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CHEMICAL KINETICS OF NITRAMINE
PROPELLANT COMBUSTION

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DEPARTMENT OF
MECHANICAL ENGINEERING

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The decomposition of many solid reactants during combustion leads to the formation of gaseous hydrocarbons and oxides of nitrogen which can react to support a flame above the surface of the solid. These flames can provide heat which is fed back to the propellant surface and thereby influence the burning rate of the solid. In the case of nitramine based solid rocket propellants, the gas phase decomposition products include significant amounts of CH_2O, HCN, NO_2, NO, N_2O and H_2. This study is intended to provide experimental data on the structure of hydrocarbon flames supported by oxides of nitrogen in order to establish the reaction mechanism for such flames. Laminar, premixed, flat flames of $\text{CH}_4/\text{NO}_2/\text{O}_2$ and $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ have been investigated and a reaction mechanism is suggested which accounts for all of the major observations in the data. (NW) (Methane)			
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I. RESEARCH OBJECTIVES

Many solid rocket propellants and other energetic materials consist of complex chemical compounds of carbon, hydrogen, oxygen and nitrogen. The decomposition of these solid reactants leads to the formation of gaseous hydrocarbons and oxides of nitrogen which can react to support a flame above the surface of the solid. These flames can provide heat which is fed back to the propellant surface and thereby influence the burning rate of the solid.

Cont'd
on pp. 123
In early studies of fuel/NO and fuel/NO₂ flames, Parker and Wolfhard³ 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^{4,5} which also show multiple luminous zones. Arden et al.⁶ and Hicks⁷ measured stable species composition profiles in a variety of these flames and provide some insight into the flame structure. 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 decomposition products are partially oxidized 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. The detailed chemistry and reaction mechanism for these hydrocarbon flames supported by oxides of nitrogen has not been described previously.

This study is intended to provide experimental data on the structure of hydrocarbon flames supported by oxides of nitrogen in order to establish the reaction mechanism for such flames. Laminar, premixed, flat flames of CH₄/NO₂/O₂ and CH₃O/NO₂/O₂ mixtures have been investigated and a reaction mechanism is suggested which accounts qualitatively for all of the major observations in the flame data.

II. STATUS OF RESEARCH

Burner Assembly

Flame reactions were followed experimentally by precise, spatially resolved measurements of species concentration and temperature profiles above a one-dimensional, laminar flat flame burner. Reactant gases, with the exception of formaldehyde, were supplied from gas cylinders and the flowrate measured and regulated by electronic, linear mass flow controllers accurate to 1% and reproducible to 0.3%. Formaldehyde cannot be supplied as a gas in a cylinder because of its reactivity, particularly with itself to form a solid polymer. Therefore a continuous flow, monomeric, gaseous formaldehyde generator was developed and used for the study⁸. The flame resulting from the reactant mixture was stabilized above the burner which was housed in a vacuum chamber at a pressure of 55 torr. The chamber allowed low pressure operation to distribute the flame reaction spatially and thus enhance spatial resolution of the measurements.

Gas temperature measurements were made using a Beryllium/Yttrium Oxide coated 0.0076 cm diameter Pt/Pt-13% Rh thermocouple. The coating recommended by Kent⁹ was followed in order to minimize the catalytic effects associated with bare platinum

wires. Gas samples were 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 Westenberg¹⁰ and procedures for minimizing these errors are in common use. The burner cross section was 2 cm by 8 cm and it was mounted on a micrometer positioning mechanism accurate to 0.01 cm. A reliable gas chromatographic concentration measurement technique for the nitrogenous species N_2 , NO, NH_3 , HCN and N_2O and the combustion products CO, CO_2 and H_2O as well as CH_4 , CH_2O , H_2 and O_2 has been developed¹¹. A computer interface between the gas chromatograph and a Hewlett-Packard 9816S laboratory computer was added to allow control of the gas chromatograph and data recording and data reduction directly by the computer.

Laser Induced Fluorescence Spectroscopy

The reactive intermediates which were measured in this study are OH, H, NH, NH_2 , 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^{12,13,14}. 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, at least at low pressure. 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. Laser induced fluorescence (LIF) is particularly suited to the measurement of minor species and reaction intermediates. Laser absorption can be used to calibrate species concentration profiles measured by LIF. Both laser induced fluorescence and laser absorption measurements have been reported for OH, NH_2 , NH, CN, CH and NO¹².

The optical arrangement for the laser absorption and laser induced fluorescence measurements is given in Figure 1. 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 50 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 pulsewidth is 5 to 20 nsec with a background of less than 1%. The combination of the excimer laser and the dye laser with the dyes available, provides high pulse energy, narrow bandwidth and extremely low background.

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 vacuum chamber 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 and scattering. The collected light from fluorescence or the attenuated light from absorption is then focused onto the entrance slit of the SPEX 1401, 0.75 m double monochromator. The signal from the photomultiplier tube is processed by a Stanford Research Systems signal averager and recorder. The Hewlett-Packard 9816S computer is used for controlling the spectrometer scan and other experimental variables and for analysis of data from the experiments.

The concentrations of CN, CH and NH were calibrated by a separate laser absorption system using a multi-pass optical cell arrangement. This makes possible the evaluation of absolute concentrations of these species. This calibration was not possible

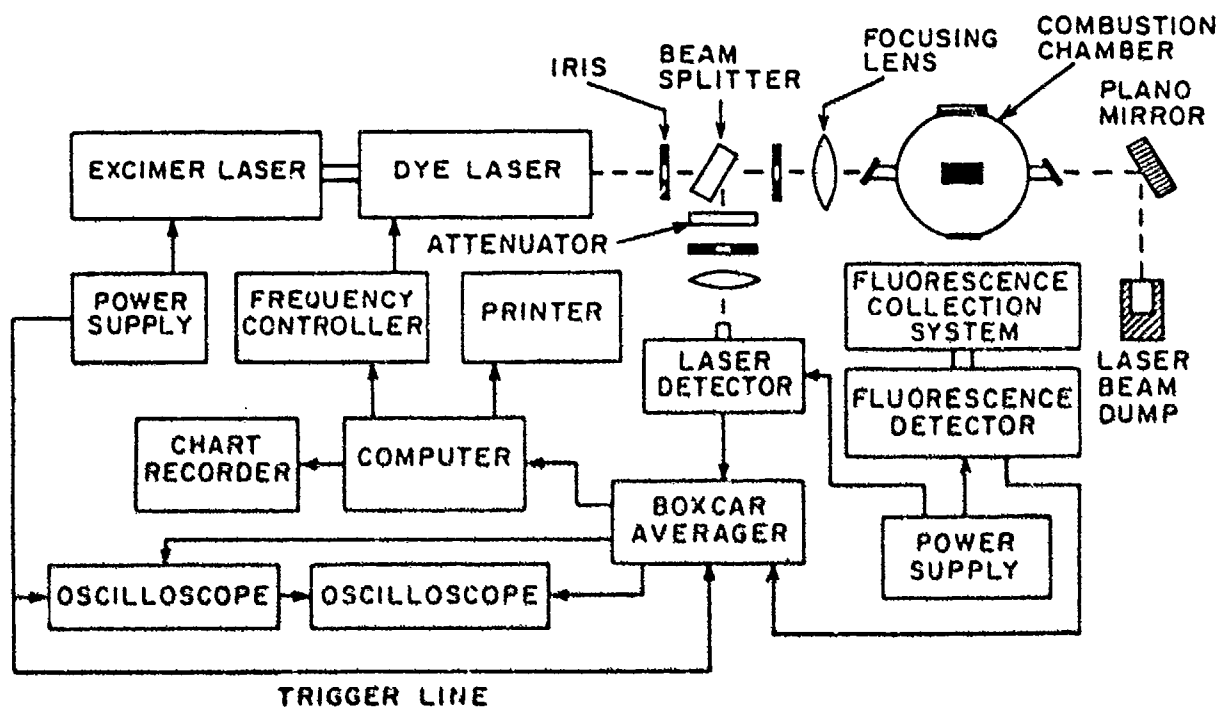


Figure 1. Schematic drawing of the laser induced fluorescence diagnostic system.

due to the lack of adequate spectroscopic data for NH_2 and was not possible for OH because the excimer laser output line at 308 nm was used directly to excite OH and the OH rotational line could not be scanned. For these reasons concentration relative to the maximum observed is plotted for NH_2 and OH.

The flame which is being studied is a premixed, laminar, flat flame. The flame is therefore nonsmoking 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 tunable dye laser system. They also have previously determined lifetimes for radiative decay. The spectral transitions used for the laser induced fluorescence measurements are given in Table I. The spectral lines used were selected so the correction for the effect of temperature on the line intensity was a minimum. In addition, the measurement of stable species concentration and of temperature in the flames by gas sampling and gas analysis aids in interpretation of the fluorescence data.

The accuracy of the stable species composition measurements is approximately 8% with a detection limit is 2000 ppm, the random error of the unstable species measurements is estimated to be 20% with a detection limit of 1 ppm and the accuracy of the temperature measurements is about 3%. The temperature measured with the thermocouple agreed with the CN rotational temperature within 25K. The flame sampling position is determined by moving the burner relative to the probes or the laser beam with a positioning micrometer. The use of irises in the laser fluorescence collection system gives a position accuracy of 200 microns and is comparable to the dimension of the probe flow disturbance.

III. RESULTS AND DISCUSSION

Flame Profiles

Complete concentration profiles are given for a lean $\text{CH}_4/\text{NO}_2/\text{O}_2$ flame in Figure 2 and for a lean $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ flame in Figure 3. The equivalence ratio ϕ_{N_2} assuming N_2 to be a final product is 0.38 for the CH_4 flame and 0.33 for the CH_2O flame. The equivalence ratio ϕ_{NO} assuming NO to be the final nitrogen product is 0.67 for the CH_4 flame and 0.56 for the CH_2O flame. Since no N_2 is formed in the CH_2O flame, ϕ_{NO} is more appropriate and since NO and N_2 are formed in the CH_4 flame, the equivalence ratio should be between ϕ_{N_2} and ϕ_{NO} . The flames with either CH_4 or CH_2O 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 blue/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 NO_2 is increased and O_2 decreased the yellow region becomes wider and brighter while the violet region becomes thinner and less bright.

Several species have concentration maxima in each of the luminous zones. In the yellow region NO_2 is at a maximum while in the violet and ultraviolet region CN,

Table I. Spectral Transitions, Fluorescence Lines and Radiative Lifetimes for Species Concentration Measurements.

Species	Transition	Radiative Lifetime
CH	$B^2\Sigma^- \rightarrow X^2\Pi$ (0,0) band at 390 nm $P_1(6)$ line. (a)	5×10^{-7} s (b)
CN	$B^2\Sigma^+ \rightarrow X^2\Sigma^+$ (0,0) band at 386 nm $R_1(14)$ line. (a)	6×10^{-8} s (b)
NH	$A^3\Pi \rightarrow X^3\Sigma^-$ (0,0) band at 336 nm $R_1(6)$ line. (c)	5×10^{-7} s (b)
OH	$A^2\Sigma^- \rightarrow X^2\Pi$ (0,0) band at 309 nm $Q_1(4)$ line. (c)	8×10^{-7} s (b)
NH ₂	$A^2A_1 \rightarrow X^2B_1$ (0,9,0) ← (0,0,0) band at 600 nm $PQ_{1,N=7}$ line of Σ Sublevel. (d)	

- (a) Thorne, et al., 1986 (Ref. 15)
(b) Bonczyk, et al., 1979 (Ref. 12)
(c) Le and Vanpee, 1985 (Ref. 17)
(d) Green and Miller, 1981 (Ref. 16)

NH, NH_2 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 and ultraviolet. The dark zones appear to result from the distinct separation of the concentration profiles of these species and from the cooled burner face. The concentration profile for CH shows a very unusual double peak with one peak occurring near the yellow luminous zone and the other much more intense in the violet zone.

The concentration profiles show that NO_2 is converted to NO and that some exothermic NO reduction occurs in the later stages of the flame when CH_4 was the fuel. As will be discussed later, radicals needed for the destruction of CH_4 and CH_2O are provided primarily by hydrogen atom attack on NO_2 and O_2 . The carbon product CO is formed early in the reaction zone and CO is oxidized to CO_2 in the later stage of the flame.

The flame profiles given in Figures 2 and 3 demonstrate that NO_2 is much less effective as an oxidizer than O_2 and much of the NO_2 remains unreacted in the burnt gas mixture. Rich mixtures with only NO_2 could not be stabilized on the burner and lean flames of CH_4/NO_2 could only be stabilized with difficulty. Measurements of CH_4/O_2 and $\text{CH}_2\text{O}/\text{O}_2$ flames show that the reaction rate with O_2 alone is much more rapid than with NO_2 . The flames in Figures 2 and 3 are all lean and generally only one of the oxygen atoms in NO_2 is available as an oxidizer.

As NO_2 is increased and O_2 decreased in the reactant mixture, the fraction conversion of NO_2 to NO does not change substantially from about 40%. The fraction of NO reduced to N_2 in the methane flames decreases significantly as NO_2 is increased indicating that O_2 facilitates the reduction in comparison to NO_2 . The limited reduction of NO to N_2 in both flames contributes to the flame temperature being much lower than the adiabatic flame temperature since NO decomposition is exothermic.

There are significant differences in the final products in the methane and the formaldehyde flames. With methane there is some reduction of the NO which is formed from NO_2 into molecular nitrogen whereas with formaldehyde little molecular nitrogen was detected. Another difference between the two flames is that the H_2 concentration is high and it remains in the burnt gas with formaldehyde even though the flame is lean whereas the H_2 is below the detection limit in the methane flame.

The intermediate species measured in the methane flame are CH, NH, CN, NH_2 and OH. All but the OH rise to a peak and then decrease quickly in the reaction zone. The CH radical is observed earliest in the flame and the profile has two peaks. The maximum concentration of all species except OH is in the primary reaction zone. In the formaldehyde flame only OH was present at concentrations which could be detected by the LIF system.

Reaction Mechanism

The conservation equations for a laminar, premixed, flat flame can be used to calculate species reaction rates in the flame in order to evaluate a reaction mechanism. The diffusion velocity, which accounts for diffusive transport of species i in a flame, is defined as

$$V_i = -\frac{D_{ij}}{x_i} \frac{dx_i}{dz}$$

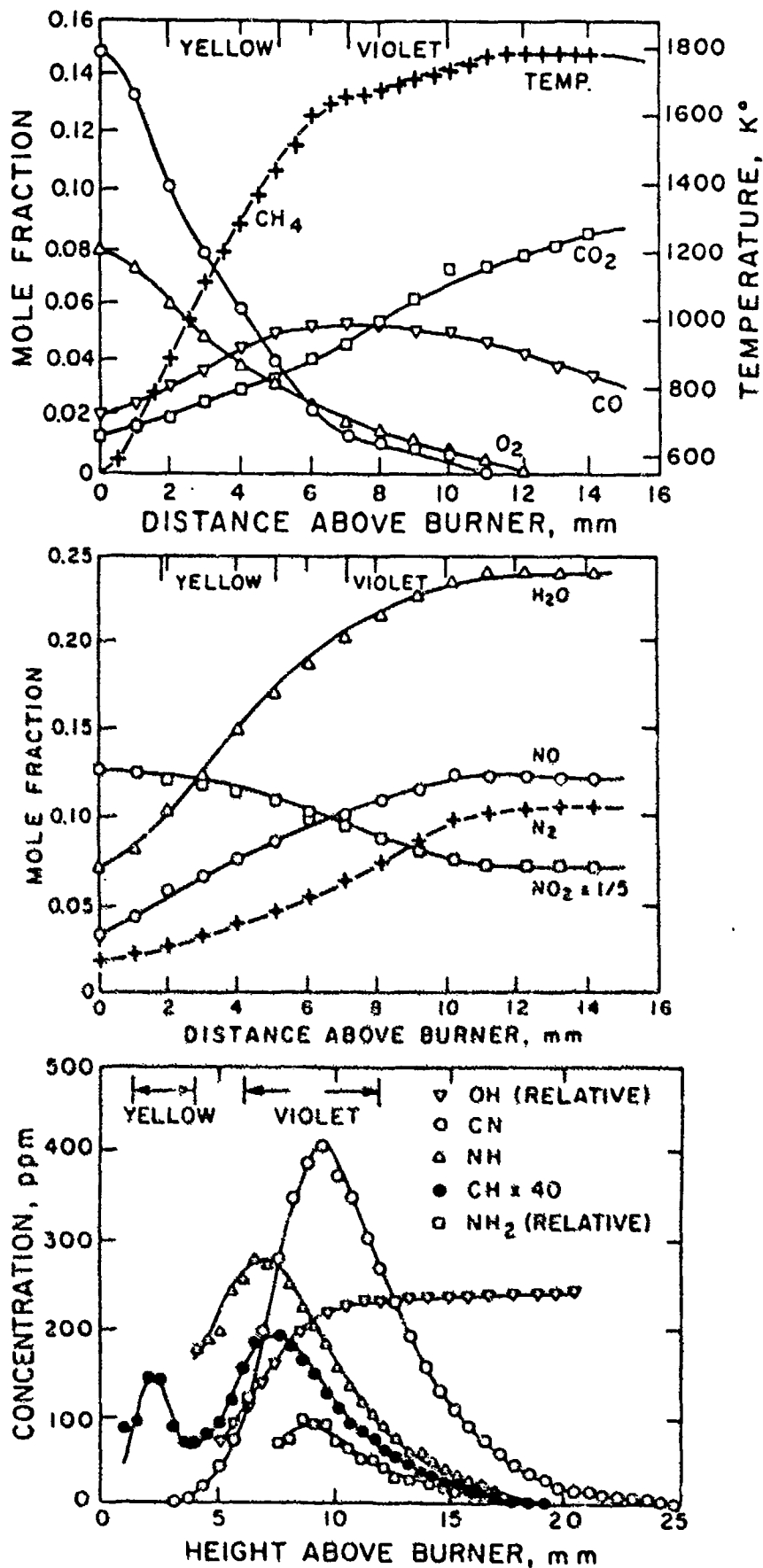


Figure 2. Composition of stable and unstable species and temperature measured in a lean, $\text{CH}_4/\text{NO}_2/\text{O}_2$ laminar, premixed flame at 55 torr. The reactant mole fractions are 0.16 CH_4 , 0.73 NO_2 , and 0.11 O_2 and the total flowrate is 2.19 standard liters per minute.

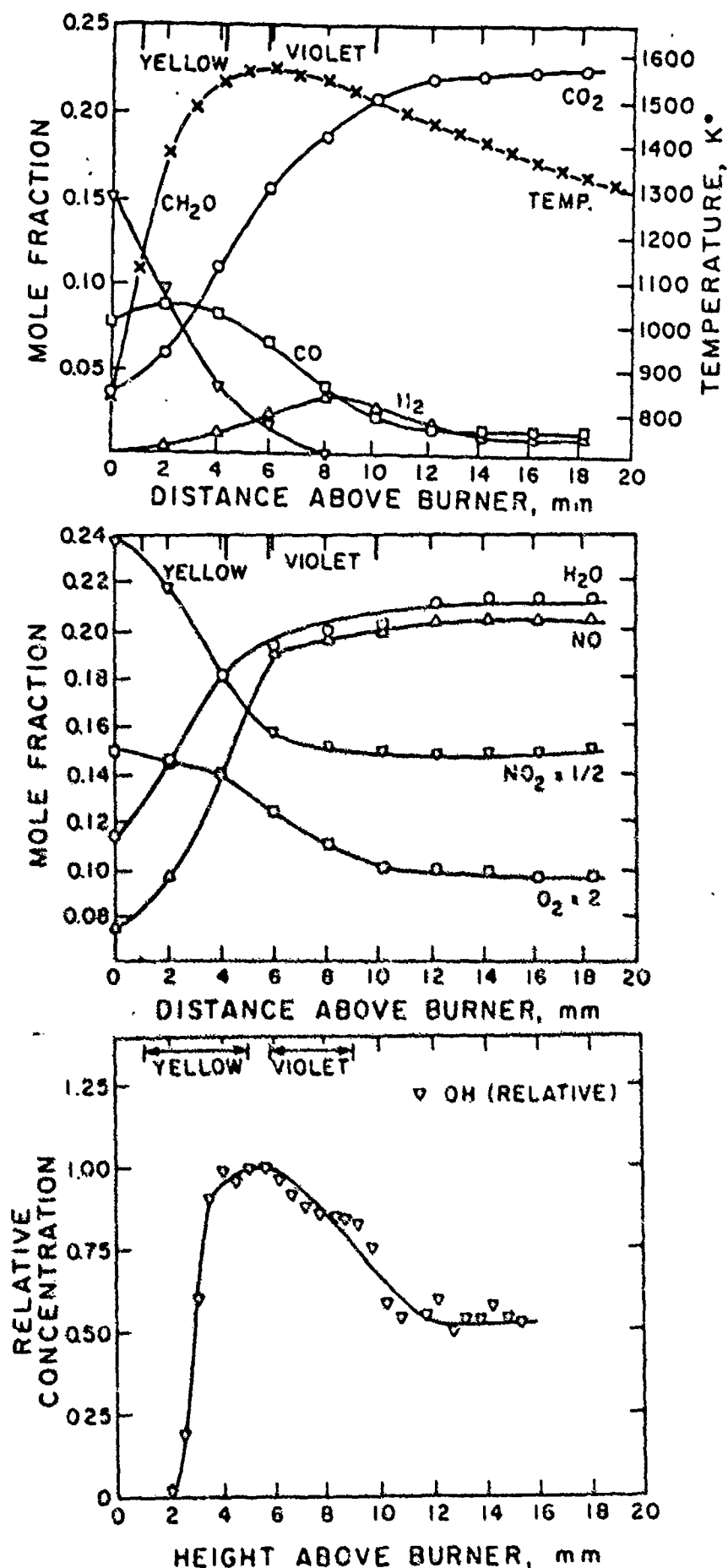


Figure 3. Composition of stable and unstable species and temperature measured in a lean, $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$, laminar, premixed flame at 55 torr. The reactant mole fractions are 0.247 CH_2O , 0.627 NO_2 , and 0.126 O_2 , and the total flowrate is 2.15 standard liters per minute.

where D_{ij} is the diffusion coefficient calculated using Reference 18 and x_i is the mole fraction of species i . The diffusion velocity can be obtained from the concentration profiles given in Figures 2 and 3. The mass flux fraction is defined as

$$G_i = N_i M_i \frac{(v + V_i)}{\rho v}$$

where N_i is the number of moles of species i , M_i is the molecular weight of species i , ρ is the local density and v is the local velocity. Using this definition of the mass flux fraction, the flame equation describing conservation of species i in a one dimensional, laminar, premixed flame can be written as¹⁰

$$\frac{\rho_0 v_0}{M_i} \frac{dG_i}{dz} = R_i$$

where ρ_0 is the reactant gas density, v_0 is the reactant gas velocity and R_i is the reaction rate of species i . All terms on the left side of the equation can be determined from the experimental data of Figures 2 and 3.

Using the concentration profiles in Figures 2 and 3 the species reaction rates have been evaluated from the species conservation equation and are plotted in Figures 4 and 5. Once the species reaction rates are known from the experimental data, they can be compared with reaction rates calculated from tabulated rate constants and the known concentrations in the flame. In this way a number of elementary reactions can be tested for their contributions to the experimentally determined reaction rates.

A comparison of the reaction rate derived from the experimental data and the reaction rate calculated from kinetic data at the point in the flame where the reaction rate is a maximum is given in Table II. The kinetic constants for the reactions are given in Table III. The first two reactions listed in Table II are unimportant for CH_4 and NO_2 disappearance since the kinetic rate is so much lower than the experimental rate. The consumption of these two species by radical attack is much faster. The close agreement between the experimental rate and the kinetic rate for the last four reactions listed suggest they could account for the observed reaction rates in the flames.

These calculations and observations from other recent studies of the kinetics of similar systems^{15,17,20} make it possible to suggest a partial reaction mechanism for the flames. The reaction mechanism is shown schematically in Figure 6 for $\text{CH}_4/\text{NO}_2/\text{O}_2$ flames and in Figure 7 for $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ flames and is discussed below in more detail.

When methane is supplied as fuel, methane conversion proceeds by the sequence below where R is any radical such as O , H , or OH



which leads to the formation of formaldehyde. Since Reaction (2) is a recombination reaction it explains why the presence of O_2 was necessary to burn CH_4 whereas no O_2 was necessary to burn the CH_2O when NO_2 is the primary oxidizer. Formaldehyde, either supplied as a fuel or formed from methane, reacts according to²⁰



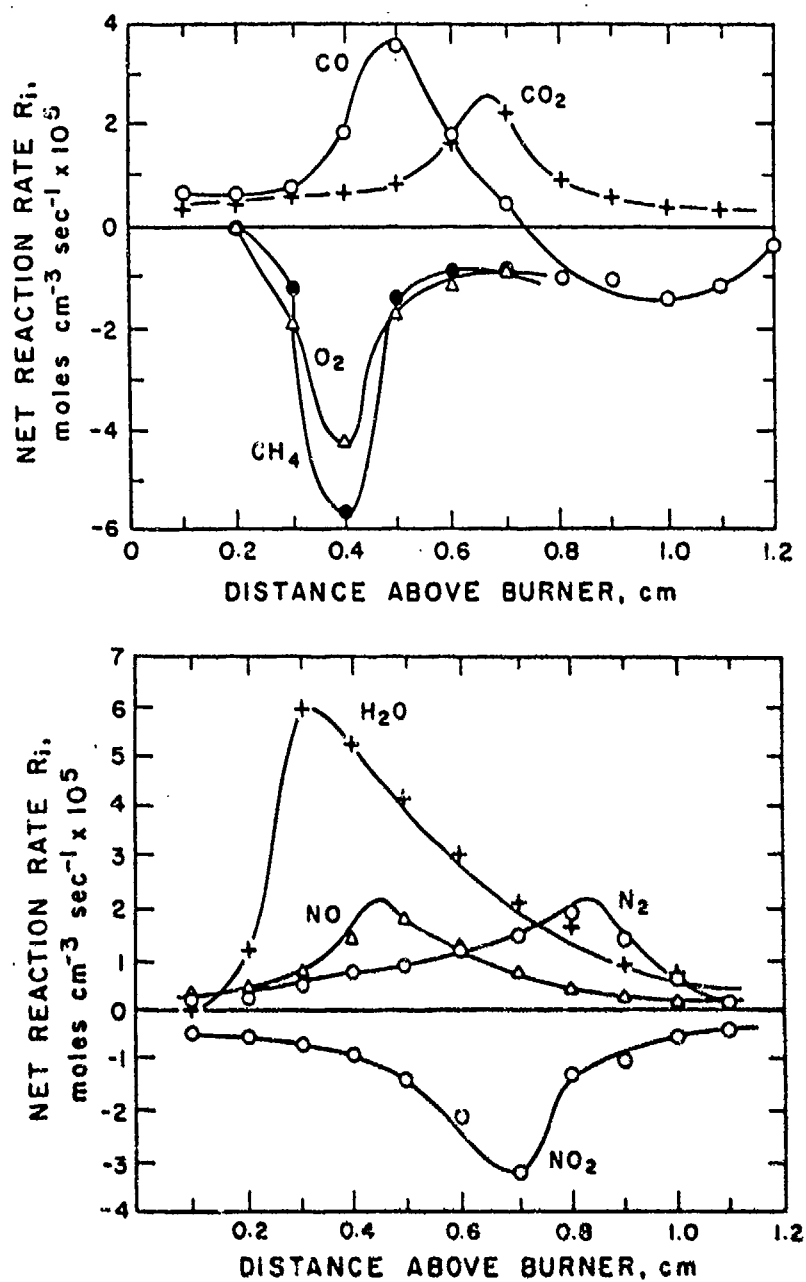


Figure 4. Reaction rate profiles for the stable species in the $\text{CH}_4/\text{NO}_2/\text{O}_2$ flame in Figure 2.

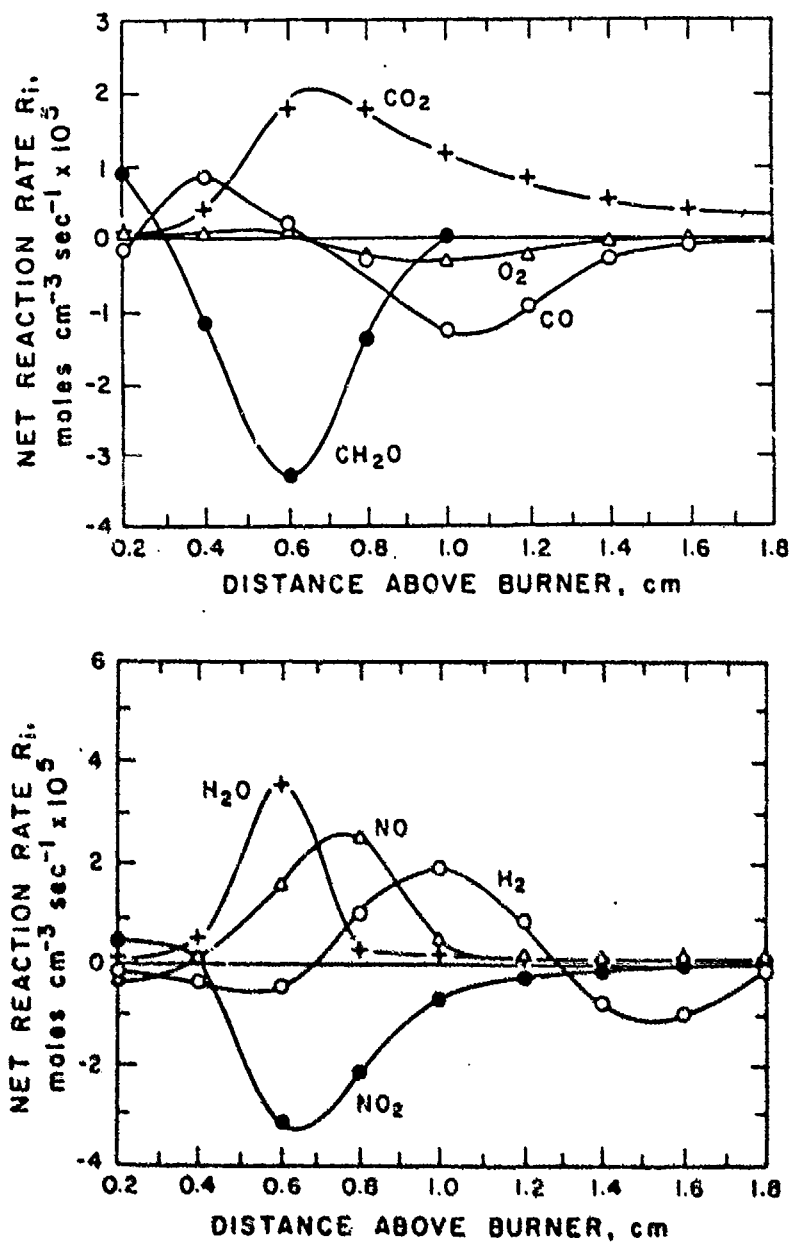


Figure 5. Reaction rate profiles for the stable species in the $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ flame in Figure 3.

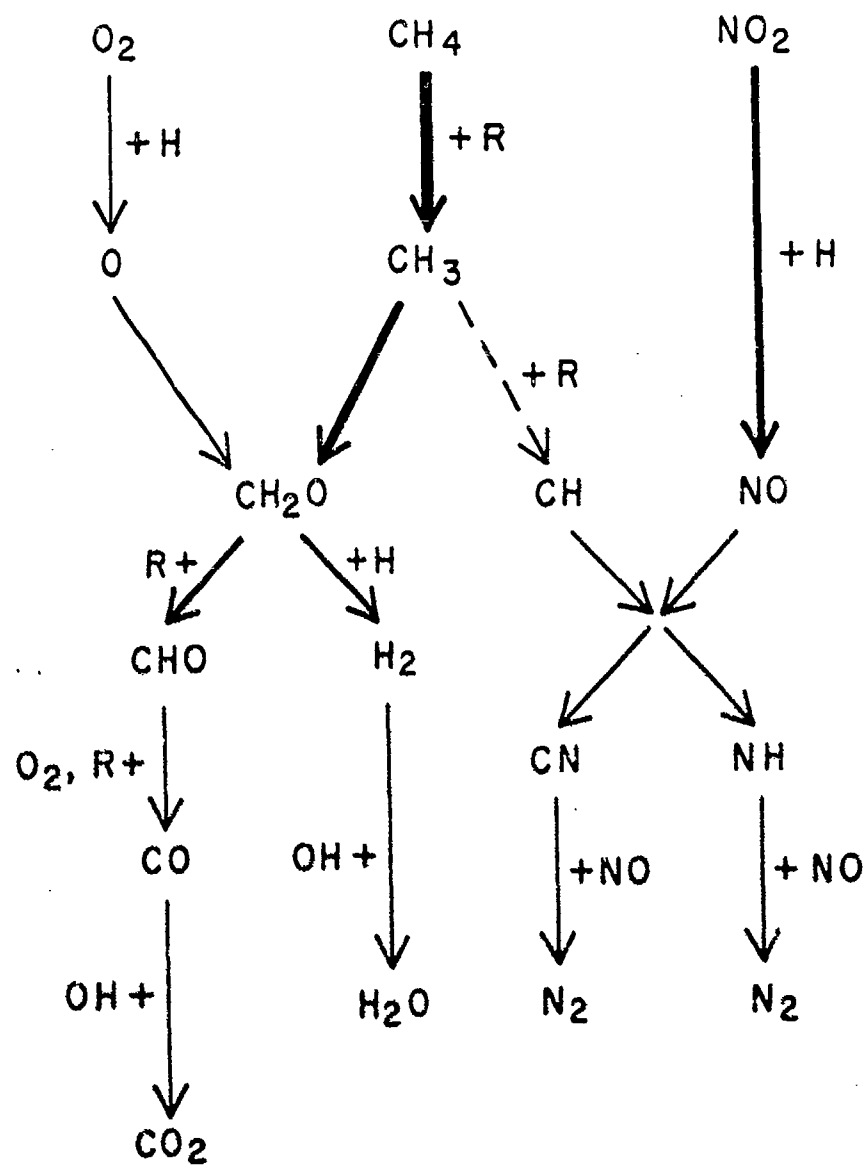


Figure 6. Schematic drawing of the reaction mechanism for $\text{CH}_4/\text{NO}_2/\text{O}_2$ flames.

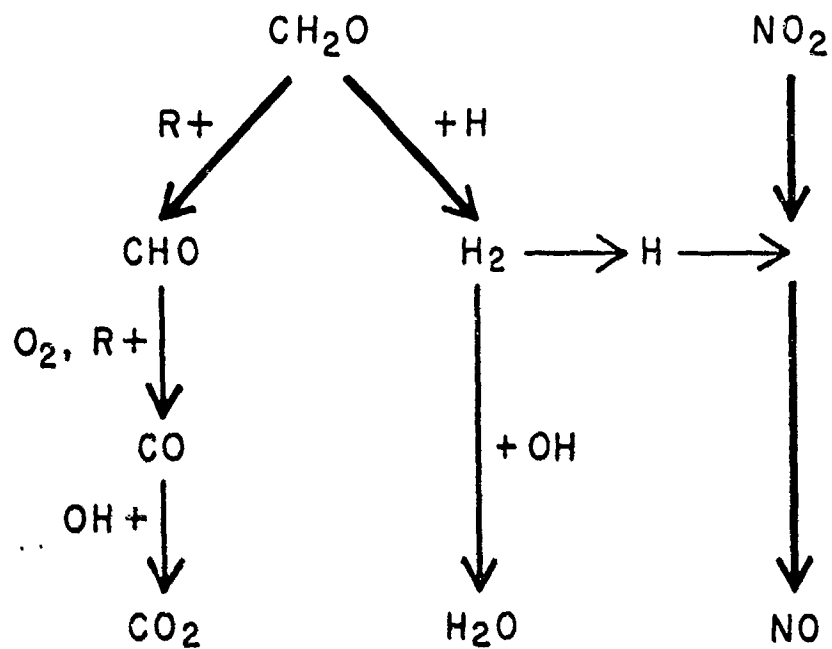


Figure 7. Schematic drawing of the reaction mechanism for $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ flames.

Table II. Comparison Between Experimentally Derived and Kinetically Calculated Net Reaction Rates.

Reaction	Temperature (K)	$R_{i,\text{exp}}$ (mol cm ⁻³ s ⁻¹)	$R_{i,\text{kinetic}}$ (mol cm ⁻³ s ⁻¹)
$\text{CH}_4 + \text{O}_2 = \text{CH}_3 + \text{OH}$	1400	5.96×10^{-5}	1.4×10^{-10}
$\text{NO}_2 + \text{M} = \text{NO} + \text{O} + \text{M}$	1400	3.00×10^{-5}	2.7×10^{-8}
$\text{CH} + \text{NO} = \text{CN} + \text{OH}$ or $\text{CH} + \text{NO} = \text{NH} + \text{CO}$	1600	0.89×10^{-5}	0.6×10^{-5}
$\text{CN} + \text{NO} = \text{N}_2 + \text{CO}$	1600	0.89×10^{-5}	1.9×10^{-5}
$\text{NH} + \text{NO} = \text{N}_2 + \text{OH}$	1600	0.89×10^{-5}	1.7×10^{-5}

Table III. Chemical Kinetic Mechanism for Methane and Formaldehyde Flames with Nitrogen Dioxide and Oxygen.
Units are mol, cm³, s, K, kcal mol⁻¹

$$k = AT^n \exp - \frac{E_a}{RT}$$

Reaction	log A	n	E	Reference
CH ₄ +M=CH ₃ +H+M	17.3	0.0	88.00	(a)
CH ₄ +H=CH ₃ +H ₂	4.35	3.0	8.750	(a)
CH ₄ +OH=CH ₃ +H ₂ O	3.54	3.08	2.000	(a)
CH ₄ +O=CH ₃ +OH	7.07	2.08	7.63	(a)
CH ₄ +O ₂ =CH ₃ +HO ₂	13.9	0.0	56.00	(a)
CH ₃ +O=CH ₂ O+H	14.11	0.0	2.000	(a)
CH ₃ +OH=CH ₂ O+H ₂	12.60	0.0	0.000	(a)
CH ₂ O+M=CHO+H+M	16.52	0.0	81.00	(a)
CH ₂ O+OH=CHO+H ₂ O	12.88	0.0	0.170	(a)
CH ₂ O+H=CHO+H ₂	14.00	0.0	4.96	(b)
CH ₂ O+O=CHO+OH	13.70	0.0	4.60	(a)
CHO+OH=CO+H ₂ O	14.00	0.0	0.000	(a)
CHO+H=CO+H ₂	14.3	0.0	0.000	(a)
CHO+O=CO+OH	14.00	0.0	0.000	(a)
CHO+M=CO+H+M	14.60	0.0	19.00	(a)
CHO+O ₂ =CO+HO ₂	12.52	0.0	7.000	(a)
CO+OH=CO ₂ +H	7.18	1.3	-0.77	(a)
CO+HO ₂ =CO ₂ +OH	13.76	0.0	22.93	(a)
O ₂ +H=OH+O	16.71	-0.82	16.51	(a)
H ₂ +O=OH+H	10.26	1.0	8.90	(a)
H ₂ +OH=H ₂ O+H	13.34	0.0	5.15	(a)
H+OH+M=H ₂ O+M	23.15	-2.0	0.00	(a)
O+H ₂ O=OH+OH	13.83	0.0	18.36	(a)
NO ₂ +M=NO+O+M	16.04	0.0	66.00	(a)
NO ₂ +H=NO+OH	14.54	0.0	1.500	(c)
CH+NO=NH+CO	14.18	0.0	0.000	(d)
CH+NO=HCN+O				
-CN+OH	14.00	0.0	0.000	(c)
NH+NO=N ₂ +OH	12.38	0.0	0.000	(e)
CN+NO=N ₂ +CO	14.03	0.0	8.000	(f)

- (a) Westbrook and Dryer, 1984 (Ref. 19)
 (b) Vandooren, et al., 1986 (Ref. 20)
 (c) Thorne, et al., 1988 (Ref. 16)
 (d) Lichtin, et al., 1984 (Ref. 21)
 (e) Kaskan and Hughes, 1973 (Ref. 22)
 (f) Philips, 1976 (Ref. 23)

It should be pointed out in particular that when R is H Reaction (3) causes the formation of H_2 in the CH_2O flame because the CH_2O concentration is high whereas little H_2 is formed in the CH_4 flames because CH_2O is much lower²⁴. The HCO formed in Reaction (3) is consumed by the reactions



The formation of CO_2 may result from either of the reactions



Some of the CH_3 formed above can react by another path to form CH, for example²⁵



The major reaction consuming NO_2 is



Once CH and NO are formed the other intermediates observed in the flames with methane can result from^{21,26}



The molecular nitrogen results from^{22,23}



This mechanism has the virtue of being able to explain nearly all of the observations on the flames we have studied. The limited effectiveness of NO_2 as an oxidizer results from the importance of the chain propagating Reaction 9 when NO_2 is oxidizer versus the chain branching reaction



which dominates when O_2 is oxidizer. This also explains why NO_2 remains in excess in these flames in comparison to the more complete consumption of O_2 .

The fact that formaldehyde reacts more readily with NO_2 than methane reacts with NO_2 results from the fact that methane must first form formaldehyde to complete its oxidation. The initial attack on the methane is well known to be relatively slow and mainly with OH ^{19,24}.

The observation that N_2 is not found in significant quantities in the formaldehyde flames arises because CHO cannot be converted to CH. Therefore, there is no straightforward path to the formation of CH in the flames with formaldehyde and the path to molecular nitrogen cannot proceed.

IV. CONCLUSIONS

Low pressure flames of methane and formaldehyde have been stabilized with mixtures of NO_2 and O_2 as oxidizer, the flame structure measured and the reaction mechanism discussed. The flames are characterized by a yellow luminous zone which results from NO_2 chemiluminescence and a separate violet/blue luminous zone due to CH and CN emission or CO chemiluminescence. Nitrogen dioxide is a poor oxidizer in relation to O_2 due to the chain propagating reaction of NO_2 with H atoms in contrast with the chain branching reaction of O_2 with H atoms. Therefore, NO_2 is converted relatively slowly to NO and much of the NO_2 remains as a diluent in the flames and results in a flame temperature well below the adiabatic flame temperature. In the methane flames some reduction of NO to N_2 is possible because of the formation of CH and subsequent reaction of CH with NO. Since formaldehyde produces CHO which cannot form CH during its oxidation, little N_2 is found in the formaldehyde flames. The results suggest that the flame reaction rates may be significantly increased if additives might be found which generate radicals that attack NO_2 and NO to increase the production of N_2 .

V. REFERENCES

1. N. Kubota, "Physiochemical Processes of HMX Propellant Combustion," *19th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 775-785, 1982.
2. K. Kuo and M. Summerfield, Ed. "Fundamentals of Solid Propellant Combustion," *Progress in Astronautics and Aeronautics*, 90, 1984.
3. W.G. Parker and H.G. Wolfhard, "Some Characteristics of Flames Supported by NO and NO_2 ," *4th Symposium (International) on Combustion*, The Williams and Wilkins Company, Baltimore, pp. 520-528, 1953.
4. A.R. Hall and H.G. Wolfhard, "Multiple Reaction Zones in Low Pressure Flames with Ethyl and Methyl Nitrate, Methyl Nitrite and Nitromethane," *6th Symposium (International) on Combustion*, Reinhold Publishing Company, New York, pp. 190-199, 1957.
5. S. De Jaegere and A. Van Tiggelen, "Comparative Study of Flame Propagation in Compounds Containing Nitrogen Oxides," *Combustion and Flame*, 3, pp. 187-200, 1959.
6. E.A. Arden and J. Powling, "The Methyl Nitrite Decomposition Flame," *6th Symposium (International) on Combustion*, Reinhold Publishing Company, New York, pp. 177-183, 1957.
7. J.A. Hicks, "The Low Pressure Decomposition Flame of Ethyl Nitrate," *8th Symposium (International) on Combustion*, The Williams and Wilkins Company, Baltimore, pp. 487-496, 1962.
8. M.E. Sadeqi and M.C. Branch, "A Continuous Flow, Gaseous Formaldehyde Generation System For Combustion Studies," *Combustion and Flame*, 71, pp. 325-329, 1988.
9. J.H. Kent, "A Noncatalytic Coating for Platinum-Rhodium Thermocouples," *Combustion and Flame*, 14, pp. 279-282, 1970.

10. R.M. Fristrom and A.A. Westenberg (1965), *Flame Structure*, McGraw-Hill, New York, 1965.
11. S.M. Banna and M.C. Branch, "Gas Chromatographic Determination of Nitrogenous Species in Combustion Products," *Combustion Science and Technology*, 24, 15-22, 1978.
12. P.A. Bonczyk, A.C. Eckbreth, and J.F. Verdieck, "Combustion Diagnostics by Laser Raman and Fluorescence Techniques," *Progress in Energy and Combustion Science*, 5, pp. 253-322, 1979.
13. D.R. Crosley, Ed., "Laser Probes for Combustion Chemistry," *ACS Symposium Series 134*, American Chemical Society, Washington, D.C., 1979
14. A.C. Eckbreth, "Recent Advances in Laser Diagnostics for Temperature and Species Concentration in Combustion, *18th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 1471-1488, 1981.
15. L. Thorne, M.C. Branch, J.A. Miller and D. Chandler, "Interactions Between Nitrogen and Carbon Species in H_2/O_2 Laminar Premixed Flames," *21st Symposium (International) on Combustion*, Combustion Institute, Pittsburgh, pp. 965-977, 1988.
16. R.M. Green and J.A. Miller, "The Measurement of Relative Concentration Profiles of NH_2 Using Laser Absorption Spectroscopy," *J. Quant. Spectrosc. Radiat. Transfer*, 26, pp. 313-327, 1981.
17. Q.N. Le and M. Vanpee, "Free Radical Concentration Measurements in Nitric Oxide-Acetylene Flames," *Combustion and Flame*, 62, pp. 193-210, 1985.
18. R.J. Kee, J. Warnatz and J.A. Miller, "A Fortran Computer code Package for the Evaluation of Gas Phase Viscosities, Conductivities and Diffusion Coefficients," *SAND 83-8209*, Sandia National Laboratories, Livermore, CA, March 1983.
19. C.K. Westbrook and F.L. Dryer, "Chemical Kinetics Modeling of Hydrocarbon Combustion," *Progress in Energy and Combustion Science*, 10, pp. 1-57, 1984.
20. J. Vandooren, L. Oldenhove de Guer'echin and P.J. Van Tiggelen, "Kinetics in a Lean Formaldehyde Flame," *Combustion and Flame*, 64, pp. 127-139, 1986.
21. D.A. Lichtin, M.R. Berman and M.C. Lin, " $NH(A^3\Pi-X^3\Sigma^-)$ Chemiluminescence from the $CH(X^3\Pi) + NO$ Reaction," *Chem. Phys. Lett.*, 108, p. 18, 1984.
22. W.E. Kaskan and D.E. Hughes, "Mechanism of Decay of Ammonia in Flame Gases from an NH_3/O_2 Flame," *Combustion and Flame*, 20, p.381, 1973.
23. L.F. Philips, "Numerical Study of the Breakdown of Cyanogen in an $H_2/O_2/N_2$ Flame," *Combustion and Flame*, 26, p. 397, 1976.
24. J. Peeters and G. Mahnen, "Reaction Mechanisms and Rate Constants of Elementary Steps in Methane Oxygen Flames," *14th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 133-146, 1973.
25. J. Warnatz, "Rate Coefficients of the C/H/O System," *Combustion Chemistry*, edited by W.C. Gardiner, Jr., Springer Verlag, New York, 1984.

26. P. Guillaume and P.J. Van Tiggelen, "Spectroscopic Investigation of Acetylene-Nitrous Oxide Flames," *20th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 751-760, 1984.

VI. RECENT PUBLICATIONS FROM THIS AND PREVIOUS AFOSR SUPPORT

1. M.C. Branch, "Flame Structure Studies by Computer-Controlled Experiments and Numerical Modeling," *Computational Methods and Experimental Measurements*, Springer-Verlag, Berlin, 2, pp. 101-110, 1986.
2. Ke Nguyen and M.C. Branch, "Ignition Temperature of Bulk 6061 Aluminum, 302 Stainless Steel and 1018 Carbon Steel in Oxygen," *Combustion Science and Technology*, 53, pp. 277-277, 1987
3. M.C. Branch, M. Sadeqi and A. Alfarayedhi, "Laser Induced Fluorescence Measurements of the Structure of $\text{CH}_4/\text{NO}_2/\text{O}_2$ Flames," *Proceedings of the 2nd ASME/JSME Thermal Engineering Conference*, 1 pp. 181-186, 1987.
4. M.C. Branch, A. Alfarayedhi and M. Sadeqi, "Flame Structure and Reaction Kinetics of $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ Flames," *Combustion Symposium Joint Conference-Western States and Japanese Sections*, The Combustion Institute, Pittsburgh, pp. 5-7, 1987
5. M.C. Branch, "Chemical Kinetics of Nitramine Propellants," *Proceedings of the AFOSR/ONR Meeting on Combustion and Rocket Propulsion*, pp. 211-214, 1987.
6. M. Sadeqi and M.C. Branch, "Structure of Laminar Premixed Flames of $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ Mixtures," *Proceedings of the 24th JANNAF Combustion Meeting*, CPIA Pub. 426, 1, pp. 343-351, 1987.
7. L. Thorne, M.C. Branch, J.A. Miller and D. Chandler, "Interaction Between Nitrogen and Carbon Species in H_2/O_2 Laminar Premixed Flames," *Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 965-977, 1988.
8. M. Sadeqi and M.C. Branch, "A Continuous Flow, Gaseous Formaldehyde Generation System for Combustion Studies," *Combustion and Flame*, 71, pp. 325-29, 1988.
9. M.C. Branch, "Chemical Kinetics of Nitramine Propellant Combustion," *Proceedings of the AFOSR/ONR Meeting on Combustion, Rocket Propulsion and Diagnostics of Reacting Flow*, California Institute of Technology, pp. 71-74, 1988.
10. M.C. Branch, A. Alfarayedhi, M. Sadeqi and P.J. Van Tiggelen, "Measurements of the Structure of Laminar Premixed Flames of $\text{CH}_4/\text{NO}_2/\text{O}_2$ and $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ Mixtures," *Combustion and Flame*, under review.

VII. PERSONNEL

1. Abdulghani Al-Farayedhi, "Laser Induced Fluorescence Measurements of CH,

CN, NH, NH_2 and OH in $\text{CH}_4/\text{NO}_2/\text{O}_2$ and $\text{CH}_2\text{O}/\text{NO}_2/\text{O}_2$ Flames, "PhD Thesis, University of Colorado, Boulder, August, 1987. (Currently a Professor in the Mechanical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.)

2. Mohammed Sadeqi, "Structure of the Multiple Luminous Zones of Flames of CH_4 and CH_2O with NO_2 and O_2 ," PhD Thesis, University of Colorado, Boulder, August 1987. (Currently a Research Engineer at the Kuwait Institute of Scientific Research, Kuwait City, Kuwait.)
3. Faud Alasfour, "Measurements and Modeling of the Flame Structure of the Gas Phase Decomposition Products of Nitramine Propellants," PhD Thesis, University of Colorado, Boulder, expected May 1989.
4. Mohammed Habeebullah, "Laser Induced Fluorescence Spectroscopy of $\text{CH}_4/\text{N}_2\text{O}$ and $\text{CH}_2\text{O}/\text{N}_2\text{O}$ Flames," PhD Thesis, University of Colorado, Boulder, expected May 1989.
5. Abdelhak Daghouche, "Numerical Chemical Kinetic Modeling of Flame Structure of Fuel/Nitrogen Dioxide Flames," MS Thesis, University of Colorado, Boulder, expected December 1988.

VIII. INTERACTIONS

The research has benefited from close interaction with related investigations on H-C-N flame reactions at Sandia Laboratories, Livermore. Professor Branch is a member of the advisory group for the Combustion of Energetic Materials Group at Sandia and participated in a workshop on "Combustion Probes for Solid Nitramines" there in June, 1986.

Interaction with Edwards Air Force Base, California has been maintained. The studies at the Air Force Aerospace Laboratory at Edwards Air Force Base are providing data on the distribution of gas product species above the surface of solid rocket propellants, including nitramines. These are among the only studies of this type being conducted. Those studies and the studies we are conducting provide a unique combination of studies on the real propellant and on flames chemically representative of the propellant.

Formal presentations of results obtained in this study have included an oral progress report and abstract entitled "Chemical Kinetics of Nitramine Propellants" presented at the AFOSR/ONR meeting on Combustion, Rocket Propulsion and Diagnostics of Reacting Flow, June 1988 at the California Institute of Technology. Other presentations and publications from this AFOSR support are summarized in the section, RECENT PUBLICATIONS FROM THIS AND PREVIOUS AFOSR SUPPORT. Recent workshops and panels related to this research are listed below.

IX. WORKSHOPS AND PANELS

1. Combustion Probes for Solid Nitramines Workshop, Sandia National Laboratories, Livermore, June 1988.
2. JANNAF Gas Phase Reactions Workshop, Naval Postgraduate School, Monterey, October 1987.

3. AFOSR Solid Rocket Motor Instability Workshop, University of Colorado, Boulder, March 1988.
4. Kinetic and Related Aspects of Propellant Combustion Chemistry Panel, Johns Hopkins University, Laurel, May 1988.
5. ONR Meeting on Coordinated Investigation of New Nitramine Compounds, Princeton University, September 1988.