JOURNAL OF PROPULSION AND POWER
Vol. 11, No. 4, July–August 1995

Structure and Chemical Kinetics of Flames Supported by Solid Propellant Combustion

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The structure and chemical kinetics of gaseous flames are important aspects of the combustion of solid propellants. Advanced diagnostics have led to specific knowledge of solid propellant decomposition products, and advanced computer programs have allowed detailed chemical kinetic modeling of these products reacting with each other. There has therefore been considerable effort aimed at measuring and modeling the structure of premixed gas flames of fuels and oxidizers representative of the chemistry occurring in actual solid propellants. Most of the recent modeling work for representative gaseous flames can be traced to a mechanism first developed to model air pollution. Comprehensive mechanisms have also been developed to model the entire gas-phase chemistry process above burning propellant surfaces. These comprehensive mechanisms also are largely traceable to the air pollution modeling mechanism. Russian researchers have also made significant advances in the comprehensive modeling of solid propellant flame structures. Overall, the current state of knowledge of the gas-phase structure of solid propellants is incomplete, but encouraging agreement exists between modeling and experimental data. Recommendations are made for additional flame and reaction studies and for a standard mechanism to use in all gaseous flame modeling.

I. Introduction

THE combustion of solid rocket propellants involves a variety of complex, multiphase, and multidimensional processes. Included among these processes is the gas-phase chemistry occurring above the propellant surface. This gas-phase chemistry can involve one-dimensional premixed flames of monopropellant decomposition products, multidimensional diffusion flames of fuel and oxidizer decomposition products, or any combination in between. The structure and chemical kinetics of gaseous flames are important because they produce the bulk of the energy release of the propellant, and set up the temperature gradient at the propellant surface, which is crucial to determining the rate of heat feedback to the condensed phases.

Due to the complex nature of solid propellant combustion, different aspects of it, including the gas-phase chemistry, must be studied separately and then integrated into an overall combustion model. An understanding of the gas-phase chemistry needs to be developed in a systematic manner, with data obtained from several different sources. Yetter et al.[1] described the hierarchical approach needed for gaseous flame studies. The first tier of data required is from shock tubes and flow reactors, to validate gas-phase kinetics and ignition. The second tier of data required is from studies of premixed flames, which are used to validate gas-phase kinetic mechanisms as they affect one-dimensional heat release and flame speeds. Premixed flame studies can also show how kinetic mechanisms are affected by transport processes, as demonstrated by Martin and Brown,[2] who showed a dramatic difference in species concentration profiles modeled in premixed flames, where diffusion and thermal conduction effects are included, vs plug flow reactors, where these physical effects do not matter. The final tier of data required is from diffusion flames, in which mechanisms can be validated in an environment involving multidimensional transport processes and flame extinction. A review of studies related to shock tubes and flow reactors is presented by Yetter and Dryer.[3] A review of diffusion flame studies is presented by Smooke and Prasad.[4] This article will review the second tier of gas-phase kinetic studies, those related to one-dimensional, steady-state flame chemistry.

A review will be made of the current knowledge of the decomposition products from burning solid propellant surfaces. This knowledge motivates the mechanistic studies that are undertaken for gaseous flames. A review will then be presented of the early gaseous flame studies that were relevant to solid propellant combustion. The computer codes CHEMKIN[5] and PREMIX,[6] which are used in detailed flame modeling, will be described. More recent mechanistic studies, including the mechanism developed by Miller and Bowman,[7] and studies that have built upon this mechanism, will then be covered. Next, the comprehensive mechanisms of Melius[8,9] and Yetter and Dryer,[10] which can model the entire gas-phase combustion process occurring above actual solid propellant surfaces, will be reviewed. The comprehensive mechanisms which Russian researchers have developed will be reviewed as well. Finally, conclusions regarding the present state of understanding of solid propellant gas-phase chemistry and areas requiring further study will be presented.

II. Propellant Gas-Phase Decomposition Products

Relevant gas-phase flame studies should involve fuels and oxidizers that are actual solid propellant decomposition products, or fuels and oxidizers that have representative chemistry of burning solid propellants. To this end, information is needed on the primary and secondary decomposition products of solid propellants. Briefly reviewed here is knowledge about this structure that has been gained from experimental and modeling studies. A detailed review of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) decomposition structure is presented by Brill.[11]

Lengellé et al.[12] stated that NO_2, aldehydes, and NO are produced at the surface of double-base propellants. It was also stated that under 100 atm, a primary flame exists involving NO_2–aldehyde reactions and a secondary flame exists involving NO–CO and NO–H_2 reactions. Fifer[13] stated that in nitrate–ester propellants, an initial flame (fizz) zone con-

Received Aug. 6, 1994; revision received Nov. 30, 1994; accepted for publication Dec. 21, 1994.

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sists of NO_2–aldehyde reactions, which is followed by a flame zone consisting of the oxidation of NO, possibly by formaldehyde.

Kishore and Giayathri[14] identified decomposition products at the surface of burning ammonium perchlorate (AP) propellants as NH_3 and $HClO_4$. Subsequent reactions were described as leading to the formation of N_2, NO, H_2O, HCl, Cl_2, O_2, and other products. Korobeinichev[15] also identified the initial decomposition products from AP to be NH_3 and $HClO_4$.

Fifer[13] reported that the following species have been detected above burning nitramine surfaces: CO_2, NO, H_2O, N_2O, CO, C_2, CN, H_2, NO_2, N_2, HCN, HCHO, and HCOOH. Brill[16] identified N_2O and NO_2 as preceding all other species from the surface of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and also identified HCN and CH_2O as important gas-phase reactants. In addition to these species, Alexander et al.[17] identified HCO, H_2CNNO_2, H_2CN, HNO, H_2CNH, H, HCNO, HNO_3, NCO, O, and NO_3 as important reactants in a conceptual mechanism for the burning of RDX propellants. Parr and Parr[18] have recently measured the species NO, NO_2, CN, NH, H_2CO, and OH above a deflagrating RDX surface.

Modeling work by Melius[8] suggested that the gas-phase chemistry for RDX decomposition follows the reaction paths shown in Fig. 1. This figure, derived from the work of Melius,[8] shows species production and destruction pathways at their general order of sequence above the propellant surface. Most of the already-mentioned species measured above RDX surfaces[13,16–18] can be seen, although some (e.g., HOCN and CH_2NNO_2) have never been experimentally confirmed. This figure also shows the importance of various hydrogen and hydrocarbon reactions with nitrogen oxides.

Yetter et al.[1] identified model flames of various fuels and oxidizers whose study would provide insight into different aspects of gas-phase RDX flame chemistry. The model fuels identified were C_2H_4, CH_4, CH_2O, HCN, CO, NH_3, H_2O, and H_2, and the model oxidizers identified were NO_2, NO, and N_2O. While some of these fuel-oxidizer reactions may not occur in large quantities above an RDX propellant's surface, their chemistry is representative of RDX flame chemistry. For instance, ammonia was cited as an important fuel to study, because it is a source of NH_2 and NH radicals, which Fig. 1 shows as important unstable intermediates.

The detailed gaseous flame studies reviewed in the article all involve fuels and oxidizers that were suggested by Yetter et al.,[1] and therefore, have the greatest relevance to nitramine combustion. Mechanisms have been developed that can model these fuel-oxidizer systems, and are studied with the goal of validating them, as well as pointing out key reactions needing isolated kinetic study, so that these mechanisms can be used in comprehensive solid propellant combustion models.

III. Flame Codes for Modeling Propellant Gas-Phase Chemistry

Most propellant flame studies involving detailed modeling use the CHEMKIN and PREMIX flame codes, developed by

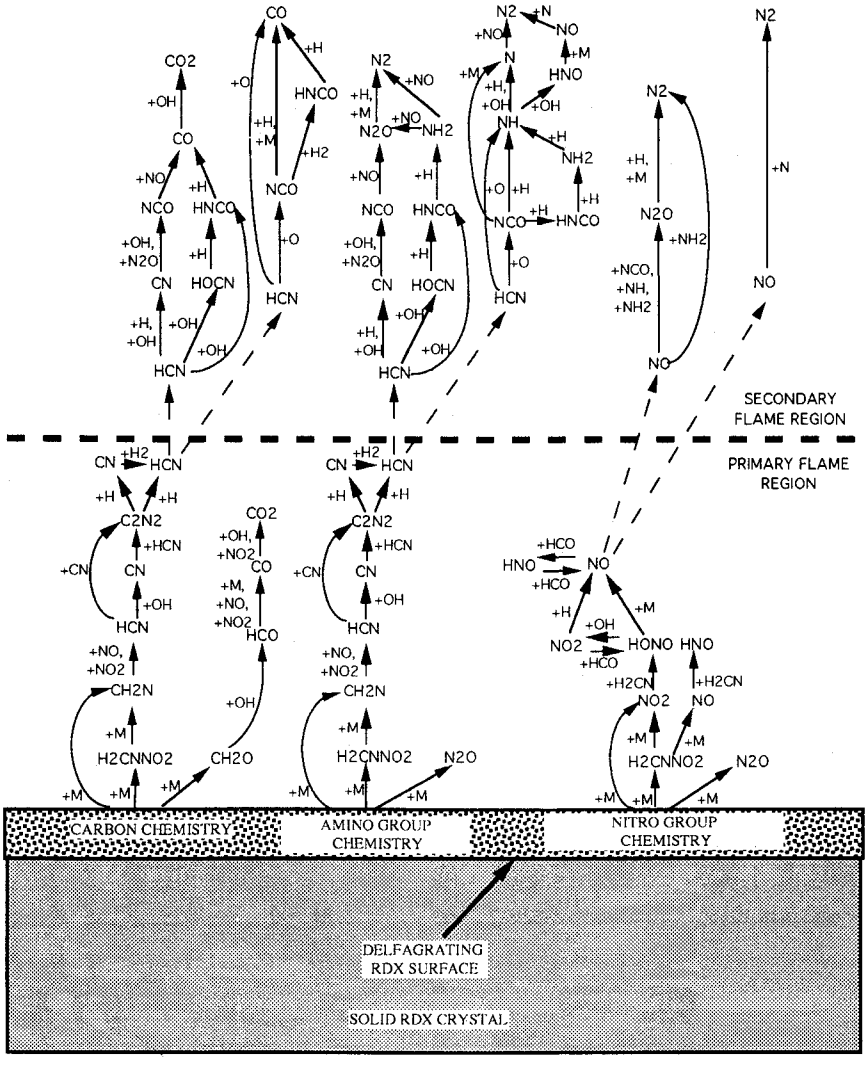

Fig. 1 Nitramine gas-phase chemistry based upon the modeling work of Melius.[8,9]

Sandia National Laboratories. These two codes are representative of a number of computer programs that have been developed to enable researchers to model detailed flame chemistry.

The CHEMKIN code takes a user-supplied chemical kinetic mechanism, thermodynamic properties, and transport properties and calculates all chemical kinetic parameters, thermodynamic variables, and transport variables needed in modeling gas-phase chemistry. The PREMIX one-dimensional flame code uses the CHEMKIN output, along with the chemical kinetic mechanism and user-supplied boundary conditions, as its input. It then uses the species, energy, and mass conservation equations to calculate the flame's species, temperature, and velocity profiles. The conservation equations are solved on a one-dimensional grid that is refined until differences between all solution variables are sufficiently small between grid points to meet the user-defined numerical accuracy. The flame can either be freely propagating or burner stabilized. For burner-stabilized flames, the option also exists to use a measured temperature profile as input to PREMIX, in which case the energy equation is not solved for, and the temperature profile is used to solve for the species and mass conservation equations. Most of the studies described in this review used this fixed-temperature option of PREMIX.

PREMIX is also used with postprocessing subroutines that perform rate-generation and sensitivity analyses. Rate-generation analysis identifies which chemical reactions are dominant in producing or consuming a species at different locations in a flame. Sensitivity analysis identifies the reactions that influence the predicted concentration of a species most significantly through the flame. Frequently, a species is found to be sensitive to a reaction that does not directly produce or consume it. A species might be sensitive, for instance, to a reaction producing a radical present in subsequent reactions that directly produce or consume the species. Rate generation and sensitivity analyses are powerful tools used to determine key reactions in flame mechanisms, and help guide mechanistic development in cases where measured and modeled data differ.

IV. Mechanistic Studies of Propellant Gas-Phase Chemistry

A large number of model gaseous flame studies have been done on fuels burning with nitrogen oxides. For the major studies reviewed here, the fuels were methane, hydrogen, acetylene, formaldehyde, carbon monoxide, ammonia, and hydrogen cyanide, and the oxidizers were NO, NO_2, and N_2O. All these reactants have been identified as decomposition products for different solid propellant systems[8,12-18] or have been specifically identified as appropriate fuels and oxidizers for nitramine-related flame studies.[1] Oxygen has sometimes also been used as an oxidizer for comparison to the more complex nitrogen chemistry. Modeling results have been compared to measurements taken in these flames to test the accuracy of current mechanisms.

At the same time that these representative gaseous flame studies have been undertaken, there have been efforts of a comprehensive nature in which large mechanisms have been used to model the entire gas-phase chemistry occurring above solid propellant surfaces. These modeling results have also been compared to experimental data. Two comprehensive mechanisms that have been used to model nitramine gas-phase chemistry are the mechanisms of Melius[8,9] and Yetter and Dryer.[10] There have also been independent efforts by Russian researchers aimed at comprehensive modeling of gas-phase chemistry in AP and nitramine propellants.

In this section, early flame studies that were undertaken prior to the advent of advanced diagnostic techniques, but whose data could nonetheless be useful in validating modern mechanisms, will be reviewed. The flame mechanism of Miller and Bowman,[7] whose development has been made possible by modern experimental and modeling tools, will be described. Recent modeling studies of propellant flames that have drawn extensively on the work of Miller and Bowman[7] will be reviewed. The comprehensive mechanisms of Melius[8,9] and Yetter and Dryer[10] will also be discussed. Finally, the comprehensive modeling work of Russian researchers will be reviewed. It is noted that all studies in this review involve premixed flames, and are thus strictly applicable to monopropellant combustion problems. Inclusion of binder effects requires a two-dimensional treatment of flame chemistry, which is covered in the work by Smooke and Prasad.[4]

A. Early Studies of Nitrogen Oxide Flames

There is a large body of data relevant to solid propellant flame chemistry that goes back to the late 1940s. These early works contained no detailed chemical kinetic flame modeling and often involved reactants that are nonideal for modern solid propellant combustion research. However, some studies provided measurements of product flame temperatures and species, and some even contained species concentration and temperature profiles. Furthermore, these early studies contained measurements of flame speeds that are not available in any modern studies. The complete tabulation of these early data and determination of their relevance to more recent mechanistic studies would be a prodigious task, but it would be of significant value to the combustion community. A tabulation of references for many of the prominent studies from the late 1940s to the mid 1960s is presented Table 1. Space precludes inclusion of all the equally valuable, but generally more well-known, studies from the 1970s and 1980s. Data from some of these more recent studies have been referenced in the validation of the mechanistic work described later in this article.

B. Miller and Bowman[7] Mechanism

Most recent research in the area of solid propellant gas-phase chemistry has involved flames that have been modeled with mechanisms closely related to or derived from the mechanism of Miller and Bowman.[7] Miller and Bowman proposed a 234-reaction basic mechanism, which had a 73-reaction submechanism specifically applicable to ammonia combustion. It was derived from a body of previous work by Miller and coworkers.[19-24] The mechanism was largely developed for the purpose of predicting the concentrations of various compounds of nitrogen formed as the result of air pollution. As such, it was devised for an environment where only small amounts of nitrogen oxides exist, being formed from oxidation of atmospheric N_2, or oxidation of the small amounts of nitrogen compounds bound in coal and coal-derived fuels. This mechanism was validated by comparing its predictions to a large amount of experimental data for flames and well-stirred reactors. The comparisons to flame data are reviewed here.

The formation of "prompt" NO, produced from radical attack on N_2, was studied by comparing modeling results to measurements made by Blauwens et al.[25] in an 18.5-torr C_2H_4–O_2–N_2 flame, with a stoichiometry ϕ of 0.97. Discrepancies found between modeling and measurements were attributed to the reaction CH + N_2 = HCN + N. Of greater significance to propellant chemistry were tests of the mechanism's ability to model the conversion of HCN to NO. To do this, modeling results were compared to measurements made by Miller et al.[19] in 25-torr H_2–O_2–Ar flames (ϕ = 0.5, 1.0, 1.5) to which trace amounts of HCN were added. The agreement between measurements and modeling was almost exact for HCN, and within about 30% for NO. Sensitivity analysis showed that HCN removal is dominated by reaction with O radicals, with reaction with OH radicals becoming significant only under highly fuel-rich conditions. The converse process of NO conversion to HCN and then N_2 was studied by comparing modeling results to measurements made by Thorne et al.[21] for two 25-torr H_2–O_2–Ar flames (ϕ = 1.5), which were doped with

Table 1 Early propellant flame studies

Reference	Flames studied	Experimental techniques	Data reported
50, 59	H_2, NH_3, hydrocarbons, CO and CS_2 reacting with NO, NO_2, and N_2O NO decomposition	Visual observation Line reversal Spectroscopic obervation	Emission spectra Temperatures Flame speeds Quenching diameters Flame appearance
60, 61	CH_3ONO $CH_3ONO-NO$ CH_3ONO-N_2O $CH_3ONO-CH_3OH$	Spectroscopic observation Fischer titration method Thermocouple	Temperatures profiles Species concentration profiles Combustion products Burning velocity
62	CH_3ONO	Thermocouple Fractional condensation	Burning velocities Final flame temperature Combustion products
63	CH_3ONO_2 $CH_3ONO_2-O_2$ $CH_3ONO_2-NO_2$ CH_3ONO_2-NO	Spectroscopic observation	Flame appearance Emission spectra Quenching diameter
64	HNO_3–hydrocarbons	Spectroscopic observation Schlieren Line reversal	Burning velocities Temperature profile Emission spectra Flame appearance
65	HNO_3–propane HNO_3–butane	Spectroscopic observation Fractional condensation	Flame speed Flashback limits Blowoff limits Emission spectra Combustion products Flame appearance
66	$H_2-O_2-N_2O-H_2O$ $C_2H_2-O_2-H_2O$	Isotope substitution Mass spectrometer Thermocouple	Species concentration profiles Temperature profiles Radical profiles Rate constants
67	CH_3ONO_2 $CH_3ONO_2-O_2$ CH_3ONO-O_2 $CH_3NO_2-O_2$ $C_2H_5ONO_2$ $C_2H_5ONO_2-O_2$ $CH_3NO_2-O_2$	Spectroscopic observation	Flame speed Emission spectra Visual observations
34	$H_2-O_2-N_2$ $H_2-N_2O-N_2$	Isotope substitution Thermocouple Flame probing	Rate constants Temperature profiles Species concentration profiles
68	$CH_4-NO_2-O_2$ $CH_3ONO-O_2-N_2$ $CH_3NO_2-O_2-N_2$	Schlieren imaging Line reversal	Flame temperatures Flame velocities
69	H_2, CO, and hydrocarbons reacting with O_2 and N_2O	Spectroscopic observation	Flame spectra OH and CH rotational temperatures
70–72	$CH_4-H_2-O_2-N_2O-Ar$ $CH_4-O_2-N_2O-Ar$ $N_2O-NO-NH_3-H_2-Ar$ N_2O-H_2-Ar $N_2O-NO-H_2-Ar$ $NH_3-H_2-O_2-Ar$ H_2-CO-O_2-Ar $N_2O-H_2-N_2$	Thermocouple and mass spectrometer Deuterium doping	Temperature and concentration profiles Reaction rates
73	NH_3-O_2 N_2H_4 decomposition	Mass spectrometer Optical spectrophotometric analysis Line reversal Thermocouple	Temperature and species concentration profiles
74	$N_2H_4-O_2$ $N_2H_4-H_2O-O_2$ NH_3-O_2 $NH_3-O_2-H_2$	Thermocouple Photographs	Flame speeds Flame temperatures
75	$C_2H_5ONO_2$	Spectroscopic observation	Flame velocities Flame spectra Flame appearance
76	N_2H_4, $N_2H_4-O_2$ N_2H_4-NO $N_2H_4-N_2O$	Schlieren	Flame speeds

C_2H_2 and HCN, and C_2H_2 and NO. The agreement between measurements and modeling was almost exact for NO, and almost as good for HCN.

To test their mechanism's ability to predict the oxidation of NH_3, Miller and Bowman[7] compared modeling results to measurements made by Bian et al.[26] for a 35-torr NH_3–O_2–Ar flame with an $NH_3/O_2/Ar$ molar ratio of 0.48/0.51/0.01. Agreement between modeling and measurements was within approximately 5% for stable species, while agreement was poorer for radicals and in particular HNO, which was overpredicted by a factor of three. Modeling analysis indicated that ammonia oxidation proceeds from successive reactions with radicals (primarily H and OH) to form NH_2, NH, and finally N. Each NH_i radical formed can also undergo reaction with O, O_2, or OH leading the formation of NO, or reaction with NO leading to the formation of N_2.

C. Model Propellant Flame Studies Based on Miller and Bowman[7] Mechanism

As already mentioned, the mechanism of Miller and Bowman was generally intended for instances in which there are low concentrations of nitrogen oxides. The model propellant flame studies covered in this section, by contrast, generally have high concentrations of nitrogen oxides that are sometimes the sole oxidizer in the flame. Although the Miller and Bowman mechanism is being used in these studies for purposes other than its original intent, it does an adequate job predicting many aspects of propellant flame chemistry. However, there have also been significant discrepancies between modeling and measurements, requiring further mechanistic development. Most flames have been studied at low pressure because they result in expanded reaction zones that facilitate the taking of measurements. Unless otherwise noted, they are modeled using a measured temperature profile as input to the PREMIX flame code.

1. Hydrogen Flame Chemistry

H_2–N_2O chemistry was studied by Sausa et al.[27] in a 20-torr, stoichiometric H_2–N_2O–Ar flame. Species concentration profiles were measured using molecular beam sampling with mass spectrometric (MB/MS) detection and laser-induced fluorescence (LIF); and temperature profiles were measured using thermocouples and the sodium line reversal (SRL) technique. A 38-reaction mechanism, most of which was derived and updated from Miller and Bowman,[7] with reactions involving species of low concentration being removed, was used to model the flame. Comparisons between modeling and measurements were made for N_2O, H_2, O_2, H_2O, N_2, NH, NO, H, OH, and O. The agreement between modeling and measurements for most of the major stable species was good, with N_2O decaying slightly more slowly in the modeling, and the final calculated N_2 and H_2O concentrations within approximated 15% of the measurements. The H_2 concentration near the burner surface was underpredicted by approximately 50%, which was possibly due to the sampling probe perturbing the flame near the burner surface. The shapes of the modeled and measured profiles for radicals NH and OH showed close agreement, with the NH peaking $\approx$1 mm later in the calculations than the measurements. The measured and computed profiles for NO agreed almost exactly, except near the burner surface. The general trends of the measured O and H concentration profiles were reproduced in the calculations.

Sensitivity and rate-generation analyses were performed as well. The consumption of N_2O was most strongly dominated by the reactions $N_2O + H = OH + N_2$ and $N_2O + M = N_2 + O + M$, with the most important colliders in N_2O decomposition being N_2O and H_2O. The significance of the reaction $N_2O + OH = HO_2 + N_2$, which previous studies had suggested was also important in consuming N_2O, was carefully examined. The only species that Sausa et al.[27] found to be significantly affected by this reaction was O_2, whose modeled profile was in almost exact agreement with experimental data when the reaction was completely removed from the mechanism. However, inclusion of the reaction, with further investigation into its rate parameters, was suggested.

Modeling and measurements both showed that the amount of NO present in the postflame region was over 40 times the amount predicted by equilibrium calculations. This relatively large presence of NO inhibits the rate of combustion because less heat is released when it is formed than when more typical products, N_2 and H_2O, are formed. This effect was demonstrated through PREMIX calculations made for freely propagating flames under conditions corresponding to those in the experimental flame. The calculated flame speed using the 38-step mechanism was only 179 cm/s, while the speed calculated using a mechanism where all of the NO reactions were removed was increased to 228.2 cm/s. Sensitivity analysis showed that the major source of NO production was $N_2O + H = NH + NO$. NO and O_2 concentration profiles best matched the measurements (within 5%) with a rate constant for this reaction that was increased at the high temperature end over that used by Miller and Bowman.[7]

Dayton et al.[28] attempted a more thorough test of the 38-reaction mechanism used by Sausa et al.[27] by comparing calculations to measurements for a lean (ϕ = 0.64), 20-torr H_2–N_2O–Ar flame. Species concentration and temperature measurements were made by MB/MS and thermocouples. The species measured were H_2, N_2O, N_2, H_2O, NO, O_2, H, O, and OH. One minor change to the mechanism was made to the rate constants for the reaction $N_2O + O = N_2 + O_2$.

The agreement between measurements and modeling was comparable to the results in the stoichiometric flame. The computed postflame concentrations for N_2 and H_2O closely matched the experimental results. The modeled rates of N_2O consumption, and H_2O and N_2 production, were faster than the measured rates near the burner surface. The H_2 was underpredicted at the burner surface by almost 50%, which was again possibly due to probe interference. The agreement between modeling and experiments for the postflame O_2 concentration was almost exact, whereas the agreement for NO was within experimental error. The postflame NO concentration again exceeded the equilibrium prediction. The calculated shapes of the O and OH concentration profiles were in good agreement with the measurements, although they peaked $\approx$2 mm earlier in the modeling than in the measurements. The calculated shape for the H profile was not in good agreement with the measurements.

Reactions $N_2O + H = OH + N_2$ and $N_2O + M = N_2 + O + M$ were still found to be major routes for nitrous oxide conversion to N_2. However, the lean conditions increased the relative importance of $N_2O + M = N_2 + O + M$ and made the reaction $N_2O + OH = HO_2 + N_2$ a significant contributor to N_2O consumption as well. Lean conditions also made the reaction $N_2O + O = 2NO$ significant in NO production and $N_2O + H = NH + NO$ less important, although not negligible. The rate parameters for $N_2O + OH = HO_2 + N_2$ was once again identified as a primary unresolved issue in N_2O-oxidized combustion.

Anderson and Faust[29] compared modeling results using the 38-reaction mechanism of Sausa et al.[27] to measured H_2–N_2O flame data at varying pressures and stoichiometries. Rate constants for two reactions, $N_2O + O = N_2 + O_2$ and $N_2O + O = NO + NO$, were updated from the values used by Sausa et al. Comparisons to data of Balaknine et al.[30] for a ϕ = 0.45, 40-torr H_2–N_2O flame, showed calculated postflame concentrations of N_2 and H_2O within approximately 5% of measured values, postflame N_2O overpredicted by a factor of 2, and postflame O_2 underpredicted by 20%. The H_2 was again underpredicted near the burner surface. An anomaly of these data, possibly attributable to measurement error, was the poor agreement for NO, whose postflame concentration was

underpredicted by a factor of 3. A comparison made with relative NH and absolute OH measurements in a stoichiometric, 7.2-torr H_2–N_2O flame by Kohse-Hoinghaus et al.[31] showed NH peaking ≈4 mm later in the modeling, while the peak calculated OH concentration was within a factor of 2 of the measured value.

Anderson and Faust[29] also made comparisons to H_2–N_2O flame data at atmospheric pressure. Comparisons with ϕ = 0.45 data of Vanderhoff et al.[32] showed nearly exact agreement for the profiles of N_2, O_2, and OH. The final amount of NO present was within 30% of the Vanderhoff et al.[32] data for ϕ = 0.45, 0.70, 0.89, and 1.0 flames. Comparisons with the stoichiometric flame data of Cattolica et al.[33] showed good agreement for the shape of the OH concentration profile and peak OH location, whereas the final flame concentration for NO was within approximately 30% of the measured value. Experimental and measured profiles agreed closely for N_2O and H_2O data in a freely propagating ϕ = 1.77 flame measured by Dixon-Lewis et al.,[34] but H_2 decayed too quickly in the modeling. Free-standing flame speed data from Dixon-Lewis et al.[34] and Duval and Van Tiggelen[35] were also compared to calculations, with the calculated speeds within 20% of the measured data in all but one fuel-rich case.

Anderson and Faust[29] also performed rate-generation and sensitivity analysis for atmospheric-pressure flames at ϕ = 0.45, 0.70, 0.89, and 1.00. These analyses reinforced the trends found by Sausa et al.[27] and Dayton et al.[28] At stoichiometric conditions, the dominant reaction producing NO is $N_2O + H = NH + NO$. As the flame becomes more lean, this reaction remains important, but $N_2O + O = NO + NO$ becomes dominant. N_2O consumption at stoichiometric conditions is dominated by $N_2O + H = OH + N_2$, but as the flame becomes leaner, $N_2O + M = N_2 + O + M$ and $N_2O + OH = N_2 + HO_2$ also become important.

Volponi and Branch[36] focused on NO_2 chemistry in studies of 25-torr flames of H_2–NO_2–Ar (ϕ = 1.09) and H_2–O_2–Ar (ϕ = 1.03). The oxygen flame was used as a basis for comparison to a well-characterized system. Measurements were made of H_2, O_2, NO_2, NO, and H_2O by MB/MS analysis, and OH and temperature measurements were made using LIF. The mechanism used to model the flame consisted of 82 reactions, the majority of which were taken from the work of Miller and Bowman.[7] Reasonable agreement was found between experiments and modeling for the O_2 flame.

In the NO_2 flame, the modeled postflame concentrations of O_2, NO, and H_2O were all in close agreement with the modeling. The agreement was the poorest for O_2, whose measured and modeled postflame concentrations differed by approximately 20%. In contrast to the flame studies of Sausa et al.,[27] Dayton et al.,[28] and Anderson and Faust,[21] the predicted H_2 concentration near the burner surface was in close agreement with the measurements. However, the shape of the OH profile was not well-represented by the modeling. Also, the overall reaction process based on the measurements was slightly slower than predicted by the modeling.

Sensitivity and rate-generation analyses for the H_2–NO_2 flame indicated that the combustion process is dominated by three reactions:

$$NO_2 + H = NO + OH$$

$$OH + H_2 = H_2O + H$$

$$H_2 + NO_2 = HNO_2 + H$$

A mechanism including just these reactions produced results within 5% of those obtained with the complete, 82-reaction mechanism. However, the limited agreement between the measurements and the modeling (primarily evident in the slower measured reaction process) led the authors to conclude that the understanding of the hydrogen–oxygen–nitrogen chemistry is not yet complete.

2. Hydrocarbon Flame Chemistry

Zabarnick[37] studied a 35-torr, CH_4–NO_2–O_2 flame at 55 torr, with a $CH_4/NO_2/O_2$ molar ratio of 0.16/0.731/0.109. Relative species concentration and temperature measurements were taken with LIF and emission spectroscopy for OH, CH, NO, NO_2, and CN. The flame was modeled using the mechanism of Miller and Bowman,[7] but it was found that the mechanism was lacking various elementary reaction steps involving NO_2. The additional chemistry resulted in a 252-reaction mechanism.

Even using the expanded mechanism, the predicted location of concentration maxima for OH, CH, NO, and CN were significantly farther from the burner surface than the measured locations (approximately 3–6 mm later). A double peak observed in the measured OH concentration profiles was not reproduced in the modeling. The modeling predicted that the NO_2 concentration would decay to zero at approximately 8 mm above the burner surface, whereas measurements showed that it decayed to zero within 3 mm of the burner surface.

By using sensitivity analysis, Zabarnick[37] was able to construct reaction pathways for the essential chemistry involving CH_4 conversion to CO_2 and NO_2 conversion to NO and N_2. The CH_4 conversion was conventional ($CH_4 \rightarrow CH_3 \rightarrow CH_3O \rightarrow CH_2O \rightarrow HCO \rightarrow CO \rightarrow CO_2$), except for the importance of intermediate species CH_3O. The NO_2 was found to be converted to NO directly from reactions with NO_2, OH, and CH_3. It was also found to react with CH_4 and HO_2 to form HONO, which then also decomposes to NO. Nitric oxide was found to be removed via reactions with NO or O. The apparent NO_2 removal rate measured in this flame suggested that more NO_2 removal reactions and/or more rapid rate constants were needed in the mechanism.

Williams et al.[38] published a subsequent study where the experimental NO_2 flow rate assumed by Zabarnick[37] was adjusted to take account for the effect of NO_2 dimerization on its heat capacity. Using the recalibrated NO_2 flow rate, the revised $CH_4/O_2/NO_2$ molar ratio was 0.36/0.24/0.40. The flame modeling was then redone using the mechanism used by Williams and Fleming[45] described below. This mechanism is very similar to the one used by Zabarnick.[37] The agreement between measurements and modeling was greatly improved. The calculated profile shapes for OH and NO_2 coincided with measurements almost exactly, with the double peak in OH being captured by the modeling. The calculated locations for the peak concentrations for NO, CH, and CN now occurred ≈1 mm earlier in the modeling than the measurements.

Zabarnick[39] also used the 252-reaction mechanism[37] to model CH_4–NO–O_2–Ar and CH_4–N_2O–Ar flames at 63 torr. The N_2O-supported flame was stoichiometric while the $CH_4/NO/O_2$ molar ratio was 0.25/0.36/0.50. LIF and absorption spectroscopy were used to measure species OH, CH, NO, NH, and CN, and LIF was used to measure flame temperatures. The CH_4–NO–O_2 flame was studied to gain greater insight into NO chemistry, with further insight coming from studying NO chemistry in the environment of the CH_4–N_2O flame.

The modeling and measurements both indicated that species generally obtained peak or final values closer to the surface in the NO flame than in the N_2O flame. Comparisons between modeling and measurements for the OH radical showed good agreement in the shape of the profiles, with the modeling overpredicting the peak concentrations by approximately a factor of 2 in the NO flame and approximately 60% in the N_2O flame. The modeled peak concentration for OH occurred at approximately the same height as the measurements in the NO flame and ≈2 mm later than the measurements in the N_2O flame. Good agreement between measurements and modeling was found for the shape of the NH concentration profile in the NO flame, although the peak concentration occurred ≈1 mm earlier in the modeling. For the N_2O flame, the calculated peak NH concentration was overpredicted by a factor of 3, with the calculated profile

wider than the experimental profile as well. The calculated peak CH concentration in the NO flame occurred ≈1 mm earlier than in the measurements, while the calculated peak CH concentration in the N_2O flame occurred ≈0.5 mm later than in the measurements.

A significant discrepancy was found in the NO flame, where the model predicted only 20% of NO removed while the experiment demonstrated at least 50% removed. In the N_2O flame, the NO concentration was modeled to peak approximately 3 mm later than in the measurements. The modeled peak CN concentration in the NO flame occurred ≈1 mm earlier than in the measurements, and was calculated to be about 3.5 times greater than in the measurements. The modeled CN peaked ≈1 mm later than in the measurements in the N_2O flame, with the peak concentration very close to the measured value.

Zabarnick[39] also used rate-generation and sensitivity analysis to determine the dominant CH_4–NO and CH_4–N_2O reaction pathways. The CH_4 removal pathway was conventional: $CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow HCO \rightarrow CO \rightarrow CO_2$. The removal of N_2O was found to primarily occur by the reaction $N_2O + M = N_2 + O + M$ and reaction with OH. The generally good agreement between modeling and measurements in the N_2O flame was attributed to the rate parameters for N_2O decomposition being well-defined. NO was found to primarily be removed by HO_2 to form NO_2, which is then converted to NO, resulting in very little NO removal in the modeling.

Analysis for the NO flame showed no single reaction dominating the removal of NO. Zabarnick[39] therefore attributed the inability of the modeling to accurately predict the NO profile, as well as the OH and CN profiles, to key reactions being missing from the NO removal mechanism, and possibly to unknown high temperature behavior of the reaction $NCO + NO = N_2O + CO$. Additional HONO removal pathways were suggested as a way to reduce the OH concentration discrepancies. Problems with NH calculations were attributed to uncertainty in the rate parameters for $H + N_2O = NH + NO$.

Habeebullah et al.[40] studied the structure of three (ϕ = 1.13, 1.04, and 0.84) CH_4–N_2O flames at 50 torr. Measurements were made of stable species using gas chromatography, unstable species using LIF, and temperatures using thermocouples and LIF. The work of Miller and Bowman[7] was the basis of an 82-reaction mechanism used for modeling the flames. Comparisons between measurements and modeling were presented for the ϕ = 1.13 flame. For species CH_4, N_2O, N_2, H_2O, CO_2, and CO, the agreement between measurements and modeling was very good for the profile shapes, with calculated postflame concentrations within 10% of measured values. For unstable species, the NH, CN, and CH concentrations peaked from 1 to 5 mm farther from the surface in the modeling than in the measurements, with good agreement for the profile shapes. The modeled OH concentration profile showed a narrower distribution of the species than shown in the measurements, although the agreement for the peak location was almost exact. The agreements between modeling and measurements for unstable species was poorer than found in the lean CH_4–N_2O flame modeled by Zabarnick.[39]

Habeebullah et al.[40] also performed rate-generation analysis. Similar to the removal path of Zabarnick,[39] CH_4 was found to be mainly consumed through H abstraction by H and OH, forming the intermediate species CH_3, which then is transformed to CH_2O or CH_2 through further reactions with O, H, and OH. Reactions between CH_2O and radicals then leads to the formation of HCO, which then forms CO, which reacts with OH to form CO_2. Reactions between CH_2 and radicals form CH, which then reacts with NO formed from N_2O decomposition to form CN and NH radicals, the first hydrocarbon–nitrogen linking reactions in the combustion process. The main sources of N_2O consumption, and N_2 production, were thermal decomposition and N_2O reactions with H, which were also found to produce the initial source of radical species required for the reaction to proceed. N_2O decomposition was found to be key in producing the OH radical, the most important radical for CH_4 decomposition and general flame propagation. Water was found to be produced mainly through reactions of OH with CH_3 and H_2.

Volponi and Branch[41] studied C_2H_2–O_2–Ar and C_2H_2–NO_2–Ar flames at 25 torr. The C_2H_2/O_2/Ar molar ratio was 0.053/0.150/0.797 and the C_2H_2/NO_2/Ar molar ratio was 0.201/0.548/0.251. Measurements were made using mass spectrometry, LIF, and thermocouples. Radical species OH and CH were measured in the O_2 flame and OH and CN were mea-

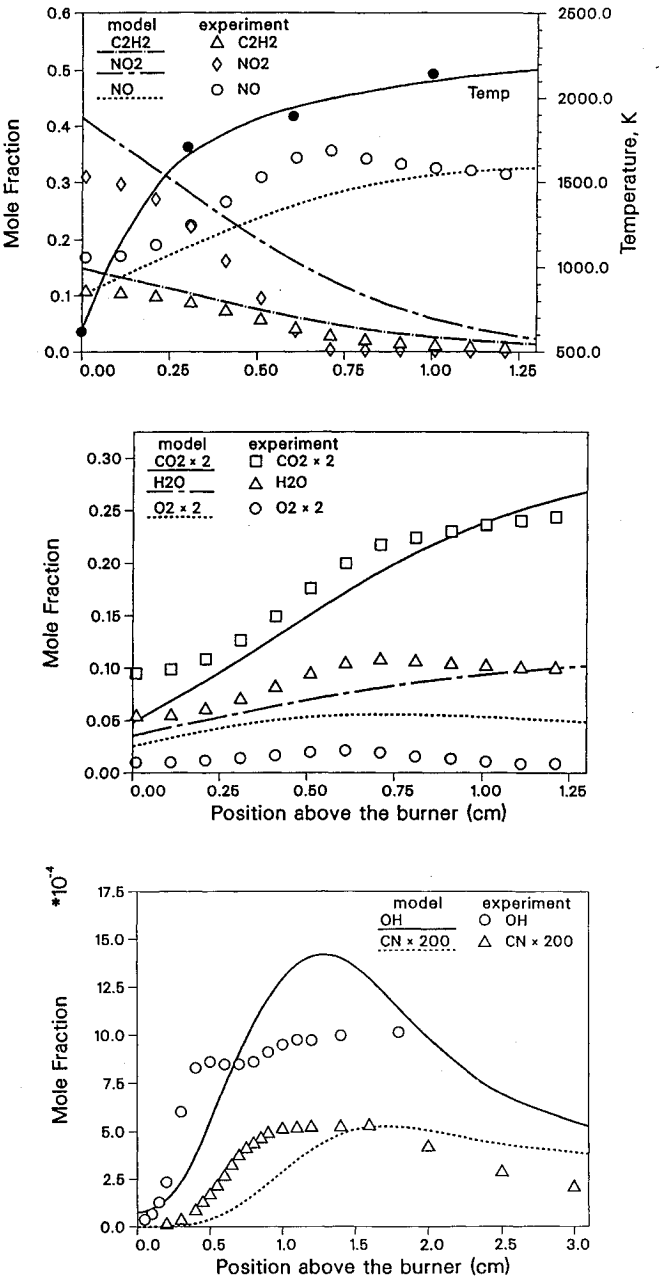

Fig. 2 Measured (symbols) and calculated (lines) profiles of composition of stable and radical species and temperature in the 25-torr, C_2H_2–NO_2–Ar laminar premixed flame of Volponi and Branch.[41] Model calculated H_2O mole fraction is corrected for radical recombination reactions in the sampling probe by adding OH mole fraction to H_2O mole fraction. Reactant mole fractions are $X(C_2H_2)$ = 0.201, $X(NO_2)$ = 0.548, X(Ar) = 0.251, and the total reactant gas flow rate is 4.01 standard liters per minute. Calibration of the OH concentration is by comparing the LIF measurements to a model prediction at 1.0 cm in a H_2–O_2–Ar flame. CN is not calibrated but is plotted relative to the CN calculation.

sured in the NO_2 flame. The flame was modeled using a 331-reaction mechanism, the core of which was taken from the work of Miller and Bowman,[7] with additional chemistry added from the studies of Volponi and Branch[36] and Miller et al.[42]

Agreement between the modeling and experiments for major species concentration profiles was better in the O_2 flame than for the NO_2 flame. In the NO_2 flame, reactants were consumed earlier in the experiment than in the modeling, as shown in Fig. 2. As in the original study by Zabarnick for the CH_4–NO_2 flame,[37] the NO_2 decayed much slower in the modeling than in the experiment. One suggested explanation given for this discrepancy was the existence of direct CH_i reactions with NO_2 not being included in the modeling. Figure 2 shows that in the NO_2 flame, the OH concentration peaks earlier in the measurements than in the modeling. The double-peak structure for OH measured by Zabarnick[37] is seen in the measured profile in Fig. 2 as well. The peak CN concentration occurs earlier in the measurements than in the modeling. CH was not present in detectable quantities in the NO_2 flame, which was as predicted in the modeling.

Sensitivity and rate-generation analyses were used to identify the key reaction pathways. In the NO_2 flame, C_2H_2 consumption was mainly through reactions with OH to produce C_2H, with additional consumption coming from reactions with C_2H, O, OH, and O_2. The most important reaction consuming NO_2 and forming NO was found to be $NO_2 + H = NO + OH$. Nitric oxide then was found to proceed to HCNO, followed by HCN, which is then converted to CN, which reacts with NO or NO_2 to finally form N_2. Carbon monoxide was found to be created mainly by reactions between HCCO + NO and $C_2H + O_2$, and then form CO_2 mainly through reaction with NO_2 and OH.

Williams and Fleming[43] studied stoichiometric, 10-torr CH_4–O_2–Ar flames doped with 0.086 mole fraction of either N_2O, NO, or NO_2. Small quantities of these oxidizers were used so that nitrogen chemical pathways could be compared under the conditions of nearly identical temperature and hydrocarbon radical profiles in the well-understood CH_4–O_2 flame. The flames were modeled using the mechanism of Miller and Bowman without alteration. The temperature and relative concentrations of the species OH, CH, NH, CN, NO, and NCO were measured using LIF.

Measurements and modeling showed that NO_2 was quickly converted to NO near the burner surface, after which the chemistry of NO_2-doped flames strongly paralleled that of flames doped with NO. In the NO and NO_2 doped flames, the measured and modeled NO removal rates both indicated that only a small portion of the NO participated in reburn reactions (defined by $CH_i + NO \rightarrow HCN \rightarrow + H_{i-1}O$, i = 1, 2, 3). However, NH, an indirect byproduct of reburn reactions, was underpredicted by approximately 40% in the NO and NO_2 flames, indicating more reburn occurring than the modeling predicted. At the same time, CN and NCO concentrations were most greatly underpredicted in the N_2O-doped flames, in which NO was overpredicted. While a single change to the mechanism to rectify all these discrepancies could not be identified, possible modifications to the mechanism were discussed. These included increasing the rate constants for the reaction $N_2O + H = NO + NH$ or $N + CH_i$ reactions. Another possibility was including NH reactions with hydrocarbon species in the mechanism.

The finding that doped NO_2 was consumed very near the burner surface was a qualitatively different finding from flames containing larger amounts of this oxidizer[36,37,41,44]; therefore, studies of methane–oxygen flames, where the oxidant is gradually changed over to NO_2, were suggested as being very instructive in understanding the chemistry of NO_2-supported flames. Williams and Fleming[45] carried out such a study, for five 15-torr CH_4–O_2–NO_2–N_2 flames, where NO_2 comprised from 0 to 40% of the oxidant in increments of 10%, with the effective ϕ for each flame kept equal to 1. LIF was used to measure the temperature and relative concentrations of H, OH, CH, NH, CN, NCO, NO_2, and CH_3O. The basic mechanism used to model the flames was that of Miller and Bowman,[7] with the added reactions suggested by Zabarnick,[37] with the exception of the HNO_3 and NO_3 reactions. Several reactions involving CN, NH, and $^3CH_2$ reacting with NO were also added. The rate constants of several other reactions, and several species' heats of formation, were modified based upon recent data in the literature.

For H, OH, and CH, the calculated profile shapes, and the trends of overall decreasing concentrations as the amount of NO_2 reactant increased, were in excellent agreement with the measurements. The double-peaked OH structure measured by Zabarnick was reproduced in both the measurements and modeling, and attributed to the reaction $NO_2 + H = NO + OH$. Experiments and modeling were also in excellent agreement for the trends in NO_2 concentration. The NO_2 was immediately depleted when it was premixed in low concentrations, while it persisted for 6–7 mm in the 40% NO_2 flame. This longevity at higher concentrations was attributed to the NO_2 completely depleting the available hydrogen atoms participating in the reaction $H + NO_2 = OH + NO$.

The measured trends for the CN, NCO, and NH concentration profiles were not reproduced well by the calculations. Compared to measurements, the modeling showed a more dramatic and consistent increase in CN and NCO concentrations as the NO_2 reactant was increased. The measured NH concentration was found to consistently decrease with high amounts of NO_2 reactant, while no clear trend was found in the calculations. These discrepancies were attributed to general problems with the nitrogen chemistry in the mechanism. A possible reaction suggested for further investigation was $CN + NO = N_2 + CO$. Since nitrogen intermediates all derive ultimately from HCN, measurements of this molecule's concentration in the flames was suggested as a means of pinpointing the difficulties with the mechanism.

The measured CH_3O profiles indicated that its peak mole fraction was approximately the same for all four flames containing NO_2, whereas the calculations showed a factor of 6 less CH_3O in the 10% vs 40% NO_2 flames. This was possibly due to radical recombination on the burner surface, which was not modeled in the flame code. However, the modeling did confirm the experimental trend of substantial increase of methoxy concentration for flames contains some NO_2. This modeling trend was attributed to the reaction $CH_3 + NO_2 = CH_3O + NO$.

3. *HCN Flame Chemistry*

Thorne and Melius[46] studied the structures of 25-torr, HCN–NO_2 flames at ϕ = 1.25 and 1.74. Species concentration and temperature measurements were taken using Fourier-transform infrared spectroscopy (FTS-IR) and compared to modeling results using a mechanism developed from the same sources as used by Miller and Bowman.[7] Sensitivity analysis was used to predict the main fuel and oxidizer consumption pathways. The primary pathway for carbon chemistry in the fuel was given as $HCN \rightarrow CN \rightarrow NCO \rightarrow CO \rightarrow CO_2$. The primary pathway for nitrogen chemistry in the fuel was given as $HCN \rightarrow CN \rightarrow NCO \rightarrow N_2O \rightarrow N_2$. The consumption of HCN in these fuel-rich flames was found to occur mainly through attack by OH and H radicals, rather than O radicals, in agreement with the predicted trends of Miller and Bowman.[7] The primary pathway for nitrogen chemistry in the oxidizer was given as $NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$. Sensitivity analysis showed that the dominant reaction controlling the burn rate was $N_2O + M = N_2 + O + M$. This was attributed to the reaction's importance in producing chain carrying O radicals, and the lack of any dominant chain-branching reaction, such as found in hydrocarbon flames.

Results calculated for a freely propagating flame at ϕ = 1.25 were compared with measurements taken in the burner-

stabilized flame. The calculated peak CO concentration was 0.28 vs a measured value of 0.32. The peak free-flame temperature was ≈500 K higher than measured above the burner surface. The modeled location of peak CN concentration above an effective burner surface corresponded to the location of violet CN emissions above the actual burner surface. However, when more realistic comparisons with the measured data were attempted by running PREMIX in a burner-stabilized mode, an unstable solution was produced with periodic oscillations. Averaging the peak calculated CO concentrations produced a mole fraction of 0.22, a poorer match with the measurements than obtained with the freely propagating calculation. The results led the authors to believe that there were inherent errors in the rate constants or mechanisms involving HCN oxidation.

4. Multiple-Flame Modeling

Branch and Cor[47] used a single mechanism to model a number of flames with different chemistries. The flames modeled included the previously mentioned flames measured by Zabarnick,[39] Volponi and Branch,[36,41] and Habeebullah et al.[40] In addition, the CO–N_2O flames measured by Dindi et al.,[48] CH_4–N_2O flames measured by Vandooren et al.,[49] and CH_4–NO_2–O_2 and CH_2O–NO_2–O_2 flames measured by Branch et al.[44] were modeled. The basis of the mechanism used was the 331-reaction mechanism of Volponi and Branch,[41] with reactions involving species with very low concentrations eliminated, resulting in a 272-reaction mechanism. Rate constants of five key reactions were varied within acceptable limits found in the literature to achieve the best fit possible with all of the data.

This mechanism did an excellent job of predicting the major species concentration profiles in the three (ϕ = 1.0, 1.32, and 1.50) 50-torr, CO–N_2O flames measured by Dindi et al.[48] It was found that four reactions were dominant in controlling the flame chemistry and produced results within 1% of those obtained using the entire mechanism. The 272-reaction mechanism did a good job of matching the concentration profiles of stable and radical species in the CH_4–N_2O flame of Habeebullah et al.,[40] and good agreement between modeling and results was also obtained for the H_2–NO_2 flame studied by Volponi and Branch.[37] For the C_2H_2–NO_2 flame, modeling results were on par with those of Volponi and Branch[41] using the full 331-reaction mechanism. When used to model the CH_4–NO–O_2 flame of Zabarnick,[39] the mechanism duplicated Zabarnick's modeling results of overpredicting the steady-state NO concentration. For radical species in this flame, the modeling led the data for the location of peak concentrations, in contrast to the modeling of Zabarnick,[39] which generally lagged the data for peak concentration locations.

The 272-reaction mechanism was also used to model the burning of free-standing flames supported by N_2O and NO_2, with the results compared to the experiments of Parker and Wolfhard.[50] The flames were also modeled using the original mechanism of Miller and Bowman[7] without the subsequent modifications made by other researchers. The 272-reaction mechanism's prediction of flame speeds were generally in better agreement with the experimental data than the mechanism of Miller and Bowman. The burning velocity of N_2O flames were found to be significantly higher than the flames using NO_2 as the oxidizer. This can perhaps be explained by the processes of converting these oxidizers to N_2. The more

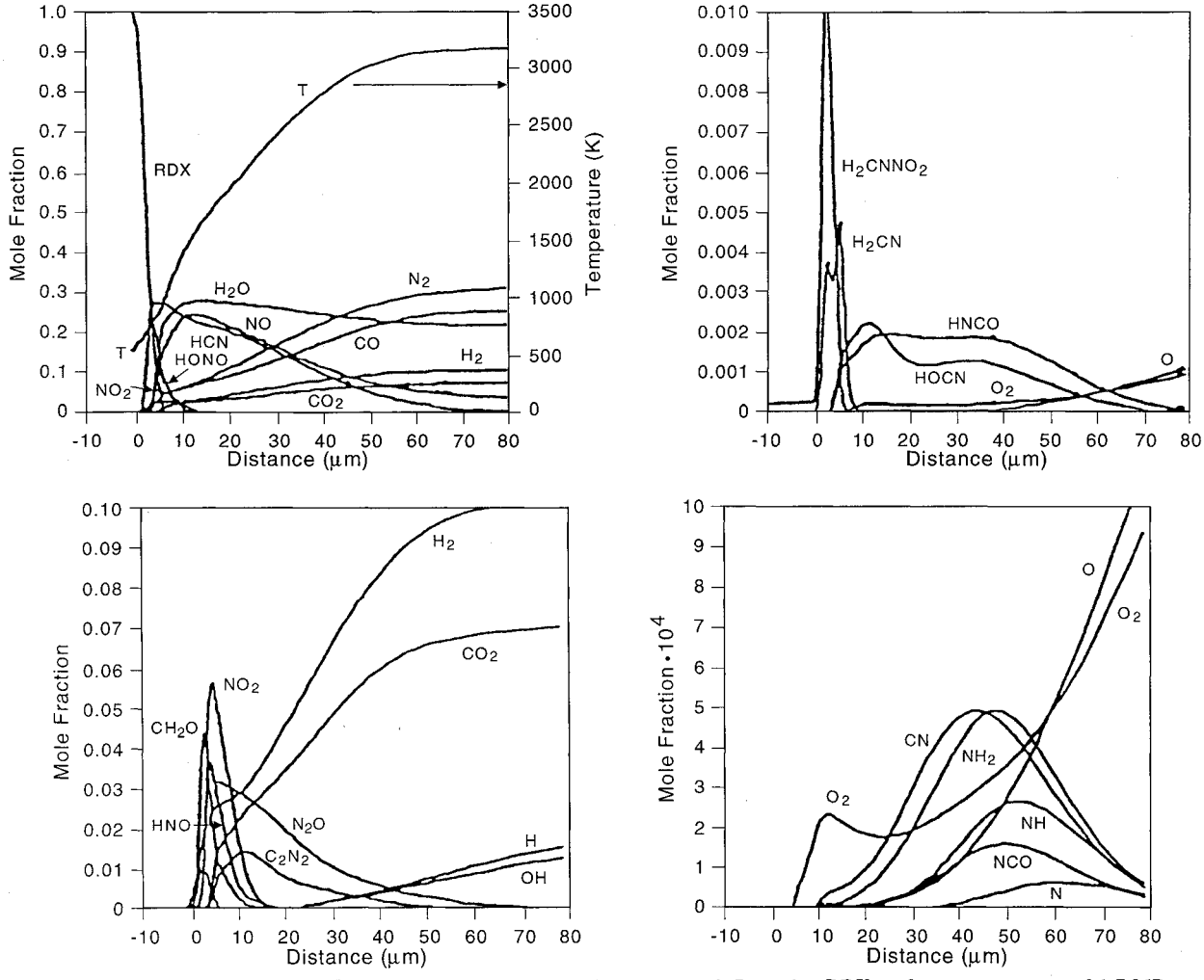

Fig. 3 Calculations by Melius[8] of major species concentrations above a deflagrating RDX surface at a pressure of 1.7 MPa.

Table 2 Comparison of measurements vs modeling of flame speeds[a]

Flame	Measured,[b] cm/s	Calculated M/B,[c] cm/s	Calculated Branch/Cor,[d] cm/s
H_2–N_2O	300	227	240
CH_4–N_2O	105	76.2	90
C_2H_2–N_2O	160	128	150
C_2H_4–N_2O	62.5	61	61

[a]All measurements and calculations for 0.1 atm and a stoichiometric mixture.
[b]Parker and Wolfhard.[50]
[c]Calculated velocity by Branch and Cor[47] using Miller and Bowman[7] mechanism.
[d]Calculated velocity using Branch and Cor[47] mechanism.

direct conversion to N_2 occurs for N_2O, while NO_2 follows a less direct and slower path to final reduction to N_2. For NO_2 flames it was also harder to obtain converged free-standing flame solutions. The measured and calculated flame speed data from the Branch and Cor[47] study are given in Table 2.

D. Melius[8,9] Mechanism

Melius developed a comprehensive mechanism for the entire gas-phase chemistry of RDX combustion. This mechanism was an extension of previous mechanistic work on hydrocarbon/air flame modeling by Miller and coworkers,[19–21] which Miller and Bowman[7] also used to develop their mechanism. The mechanism used by Melius[9] consisted of 158 reactions. Over half of these reactions are also included in the Miller and Bowman mechanism; but there are a considerable number of reactions involving nitrogen chemistry and large hydrocarbons, as well as RDX reactions, not found in the Miller and Bowman mechanism. The Sandia flame codes[5,6] were used to solve the gas-phase chemistry, with the solid RDX surface treated as a "pseudo" gas, with the density and thermal conductivity of a solid, and no diffusion of the RDX being allowed. Results for the calculations at a pressure of 1.7 MPa are shown in Fig. 3.

Rate generation and sensitivity analysis for the 1.7-MPa flame demonstrated that a two-stage flame exists. The first-stage flame, or primary flame, is located between 2–30 μm above the surface. It begins with a decomposition region, from 2–7 μm, which is dominated by the formation of HCN, and secondarily by the formation of CH_2O, N_2O, HONO, and HNO. The primary flame's combustion region, from 6–20 μm, features the partial conversion of HCN to C_2N_2, and production of CO_2, NO, and more HNO. This region is followed by a postprimary-flame zone from 15–30 μm, where the C_2N_2 is converted back to HCN. The second-stage flame, or secondary flame, located between 20–100 μm above the surface, features the final conversion of HCN to CO, CO_2, and N_2, and conversion of NO to N_2. The dominant RDX combustion pathways as determined by Melius[8,9] are shown in Fig. 1.

Sensitivity analysis of the burning rate to gas-phase reactions showed the greatest sensitivity to a reaction occurring in the secondary flame: $N_2O + M = N_2 + O + M$. This is because N_2O thermal decomposition is the major generator of radicals for the secondary flame. The major generator of radicals for the primary flame was found to be HONO thermal decomposition.

Calculations were also performed for 0.05-MPa[8] and 1.0-MPa[9] flames, which showed similar behavior to the reaction pathways for the 1.7-MPa flame when distances were scaled up. The modeled 0.05-MPa flame results were also compared to experimental data of Korobeinichev[51] (Fig. 4) taken at the same pressure, with good agreement found for the profiles of species HCN, NO, H_2O, N_2, CO, and CO_2. The theoretical flame zone was smaller by 30% and the theoretical flame speed was smaller by a factor of 2.

Kuo and Lu[52] have incorporated the Melius[9] mechanism into an all-encompassing model of RDX combustion. This model covers the decomposition of the solid propellant, in the melt or foam layer, which includes the physics and chemistry of gas bubbles forming in that layer; and a gaseous flame region. The mechanism of Melius[9] is included in the modeling of the gaseous domain. This modeling effort is still in its earliest stages of development, and emphasis to date has been placed on the physics of the foam layer.

E. Yetter and Dryer[10] Mechanism

Yetter and Dryer have developed and are maintaining a standard RDX flame mechanism that has been taken in large part from the RDX mechanism of Melius.[9] The Melius mechanism was updated and expanded using several different sources, but mainly from the kinetic data of Tsang and Herron[53] and Tsang.[54] The Yetter and Dryer mechanism is intended to

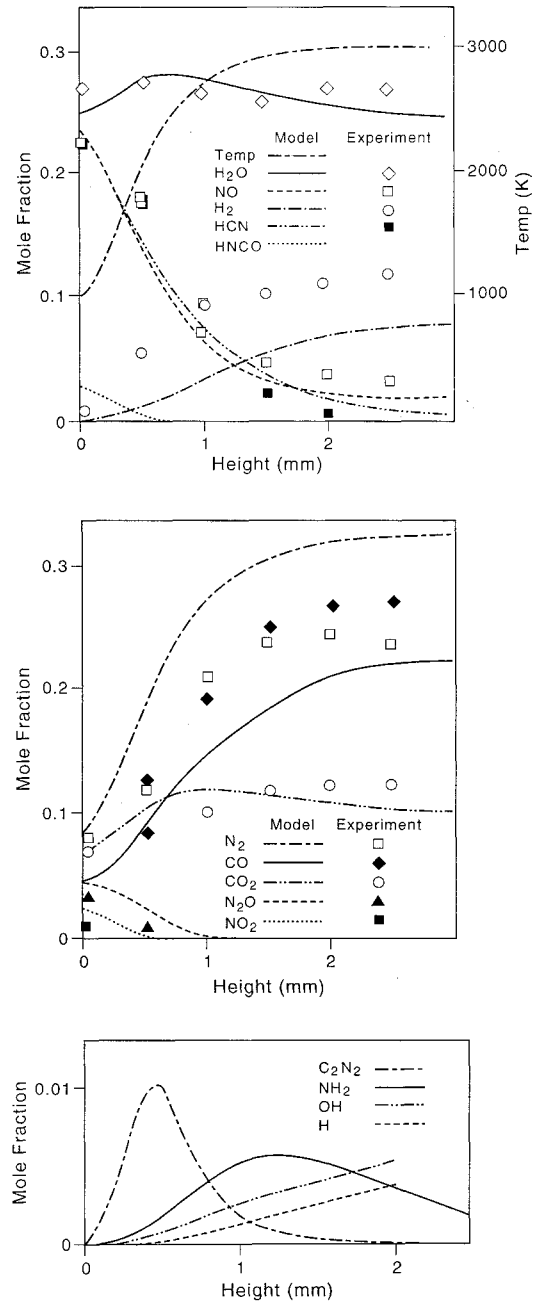

Fig. 4 Measured (symbols) and calculated (lines) profiles of species and temperature above the deflagrating RDX surface modeled by Ermolin et al.[56] and measured by Korobeinichev[51] at a pressure of 0.05 MPa.

be generally applicable to RDX flame studies. It has many reactions in common with the mechanism of Miller and Bowman,[7] but most of the common reactions have rate constants based on the more recent sources. Thus, it is important that flame modelers basing their work on the Miller and Bowman mechanism ensure that the rate constants they are using are current with the recommendations of Yetter and Dryer. A detailed description of the most recent modeling work done using this mechanism is described by Litzinger and Fetherolf.[55]

F. Russian Propellant Flame Modeling

Korobeinichev[15] studied the gas-phase chemistry of ammonium perchlorate. Mass spectrometric measurements above a burning AP surface were compared to calculations using a 17-reaction mechanism. The mass, energy, and species conservation equations were solved for with the surface temperature and stable species concentrations at both computational boundaries supplied as input. Measurements of the AP flame were taken up to a height of 1.5 mm and compared to calculations for the temperature and concentrations of H_2O, O_2, HCl, Cl_2, ClOH, N_2O, N_2, NO, NO_2, $HClO_4$, and ClO_2. Several reactions rate constants were adjusted to obtain the best agreement with the data. Agreement between the measurements and the calculations was almost exact except for the species Cl_2 and HCl. Experimental results indicated that the initial decomposition products were NH_3 and $HClO_4$, and so measurements were also taken above a premixed flame of these two reactants, and this flame was modeled using the AP mechanism. Reasonable agreement was found between the measurements and modeling once again.

In similar mechanistic studies done for an RDX propellant, Ermolin et al.[56] modeled an RDX flame using a mechanism of 23 species and 49 reactions and compared the results to the experimental data of Korobeinichev[51] at a pressure of 0.05 MPa. The reaction rates for several reactions were not well-known and so were varied to get a good fit with the experimental data. Agreement was found to be good between the measurements and modeling for HCN, CO_2, NO, NO_2, N_2O, and H_2O, with agreement poorer for H_2, N_2, and CO. The modeling and experimental results are shown in Fig. 4.

V. Conclusions

A review has been presented of the current state of understanding of the gas-phase chemical kinetics of flames above solid propellant surfaces. This review began with a survey of studies of flames featuring nitrogen chemistry going back to the late 1940s. These early studies contain most of the flame-speed data which are available, and frequently have species concentration and temperature data. While Table 1 lists prominent flame studies up to the mid 1960s, data from the 1970s and 1980s also exist that are valuable to validation of modern mechanisms. Modelers should be aware of the large database that exists to assist in mechanistic validation in addition to the most recent data that have been included in this review.

Recent modeling studies of premixed gas-phase chemistry relevant to solid propellant combustion have been reviewed. These studies have built upon the mechanism first developed by Miller and Bowman.[7] Different researchers have made different modifications to the mechanism to match the specific chemistry they have studied; however, there is no clear consensus on what reactions should be included in a general mechanism, or what those rate constants should be. A commonly agreed upon mechanism, with standard rate constants, applicable to a wide variety of flames, would be useful in modeling gaseous propellant flames. An example of such a mechanism would be that used by Branch and Cor.[47] All flame studies could then be based upon this standard mechanism, with a standard basis of comparison for modeling results.

Overall, there is encouraging agreement between measurements and modeling in the different gaseous flame studies reviewed; however, knowledge of gas-phase structure is incomplete. Specifically, the rate parameters for reactions identified by Volponi and Branch[36] as dominating H_2–NO_2 flame chemistry need careful examination. Other studies indicate that rate parameters for $NO_2 + H = NO + OH$, $NCO + NO = NH + NO$, $N_2O + OH = HO_2 + N_2$, $NCO + NO = N_2O + CO$, $CN + NO = N_2 + CO$, $N + CH_i$ reactions and $N_2O + M = N_2 + O + M$ need careful examination. For the N_2O decomposition reaction, careful shock tube study should be undertaken for as many different colliders as possible. The finding of Sausa et al.,[27] that the reaction $N_2O + H = NO + NH$, needs a higher rate constant at the high temperature end has now been confirmed by two recent theoretical studies,[57,58] and the rate parameters from these studies should be incorporated into modeling. Mechanisms might also be improved by the addition of more HONO removal pathways and NH–hydrocarbon chemistry.

Flame studies should be undertaken that feature the still-incomplete chemistry of NO removal and reburn mechanisms. The results of Thorne and Melius[44] suggest that the chemistry of HCN oxidation is deficient and needs more study. All experimental studies that have incorporated NO_2 as an oxidizer should be reviewed to eliminate the NO_2 flowmeter calibration problem identified by Williams et al.[38] as a source of error. This problem with NO_2 flowmeter calibration should be borne in mind by future experimentalists and modelers.

Experimental gas flame studies need to be extended to pressures of atmospheric and higher. Such studies are needed to extend the validity of mechanisms being developed at low pressures to the more realistic pressures present in actual rocket motors. Although such studies will reduce the size of the reaction zone and not allow as detailed a study of intermediate chemistry, measurements of final flame products can help determine the validity of propellant flame mechanisms as they are extended to rocket motor operating pressures.

Two comprehensive flame mechanisms, those of Melius[9] and Yetter and Dryer,[10] have also been reviewed in this article. The mechanism of Melius has produced encouraging agreement between measurements and modeling for the gas-phase structure of an RDX propellant. While both of these comprehensive mechanisms contain reactions involving species that obviously would not be included in simpler model flame chemistry, there are important differences between these comprehensive mechanisms and the mechanism of Miller and Bowman.[7] There are numerous reactions involving nitrogen–oxide species which are included in the Melius mechanism that are not found in the Miller and Bowman mechanism. Also, the rate constants of Yetter and Dryer have been updated so that they frequently differ from the constants used by Miller and Bowman. Conversely, these comprehensive mechanisms are deficient in reactions important in model flame studies. For example, hydrocarbon reactions required for model fuels such as CH_4 to burn are not included in these comprehensive propellant mechanisms.

Therefore, an all-encompassing, standard model flame mechanism, applicable to propellant and gaseous flame studies, such as the standard Yetter and Dryer mechanism, needs to be developed from several sources. An initial step toward such a mechanism could be an updated Miller and Bowman mechanism that includes all relevant nitrogen chemistry in the Melius and Yetter and Dryer mechanisms. In addition, it would contain all the model flame chemistry of the Volponi and Branch mechanism. The rate constants used in this mechanism would need to be continuously updated. Such a standard, updated mechanism would also help ensure that the relevant findings of gaseous flame studies quickly find their way into the comprehensive flame modeling efforts, and vice versa.

At the same time that standard, large mechanisms are being developed, more studies should be undertaken to reduce the sizes of mechanisms, such as the work described by Branch

and Cor[47] for $CO-N_2O$ flames, and Volponi and Branch[40] for H_2-NO_2 flames. Reduced mechanisms are needed because the mechanisms must ultimately be rolled into larger, all-encompassing propellant combustion models, such as that of Kuo and Lu.[50] These models are necessarily large and complex, and flame chemistry is only one of many different physical processes involved in them. The flame chemistry must therefore be describable in as small a number of reactions as possible.

Significant studies of propellant gas flame structure have been made by Russian researchers. These studies have involved modeling of flame chemistry above solid propellant surfaces that has had encouraging agreement with experimental results. Modelers should review these studies with special attention paid to reactions included in the mechanisms, the rate constants for those reactions, and the comprehensive flame modeling schemes used.

Acknowledgment

This research was supported by the Air Force Office of Scientific Research under Grant DOD-F49620-93-0430.

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