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IONIC MECHANISMS OF CARBON FORMATION IN FLAMES. (U)

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An experimental program is underway to determine the mechanism of soot formation in flames, with particular emphasis on ionic mechanisms. Mass spectroscopic measurements of positive ion profiles through sooting and non-sooting, flat premixed flames show a large increase in the variety of ions produced when sooting occurs, with dramatic increases in the concentration of heavier ions as the combustion mixture is made fuel rich. In sooting flames, masses above 165 amu display two maxima in ion profiles through the flame. This has been confirmed by electrostatic probe measurements. The effect of changing the

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Initial, and thus adiabatic flame temperature, on the critical equivalence ratio for soot formation was determined for acetylene and benzene. For acetylene the tendency to soot decreases with increasing adiabatic flame temperature; for benzene the tendency to soot first increases and then decreases.

The data obtained in this program and data in the literature are interpreted in terms of a detailed ionic mechanism for soot formation in which chemi-ions grow by adding acetylene, polyacetylenes, and C_2H .

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I. INTRODUCTION

This is the second annual report on a program designed to determine the mechanism of soot formation in air-breathing engines. The working hypothesis is that flame ions produced by chemi-ionization are the precursors of soot and that large hydrocarbon ions are produced by very rapid ion-molecule reactions. This hypothesis is being examined by ion mass spectrometer studies of low pressure, flat, premixed flames and by detailed analysis of the data reported in the literature by others. Considerable progress has been made during this period on formulating mechanisms and interpreting data both from our results on acetylene-oxygen and benzene-oxygen flames and from the data in the literature. We have experienced more experimental difficulties than anticipated; these were concerned with "singing flames," and seem to be related to the burners. In this report we will summarize our progress and problems with respect to the specific items in the statement of work. Two papers, now in preparation, will present the work in detail; that data and discussion will not be duplicated here. The basic mechanism developed in those papers is summarized in Section II.E.

II. TECHNICAL DISCUSSION

A. EFFECT OF FUEL TYPE

"Determine the effect of fuel type (representative of coal and petroleum derived fuels) on carbon and ion formation processes in both premixed and diffusion flames. An ion mass spectrometer will be used for ion profile identification; and other techniques, using e.g., electrostatic probes, microwave cavities, gas sampling probes, thermocouple probes and emission and absorption spectrometers will be used as required during the progress of the work. Included will be mass spectrometric identification of the ions present in the soot nucleation and particle growth zones of flames of a number of fuels, at equivalence ratios near and in excess of those necessary for smoke formation."*

Improvements were made in the mass spectrometer instrumentation both to increase the accuracy and reproducibility of the data and to increase the rate at which data could be acquired. Data had been obtained point by point;

* From Statement of Work

this was not only time-consuming but led to inaccuracies due to meter readings and instrument drifts during the long periods of time required to take a complete set of data on a given flame. This might consist of 30 to 50 individual ion profiles through the flame. With the instrumentation modifications it is now possible to automatically record a given mass profile through the flame by moving the burner with respect to the mass spectrometer sampling cone. This scan takes about one minute. Or, at fixed flame position, the instrument can be scanned over the 19 to 300 mass unit range in one to two minutes.

Difficulties were experienced with flame oscillations at certain critical conditions of equivalence ratio, burner position, and pressure. These oscillations altered the shape of ion profiles through the flame; they did not show up as noise. Flame oscillations were experienced on burners which have been used for many years without trouble for lean, and stoichiometric, but not rich flames. The oscillations are apparently burner related; two burners, 18 and 9 cm diam, constructed of 5500 and 1400 1 mm diam, 3 cm long stainless steel hypodermic needle tubes soldered into a water jacket, showed oscillations when operating at close to 2.5 kPa. The burner currently being used does not give oscillations; it is made of alternate layers of flat and corrugated 0.013 cm thick stainless steel sheets wound in a spiral 15 cm in diameter. This burner is not water cooled and operates well at pressures below about 2.5 kPa.

In the mass spectrometer studies we concentrated on the two fuels, benzene and acetylene, because they have the same C/H ratio; benzene is representative of coal derived aromatic type fuels and acetylene flames have been studied extensively by others. By working at the same conditions as others, primarily Homann and Wagner and their associates in Germany^{1,2} and Howard and associates at MIT,^{3,4} we can develop a complete description of at least one flame by using their extensive measurements of the various properties of the flame to supplement our measurements. This will make it possible to develop computer models at an early date to demonstrate the validity (or non-validity) of our mechanism.

The detailed flame profiles on benzene and acetylene are still being interpreted and since more data must be acquired they will not be discussed here. The most striking and unexpected observation has been the appearance of two maxima in the ion profiles of sooting flames. These occur only for ions of mass greater than 165 amu and occur in both benzene and acetylene flames. We have thus far found it difficult to rationalize an acceptable mechanism to

explain them. Our first thought was that they were an artifice of the experiment but subsequent experiments have convinced us that they are real. Similar double maxima have been observed by Delfau, Michaud, and Barassin at Orleans.⁵

To further examine the appearance of double maxima in the ion profiles and to estimate the total ion concentration, electrostatic probe measurements were made in acetylene, benzene, n-hexane, and cyclohexane flames. The double maxima were confirmed. Because these data will not be published in the forthcoming publications they are presented here, Figs. 1 to 4.

B. EFFECT OF PRESSURE

"Determine the effect of pressure on carbon and ion production processes in the combustion of some representative fuels."

Very little additional work was done on the effect of pressure because the experiments last year indicated that pressure has little effect on the critical equivalence ratio for soot formation. Further experiments are planned, however, because even a small pressure dependence of soot formation would be of practical importance since combustors operate over very wide pressure ranges.

Some preliminary experiments were, however, done on the effect of temperature on the critical equivalence ratio at which soot is produced. The results were surprising, and thus interesting. They were not pursued further because the effort involved is beyond the scope of the present program. The results of preheating the fuel-air mixture are reported in Figs. 5 and 6. The curve on Fig. 5 has been drawn through the lowest equivalence ratios at which soot is observed; because of the difficulty of observing the critical ratio for soot formation in acetylene these points should be the most accurate. The smoothed curves have been replotted in Fig. 6 against the calculated adiabatic flame temperatures, with the arrows indicating the direction of increasing initial temperatures. Acetylene behaves as one might expect; increasing adiabatic flame temperature decreases the tendency to soot (higher critical equivalence ratio for soot formation), but benzene behaves rather strangely. Note that there are two competing processes, the increasing fuel/oxygen ratio and the increasing preheat temperature. While there may be problems with these data, e.g., the flames may not be adiabatic--experimental flame temperatures should be measured--it is difficult to rationalize that the data are so far off as to cause this distortion of the benzene curve.

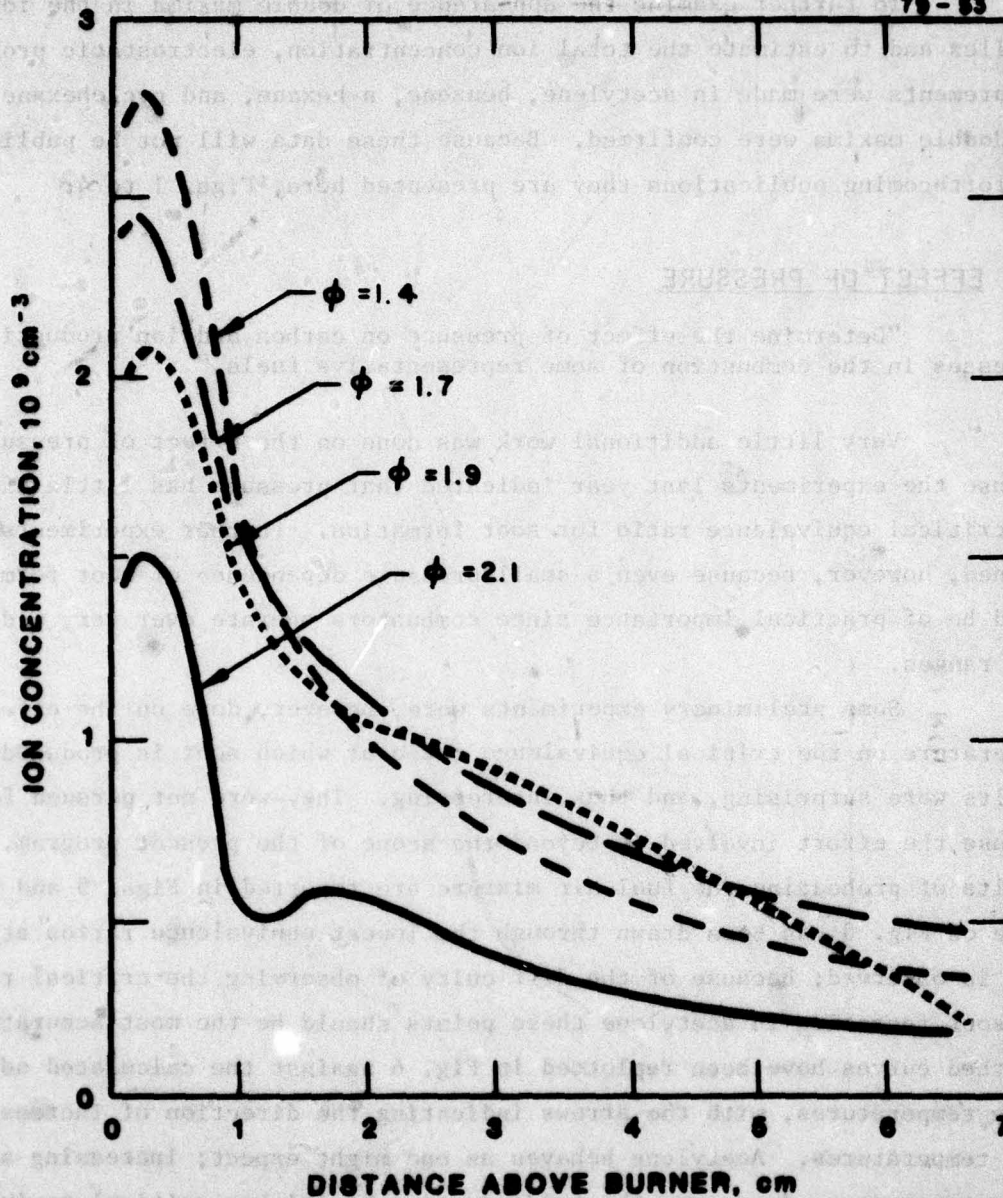


FIGURE 1 TOTAL POSITIVE ION CONCENTRATION IN ACETYLENE-AIR FLAME
AT 6.7 kPa

Air flow = $100 \text{ STP cm}^3 \text{ s}^{-1}$; $\phi_g = 2.05$.

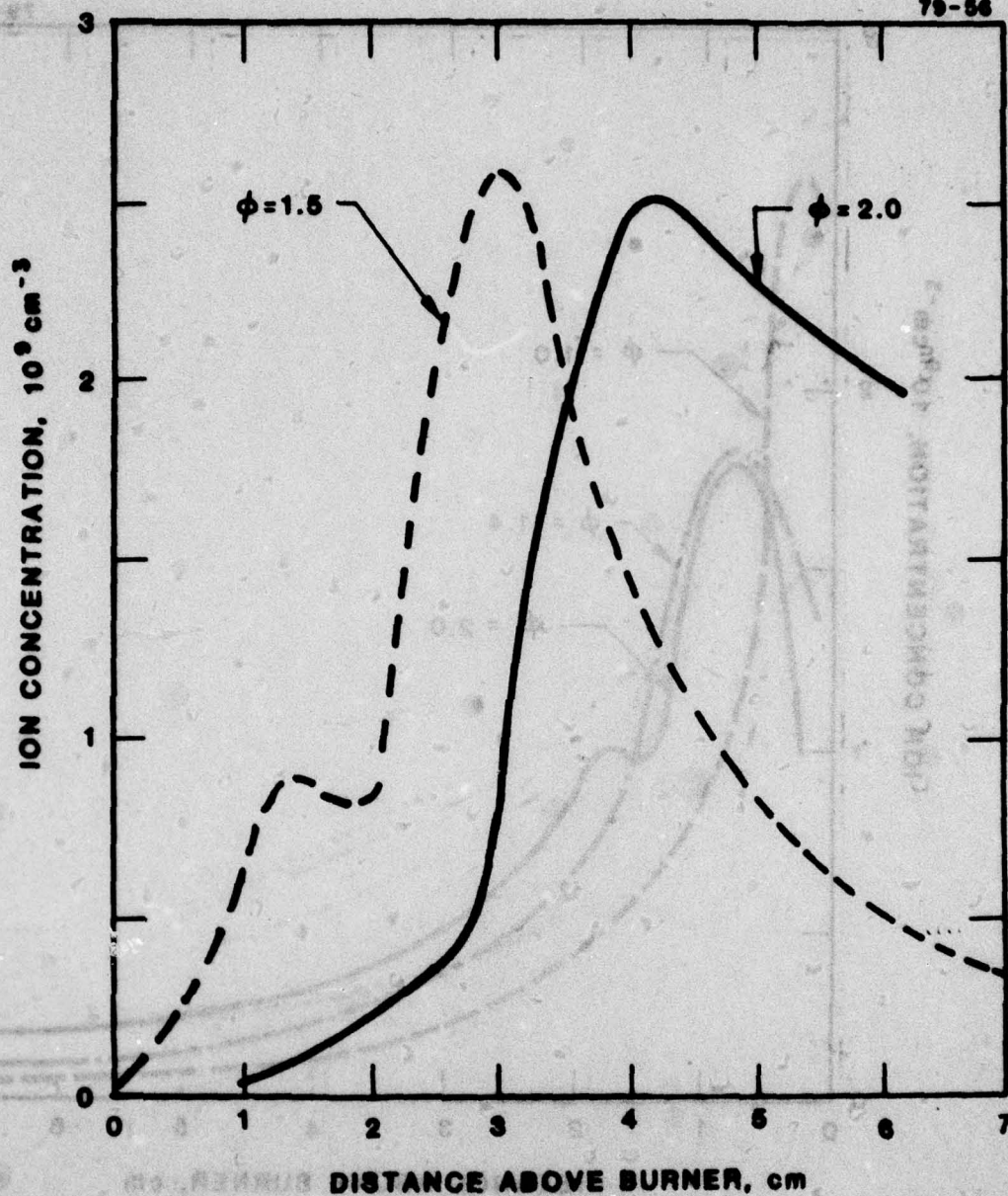


FIGURE 2 TOTAL POSITIVE ION CONCENTRATION IN BENZENE-AIR FLAME
AT 6.7 kPa

Air flow = $21.5 \text{ STP cm}^3 \text{ s}^{-1}$; $\phi_s = 1.55$.

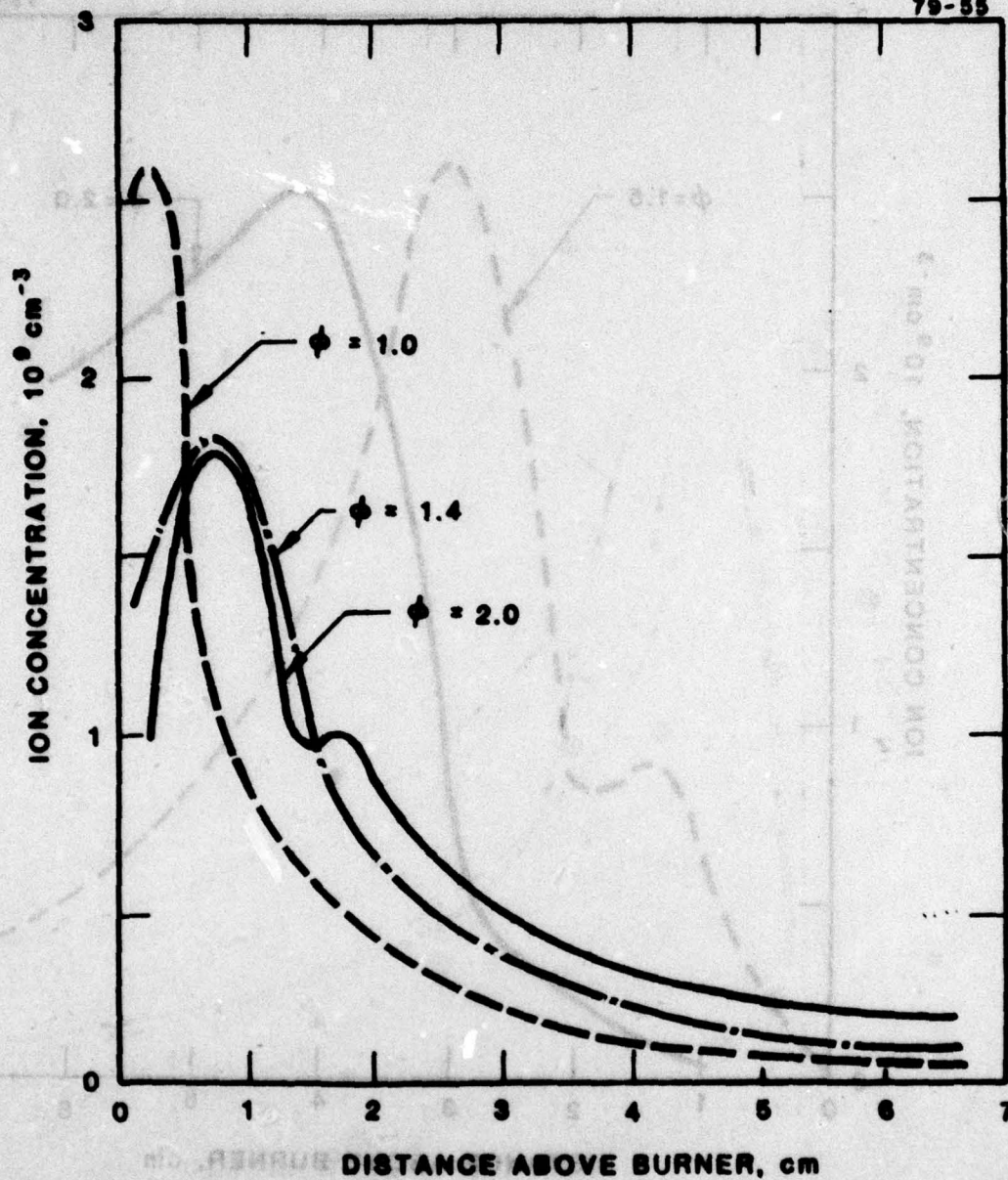


FIGURE 3 TOTAL POSITIVE ION CONCENTRATION IN n-HEXANE-AIR FLAME
AT 6.7 kPa

Air flow = $10.8 \text{ STP cm}^3 \text{ s}^{-1}$; $\phi_s = 1.63$.

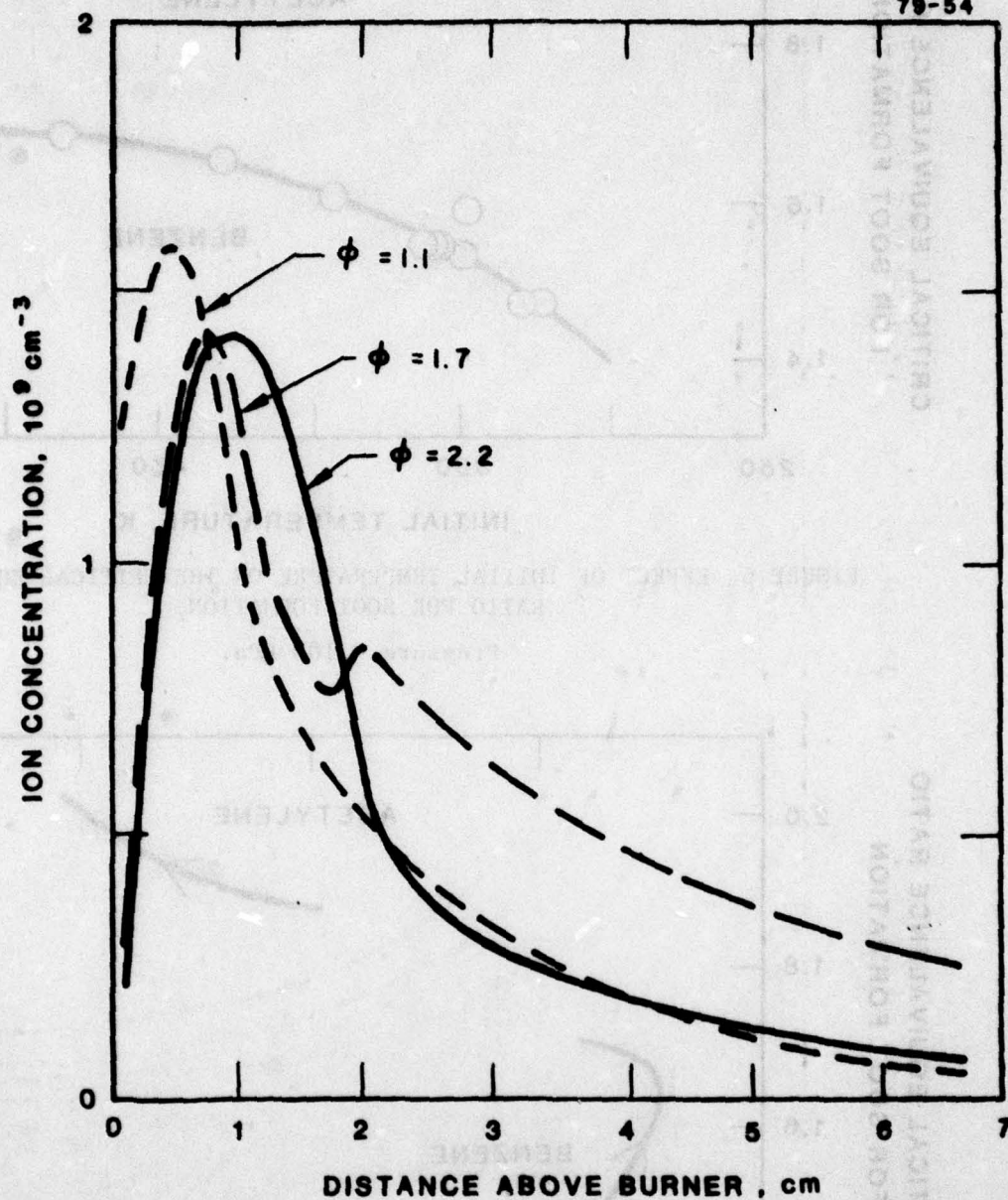


FIGURE 4 TOTAL POSITIVE ION CONCENTRATION IN CYCLOHEXANE-AIR FLAME
AT 6.7 kPa

Air flow = $10.8 \text{ STP cm}^3 \text{ s}^{-1}$; $\phi_s = 1.7$.

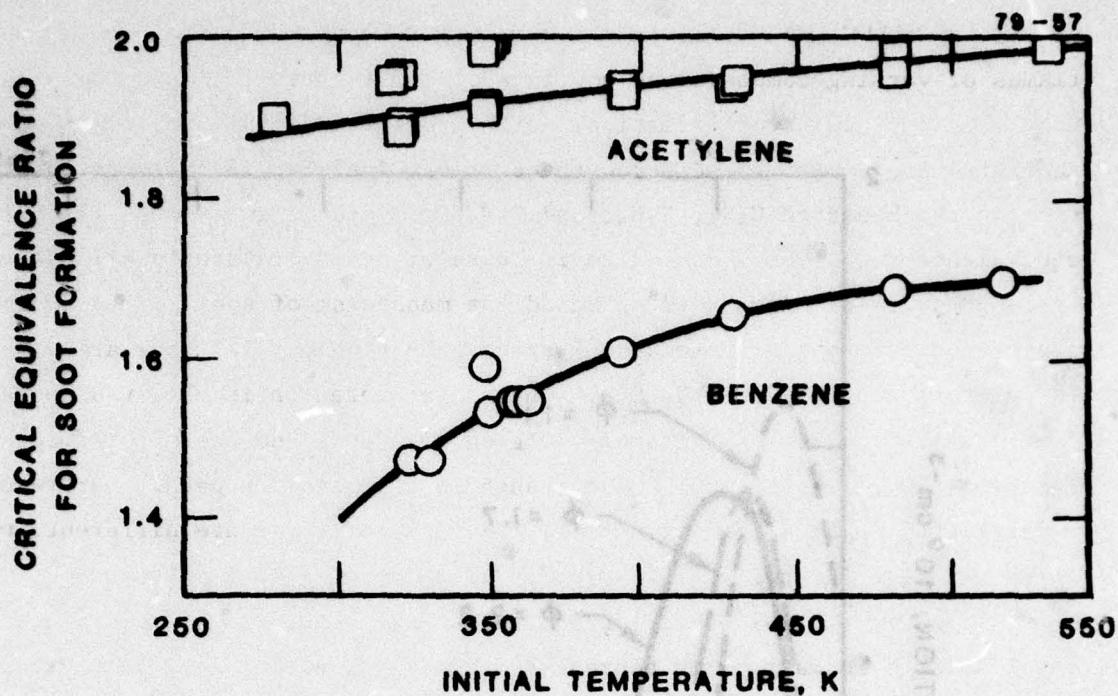


FIGURE 5 EFFECT OF INITIAL TEMPERATURE ON THE CRITICAL EQUIVALENCE RATIO FOR SOOT FORMATION

Pressure = 100 kPa.

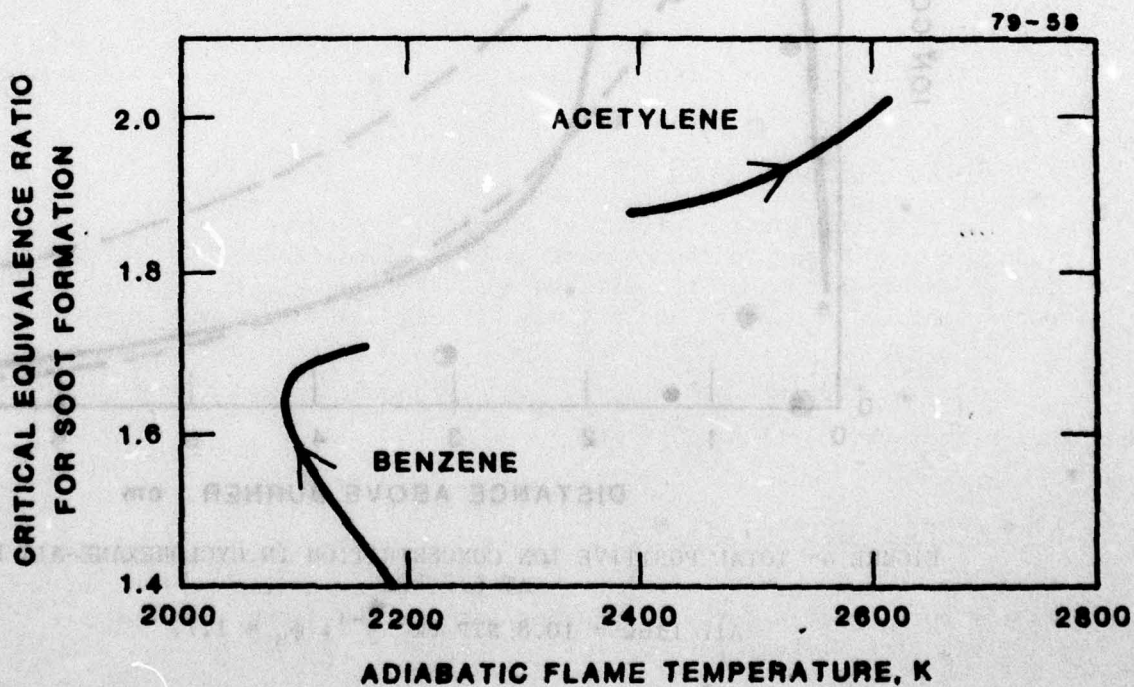


FIGURE 6 EFFECT OF ADIABATIC FLAME TEMPERATURE ON THE CRITICAL EQUIVALENCE RATIO FOR SOOT FORMATION

Pressure = 100 kPa. Arrows indicate direction of increasing initial temperature.

Millikan⁶ measured the flame temperature of premixed ethylene-air flames of varying compositions and interpreted the results in terms of an activation energy for soot formation--no abnormal temperature behavior was noted. Radcliffe and Appleton⁷ measured the critical fuel-oxygen ratio for soot formation in shock heated C_2H_2 , C_2H_4 , and C_2H_6/O_2 mixtures in argon. The critical equivalence ratio was observed to increase with temperature in all cases. Graham, Homer, and Rosenfeld⁸ studied the mechanism of soot formation in the shock-tube pyrolysis of aromatic hydrocarbons highly diluted in argon over the temperature range 1600 to 2300 K. They interpreted their observed increase in soot yield with increasing temperature up to 1750 K and rapid fall with increasing temperature above 1800 K to a change in the reaction path. Our results are consistent with this although the critical temperatures are different, which is to be expected for the two grossly different experimental systems.

Our initial objective in these experiments was to determine the onset of soot formation for benzene and acetylene at the same temperatures to eliminate the effect of temperature on the kinetics of soot formation in benzene and acetylene. Clearly, Fig. 6, that objective was not attained. The benzene could not be sufficiently preheated without having it pyrolyze in the burner. To accomplish our objective we will have to cool the acetylene below room temperature.

Clearly the effect of temperature deserves more detailed study.

C. CHEMICAL ADDITIVES

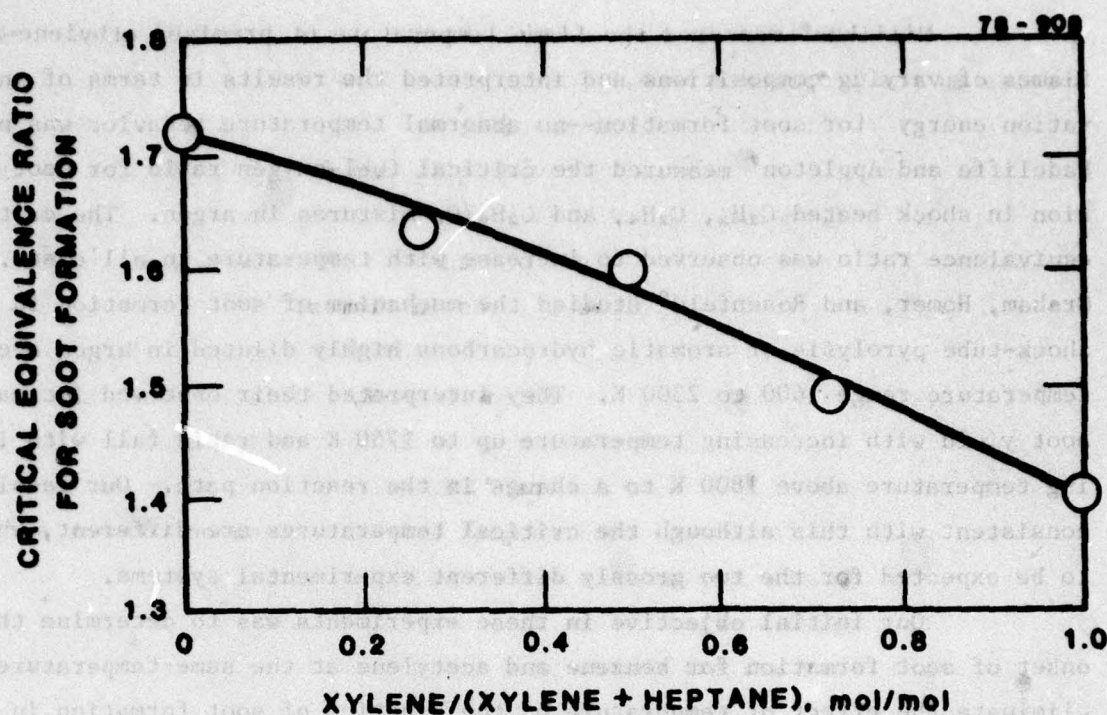
"Determine the effect of chemical additives on carbon and ion production processes in the combustion of some representative fuels. Included will be determination of the effects of alkali and alkaline earth additives on soot formation parameters and a study of their influence on flame ion chemistry."

Nothing was done on this task; the effort was placed on the effect of fuel structure, Sections II.A and E.

D. HYDROCARBON MIXTURES

"Study of the sooting characteristics of flames of mixed hydrocarbons for the purpose of ascertaining synergistic effects and developing a means for predicting the smoke tendency of real fuel systems."

Critical equivalence ratios for soot formation in mixtures of m-xylene (aromatic) and heptane (aliphatic), molecular weights 100 and 106, respectively, were run at ambient pressure. Each point, Fig. 7, is the result

FIGURE 7 SOOT ONSET FOR *m*-XYLENE HEPTANE MIXTURE

of measurements over a range of total flow rates, using the equivalence ratio that plateaued with increasing total flow velocity. The results, Fig. 7, indicate an almost linear effect.

E. MECHANISM FOR SOOT FORMATION

"Interpret, as the work progresses, the results from the above experiments, and data already in the literature, in terms of an ionic mechanism of carbon formation in flames."

A detailed mechanism has been developed for soot formation in flames based upon the results obtained in this program and data in the literature. Because the arguments which lead to the mechanisms will be presented in detail in two forthcoming publications, they will not be repeated here. We will simply summarize the basic reaction steps which we think are important. Our program consists in confirming these steps by further experimental work and by the development of a computer model to compare the predictions of the mechanism to the detailed experimental profiles--certainly some changes can be contemplated in the light of future work. The main difficulty in preparing such a model is the lack of chemical kinetics data for the individual reactions, a situation

made even more difficult by the lack of thermodynamic data for many of the species in the proposed scheme. Nevertheless, the principles for making these estimates are available^{9,10} although tedious.

The basic mechanism we envision is summarized in Fig. 8. Primary ions are produced by the generally accepted reactions for producing chemi-ionization; C_xH_y neutral species are produced by the same set of reactions used to explain the formation of polyacetylenes in flames.¹¹⁻¹³ The products of these two sets of reactions react to produce hydrocarbon ions, $C_zH_w^+$, which grow further by the addition of more neutral C_xH_y species; these ions (for non-aromatic fuels) rearrange to produce polycyclic (aromatic) ions which grow further by the addition of more neutral C_xH_y species, and so on to larger ions, followed by agglomeration, neutralization, oxidation, and on to soot particles.

The specific sets of reactions which are our current candidates follow. All involve species observed in sooting flames and, to the extent data are available, they are all thermodynamically acceptable.

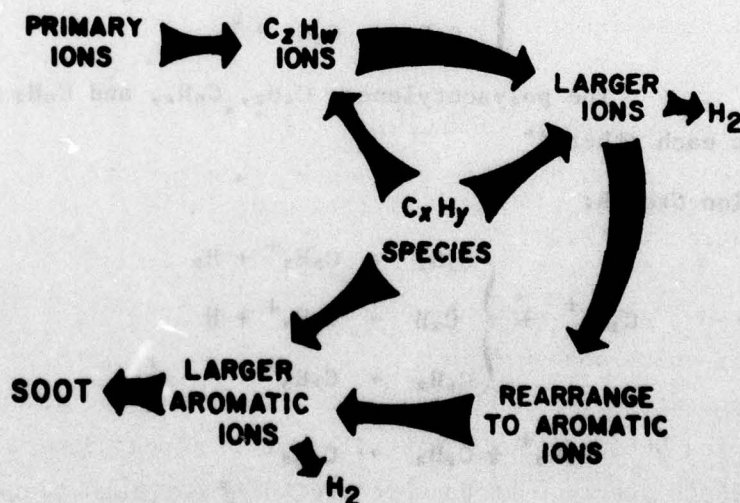
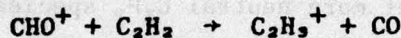
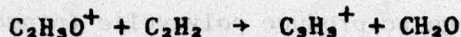
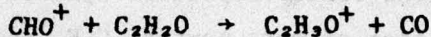
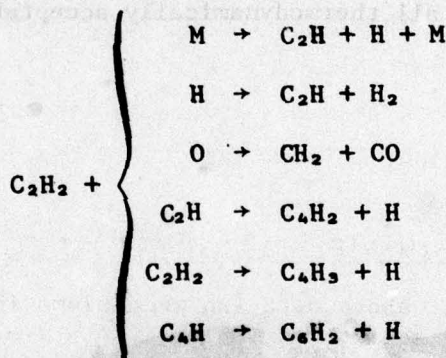


FIGURE 8 IONIC MECHANISM OF SOOT FORMATION

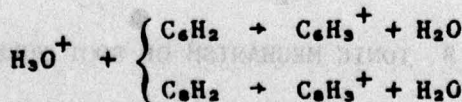
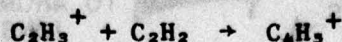
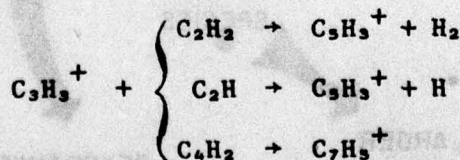
1. Primary ions:

a. Chemi-ionization:

b. Charge transfer (typical of reactions producing C_3H_3^+ from CHO^+):2. Neutral, C_xH_y Species:

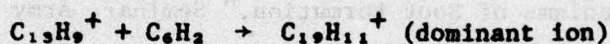
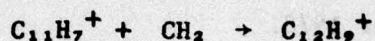
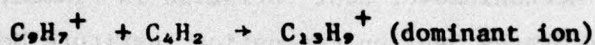
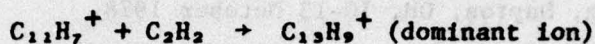
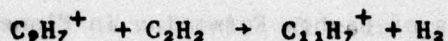
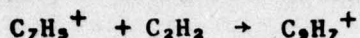
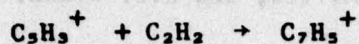
The polyacetylenes, C_4H_2 , C_6H_2 , and C_8H_2 are in equilibrium with each other.¹⁴

3. Ion Growth:



This is followed by additional ion growth reactions, including rearrangement to polycyclic structures, for which the step is not separately identified.

Rearrangement is assumed to occur rapidly during an ion molecule reaction when the polycyclic structure is the more favored thermodynamic structure.



It is easy to see how the process would continue with ion clustering also increasing the ion size at the expense of the number density. Ion recombination, of course, removes ions. As the molecules become larger, their properties approach those of particles and they are ionized thermally because of their low work function. The change from molecular to particle properties occurs at a molecular weight of about 10^4 and a particle radius of about $15 \text{ \AA}$.

F. SOOT FORMATION IN AIR BREATHING ENGINES

"Interpret the above data and mechanisms in terms of the potential effects of new fuels on soot formation in air breathing engines, and possible means of minimizing soot formation in air breathing engines."

Nothing was done on this task.

III. PERSONNEL

The authors are pleased to acknowledge the assistance of Dr. H.N. Volltrauer for improving the instrumentation and R.W. Bowser and L.R. Koenig who assisted with the experiments:

IV. PUBLICATIONS AND PRESENTATIONS

Two publications are in preparation:

1. For the AIAA Journal, a review paper on the "Mechanism of Soot Formation in Flames" based on the invited paper given by H.F. Calcote at the AIAA Annual Meeting, New Orleans, LA, 15-17 January 1979.

2. For Combustion and Flame, a paper entitled "A Mass Spectroscopic Study of Ionic Mechanisms of Soot Formation in Acetylene and Benzene Flames" by H.F. Calcote, W.J. Miller, and D.B. Olson.

The following presentations were given or prepared during the year by H.F. Calcote.

1. "Ionic Mechanisms of Carbon Formation in Flames," AFOSR Contractors Meeting, Dayton, OH, 10-13 October 1978.
2. "Ionic Mechanisms of Soot Formation in Flames," Invited Paper, Eastern States Section Combustion Institute Meeting, Miami, FL, 29 November-1 December 1978.
3. "Mechanisms of Soot Formation," Seminar, Army Ballistic Research Laboratories, Aberdeen, MD, 10 January 1979.
4. "Mechanisms of Soot Formation in Flames - An Invited Review," AIAA Meeting, New Orleans, LA, 15-17 January 1979.

V. NEW TECHNOLOGY

There is no new technology to report.

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