

## TRACE ORGANIC COMPOUNDS IN NATURAL GAS COMBUSTION

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## INTRODUCTION

Complete combustion is decidedly easier to obtain with natural gas than with any other fossil fuel.<sup>5</sup> Under normal operating conditions, the flue products of natural-gas-burning equipment are relatively free of unburned hydrocarbons and partial combustion products. However, under fuel-rich conditions, small quantities of organic derivatives are produced. The investigation reported in this paper to identify and determine the quantities of these trace compounds, particularly when combustion occurs under low-aeration conditions, was carried out at the Institute of Gas Technology, with financial support of the American Gas Association.

Classical wet chemical procedures lack the sensitivity and selectivity for analyses of these trace organic compounds. Consequently, highly sensitive instrumental methods were used, with modifications whenever necessary.

## EQUIPMENT

The source of combustion products was the burner system shown in Fig. 1. It consists of a burner, transite base, and glass chimney. When the burner is operated at the low flow rates employed in this study, a bunsen-type flame is obtained. Disturbance of the flame by air currents, and dilution of the exhaust gases by surrounding air, were prevented by enclosing the burner in a pyrex glass chimney. Samples of flue products were withdrawn either from the top of the chimney or through the probe.

Early in the investigation, the base of the burner system was modified as shown in Fig. 2; a secondary air chamber, with 1/8-in. steel spheres in it to facilitate diffusion, was installed.

The burner was operated on 1000 Btu natural gas similar in composition to that shown in Table 1, and numerous experiments were carried out under a variety of conditions. Since space does not permit a detailed description of the experimental techniques, only a few comments can be made here.

Combustion conditions varied from fuel-rich to stoichiometric operation. The extreme fuel-rich variable corresponded to flow rates of 2 CF/hr of natural gas, no primary air, and 10 CF/hr of secondary air. Stoichiometric conditions corresponded to flow rates of 2 CF/hr of natural gas and 17.5 CF/hr of primary air. Secondary air was employed in selected stoichiometric experiments. Sufficient experiments were carried out to insure the reproducibility of the analytical determinations under the specific operating conditions. All determinations of specific

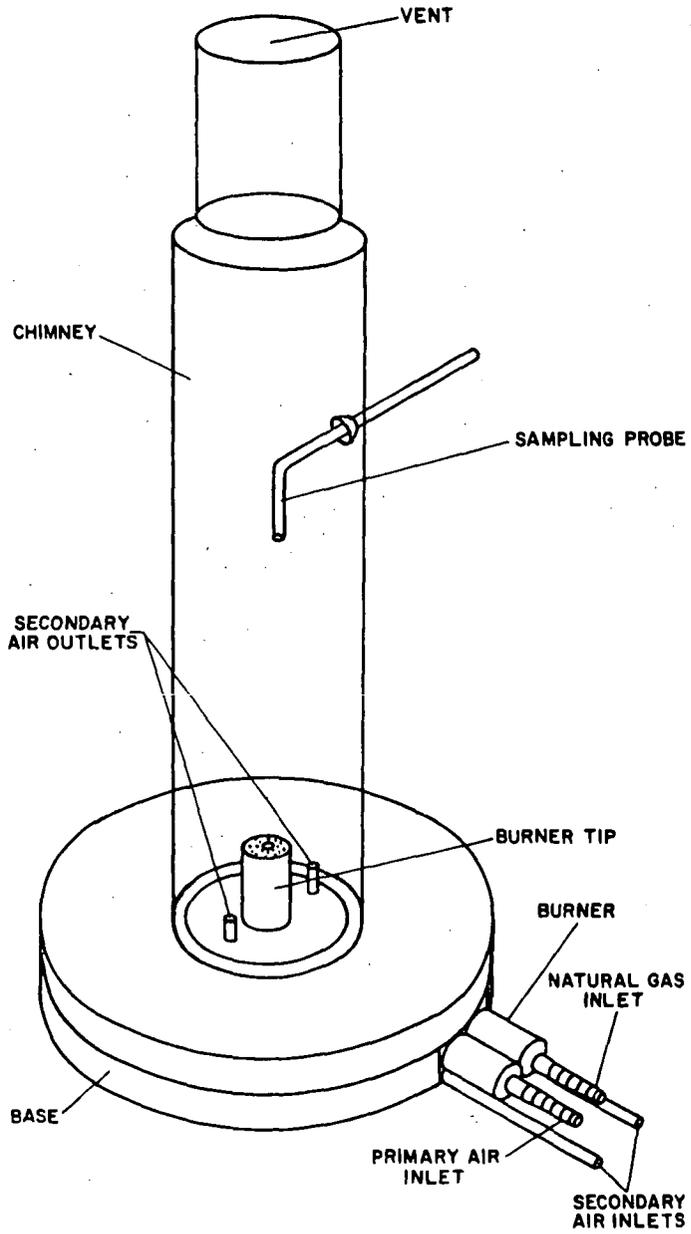


Fig. 1.-CLOSED BURNER SYSTEM FOR COMBUSTION OF NATURAL GAS

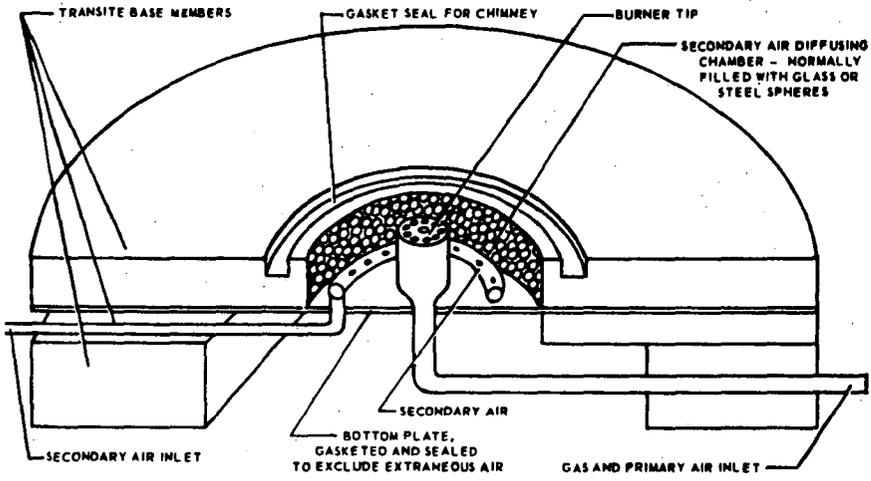


Fig. 2.—MODIFIED BURNER BASE

flue products were normalized to percentages of the total flue products

## RESULTS

During this investigation, a large number of saturated and unsaturated aliphatic, polynuclear aromatic, and oxygenated hydrocarbons were identified. Many were determined quantitatively in the ppb (parts per  $10^9$ ) concentration range. Table 2 gives a partial list of the organic compounds found in the combustion products under stoichiometric and fuel-rich operating conditions.

Gas chromatography with a flame ionization detector was employed to measure  $C_1$  to  $C_5$  saturated and unsaturated aliphatic hydrocarbons. Under essentially complete combustion conditions, the  $C_1$  to  $C_5$  hydrocarbons were present in the flue products in the ppb range, and several  $C_4$  and  $C_5$  compounds were below limits of detectability, as shown in Tables 3 and 4. When primary air was absent, concentrations of the  $C_1$  to  $C_5$  hydrocarbons varied inversely with the secondary air flow. Total  $C_5$  + hydrocarbons were determined by reversing carrier gas flow in the chromatographic column and backflushing after the emergence of n-butane. Again, the inverse relationship of concentration to secondary air flow was observed, as shown in Table 5.

An alumina column operated at  $80^\circ\text{C}$  with argon carrier gas served to separate the  $C_1$  to  $C_3$  fraction. The  $C_4$  to  $C_5$  fraction was separated on a  $1/8$  in. x 15 ft column of 28% dimethylsulfolane on Chromasoro P. Separation of total  $C_5$ + hydrocarbons was effected on a  $1/8$  in. x 6 ft alumina column operating at  $100^\circ\text{C}$ .

Polynuclear aromatic hydrocarbons were collected in a low-temperature trapping system, and separated by means of liquid extractive procedures and column, paper, and gas chromatography. Ultraviolet absorption and fluorescence spectrophotometry were then employed to identify the separated fractions. By these techniques, fifteen polynuclear aromatic compounds were identified; seven of these were determined quantitatively. Quantitative determination was based on separation via column chromatography, and identification and measurement were accomplished by ultraviolet fluorescence spectrophotometry. Table 6 shows that the concentrations ranged from less than 0.1 ppb for o-phenylenepyrene under conditions of essentially complete combustion, to 1040 ppb for pyrene under fuel-rich conditions.

Several classes of oxygenated hydrocarbons were investigated, including aldehydes, phenols, and ketones. Because aldehydes are always produced during incomplete combustion,<sup>18</sup> these compounds were studied in some detail. The spectrophotometric methods used are specific for formaldehyde, acrolein, total aliphatic aldehydes and total aldehydes. Table 7 shows that when only secondary air was present, the concentration of total aldehydes was inversely related to the flow of secondary air. In the absence of secondary air, but with sufficient primary air to ensure essentially complete combustion, aldehydes were produced in only ppb concentrations. Formaldehyde was predominant, and persisted under all but stoichiometric combustion conditions. With increased secondary air, a generally increasing ratio of formaldehyde to other aldehydes was observed. These findings are consistent with the reported stability of formaldehyde.<sup>18</sup>

Table 1.—Typical Analysis of Chicago Natural Gas

Component	Mole %	Component	Mole %
Air	3.21	Propane	1.21
Helium	0.08	n-Butane	0.17
Nitrogen	1.79*	i-Butane	0.08
Carbon dioxide	0.63	Pentanes	0.04
Methane	88.21	Hexanes	0.03
Ethane	4.51	Heptanes	0.04
			100.00

Heating Value - 1001 Btu/SCF, Saturated gas at 60°F, 30 in. Hg.

\*Nitrogen in excess of that included in air.

Table 2.—TYPES AND QUANTITIES OF ORGANIC COMPOUNDS FOUND IN THE COMBUSTION PRODUCTS OF A NATURAL GAS FLAME

Type of Compound	Concentration Found after	
	Stoichiometric Combustion	Fuel-Rich Combustion
<b>Aldehydes:</b>		
Formaldehyde	< 0.02 ppm	20 ppm
Other Aliphatic Aldehydes	< 0.02	13
Nonaliphatic Aldehydes	< 0.02	6
Total Aldehydes	< 0.02	39
<b>Polynuclear Aromatics:</b>		
Anthanthrene	< 3.0 ppb	275 ppb
Anthracene	< 0.4	46
Benzo [a] pyrene	0.4	89
Fluoranthene	6.0	468
1-Methylpyrene	0.6	78
o-Phenylene-pyrene	0.1	84
Pyrene	14.0	1040
<b>Other Hydrocarbons:</b>		
Methane	0.08 ppm	60,000 ppm
Ethane	0.13	3,500
Propane	0.10	900
i-Butane	< 0.01	50
n-Butane	< 0.01	70
Pentane plus	< 5.00	120
Acetylene	< 0.01	2,500
Ethylene	0.06	4,000
Propylene	< 0.01	260

Table 3.—CONCENTRATION OF SOME C<sub>1</sub> - C<sub>4</sub> HYDROCARBONS AT VARIOUS AERATION LEVELS

Air Input, CF/hr		Concentration ppm									
Primary	Secondary	Alkanes				Alkenes				Acetylene	
		Methane	Ethane	Propane	i-Butane	n-Butane	Ethylene	Propylene	Acetylene		
0	30	0.08*	-	0.02	<0.01	<0.01	0.09	<0.01	<0.01	<0.01	
		0.08*	-	0.11	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	
0	25	3.4	0.16	0.11	<0.01	<0.01	0.84	0.07	0.07	4.6	
		1.6	0.09	0.04	<0.01	<0.01	0.61	<0.02	<0.02	3.3	
		5.2	0.16	0.01	<0.01	<0.01	1.37	0.03	0.03	4.7	
0	20	2800	23.3	0.17	<0.02	<0.02	161	2.3	2.3	240	
		2100	25.0	0.13	<0.02	<0.02	162	2.1	2.1	240	
		1900	22.1	0.16	<0.02	<0.02	182	2.1	2.1	250	
0	17.5	7000	72	1.3	<0.02	<0.02	410	7.8	7.8	910	
		7300	72	1.3	<0.02	<0.02	470	7.7	7.7	850	
		7300	69	1.3	<0.02	<0.02	470	7.9	7.9	880	
0	15	12,500	117	2.3	0.06	0.06	910	17.5	17.5	1400	
		16,300	138	2.2	0.05	0.04	1080	20.2	20.2	1500	
		14,600	-	2.5	0.8	0.06	1030	20.1	20.1	1500	
0	12.5	26,200	343	7.0	-	0.25	1700	68.0	68.0	1900	
		29,200	352	6.9	0.04	0.17	1800	58.5	58.5	2000	
		29,000	441	6.2	0.13	0.20	1800	57.5	57.5	2000	
0	10	58,300	1223	45.4	2.2	3.8	3700	118	118	2600	
		39,100	964	42.1	1.5	2.2	3100	108	108	2600	
		33,200	1048	48.7	0.6	3.9	2700	97	97	2300	
20	0	0.04*	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
		0.04*	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
		0.04*	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
15	0	0.41*	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
		0.37*	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
		0.44*	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
12.5	0	12.8*	-	<0.01	<0.01	<0.01	1.5	<0.01	<0.01	5.2	
		5.4*	-	<0.01	<0.01	<0.01	.5	<0.01	<0.01	2.4	
		15.4*	-	<0.01	<0.01	<0.01	2.4	<0.01	<0.01	9.2	
		19.2*	-	<0.01	<0.01	<0.01	3.2	<0.01	<0.01	-	
10	10	.05*	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
		.05*	-	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	

\* Composite methane and ethane peak.

Table 4. - AIR FLOW VS. C<sub>4</sub>-C<sub>5</sub> CONCENTRATIONS

Run No.	<u>41b</u>	<u>40a</u>	<u>40b</u>	<u>41a</u>	<u>42a</u>
Flow Rates, CF/hr					
Primary Air	0	0	0	0	17.5
Secondary Air	10	15	20	25	0
Natural Gas	2	2	2	2	2
Concentration, ppm*					
Butene-1	1820	550	165	17	<0.05
<u>i</u> -Butene	<0.05	<0.05	<0.05	<0.05	<0.05
<u>trans</u> -Butene-2	50	8	2	<0.05	<0.05
<u>i</u> -Pentane	<0.05	<0.05	<0.05	<0.05	<0.05
<u>cis</u> -Butene-2	<0.05	<0.05	<0.05	<0.05	<0.05
Pentane	<0.05	<0.05	<0.05	<0.05	<0.05
3-Methylbutene-1	<0.05	<0.05	<0.05	<0.05	<0.05
1,3-Butadiene	40	9	1	<0.05	<0.05
Pentene-1	118	43	7	<0.05	<0.05

\* Chromatograph calibrated on basis of response to n-butane

Table 5. - C<sub>5</sub> + HYDROCARBONS

*Air Input, CF/hr,		Total C <sub>5</sub> + Hydrocarbons,	Air Input, CF/hr		Total C <sub>5</sub> + Hydrocarbons,
Primary	Secondary	ppm	Primary	Secondary	ppm
5	10	<5	0	25	<5
5	5	30	0	20	<5
			0	15	<5
			0	12.5	80
2.5	10	<5	0	12.5	100
2.5	7.5	20	0	10	90
2.5	7.5	14	0	7.5	110
2.5	5	85	0	7.5	144

\* Natural Gas Input, 1 CF/hr

Table 6.-POLYNUCLEAR AROMATIC HYDROCARBONS  
DETERMINED IN NATURAL GAS COMBUSTION PRODUCTS

<u>Aeration Conditions</u>	<u>Flow Rate, CF/hr</u>				
	<u>Run No.</u>				
	<u>9</u>	<u>5R</u>	<u>7</u>	<u>8</u>	<u>10</u>
Primary air	0	0	0	0	17.5
Secondary air	10	15	20	25	0
Natural gas	2	2	2	2	2
<u>Component</u>	<u>Concentration, ppb</u>				
Anthanthrene	240	275	11	<3	<3
Anthracene	26	46	6	6	<0.4
Benzo[a] pyrene	89	78	40	11	0.4
Fluoranthene	434	468	256	117	6
1-Methylpyrene	78	48	11	4	0.6
o-Phenylene pyrene	75	75	84	43	<0.1
Pyrene	1040	454	155	103	14

Table 7.-AIR FLOW VS. ALDEHYDE PRODUCTION

<u>Run No.</u>	<u>Flow Rates, CF/hr</u>			<u>Aldehyde Concentration, ppm</u>		
	<u>Primary Air</u>	<u>Secondary Air</u>	<u>Natural Gas</u>	<u>Formaldehyde</u>	<u>Aliphatic Aldehydes</u>	<u>Total Aldehydes</u>
3	0	10	2	19.4	32.9	39.3
4	0	15	2	18.4	25.6	34.6
5	0	20	2	13.4	13.1	18.5
6	0	25	2	2.4	1.9	6.0
8	17.5	0	2	<0.02	<0.01	<0.02

The unsaturated aldehyde acrolein occurs in the exhaust gases from most combustion processes.<sup>2,7,8,12</sup> Under fuel-rich combustion conditions, acrolein concentrations ranging from less than 0.03 ppm (parts per million) to about 6 ppm (Table 8) were determined by a spectrophotometric method.

Phenols are another group of oxygenated organic derivatives that is known to be present in combustion products from natural gas flames.<sup>13</sup> Total phenol concentrations varied from 0.007 ppm to about 4 ppm (Table 9).

Several spectrophotometric procedures were investigated for determination of ketones, but interference from water and formaldehyde introduced excessive error. Gas chromatography, however, resulted in accurate determinations of several ketones, as shown in Table 10.

Chromatographic studies gave tentative evidence of the presence of methyl and ethyl alcohols in the flue products. Quantitative measurements were not made, but methyl alcohol peak areas indicated concentrations of about 3 ppm.

## DISCUSSION

The experimental data collected in our investigation of the flue products from fuel-rich flames might be interpreted in terms of numerous hypothetical reaction mechanisms that have no real meaning. Instead, let us consider how the formation of trace components produced under poor combustion conditions can be rationalized and qualitatively explained in terms of a few reaction mechanisms which are known to be operative in fuel-rich flames. (Carbenes and perhaps methyne are very likely involved in the formation of flue-gas combustion products; but they are not considered in this treatment.)

Many of the major mechanisms operative in lean flames are reasonably well understood, but the organic chemistry of fuel-rich flames presents a considerably more complex situation.<sup>3</sup> The initial reactions in a fuel-rich methane-oxygen flame have been shown to involve formation of methyl radicals, which are probably produced by hydrogen atom abstraction:



The methyl radicals might be called the "key intermediates" in the combustion of methane in fuel-rich systems because their concentration is sufficient to produce other structures by conversion to higher molecular weight intermediates. Subsequent chemical reactions of methyl radicals in fuel-rich flames therefore determine, to a large extent, the structures of the partial combustion products. We should thus be able to relate our experimental results to these methyl radical reactions, especially those that occur with small or essentially zero activation energies.

First, the reaction of methyl radicals with oxygen would not be expected to be the dominant one in an oxygen-deficient flame, but the reaction should occur to some degree with formation of peroxy radicals:

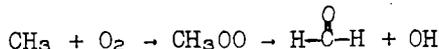


Table 8. -AIR FLOW VS. ACROLEIN PRODUCTION

Run	Natural Gas, CF/hr	Air, CF/hr		Acrolein, ppm
		Primary	Secondary	
21	2	17.5	0	<0.03
22	2	0	10	6.3
23	2	0	15	5.6
24	2	0	20	5.3
25	2	0	25	2.9

Table 9. -AIR FLOW VS. PHENOL PRODUCTION

Run No.	Flow Rates, CF/hr			Phenol Concentration, ppm*
	Primary Air	Secondary Air	Natural Gas	
4	0	10	2	4.0
5	0	15	2	4.1
6	0	20	2	1.0
7	0	25	2	0.5
8	17.5	0	2	0.026
9	25.0	0	2	0.007

\* Calibration curves were prepared with phenol solutions as standards.

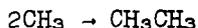
Table 10. -AIR FLOW VS. CARBONYL PRODUCTION

Run	Natural Gas, CF/hr	Air, CF/hr		Carbonyl Production, ppm			
		Primary	Secondary	Acetaldehyde	Acrolein-Acetone	Propionaldehyde	2-Butanone
3637-1	2	0	10	6.2	1.5	0.07	1.6
3637-2	2	0	15	3.4	0.8	0.03	1.0
3637-3	2	0	20	2.9	1.2	0.05	1.8
3637-4	2	0	25	5.0	1.5	0.01	2.8

These radicals are known to decompose rapidly to yield formaldehyde.<sup>14,17</sup> Further oxidation of formaldehyde would be expected, even in an oxygen-deficient flame, because of the high reactivity of aldehyde groups.

Since the rate of formation of formaldehyde should be greater than the rates of formation of the higher aldehydes from the methyl-radical-derived intermediates that will be discussed later, we would expect formaldehyde to be present in higher concentrations than the other aldehydes in the flue gases. As already shown in Tables 2 and 7, over half of the total aldehydes in almost all of our experiments was formaldehyde when the flue products were produced under oxygen-deficient conditions.

Recombination of excess methyl radicals in oxygen-deficient flames:



would be favored over methyl radical-oxygen reactions, so larger concentrations of ethane relative to formaldehyde would be expected in the flue gases. The formation of ethane in this type of recombination reaction, however, is not as simple as it appears. When the new carbon-to-carbon bond is formed, a large amount of energy is liberated. This energy, along with the original thermal energy carried by the methyl radicals, can dissociate ethane back to methyl radicals, or the resulting vibrationally excited ethane molecules can be deactivated by a three-body collision process. In the presence of a third body, such as another molecule with which the energy-rich ethane molecules collide, the excess energy can be transferred with concurrent formation of substantial amounts of ethane without homolytic dissociation to methyl radicals. However, according to Kistiakowsky,<sup>4</sup> the energy-rich ethane molecules initially produced do not necessarily require a three-body process to prevent dissociation.

Since methyl radical recombination is a direct one-step path to a stable paraffin, one would expect larger concentrations of ethane than the higher paraffins in the flue gases. This conclusion is supported by the results summarized in Table 2. Significantly higher concentrations of ethane than propane were detected in the flue products under oxygen-deficient conditions. The concentrations of propane were in turn higher than the total C<sub>4</sub>+ paraffin concentrations. The natural gases studied in this investigation contained a few percent ethane and propane, but the relative ratios of these hydrocarbons in the flue gases should still be indicative of the combustion mechanism.

The mechanism of formation of ethylene and acetylene in a methane-rich flame has not been fully established, but the general course of the reactions is believed to proceed through C<sub>2</sub> radical intermediates.<sup>11</sup> Successive dehydrogenation of ethane yields ethylene and acetylene. The detailed mechanism of the dehydrogenation is not known.<sup>9</sup> Homolytic C-H bond rupture by unimolecular decomposition or hydrogen atom abstraction should be facilitated in methane-rich flames, because methyl radical recombination affords energy-rich ethane molecules. We therefore expect that stepwise dehydrogenation of ethane proceeds via an ethyl radical intermediate:



to yield substantial amounts of ethylene and acetylene relative to the

other unsaturates. Formation of ethyl radicals subsequently provides direct routes to propane and the butanes, but dehydrogenation should be the preferred reaction path because of the favorable kinetics at high temperatures.<sup>9</sup>

Thus, the formation and relative concentration of the major oxygenated and saturated and unsaturated aliphatic compounds detected as trace components in the flue gases of methane-rich flames have been rationalized on the basis of a few known radical reactions. It should be emphasized that these reactions are by no means the only paths to the observed compounds, but their relationship to the experimental results indicates that they are important.

It is much more difficult to explain the formation of the polynuclear aromatics listed in Table 2. Grossly empirical reaction mechanisms must be postulated because of the complexity of polynuclear aromatic structures.<sup>15</sup> Nevertheless, we believe that a few important conclusions can be drawn from the data collected in our work.

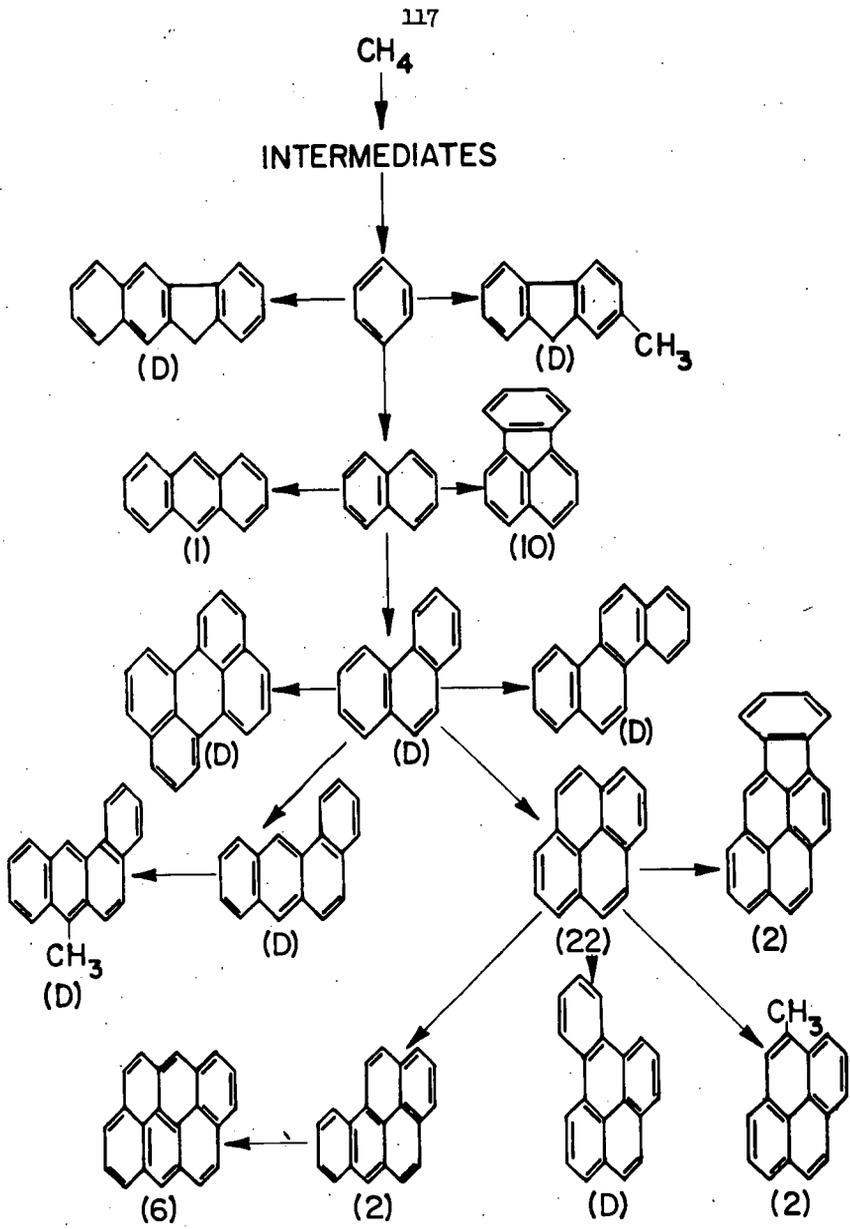
Most investigators who have studied the formation of polynuclear aromatics found that these compounds generally form under fuel-rich conditions.<sup>6,15</sup> Our data, which include determinations of both aliphatic and aromatic compounds, show that fuel-rich conditions promote polynuclear aromatics formation, but at very low levels relative to the concentrations of the aliphatic compounds. It is therefore difficult to select a particular aliphatic compound, or group of compounds, as key intermediates in the mechanism of formation of the aromatic compounds.

Aliphatic intermediates are, however, clearly the precursors of the aromatic compounds because the natural gases used in our experiments contained zero polynuclear aromatics. Various investigators have suggested that methyne and unsaturates such as ethylene and acetylene play an important role as intermediates.<sup>6,10,11,15</sup> Empirical reaction paths have also been postulated to account for the formation of polynuclear aromatics from these and other intermediates.<sup>15</sup>

In several experiments, our determinations of the polynuclear aromatics formed in fuel-rich flames tend to fall into a particular pattern. The higher molecular weight polynuclear aromatics in the flue gas were consistently present in lower concentrations than those of lower molecular weight. Although other investigators have reported similar results,<sup>10</sup> this information is insufficient for valid conclusions regarding the mechanisms of formation.

However, significant observations can be made. The distribution of the aromatics was about the same in each of our experiments, as shown in Table 6. Furthermore, this distribution corresponds essentially to that reported by others.<sup>6,10,15</sup> Finally, we observed that the relative concentrations of a few specific polynuclear aromatics are consistently higher than the concentrations of the other aromatics.

These observations suggest that the overall scheme shown in Fig. 3 is a plausible route to the various aromatic compounds identified in our studies. The reactive species and fragments involved in the many reactions required to produce the polynuclear aromatics are, of course, not known. But our results and their apparent relationship to the scheme in Fig. 3 support a stepwise buildup of the higher aromatics through common intermediates. A similar scheme can also be developed with Lindsey's data.<sup>10</sup>



A-56493

Fig. 3.—POSSIBLE ROUTES TO POLYNUCLEAR AROMATIC COMPOUNDS

Other interpretations of the distribution of the aromatics (Table 2), such as consideration of their relative stabilities, can be employed to rationalize the results. For example, linearly annelated acenes are known to be more reactive than phenes containing the same number of rings.<sup>1</sup> Thus, one would not expect a large concentration of acenes relative to the angularly annelated phenes in the flue products. Our experimental data show that only one acene, anthracene, was detected. Most of the polynuclear aromatics determined in this investigation contain the phenanthrene nucleus.

Quantitative treatment of the distribution of polynuclear aromatics in terms of electron densities and bond localization energies will be attempted when additional data have been compiled.

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