

CHEMICAL REACTIONS IN DIFFUSION FLAMES

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ABSTRACT

A review of the study of the chemical reactions in a series of hydrocarbon, ketone and alcohol diffusion flames determined by removing samples from various regions inside and outside the glowing mantle of the flame with a specially constructed fine quartz probe is presented. The samples removed from flames have been carefully analyzed by mass spectrometer and gas chromatography techniques. From the product analysis it is indicated that the fuel is pyrolyzed in the inner mantle by a free radical mechanism, and the pyrolysis products are oxidized in the high temperature combustion zone and the edge of the flame.

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INTRODUCTION

Most of the work that has been carried out in the studies of flames has involved studies of the physical properties -- structure, flame velocity and temperature. Only a limited amount of work has been carried out in an attempt to elucidate the chemical processes in flames.

In 1861 Faraday (1) published a book entitled "Chemical History of a Candle," which was made up of a series of lectures given to the English equivalent of high school students where the candle flame is used in a series of experiments to demonstrate the scientific method. With a long glass tube Faraday removed pre-combustion products from the neighborhood of the wick of the candle and reignited them to demonstrate that the wax pyrolyzed to lighter molecules before it was burned. Eltenton (2) studied samples rapidly removed from a methane flame into a mass spectrometer with a view to identifying free radicals. Foner and Hudson (3) have used mass spectrometric techniques for the identification of H, O and OH radicals in hydrogen-oxygen flames, and for the identification of the methyl radical and stable intermediates in the methane-oxygen flame. Prescott, et al. (4) have described the composition profile in a pre-mixed propane air flame by probing samples from the flame and analyzing them with a mass spectrometer. Fristrom, Prescott and Grumfelder (5) have described their flame probing technique and have given the results of analysis of samples removed from a propane flame. Parker and Wolfhard (6) have examined the various zones of a diffusion flame spectroscopically and have identified free radicals in the flame and have deduced that pyrolysis must play a role in the mechanism of burning. Needham and Powling (7) have studied the decomposition flame of ethyl nitrate by probing samples and analyzing them by infrared techniques.

The authors (8-12) have studied the chemistry of combustion in a series of hydrocarbon and oxygenate flames by probing samples from the flame with a quartz probe and analyzing these samples by means of precise mass spectrometric and gas chromatographic techniques. These results show that a pyrolysis mechanism is the only route for the disappearance of the fuel.

APPARATUS AND PROCEDURES

Our experimental procedure has involved establishing the flame on a burner placed on a micromanipulator in a plexiglas hood that eliminates the effects of air currents on the flame. For gaseous fuels a diffusion flame burner with a 27 mm port was used, and for liquid fuels an alcohol lamp with a Fibreglas wick was used. A quartz probe 0.5 mm OD at the tip and an ID of 0.2 mm with a constricted opening whose average diameter is 0.06 mm was sealed into position above the burner, and any portion of the flame can be sampled by adjustment of the micromanipulator supporting the burner.

During an experiment the probe is continually vented to the house-vac and when the flame is to be sampled a three-way stopcock diverts the sample to a

previously evacuated flask. Simultaneously with sampling the system is photographed so that the precise position of the probe with respect to the flame can be determined.

The probe is constructed by drawing a piece of quartz tubing to 0.5 mm OD and sealing off the tip. The tip is then ground with fine carborundum paper until it is reopened. This probe gives no visual disturbance of the flame during sampling and adequate size sample for analysis can be withdrawn in between 15 seconds and 1 minute.

Probe techniques are often criticized because of the possibility of catalysis or flame disturbance. The probe that we have used in these experiments rapidly drops the pressure from 1 atmosphere to between < 1 mm and 20 mm and the residence time of the gases inside the hot portion of the probe has been calculated to be less than 5 millisecon. With the low pressures inside the probe, and short residence time there does not appear to be much likelihood for catalysis by the probe surfaces. Various changes were made in the probe design to vary the residence time of the gas inside the hot zone by a factor of 10 without appreciably changing the composition of the sample. We have also sampled the same point of the flame by probing through the hot zone at the edge and up through the port; these analyses checked each other and showed that the gases were in the hot section of the probe for too short a time to permit further reaction. We have concluded that any probe that rapidly removes a sample from a zone of the flame and rapidly quenches it by expansion to low pressure gives an accurate picture of the composition of stable compounds of that zone.

The quantitative analysis of the samples has been carried out with a Consolidated Electrodynamics Corporation Model 21-103 analytical mass spectrometer. The mass spectra were analyzed by starting at the high mass fragments and successively subtracting the patterns of each component. Identification of the components of the samples has been aided by thermal fractionation of the samples from a series of temperatures from liquid nitrogen to room temperature and the examination of the spectrum of each fraction. The use of gas chromatography (12) in conjunction with mass spectrometer identification of the separated and collected fractions has been used to separate and identify products. Samples of effluent gas from the chromatography column coincident with peaks on the recorder were collected and analyzed with the mass spectrometer. In this way, for example, it has been possible to analyze quantitatively allene in the presence of propyne, and to analyze mixtures of the butene isomers. The mass spectrometer used has high resolution slits. This has made it possible to unambiguously identify ethane in the presence of formaldehyde and isotopes at mass 30 due to $C^{13}C^{12}H_6$ and $C^{12}O^{18}$.

Temperatures of the flames have been measured with 1 mil Pt-Pt 10% Rh hairpin thermocouple enclosed in a four mil OD quartz tube. Although the quartz tube reduces the response and spatial sensitivity of the thermocouple, without this coating catalytic reactions on the platinum make the temperature measurements meaningless. The temperatures measured at the edge of the flame where gradients are large are low due to conductivity losses, but in the central pyrolysis region where temperature gradients are small the error of measurement is not serious.

DISCUSSION

Study of the analyses of the precombustion products indicates that the mechanism of burning in the flame proceeds via a free radical attack on the parent molecule and the abstraction of a hydrogen by this free radical. The hydrogen can be abstracted from the various sites on the molecules, and the abstraction from any particular site depends on the energy of activation and the probability factor.

In a diffusion flame there is a large thermal gradient from about 1400°C-1500°C at the edge to about 400°C-600°C in the interior of the mantle. Also, there is extremely rapid diffusion of species throughout the flame, amply demonstrated by the fact that in no part of the flame is there less than 30 percent nitrogen. Non-free radical products formed in the primary pyrolysis reactions also undergo attack by free radicals forming a secondary set of products. Then, in addition to these pyrolysis reactions, there are polymerization reactions which are responsible for the formation of the benzene and carbon. Thus, no quantitative kinetic picture can be given for the reactions; however, qualitatively, the analysis of the samples probed from the flame can allow us to study the homogeneous mechanism for the pyrolysis and oxidation of the fuel, and presents a picture of the locations and concentration of the various species of the flame.

Figure 1 shows the results of probing a methane diffusion flame. The bottom abscissa indicates the relative distance of the probe between the luminous edge and the central axis of the flame. The top abscissa indicates the temperature measured with a quartz coated 1 mil Pt-Pt 10% Rh thermocouple.

There is a rapid decrease in the concentration of methane in the samples as one probes from the central axis to the edge of the flame. This decrease is not matched by a corresponding increase in hydrogen or hydrocarbon intermediates. The hydrogen content is quite low (1-2%) and relatively constant inside the flame cone, and begins to decrease only at the edge of the flame where the temperature rises and the concentration of oxygen begins to increase. The concentration profile presented by the hydrogen is similar to the distribution of other hydrocarbons formed in the flame. The hydrogen formed in the pyrolysis diffuses rapidly to the edge of the flame where it is consumed. The carbon formed in the pyrolysis must eventually polymerize to high molecular weight carbonaceous material since no evidence of its history appears in the compounds sampled in the flame cone.

At the edge of the flame carbon dioxide and water are maximized, indicating that these compounds are generated here from the oxidation of carbon and hydrogen that diffuse to the edge of the flame.

At the temperatures measured in the center of the flame cone methane is normally inert (14) and no pyrolysis occurs to any extent at temperatures several hundred degrees higher, so that the small amount of oxygen which penetrates into the central cone of the flame primarily through the low temperature zone in the neighborhood of the port must play a vital role in the mechanism of pyrolysis. The role of small traces of oxygen in rapidly changing the rate of decomposition is under investigation in our laboratory in a flow system where contact times and temperatures of the flames can be simulated.

The mechanism for the pyrolysis of the methane to account for the products found is shown below



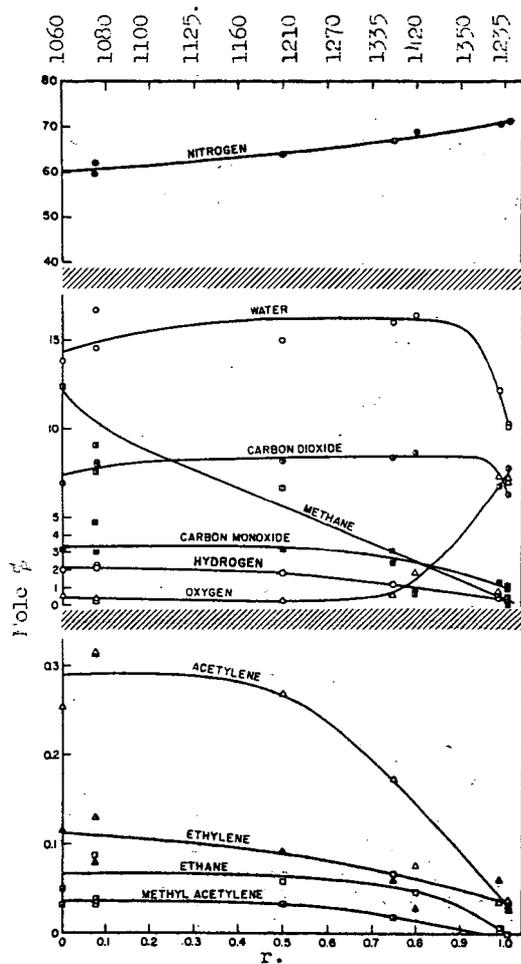


FIG. 1. Composition of sample probed from flame 20 mm. above port. (r = ratio of distance of probe to central axis to radius of flame).

The examination of the precombustion products indicates that only small traces of formaldehyde (<0.1%) and methyl alcohol (<0.2%) are the only oxygenates found in the precombustion products. Since formaldehyde and methyl alcohol are generally proposed as intermediates in describing the mechanism of combustion in flames, a concerted effort has been made to find these compounds. Large samples were probed from the methane flame and these samples were treated with Schiff's reagent. These chemical tests indicated that formaldehyde was present in concentrations of < 1 part in 10^5 and confirmed analyses of duplicate samples that were obtained using high resolution techniques on the mass spectrometer.

We also wished to determine if the sampling and analytical techniques used in these experiments were capable of detecting and measuring formaldehyde if we were certain that it was present in the flame. Pellets of paraformaldehyde were placed on the port of the burner and vaporized into the fuel stream. The results of sampling this flame are shown in Table 1. It is seen that on the central axis a sample with >2% formaldehyde was withdrawn.

TABLE 1. Comparison of Samples Probed from Methane Diffusion Flame, with and without Added Formaldehyde.

	<u>Sampled close to central axis</u>		<u>Sampled close to edge of flame</u>	
	<u>Normal Flame</u>	<u>Paraformaldehyde Added</u>	<u>Normal Flame</u>	<u>Paraformaldehyde Added</u>
Benzene			0.006	0.007
Vinyl acetylene			0.01	0.007
Diacetylene			0.005	0.004
Carbon dioxide	6.03	5.96	9.03	9.06
Propylene				0.004
Methyl acetylene	0.03	0.01	0.03	0.02
Argon	0.61	0.60	0.75	0.74
Oxygen	1.15	0.17	0.42	0.19
Formaldehyde		2.04	0.01	0.08
Ethane	0.08	0.05	0.07	0.05
Ethylene	0.12	0.24	0.10	0.11
Acetylene	0.22	0.22	0.26	0.29
* Water	-	-	-	-
Methane	27.82	21.12	7.55	5.46
Nitrogen	58.92	56.69	76.55	76.41
Carbon monoxide	2.79	8.73	3.30	5.11
Hydrogen	2.23	4.18	1.89	2.47

* Analysis on water free basis.

The oxidation of methane in flow systems at high temperatures with short contact times (15) leads to appreciable concentrations of formaldehyde in the products. However, on the basis of the experiments described, it does not appear to be an intermediate in the oxidation of methane in a diffusion flame.

Formaldehyde is found in the precombustion products of a flame when it is a reasonable result of a free radical attack on the parent fuel. This is the case in the methanol diffusion flame where formaldehyde is the major precombustion product. The methanol burns according to the following scheme:

However, very little ethane is formed as a result of hydrogen abstraction by ethyl radicals compared to the concentration of methane in the acetone flame, and most of the ethane could be formed by the recombination of methyl radicals as in the acetone flame, as indicated by the comparison of methane and ethane concentrations of three ketone flames, Table 3, where each flame was sampled on the central axis about 0.3 of the distance from the base to the tip of the flame.

TABLE 3. Comparison of methane and Ethane Concentrations in Ketone Flames

	<u>Acetone</u>	<u>Methyl Ethyl Ketone</u>	<u>Diethyl Ketone</u>
CH ₄	4.4	2.3	0.8
C ₂ H ₆	1.1	0.6	0.3

The inability of the ethyl radical to abstract hydrogen and form ethane is consistent with the fate of the n-propyl and isopropyl radicals (in the dinormal and diisopropyl-ketone flames) which pyrolyze to propylene and ethylene rather than form propane. The ethyl radicals must efficiently lose hydrogen to form ethylene and this compound dominates the precombustion products of the flame. It should be noted that in the study of the flames of various paraffin hydrocarbons it has been noted that the rate of decomposition of methane, ethane and propane do not differ greatly and are relatively slow, so that if a large amount of ethane were formed by the abstraction of hydrogen by the ethyl radicals in these flames a large steady state concentration of ethane would be found by our probing techniques.

Only the fate of the primary free radicals and products formed by the attack on the parent fuel has been discussed here. In addition to the primary pyrolysis products, secondary pyrolysis products also exist, such as ethylene and acetylene by the dehydrogenation of ethane and polymerization reactions which give rise to propyne, allene, diacetylene, benzene and toluene.

From the studies of the precombustion products of the diffusion flames that we have carried out, we feel that we can make some deductions about the formation of carbon in flames.

Porter (15) has postulated that in flame and explosion processes carbon particles are formed by the pyrolysis of acetylene. In many of the diffusion flames we have studied there does indeed appear to be a correlation between the sootiness of the flame and the stationary concentration of acetylene in the flame mantle. However, our results have indicated that there are many difficulties with this approach. First, benzene itself creates a very sooty flame but has a stationary concentration of acetylene in the mantle less than the methane flame which is a sootless flame. Also, in the examination of the alcohol flames we have observed an increasing amount of carbon production as one proceeds from the C₁ to C₄ alcohols. The methanol flame produces no carbon, the ethanol flame a small amount of yellow tipping, and the propanol and butanol flames produce relatively large amounts of carbon. Analysis shows no benzene and less than 0.004% acetylene in the precombustion products sampled on the central axis of the methanol flame, but the amounts of these precombustion products in the ethanol, propanol and butanol flames are very similar, benzene (0.02% and acetylene (1-2%). The temperature profiles of these flames are quite similar so that this lack of correlation of sooting ability indicates that the tendency toward carbon formation does not depend on the steady state concentration of these constituents in the flame.

Cole and Minkoff (16) have recently reported the results of a series of studies on carbon formation in diffusion flames of the simple hydrocarbons. Flat diffusion flames were examined with a specially constructed narrow beam recording infrared spectrometer and the 729 cm⁻¹ band of acetylene was monitored. No correlation between sooting ability and intensity of the acetylene absorption band was found by this independent technique.

The techniques outlined above for the study of these flames have been applied to preliminary studies of premixed methane-oxygen flames also. The results indicate the same reactions occur at much faster rates consistent with the higher temperatures, making the probing technique less sensitive in the determination of minor intermediates. These preliminary results on premixed flames are consistent with those obtained by Grumer and Singer (18) whose results on probing premixed propane-air flames are consistent with those that we have obtained from the study of propane diffusion flames.

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