

LEVEL III

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NAVSEA Propulsion Research Program

Program Element 61153N

Decomposition and Interaction of
Propellant Ingredients

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Technical Objective:

Investigate decomposition, deflagration, and interaction of conventional and new propellant ingredients with the goal of improving performance and safety, reducing cost to achieve specified performance, and providing methods to assure reproducibility during production and usage.

Background:

There is a continuous need in the field of solid propellant combustion to understand and solve problems such as cook-off hazards, burn rate anomalies, burn rate tailoring and control, combustion stability, combustion efficiency, and the use of high energy or highly aluminized propellants. The research effort of this program supplies knowledge and fundamental data necessary to understand and to solve combustion problems. It also generates the basis for the control of propellant combustion behavior, the development of new propellant systems, the use of novel ingredients, and the quality control of ingredients. The research data and results are indispensable for consultation in the combustion community, for the achievement of specific combustion goals, and for a critical assessment and application of data reported in the literature.

Approach:

The program utilizes a wide variety of experimental methods as well as theoretical studies in specific areas such as burn rate modeling. These methods have been well documented in numerous presentations, publications, and patents. They allow the study of catalyzed and uncatalyzed decomposition of propellant oxidizers, binders, and metal fuels, and the evaluation of combustion characteristics, combustion performance, and combustion stability of experimental and production lot propellants. Where required, established test methods are modified or new methods are developed to meet specific needs such as in particle size analysis or ingredient modification. In-house or commercial analytical capabilities are employed whenever feasible or promising. The interpretation of results is facilitated by limiting the number of sample and test parameters as much as possible and by rigorous control of test variables. In the process, new options for tailoring of propellant combustion behavior, new propellant systems, and quality control of ingredients are evolved.

Progress

The decomposition and combustion of HMX were studied extensively in the past to promote the efficient use of this ingredient in solid propellant technology. The number of proposed decomposition steps and the range of kinetic data suggest a rather complex decomposition behavior of HMX. This work constitutes an effort to gain additional details and clarification of the HMX thermal decomposition mechanism. Most important, such decomposition data are being sought which would support and enhance the tailoring of HMX combustion behavior.

During the past year, the study of HMX decomposition has been continued and expanded. Incomplete work¹ was completed and specific reactions such as HMX liquefaction were studied in more detail. The burn rates of HMX/additive mixtures were measured to test the screening of potential burn rate modifiers by differential thermal analysis.

Decomposition and Liquefaction of HMX

The evaluation of the decomposition kinetics of solid HMX by weight loss measurements has been completed during the reporting period. The data were obtained in the temperature range 229–269°C in gaseous environments consisting of oxygen, air and nitrogen at atmospheric pressure (93 kPa). Details of the weight loss versus time curves are contained in a paper which was submitted for publication.² From these curves, rate constants were derived for a first order reaction. The temperature sensitivity of the rate constants as shown in Figure 1 can be expressed by the equations:

in oxygen	$k = 1.2 \times 10^{17} \exp (-49,700/RT) \text{ sec}^{-1}$
in air	$k = 9.3 \times 10^{16} \exp (-49,000/RT) \text{ sec}^{-1}$
in nitrogen	$k = 3.2 \times 10^{11} \exp (-35,100/RT) \text{ sec}^{-1}$

The results suggest the breakage of the N-NO₂ bond as rate determining step of decomposition in oxygen containing gases.² Oxygen clearly had the effect of an inhibitor. Its removal increased the decomposition rates and lowered the activation energy and preexponential factor. Intramolecular and intermolecular oxygen transfer was proposed as possible reaction parallel to N-NO₂ fission in order to interpret this unexpected result. Additional measurements, particularly product analysis, will be necessary to determine the prevalence of one or the other steps depending on experimental conditions.

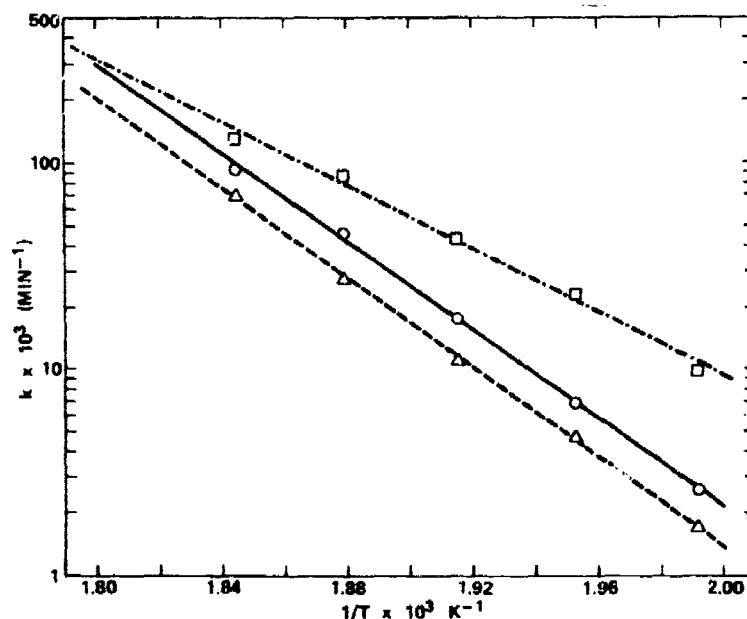


Figure 1. Temperature Dependence of Rate Constants for the Decomposition of HMX in 93 kPa of Nitrogen (---), Air (—), and Oxygen (---).

Nonisothermal differential thermal analysis of HMX was started to investigate the decomposition kinetics based on the exothermicity of HMX reaction and to study the influence of experimental parameters on the location and amount of heat release. To date, two test series have been completed in air at atmospheric pressure. A third test series was performed in 3.54 MPa of nitrogen. Figure 2 shows the results as evaluated by Kissinger's Method. The following temperature dependence of the rate constants was obtained from the data of Figure 2.

in 93 kPa air for

$$\begin{array}{ll} 4 \text{ mg samples} & k = 7.6 \times 10^{15} \exp (-44,700/RT) \text{ sec}^{-1} \\ 5 \text{ mg samples} & k = 4.5 \times 10^{15} \exp (-44,800/RT) \text{ sec}^{-1} \end{array}$$

and in 3.54 MPa nitrogen for

$$2 \text{ mg samples} \quad k = 2.9 \times 10^8 \exp (-25,900/RT) \text{ sec}^{-1}$$

The kinetic parameters at atmospheric pressure are comparable with those obtained from weight loss measurements in oxygen containing gases. It is interesting to note that in the case of 4 mg samples, crossing of the liquefaction point in Figure 2 ($1/T = 1.8078 \times 10^{-3} \text{ K}^{-1}$) did not cause a change in slope. Thus the phase change seems to be without effect on the kinetics under the given conditions. The same conclusion is indicated by preliminary results obtained from differential thermal analysis of liquid HMX in an open system. In contrast, the exothermicity in closed systems tends to increase appreciably and frequently leads to ignition. Under these circumstances, high activation energies must be expected because of self-heating of reacting decomposition products which are hindered in their mobility away from the primary (endothermic) source.

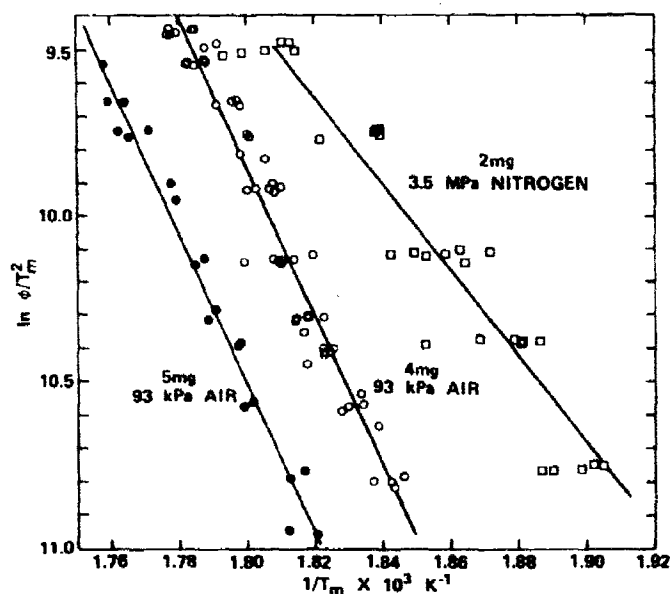


Figure 2. Plot of Differential Thermal Analysis Data According to Kissinger.⁷ ϕ =Heating Rate, T_m =Peak Temperature of DTA Exotherm. Data are for the Thermal Decomposition of 5 mg samples (—•—) and 4 mg samples (—○—) of HMX in 93 kPa of Air and for 2 mg samples (---□---) in 3.54 MPa of Nitrogen.

A similar mechanism may explain the high temperature sensitivity of the liquefaction of HMX. Figure 3 shows the time needed to liquefy HMX samples of approximately 7 mg upon isothermal heating at temperatures in the range 266-275°C. The slope of the straight line yielded the following temperature dependence of the time to liquefaction.

$$\ln t = -182 + 202,200/RT \text{ sec}$$

Variation of sample size, of particle size, and of the ability of decomposition products to escape influenced the liquefaction behavior of HMX (for details see reference (2)). Some important conclusions could be drawn:

1. At constant sample size, liquefaction depends on particle size. Processes occurring within a particle seem to be more important than surface processes.
2. A minimum particle size is necessary for liquefaction at 266°C. Large particles have a lower limiting temperature.
3. The importance of the gaseous environment is shown by the return of liquefaction in a covered furnace at constant particle size and sample size. This could be due to a decreasing flow of gaseous reaction products from the interior of the particles as the outside pressure of the species builds up, to increased heterogeneous surface reactions, or to both.

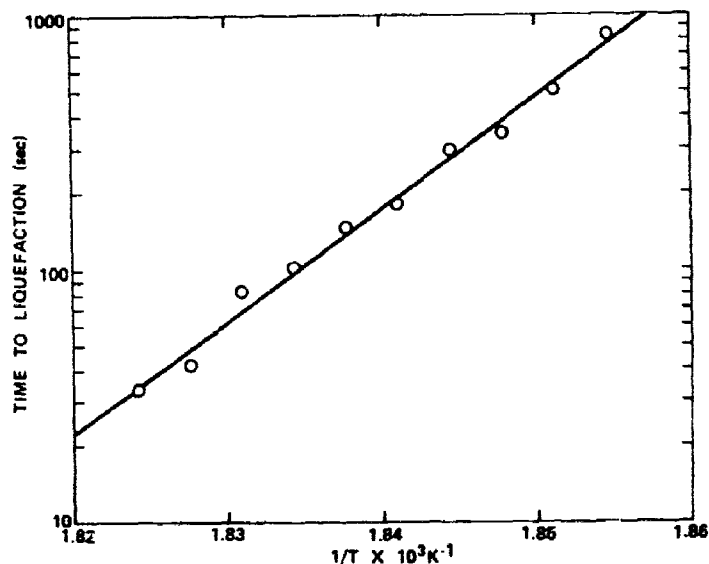


Figure 3. Plot Showing the Temperature Sensitivity of HMX Liquefaction. Test Results Cover the Temperature Range 266-275°C.

4. There is a minimum sample size for liquefaction.

5. At constant sample size, large particles liquefy faster than small particles.

Liquefaction mechanisms which are compatible with these observations may be suggested. They have to include thermal decomposition as a major process, the generation of gaseous decomposition products, and interaction with the condensed phase and surrounding gas phase. The concept of self-heating appears most promising at this time for the analysis of liquefaction and probably also for the treatment of the reaction of liquid HMX. A check for an increase of the heats of reaction and the acceleration of the decomposition kinetics³ as a function of "escape of decomposition products" may indeed help to resolve uncertainties concerning reaction mechanisms and activation energies. It may also supply clues with regard to the best point of attack in burn rate modification.

Decomposition and Combustion of HMX/Additive Mixtures

Several mixtures of HMX with ammonium compounds have been investigated by DTA. These additives were expected to supply NH_3 which was found earlier to have a positive effect on HMX decomposition.¹ After DTA testing, pellets were pressed from the mixed powders and fired in the window bomb to determine the burning rates. No burn rate effects were found at the 2.9% additive level. In contrast, the effect of ammonium perchlorate (AP) on the decomposition and combustion of AP/HMX mixtures was positive and DTA, as well as burn rate screening, showed the same trend. However, the concentrations of AP were too high to be considered as an additive. Compounds which promote the heat release in or near the condensed phase by chemical reaction with HMX or other propellant ingredients seem to be most promising for the burn rate control of HMX. At present, combustion and burn rate measurements are more reliable for the screening of additives than the cheaper and faster thermal analysis.

Plans

CFY

1. Investigate decomposition of HMX in solid and liquid phase.
2. Study HMX decomposition as function of gaseous environment and pressure.
3. Study changes of HMX reaction due to liquefaction.
4. Continue investigation of burn rate modification for HMX.

CFY + 1

1. Continue above. Apply results in the combustion of high energy propellants.
2. Study aluminum combustion in the presence of HMX.

3. Apply novel binders in high energy propellants.
4. Study ignition of nitramine containing propellants.

CFY + 2

1. Continue items under CFY + 1

Milestones

MILESTONES	FY 82	FY 83
• HMX DECOMPOSITION		
• IN NITROGEN	_____	
• IN OXYGEN	_____	
• AT LIQUEFACTION	_____	
• IN LIQUID PHASE	_____	
• AT SUPERATMOSPHERIC PRESSURE	_____	_____
• HOT STAGE MICROSCOPY		
• BURN RATE MODIFICATION		
• HIGH ENERGY PROPELLANTS		
• COMBUSTION OF ALUMINUM		_____
• EFFECT OF BINDER		_____
• IGNITION		_____

References

1. Kraeutle, K. J., "A Contribution to the Knowledge of HMX Decomposition and Application of Results," Proceedings of the 17th JANNAF Combustion Meeting, CPIA Publication 329, Vol. II, November 1980.
2. Kraeutle, K. J., "The Thermal Decomposition of HMX: Effect of Experimental Conditions and of Additives," presented at the 18th JANNAF Combustion Meeting, October 19-23, 1981, Jet Propulsion Lab, Pasadena, Calif. To be published in the proceedings of the meeting.
3. Tarver, C. M., McGuire, R. R., Lee, E. L., Wrenn, E. W., and Brein, K. R., "The Thermal Decomposition of Explosives with Full Containment in One-Dimensional Geometries," University of California, Lawrence Livermore Laboratory Report 80435, December 1978.