Our efforts to assemble an ion-molecule reaction mechanism for soot formation have identified a number of areas where additional fundamental work is required.

C. ION-ELECTRON RECOMBINATION

The ions disappear by either ion-electron or positive ion-negative ion recombination reactions. Negative ion recombination rate coefficients are about an order of magnitude slower than electron recombination rate coefficients. Further, negative ion concentrations which have been measured are about two orders of magnitude smaller than electron concentrations²² but there are no good measurements of electron concentrations or negative ions in soot forming flames. There is, however, evidence for the presence of large negative ions in soot forming flames.^{3,23} We neglect negative ions for the present; should the ion decay be observed in the model to exceed that observed experimentally, we will reconsider the negative ion possibility. The ion-electron mechanism and rate coefficients are presented in Table III.

In choosing product channels for the large ion-electron dissociative recombination reactions, only molecules observed by Bockhorn et al.²⁴ have been considered as products. Reaction rate coefficients for ion-electron reactions are not strongly temperature dependent, but they do increase with the size of the ion.

We estimate the rate of ion recombination, α , by the equation for the rate of collision of electrons with particles²⁵

$$\alpha = \frac{\pi d^2}{4} \left[\frac{8kT}{\pi m_e} \right]^{1/2} \left[1 + \frac{e^2}{(2\pi\epsilon_0 d)kT} \right] \quad (2)$$

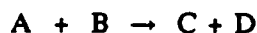
in which d = the ion diameter, m_e = the electron mass, and ϵ_0 = dielectric constant of free space. The ion diameters were calculated from ion mobilities by use of the Langevin equation

for ion mobilities. Equation (2) gives a $T^{-1/2}$ temperature dependence which compares favorably with experiments of Ogram et al.²⁶ for H_3O^+ . The values calculated by Eq. (2) were about twice the measured values of Ogram, so we have divided the calculated values by 2.

If there is an error in the data in Table III, it will be on the high side. This will be determinable by comparing experiment and computer runs. The computer run should be consistent, if we are correct above, with an interpretation that for smaller ions the recombination coefficients are correct and for larger ions they are too large. Generally, in the computer runs to date,⁴ most large ions--there are exceptions--are computed to have far too small a concentration and a more rapid decay rate than observed experimentally. The small concentration may be due to the ion-molecule rates being too small, or due to too fast a loss rate by ion-electron recombination. This could indicate the presence of significant concentrations of negative ions; their rates of recombination are smaller than for electrons. Of course, the recombination of a large positive ion and a large negative ion would double the size of the carbon species, albeit neutral, and could be interpreted as the first step in coagulation. Such collisions are favored, by electric charge effects, over ion-neutral or neutral-neutral collisions.

V. COMPARISON OF THE RATE OF CARBON SPECIES GROWTH FOR NEUTRAL AND IONIC MECHANISMS

The main objective of this program is to compare the rate of formation of large carbon species, which presumably lead to soot, by the free radical mechanism and the ionic mechanism. We have performed a comparison of the two rates by an oversimplified means, but one which should be quite accurate. Experimental measurements of concentrations of both neutral and ionic species in the standard acetylene flame²⁷ were combined with the rate coefficients for the growth of that species to the next larger species in the sequence, and a time was calculated for each of these steps. The times for the species to add a specified number of carbon atoms by the two mechanisms was then compared. Thus, for the reaction:



the rate of reaction is given by:

$$R = \frac{dC}{dt} = kAB \quad (3)$$

For this analysis we use the maximum (with respect to distance from the burner) experimental concentrations of A, and use the measured value of B at the position in the flame where the concentration of A is maximum. The appropriate rate coefficient for k is used for either the free radical or the ionic mechanism. In the free radical mechanism,^{28,29} A is a stable

species or a free radical and C is a free radical with the same number of carbon atoms as A, or a stable species with two more carbon atoms than A; B is a hydrogen atom or acetylene. In the ionic mechanism, A is an ion and C is an ion with two more carbon atoms than A; B is acetylene.

The time for a number, n , of the same species per unit volume to react is:

$$\tau = n/R. \quad (4)$$

where R is the appropriate rate constant for that step.

For this exercise, we chose n as the maximum soot number density observed in this flame, $4 \times 10^9 \text{ cm}^{-3}$. The number is not important for the comparison, but, as we will see, the use of the maximum number of soot particles has interesting implications. Thus we write the mechanism for adding ten carbons in the free radical mechanism and in the ionic mechanism, Tables IV and V, respectively. The time for each step is calculated by Eq. (4) using the free radical rate coefficients from Frenklach et al.²⁹:

$$\text{for } A + H\cdot (-H_2) \quad k = 1 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\text{and} \quad \text{for } A + C_2H_2 (-H\cdot) \quad k = 1 \times 10^{13}$$

and the ion-molecule reaction rate coefficient:

$$\text{for } A^+ + C_2H_2 (-D) \quad k = 6 \times 10^{14}.$$

In calculating the reaction times, only the forward reactions are considered for both mechanisms.

The total times required to add ten carbon atoms, Tables IV and V, are comparable for the two mechanisms: $9.7 \mu\text{s}$ for the free radical mechanism and $5.6 \mu\text{s}$ for the ionic mechanism. The higher concentration of neutral species is balanced by the greater reaction rate coefficients for ion-molecule reactions and the fewer number of steps involved in adding a specific number of carbon atoms to the growing species for the ionic mechanism than for the neutral mechanism.

Consideration for larger carbon containing species is not possible for the free radical mechanism because experimental data on large neutral species are not available in the standard flame, presumably because the concentrations are below detection limits. In fact, in the calculations of reaction times reported in Table IV, the neutral species concentrations above $C_{14}H_8$ were estimated from measurements in a different flame²⁴ because they are not available in the standard flame. Note the decrease in maximum concentration in going from C_6H_6 to $C_{14}H_8$ in the standard flame:

benzene	C_6H_6	7.8×10^{12} per cm^{-3}
naphthalene	$C_{10}H_8$	1.8×10^{11}
ethynylnaphthalene	$C_{12}H_8$	6.9×10^{10}
	$C_{14}H_8$	1.7×10^{10}

This is a decrease in concentration of about a factor of 60 per carbon atom added. Bockhorn's results,²⁴ which cover a larger range of carbon species do not indicate such a rapid decay, but unfortunately they are in a different flame.

For ions the decay in concentration is much less,³ e.g.:

$C_3H_3^+$	4.7×10^8 per cm^{-3}
$C_{30}H_{15}^+$	1.9×10^7
$C_{45}H_{17}^+$	1.9×10^6

This is a decrease in concentration of about a factor of 6 per carbon atom added, about one-tenth that indicated above for neutral species!

Clearly a comparison of the two mechanisms requires extension to much larger species than is done in Tables IV and V. The computer modeling effort will thus have to be extended to greater masses than are currently in the computer model.

We now consider the implications of the above calculations of reaction times. The maximum concentration of soot number density is reached at about 35 mm above the burner, or about 6.7 ms from the position in the flame at which large carbon containing species maximize. This is a good estimate of the time available, τ_s , for soot particles to be formed from molecular species. If we assume the time for addition of one carbon atom to the growing species is τ_c , then the number of carbon atoms, N_c , that can be added to the growing nuclei is:

$$N_c = \frac{\tau_s}{\tau_c} = \frac{6.7 \times 10^{-3}}{7.4 \times 10^{-7}} \approx 9,000 \text{ carbon atoms.}$$

τ_c is taken as the average for the neutral and ion mechanisms, Table IV and V. 9,000 carbon atoms corresponds to a molecular weight of about 110,000 amu. This is equivalent to a particle diameter of about 4.5 or 3.0 nm, depending upon whether the particle is planar or spherical, respectively.³⁰ The experimentally observed particle diameters at 35 mm above the burner surface are 9-13 nm for neutral particles and 3-6 nm for charged particles. One of the interesting observations is that the calculated diameter, assuming the equivalent of a fixed rate (fixed time) for adding carbon atoms to the growing species, neutral or ion, leads to a diameter of the carbon particle very close to that observed, within the accuracy of the calculation and the measurement.

The main point of the above discussion with respect to our primary objective, is that examining relatively small carbon species does not permit a decision between the rate of soot nucleation by the neutral and the ionic mechanism; they both have about the same reaction times with the data that have been analyzed. To make a distinction between the two mechanisms one must examine reactions involving larger numbers of carbon atoms than are in the present computer model.

VI. PUBLICATIONS

A publication of the thermodynamic data base developed for this program will probably be submitted for publication with Steve Stein at NIST who has also developed thermodynamic data on large ions, a few overlapping ours. A manuscript will be submitted to Blackwell who is publishing the plenary lectures of the Third International Seminar on Flame Structure at Alma Ata (USSR), September 1989. Our title was "The Role of Ions in Soot Formation"; the subject matter of Section V of this report was presented.

VII. PROFESSIONAL PARTICIPATION

The Principal Investigator on the program is H. F. Calcote who has been responsible for developing the reaction mechanism and collecting the reaction kinetics data. Dr. R. J. Gill has been responsible for collecting and calculating the thermodynamics data. We both acknowledge fruitful discussions with Drs. W. Felder and D. G. Keil.

VIII. TECHNICAL INTERACTIONS

During this period Prof. Phil Westmoreland and his student visited AeroChem to consult with us on their setting up a mass spectrometer to study flames (incidentally ours is idle !). We have consulted with a number of people from whom we have solicited help in setting up our mechanism. These have included: William Gardiner; Dave Golden; Sharon G. Lias; Steve Stein; and Phil Westmoreland.

IX. INVENTIONS

None.

X. REFERENCES

1. Eraslan, A.N. and Brown, R.C., "Chemiiionization and Ion-Molecule Reactions in Fuel-Rich Acetylene," *Combust. Flame* 74, 19 (1988).
2. Brown, R.C. and Eraslan, A.N., "Simulation of Ionic Structure in Lean and Close-to-Stoichiometric Acetylene Flames," *Combust. Flame* 73, 1 (1988).
3. Calcote, H.F. and Keil, D.G., "Ion-Molecule Reactions in Sooting Acetylene-Oxygen Flames," *Combust. Flame* 74, 131 (1988).
4. Frenklach, M., "Computer Modeling of Soot Formation Comparing Free Radical and Ionic Mechanisms," Annual Technical Report, in preparation.
5. Keil, D.G., Gill, R.J., Olson, D.B., and Calcote, H.F., "Ionization and Soot Formation in Premixed Flames," Twentieth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1985) p. 1129.
6. Keil, D.G., Gill, R.J., Olson, D.B., and Calcote, H.F., "Ion Concentrations in Premixed Acetylene-Oxygen Flames Near the Soot Threshold," in The Chemistry of Combustion Processes, T.M. Sloane, Ed., ACS Symposium Series 249 (American Chemical Society, Washington, DC, 1984) p. 33.
7. Bittner, J.D. and Howard, J.B., "Pre-Particle Chemistry of Soot Formation," in Particulate Carbon: Formation During Combustion, D.G. Siegl and G.W. Smith, Eds. (Plenum, New York, 1981) p. 109.
8. Calcote, H.F. and Gill, R.J., "Computer Modeling of Soot Formation Comparing Free Radical and Ionic Mechanisms," Annual Report, AeroChem TP-482, March 1989.
9. NIST/EPA/MSDC Mass Spectral Database, P.C. Version 2.0, January 1989.
10. Hwang, S.M., Gardiner, W.C., Jr., Frenklach, M., and Hidaka, Y., "Induction Zone Exothermicity of Acetylene Ignition," *Combust. Flame* 67, 65 (1987).
11. Cool, T.A. and Tjossem, J.H., "Direct Observation of Chemi-ionization in Hydrocarbon Flames Enhanced by Laser Excited $\text{CH}^*(\text{A}^2\Delta)$ and $\text{CH}^*(\text{B}^2\Sigma)$," *Chem. Phys. Lett.* 111, 82 (1984).
12. Westmoreland, P.R., "Importance of Obvious and Disguised Association Reactions in Combustion," submitted to *J. Phys. Chem.*, September 1989.

13. Westmoreland, P.R., Personal communication on chemiionization, 9 October 1989.
14. Su, T. and Bowers, M.T., in Gas Phase Ion Chemistry, M. T. Bowers, Ed. (Academic Press, New York, 1979), Ch. 3.
15. Bates, D.R., "Density of Quantum States of Ion-Molecule Association Complex and Temperature Dependence of Radiative Association Coefficient," J. Chem. Phys. 73, 1000 (1980).
16. Bates, D.B., "Temperature Dependence of Ion-Molecule Association," J. Chem. Phys. 71, 2318 (1979).
17. Chang, J.S. and Golden, D.M., "Kinetics and Thermodynamics for Ion-Molecule Association Reactions," J. Am. Chem. Soc. 103, 496 (1981).
18. Patrick, R. and Golden, D.M., "The Temperature Dependence of Ion-Molecule Association Reactions," J. Chem. Phys. 82, 75 (1985).
19. Dodds, J.A., Golden, D.M., and Brauman, J.I., "Entropy Bottlenecks in Ion-Molecule Reactions," J. Chem. Phys. 80, 1894 (1984).
20. Smith, D. and Adams, N.G., "Cyclic and Linear Isomers of $C_3H_2^+$ and $C_3H_3^+$: The $C_3H_2 + H_2$ Reaction," Int. J. Mass Spectr. Ion Proc. 76, 307 (1987).
21. Gioumousis, G. and Stevenson, D.P., "Reactions of Gaseous Molecule Ions with Gaseous Molecules. V. Theory," J. Chem. Phys. 29, 294 (1958).
22. Calcote, H.F., Kurzius, S.C., and Miller, W.J., "Negative and Secondary Ion Formation in Low Pressure Flames," Tenth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1965) p. 605.
23. Homann, K.H. and Stroefer, E., "Charged Soot Particles in Unseeded and Seeded Flames," in Soot in Combustion Systems, J. Lahaye and G. Prado, Eds. (Plenum Press, New York, 1981) p. 217.
24. Bockhorn, H., Fetting, F., and Wenz, H.W., "Investigation of the Formation of High Molecular Hydrocarbons in Premixed Hydrocarbon-Oxygen Flames," Ber. Bunsenges. Phys. Chem. 87, 1067 (1983).
25. Sodha, M.S. and Guha, S., Adv. Plasma Phys. 4, 219 (1971).
26. Ogram, G.L., Chang, J.-S., and Hobson, R.M., "Dissociative Recombination of H_3O^+ and D_3O^+ at Elevated Electron and Gas Temperatures," Phys. Rev. 21, 982 (1980).

27. Calcote, H.F., Olson, D.B., and Keil, D.G., "Are Ions Important in Soot Formation," *Energy & Fuels* 2, 494 (1988).
28. Frenklach, M. and Warnatz, J., "Detailed Modeling of PAH Profiles in a Sooting Low Pressure Acetylene Flame," *Combust. Sci. Techn.* 51, 265 (1987).
29. Frenklach, M., Clary, D.W., Gardiner, W.G., Jr., and Stein, S.F., "Detailed Kinetic Modeling of Soot Formation in Shock-Tube Pyrolysis of Acetylene," Twentieth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1984) p. 887.
30. Calcote, H.F., "Mechanisms of Soot Formation in Flames-A Critical Review," *Combust. Flame* 42, 215 (1981).

TABLE I

EXCITED STATE/CHEMIIONIZATION REACTIONS

$$k = AT^n \exp(-E(\text{kJ})/RT), \text{ cm}^3, \text{ mol}, \text{ s}$$

No.	REACTION		A	n	E, kJ
1	$\text{C}_2 + \text{OH}$	$\rightarrow \text{CH}({}^2\Delta) + \text{CO}$	$3.4\text{E}+12$	0.0	0
2	$\text{C}_2\text{H} + \text{O}$	$\rightarrow \text{CH}({}^2\Delta) + \text{CO}$	$7.1\text{E}+11$	0.0	0
3	$\text{C}_2\text{H} + \text{O}_2$	$\rightarrow \text{CH}({}^2\Delta) + \text{CO}_2$	$4.5\text{E}+15$	0.0	105
4	$\text{CH}({}^2\Delta) + \text{M}$	$\rightarrow \text{CH}({}^2\Pi) + \text{M}$	$4.0\text{E}+10$	0.5	0
5	$\text{CH}({}^2\Delta) + \text{O}_2$	$\rightarrow \text{CH}({}^2\Pi) + \text{O}_2$	$2.4\text{E}+12$	0.5	0
6	$\text{CH}({}^2\Delta)$	$\rightarrow \text{CH}({}^2\Pi)$	$1.7\text{E}+06$	0.0	0
7	$\text{CH}({}^2\Pi) + \text{O}({}^3\text{P})$	$\rightarrow \text{HCO}^+ + \text{e}$	$4.6\text{E}+08$	0.73	-2.56
8	$\text{CH}({}^2\Pi) + \text{O}({}^3\text{P})$	$\rightarrow \text{H} + \text{CO}$	$3.1\text{E}+14$	-0.25	1.1
9	$\text{CH}({}^2\Delta) + \text{O}({}^3\text{P})$	$\rightarrow \text{HCO}^+ + \text{e}$	$4.8\text{E}+14$	0.0	0

TABLE II
ION-MOLECULE REACTIONS

$$k = AT^n \exp(-E(\text{kJ})/RT), \text{ cm}^3, \text{ mol}, \text{ s}$$

Codes for molecular structure: $\text{C}_3\text{H}_3^+ = \text{C}_3\text{H}_3^+(1)$; $\text{H}_3\text{C}_3^+ = \text{C}_3\text{H}_3^+(c)$; $\text{C}_3\text{H}_4 = \text{C}_3\text{H}_4(\text{allene})$; $\text{H}_4\text{C}_3 = \text{C}_3\text{H}_4(\text{propyne})$; $\text{C}_6\text{H}_5^+ = \text{C}_6\text{H}_5^+(\text{linear})$; $\text{C}_2\text{H}_3 = \text{C}_2\text{H}_3(1)$; $\text{C}_7\text{H}_7^+ = \text{benzyl}$; $\text{C}_3\text{H}_2 = \text{H-C}\equiv\text{CH}$; $\text{HC} = \text{CH}^*$ (electronic state: $^2\Delta$); C_xH_y^+ , H_yC_x^+ , and $\text{C}_x\text{H}_{(y-n)}\text{H}_n$ represent three different isomers of the same ion.

No.	REACTION		A	n	E, kJ
1	HCO^+	$+ \text{C}_2\text{H}_2 = \text{C}_2\text{H}_3^+ + \text{CO}$	$8.3\text{E}+14$	0.0	0
2	HCO^+	$+ \text{C}_3\text{H}_2 = \text{C}_3\text{H}_3^+ + \text{CO}$	$7.3\text{E}+14$	0.0	0
3	HCO^+	$+ \text{C}_3\text{H}_4 = \text{C}_3\text{H}_3^+ + \text{H}_2 + \text{CO}$	$7.0\text{E}+14$	0.0	0
4	HCO^+	$+ \text{C}_4\text{H}_2 = \text{C}_4\text{H}_3^+ + \text{CO}$	$6.0\text{E}+14$	0.0	0
5	HCO^+	$+ \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CO}$	$1.9\text{E}+15$	0.0	0
6	H_3O^+	$+ \text{C}_4\text{H}_2 = \text{C}_4\text{H}_3^+ + \text{H}_2\text{O}$	$8.6\text{E}+14$	0.0	0
7	H_3O^+	$+ \text{C}_3\text{H}_2 = \text{C}_3\text{H}_3^+ + \text{H}_2\text{O}$	$8.6\text{E}+14$	0.0	0
8	C_2H_3^+	$+ \text{C}_2\text{H}_2 = \text{C}_4\text{H}_3^+ + \text{H}_2$	$3.0\text{E}+14$	0.0	0
9	C_3H_3^+	$+ \text{C}_3\text{H}_4 = \text{C}_4\text{H}_3^+ + \text{C}_2\text{H}_4$	$6.6\text{E}+14$	0.0	0
10	C_3H_3^+	$+ \text{C}_3\text{H}_4 = \text{C}_4\text{H}_5^+ + \text{C}_2\text{H}_2$	$7.5\text{E}+14$	0.0	0
11	C_3H_3^+	$+ \text{C}_4\text{H}_2 = \text{C}_5\text{H}_3^+ + \text{C}_2\text{H}_2$	$8.4\text{E}+14$	0.0	0
12	C_3H_3^+	$+ \text{C}_2\text{H}_2 = \text{C}_5\text{H}_3^+ + \text{H}_2$	$3.0\text{E}+14$	0.0	0
13	C_3H_3^+	$+ \text{C}_3\text{H}_4 = \text{C}_6\text{H}_5^+ + \text{H}_2$	$6.6\text{E}+14$	0.0	0
14	C_3H_3^+	$+ \text{M} = \text{H}_3\text{C}_3^+ + \text{M}$	$3.2\text{E}+15$	0.0	0
15	C_3H_3^+	$+ \text{OH} = \text{HCO}^+ + \text{C}_2\text{H}_3$	$7.6\text{E}+14$	-0.1	125
16	C_4H_3^+	$+ \text{C}_3\text{H}_4 = \text{C}_7\text{H}_7^+$	$6.0\text{E}+14$	0.0	0
17	C_4H_3^+	$+ \text{C}_3\text{H}_4 = \text{C}_7\text{H}_5^+ + \text{H}_2$	$7.6\text{E}+14$	0.0	0
18	C_4H_5^+	$+ \text{C}_2\text{H}_2 = \text{C}_6\text{H}_5^+ + \text{H}_2$	$6.0\text{E}+14$	0.0	0
19	C_4H_5^+	$+ \text{C}_4\text{H}_2 = \text{C}_8\text{H}_7^+$	$6.0\text{E}+14$	0.0	0
20	C_4H_5^+	$+ \text{C}_3\text{H}_4 = \text{C}_7\text{H}_7^+ + \text{H}_2$	$6.0\text{E}+14$	0.0	0
21	C_5H_3^+	$+ \text{C}_3\text{H}_4 = \text{C}_6\text{H}_5^+ + \text{C}_2\text{H}_2$	$6.6\text{E}+14$	0.0	0
22	C_6H_5^+	$+ \text{C}_3\text{H}_4 = \text{C}_7\text{H}_7^+ + \text{C}_2\text{H}_2$	$6.5\text{E}+14$	0.0	0
23	C_6H_5^+	$+ \text{C}_3\text{H}_4 = \text{C}_9\text{H}_7^+ + \text{H}_2$	$6.0\text{E}+14$	0.0	0
24	C_7H_5^+	$+ \text{C}_3\text{H}_4 = \text{C}_8\text{H}_7^+ + \text{C}_2\text{H}_2$	$6.0\text{E}+14$	0.0	0

TABLE II (continued)

No.	REACTION	A	n	E, kJ
25	$C_7H_5^+ + C_3H_4 = C_{10}H_9^+$	6.0E+14	0.0	0
26	$C_7H_5^+ + C_3H_4 = H_9C_{10}^+$	6.0E+14	0.0	0
27	$C_7H_5^+ + C_2H_2 = C_9H_7^+$	6.0E+14	0.0	0
28	$C_7H_7^+ + C_3H_4 = C_{10}H_9^+ + H_2$	6.0E+14	0.0	0
29	$C_8H_7^+ + C_2H_2 = C_{10}H_9^+$	6.0E+14	0.0	0
30	$C_8H_7^+ + C_4H_2 = C_{12}H_9^+$	6.0E+14	0.0	0
31	$C_8H_7^+ + C_3H_4 = H_9C_{11}^+ + H_2$	6.0E+14	0.0	0
32	$C_9H_7^+ + C_3H_4 = C_{10}H_9^+ + C_2H_2$	6.0E+14	0.0	0
33	$C_9H_7^+ + C_3H_4 = H_9C_{10}^+ + C_2H_2$	6.0E+14	0.0	0
34	$C_{10}H_9^+ + C_2H_2 = C_{12}H_9^+ + H_2$	6.0E+14	0.0	0
35	$C_{10}H_9^+ + C_4H_2 = C_{12}H_9^+ + C_2H_2$	6.0E+14	0.0	0
36	$C_{11}H_9^+ + C_2H_2 = C_{13}H_9^+ + H_2$	6.0E+14	0.0	0
37	$C_{11}H_9^+ + C_2H_2 = C_{13}H_8H^+ + H_2$	6.0E+14	0.0	0
38	$C_{11}H_9^+ + C_4H_2 = C_{13}H_9^+ + C_2H_2$	6.0E+14	0.0	0
39	$C_{11}H_9^+ + C_4H_2 = C_{13}H_8H^+ + C_2H_2$	6.0E+14	0.0	0
40	$C_{12}H_9^+ + C_4H_2 = C_{16}H_{11}^+$	6.0E+14	0.0	0
41	$C_{13}H_9^+ + C_4H_2 = C_{17}H_{11}^+$	6.0E+14	0.0	0
42	$C_{13}H_9^+ + C_4H_2 = H_{11}C_{17}^+$	6.0E+14	0.0	0
43	$C_{15}H_{11}^+ + C_2H_2 = C_{17}H_{11}^+ + H_2$	6.0E+14	0.0	0
44	$C_{15}H_{11}^+ + C_4H_2 = C_{17}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
45	$C_{15}H_{11}^+ + C_4H_2 = H_{11}C_{17}^+ + C_2H_2$	6.0E+14	0.0	0
46	$C_{15}H_{11}^+ + C_2H_2 = H_{11}C_{17}^+ + H_2$	6.0E+14	0.0	0
47	$C_{16}H_{11}^+ + C_4H_2 = H_{11}C_{20}^+ + H_2$	6.0E+14	0.0	0
48	$C_{17}H_{11}^+ + C_4H_2 = C_{19}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
49	$C_{17}H_{11}^+ + C_2H_2 = C_{19}H_{11}^+ + H_2$	6.0E+14	0.0	0
50	$C_{17}H_{11}^+ + C_4H_2 = C_{21}H_{11}^+ + H_2$	6.0E+14	0.0	0
51	$C_{18}H_{11}^+ + C_2H_2 = C_{20}H_{11}^+ + H_2$	6.0E+14	0.0	0
52	$C_{18}H_{11}^+ + C_4H_2 = C_{20}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
53	$C_{18}H_{11}^+ + C_4H_2 = C_{22}H_{13}^+$	6.0E+14	0.0	0
54	$C_{18}H_{11}^+ + C_2H_2 = H_{11}C_{20}^+ + H_2$	6.0E+14	0.0	0

TABLE II (continued)

No.	REACTION	A	n	E, kJ
55	$C_{18}H_{11}^+ + C_4H_2 = H_{11}C_{20}^+ + C_2H_2$	6.0E+14	0.0	0
56	$C_{19}H_{11}^+ + C_4H_2 = C_{21}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
57	$C_{19}H_{11}^+ + C_2H_2 = C_{21}H_{11}^+ + H_2$	6.0E+14	0.0	0
58	$C_{19}H_{11}^+ + C_3H_4 = C_{22}H_{13}^+ + H_2$	6.0E+14	0.0	0
59	$C_{20}H_{11}^+ + C_2H_2 = C_{22}H_{13}^+$	6.0E+14	0.0	0
60	$C_{20}H_{11}^+ + C_3H_4 = C_{23}H_{13}^+ + H_2$	6.0E+14	0.0	0
61	$C_{20}H_{11}^+ + C_4H_2 = C_{24}H_{13}^+$	6.0E+14	0.0	0
62	$C_{21}H_{11}^+ + C_3H_4 = C_{22}H_{13}^+ + C_2H_2$	6.0E+14	0.0	0
63	$C_{21}H_{11}^+ + C_3H_4 = C_{24}H_{13}^+ + H_2$	6.0E+14	0.0	0
64	$C_{22}H_{13}^+ + C_2H_2 = C_{24}H_{13}^+ + H_2$	6.0E+14	0.0	0
65	$C_{22}H_{13}^+ + C_4H_2 = C_{24}H_{13}^+ + C_2H_2$	6.0E+14	0.0	0
66	$H_9C_{10}^+ + C_2H_2 = C_{12}H_9^+ + H_2$	6.0E+14	0.0	0
67	$H_9C_{10}^+ + C_2H_2 = H_9C_{12}^+ + H_2$	6.0E+14	0.0	0
68	$H_9C_{10}^+ + C_3H_4 = C_{13}H_8H^+ + H_2 + H_2$	6.0E+14	0.0	0
69	$H_9C_{10}^+ + C_3H_4 = C_{13}H_9^+ + H_2 + H_2$	6.0E+14	0.0	0
70	$H_9C_{10}^+ + C_4H_2 = C_{12}H_9^+ + C_2H_2$	6.0E+14	0.0	0
71	$H_9C_{10}^+ + C_4H_2 = H_9C_{12}^+ + C_2H_2$	6.0E+14	0.0	0
72	$H_9C_{11}^+ + M = C_{11}H_9^+ + M$	1.0E+14	0.0	0
73	$H_9C_{11}^+ + C_2H_2 = C_{13}H_8H^+ + H_2$	6.0E+14	0.0	0
74	$H_9C_{11}^+ + C_4H_2 = C_{13}H_8H^+ + C_2H_2$	6.0E+14	0.0	0
75	$H_9C_{11}^+ + C_4H_2 = C_{13}H_9^+ + C_2H_2$	6.0E+14	0.0	0
76	$H_9C_{12}^+ + C_3H_4 = C_{15}H_{11}^+ + H_2$	6.0E+14	0.0	0
77	$H_9C_{12}^+ + C_4H_2 = C_{16}H_{11}^+$	6.0E+14	0.0	0
78	$C_{13}H_8H^+ + C_3H_4 = H_{11}C_{16}^+ + H_2$	6.0E+14	0.0	0
79	$C_{13}H_8H^+ + C_3H_4 = C_{16}H_{11}^+ + H_2$	6.0E+14	0.0	0
80	$C_{13}H_8H^+ + C_4H_2 = H_{11}C_{17}^+$	6.0E+14	0.0	0
81	$C_{13}H_8H^+ + C_4H_2 = C_{17}H_{11}^+$	6.0E+14	0.0	0
82	$H_{11}C_{16}^+ + C_2H_2 = H_{11}C_{18}^+ + H_2$	6.0E+14	0.0	0
83	$H_{11}C_{16}^+ + C_2H_2 = C_{18}H_{11}^+ + H_2$	6.0E+14	0.0	0
84	$H_{11}C_{16}^+ + C_4H_2 = H_{11}C_{20}^+ + H_2$	6.0E+14	0.0	0

TABLE II (continued)

No.	REACTION	A	n	E, kJ
85	$H_{11}C_{16}^+ + C_4H_2 = H_{11}C_{18}^+ + C_2H_2$	6.0E+14	0.0	0
86	$H_{11}C_{16}^+ + C_4H_2 = C_{18}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
87	$H_{11}C_{16}^+ + C_4H_2 = C_{20}H_{11}^+ + H_2$	6.0E+14	0.0	0
88	$H_{11}C_{17}^+ + C_2H_2 = C_{19}H_{11}^+ + H_2$	6.0E+14	0.0	0
89	$H_{11}C_{17}^+ + C_4H_2 = C_{19}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
90	$H_{11}C_{17}^+ + C_4H_2 = C_{21}H_{11}^+ + H_2$	6.0E+14	0.0	0
91	$H_{11}C_{18}^+ + C_2H_2 = H_{11}C_{20}^+ + H_2$	6.0E+14	0.0	0
92	$H_{11}C_{18}^+ + C_4H_2 = C_{22}H_{13}^+$	6.0E+14	0.0	0
93	$H_{11}C_{18}^+ + C_4H_2 = H_{11}C_{20}^+ + C_2H_2$	6.0E+14	0.0	0
94	$H_{11}C_{20}^+ + C_2H_2 = C_{22}H_{13}^+$	6.0E+14	0.0	0
95	$H_{11}C_{20}^+ + C_3H_4 = C_{23}H_{13}^+ + H_2$	6.0E+14	0.0	0
96	$H_{11}C_{20}^+ + C_4H_2 = C_{24}H_{13}^+$	6.0E+14	0.0	0

TABLE III
ION-ELECTRON RECOMBINATION REACTIONS

$$k = AT^n \exp(-E(\text{kJ})/RT), \text{ cm}^3, \text{ mol}, \text{ s}$$

Codes for ion structures: $\text{C}_3\text{H}_3^+ = \text{C}_3\text{H}_3^+(1)$; $\text{H}_3\text{C}_3^+ = \text{C}_3\text{H}_3^+(c)$; $\text{C}_6\text{H}_5^+ = \text{C}_6\text{H}_5^+(\text{linear})$; $\text{C}_7\text{H}_7^+ = \text{benzyl ion}$; $\text{HC} = \text{CH}^*$ (electronic state: $^2\Delta$); C_xH_y^+ , H_yC_x^+ , and $\text{C}_x\text{H}_{y-1}\text{H}$ represent three different isomers of the same ion.

No.	REACTION		A	n	E, kJ
1	$\text{H}_3\text{O}^+ + e$	$\rightarrow \text{H}_2\text{O} + \text{H}$	$1.3\text{E}+19$	0.5	0.0
2	$\text{HCO}^+ + e$	$\rightarrow \text{CO} + \text{H}$	$7.4\text{E}+18$	0.69	0.0
3	$\text{CH}_3^+ + e$	$\rightarrow \text{CH} + \text{H}_2$	$5.3\text{E}+18$	0.5	0.0
4	$\text{C}_2\text{H}_3^+ + e$	$\rightarrow \text{C}_2\text{H} + \text{H}_2$	$8.5\text{E}+18$	0.5	0.0
5	$\text{C}_3\text{H}_3^+ + e$	$\rightarrow \text{C}_2\text{H}_2 + \text{CH}$	$1.1\text{E}+19$	0.5	0.0
6	$\text{H}_3\text{C}_3^+ + e$	$\rightarrow \text{C}_2\text{H}_2 + \text{CH}$	$1.1\text{E}+19$	0.5	0.0
7	$\text{C}_4\text{H}_3^+ + e$	$\rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}$	$1.2\text{E}+19$	0.5	0.0
8	$\text{C}_4\text{H}_5^+ + e$	$\rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_3$	$1.2\text{E}+19$	0.5	0.0
9	$\text{C}_5\text{H}_3^+ + e$	$\rightarrow \text{C}_3\text{H}_3 + \text{C}_2$	$1.3\text{E}+19$	0.5	0.0
10	$\text{C}_5\text{H}_5^+ + e$	$\rightarrow \text{C}_2\text{H} + \text{C}_3\text{H}_2$	$1.3\text{E}+19$	0.5	0.0
11	$\text{C}_7\text{H}_5^+ + e$	$\rightarrow \text{C}_4\text{H}_2 + \text{C}_3\text{H}_3$	$1.5\text{E}+19$	0.5	0.0
12	$\text{C}_6\text{H}_5^+ + e$	$\rightarrow \text{C}_4\text{H}_4 + \text{C}_2\text{H}$	$1.4\text{E}+19$	0.5	0.0
13	$\text{C}_7\text{H}_5^+ + e$	$\rightarrow \text{C}_5\text{H}_5 + \text{C}_2$	$1.5\text{E}+19$	0.5	0.0
14	$\text{C}_7\text{H}_7^+ + e$	$\rightarrow \text{C}_6\text{H}_4 + \text{CH}_3$	$1.5\text{E}+19$	0.5	0.0
15	$\text{C}_7\text{H}_7^+ + e$	$\rightarrow \text{C}_6\text{H}_6 + \text{CH}$	$1.5\text{E}+19$	0.5	0.0
16	$\text{C}_8\text{H}_7^+ + e$	$\rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}$	$1.6\text{E}+19$	0.5	0.0
17	$\text{C}_9\text{H}_7^+ + e$	$\rightarrow \text{C}_8\text{H}_6 + \text{CH}$	$1.7\text{E}+19$	0.5	0.0
18	$\text{C}_{10}\text{H}_9^+ + e$	$\rightarrow \text{C}_{10}\text{H}_8 + \text{H}$	$1.8\text{E}+19$	0.5	0.0
19	$\text{H}_9\text{C}_{10}^+ + e$	$\rightarrow \text{C}_8\text{H}_6 + \text{C}_2\text{H}_3$	$1.8\text{E}+19$	0.5	0.0
20	$\text{C}_{11}\text{H}_9^+ + e$	$\rightarrow \text{C}_{10}\text{H}_8 + \text{CH}$	$1.9\text{E}+19$	0.5	0.0
21	$\text{H}_9\text{C}_{11}^+ + e$	$\rightarrow \text{C}_8\text{H}_6 + \text{C}_3\text{H}_3$	$1.9\text{E}+19$	0.5	0.0
22	$\text{C}_{12}\text{H}_9^+ + e$	$\rightarrow \text{C}_{12}\text{H}_8 + \text{H}$	$1.9\text{E}+19$	0.5	0.0
23	$\text{H}_9\text{C}_{12}^+ + e$	$\rightarrow \text{C}_{10}\text{H}_8 + \text{C}_2\text{H}$	$1.9\text{E}+19$	0.5	0.0
24	$\text{C}_{13}\text{H}_9^+ + e$	$\rightarrow \text{C}_{13}\text{H}_9$	$2.0\text{E}+19$	0.5	0.0
25	$\text{C}_{13}\text{H}_9^+ + e$	$\rightarrow \text{C}_{12}\text{H}_8 + \text{CH}$	$2.0\text{E}+19$	0.5	0.0

TABLE III (continued)

No.	REACTION	A	n	E, kJ
26	$C_{14}H_{11}^+ + e \rightarrow C_{14}H_{10} + H$	2.1E+19	0.5	0.0
27	$C_{14}H_{11}^+ + e \rightarrow C_{14}H_{11}$	2.1E+19	0.5	0.0
28	$C_{15}H_{11}^+ + e \rightarrow C_{14}H_{10} + CH$	2.1E+19	0.5	0.0
29	$C_{15}H_{11}^+ + e \rightarrow C_{15}H_{11}$	2.1E+19	0.5	0.0
30	$C_{16}H_{11}^+ + e \rightarrow C_{16}H_{10} + H$	2.2E+19	0.5	0.0
31	$C_{17}H_{11}^+ + e \rightarrow C_{17}H_{10} + H$	2.2E+19	0.5	0.0
32	$C_{17}H_{11}^+ + e \rightarrow C_{16}H_{10} + CH$	2.2E+19	0.5	0.0
33	$H_{11}C_{17}^+ + e \rightarrow C_{17}H_{11}$	2.2E+19	0.5	0.0
34	$H_{11}C_{18}^+ + e \rightarrow C_{16}H_{10} + C_2H$	2.3E+19	0.5	0.0
35	$C_{18}H_{10}H^+ + e \rightarrow C_{18}H_{10} + H$	2.3E+19	0.5	0.0
36	$C_{19}H_{11}^+ + e \rightarrow C_{19}H_{11}$	2.3E+19	0.5	0.0
37	$C_{19}H_{11}^+ + e \rightarrow C_{18}H_{10} + CH$	2.3E+19	0.5	0.0
38	$C_{20}H_{11}^+ + e \rightarrow C_{18}H_{10} + C_2H$	2.4E+19	0.5	0.0
39	$H_{11}C_{20}^+ + e \rightarrow C_{20}H_{11}$	2.4E+19	0.5	0.0
40	$C_{21}H_{11}^+ + e \rightarrow C_{21}H_{11}$	2.4E+19	0.5	0.0
41	$C_{21}H_{11}^+ + e \rightarrow C_{18}H_{10} + C_3H$	2.4E+19	0.5	0.0
42	$C_{22}H_{13}^+ + e \rightarrow C_{22}H_{12} + H$	2.5E+19	0.5	0.0
43	$C_{23}H_{13}^+ + e \rightarrow C_{22}H_{12} + CH$	2.5E+19	0.5	0.0
44	$C_{23}H_{13}^+ + e \rightarrow C_{23}H_{13}$	2.5E+19	0.5	0.0
45	$C_{24}H_{13}^+ + e \rightarrow C_{24}H_{12} + H$	2.5E+19	0.5	0.0
46	$C_{24}H_{13}^+ + e \rightarrow C_{24}H_{12} + H$	2.5E+20	0.5	0.0

TABLE IV
TO ADD TEN CARBON ATOMS BY THE FREE RADICAL MECHANISM

$C_{10}H_8$			
↓ ↑	+ H• (- H ₂)	0.27 μs	
$C_{10}H_7•$			
↓	+ C ₂ H ₂ (- H•)	0.11 μs	
$C_{12}H_8$			
↓ ↑	+ H• (- H ₂)	0.64 μs	
$C_{12}H_7•$			
↓ ↑	+ C ₂ H ₂ (- H•)	0.16 μs	
$C_{14}H_8$			
↓	+ H • (- H ₂)	2.7 μs	
$C_{14}H_7•$			
↓	+ C ₂ H ₂	1.1 μs	
$C_{16}H_9•$			
↓ ↑	cyclizes		
$C_{16}H_9•$			
↓ ↑	+ C ₂ H ₂ (- H•)	1.1 μs	
$C_{18}H_{10}$			
↓	+ H • (- H ₂)	2.9 μs	
$C_{18}H_9•$			
↓ ↑	+ C ₂ H ₂ (- H•)	0.69 μs	
$C_{20}H_{10}$			

Total Time = 9.7 μs

TABLE V
TO ADD TEN CARBON ATOMS BY THE IONIC MECHANISM

$C_{11}H_9^+$		
↓	+ C_2H_2 (- H_2)	3.1 μs
$C_{13}H_9^+$		
↓ †	+ C_2H_2	0.40 μs
$C_{15}H_{11}^+$		
↓	+ C_2H_2 (- H_2)	0.42 μs
$C_{17}H_{11}^+$		
↓	+ C_2H_2 (- H_2)	1.2 μs
$C_{19}H_{11}^+$		
↓	+ C_2H_2 (- H_2)	0.50 μs
$C_{21}H_{11}^+$		
Total Time = 5.6 μs		