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Structure of Model Gas Flames in Nitramines

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The purpose of this paper is to summarize the current status of studies we have undertaken of model gas phase flames associated with the combustion of nitramine based solid rocket propellants. These studies consist of measurements of the structure of stable and unstable species concentration profiles and temperature in laminar, premixed, flat flames of fuel/NOx mixtures at low pressure. The experimental measurements are then compared to calculations of the concentration profiles using a one dimensional flame code which models the transport processes and chemistry of the flame. The transport processes include species diffusion and thermal conduction through the flame and the chemistry is modeled by a detailed chemical kinetic reaction mechanism. The flames which have been studied thus far are supplied with CH4, CH2O or CO as fuel and NO2, N2O or O2 as oxidizer. The overall characteristics of the flames are presented in the paper and the preliminary conclusions of the flame modeling are discussed.

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I. RESEARCH OBJECTIVES

The combustion of solid rocket propellants and other energetic materials is a complex multidimensional and multiphase process involving a wide variety of chemical species (1). The very high pressure and temperature conditions of practical rocket combustion chambers are at present inaccessible by most conventional diagnostic techniques. The study of these coupled phenomena in situ, therefore, has not been possible in sufficient detail to develop a complete understanding of the chemistry and physics of the combustion process. Æ been to study separate aspects of the overall process in an effort to provide a comprehensive understanding of the combustion mechanism. This study is one component of that coordinated investigation and has as its focus the gas phase reactions associated with the combustion of these solid fuels.

The decomposition of many of these solid energetic materials during combustion leads to the formation of gaseous hydrocarbon fuel species and oxides of nitrogen which serve as oxidizers. The reactions of these decomposition products above the propellant surface leads to a gaseous flame which can provide heat which is transferred back to the propellant surface and can thereby influence the burning rate. We have initiated a study of these gas phase reactions by investigating the structure of model flames under conditions which are idealized for the gas phase measurements. The compositions of the reactant species can be varied independently to study individual reactant systems which can then be integrated into an overall reaction system. Although the temperature of the model flames is near that of the propellant flames, it is necessary to conduct the flame studies at low pressure in order to have sufficient spatial resolution to resolve the chemical kinetic mechanism of the reaction.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The laminar, premixed, flat flames which were studied were stabilized on a 2 cm by 8 cm rectangular burner housed in a chamber evacuated to a pressure of 50 torr. The reactant gases, with the exception of formaldehyde, were supplied from gas cylinders and controlled by linear mass flow regulators. Formaldehyde cannot be supplied as a gas in a cylinder because of its extreme reactivity, particularly with itself, to form a solid polymer. Therefore, a continuous flow, monomeric, gaseous formaldehyde generator was developed and used for the study (2).

Flame measurements were made of the concentration of stable species and of selected intermediate species and of temperature through the reaction zone. Stable species were measured by a sampling microprobe and gas chromatographic analysis. Unstable species were measured by laser induced fluorescence and laser absorption using an excimer pumped dye laser system. The laser absorption results were used to calibrate the linear fluorescence concentration profiles. The gas temperature was determined by a BeO/Y_2O_3 coated Pt-Pt/13%Rh thermocouple corrected for radiation losses and by spectroscopic rotational temperature measurements.

The accuracy of the of the stable species composition measurements is approximately 8%, the accuracy of the unstable species measurements is estimated to be 20% and the accuracy of the temperature measurements is about 3%. 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 slits in the laser induced fluorescence collection system gives a position.Æ disturbance. A more detailed description of the experimental system is given in Reference 3.

III. RESULTS AND DISCUSSION

A. LAMINAR PREMIXED $CH_4/NO_2/O_2$ and $CH_2O/NO_2/O_2$ FLAMES

Flame Structure. Complete composition and temperature profiles were measured for three lean $CH_4/NO_2/O_2$ flames and two lean $CH_2O/NO_2/O_2$ flames and results from one flame in each group is given in Figure 1. 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 only 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 stages of the flame.

The flame profiles indicate that NO_2 is a much less effective oxidizer than N_2O or O_2 and much of the NO_2 remains unreacted in the burnt gas mixture. Mixtures with only CH_2O and NO_2 could not be stabilized and mixtures with only CH_4 and NO_2 could only bee stabilized in very lean mixtures with great difficulty. Small amounts of O_2 added rendered the reactant mixtures sufficiently stable that probe sampling became possible. Measurements of CH_4/O_2 and CH_2O/O_2 flames showed that the reaction rate with O_2 alone is much more rapid than with combinations of NO_2 and O_2 with the same stoichiometry. The profiles suggest that only one of the oxygen atoms in the NO_2 is available as an oxidizer with the other remaining bound in the NO.

There are significant differences in the final products in the methane and in 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 concentration is high and remains high in the burnt gas with formaldehyde even though the flames are lean whereas the H_2 is below the detection limit in the methane flame.

The intermediate species measured in the methane flame are CH, CN, NH, NH_2 and OH. All but the OH rise to a maximum and then decrease quickly in the reaction zone. The CH radical is observed earliest in the reaction zone and the profile has two peaks. In the formaldehyde flame only CN and OH were detected by the LIF system.

Reaction Mechanism. The reaction mechanism of the flames of CH_4 and CH_2O with

NO_2 and O_2 has been evaluated by calculating the reaction rates of the species measured in the flame and comparing these rates to those calculated for elementary reactions. In addition, calculations of the flame structure using a flame code (4) were compared to the experimental measurements. The reaction mechanism is based on the hydrocarbon reactions given in Warnatz (5) and the nitrogen reactionsÆ kinetic calculations and the associated sensitivity analysis provide a preliminary explanation of the major reaction pathways in the flame. Most aspects of the reaction mechanism are consistent with current understanding of methane and formaldehyde combustion. However there are a number of problems which are raised by the use of NO_2 as oxidizer which will be emphasized here.

The consumption of methane proceeds primarily by the sequence of reactions

$$\begin{aligned} CH_4 + R &= CH_3 + RH \\ CH_3 + O_2 &= CH2O + OH \end{aligned}$$

followed by the formaldehyde reactions

$$\begin{aligned} CH_2O + R &= HCO + RH \\ HCO + R &= CO + RH \end{aligned}$$

where R can represent H, O or OH. In addition, the CH3 radical from CH_4 can undergo a series of hydrogen abstractions to give CH. Note, however, that if CH_2O is the only fuel, no CH is produced because of the extreme difficulty of producing CH from HCO. Several aspects of the experimental results derive easily from this mechanism. The relative ease with which H_2 is formed in CH_2O flames arises from the importance of H in the CH_2O reactions above. The fact that no N_2 is formed in the CH_2O flames arises from the fact that CH reactions with NO or other nitrogen containing species to form N_2, as will be discussed below.

The reactions involving nitrogen species are rather more interesting. The consumption of NO_2 in many combustion systems is usually by reaction with H to form NO and OH. Likewise the most important reaction for CO oxidation is with OH to form CO_2 and H. These reactions are not sufficient to describe either the rate of consumption of NO_2 in the flames or the rate of conversion of CO to CO_2. It is necessary to add the reaction

$$NO_2 + CO = NO + CO_2 \qquad (1)$$

in order to improve the agreement between the calculated profiles and the flame data. The literature value of the rate constant cited in Table I was used (Reference 7). In addition, in order to calculate the N_2 formation which was observed, the reactions below were used

$$\begin{aligned} CH + NO &= (HCN + O) = NH + CO \\ NH + NO &= N_2 + OH \end{aligned}$$

This sequence in which CH is needed to form NO explains the absence of N_2 in the CH_2O flames; however, the literature values of rate constants for these reactions are not sufficiently

fast to give as much N_2 formation as observed in the CH_4 flames. The relative stability of NO also suggests why the flames with NO_2 require some small amount of O_2 for flame stabilization. The reaction of NO_2 with H is chain propagating whereas the reaction of O_2 with H is chain branching. This results in essentially only one oxygen atom being available as an oxidantÆ

B. LAMINAR PREMIXED CH_4/N_2O AND CH_2O/N_2O FLAMES

Flame Structure. Complete flame profiles were measured for three CH_4/N_2O flames and two CH_2O/N_2O flames and some representative data are given in Figure 2 for each fuel. With N_2O as oxidizer it was possible to stabilize flames under lean or rich conditions and the flames were generally much more stable than with NO_2. The N_2O was converted nearly completely to N_2 in rich or stoichiometric flames and there was also some formation of NO from N_2O in the post flame gases. It was likewise found in these flames that CO was produced as an intermediate and then converted partially to CO_2.

Several aspects of the flame structure were different depending on whether CH_4 or CH_2O was the fuel. With CH_2O as fuel there was rather more CO formed and there was again some H_2 formed even in the lean mixtures. With N_2O as oxidizer there was some NO measured in flames with both CH_4 and CH_2O. As will be discussed below, this is a result of the fact that N_2O can form NO directly even though N_2 is the primary decomposition product.

The measurements of the unstable species in the N_2O flames showed that there was again CH, CN, NH and OH in the CH_4 Flame but no CH was observed in the CH_2O flame. The OH profile persisted into the postflame gases whereas the other intermediates had a concentration maximum in the reaction zone. As with the NO_2 flames the CH peak was the first to occur in the N_2O flame.

Reaction Mechanism. The reaction mechanism for the N_2O flames was also evaluated by calculating the flame structure using the mechanism in Table I and comparing the results to the measured profiles. The preliminary reactions of CH_4 and CH_2O in this system are essentially the same as those for the NO_2 system. This mechanism again suggests that rather more CO will result from CH_2O because of the formation of HCO which reacts almost exclusively to form CO. The formation of H_2 from CH_2O is also more significant.

The reactions of the nitrogen containing species are dominated by

$$N_2O + H = N_2 + OH$$
$$N_2O + H = NO + NH$$

with the second reaction contributing no more than 5% to the total N_2O consumption. It was again found that the rate of consumption of the oxidizer and the rate of conversion of CO to CO_2 was not adequately represented unless the reaction

$$N_2O + CO = N_2 + CO_2 \qquad (2)$$

was added, again using literature values for the rate constant (Reference 8).

C. LAMINAR PREMIXED CO/N_2O FLAMES

The results discussed above suggest that a study of flames of CO with NO_2 and N_2O would be very useful for the understanding of the CH_4 and CH_2O flames. By studying these flames it would be possible to obtain data on the rate of the reaction of CO with both NO_2 and N_2O, reactions which are important in the systems described above and which have limited high temperature kinetic data currently available.

Another motivation for the study of the CO flames arises from the as yet unexplained presence of CN in the CH_2O flames. As discussed in describing the $CH_2O/NO_2/O_2$ and CH_2O/N_2O flames, no CH was expected or observed in the flame. The mechanism discussed above would also suggest that no CN should be found in the flame as well. The chemical kinetic path most often suggested for the formation of CN is by a reaction between CH and NO to form HCN followed by a reaction to form CN. From our experimental observations, however, it appears that there is a mechanism for the formation of CN from CH_2O without CH being present.

We have, therefore, established laminar premixed flat flames of CO with N_2O to which small amounts of CH_4 or CH_2O might be added. Laser induced fluorescence measurements in the pure CO/N_2O flame give no detectable fluorescence signal for CH or CN (or of NH, NH_2 or OH since no hydrogen was present). This suggests that the formation of CN in the CH_2O flames occurs before the fuel is converted to CO and most likely by reactions between HCO and NO or N_2O. Measurements with as little as 1% added CH_4 give a distinct CH peak followed by a CN peak in the reaction zone. Measurements with added CH_2O have not yet been completed.

IV. CONCLUSIONS

Low pressure, laminar, premixed flames of CH_4, CH_2O and CO have been stabilized with NO_2, N_2O and O_2 as oxidizer, the flame structure measured and the reaction mechanism discussed. 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 rather slowly and incompletely to NO and much of the NO_2 remains unreacted in the burnt gas. In flames with NO_2 and CH_4, some reduction of NO to N_2 was possible because of the reaction of CH with NO. In flames with NO_2 and CH_2O no CH is formed so that no molecular nitrogen is detected. In flames with N_2O as oxidizer both N_2 and NO are produced from the reaction of N_2O with H atoms. The reaction mechanism presented is capable of explaining all the experimental observations except the presence of CN in the CH_2O flames. Measurements on flames of CO and N_2O suggest that this species results from a reaction between HCO and NO or N_2O.

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VI. RECENT PUBLICATIONS FROM THIS AND PREVIOUS AFOSR SUPPORT

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VII. PERSONNEL

1. Abdulghani Al-Farayedhi, "Laser Induced Fluorescence Measuremenets of CH, CN, NH, NH2 and OH in CH4/NO2/O2 and CH2O/NO2/O2 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 CH4 and CH2O with NO2 and O2," **PhD Thesis**, University of Colorado, Boulder, August 1987. (Currently a Research Engineer at the Kuwait Institute of Scientific Research.)

3. Faud Alasfour, "Structure and Kinetics of Flames of Methane and Formaldehyde with Nitrous Oxide," **Phd Thesis**, University of Colorado, Boulder, May 1989. (Currently a Professor in the Mechanical Engineering Department at Kuwait University, Kuwait City, Kuwait.)

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5. Abdelhak Daghouche, "Modeling of the Structure and Kinetics of CH4/NO2/O2 and CH2O/NO2/O2 Flames," **MS Thesis**, University of Colorado, Boulder, August 1989.

VIII. 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.

6. ARO Meeting of Combustion of Energetic Materials, Picatinny Arsenal, New Jersey, June 13-14, 1989.

Table I

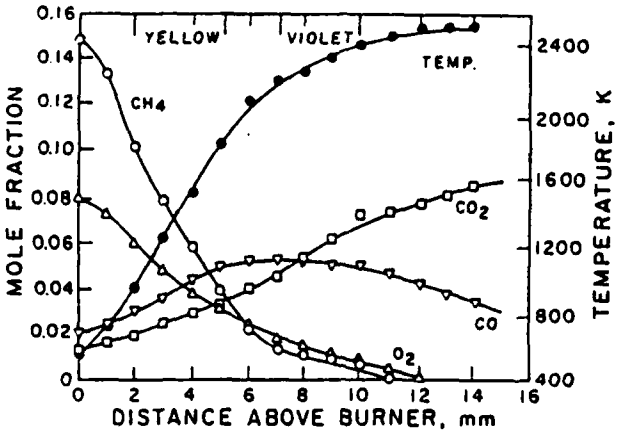
Combined Reaction Mechanism for $CH_4/NO_2/O_2$ and $CH_2O/NO_2/O_2$ flames. Rate Coefficients are in the form $K(T) = AT^n \exp[-E/(RT)]$. The units are moles, cm^3, seconds, K, and cal/mole.

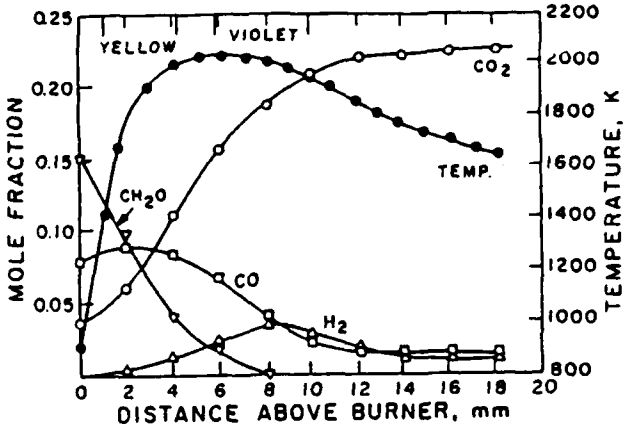
No.	REACTION	A	n	E	Ref.
1	$CH_3 + H + M = CH_4 + M$	8.00E+26	-3.00	0.0	3
2.	$CH_4 + O_2 = CH_3 + HO_2$	7.90E+13	0.00	56000.0	3
3	$CH_4 + O = CH_3 + OH$	1.20E+07	2.10	7620.0	1
4.	$CH_4 + H = CH_3 + H_2$	2.20E+04	3.00	8750.0	3
5	$CH_4 + OH = CH_3 + H_2O$	1.60E+06	2.10	2460.0	3
6	$CH_4 + HO_2 = CH_3 + H_2O_2$	1.80E+11	0.00	18700.0	3
7.	$CH_3 + O_2 = CH_2O + H + O$	1.50E+13	0.00	28680.0	1
8.	$CH_3 + HO_2 = CH_3O + OH$	2.00E+13	0.00	0.0	3
9	$CH_3 + O_2 = CH_3O + O$	2.05E+19	-1.57	29229.0	3
10	$CH_3 + O = CH_2O + H$	8.00E+13	0.00	0.0	3
11	$CH_3 + NO = NH + CH_2O$	6.00E+11	0.00	0.0	8
12.	$CH_3 + OH = CH_2 + H_2O$	7.50E+06	2.00	5000.0	3
13	$CH_3 + H = CH_2 + H_2$	9.00E+13	0.00	15100.0	3
14	$CH_3 + NO = HCN + H_2O$	1.00E+11	0.00	15000.0	3
15.	$CH_3O + M = CH_2O + H + M$	1.00E+14	0.00	25000.0	3
16.	$CH_3O + H = CH_3 + OH$	1.00E+14	0.00	0.0	3
17.	$CH_3O + H = CH_2O + H_2$	2.00E+13	0.00	0.0	3
18.	$CH_3O + OH = CH_2O + H_2O$	1.00E+13	0.00	0.0	3
19.	$CH_3O + O = CH_2O + OH$	1.00E+13	0.00	0.0	3
20.	$CH_3O + O_2 = CH_2O + HO_2$	1.00E+14	0.00	7600.0	1
21	$CH_2O + M = HCO + H + M$	3.31E+16	0.00	81000.0	3
22.	$CH_2O + M = CO + H_2 + M$	5.05E+16	0.00	71940.0	7
23	$CH_2O + OH = HCO + H_2O$	1.81E+13	0.00	437.0	2
24	$CH_2O + O = HCO + OH$	5.00E+13	0.00	4600.0	4
25	$CH_2O + H = HCO + H_2$	1.00E+14	0.00	4927.7	2
26	$CH_2O + HO_2 = HCO + H_2O_2$	1.00E+12	0.00	9338.0	2
27	$HCO + O = CO_2 + H$	3.00E+13	0.00	0.0	1
28	$HCO + OH = CO + H_2O$	5.00E+13	0.00	0.0	1
29	$HCO + H = CO + H_2$	2.00E+14	0.00	0.0	1
30	$HCO + O = CO + OH$	3.00E+13	0.00	0.0	1
31	$HCO + M = CO + H + M$	5.00E+12	0.00	19120.0	1
32	$HCO + O_2 = CO + HO_2$	3.00E+12	0.00	0.0	1
33	$CO + OH = CO_2 + H$	1.51E+07	1.30	-758.0	3
34	$CO + HO_2 = CO_2 + OH$	3.46E+12	0.00	8196.0	2
35	$CO + O + M = CO_2 + M$	6.17E+14	0.00	3000.0	3
36	$CO + O_2 = CO_2 + O$	2.50E+12	0.00	47800.0	1
37	$CO + CO + O = CO_2 + CO$	5.30E+13	0.00	4541.0	1
38	$CO + H + H_2 = HCO + H_2$	6.90E+14	0.00	1673.0	1
39	$NO_2 + M = NO + O + M$	4.67E+18	-1.50	72000.0	5
40	$NO_2 + H = NO + OH$	3.50E+14	0.00	1500.0	3
41	$NO_2 + O = NO + O_2$	1.00E+13	0.00	600.0	3
42	$HO_2 + NO = NO_2 + OH$	2.11E+12	0.00	-479.0	3
43	$NO_2 + CO = CO_2 + NO$	1.20E+13	0.00	31600.0	6
44	$H_2 + O_2 = OH + OH$	1.70E+13	0.00	47780.0	3
45	$OH + H_2 = H_2O + H$	1.17E-09	1.30	3626.0	3
46	$O + OH = O_2 + H$	4.00E+14	-0.50	0.0	3
47	$O + H_2 = OH + H$	5.06E-04	2.67	6290.0	3
48.	$OH + HO_2 = H_2O + O_2$	7.50E-12	0.00	0.0	3
49.	$H + HO_2 = OH + OH$	1.40E+14	0.00	1073.0	3
50.	$O + HO_2 = O_2 + OH$	1.40E+13	0.00	1073.0	3
51	$OH + OH = O + H_2O$	6.00E-08	1.30	0.0	3
52.	$2H + M = H_2 + M$	1.00E-18	-1.00	0.0	3
53.	$H + H + H_2 = H_2 + H_2$	9.20E-16	-0.60	0.0	3
54.	$H + H + H_2O = H_2 + H_2O$	6.00E-19	-1.25	0.0	3
55.	$H + H + CO_2 = H_2 + CO_2$	5.49E-20	-2.00	0.0	3
56.	$H + OH + M = H_2O + M$	1.60E-22	-2.00	0.0	3
57	$H + O + M = OH + M$	6.20E-16	-0.60	0.0	3
58.	$2O + M = O_2 + M$	1.89E-13	0.00	-1788.0	3
59.	$H + HO_2 = H_2 + O_2$	1.25E-13	0.00	0.0	3
60	$HO_2 + HO_2 = H_2O_2 + O_2$	2.00E-12	0.00	0.0	3
61.	$H_2O_2 + M = OH + OH + M$	1.30E-17	0.00	45500.0	3
62.	$H_2O_2 + H = HO_2 + H_2$	1.60E-12	0.00	3800.0	3
63.	$H_2O_2 + OH = H_2O + HO_2$	1.00E-13	0.00	1800.0	3
64.	$CH_2 + H = CH + H_2$	1.00E+18	-1.56	0.00	3
65.	$CH_2 + OH = CH + H_2O$	1.13E-07	2.00	3000.0	3
66.	$CH_2 + OH = CH_2O + H$	2.50E+13	0.00	0.0	3
67	$CH_2 + CO_2 = CH_2O + CO$	1.10E+11	0.00	1000.0	3
68.	$CH_2 + O = CO + 2H$	5.00E+13	0.00	0.0	3
69	$CH_2 + O = CO + H_2$	3.00E+13	0.00	0.0	3
70.	$CH_2 + O_2 = CO_2 + 2H$	1.60E+12	0.00	1000.0	3
71	$CH_2 + O_2 = CH_2O + O$	5.00E+13	0.00	0.0	3
72	$CH_2 + O_2 = CO_2 + H - 2$	6.90E+11	0.00	500.0	3
73	$CH_2 + O_2 = CO + H_2O$	1.90E+10	0.00	-1000.0	3
74	$CH_2 + O_2 = HCO + OH$	4.30E+10	0.00	-500.0	3
75	$CH_2 + CH_4 = CH_3 + CH_3$	4.00E+13	0.00	0.0	3
76	$CH_2 + O_2 = CO + OH + H$	3.00E+13	0.00	0.0	3
77	$CH_2 + N_2 = HCN + NH$	1.00E+13	0.00	74000.0	3
78	$CH_2 + NO = HCN + OH$	2.00E+13	0.00	0.0	3
79	$CH_2 + N = HCN + H$	5.00E+13	0.00	0.0	3
80	$CH + O_2 = HCO + O$	3.30E+13	0.00	0.0	3
81	$CH + O = CO + H$	5.70E+13	0.00	0.0	3
82	$CH + OH = HCO + H$	3.00E+13	0.00	0.0	3
83	$CH + CO_2 = HCO + CO$	3.40E+12	0.00	690.0	3
84	$CH + H = C + H_2$	1.50E+14	0.00	0.0	3
85	$CH + H_2O = CH_2O + H$	4.57E+14	-0.75	0.0	3
86	$CH + N_2 = HCN + N$	2.00E-11	0.00	13600.0	3
87	$CH + NO = HCN + O$	1.10E+14	0.00	0.0	3
88	$CH + N = CN + H$	1.30E+13	0.00	0.0	3
89	$CO_2 + N = NO + CO$	1.90E+11	0.00	3400.0	3
90	$HCN + OH = CN + H_2O$	1.45E+13	0.00	10929.0	3
91	$HCN + O = NCO + H$	1.38E+04	2.64	4980.0	3
92	$HCN + O = NH + CO$	3.45E+03	2.64	4980.0	3

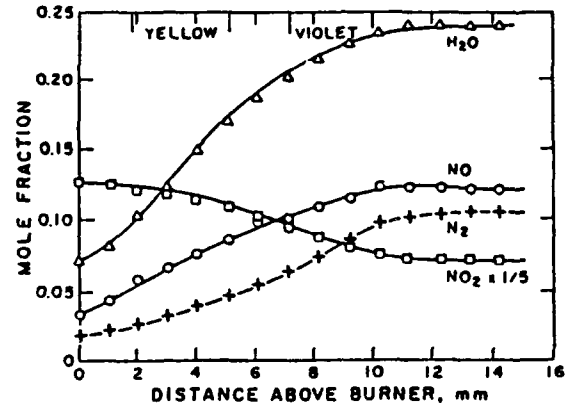
Table I (cont.)

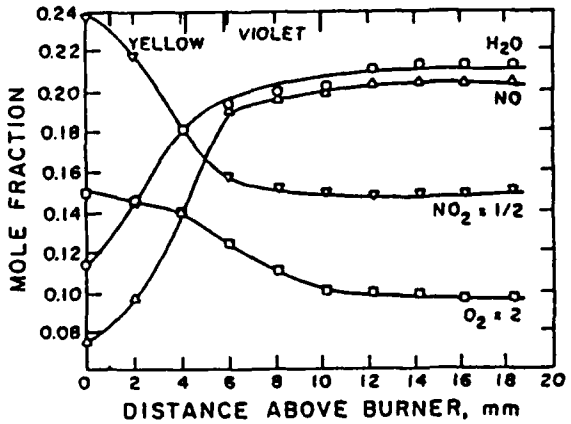
No.	REACTION	A	n	E	Ref.
93	$HCN + O = CN + OH$	2.70E+09	1.58	29200.0	3
94	$CN + H_2 = HCN + H$	2.95E+05	2.45	2237.0	3
95	$CN + O = CO + N$	1.80E+13	0.00	0.0	3
96	$CN + O_2 = NCO + O$	5.60E+12	0.00	0.0	3
97	$CN + OH = NCO + H$	6.00E+13	0.00	0.0	3
98	$CN + NO_2 = NCO + NO$	3.00E+13	0.00	0.0	3
99	$CN + N2_O = NCO + N_2$	1.00E-13	0.00	0.00	3
100	$NCO + H = NH + CO$	5.00E-13	0.00	0.0	3
101	$NCO + O = NO + CO$	2.00E-13	0.00	0.0	3
102	$NCO + N = N_2 + CO$	2.00E+13	0.00	0.00	3
103	$NCO + OH = NO + CO + H$	1.00E+13	0.00	0.0	3
104.	$NCO + M = N + CO + M$	3.10E+16	-0.50	48000.0	3
105	$NCO + H2 = HNCO + H$	8.58E+12	0.0	9000.0	3
106	$NCO + NO = N_2O + CO$	1.00E+13	0.00	-300.0	3
107	$NH + O_2 = HNO + O$	1.00E+13	0.00	12000.0	3
108	$NH + O_2 = NO + OH$	7.60E+10	0.00	1530.0	3
109.	$NH + NO = N_2O + H$	2.40E+15	-0.80	0.0	3
110	$NH + OH = HNO + H$	2.00E+13	0.00	0.0	3
111	$NH + OH = N + H_2O$	5.00E+11	0.50	2000.0	3
112	$NH + N = N_2 + H$	3.00E+13	0.00	0.0	3
113	$NH + H = N + H_2$	1.00E+14	0.00	0.0	3
114	$NH + NO = N_2 + OH$	2.40E+15	-0.80	0.0	3
115	$N_2O + M = N_2 + O + M$	1.60E+14	0.00	51600.0	3
116	$N_2O + OH = N_2 + HO_2$	2.00E+12	0.00	10000.0	3
117	$N_2O + H = N_2 + OH$	7.60E+13	0.00	15200.00	3
118	$N_2O + O = N_2 + O_2$	1.00E+14	0.00	28200.00	3
119	$N_2O + O = NO + NO$	1.00E+14	0.00	28200.00	3
120	$HNO + HNO = N_2O + H_2O$	3.95E+12	0.00	5000.0	3
121	$HNO + NO = N_2O + OH$	2.00E+12	0.00	26000.0	3
122	$HNO + M = H + NO + M$	1.50E+16	0.00	48680.0	3
123	$HNO + H = H_2 + NO$	5.00E+12	0.00	0.0	3
124	$N + NO = N_2 + O$	3.27E+12	0.30	0.0	3
125	$N + O_2 = NO + O$	6.40E+09	1.00	6280.0	3
126	$N + OH = NO + H$	3.80E+13	0.00	0.0	3

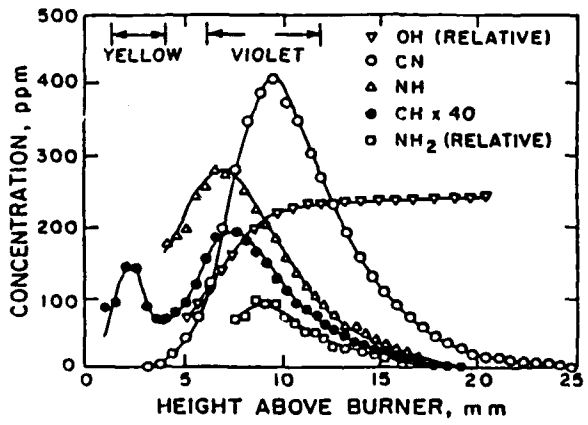
1. Gardiner, W.C. (1984)
2. Vandooren *et al.* (1986)
3. Miller and Bowman (1988)
4. Pitz et al. (1984)
5. Hiraoka and Hardwick (1963)
6. Milks and Matula (1972)
7. Dean *et al.* (1978)
8. Suggested reaction











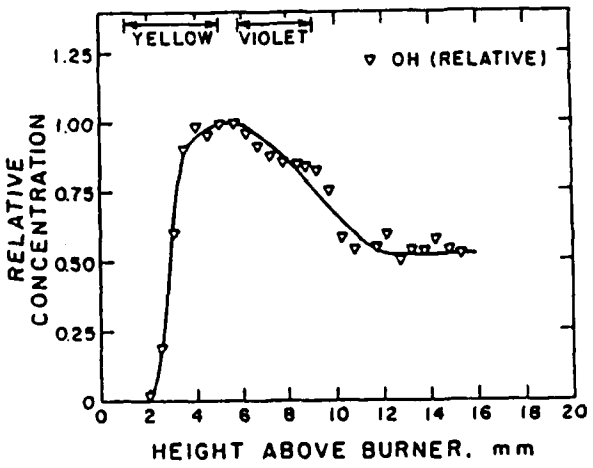


Figure 1A: Composition of stable species and temperature (upper graphs) and unstable species (lower graph) measured in a lean, laminar, premixed $CH_4/NO_2/O_2$ flame at 55 torr. The reactant mole fractions are 0.16 CH_4, 0.73 NO_2, and 0.11 O_2. The total flowrate is 2.19 standard liters per minute.

Figure 1B: Composition of stable species and temperature (upper graphs) and unstable species (lower graph) measured in a lean, laminar, premixed $CH_2O/NO_2/O_2$ flame at 55 torr. The reactant mole fractions are 0.247 CH_2O, 0.627 NO_2, and 0.126 O_2. The total flowrate is 2.15 standard liters per minute.

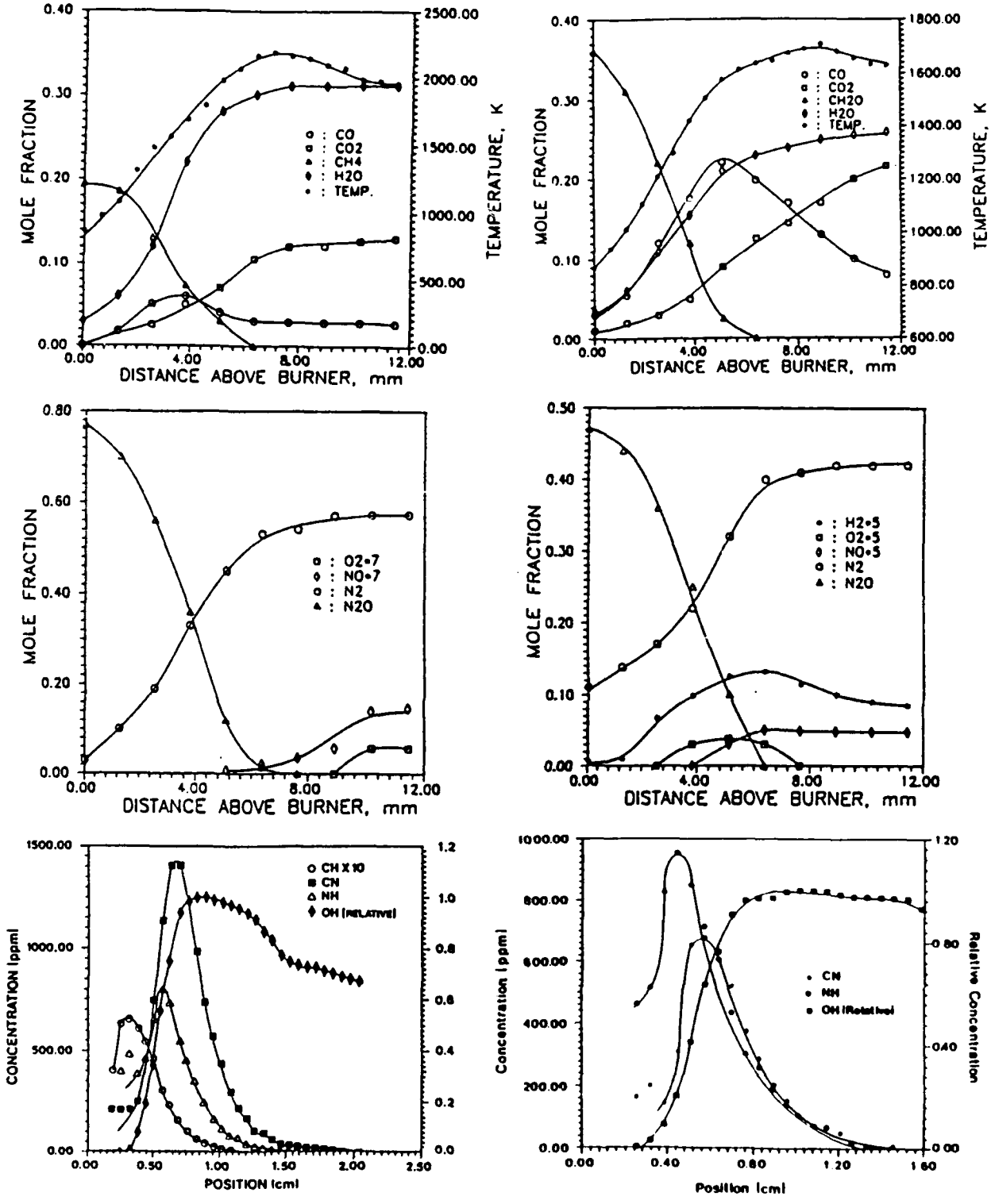


Figure 2A: Composition of stable species and temperature (upper graphs) and unstable species (lower graph) measured in a laminar, premixed CH_4/N_2O flame at 50 torr. The reactant mole fractions are 0.21 CH_4 and 0.79 N_2O. The total flowrate is 2.18 standard liters per minute.

Figure 2B: Composition of stable species and temperature (upper graphs) and unstable species (lower graph) measured in a laminar, premixed CH_2O/N_2O flame at 50 torr. The reactant mole fractions are 0.43 CH_4, 0.57 N_2O. The total flowrate is 2.01 standard liters per minute.