THEORY OF COMBUSTION OF LIQUID PROPELLANTS BASED ON HYDROXYLAMMONIUM NITRATE

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13. ABSTRACT (*Maximum 200 words*)

Deflagration velocities of liquid propellants based on hydroxylammonium nitrate are controlled by the chemistry of decomposition of this oxidizer in aqueous solutions. Theory was developed for the deflagration velocity and its dependence on oxidizer concentration, giving excellent agreement with experiment and suggesting that the rate of the initial proton-transfer step determines the deflagration rate. Nitramine deflagration also was considered, with two-phase flow in the reaction zone taken into account, employing empirical one-step Arrhenius chemistry. Although excellent agreement of theoretical deflagration rates with experiment was obtained from 0.5 to 10^3 atm, attempts to relate the one-step rate constants to rates of known elementary steps were only partially successful. Asymptotic analysis was also completed for the structure and burning velocity of carbon monoxide-nitrous oxide flames, which have some relevance to propellant deflagration. For these last flames, there is good agreement with numerical integrations, and differences from experiment are explicable. In general, the research advances our understanding of homogeneous propellant deflagration.

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THEORY OF COMBUSTION OF LIQUID PROPELLANTS BASED ON HYDROXYLAMMONIUM NITRATE

by

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1. PROBLEM STATEMENT

The summary statement of the problem initially proposed for investigation, as it appeared in the abstract of the research proposal, is the following:

Hydroxylammonium nitrate (HAN) is a major constituent in a new class of liquid monopropellants that have many attractive characteristics. Experimental studies in recent years have now provided enough information on the properties of these propellants to enable reasonable theoretical analyses of their deflagration to be initiated. Deflagration theory of the type that has achieved success for describing the burning rates of ammonium perchlorate and of nitramines will be applied to HAN-based propellants for investigating the structure of the combustion zone. The theory considers the chemical kinetics, energetics and fluid dynamics of the combustion, making use of asymptotic analysis to decide what combustion mechanisms would be consistent with available data. On the basis of these results, predictions will be made of burning mechanisms and burning rates for conditions not yet investigated experimentally. The interaction of theory with experiment can then enhance understanding of the combustion of HAN-based propellants.

This objective was accomplished quickly enough to extend the studies to other deflagration problems related to propellant combustion. Nitramine deflagration and deflagration of gaseous reactants released during propellant combustion were therefore also considered. Attention was still restricted to systems for which measurements of

deflagration velocities were available, so that predictions of the asymptotic analyses could be compared with experiment.

2. PRINCIPAL RESULTS

The study of HAN combustion first employed experimental and theoretical results, obtained mainly at the Combustion Research Facility of SANDIA in Livermore CA to determine that the propellant deflagration velocity usually is controlled mainly by the HAN decomposition rate and that the observed pressure dependence can be explained by hydrodynamic effects, with a pressure-independent local planar front propagation velocity. At lower pressures front curvature and corrugation through hydrodynamic instability leads to an apparent deflagration velocity that decreases with increasing pressure. At high enough pressures, the deflagration velocity is nearly independent of pressure and the front more nearly planar. The present research addressed this high-pressure regime and derived theoretical expressions for the deflagration velocity that were compared with the high-pressure experimental results. Attention was focused in particular on the increase in the deflagration velocity with increasing HAN concentration.

Deflagration theory of the type that has achieved success for describing burning rates of ammonium perchlorate and nitramine propellants was applied to aqueous solutions of hydroxylammonium nitrate (HAN). The theory considered the chemical kinetics, energetics and fluid dynamics of the combustion zone, making use of asymptotic analysis to decide what combustion mechanisms are consistent with the available data. The model was used in conjunction with experimental results to obtain frequency factors and overall activation energies for HAN decomposition. Results suggest that deflagration rates are controlled by condensed-phase combustion with production of water dominating the heat release and that phase and chemical equilibria are not approached in the condensed-phase

combustion zone. The results also tend to support the postulate that the rate of HAN decomposition is controlled by the rate of proton transfer from NH_3OH^+ to NO_3^-. Theoretical predictions of deflagration rates are in good agreement with experimental data. The results are reported in a paper that has been submitted for publication.[1]

The research on nitramine deflagration first adopted a one-step, empirical, Arrhenius description of the gas-phase chemistry and proceeded to analyze effects of two-phase flow in the melt layer. Methods of asymptotic analysis were employed to extend an earlier model for the deflagration of nitramines (both HMX and RDX) to account for the presence of bubbles and droplets in a two-phase layer at the propellant surface during combustion. Two zones were identified in the two-phase region: one, at higher liquid volume fractions, maintains evaporative equilibrium, whereas the other, at lower liquid volume fractions, exhibits nonequilibrium vaporization. By introducing the most reasonable estimates for two-phase behavior of nitramines, the steady burning rates were found to be close to those obtained for models with a sharp liquid-gas interface. Good agreement with measured burning rates and pressure and temperature sensitivities were achieved through reasonable approximations concerning overall chemical-kinetic parameters. This work has now been published.[2]

Next, attempts were pursued to derive the successful empirical rate parameters for nitramine from the full gas-phase chemical kinetics by suitable development of reduced chemical-kinetic mechanisms through asymptotics.[3] To remove the complicating influence of condensed-phase chemistry, this work is focusing on RDX deflagration. Entirely satisfactory reductions of kinetic mechanisms still have not been obtained. However, it has become clear that unimolecular RDX decomposition cannot be the sole initiating step. There must be significant bimolecular contributions of some kind if the observed pressure dependence of the deflagration rate is to be predicted correctly. The work has not yet

identified which bimolecular steps are likely to be most important. The studies are continuing (at present, without funding) towards adoption of a preferred reduced mechanism capable of producing agreement with observed deflagration velocities while maintaining consistency with known rates of elementary steps.

In a further problem related to the gas-phase chemistry, asymptotic analysis was employed to investigate the carbon monoxide-nitrous oxide premixed flame structure. Activation-energy asymptotics were applied to a non-adiabatic premixed laminar flame of carbon monoxide and nitrous oxide which had been studied experimentally. Since the reaction proceeds mainly through the one-step process $CO + N_2O \rightarrow CO_2 + N_2$, analysis of this flame provides a unique illustration of the predictive capability of activation-energy asymptotics. One- and two-term expansions in the reciprocal of the Zel'dovich number were used for predicting the burning velocity in a two-reactant, four-species flame with one-step irreversible chemistry. The effects of variable transport and thermodynamic properties and of variable mean molecular weight were included. The predicted burning rate and the flame structure were compared with numerical calculations and with recently reported experimental measurements for fuel/oxidizer equivalence ratios of 1.0, 1.32 and 1.5, flame temperatures near 2062 K, and a pressure of 50 torr. While there is good agreement between the numerical and asymptotic results, the experimental burning velocity is larger by about a factor of three, a difference that is consistent with estimated influences of possible non-one-dimensional effects in the experiment. Results of this research have been submitted for publication.[4]

In general, this research has provided some advances in our understanding of propellant deflagration, by use of asymptotic analysis. However, more needs to be done along these lines, especially for nitramines and other homogeneous propellants.

3. SCIENTIFIC PERSONNEL

Besides the principal investigator, there are a number of fresh Ph.D.'s who were supported on this project, for a limited time each:

S.H. Chung, currently at Seoul National University, Korea

B.D. Shaw, currently at University of California, Davis

S.C. Li, currently at UCSD

G.T. Linteris, currently at UCSD

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