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IONIC MECHANISMS OF CARBON FORMATION IN FLAMES. (U)
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AEROCHEM-TP-371

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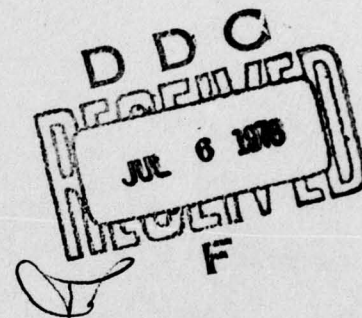
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IONIC MECHANISMS OF CARBON FORMATION IN FLAMES

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May 1978

Annual Report for Period 1 January 1977 - 31 December 1977

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Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
BOLLING AIR FORCE BASE
WASHINGTON, DC 20332

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR-78-1082	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) IONIC MECHANISMS OF CARBON FORMATION IN FLAMES	5. TYPE OF REPORT & PERIOD COVERED INTERIM Jan 77 - 31 Dec 77	
6. AUTHOR(s) HARTWELL S. CALCOTE WILLIAM J. MILLER	7. PERFORMING ORG. REPORT NUMBER AEROCHEM-TP-371	
8. PERFORMING ORGANIZATION NAME AND ADDRESS AEROCHEM RESEARCH LABORATORIES, INC PO BOX 12 PRINCETON, NJ 08540	9. CONTRACT OR GRANT NUMBER(s) F49620-77-C-0029	
10. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D C 20332	11. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT 2308A2 61102F	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 35 p.	13. REPORT DATE May 1978	
	14. NUMBER OF PAGES 32	
	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Annual Rept. 1 Jan - 31 Dec 77		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) SOOT FORMATION HYDROCARBON FLAMES ION PRODUCTION ION-MOLECULE REACTIONS		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This program is directed toward the elucidation of soot formation mechanisms in air breathing engines with particular emphasis on the possible causal relationship between charged species chemistry and soot production. Premixed laboratory test flames of a number of hydrocarbons have been examined to determine the effects of pressure and fuel structure on the critical fuel air mixture ratio for soot onset. The tendency for flames to soot increases, in general, with the aromaticity and molecular weight of the fuel; pressure has little effect. Mass spectrometric probing of nearly sooting acetylene/air and benzene/air flames		

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reveals a wide variety of naturally occurring high molecular weight hydrocarbon ions. As the equivalence ratio at which soot appears is approached, the average molecular weight of these flame ions increases. Both fuels give rise to very similar ionic species in the mass range above about 150 amu. These ions are separated by 12 or 13 amu and correlate with the molecular weights of stable polycyclic aromatic species or free radicals. Distinct differences appear in the charged species distributions of benzene and acetylene flames in the mass range below about 150 amu, i.e., in the nucleation and early polymerization processes. The reactions subsequent to this early reaction mechanism apparently lead to aromatic species which are essentially independent of the identity of the fuel and which can grow rapidly to a complex array of polycyclic aromatics and soot.

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I. INTRODUCTION

This is the first annual report on a program designed to determine the mechanism of soot formation in air-breathing engines. Because of the extensive evidence accumulated over the last decade indicating that flame ionization and soot formation are related,¹⁻⁴ the objective of this program is to determine exactly what the relationship is. The working hypothesis is that soot precursors are ions which, in very rapid ion molecule reactions, grow to incipient soot particles.

The work is further motivated by the anticipated future use of so called "new fuels" produced from coal, tar sand, and shale oil. These fuels are expected to have higher molecular weights, more aromatics and polycyclics, and greater C/H ratios than current petroleum-derived fuels. These properties all increase the smoking or sooting tendency in combustion systems.

Because of the great extent to which fuel structure will probably change as petroleum-derived fuels are replaced by coal or shale oil-derived fuels, a major effort in this program has been placed on the effect of fuel structure. Thus, simultaneously with experimental studies of ionization in sooting flames, experiments are being pursued on the effect of molecular structure on the critical equivalence ratio at which soot is produced. After describing the experimental techniques being employed, these two efforts will be discussed separately.

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II. EXPERIMENTAL

In reviewing previous work⁵⁻⁸ in which observations were made of the fuel concentration at the onset of soot formation, it became obvious that the critical stoichiometry at which soot is produced is a function of flame geometry. Meker type flames and flat flames tend to become cellular as the fuel flow is increased and soot sets in at the tip of each of the individual cells. Similarly, in Bunsen flames, it is at the tip of the conical primary flame zone that soot is first observed. These effects are described in more detail in the review by Homann.⁷ Thus, in order to correlate the relative tendencies of various fuels to soot, one must take into account changes in flame geometry which, in turn, are a sensitive function of unburned gas flow rate and burner configuration.

The two burners being used in the present study are annular shielded flame Meker burners as shown in Fig. 1. One is a water-cooled version fabricated from bundles of hypodermic tubing of 0.75 mm internal diameter; the other is identical in size with a sintered stainless steel top welded in place to facilitate higher input feed gas temperatures. The temperature of the input fuel-air mixture is determined with a thermocouple, located in a well within the plenum upstream of the sintered burner top. Flames are stabilized on either burner top as a number of small "cells" or inverted dome-shaped combustion zones. The central test flame is 2.5 cm in diameter and is supplied with the fuel/air mixture under investigation; the annulus surrounding it has an outside diameter of 4.7 cm and supports a near stoichiometric C_3H_8 /air flame which shrouds the test flame from unwanted cool ambient air and provides an ever-present ignition source. The entire burner is enclosed in a 30 cm diam stainless steel vacuum housing which is exhausted, when desired, by a 150 l sec^{-1} mechanical pump. The apparatus is therefore capable of providing flames at pressures of 1 atm down to a few Torr at virtually any unburned gas flow rate and fuel-air ratio at which combustion can be sustained.

The propane and air for the shroud flame are provided via critical orifice flow meters and mixed in a 100 ml mixing vessel upstream of the burner and outside the vacuum housing. The mixing vessel for the test flame is similarly supplied with air but from two meters; one stream of about 30 ml sec^{-1} provides the "propellant" for an atomizer built into one end of a 0.8 l mixing vessel; the remainder of the air sweeps through the vessel and mixes with the fuel and

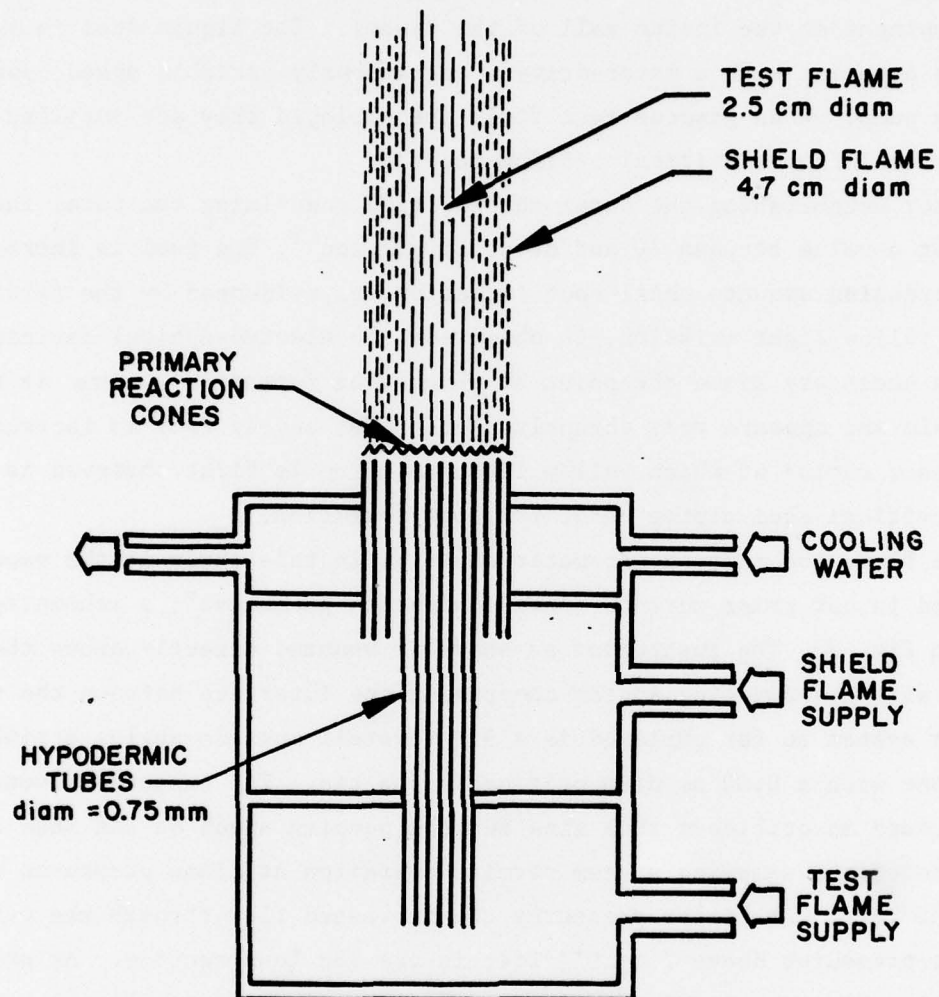


FIGURE 1 SHIELDED FLAME MEKER BURNER

atomizer air before flowing to the inner portion of the burner. The entire mixing vessel and aspirator are enclosed in a small laboratory oven operated at a temperature high enough to insure vaporization of the atomized liquid fuel as it impinges on the inside wall of the vessel. The liquid fuel is metered into the atomizer with a motor-driven, continuously variable speed hypodermic infusion pump. When gaseous test fuels are employed they are supplied directly to the vessel from a critical orifice meter.

After establishing the outer shroud flame and fixing the total inner air supply at a value between 30 and about 250 ml sec⁻¹, the fuel is introduced in ever-increasing amounts until soot formation, as evidenced by the first appearance of yellow light emission, is observed. No electro-optical devices have yet been necessary since the point at which soot formation occurs is readily observable and appears very abruptly as the fuel supply rate is increased. The equivalence ratio* at which yellow light emission is first observed is defined as the critical equivalence ratio for soot formation, ϕ_s .

The flame ion mass spectrometer employed in this study is the same instrument used in our prior work on flame ionization phenomena⁹; a schematic is given in Fig. 2. The instrument as shown is mounted directly above the burner housing with its sampling system comprising the interface between the two. The sampling system so far employed is a 95° (overall outside angle) stainless steel cone with a 0.09 mm diam orifice in the tip. The balance between gas flow through an orifice of this size and the pumping speed on the mass spectrometer side of the sampling system permits operation at flame pressures up to about 250 Torr. At higher pressures the increased flow through the orifice leads to pressures above 2×10^{-4} Torr in the ion lens section. At pressures above this value, chemical reaction rates in the lens region become rapid enough to cause appreciable errors. The mass spectrometer now in use has an upper mass limit of 550 amu. It is a low resolution, high transmission quadrupole ideally suited for rapid, qualitative survey experiments.

As will be seen, two of the experimental problems in this study are the complex nature of the mass spectra and the large changes in mass distribution that result from small changes in experimental parameters. In principle, the

*

$$\text{Equivalence ratio, } \phi \equiv \frac{(\text{fuel flow/oxidizer flow})_{\text{experiment}}}{(\text{fuel flow/oxidizer flow})_{\text{stoichiometric}}}$$

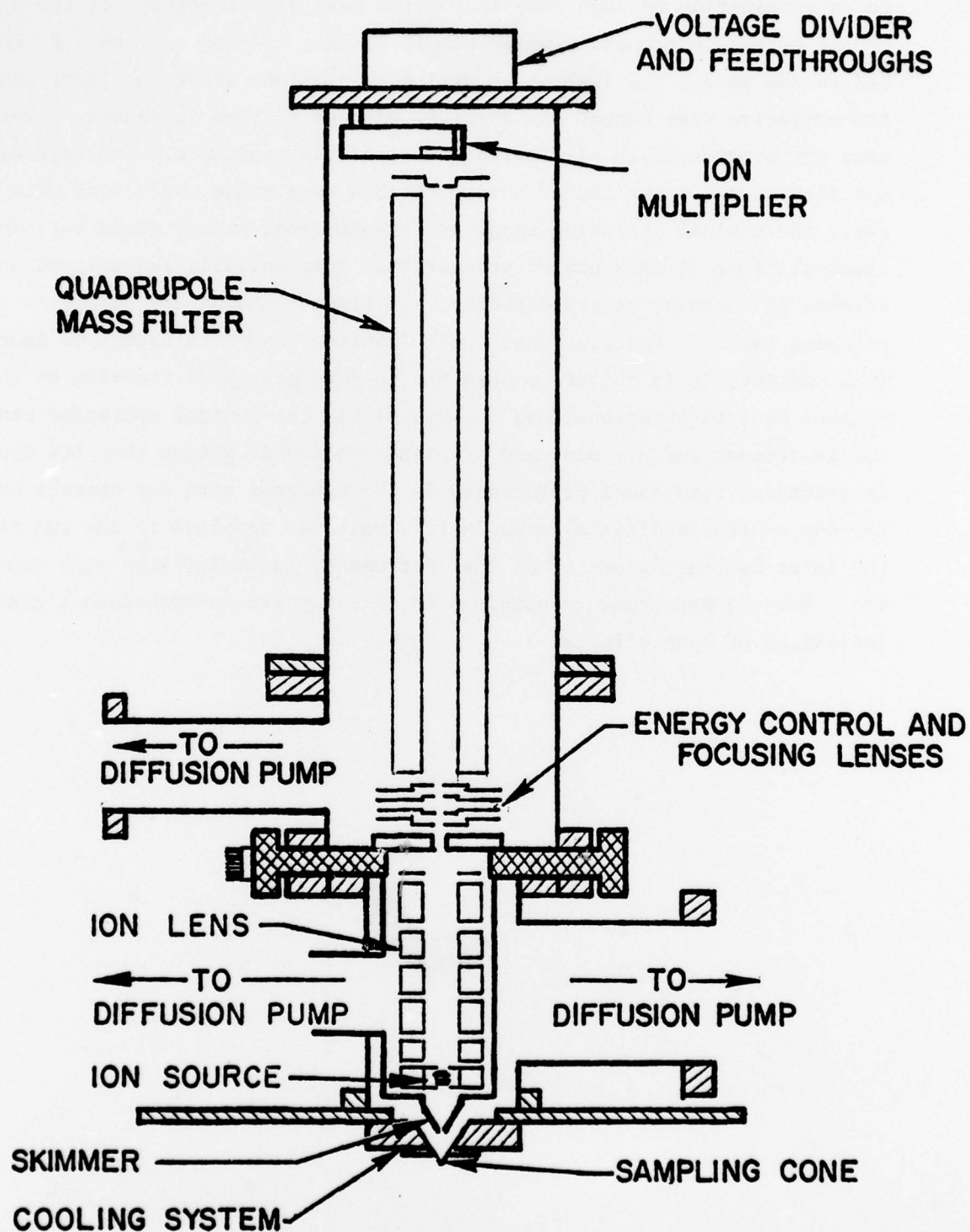


FIGURE 2 FLAME ION MASS SPECTROMETER

operating characteristics of a quadrupole mass filter are uniquely well suited to an examination of such complicated ion mass distributions; if the d.c. component of the instrument's power supply is shut off and only an r.f. voltage fed to the poles, the instrument will pass all ions above the lower limit of its operative mass range. As the r.f. voltage is then increased, lower mass ions are progressively eliminated until, at the maximum r.f. voltage corresponding to the upper end of the accessible mass range, only ions with masses above the nominal operating range are transmitted. At any given r.f. voltage, then, all ions of mass number greater than that normally transmitted at that voltage will appear at the detector; all lighter masses are rejected. By scanning the r.f. voltage range while sampling ions from flames of increasing fuel content, it is therefore possible to determine what fraction of the ions present fall into various mass classes within the nominal operating range of the instrument and how many are of higher molecular weight than its upper limit. In practice, this ideal performance is not achieved with our present mass filter due to the small imbalances in r.f. voltages supplied to the two pole pairs, the inlet aperture geometry of the instrument, ion multiplier mass sensitivity, etc., but the measurements obtained in this way are nevertheless a qualitative indication of such effects.

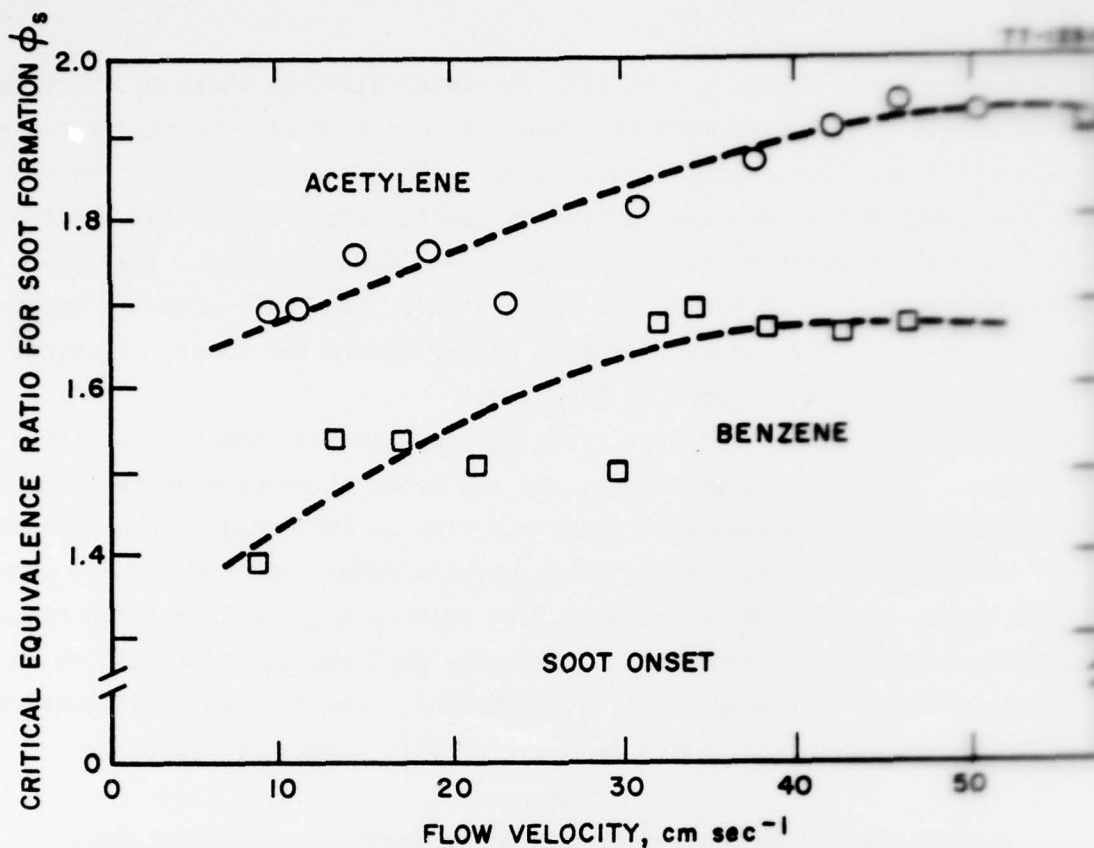


FIGURE 3 EFFECT OF FLOW VELOCITY ON SOOT FORMATION
Water-cooled burner; inlet temperature = 360 K

III. EFFECT OF FUEL STRUCTURE ON SOOT FORMATION

The first efforts were directed toward determining the effect of fuel structure on soot formation. There are, of course, some data in the literature^{5,6,8} on the subject but they pertain to different burner configurations from those used in this study or to different combustion systems, i.e., diffusion flames or aerosol fuels. The system so far used in this study involves premixed gaseous fuels and air. It will be useful to compare the critical equivalence ratios for soot formation in these various systems.

The effect of unburned gas flow velocity on the critical equivalence ratio for soot formation was first determined for a variety of fuels. The results are presented in Fig. 3. The apparent large scatter is real and not simply experimental scatter. As the flow rate changes, the shape of the flame changes from cellular flames with varying numbers of cells, to fluttering cellular flames, to single well-formed cones. These changes are usually very abrupt and

the equivalence ratio at which soot sets in varies with the shape of the flame. The variation in flame shape with flow has, of course, been observed previously and has been studied extensively, especially by Markstein.¹⁰ These phenomena are certainly related to relative diffusion coefficients of fuel and oxidizer on soot precursor reactants, e.g. ions, and merit further study. They could be important to soot formation in jet engines where the flame shape is determined by turbulence. The present program cannot afford the luxury of digressing to consider this problem further at this time.

In general, at the higher flow rates employed in this study, the flames become better defined and more stable, and the point at which soot is observed becomes essentially independent of total gas flow as indicated by the data in Fig. 3. Because this occurs over a range of high flows, it appears that under these conditions heat transfer to the burner becomes negligible and the flame temperatures attained are constant and probably approach the adiabatic value.

Values of ϕ_s under these relatively constant, reproducible conditions are tabulated for all the fuels tested to date in Table I, together with the

TABLE I
CRITICAL EQUIVALENCE RATIOS FOR SOOT FORMATION IN SELECTED FUELS
(1 atm flames)

	Vapor Fuel (This study)	Aerosol Fuel Street & Thomas ^a	Δ
<u>Alkanes</u>			
Propane C ₃ H ₈	1.74	1.56	0.18
n-Hexane C ₆ H ₁₄	1.63	1.45	0.18
c-Hexane C ₆ H ₁₂	1.70	1.51	0.19
n-Heptane C ₇ H ₁₆	1.69	---	
n-Octane C ₈ H ₁₈	1.71	1.39	0.32
<u>Alkenes</u>			
Ethylene C ₂ H ₄	1.84	1.82	0.02
<u>Alkyne</u>			
Acetylene	2.05	2.07	- 0.02
<u>Aromatics</u>			
Benzene C ₆ H ₆	1.55	1.42	0.13
Toluene C ₇ H ₈	1.43	1.33	0.10
Xylene C ₈ H ₁₀	1.43	1.27	0.16
Cumene C ₉ H ₁₂	1.56	1.28	0.28

analogous values from the prior work of Street and Thomas.⁸ In the work of Street and Thomas the fuel was sprayed into the air stream of a Bunsen burner so that, in most cases, the fuel entered the flame as a gas/aerosol mixture. The differences in the critical equivalence ratios are not small and tend to increase with increasing boiling points. It is tempting to assume that this is due to the heat of vaporization affecting the flame temperature; this assumption is supported by the similarities in adiabatic flame temperatures given in Table II. It also seems likely that the fuel rich mixtures that occur locally around burning or evaporating droplets, or groups of droplets, are more apt to produce soot so that the average ϕ_s for aerosols is less than for vapors where a premixed homogeneous condition exists.

TABLE II
ADIABATIC FLAME TEMPERATURES FOR THERMODYNAMIC AND EXPERIMENTAL
CRITICAL EQUIVALENCE RATIOS AT WHICH SOOT IS FORMED

	Thermodynamic		Experimental	
	ϕ_s	T, K	ϕ_s	T, K
Benzene: vapor	2.52	1460	1.55	2200
aerosol	2.47	1350	1.4	2180
n-Hexane: vapor	2.88	1150	1.63	1850
aerosol	2.76	1100	1.5	1870

Flames of three fuels, viz. acetylene C_2H_2 , benzene C_6H_6 , and cumene C_9H_{12} , have also been examined for their tendency to soot at reduced pressures, see Table III. The experiments described above for 1 atm flames were duplicated at pressures down to 70 Torr. Because of the increase in linear flow

TABLE III
EFFECT OF PRESSURE ON THE CRITICAL EQUIVALENCE RATIO FOR SOOT FORMATION
Unburned gas temperature = 90°C

	Pressure, Torr						Mean ϕ_s
	70	120	200	350	500	760	
Acetylene	2.06	2.00	1.93	2.16	2.15	2.05	2.06
Benzene	1.81	1.67	1.64	1.48	1.66	1.55	1.64
Cumene	1.60	1.48	---	1.60	---	1.56	1.56

velocity of unburned gas at lower pressures and dependence of flame speed on pressure over this range, it was necessary to work at smaller total gas flow rates. At 70 Torr, stable well-structured flames could only be obtained at total flow rates below $80 \text{ ml(STP)sec}^{-1}$. The corresponding decrease in fuel flow caused some imprecision in feed rate measurements and led to less reproducibility in the low pressure data than at 1 atm. Notwithstanding these difficulties, it can still be concluded, at least in this pressure range, that ϕ_s changes little with pressure. This is in substantial agreement with the results of McFarlane et al.¹¹ at pressures above 1 atm.

Other laboratory studies^{5,7} have demonstrated an increasing tendency to soot formation with increasing pressure. Gaydon and Wolfhard,⁶ however, question the interpretation of a pressure effect; they cite evidence that the observed effects are due to changes in flame temperature resulting from heat loss to the burner (compare discussion above) which is dependent on pressure in many experiments. They conclude, however, that once carbon is set free, the proportion of fuel converted to soot does increase with increasing pressure. The effect of pressure merits further study because increasing the operating pressure in a jet engine apparently does increase the tendency to smoke. For example, increasing the combustor pressure in a Rolls-Royce RA24 engine, operating at an overall equivalence ratio of 0.24 from 140 to 190 psia increased the exhaust emission from about 23 to 58 P.S.U. (photo smoke unit $\approx 1 \mu\text{g}$ soot per liter).⁹ Before the results reported in Table III are published they will be repeated--the scatter seems excessive.

The effect of molecular structure on the critical equivalence ratio for soot formation is demonstrated in Fig. 4, for a variety of fuels, as a function of C/H ratio. The tendency to soot in general decreases in order: aromatics > alkanes > alkenes > acetylene. Clearly to complete this picture some other substances have to be examined, e.g., a higher molecular weight acetylene and mixtures, e.g., acetylene and benzene. Such studies are in progress. With respect to the motivation for this study, i.e., the anticipated use of coal-derived fuels, the general increasing tendency to soot with increasing C/H ratio--with the exception of acetylene--demonstrates the importance of this study. This is rather dramatically presented in Fig. 5. If we are to efficiently utilize coal in producing liquid fuels, and are not to consume a major portion of the available energy just in reducing the C/H ratio, we will have to burn more aromatic fuels. This means we must find a means of reducing the

experimental temperature is the adiabatic flame temperature calculated for that equivalence ratio. No carbon product is predicted by an equilibrium calculation at this temperature. This table clearly demonstrates that soot formation is a non-equilibrium process--that, of course, is one reason why it is interesting.

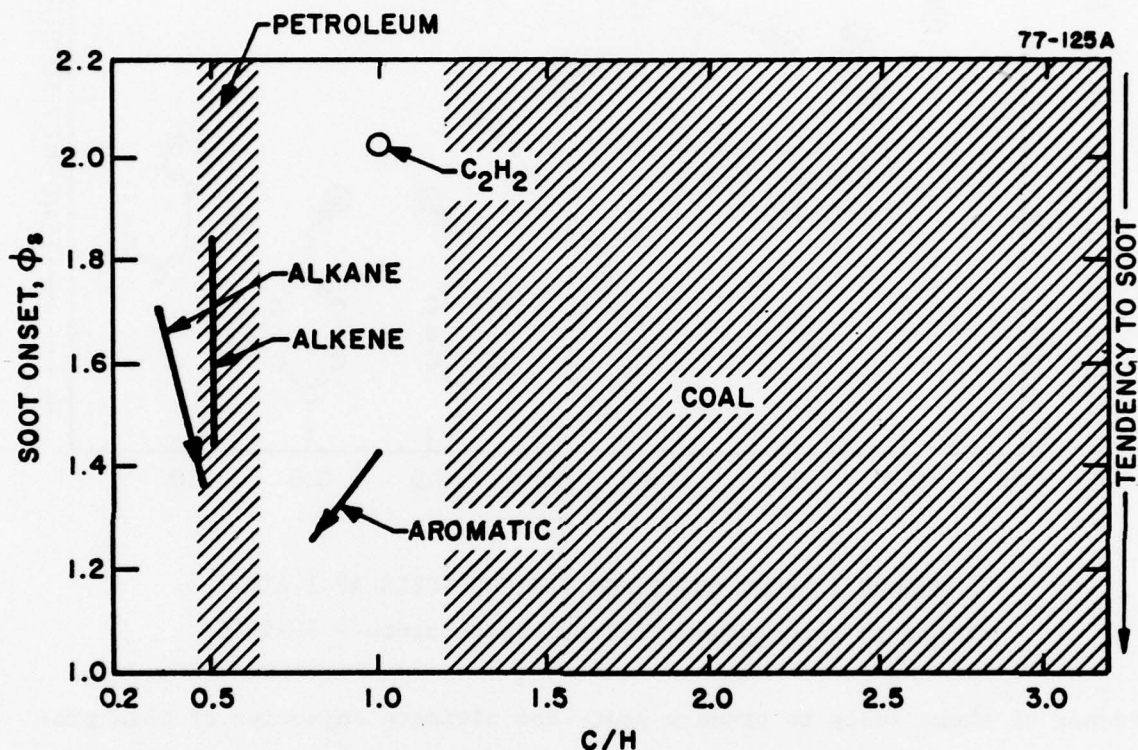


FIGURE 5 COMPARISON OF FUEL SOOTING TENDENCY WITH C/H IN PETROLEUM AND COAL

Data from this study and Street and Thomas.⁸ Arrows on lines indicate increasing molecular weight.

TABLE IV
COMPARISON OF THERMODYNAMIC AND EXPERIMENTAL FLAME
TEMPERATURES FOR SOOT FORMATION

	<u>Thermodynamic</u>		<u>Experimental</u>		
	ϕ_s	T, K	ϕ_s	T, K	ϕ_{Th}/ϕ_{Ex}
Acetylene	2.5	2140	2.05	2380	1.3
Benzene	2.5	1350	1.55	2200	1.6
n-Hexane	2.8	1100	1.63	1850	1.7

IV. IONIZATION IN SOOTING FLAMES

The main objective of this program is to examine the hypothesis that chemi-ionization flame ions play a major role in soot formation in hydrocarbon flames. The main experimental tool is an ion sampling mass spectrometer. In this section the results of the mass spectrometer study are summarized. It would be presumptuous, after a year's study, to claim that all of the free-radical mechanisms previously proposed were incorrect and had to be replaced by an ionic mechanism. We will show, however, that an ionic mechanism is consistent with the data obtained in this study; in subsequent work the ionic and free radical mechanisms will be compared.

Figure 6 demonstrates how the ion spectra change as the equivalence ratio is increased. This flame showed visible soot at an equivalence ratio just over 2.10. Only the lower 1% of the spectra is shown; the peaks have been cut off. The total ion concentration under the three sets of conditions is nearly the same--it decreases less than 10% between $\phi = 1.9$ and 2.1, but the distribution of ion masses shifts dramatically to higher masses as the equivalence ratio is increased. The H_3O^+ ion concentration is low, only about 10% of the total ion concentration. In the leanest flame of the three, the dominant ions are at masses 39, 53, and 63, corresponding to $C_3H_3^+$, $C_4H_5^+$, and $C_5H_7^+$, respectively. These three ions remain abundant as the fuel content is increased but higher molecular weight species become rapidly more prevalent. The heavier ions, above mass 63, appear to be separated by an average of 13 amu (corresponding to CH), and the more massive the ion, the greater is its sensitivity to fuel concentration. In the richest condition of Fig. 6, the ion spectrum is dominated by 39, 63, 89, 127, and 165.

Figure 7 shows the relative abundances of the ions in three different mass classes in C_2H_2 /air flames at 55 Torr at a position well downstream of the flame front as a function of equivalence ratio. It should be noted that the numbers are not a quantitative indication of relative proportions but serve only to demonstrate that an increase in heavy masses accompanies the onset of soot formation. The predominance of low molecular weight species, in this case mainly mass 39, $C_3H_3^+$, is also apparent as is the fact that the ions in the intermediate mass range from 180 to 300 amu and in the large mass range, greater than 300 amu, comprise a relatively small fraction of the total ion spectra at the position in the flame where soot is first produced.

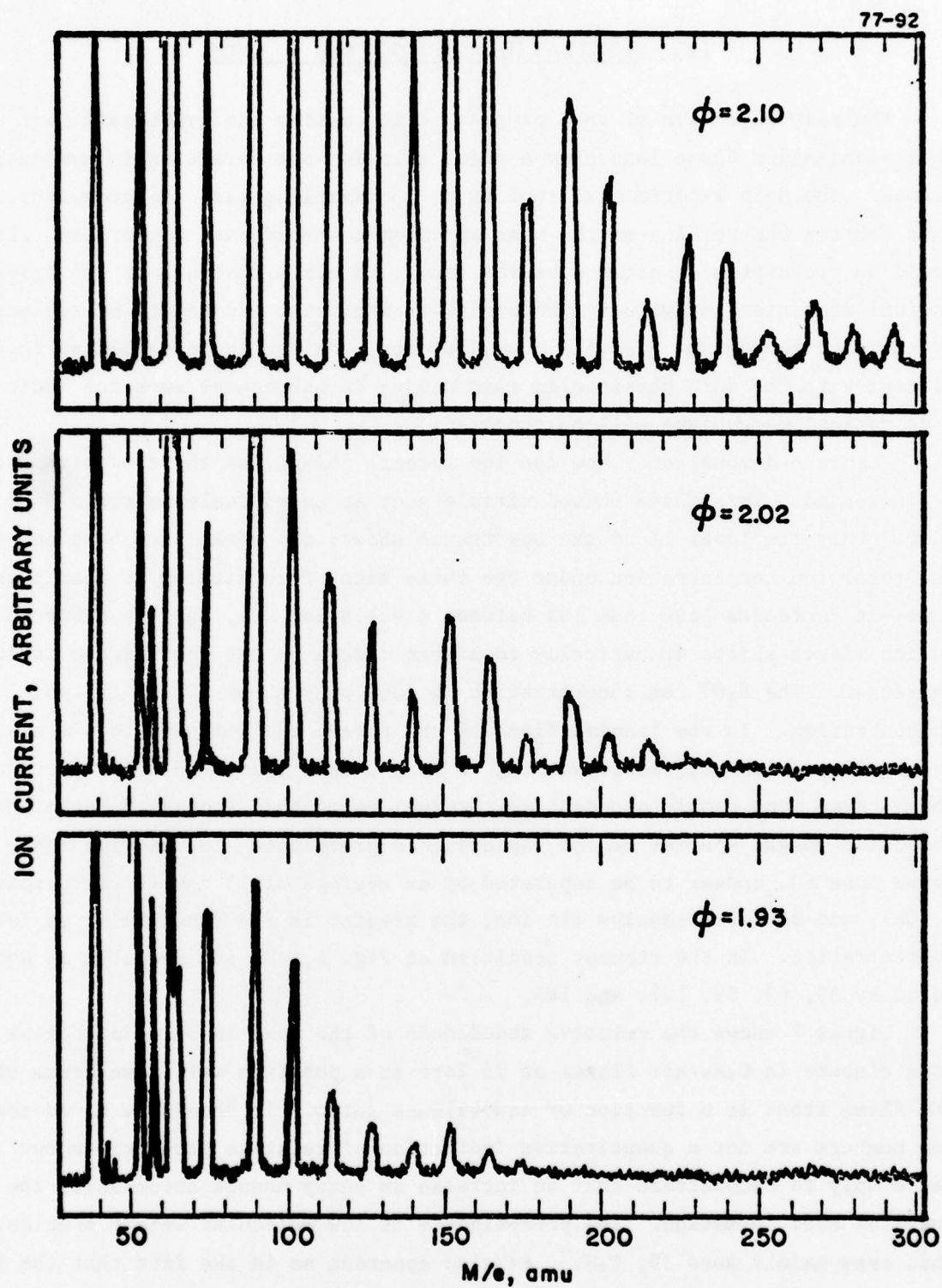


FIGURE 6 ION SPECTRA OF FUEL RICH ACETYLENE/AIR FLAMES
P = 200 Torr

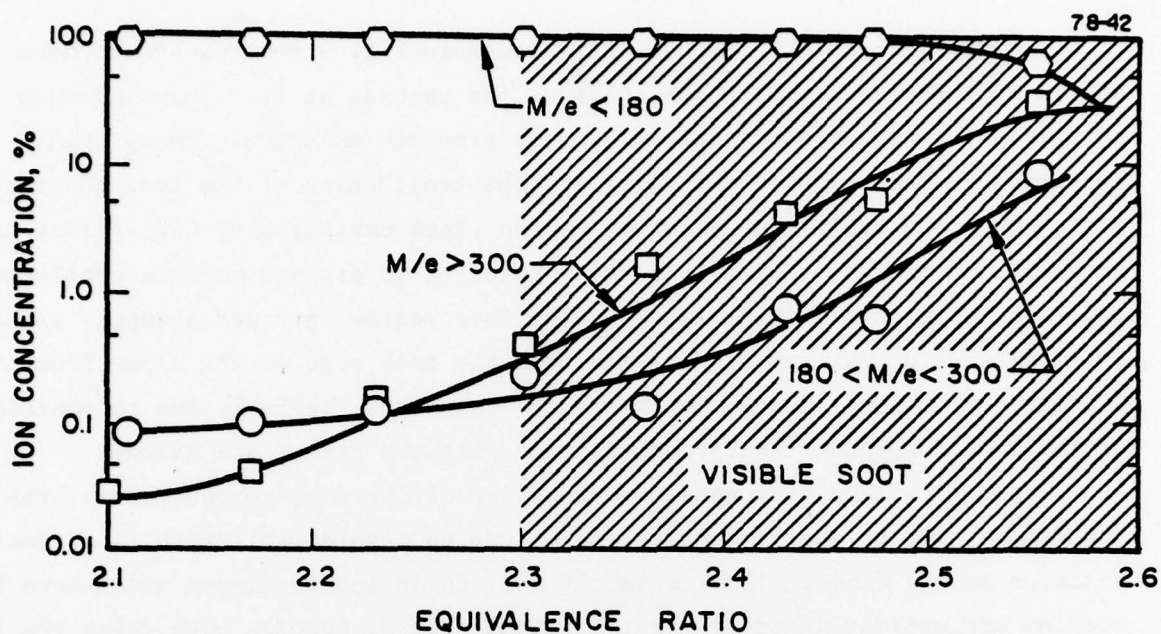


FIGURE 7 EFFECT OF EQUIVALENCE RATIO ON ION CONTENT
IN AN ACETYLENE-AIR FLAME

$P = 55$ Torr; $T_u = 165^\circ\text{C}$

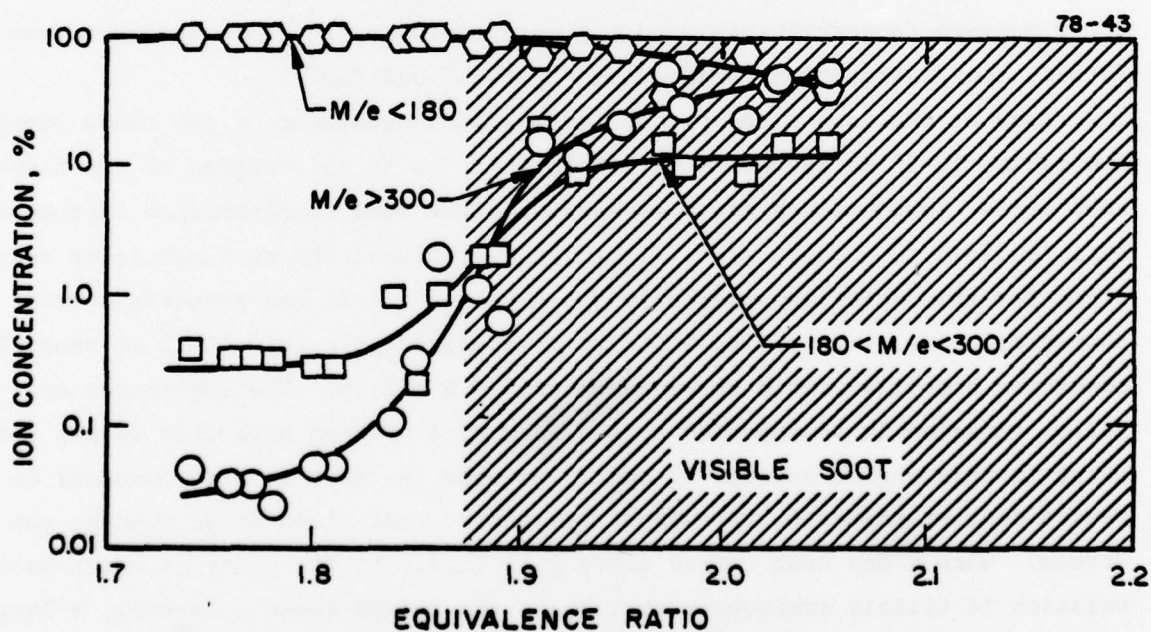


FIGURE 8 EFFECT OF EQUIVALENCE RATIO ON ION CONTENT
IN A BENZENE-AIR FLAME

$P = 55$ Torr; $T_u = 200^\circ\text{C}$

The analogous plots for C_6H_6 /air flames in Fig. 8 reflect a much more abrupt appearance of higher molecular weight species at ϕ_s . This behavior is paralleled by visual observations of soot particle emission. The gradual increases in the emission intensity and the lengthening of the soot-containing region over the whole cross-section of the flame exhibited by C_2H_2 flames are not apparent in C_6H_6 flames. As the ϕ required to produce visible continuum emission is reached in C_6H_6 flames, a diffuse yellow streamer abruptly appears which extends downstream all the way from the back edge of the flame front to a point 6-8 cm above the burner where it disappears, probably due to admixing of the leaner shroud flame product stream with the test flame stream.

Besides being a very sensitive function of the fuel concentration, the ion composition of nearly sooting flames varies considerably with flow time or position in the flame. This is partly due, as in leaner flames which have been studied extensively in prior work,¹² to the neutral species with which the ions interact, changing continuously with time as the fuel and oxidizer are consumed and products evolve. The complexity of the resultant ion profiles is illustrated in Fig. 9 in which relative ion concentrations are given as a function of distance from the burner top in a nearly sooting ($\phi = 2.2$ where $\phi_s = 2.3$) C_2H_2 /air flame. It can be seen from this figure that different ions reach their maximum concentrations at different points in the flame and that downstream, the distribution is dominated by $C_3H_3^+$ and C_5H^+ .

Many of the ions display a second maximum downstream of the flame front in the region 10-20 mm above the burner top. It is in this region of the flame that yellow luminescence first appears when the fuel concentration approaches that required to produce soot. In these C_2H_2 flames, the soot particles responsible for this emission apparently "burn up" as the stream proceeds further downstream, i.e., the yellow emission disappears above this 10-20 mm zone. This condition prevails within the interval $2.3 < \phi < 2.75$. The appearance of yellow emission is accompanied by the formation of high molecular weight ions, first in this region between 10 and 20 mm when the soot is also confined to this region and, at higher ϕ , throughout the entire post flame front product gas stream. When ϕ has been raised above 2.75 (i.e., to the point at which yellow emission is visible everywhere throughout the burned gases), however, a large proportion of the charged species are of a molecular weight greater than 300 amu and thus lie beyond the range of the mass spectrometer being used when these experiments were carried out.

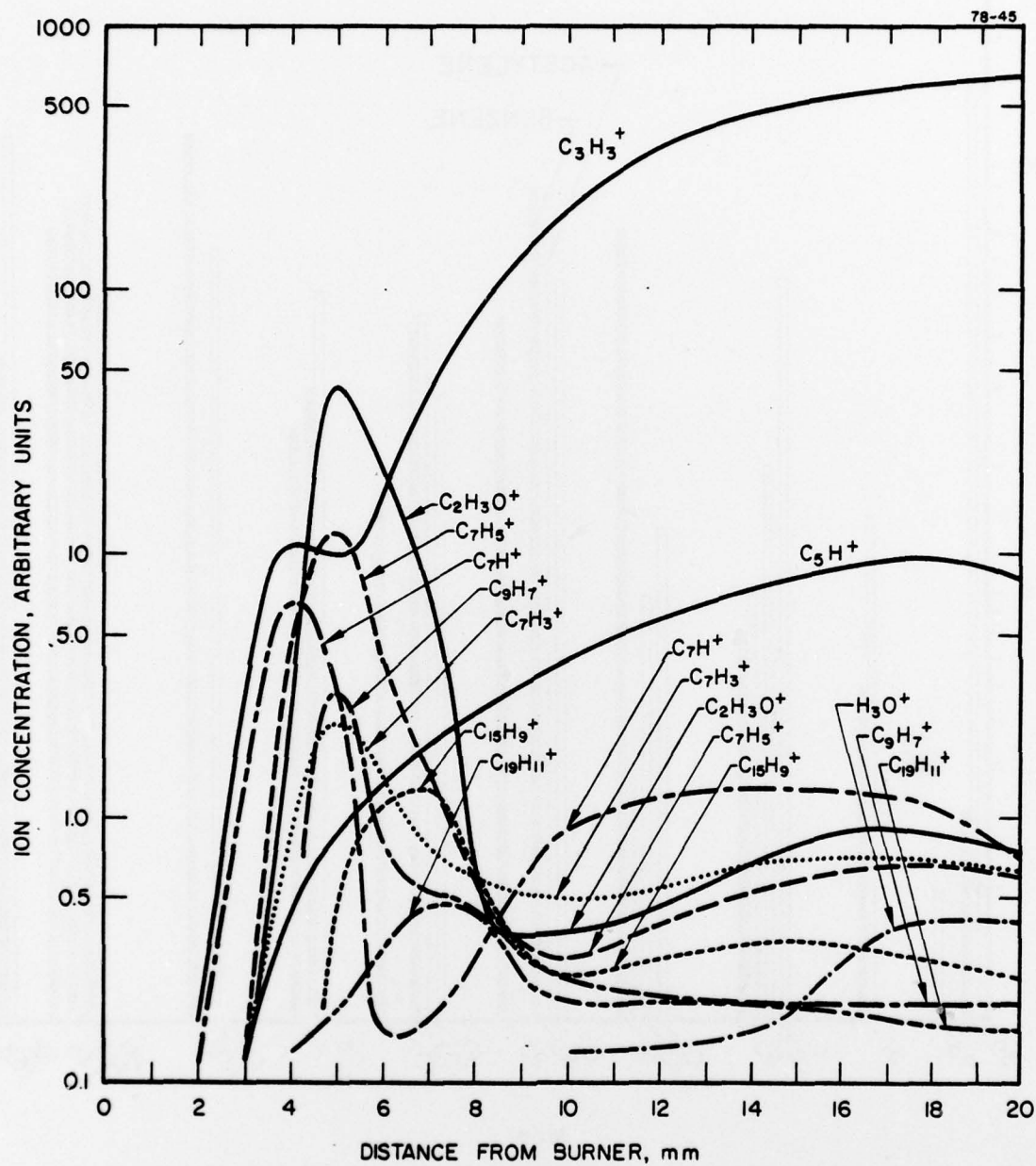


FIGURE 9 VARIATION OF ION CONCENTRATION THROUGH AN ACETYLENE-AIR FLAME
 $P = 56$ Torr; $T_u = 220^\circ\text{C}$; $\phi = 2.2$; $\phi_s = 2.3$; linear gas flow velocity in
 unburned gas $= 180 \text{ cm sec}^{-1}$

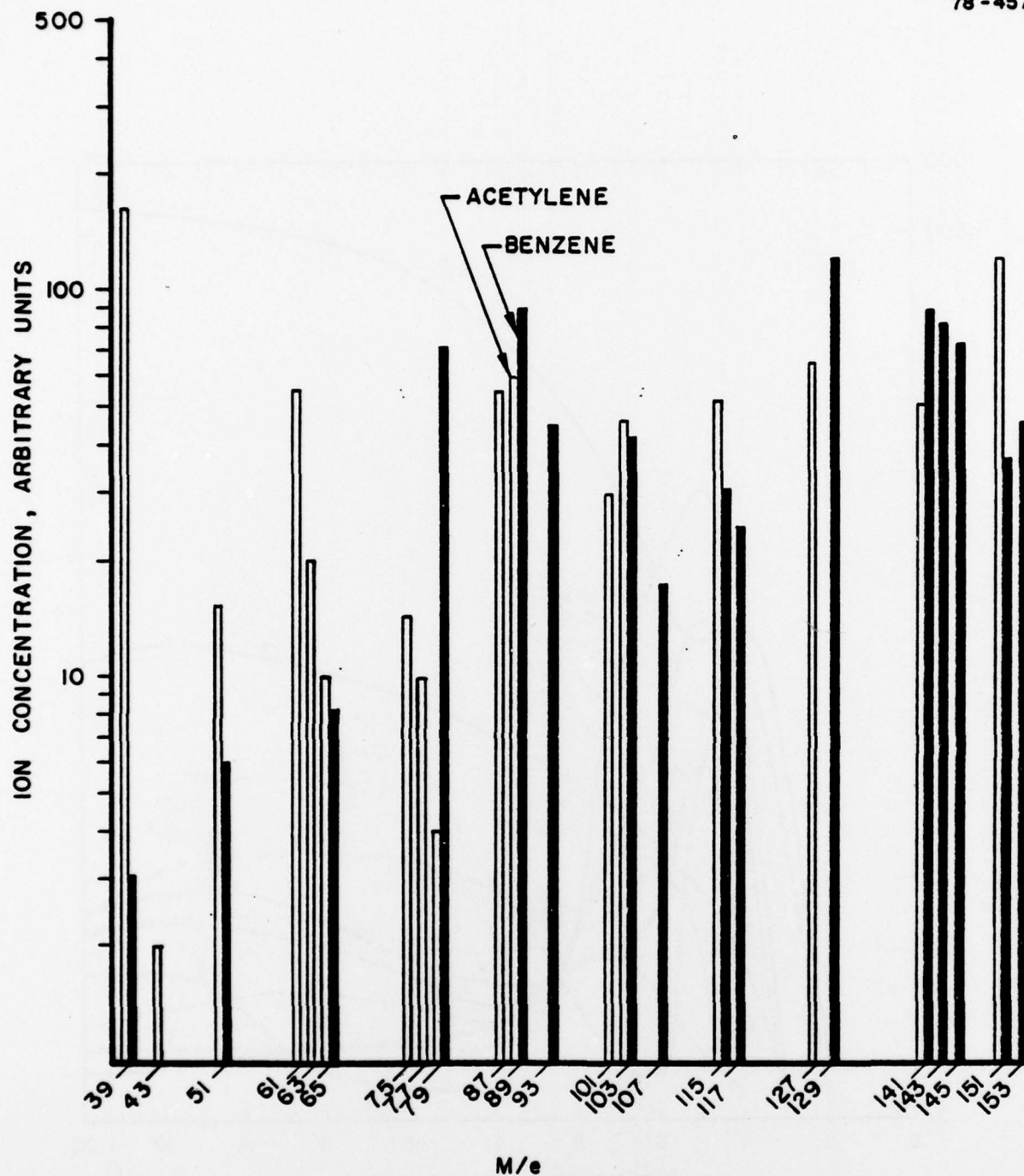
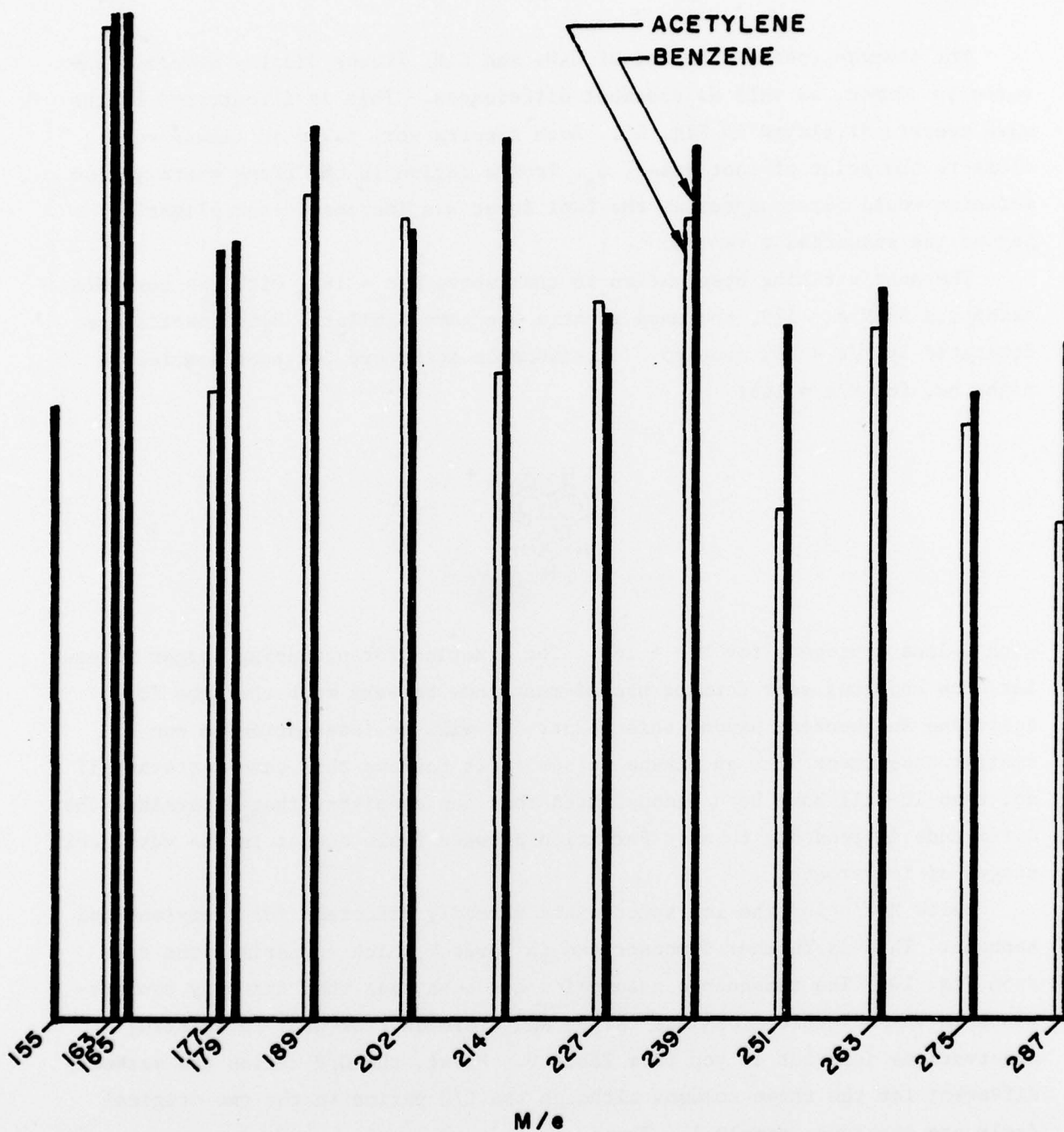


FIGURE 10 COMPARISON OF ACETYLENE-AIR AND
 P = 55 Torr; inlet gas temperature = 220°C;
 distance above

Experimental Equivalence Ratio, ϕ
 Critical Equivalence Ratio for
 Soot Formation, ϕ_s



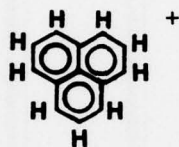
BENZENE-AIR ION SPECTRA IN LUMINOUS FLAME ZONE

air flow rate = 16 ml(STP)sec⁻¹; probe
burner = 12 mm

<u>Acetylene</u>	<u>Benzene</u>
2.20	1.90
2.25	1.95

The charged species content of C_2H_2 and C_6H_6 flames display several features in common, as well as distinct differences. This is illustrated by the mass spectra displayed in Fig. 10. Both spectra were taken in flames very close to the point of soot onset, ϕ_s , from a region in the flame where yellow emission would first appear as the fuel input was increased just slightly beyond the specified ϕ values.

The most striking observation is that above $M/e = 163$, with the possible exception of $M/e = 179$, the mass spectra are very similar. Both spectra are dominated by $M/e = 163$ and 165 . A reasonable structure for such a molecule might be, for $M/e = 165$:



with 2 less hydrogens for $M/e = 163$. The kinetics for producing larger molecular ions and thus soot forming nuclei must thus be very much the same for acetylene and benzene beyond this point. It will be interesting to run a similar experiment with an alkane to see if it follows this same pattern. If so, then it will have been demonstrated that the chemistry that determines the difference in tendency to soot formation between fuels occurs in the very early stages of ion growth.

Below $M/e = 163$ the ion spectra are markedly different for acetylene and benzene. This is further demonstrated in Table V which summarizes the data from Fig. 10. The reasonable assumption has been made that the only two elements in the molecular ions are carbon and hydrogen. Several interesting observations jump out at you from Table V. First, the C/H ratios are markedly different for the three columns although the C/H ratios in the two original fuels are the same, namely 1. Thus:

C/H for ions unique to acetylene	1.72
C/H for ions in common	1.42
C/H for ions unique to benzene	1.03

Interestingly C/H for the ions in common lies between the two fuels. An obvious interpretation of this data is that an aromatic molecular ion must be formed to produce higher molecular weight ions. This is consistent with the

TABLE V
ION COMPOSITIONS UNIQUE TO ACETYLENE OR BENZENE AND COMMON TO BOTH
(From Fig. 10)

Number Carbons	Unique to Acetylene	Unique to Benzene	Common
3	$C_3H_3^+$ ^a	---	---
4	---	---	51 $C_4H_3^+$
5	61 C_5H^+ , 63 $C_5H_3^+$	---	65 $C_5H_3^+$
6	75 $C_6H_3^+$, 77 $C_6H_5^+$	---	79 $C_6H_4^+$
7	87 $C_7H_3^+$	93 $C_7H_9^+$	89 $C_7H_7^+$
8	101 $C_8H_5^+$	107 C_8H^+	103 $C_8H_7^+$
9	---	117 $C_9H_9^+$	115 $C_9H_7^+$
10	127 $C_{10}H_7^+$	129 $C_{10}H_9^+$	---
11	---	143 $C_{11}H_{11}^+$, 145 $C_{11}H_{13}^+$	141 $C_{11}H_9^+$
12	---	153 $C_{12}H_9^+$, 155 $C_{12}H_{11}^+$	151 $C_{12}H_7^+$
13	---	---	163 $C_{13}H_7^+$, 165 $C_{13}H_9^+$
14	---	179 $C_{14}H_{11}^+$	177 $C_{14}H_9^+$

^a Included with acetylene because in benzene it is so much lower.

observation, above, that the change in ion concentration with equivalence ratio and change in appearance of soot are very abrupt for benzene flames and less abrupt for acetylene flames, Figs. 7 and 8. In the case of benzene, a molecule (or molecules) is present by which proton transfer can readily produce an aromatic molecular ion. In acetylene, the aromatic ion has to be produced.

Another clue to the mechanism, or possibly only to the thermal stability of molecular ions at high temperatures, is the observation of the number of hydrogen atoms on the ions, see Table VI. The dominance of odd numbers of hydrogen atoms begs for an explanation as do the "observations" noted in the table.

Spectra have also been taken repeatedly at higher resolving power in order to determine the mass numbers of observed species with more accuracy than is possible from rapid, higher sensitivity runs exemplified by Fig. 10. Figure 11 is a sample of such a higher resolution spectrum taken from the reaction zone of a C_2H_2 /air flame under fuel-rich conditions similar to those of Fig. 10, but at an equivalence ratio somewhat further from the point of soot onset. These data illustrate the complexity of the ion content of these flames in that many

TABLE VI
NUMBER OF H ATOMS ON MOLECULAR IONS
(From Table V)

<u>Number H Atoms</u>	<u>Number Molecular Ions in Table V</u>	<u>Observations</u>
1	1	
2	0	
3	5	4 from C_2H_2
4	1	from common
5	4	none from benzene
6	1	
7	4	from common only
8	0	
9	7	5 from benzene
10	0	
11	3	all from benzene
12	0	
13	1	

of the peaks of Fig. 10 can be seen under higher resolution to comprise groups of several species differing by only a few mass units. An analogous situation obtains in C_6H_6 flames. It is also apparent from a comparison of Figs. 10 and 11 that only a small change in fuel concentration can produce distinct changes in relative ion concentrations within the groups. In Fig. 11, for example, the ions at 87, 89, and 91 amu are all of comparable intensity whereas, despite the lack of resolution, it is apparent in the mass spectra which led to Fig. 10 that mass 91 is negligible compared to the other two. Similar changes occur in many of the other groupings, but, in general, it appears that as the flame is made more fuel rich, the higher molecular weight ions within any given group become more abundant. Assuming the ions contain only C and H, this observation implies that a structure with increasing H content is approached as the stoichiometry is increased toward soot formation. This would be consistent with the discussion above on the data in Table V and the observation that the C/H ratio for the ions unique to acetylene flames is greater than that for ions unique to benzene flames and is also greater than for the ions observed in both flames. To produce large molecular ions, the

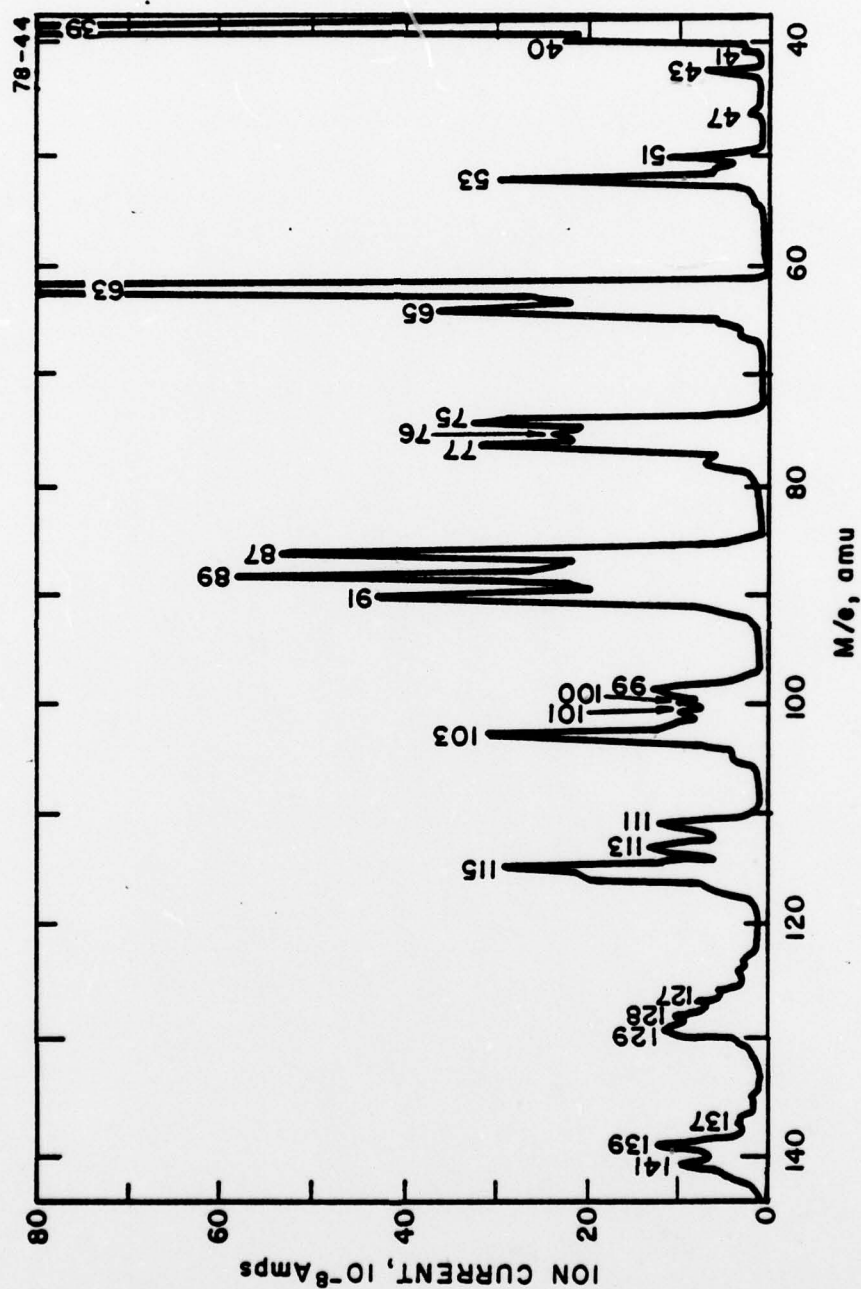


FIGURE 11 HIGHER RESOLUTION MASS SPECTRUM SEGMENT FROM ACETYLENE-AIR
FLAME AT 55 TORR
 $\phi = 1.8$ in the flame zone

presumed precursors of soot nuclei, the ions have to go through an aromatic structure which means, for acetylene flame ions, adding hydrogen.

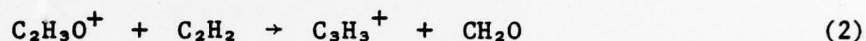
V. AN IONIC MECHANISM OF SOOT FORMATION

At this stage it is worthwhile considering some mechanisms in an attempt to explain the data and to serve as a guide for defining future experiments.

The primary ion must be produced by the chemi-ionization reaction^{12,13}

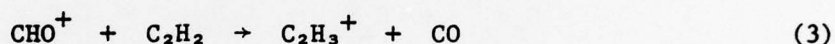


The prominent ion, $\text{C}_2\text{H}_3\text{O}^+$, in Fig. 9 is produced by^{14,15}



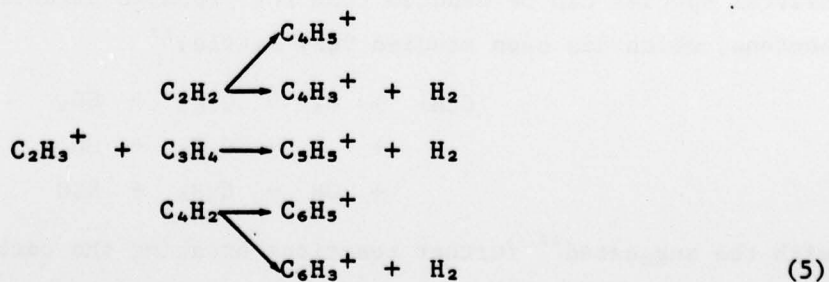
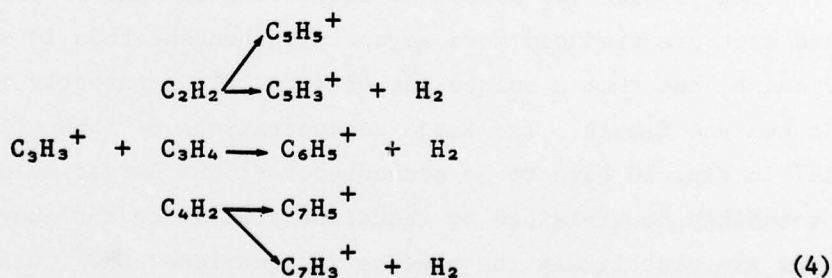
This is certainly consistent with the increase in C_3H_3^+ as $\text{C}_2\text{H}_3\text{O}^+$ decays in Fig. 9.

Other simple ions might be produced such as C_2H_3^+ , observed by Vinckier et al¹³

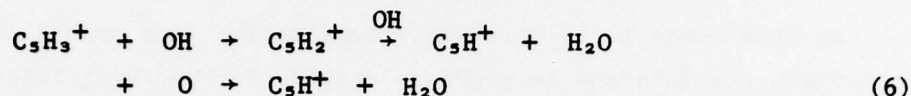


The lack of appearance of C_2H_3^+ in our system does not mean it does not form; its removal reactions may be much faster than the formation reactions.

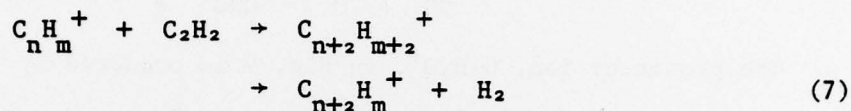
The neutral species building blocks, from the work of Homann et al,^{7,16} are: CH, CH_2 , C_2H , C_3H_4 , C_4H_2 , and C_6H_2 . Using only a few of these with the above two ions, C_3H_3^+ and C_2H_3^+ , the initially observed intermediate mass ions are readily produced:



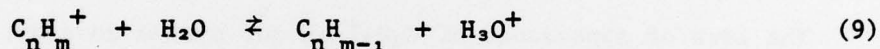
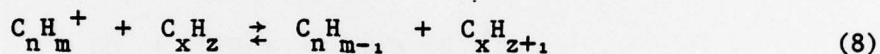
To account for the large concentrations of C_3H^+ , Figs. 9 and 10, oxidation reactions have to be invoked to remove hydrogen, e.g.:



Generalizing Reactions (5) and (6), larger molecular ions are formed by:

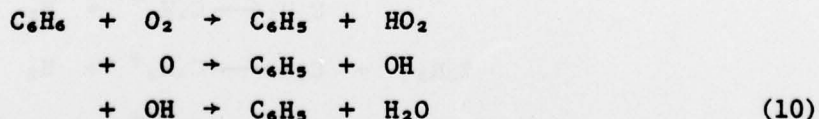


It might be expected that a proton, or even a hydrogen atom, would shuffle from molecule to molecule so that the number of hydrogens on a carbon skeleton might vary with the composition, temperature, and pressure of the environment. Reactions of the following type would be expected to contribute:

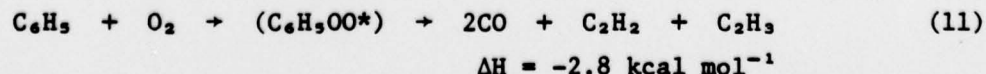


The H_3O^+ formed in Reaction (9) would serve as an intermediary, giving its proton to another large molecule. The data in Table V and Fig. 11 would generally require that two hydrogen atoms be shuffled at a time or that two shuffling reactions occur very quickly. Clearly more work is required.

The problem now arises of accounting for the observation that large ions and soot are produced more abruptly in benzene than in acetylene flames, Figs. 7 and 8, and that a unique set of ions, all apparently aromatic, are produced in benzene flames. The large concentrations of ions of mass 79, 93, 107, and 117 in Fig. 10 have to be accounted for; the larger molecular ions can then presumably be explained by reactions similar to the above. The basic starting ions are most likely the same as in acetylene: CHO^+ , $C_2H_3^+$, and $C_3H_3^+$. The neutral species can be deduced from the probable oxidation mechanism for benzene, which has been studied very little,¹⁷

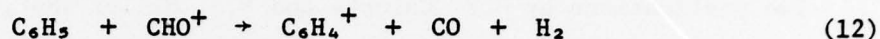


with the suggested¹⁷ further reactions breaking the carbon-carbon bond:

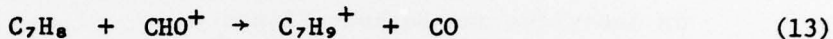


The molecular ions in benzene flames might then be produced as follows:

For amu 79:

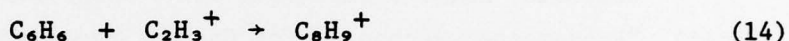


Amu 93 is difficult to account for in one step from the above set of neutrals and ions. Should toluene be present, the reaction



would be expected.

For amu 107:



For amu 117:



In explaining the larger ions in the benzene flame it will be necessary to explain why they are unique to that flame and do not also occur in the acetylene flame. For example, to explain the unique formation of amu 107, C_8H_9^+ , in the benzene flame, we cannot go through C_8H_7^+ because that ion is common to acetylene and benzene, Table V, and the amu 107 ion does not occur in the acetylene flame.

The above seems a rational explanation of the appearance of specific ions in acetylene and benzene flames as well as why benzene flames produce soot and ions more abruptly with increasing equivalence ratio. The assumption is being made that to produce soot the ions must take on an aromatic ring structure. In benzene, the aromatic ion is produced from the parent fuel molecule or a first derivative of that molecule, while in acetylene the ion must grow by ion molecule reaction and then the new molecular ion must rearrange to produce an aromatic molecular ion. Discussion of these mechanisms will be left to the future.

VI. PUBLICATIONS AND PRESENTATIONS

Two publications by H.F. Calcote and W.J. Miller should be submitted by year end to the journal, Combustion and Flame. They will be entitled:

- (i) Effect of Fuel Structure on Soot Formation
- (ii) A Mass Spectrometric Study of Ionic Mechanisms of Soot Formation in Acetylene and Benzene Flames

The authors participated in the following meetings and workshops:

- (i) Project SQUID Workshop on Alternate Hydrocarbon Fuels for Engines, Columbia, MD, 7-9 September 1977; H.F. Calcote was a Panel Member.
- (ii) "Fundamental Mechanisms of Carbon Formation in Hydrocarbon and Synthetic Fuel Combustion," presented by H.F. Calcote, 1977 AFOSR Meeting on Air-Breathing Combustion Dynamics, West Lafayette, IN, 12-16 September 1977.
- (iii) "Ionic Mechanism of Carbon Formation in Flames," presented by W.J. Miller, Fall Technical Meeting, Eastern Section: The Combustion Institute, United Technologies Research Center, East Hartford, CT, 10-11 November 1977.
- (iv) "Ionic Mechanisms of Carbon Formation in Flames," presented by H.F. Calcote, School of Engineering and Applied Science, Princeton University, 6 December 1977.
- (v) "Ionic Mechanism of Carbon Formation in Flames," presented by H.F. Calcote, National Bureau of Standards, Washington, DC, 13 December 1977.
- (vi) Project SQUID Workshop on Gas Turbine Combustion Design Problems, H.F. Calcote attending, Purdue University, West Lafayette, IN, 31 May-1 June 1978.
- (vii) "Ionic Mechanisms of Soot Formation in Flames," H.F. Calcote will be invited speaker at the Fall Technical Meeting, Eastern Section: The Combustion Institute, Miami Beach, FL, 29 November-1 December 1978.

VII. RESEARCH PARTICIPANTS

In addition to the authors, Ms. Rita M. Bowser assisted with the experiments.

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