This report describes a pumped dye laser system used in studies of the combustion of nitramine based solid rocket propellants. Although these propellants have advantages of high specific impulse and low infrared and smoke emissions from their exhaust, better control of the burn rate is needed. Propellant additives have been suggested for burn rate control but the understanding of the chemical mechanism of burning is not well enough developed to predict the effects of these burn rate modifiers. The objective of our studies is to describe the detailed chemistry of reactions of gas phase species which are important in the combustion of nitramine propellants and additives. Species composition, temperature and burning rate have been measured for reacting gas mixtures representative of the pyrolysis products of nitramines and nitramines with additives. Chemical kinetic and fluid mechanic modeling of the flame structure is used to correlate the experimental data and evaluate critical reaction paths and energetics and their importance in burn rate control. The excimer laser pumped dye laser described in this report is used for laser
INTRODUCTION

This report describes an excimer pumped dye laser system and associated instrumentation which has been used in studies of gas phase reactions representative of the decomposition products of nitramine based solid rocket propellants. The laser diagnostic system was provided by a Department of Defense University Research Equipment Grant to be used in ongoing studies of solid rocket propellant combustion supported by the Air Force Office of Scientific Research. The focus of this report is the description of the laser diagnostic system provided by the equipment grant and demonstration of the implementation of the system in measurements on CH4//NO2/O2 flames. Although the dye laser is described with reference to studies of nitramine propellants, it should be emphasized that because tuning is possible with the dye laser, the equipment has a very wide range of application to the measurement of unstable reaction intermediates. It therefore represents a new capability which can be used in support of future research on significantly different chemical systems. The nitramine propellant combustion studies in progress are described below as a prototype of studies of this general type which are possible with the dye laser. The importance of certain very specific intermediates is emphasized to demonstrate the contribution which this equipment can make to the conclusiveness of the study.

The use of nitramine based solid rocket propellants has the advantages of high specific impulse due to low molecular weight products, reduced infrared radiation emissions in the exhaust plume due to relatively lower CO2 and H2O in the products, reduced smoke and less corrosive products (Kubota, 1982). There remains considerable uncertainty, however, about the basic chemical and physical processes which control the combustion of these propellants. This is particularly true of the gas phase reactions above the surface of the propellant during combustion.

The decomposition of the nitramines RDX (1,3,5, trinitro hexahydro 1,3,5 triazine) and HMX (1,3,5,7 tetranitro 1,3,5,7 tetracyclooctane) has been considered by several investigators (Schroeder, 1985). When heated the solid RDX or HMX first undergoes solid-solid then solid-liquid phase changes before gaseous products are formed. The major gaseous nitrogen species found are NO2, N2O, NO, N2 and NH3 and the gaseous carbon species formed are primarily CH2O, HCN, CO and CO2. The relative yield of the products has been found to be a function of the pressure and heating rate. Low pressure and high heating rates were found to favor the formation of CH2O and NO2. High pressure and low heating rates, on the other hand, were found to favor the formation of HCN and NO2. Under actual combustion conditions of high pressure and high heating rate, it is likely that CH2O, HCN and NO2 are all important. Reactions of these decomposition products support the gas phase flame reactions near the propellant surface and thereby influence the burning rate.

Several distinct luminous flame zones are observed in the combustion of nitramine propellants which have also been seen in hydrocarbon flames with NO2 as an oxidizer. A very rapid, luminous reaction zone is found adjacent to the surface of the propellant followed by
a dark, nonluminous zone at greater distances from the surface. Finally, an additional visible flame zone appears after the dark zone. The detailed chemistry of this flame structure is not known at the present time.

In early studies of fuel/NO and fuel/NO2 flames, Parker and Wolfhard (1953) qualitatively characterized flames supported by NO and NO2. They observed multiple luminous zones in flames with a number of different hydrocarbons as fuels and they also were able to establish a pure NO decomposition flame. More quantitative data have been reported on methyl nitrite, methyl nitrate and ethyl nitrate decomposition flames (Hall and Wolfhard, 1957) which also show multiple luminous zones. Arden et al. (1957) and Hicks (1962) measured stable species composition profiles in a variety of these flames and provide some insight into the structure of the multiple luminous zones. The fuel evaporates from the liquid pool and rapidly decomposes into a variety of products which then react in the gas phase. In the case of the nitrites, the decomposition products are hydrocarbons and NO. In the case of the nitrates the products are hydrocarbons and NO2. When NO2 is formed as a decomposition product, rapid reaction between the hydrocarbon intermediates and NO2 is observed leading to the formation of NO. In all of the flames where NO is formed, there is the possibility of the exothermic decomposition of NO if the temperature is sufficiently high.

We have completed low pressure flame studies of CH4/NO2/O2 mixtures which identify reactant, intermediate, and product species profiles through the flame. These measurements represent the first data on intermediates in the reaction of hydrocarbons with NO2 in flames. The comparison of these measurements to a flame model including kinetics can be used to evaluate the quantitative accuracy of a kinetic mechanism.

**STATUS OF RESEARCH**

**Burner Assembly**

Flame reactions are followed experimentally by precise, spatially resolved measurements of species concentration and temperature profiles above a one dimensional, laminar flat flame burner (Figure 1). Reactant gases are metered by Tylan electronic, linear mass flow controllers accurate to 1% and reproducible to 0.3%. The flame resulting from the reactant mixture is stabilized above the burner which is housed in a reaction chamber. The chamber allows low pressure operation to distribute the flame reaction spatially and thus enhance spatial resolution of the measurements.

Gas temperature measurements are made using a silica coated 0.0076 cm diameter Pt/Pt-13% Rh thermocouple. The coating recommended by Fristrom and Westenberg (1965) is followed in order to minimize the catalytic effects associated with bare platinum wires. Gas samples are withdrawn by quenching quartz microprobes and analyzed by a Varian 3700 gas chromatograph. Possible errors and limitations associated with flame probing have been described by Fristrom and Westenberg (1965) and procedures for minimizing these errors are in common use. The burner is mounted on a micrometer positioning mechanism accurate to .01 cm. A reliable gas chromatographic concentration measurement technique
Figure 1. Schematic of the low pressure, laminar, flat flame burner assembly showing the gas supply system (above) and gas sampling system (below). Samples of stable gases are withdrawn to the gas chromatograph by a vacuum pump.
for the nitrogenous species N2, NO, NH3, HCN and N2O and the combustion products CO, CO2, CH4 and H2 has been developed (Banna and Branch, 1978).

In order to provide a computer interface between the gas chromatograph and the Hewlett Packard 9816S laboratory computer two new logic circuits had to be designed. The operation of the Varian 3700 gas chromatograph including digital integration is controlled by Varian CDS111 data system. A new input interface for the HP computer and a dual rate output buffer for the CDS111 to the HP computer were designed and added to the CDS111. These changes allowed control of the gas chromatograph and data recording and data reduction directly by the HP computer.

Laser Induced Fluorescence Spectroscopy

The reactive intermediates which are of interest in this study are primarily OH, H, NH, NH2, CH, and CN. Identification and quantitative measurements of most of these species and of NO is possible by laser spectroscopy. In addition, gas temperature can be measured by spectroscopy for comparison to thermocouple readings.

Several spectroscopic techniques have been used to probe concentrations and temperature of particular species in flames (Bonczyk, et al., 1979 and Crosley, 1979). Since lasers can be focused down to very small diameters, spatial accuracy can be obtained which is sufficient to resolve even the very steep concentration gradients characteristic of flame reaction zones. Interaction of laser radiation with specific energy modes of the reactant species also provides considerable selectivity in identification and measurement of species concentration and temperature. The technique of laser induced fluorescence (LIF) is particularly suited to the measurement of minor species and reaction intermediates. Although less sensitive than LIF, laser absorption can be used to measure species which may not be accessible by LIF. Both laser induced fluorescence and laser absorption measurements have been reported for OH, NH2, NH, CN, CH, and NO.

The optical arrangement for the laser absorption and laser induced fluorescence measurements is given in Figure 2. A Lambda Physik EMG 53 MSG Excimer Gas Laser is used to pump a Lambda Physik FL2001 Dye Laser. The excimer laser pulses at 0.1 to 100 Hz and has a pulse energy of 50 mJ at 308 nm. The Lambda Physik FL2001 Dye Laser has a wavelength range of 320 to 970 nm and a bandwidth of 0.22 cm\(^{-1}\) at 580 nm. Typical pulse energies are 10 to 15 mJ and pulsewidth is 5 to 20 nsec with background of less than 1%. The combination of the excimer laser and the dye laser with the dyes available, provide high pulse energy, narrow bandwidth and extremely low background.

Following the optical path in Figure 2, the laser light output from the dye laser is filtered and a beam splitter used to divert part of the beam to a power meter monitor. Light then passes through the burner pressure vessel and is focused through the flame. Separate focusing arrangements and mirrors are used for the laser absorption and laser fluorescence measurements to avoid window fluorescence. The collected light from fluorescence or the attenuated light from absorption is then focused onto the entrance slit of the SPEX 1401, 0.75m double monochrometer. The signal from the photomultiplier tube is processed by
Figure 2. Schematic of the optical arrangement for the laser induced fluorescence system.
a Stanford Research Systems signal averager and recorded. The Hewlett-Packard 9816S computer is available for controlling the spectrometer scan and other experimental variables and analysis of data from the experiments.

The flame which is being studied is a premixed, laminar, flat flame. The flame is therefore nonsooting to minimize soot extinction and limit background luminosity and laser induced particulate fluorescence. Since the path length through the flame is 8 cm, defocusing is minimal. Laminar flow and the use of electronic mass flow controllers accurate to 1% also eliminate temporal variations in the flowfield. Beam trapping helps avoid spurious scattering of laser light.

The species of interest in the flame studies we are conducting generally have known absorption and emission spectra and are all accessible by the turnable dye laser system. They also have previously determined lifetimes for radiative decay. Data from the previous observations of these species in other chemical systems aid in the interpretation of the fluorescence and absorption spectra. In addition, the measurement of stable species concentration and of temperature in the flames by gas sampling and gas analysis also aids in interpretation of the fluorescence data. These and other requirements of signal interpretation are discussed in detail in Eckbreth (1981), Bonczyk et al. (1979) and Crosley (1979). Although all necessary corrections are not completely characterized, saturated fluorescence and fluorescence calibrated by absorption of some other technique have been successful in giving reliable species concentration data for laboratory flames. A typical laser induced fluorescence spectrum for CH is given in Figure 3.

Flame Modeling

The data generated by the experimental measurements consist of one-dimensional profiles of species composition and temperature throughout the flame. The data can then be compared to a numerical model of the multicomponent reacting flow including an elementary reaction mechanism for the detailed chemistry of major species and intermediates. The comparison between the experimental profiles and those generated by the numerical model provide insight into the appropriateness of the reaction mechanism and fluid mechanics of the process.

RESULTS AND DISCUSSION

Profiles of stable and unstable species and temperature have been measured in a lean, laminar premixed flat flame stabilized on a Cercor ceramic burner. The burner has a width of 2.0 cm and a length of 8.0 cm and is enclosed in a vacuum chamber with the pressure maintained at 30 torr. During sampling for stable species the quartz sampling microprobe and vacuum chamber are held in a fixed position and the burner is moved by means of a micrometer positioner accurate to .01 mm. The sampling probe is surrounded by a cooling water jacket which begins 2.54 cm above the tip of the probe. During the laser fluorescence measurements the optics are similarly held in a fixed position and the burner moved to provide a traverse of the flame gases.
Figure 3. Laser Induced Fluorescence spectrum of CN in a lean CH4/N2/O2 premixed flame.
The flames of CH4/NO2/O2 were characterized by two distinct luminous zones separated by dark zones. At the face of the burner where the gas temperature was generally low, there was a dark or nonluminous zone usually a few mm in thickness. Next there was a yellow/orange region which was typically 3 or 4 mm thick followed by the second dark zone. Finally there was a violet luminous zone about 5 mm in thickness. The thickness of the zones could be changed by changing the relative proportion of the reactants. For example, if NO2 is increased and O2 decreased the yellow region becomes wider and brighter while the violet region becomes thinner and less bright.

It was found in these low pressure flames that oxygen was necessary in order to stabilize the flames with NO2. Table I gives the minimum oxygen flow in order to stabilize the flame as a function of NO2 flowrate in our burner. If the O2 is decreased below these limits the flame first begins to oscillate rapidly and then is extinguished. Earlier qualitative observations of hydrocarbon/NO2 flames (Parker and Wolfhard, 1953) were at significantly higher pressure where it was possible to stabilize pure hydrocarbon/NO2 flames. The measured stable species concentrations suggest that the overall reaction has a stoichiometry given by

\[ CH_4 + 2NO_2 = 2H_2O + CO_2 + N_2 \]

The added oxygen appears to be necessary to initiate the early reaction of CH4 even though the mixture is quite fuel lean.

The measured species concentrations and temperature are given in Figures 4-6. The spectral transitions used for the laser induced fluorescence measurements are given in Table II. The spectral lines used were selected so that the correction for the effect of temperature on the line intensity was a minimum. Also shown on each of the figures is the location of the dark and luminous zones in the flame.

The concentration profiles show that NO2 is converted largely to NO and that exothermic NO reduction occurs in the later stages of the flame. Oxygen needed for the oxidation of CH4 is provided primarily by the early decomposition of NO2 to NO. The carbon products CO and CO2 are formed early in the reaction zone and CO continues to be oxidized to CO2 throughout most of the flame. The concentration of the intermediates CN and CH is plotted relative to the maximum concentration of each species in Figure 6. The CH concentration profile is unusual in that it has two distinct peaks. Although the flame modeling is not complete, preliminary evidence suggests that the first peak is associated with flame initiation of CH4/O2 while the second peak is due to CH4/NO2.

Several species have concentration maxima in each of the luminous zones. In the yellow region NO2 is at a maximum while in the violet region CN, NH, NH2 and NO are all at their maximum concentrations. Nitrogen dioxide chemiluminescence in the yellow/orange is strong and CN, NH and NO have strong emission bands in the violet. The dark zones appear to result from the distinct separation of the concentration profiles of these species and from the cooled burner face as discussed above.

The interpretation of the mechanism for formation of CH and CN is possible with the aid of recent studies of carbon-nitrogen interactions in flames (Thorne, et al., 1986 and Le and...
TABLE I. Limiting Oxygen Flowrate for Stable CH$_4$/NO$_2$/O$_2$ Flames at 30 torr.

<table>
<thead>
<tr>
<th>Flame</th>
<th>CH$_4$</th>
<th>NO$_2$</th>
<th>O$_2$</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>0.4</td>
<td>0.43</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>0.8</td>
<td>0.33</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>1.2</td>
<td>0.28</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>1.6</td>
<td>0.22</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Flowrates are in standard liters per minute.*
<table>
<thead>
<tr>
<th>Species</th>
<th>Transition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>B²Σ⁻⁺ → X²Π⁺&lt;br&gt;(0,0) band at 390 nm&lt;br&gt;P₁(6) line</td>
<td>Thorne, et al (1986)</td>
</tr>
<tr>
<td>CN</td>
<td>B²Σ⁺ → X²Σ⁺&lt;br&gt;(0,0) band at 386 nm&lt;br&gt;R₁(14) line</td>
<td>Thorne, et al (1986)</td>
</tr>
<tr>
<td>NH₂</td>
<td>A²A₁ → X²B₁&lt;br&gt;(0,0,0) ← (0,0,0) band at 600 nm&lt;br&gt;P₁,Q₁,N=7 line of Σ Sublevel</td>
<td>Green &amp; Miller (1981)</td>
</tr>
<tr>
<td>*NH</td>
<td>A³Π → X³Σ⁻&lt;br&gt;(0,0) band at 336 nm&lt;br&gt;R₁(6) line</td>
<td>Le &amp; Vanpee (1985)</td>
</tr>
<tr>
<td>*OH</td>
<td>A²Σ⁻ → X²Π⁺&lt;br&gt;(0,0) band at 309 nm&lt;br&gt;Q₁(4) line</td>
<td>Le &amp; Vanpee (1985)</td>
</tr>
</tbody>
</table>

*Species observed and identified but no quantitative data.
Figure 4. Profiles of nitrogen and carbon containing species measured in a CH4/NO2/O2 flame. The reactant mole fractions are 0.24 CH4, 0.56 NO2 and 0.20 O2.
Figure 5. Temperature profiles measured with a thermocouple and by CN rotational temperature for the flame in Figure 4 (Flame 2) and for a flame of .2 CH4 and .8 O2 (Flame 4).
Figure 6. Profiles of intermediate species measured in a CH4/NO2/O2 premixed flame. The reactant mole fractions are the same as those of Figure 3.
Vanpee, 1985). The reaction is initiated by hydrogen abstractions from CH4 leading to the formation of CH2. An additional reaction such as

$$CH2 + H = CH + H2$$

is usually the most important step in the formation of CH. Once CH is formed, several paths are reasonable to form CN, for example

$$CH + NO = CN + OH$$

or

$$CH + H = C + H2$$
$$C + NO = CN + O$$

In view of the high concentration of NO formed from the decomposition of NO2, the first path is probably most likely and may proceed through the formation of HCN. Both possibilities are consistent with the observation that the CH concentration peak precedes the CN peak. The complete results of the flame structure measurements are given in Branch (1987) and Branch et al (1987).

CONCLUSIONS

Experimental measurements of the concentration profiles of major and minor species have been made in laminar, premixed flat flames of CH4/NO2/O2. These provide new data which may be used in the interpretation of the multiple reaction zones characteristic of some solid rocket propellant flames. With this understanding it may be possible to modify the composition of the propellant to influence the burning rate and the range of products formed.

REFERENCES


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