BURN-RATE MODELING AND COMBUSTION DIAGNOSTICS FOR ENVIRONMENTALLY FRIENDLY, SOLID ROCKET PROPELLANTS

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ABSTRACT

Advanced, burn-rate, propellant modeling is critical for developing new rocket-missile and gun propellants for Future Combat Systems and for providing a fundamental screening tool that can result in substantial cost savings compared to missile and gun firings. In this paper, we report the detailed chemical kinetics and burn rate prediction of tri-amino-guanidinium azotetrazolate (TAGzT) and nitrocellulose (NC).

1. INTRODUCTION

Most composite formulations in tactical rocket and missile systems contain about 70 to 80% ammonium perchlorate (AP), an environmentally, hazardous compound. AP contributes to ground water pollution, and its combustion yields copious quantities of toxic hydrochloric acid and an undesirable smoke signature. Thus, it is desirable to replace it with insensitive, high-energy materials that are safer and have reduced smoke signatures.

We are employing advanced flame diagnostics and burn-rate, propellant modeling to characterize new oxidizers and high-energetic binders and nitrate esters with high-nitrogen compound additives, such as 5-aminotetrazole (5-AT), biz-tetrazolyl-amino-tetrazine (BTATz), or tri-amino-guanidinium azotetrazolate (TAGzT), to determine their viability in rocket-missile propellants for energy-managed systems that require lower sensitivity, greater range, and flexibility (Sausa and Anderson, 2005). In this paper, we report our modeling and experimental efforts on nitrocellulose (NC) and TAGzT.

2. EXPERIMENTAL APPARATUS AND MODELING

The experimental apparatus and modeling are described in detail in our previous publications (Anderson and Fontijn, 2005, Miller and Anderson, 2004, Sausa, Venizelos, and Cabalo, 2006, Venizelos and Sausa, 1998, and Venizelos and Sausa, 2000). Briefly, the burn rates of NC and TAGzT are calculated over a broad pressure range using Cyclops, a burn-rate predictor developed at the US Army Research Laboratory (Miller and Anderson, 2004). The predictor employs a detailed chemical mechanism containing about 400 elementary reactions involving 100 species, which we obtained from a critical literature review. We tested parts of this mechanism with our burner flame apparatus shown in figure 1 using H_2,NH_3/N_2O,NO_2/Ar flames. We measured the flame temperatures by thin-wire thermometry, and the stable and radical species concentrations by laser spectroscopy, molecular beam mass spectrometry, or both. The experimental species concentrations are then compared to those obtained with the SANDIA PREMIX flame code containing subsets of the detailed chemical mechanism.

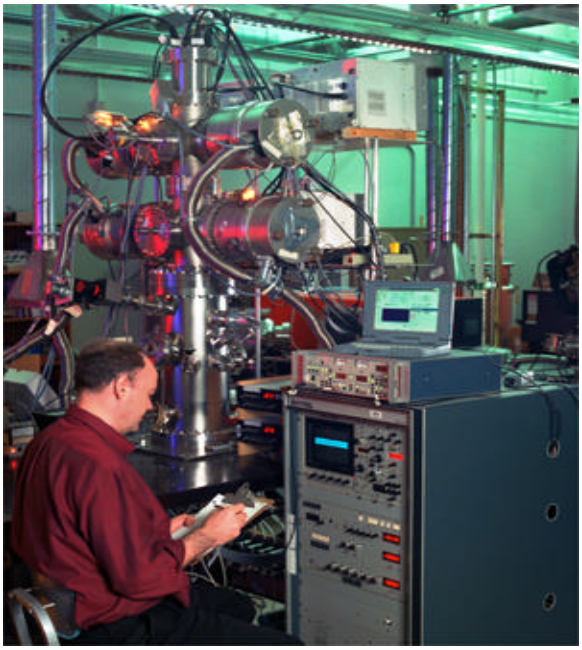

Figure 1. A photograph of our experimental apparatus. Apparatus consists of a low pressure burner equipped for MB-MS, LIF, and thin-wire thermometrv.

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3. RESULTS

The PREMIX calculations predict very well the H_2, N_2O, NH_3, NO_2, N_2, and NO, O_2, and H_2O stable species concentrations, as well as the OH, NH, and O radical profiles in the flames studied. Figure 2 shows the experimental and modeled OH profiles for the $H_2/N_2O/NO_2$ flame. The experimental LIF concentrations are converted to mole fractions using the measured flame temperatures and then normalized to the calculated mole fractions for comparison purposes. The model calculations predict well the shape of the OH radical throughout the flame, including a peak near 3.0 mm. Williams and Fleming observed a similar peak in their OH profile of premixed methane flames with O_2 and NO_2 oxidizers, and attributed it to the exothermic reaction $H+NO_2=OH+NO$ (Williams and Fleming, 1991). Our model calculations also predict well the shapes of the OH profiles of the H_2/N_2O and $H_2/NH_3/N_2O$ flames. The calculations show approximately a 55% decrease in the postflame OH mole fraction when ~4% NH_3 is added to the H_2/N_2O flame. This decrease agrees well with the observed OH decrease of ~45% (Sausa, Venizelos, and Cabalo, 2006).

OH rate analysis for the $H_2/N_2O/NO_2$ flame reveals that OH is formed mainly from the reactions $NO_2+H=NO+OH$ and $N_2O+H=OH+N_2$, and that it is consumed mostly from reactions $OH+OH=H_2O+O$ and $H_2+OH=H_2O+H$. The peak observed in the OH profiles shown in figure 2 results from the interplay between reactions $NO_2+H=NO+OH$ and $H_2+OH=H_2O+H$. In contrast, our OH rate analysis of the H_2/N_2O flame reveals that over 90% of OH is formed from the $N_2O + H = OH + N_2$ reaction, and ~94% is consumed from the $H_2+OH=H_2O+H$ reaction. A similar trend is observed for the $H_2/NH_3/N_2O$ flame. However, the $NH_3+OH=NH_2+H_2O$ reaction in the NH_3-doped flame plays more of a role in the consumption of OH, ~8%, compared to that in the neat flame (<0.01%).

Figure 3 is a pathway diagram of our modeled results showing the nitrogen chemistry occurring in the $NH_3/N_2O/Ar$ flame. The numbers in parentheses are the relative integrated net reaction rates from 0 to 30.0 mm for the disappearance of the indicated reactant by the various reactions. These integrated rates are normalized to 100 (2.55 x 10^{-5} mol/cm^2-sec) for the $NH_3 + OH = NH_2 + H_2O$ reaction. The N_2O reactant is consumed primarily by reactions

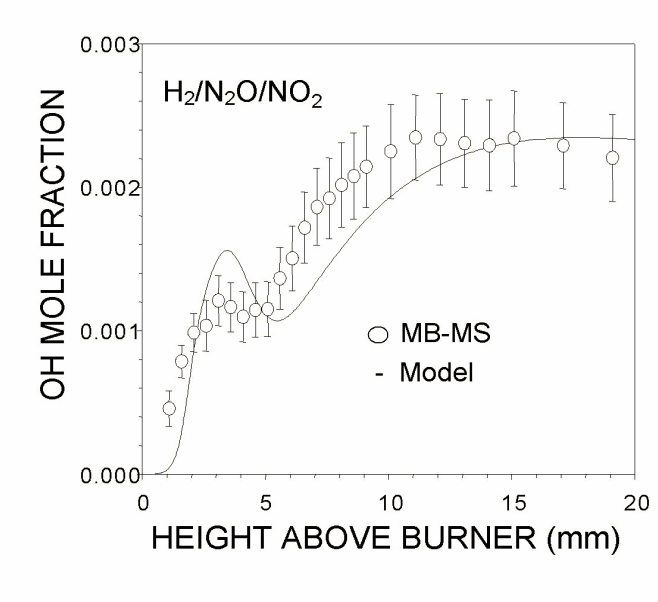

Figure 2. Experimental and calculated OH profiles of $H_2/N_2O/NO_2$ flame

with H and M to form N_2, whereas its companion reactant, NH_3, is consumed by reactions involving the OH, H, and O species to form NH_2. NH_3 is regenerated to some extent mainly from NH_2 species reacting with themselves. Although the reactions involving N_2O with H and M are the major routes for N_2 formation, ~ 32% of N_2 is formed from the NNH, NH_2, NH, NO, and N species.

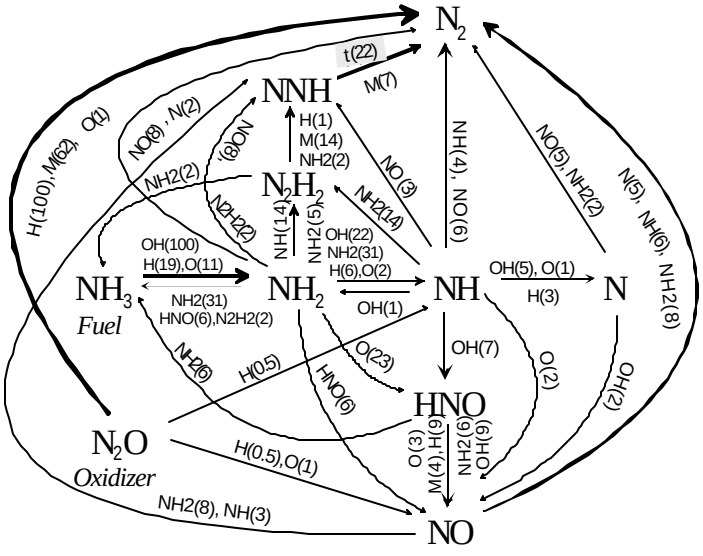

Figure 3. Pathway diagram of an NH_3/N_2O flame

Figure 4 shows a burning propellant and the nature of the burning propellant with thermochemical and physical processes that illustrate the complexity of the overall process. We modeled the gas phase at a high level of detail and finessed the condensed phase by a semi-empirical approach (Miller and Anderson, 2004).

Figure 5 shows both modeled and measured burn rates of nitrocellulose in the 1-100 MPa range, whereas figure 6 shows those of TAGZT in the 0.1 to 30 MPa range. Our model predicts the observed data extremely well for both NC (Miller and Anderson, 2004) and TAGzT (Tappen et al., 2006). We also computed the combustion products of TAGzT using our burn rate predictor at 1 MPa; their identity along with their mole fraction is as follows: N_2 – 0.446; H_2 – 0.211; NH_3 – 0.120; and HCN – 0.220. These values agree well with those observed by Tappen and coworkers except for H_2, which they could not observe because of a limitation in their experimental apparatus (Tappen et al., 2006)

4. CONCLUSION

Our advanced experimental and modeling capabilities provide the necessary tools for characterizing environmentally benign rocket-missile propellants with low sensitivity and signatures. We have developed a burning rate model with detailed chemical kinetics for solid propellants, and presented our results for nitrocellulose and TAGzT. Overall, our model predicts very well the burn rates of NC and TAGzT over a wide range of pressure.

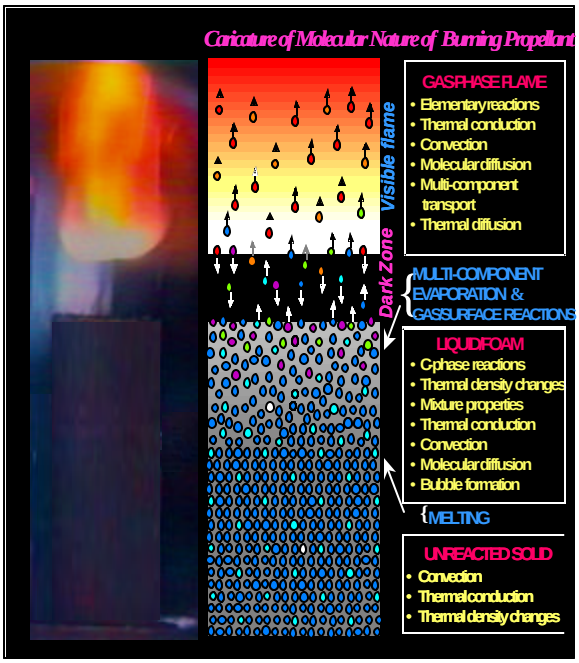

Figure 4. Molecular depiction (right) of a burning propellant strand (left).

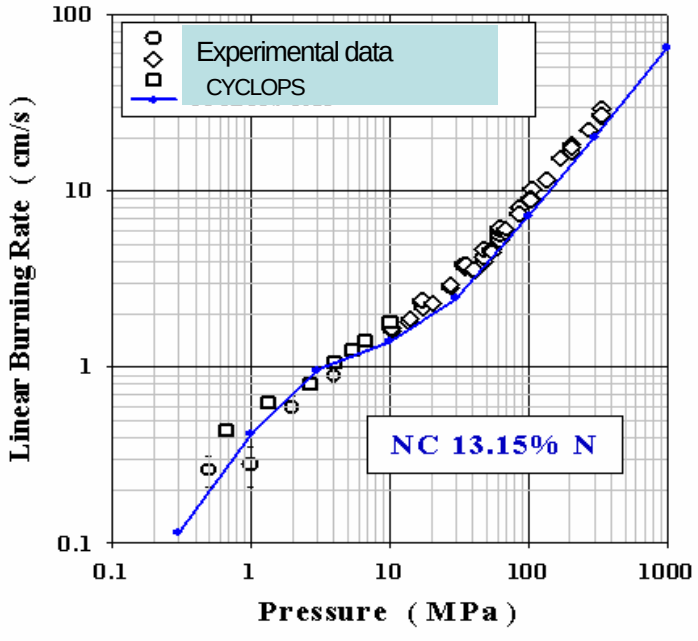

Figure 5. Calculated and observed burning rates of nitrocellulose

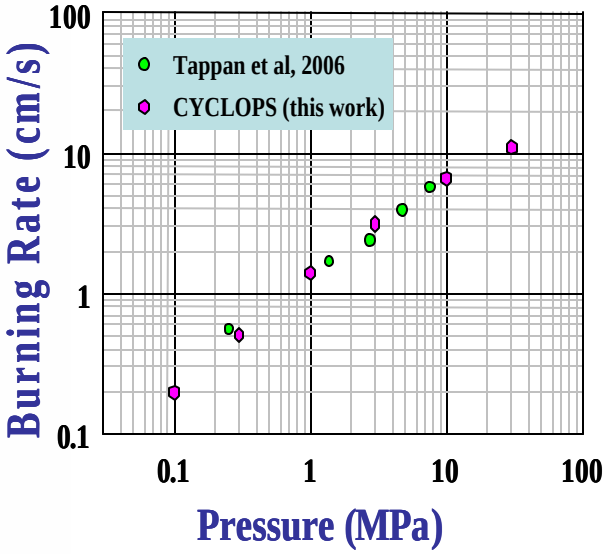

Figure 6. Calculated and observed burning rates of TAGzT.

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REFERENCES

Anderson, W. and Fontijn, A., 2005: Gas-Phase Kinetics for Propellant Combustion Modeling: Requirements and Experiments," in: *Overviews of Recent Research on Energetic Materials*, R.W. Shaw, T.B. Brill, and D.L. Thompson, Eds., Advanced Series in Physical Chemistry Vol. 16 (World Scientific, London, chapter 7, and references therein.

Miller, M. and Anderson, W., 2004: Burning-Rate Predictor for Multi-Ingredient Propellants: Nitrate-Ester Propellants, *J. Prop. Power*, **20**, 440-454, and references therein.

Sausa, R. and Anderson, W., 2005: Environmentally Benign Replacement Ingredients for Insensitive, Smokeless, Solid Rocket Propellants, Proceedings of the Partners in Environmental technology Technical Symposium and Workshop, Washington DC, November.

Sausa, R., Venizelos, D., and Cabalo, J., 2006: Mass Spectrometric, Laser-Induced Fluorescence, and Chemical Kinetic Modeling Studies of N2O and NO2, Burner-Stabilized Flames, *Annals of International Heat Transfer*, **13**, in press.

Tappan, B., Ali, A., Son, S., and Brill, T., 2006: Decomposition and Ignition of the High-Nitrogen Compound Triaminoguanidinium Azotetrazolate (TAGzT), *Propellants, Explosives, Pyrotechnics*, **31**, 163-169.

Venizelos, D. and Sausa, R., 2000: Detailed Chemical Kinetics Studies of an $NH_3/N_2O/Ar$ Flame by Laser-Induced Fluorescence, Mass Spectrometry, and Modeling, *Twenty-eight Symposium (International) on Combustion, The Combustion Institute*, **28,** 2411-2418, and references therein.

Venizelos, D. and Sausa, R., 1998: Laser-Induced Fluorescence, Mass Spectrometric, and Modeling Studies of Neat and NH_3-doped $H_2/N_2O/Ar$ Flames, *Combust. and Flame,* **115**, 313-326.

Williams, B. and Fleming, J., 1995: Comparison of Species Profiles Between O_2 and NO_2 Oxidizers in Premixed Methane Flames, *Combustion and Flame,* **100**, 571-590.