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AFOSR 67-1788

Service through Science

Quarterly Technical Summary Report No. 6

March 1, 1967 to May 31, 1967

RESEARCH ON THE DEFLAGRATION
OF HIGH-ENERGY SOLID OXIDIZERS

Contract No. AF 49(638)-1645

AD818227

To:

Air Force Office of Scientific Research
Washington, D. C.

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Kinetics and Combustion Group
Research Division

June 30, 1967

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ATLANTIC RESEARCH CORPORATION
ALEXANDRIA, VIRGINIA

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RESEARCH ON THE DEFLAGRATION
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To:

Air Force Office of Scientific Research
Washington, D. C.

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I. ABSTRACT AND INTRODUCTION

During this quarter, the study of the deflagration of hydroxyl-ammonium perchlorate (HAP) was completed. The results obtained since the previous report are given, together with further analysis of the HAP deflagration process. Some data on ammonium perchlorate (AP) have also been obtained and these are presented. The AP deflagration process is also analyzed and a concept of cellular flame structure is advanced.

II. FURTHER EXPERIMENTS ON HAP AND AP

In the previous report (1), the deflagration rate of HAP as a function of pressure, the effect of H_2O on the deflagration, and the critical tube diameter for quenching of the deflagration were studied. Some experiments on AP quenching and burning rates were also reported. This report presents further results and analysis of HAP and AP deflagration.

The technique of burning solid oxidizers in glass tubes, which act as heat sinks, requires that the effect of the tubes on the deflagration rates be known. For HAP we have measured the burning rates at 200 atm as a function of tube diameter. These are shown in the table below.

| <u>Pyrex Tube i.d. (mm)</u> | <u>\dot{m} (g/cm² sec)</u> |
|-----------------------------|--|
| 3.8 | 4.08 4.24 |
| 5.8 | 4.52 4.63 |
| 8.0 | 5.25 (averg.) |

The last value is an average of several experiments. A monotonic increase in \dot{m} with increasing tube diameter is found, continuing even up to 8 mm i.d. tubes, which exceed the quenching diameter by a factor of three at 200 atm. We do not believe the reported (1) pressure dependence of the deflagration

rate is substantially affected by this finding, but the low value of the measured flame temperature (see below), which is less than the calculated adiabatic value, may be partially due to this.

The deflagration rate for AP also varies with tube diameter and with particle size. In figure 1 are presented the complete results of the mass rates vs. pressure, which were only partially completed last report period. The figure is self-explanatory. The data are necessary for interpretation of the quenching diameter results (1) but we have nothing to add to the discussion beyond what was presented previously (1).

When burning AP powder compacted to only ~60% of crystal density, ~40% of the strand is void space filled with high pressure gas. This gas dilutes the combustion product gases and lowers the flame temperature. It was calculated (1) that at 100 atm, the flame temperature of AP would be lowered approximately 50°C and this would result in a decrease of \dot{m} of about 20%. To determine if this assumption is correct, we have burned 21 μ AP at 60% crystal density in 8 mm i.d. tubes at 70 atm using He and Ar as pressurizing gases. The mass rates were the same for both gases, 1.41 g/cm² sec (average of several), and about 10% higher than the rate using N₂ as pressurizing gas, 1.27 g/cm² sec. Since the heat capacities of He and Ar are the same and lower than N₂, but the thermal conductivities of He and Ar vary greatly, this establishes that there are no significant superimposed thermal conduction effects.

The product gas temperature for deflagrating HAP has been measured using fine thermocouples. The method was essentially the same as in previous work (2). It consisted of imbedding thermocouples in strands compacted to ~98% of crystal density and measuring the voltage output with a recording oscillograph as the deflagration wave overran the couple. Chromel-Alumel of 2 mil wire diameter was used and the measured temperature was corrected for radiation heat loss of the bead. This correction was 25°. The flame temperatures were 1320 and 1290°K at 200 atm. The average of these is 1305°K and this compares with the calculated value at 200 atm at 1413°K. For comparison the calculated and measured values for AP at 100 atm are 1440 and 1203°K, respectively (4).

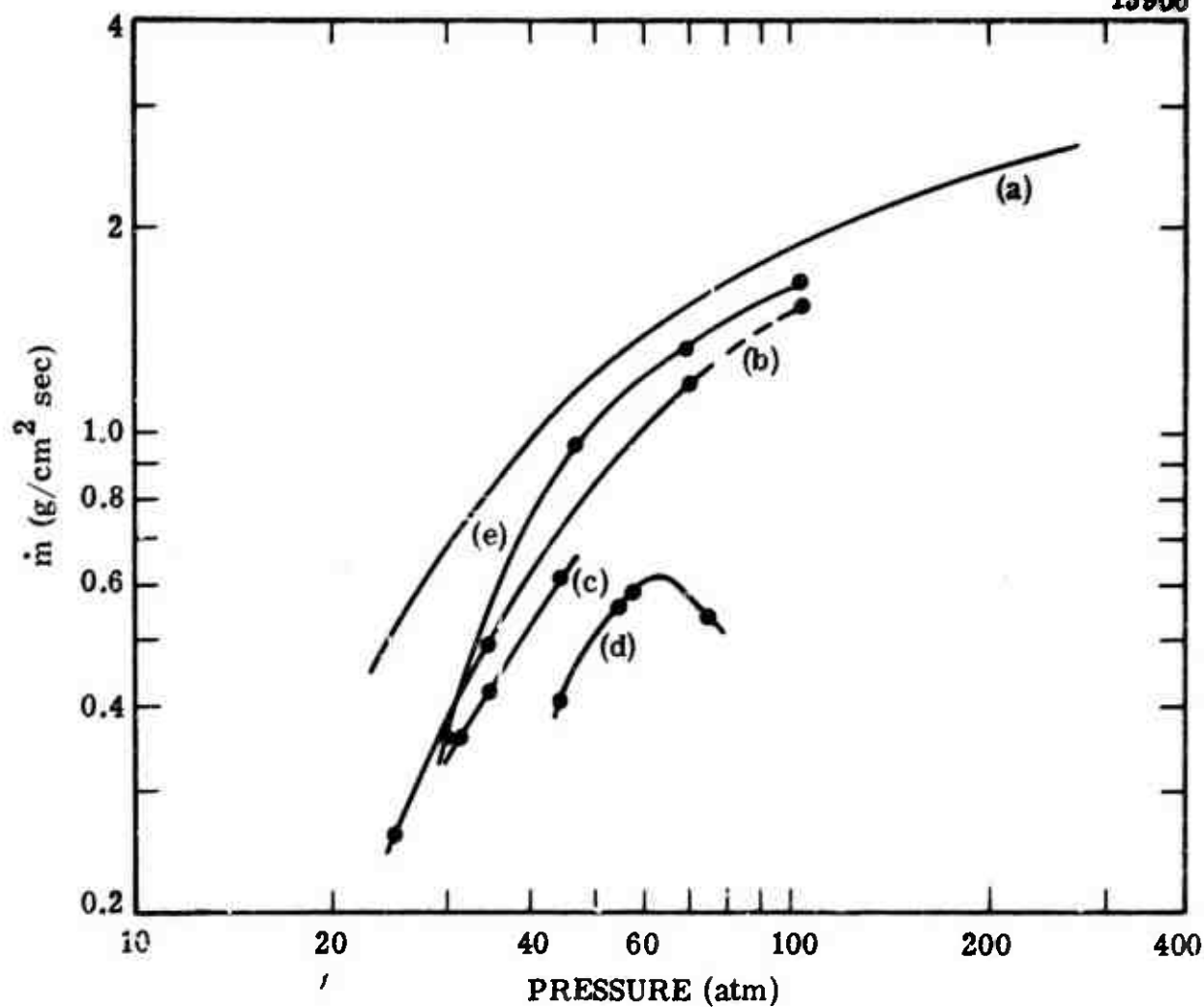


Figure 1. Mass Deflagration Rate Versus Pressure for AP. (a) Data from Reference 3 for Compacted Strands Near Crystal Density; (b) 21μ AP, 1.15 g/cc Density, 6mm Pyrex Tubes; (c) 21μ AP, 1.15 g/cc Density, 3.3mm Pyrex Tubes; (d) 203μ AP, 1.28 g/cc Density, 5.7mm Pyrex Tubes; (e) 21μ AP, 1.15 g/cc Density, 8.0 mm Pyrex Tubes.

III. ANALYSIS OF DEFLAGRATION PROCESS OF HAP AND AP

It is instructive to compare the deflagration rate vs. pressure curves for HAP and AP (1). When HAP does burn, it burns at approximately twice the rate of AP, but it has a lower inflammability limit of ~ 140 atm which compares to the lower pressure limit of AP of ~ 20 atm. This occurs even though the flame temperature of HAP is $\sim 100^\circ$ above that for AP, and the heat of vaporization is only about half of that for AP. A reasonable explanation for this difference in burning behavior between HAP and AP could be the difference in the extent of condensed phase heat release in the two monopropellants. We postulate that in HAP heat release at or just below the surface is necessary to drive the deflagration. The condensed phase reactions in turn require a heat flux from the gas phase to sustain them. As pressure falls, this flux decreases and the condensed phase reactions diminish due to the lowering of surface temperature. Such a mechanism can account for the relatively fast rates observed for HAP deflagration and yet allow for the fact that it has a lower-pressure inflammability limit many times higher than AP. The model can be formulated one dimensionally by writing a heat balance at the surface of the deflagrating solid:

$$\lambda \left. \frac{dt}{dx} \right|_g = \dot{m} [c_p (T_s - T_u) + Q_{vap} - Q_{c\phi}] ,$$

which for an assumed linear temperature gradient in the gas yields

$$\dot{m} = \frac{\lambda (T_f - T_s)}{L [c_p (T_s - T_u) + Q_{vap} - Q_{c\phi}]}$$

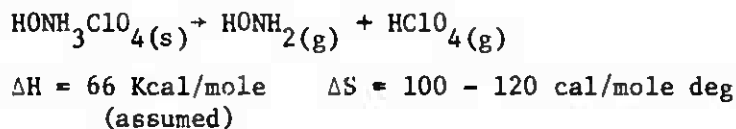
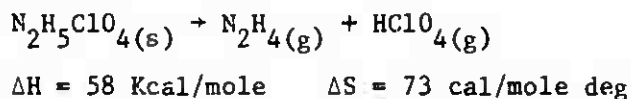
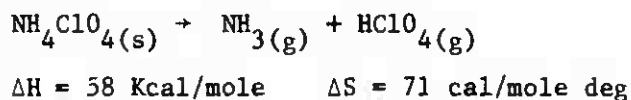
L is the gas reaction zone thickness and $Q_{c\phi}$ is the heat liberated in the surface plane. For AP, if $Q_{c\phi}$ is neglected, and the following values for the other terms are chosen (these have been either measured or are acceptable estimates)

| | |
|----------------------------|--------|
| T_f (°C) | 930 |
| $(T_f - T_s)$ | 400 |
| $C_p (T_s - T_u)$ (cal/g) | 150 |
| Q_{vap} (cal/g) | 500 |
| λ (cal/cm sec deg) | .00015 |

one calculates that the flame standoff distance must be approximately 0.3 microns at 150 atm to obtain a mass burning rate of $3 \text{ g/cm}^2 \text{ sec}$. In the case of HAP, $T_f = 1035^\circ\text{C}$, $Q_{vap} = 250 \text{ cal/g}$, and if T_s is taken as $\sim 400^\circ\text{C}$ (arbitrarily selected as the approximate 1 atm boiling point obtained by extrapolation of data in (5)) then at 150 atm where $\dot{m} = 6 \text{ g/cm}^2 \text{ sec}$, L is calculated to be 0.45 microns, if $Q_{c\phi}$ is neglected (C_p and λ are estimated to be the same as for AP). This accounts for the faster burning rates observed for HAP but gives no clue as to why HAP then should not sustain deflagration down to pressures comparable to the lower limit of AP. The higher inflammability limit requires an adjustment of the model, i.e., we consider $Q_{c\phi}$. If the condensed phase heat release is assumed to be approximately of the same magnitude as Q_{vap} , then for the values given above at 150 atm, $L = 1.6\mu$. Thus, HAP will burn faster than AP even though the gas kinetics are slower, but since the gas heat flux is necessary to drive the surface reactions and thereby sustain the combustion, HAP can show a higher lower-pressure limit. We note that HAP deflagration rates will show a positive pressure exponent which will be contained in the L term of the above equation. Also there is no evidence in the foregoing discussion that condensed phase heat release may not occur to some extent in AP deflagration. In fact if $Q_{c\phi}$ in AP is 90% of the heat necessary to supply the sensible heat plus the heat of vaporization, L at 150 atm is still only 3μ .

One final point to be discussed in connection with HAP is its mode of vaporization. In the case of AP and hydrazine perchlorate (HP), vaporization is believed to occur with dissociation. The evidence is fairly strong and is given in references 6 and 7. This being the case, the heat

of vaporization is then 2R times the slope of the line obtained from a Clausius-Claperon plot of vapor pressure-temperature data. For HAP the vapor pressure as a function of temperature has been measured (5) by the Knudsen and Langmuir techniques, and although the actual magnitude of the pressures at the same temperatures differ by approximately a factor of 7, the slopes of the two curves both yield a heat of vaporization of 33 ± 1 kcal/mole. This assumes no dissociation and the value would be 66 kcal/mole with dissociation. In the absence of experimental evidence, one can check the validity of the non-dissociative assumption by examining the entropies of vaporization for the three oxidizers. The entropy is given by Q_{vap}/T , where T must be a temperature selected for each oxidizer where the vapor pressures are equal. Usually the 1 atm boiling temperature is used. Below we list the calculated entropies for AP, HP and HAP.



If vaporization occurred in the same way for all three compounds, one would expect to find all the ΔS 's approximately equal (as they are for AP, HP and other similar solids, see (6)). Since HAP exhibits an inordinately high ΔS_{vap} when calculated in this way, the argument favors a non-dissociative vaporization with an enthalpy of 33 kcal/mole.

In the course of our studies of the self-deflagration of solid oxidizers and the analysis of the results in terms of the structure of combustion waves, we have been led to the conclusion that ammonium perchlorate must exhibit cellular structure. Cellular flames have long been

known for gaseous combustion mixtures and are discussed in reference (8). They spontaneously form when the combustible mixture is stoichiometrically unbalanced and the diffusivity of the deficient component is higher than that of the component in excess. The ammonium perchlorate system meets these criteria, being oxidizer rich and NH_3 having a much higher diffusivity than the HClO_4 component. Under these conditions cells would be expected to form which should appear similar to the illustration of Figure 2 (not to scale). The dashed line above the solid AP represents the reaction zone boundary. Within a cell the diffusional stratification of gasified re-

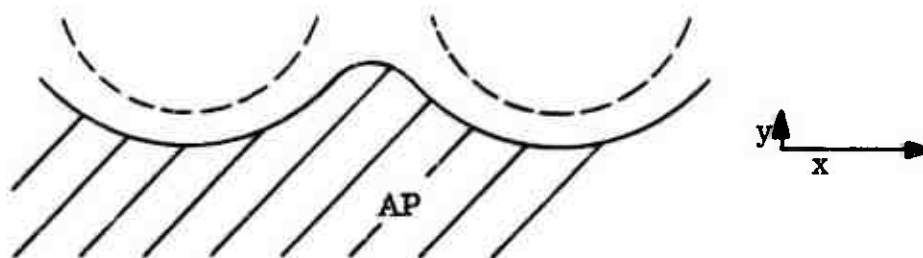


Figure 2. Cellular Flame Structure of Ammonium Perchlorate

actants yields a mixture of NH_3 and HClO_4 richer in NH_3 and more stoichiometrically balanced. The burning velocity will therefore be higher than between cells where the reactant mixture will be very fuel lean. Correspondingly, the heat flux back to the solid will be greater within the cells. During the burning of a single crystal of AP, cellular flames would be expected to engrave a pattern on the surface. Such an engraved pattern has been found by Price and Hightower (9) in their studies of the deflagration of single AP crystals, in which they quenched the combustion and examined the surface.

Another criterion which we believe must be met for cellular flames to form is the diffusion distance of an element of reactant should be

comparable to or larger than the reaction zone thickness. For AP at 80 atm pressure a one-dimensional treatment such as previously given yields a reaction zone of ~ 0.5 microns. An average diffusion distance, x , can be estimated from

$$x = \sqrt{2Dt} = \sqrt{2Dy/v_g}$$

where D is the diffusivity of NH_3 estimated to be $0.015 \text{ cm}^2/\text{sec}$ at 1000° and 80 atm, t is the average time spent in the reaction zone estimated as y/v_g where y is 0.5 microns and v_g is the average gas velocity which we calculate to be approximately 34 cm/sec. x therefore is 2 microns, and the ratio x/y is about 4. For the cellular flames of butane-air studied by Markstein (10) we estimate the analogous x/y ratio to be about 2. This criterion seems to be better fulfilled for the AP system. We further estimate the cell size to be approximately 100 times the reaction zone thickness based on comparison with the butane-air cells. This would predict a cell size at 80 atm of $\sim 50\mu$, which is approximately the dimension of the engraved pattern observed by Price and Hightower at 80 atm.

Cellular structure may be an important consideration when interpreting some combustion behavior of AP. It is likely not to be important when considering the burning of a single AP particle embedded in a propellant binder matrix. Also in the deflagration of pressed strands of the oxidizer made from AP of various particle sizes it probably becomes washed out. Conditions are fulfilled to a greater or lesser extent in other monopropellant-type oxidizer systems for formation of cellular flames although they too may be washed out and never observed by the melting and heterogeneity of the samples.

IV. PLANS FOR FUTURE WORK

Studies of extinguishment of propellants by rapid depressurization, mentioned in previous reports in this series, are now underway. The apparatus has been built and instrumented and some initial experiments were made. During the next quarter it is expected that preliminary results will be obtained and a complete report on the work will then be given.

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UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

| | | | |
|---|--|--|-----------------------|
| 1. ORIGINATING ACTIVITY (Corporate author) Atlantic Research Corporation Alexandria, Virginia | | 2a. REPORT SECURITY CLASSIFICATION Unclassified | |
| | | 2b. GROUP | |
| 3. REPORT TITLE RESEARCH ON THE DEFLAGRATION OF HIGH-ENERGY SOLID OXIDIZERS | | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) QPR - March 1, 1967 to May 31, 1967 | | | |
| 5. AUTHOR(S) (First name, middle initial, last name) G. von Elbe R. Friedman E. T. McHale J. B. Levy | | | |
| 6. REPORT DATE June 30, 1967 | | 7a. TOTAL NO. OF PAGES 9 | 7b. NO. OF REFS 10 |
| 8a. CONTRACT OR GRANT NO. AF 49(638)-1645 | | 8b. ORIGINATOR'S REPORT NUMBER(S) | |
| b. PROJECT NO. | | | |
| c. | | 8c. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | |
| d. | | AFOSR 67-1788 | |
| 10. DISTRIBUTION STATEMENT | | | |
| 11. SUPPLEMENTARY NOTES | | 12. SPONSORING MILITARY ACTIVITY Air Force Office of Scientific Research Washington, D. C. | |
| 13. ABSTRACT During this quarter, the study of the deflagration of hydroxylammonium perchlorate (HAP) was completed. The results obtained since the previous report are given, together with further analysis of the HAP deflagration process. Some data on ammonium perchlorate (AP) have also been obtained and these are presented. The AP deflagration process is also analyzed and a concept of cellular flame structure is advanced. | | | |

DD FORM 1 NOV 66 1473

UNCLASSIFIED

Security Classification

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Security Classification

| 14 | KEY WORDS | LINK A | | LINK B | | LINK C | |
|----|---|--------|----|--------|----|--------|----|
| | | ROLE | WT | ROLE | WT | ROLE | WT |
| | Hydroxylammonium perchlorate Ammonium perchlorate Deflagration Solid oxidizers Cellular flame structure | | | | | | |

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Security Classification