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FLAME INHIBITION RESEARCH
QUARTERLY PROGRESS REPORT

1 May - 31 July 1961

R. M. FRISTROM --- PROJECT COORDINATOR

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SUMMARY OF PROGRESS, 1 May - 31 July 1961

(1) A set of composition and temperature profiles was determined for a flat methane-oxygen flame (CH$_4$ - 0.078, O$_2$ - 0.02, P = 0.05 atm) with and without added HBr. Corrosion was so severe that the burner assembly became unusable. A new teflon-glass-ceramic system including traps to protect the pumps has been designed and is being fabricated.

(2) A program to measure the high-temperature diffusion coefficients for the analysis of the inhibited flames has been started. The apparatus has been activated and tested at 300 °K and 500 °K on the well-known He-N$_2$ system. Measurements have been started on the Ar-H$_2$ system.

(3) Scavenger probe studies of radical concentrations in flames have been continued. The use of chlorinated hydrocarbons as scavenger for H atoms has been shown to be proportional to H, but the scavenging efficiency was found to be only 10%. Studies of oxygen-atom concentration using NO$_2$ as a scavenger have been made. The efficiency of scavenging appears to be high and may approach 100%.
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FLAME INHIBITION RESEARCH

I. BACKGROUND MATERIAL

REPORT ORGANIZATION

This report is divided into four sections: I. Background Material, II. Program Outline, III. Summary of the program to the beginning of the reported quarter, and IV. Quarterly Progress. Only the fourth section contains new material (although Section III is updated quarterly). It is hoped that the background material will aid the unfamiliar reader in following the program without extensive references; it will be single-spaced to conserve space. Those who are familiar with the work may find it profitable to turn directly to the fourth section.

PROGRAM OBJECTIVE

The objective of this program is to obtain a scientific understanding of the mechanism of chemical inhibition of flames. Although this research is primarily restricted to the fundamental aspects of the problem, there are several potential practical by-products. A quantitative understanding of flame inhibition should allow the prediction of the relative effectiveness of inhibitors on a flame system from their known chemical kinetics. Thus, a rational initial choice of inhibitor should be possible without extensive empirical studies. (This factor may become of increasing importance as "exotic" fuels become common.) It would also seem possible to set an absolute upper limit for the effect of an inhibitor, so that their efficiencies can be evaluated.

HISTORICAL SUMMARY

Over the past two decades, a number of studies have been made on flame inhibition of hydrocarbon-oxygen flames by halogen-containing compounds (Refs. 1,2). The experimental evidence suggests that the effectiveness of these materials is due to an effect on the chemical reactions in such flames. It has been established that the inhibition is a function of the concentration of the halogen, and that the order of effectiveness of the halogens is inverse to the reactivity of the free atoms, i.e., F<Cl<Br<I. Most practical extinguishers contain bromine compounds. Iodine compounds are either unstable or expensive.

It is generally accepted that the mechanism for such flame inhibition is the exchange reactions between the inhibitor and the free radicals that are responsible for the primary propagation reactions in flames. Such reactions lead to the formation of stable
molecules and free halogen atoms, which are much less reactive than the flame radicals. In hydrocarbon-oxygen flames the important radicals are hydrogen atoms, oxygen atoms, hydroxyl radicals, and possibly methyl radicals. Other radicals exist in flames, but these are probably less important to the flame propagation. On this hypothesis one would expect that the following reactions would be important in flame inhibition:

1) \[ RX + H^\cdot \rightarrow HR + X^\cdot \]
2) \[ RX + OH^\cdot \rightarrow ROH + X^\cdot \]
3) \[ RX + O^\cdot \rightarrow RO^\cdot + X^\cdot \]

Here, R represents a hydrogen or hydrocarbon radical, and X represents a halogen. Dots indicate unpaired electrons. Reactions of this type are well known (Ref. 3), but much of the available data is too fragmentary to allow extrapolation of the kinetic information from the low-temperature regime of most laboratory studies to radical reactions at the high temperatures encountered in flames.
II. PROGRAM OUTLINE

The research program will utilize studies of the detailed microstructure of flames (Ref. 4) with and without added inhibitor, together with such other chemical and physical studies as seem necessary to elucidate the detailed mechanisms of chemical inhibition of flames. The relation between these studies can be visualized in Fig. 1. Following this figure the report will be divided into five major sections (flame structure studies, simple reaction studies, analysis, interpretation, and recommendations on flame inhibition), and eight minor sections (temperature profiles, composition profiles, aerodynamic profiles, and atomic and free-radical composition profiles). This is a long-range program of modest scale whose completion is expected to take from three to five years. Therefore, although work is planned in all of these categories, current work will usually occupy only a few of these sections.

The number of possible inhibitors and the number of possible flame systems are both large, and the number of flame-inhibitor systems which may be of interest is even larger since it is the product of these two numbers. The situation can be represented by a very large "matrix" in which one index of the terms represents the flame system and the other represents the inhibitor system. (See Fig. 2.) Since it is impractical to study such a large number of systems, two possible approaches suggest themselves: The synthetic method, in which one would study the chemistry of inhibitors with radicals, and a separate study of the uninhibited flame systems. This is equivalent to studying the initial row and initial column in the "matrix". A satisfactory theory would allow the prediction of the effect of any inhibitor on any flame from this information. The other approach is the statistical technique, which is often used in agriculture. Studies would be made of a randomized set of these systems using one of the patterns of experiment design, such as the Latin square. By studying this fraction of the systems, a satisfactory theory should allow the derivation of information sufficient to predict the effect of any specific inhibitor on any specific flame system.

Both approaches assume that an adequate theory is developed. Therefore, a judicious combination of these two approaches seems in order. Early studies should be aimed at developing a theory, subsequent studies should be aimed at making a randomized statistical test of the efficacy of the theory, and final studies should be aimed at the accumulation of data. On this basis we propose to make a very detailed study of the methane-oxygen flame with a simple inhibitor (probably HBr) to develop the theory. This will be followed by a randomized test on a restricted number of systems, and finally by a systematic study of parameters. The program is illustrated by Fig. 2 and Table I. It is discussed in more detail in Ref. 4.
Fig. 1 FLOW OF INFORMATION IN THE PROGRAM TO STUDY FLAME INHIBITION
## Fig. 2 OVER-ALL PROGRAM TO STUDY FLAME INHIBITION

**Initial Study, I** – An intensive study of one inhibitor-flame system is directed toward the goal of a simplified theory of flame inhibition. The chosen system is methane-oxygen with HBr (and/or DBr) as an inhibitor.

**Test of Theory, T** – The theory from the initial study should then be tested on representative inhibitor-flame systems to confirm its generality.

**Data for Application, D** – If the theory seems satisfactory, then a store of data should be developed to permit its broad application. Such data is most readily obtained from simple systems – the flame systems alone and inhibitor-radical reaction systems. The required data include those of chemical kinetics, transport coefficients, and thermodynamic properties.
### Table I

**APL and JHU Programs of Interest in Flame Inhibition**

<table>
<thead>
<tr>
<th>Program</th>
<th>Investigator</th>
<th>Laboratories</th>
<th>Sponsor</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Temperature Chemical Kinetics in Laminar Flames</td>
<td>Fristrom, Grunfelder, Favin, Westenberg</td>
<td>APL</td>
<td>ARPA</td>
</tr>
<tr>
<td>Thermal Conductivity of Gases by a New Technique</td>
<td>Walker, deHaas, Westenberg</td>
<td>APL</td>
<td>ARPA</td>
</tr>
<tr>
<td>Transport Properties in Dissociated Gases</td>
<td>Walker and Westenberg</td>
<td>APL</td>
<td>ARPA</td>
</tr>
<tr>
<td>High Temperature Chemical Kinetics from a Reacting Point Source</td>
<td>Snow and Westenberg</td>
<td>APL</td>
<td>ARPA</td>
</tr>
<tr>
<td>Flame Inhibition Research</td>
<td>Fristrom, Grunfelder, Favin</td>
<td>APL</td>
<td>U.S. Army Eng. Res. &amp; Dev. Lab. (Civil Dept.)</td>
</tr>
</tbody>
</table>
FLAME STRUCTURE EXPERIMENTAL STUDIES

It is planned to use flame structure studies in this research, for flames both with and without inhibitors. These techniques have been discussed in the literature (Refs. 5, 6) and offer certain advantages for studying chemical reactions: 1) flames offer a steady-state system for study, 2) there is no wall problem, 3) there are no mixing problems for studying fast reactions. The disadvantages are: 1) data analysis is complex and, 2) high precision is required of the data for obtaining kinetic information. These techniques nevertheless offer an excellent method for studying fast, high-temperature reactions and, in particular, offer the ideal technique for studying flame inhibition reactions in situ.

To characterize a flame system, it is necessary to specify at least \(N + 1\) variables, where \(N\) is the number of molecular species (Ref. 5). The independent variable usually chosen is distance through the flame front, while the dependent variables are composition, temperature, velocity, or area ratio. Experimentally, it is common to classify the profiles in four categories according to the techniques required to measure them. These are: composition profiles, atomic and free-radical composition profiles, temperature profiles, and aerodynamic profiles. An example of such a set is given in Fig. 2.

Composition Profiles

From the chemical standpoint, the most important information is the concentration profiles. The most satisfactory technique developed for making such studies is the microprobe sampling technique, which is followed by mass spectral analysis. The technique consists of withdrawing a sample of gas from the flame using a small, tapered quartz probe. The probe can be made small enough so that its effect on the flame is small, and the low pressure and rapid pressure drop in such a tapered probe quenches the sample so that reproducible meaningful samples can be obtained. Radical concentrations are not obtained by these techniques and are discussed in the next section. This technique is discussed in detail in the literature (Ref. 7).

Radical-Atom Concentration Profiles

Logically, atom-radical concentration flame studies are part of the concentration profile determinations. However, since their study requires special techniques, they are considered separately.

Radicals and atoms are not susceptible to conventional sampling techniques because of their extreme reactivity which transforms them into stable species before analysis is possible. In most flame structure studies (Refs. 5, 7) these concentrations are considered (usually correctly)
Fig. 3 CHARACTERISTIC PROFILES FOR A METHANE-OXYGEN FLAME
(CH₄ - 0.078, O₂ - 0.92, PRESSURE 7.6 cm Hg) (REF. 6))
(a) Major Species
(b) Concentration (f) and Flux Fraction (G) Profiles of Methane through Flame Zone
to be negligible compared with the concentrations of the stable species, and are therefore neglected in the analysis. This reasonable approximation is, of course, only a stopgap measure to obtain information while satisfactory methods are developed for determining atom and radical concentrations. None of the techniques thus far developed (Refs. 8 through 10) possess the generality and spatial resolution necessary for the quantitative interpretation which we wish to make. Therefore, we are developing a new technique for studying radical concentration profiles under a companion flame structure study supported by ARPA (Task R). This is the scavenger probe method, which combines the techniques of probe sampling with those of chemical scavenging. A sample is taken through a probe, and the radical-containing gases are mixed rapidly with a large excess of a suitable "scavenger" gas which reacts with the radical to produce a characteristic product. Scavenger studies are well known in radiochemistry and photochemistry (Ref. 11), and mass spectrometer studies (Ref. 12) have indicated that radicals can be sampled successfully through orifices.

An absolute measurement of concentration can be made if 1) there is a one-to-one correspondence between the reaction product and the precursor radical and, 2) the analytical system (mass spectrometer) can be calibrated for the stable reaction product. This is a significant advantage since it is notoriously difficult to obtain absolute radical concentrations. Spatial resolution will be limited by the probe diameter, and sensitivity should be as high as the analytical system allows for stable species. As this technique is developed it will be used in these studies.

Temperature Profiles

Temperature profiles offer an important technique for characterizing flame fronts. Three methods have been used at this Laboratory: thermocouple traverses, aerodynamic measurements, and pneumatic probe measurements. Their data are in essential agreement (Ref. 6), although of varying precision.

The most precise method is that with thermocouple traverses in which temperatures are measured with fine (0.0005") Pt-Pt 10% Rh thermocouples coated with silica. Profiles with a precision of 10°K and excellent spatial reproducibility are obtained.

Temperature can be determined by using aerodynamic measurements of velocity and area ratio, deriving the point-by-point density through the continuity relations, and then applying the perfect gas law. The results are not of high precision (2-4%), but within their limits, they provide a reliable measure of the translational temperature of the gas.
Temperatures can also be measured with a pneumatic probe (Ref. 13). This device is a quartz probe similar to those used in the composition studies. If gas flows under choking conditions through two orifices in series, and the temperature is known at the second orifice, temperature at the inlet orifice of such a probe can be derived from the relation between ambient pressure and the pressure between the two orifices. This technique provides a moderately precise (1-2%) and reliable method for determining temperature and has the added advantage that it can be directly associated with a composition, since it can also be used for composition sampling.

**Aerodynamic Profiles**

Flames can be characterized aerodynamically by two profiles - velocity and area ratio. As mentioned under temperature measurements, these can be combined to derive a density profile. The area ratio is simply the geometry of the stream tubes of flow through the flame front. In the general case it is necessary to make this measurement, since stream tube expansion through the flame is appreciable. With a symmetrical flame, such as the spherical flame, it is unnecessary to make this measurement, since it can be obtained directly from the geometry of the position determinations. Direct aerodynamic measurements are made by introducing MgO particles as a tracer and photographically visualizing their paths through the flame front, using a Zr flashbulb for the stream tube measurements and a pulsed electronic flashlamp for the direct velocity measurements (Ref. 14).

**Simple Reaction Studies**

Flame systems have relatively complex chemistry (see Table II) which makes the identification of the dominant reactions difficult. For this reason it is desirable to supplement the flame studies with studies of the individual reactions with simplified chemistry. A second reason for doing so is that these studies will be made at lower temperatures, thus enabling more precise estimates to be made of the activation energy.

The activation energy of most flame reactions lies below 10 kilocalories per mole, so that at flame temperatures the rate is a very insensitive function of the activation energy. On the other hand for this very reason, flame studies allow an accurate determination of the steric factor and may ultimately allow a determination of its temperature dependence - a problem which has plagued chemical kineticists for many years.

The techniques we propose to use are the conventional discharge tube-mixing techniques, with the addition of direct measurement of radical concentrations using the scavenger probe technique being developed. This work has been summarized by Steacie (Ref. 3) to 1954. More recent work has been carried out by a number of authors (Ref. 15).
Table II

Methane-Oxygen Flame Reaction Kinetic Constants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation Energy, $E$ (kcal mole$^{-1}$)</th>
<th>Frequency Factor, $A$ ($10^{14}$ cm$^3$ mole$^{-1}$ sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ + OH $\rightarrow$ CH$_3$ + H$_2$O</td>
<td>8.5</td>
<td>2</td>
</tr>
<tr>
<td>CH$_4$ + O $\rightarrow$ CH$_3$ + OH</td>
<td>8</td>
<td>$2^*$</td>
</tr>
<tr>
<td>CH$_3$ + O$_2$ $\rightarrow$ OH + H$_2$CO</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>H$_2$CO + OH $\rightarrow$ HCO + H$_2$O</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>HCO + OH $\rightarrow$ CO + H$_2$O</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>CO + OH $\rightarrow$ CO$_2$ + H</td>
<td>7</td>
<td>0.3</td>
</tr>
<tr>
<td>H + H$_2$O $\rightarrow$ OH + H$_2$</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>OH + H$_2$ $\rightarrow$ H$_2$O + H</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>O + H$_2$ $\rightarrow$ OH + H</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>OH + OH $\rightarrow$ H$_2$O + O</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>O + O + M $\rightarrow$ O$_2$ + M</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>H + O$_2$ $\rightarrow$ OH + O</td>
<td>18</td>
<td>5</td>
</tr>
</tbody>
</table>

$^*$The value given is an estimate, normal for this type of reaction.
DATA ANALYSIS

To make quantitative interpretation of flame structure information it is necessary to analyze the data. An analysis consists of calculating the actual flux profiles and rate of species and heat production profiles by quantitatively accounting for the effects of molecular diffusion and thermal conductivity. This step is necessary to avoid false impressions of the rate processes involved (Fig. 3), since in many flames the effects of diffusion and thermal conduction are large.

This analysis is based on the flame equations consisting of conservation laws and the differential equations of transport and chemical kinetics. They have been formulated in generality by Hirschfelder (Ref. 16) and adapted for flame structure analysis by Westenberg (Refs. 17, 18).

Thermodynamic Information

The thermodynamic functions of interest are enthalpies and heat capacities. This information is generally available for almost all of the species found in flame inhibition studies over the temperature range of interest. Several standard reference sources are available (such as Ref. 19) which provide data of sufficient accuracy for our purposes.

Transport Coefficient Studies

Transport coefficient information is necessary for the quantitative interpretation of flame structure data. The required data are the binary diffusion coefficients for the species being studied and the thermal conductivities of the mixtures. The multicomponent diffusion coefficients necessary for the interpretation of such systems are a complex function of all of the binary diffusion coefficients (Ref. 16). To avoid this problem it is usual to choose systems in which one species can be considered dominant; in this case, the true multicomponent diffusion coefficients can be accurately approximated by a set of binary diffusion coefficients of the individual species with the dominant species. The general case, with no single dominant species, could also be handled, but only at the expense of an order of magnitude increase in the necessary diffusion coefficient information (in the general multicomponent case, it is necessary to know the diffusion coefficients of all of the possible pairs of species) (Ref. 20).
The principal problem is to obtain precise, reliable data at sufficiently high temperatures to be useful in the flame studies. A new technique has been developed at APL which allows such measurements (Ref. 21). Diffusion coefficient data are available for the methane-oxygen system (Ref. 22).

The problem of thermal conductivities of mixtures is in a less satisfactory state, but fortunately this information is unnecessary for kinetic studies. An analogous "point source" technique is being developed at APL under Task R for making such measurements (Ref. 23).

**INTERPRETATION**

The interpretation of this information on flame structure consists of deriving chemical kinetic information and information on flame processes (Refs. 24 through 26). The analysis provides data on rates and fluxes of enthalpy and the various molecular species. Such a description is unambiguous and complete, but if the information is to be useful on other systems it is necessary to deduce the detailed reaction scheme and derive the appropriate kinetic constants, activation energies and steric factors. This step is largely an art, since in a real system all possible reactions occur to some extent. What is desired is to provide a description of the dominant reactions. For this reason there may be several interpretations with varying levels of sophistication and complexity. For flame inhibition work what is usually desired is the simplest possible interpretation consistent with a quantitative description.

**Chemical Kinetic Information**

Once a mechanism is assigned, the derivation of chemical kinetic data from flame structure and simple reaction rate information is straightforward. The choice of mechanism is largely a subjective process. We will not discuss the process other than to point out that a useful beginning is often a systematic collection of the possible reactions. The data which we have available from flame structure and simple reaction studies are: temperature, concentrations, and rates. The constants which are of interest are: the activation energy $E_a$, the steric factor $F$, and the temperature dependence of the steric factor $n$. In most kinetic studies, and probably in our initial work, the precision is not sufficient to allow separation of the temperature dependence factor from the exponential dependence of the activation energy. Flame studies, however, do offer information in a temperature regime which may ultimately allow such a separation to be made. If this is possible, it will represent an important addition to kinetic information. The relation of the exponential and power dependence of the reaction rate
on temperature is best visualized by expanding the Arrhenius exponential factor as a series:

$$R_i = R_j = X_i Z P T^n e^{-E/RT}$$

$$= X_i Z P \left\{ \frac{Z}{T_0^{1/2}} \left( T_0^{n-1/2} - \frac{E}{RT_0} T_0^{n-3/2} \right) + \frac{E^2}{2^n R^2} T_0^{n-5/2} + \text{----} \right\}$$

Since the species are interrelated, a number of cross checks should be possible on the derived kinetic constants, so that there will be a reasonable assurance of the essential correctness of the derived mechanism.

**Simplified Theory**

The goal of these studies is to provide a description of flame inhibition which is relatively simple and yet still will yield quantitative predictions. This may not always be possible, but it appears that in the case of the methane-oxygen flame a start can be made. The goal of such a simplified theory would be to enable quantitative predictions to be made of the effect of inhibitor on flame reactions (and hence burning velocity) with a precision of 20 per cent. In a sense this simply represents the limit of interpretations, since all mechanisms represent abstractions of the true system.

**RECOMMENDATIONS ON FLAME INHIBITION**

As a result of this work it is hoped that it will be possible to make some practical recommendations on flame inhibition. It is hardly possible to predict in advance what such recommendations will be, but it seems reasonable to expect that they will include recommendations of specific inhibitors for specific flame systems.
III. SUMMARY OF PREVIOUS WORK

SUMMARY OF WORK PRIOR TO 1 NOV. 1960

The work prior to the initiation of this contract (on 1 November 1960) consisted of a survey of the possibilities of applying flame structure data to flame inhibition studies, and a suggested program for such studies. This work was summarized in a proposal submitted to the U. S. Army Engineering Research and Development Laboratory in October 1960 (Ref. 4).

SUMMARY OF PROGRESS, 1 NOV. 1960 - 31 JAN. 1961

(1) A flat flame burner was set up for flame inhibition studies. The previously studied methane flame (CH₄ - 0.078, O₂ - 0.92; pressure 0.05 atm) was successfully stabilized with added inhibitor (HBr) up to concentrations of 0.0035 mole fraction.

(2) Using the uninhibited flame, two flame composition profiles were run on the new time-of-flight mass spectrometer. A third run was made on an inhibited flame to test the sensitivity of the instrument for HBr. From these test runs it was concluded that the instrument requires the addition of a trap current regulator to allow quantitative work and a forepump trap to shorten the HBr pump-out time. These items have been ordered, and the inhibitor studies have been temporarily transferred to the CEC magnetic-deflection spectrometer.

(3) A computing machine routine for the automatic reduction of flame structure data has been developed.

(4) A report on the flame inhibition program was presented 15 November 1960 at the meeting on "Inhibition of Ignition and Flames with Chemicals". This meeting was sponsored by the Committee on Fire Research of the National Academy of Sciences, National Research Council.

SUMMARY OF PROGRESS, 1 FEB. - 30 APR. 1961.

(1) A spherical flame apparatus was set up for inhibition studies on the system (CH₄ - 0.09, O₂ - 0.179, Ar - 0.727, pressure 0.05 atm). Composition profiles were measured for both the inhibited and uninhibited flames with the same total mass flow. In addition to measuring the concentrations of the species which were stable to sampling, an attempt was made to measure hydrogen-atom concentration profiles using a new device, "the scavenger sampling probe". Qualitative consideration of these results yields the following information:

(a) The addition of this amount of inhibitor (X(HBr) = 0.0015) appreciably lowers the rate of reaction of the major species (CH₄, O₂, and CO).
(b) Peak concentrations of the intermediate species (OCH₂, CO, and H₂) are changed and shifted relative to the major species. When data on diffusion and temperature become available, a quantitative interpretation may yield H, OH, and CH₃ radical concentration data.

(c) The apparent concentration of H atoms was depressed almost five-fold by the addition of HBr even in the equilibrium region.

(d) HBr was the only bromine-containing compound detected (X(Br₂) < 10⁻⁴).

These latter two results are probably artifacts of the techniques. They may, however, yield useful information and provide a guide for subsequent work.

(2) A series of computer calculations were made of the adiabatic temperatures and compositions of the equilibrium burned gases of some CH₄ - O₂ - Ar mixtures and of the effect of adding small amounts of HBr. A routine developed by the U. S. Naval Ordnance Test Station was used on the APL computer to determine these flame properties. One of the most interesting points developed was that the HBr is almost completely dissociated and that bromine atoms are the commonest inhibitor species in the burned gases.
IV. REPORT ON PROGRESS 1 MAY 1961 - 31 JULY 1961

FLAME STRUCTURE STUDIES

A series of runs were made on the flat, twentieth-atmosphere flame (CH\(_4\) - 0.078, O\(_2\) - 0.92) which has been studied in detail in this laboratory (Refs. 5, 26). It was hoped that the study of this flame inhibited with 0.003 HBr would allow an early analysis of the effects of HBr on the rates of reaction in the methane-oxygen system. A complete analysis has been made of the uninhibited flame, and diffusion coefficients are available for all of the species except HBr and Br\(_2\).

The results obtained using the standard techniques (pp. 4 - 9) are given in Figs. 4, 5. Compositions were determined using micro-probe sampling techniques. The temperature profile was measured with a silica-coated Pt - Pt, 10% Rh thermocouple, and the velocity was calculated from the initial mass flows and the assumption that the flame is geometrically similar to the uninhibited flame. The run turned out to be a problem because of the corrosive effects of the burned gases (presumably the reactive species is bromine atom). These gases attacked not only the brass, but also the stainless-steel parts of the burner and greatly shortened the life of the Pt - Pt, 10% Rh thermocouple used for temperature measurements. The attack on the stainless-steel parts of the burner resulted in the formation of ferric bromide, which distilled through the burner, finally contaminating the system so badly that the run had to be discontinued. At the time it was thought that a complete run had been made although it was not expected to be of high quality. When the data were analyzed, however, it was discovered that the HBr had corroded the inlet orifice mounting so that almost half of the composition profile run was made with continuously varying HBr concentration, and the data had to be discarded.

The burner system was so badly corroded that it was decided not to make a second run, and the burner was retired. On the basis of this experience a new burner system was designed. It is a spherical-flame system with the parts made of glass, teflon, and ceramic. In addition, a sodium hydroxide stick trap was designed to protect the pumps and pump oils from contamination by HBr and Br\(_2\). This equipment
Fig. 4 TEMPERATURE AND VELOCITY PROFILES OF A FUEL-LEAN, FLAT FLAME

(CH$_4$ - 0.078, O$_2$ - 0.92, Ar - 0.002, P = 0.05 atm, with and without 0.003 HBr inhibitor.) Temperatures were measured using a Pt-Pt-10%Rh silica-coated thermocouple. Velocities of the inhibited flame were inferred from the temperature profile and the assumption that the inhibited and uninhibited flames were geometrically similar. Values for the uninhibited flame were taken from Ref. 30.
Fig. 5 COMPOSITION PROFILES OF A FUEL-LEAN, FLAT FLAME

(CH₄ - 0.078, O₂ - 0.92, Ar - 0.002, P = 0.05 atm, with and without 0.003 HBr inhibitor.) Compositions were measured using a quartz microprobe for sampling with mass spectrometric analysis. Values for the uninhibited flame were taken from Ref. 30.
is being fabricated, and will be used for subsequent flame inhibition studies.

**HIGH-TEMPERATURE DIFFUSION COEFFICIENTS**

Reliable diffusion coefficients are necessary for the analysis of flame structure data. A program has been initiated to measure the diffusion coefficients required for the analysis of available flame structure data. These data are on an argon-diluted methane-oxygen flame (Ref. 27). It is projected to measure binary diffusion coefficients for the flame species in an argon carrier (H₂, HBr, Br₂, CH₄, O₂, CO, CO₂, and H₂O), using the point-source method developed at this Laboratory (Ref. 28). During the quarter the apparatus was set up (see Fig. 6) and tested at two temperatures on the He-N₂ system. Satisfactory checks were obtained with previous data (Table III). A study of the hydrogen-argon system has been initiated.

**CONCENTRATIONS OF ATOMS AND RADICALS IN FLAMES**

The most important class of species in the flame are the reactive atoms and radicals which enter into all of the important reactions (Table II). Their concentration cannot be determined by the usual microprobe-sampling techniques because of their reactivity. Therefore, special techniques must be devised for their determination. One possible method is the radical scavenger technique (Ref. 27), which has been under study in this Laboratory for the past year under Task R (Ref. 29). Because of the importance of the success of these studies to the flame inhibition program and because of the hiatus created by the construction of the corrosion-proof burner, an intensive effort was put on the scavenger-probe studies this past quarter.

The radicals are presumed to be sampled quantitatively under frozen flow conditions by the scavenger-probe nozzle. Therefore, if a "scavenger" can be rapidly mixed with the incoming sample, and the reaction of scavenger and radical is rapid compared with the radical recombination rate, there will be a one-to-one correspondence between initial radicals and the resulting stable product.

As reported last quarter, the reaction of hydrogen atoms with chlorinated hydrocarbons is one such reaction, and initial studies
Fig. 6 POINT-SOURCE APPARATUS FOR MEASURING DIFFUSION COEFFICIENTS OF GASES

(a) Flow Diagram of Gas Handling and Analysis System

(b) Schematic Diagram of Point Source in a Laminar Flow
TABLE III

Test of Point-Source Diffusion Coefficient Apparatus*

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>TEMP. °C</th>
<th>OBSERVED VALUE $\text{cm}^2/\text{sec}$</th>
<th>LITERATURE $\text{cm}^2/\text{sec}$</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$-$\text{He}$</td>
<td>24.</td>
<td>0.723</td>
<td>0.723, 0.736</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>2.63</td>
<td>2.00</td>
<td>1.99</td>
<td>(2)</td>
</tr>
</tbody>
</table>

(1) Walker, R. E., PhD Thesis, 1958, Dept. of Physics, University of Maryland, College Park, Maryland.


*To test the operation of the rebuilt point-source apparatus, the values were obtained for a well-known system ($\text{He}$-$\text{N}_2$) at two temperatures and compared with the literature. The check was considered satisfactory ($\pm$ 1%).
(Ref. 27) gave qualitative confirmation of this assumption. In the regime of operation the reaction appeared to give results proportional to H-atom concentration but with only 10-20% efficiency. Studies this past quarter have indicated that there is no regime for quantitative application of this reaction (unless perhaps reaction flasks at least as large as 50 liters are used).

For this reason work was shifted to oxygen atoms using the reaction:

$$0 + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2,$$

which is so rapid that no measurement of its speed has yet been possible (Ref. 30). The apparatus was modified to accommodate these studies (Fig. 7). Initial studies indicated that this reaction is suitable for scavenger sampling studies, and experimental concentrations in the equilibrium burned gas regions are quite close to those calculated assuming adiabatic reaction. (Table IV). The concentration profiles are similar to those obtained with the hydrogen-atom studies (Ref. 27) showing a peak in the reaction zone at 3 to 4 times the concentration in the equilibrium gases. The precision of the present results is poorer than originally expected because of the bad behavior of \text{NO}_2 in the mass spectrometer. The \text{NO}_2 presumably is decomposed and attacks the hot rhenium filament. This changes the true cracking pattern. In spite of these difficulties it appears to be possible to determine meaningful oxygen-atom concentration profiles in flames by this technique.
Fig. 7  SCHEMATIC DIAGRAM OF SCAVENGER PROBE USED IN MEASURING OXYGEN-ATOM CONCENTRATIONS
(Ref. 27)
TABLE IV

Test of Oxygen-Atom Scavenger Probe*

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>CH₄</th>
<th>O₂</th>
<th>Ar</th>
<th>T₀ (°K)</th>
<th>P (atm)</th>
<th>Exptl.</th>
<th>Calculated**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.078</td>
<td>0.92</td>
<td>0.002</td>
<td>313</td>
<td>4.1</td>
<td>0.0019</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.18</td>
<td>0.72</td>
<td>313</td>
<td>3.8</td>
<td>0.0030</td>
<td>0.00325</td>
</tr>
</tbody>
</table>

*Using the reaction \(0 + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2\) for scavenging in flame microprobe-sampling studies (see Fig. 7), the O-atom concentrations were found in the equilibrium burned gas region.

**Values interpolated from calculation made using \(T₀ = 400 \, \text{°K}\).
REFERENCES


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