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Quarterly Technical Summary Report No. 12 March 1, 1965 to May 31, 1965

> RESEARCH ON THE DEFLAGRATION OF HIGH-ENERGY SOLID OXIDIZERS (U)

Contract No. AF 49(638)-1169

to

Air Force Office of Scientific Research Washington 25, D. C.

from

Kinetics and Combustion Group Atlantic Research Corporation Alexandria, Virginia

August 11, 1965

Chief Investigator: J. B. Levy Internal Consultants: G. von Elbe and R. Friedman Chemist: E. T. McHale Chemist: C. Midkiff



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RESEARCH ON THE DEFLAGRATION OF HIGH-ENERGY SOLID OXIDIZERS (U)

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RESEARCH ON THE DEFLAGRATION OF HIGH-ENERGY SOLID OXIDIZERS(U)

I. ABSTRACT

The measurements of the flame temperature of deflagrating hydrazine diperchlorate using fine Chromel-Alumel thermocouples have been completed at 28 atm. A value of 1385 ± 35 K (corrected for radiation heat loss of the thermocouple) was obtained. Experiments at 55 atm have tentatively put the flame temperature at above 1500 K at this pressure. Both temperatures are below the theoretical value of 1600 K and indicate that thermodynamic equilibrium is not attained in the flame, although it may be at higher pressures.

The temperature profile through the combustion wave was obtained for deflagration at 28 atm. No indication of heat release up to 190°C (the melting point of HDP) in the condensed heated zone of the oxidizer was observed. The thickness of the preheat zone was measured as 550 ± 80 microns, and the thermal diffusivity was determined to be $0.0015 \pm .0005$ cm²/sec, for HDP of 2.1 g/cc density.

Further measurements of the deflagration rate were made as a function of pressure. The present experiments were performed in the 200-350 atm range and these data are combined with previous data. The lower pressure limit of deflagration is discussed in the light of the experimentally determined temperature profile and compustion theory.

II. INTRODUCTION

In this program we are studying the deflagration of a series of high-energy oxidizers. In earlier work in this laboratory the self-deflagration of ammonium perchlorate has been studied in some detail (5). In the present program we have examined the behavior of hydrazine perchlorate and have recently reported our results and conclusions on the deflagration of this oxidizer (2). The investigation of hydrazine diperchlorate (HDP) has been underway for some time and the following lines of research are being pursued: the selfdeflagration of HDP in inert gas at elevated pressures; the effects of

> catalysts on the deflagration rate; the thermal decomposition of HDP, both pure and catalyzed; the measurement of the flame temperature of deflagrating HDP at various pressures; and the measurement of the temperature profile through the combustion wave.

III. PROGRESS DURING PRESENT PERIOD

During the present period we have performed further experiments on the flame temperature of HDP, and the temperature profile through the deflagration wave. The deflagration rate as a function of pressure has been measured at high pressures (200-350 atm). The results are discussed below.

A. The Flame Temperature of Hydrazine Diperchlorate

As discussed in the previous report (1), early attempts to measure the flame temperature of hydrazine diperchlorate by means of fine thermocouples were hampered by irreproducibility. The use of uncoated Chromel-Alumel thermocouples made from 1 mil diameter wire seemed to yield consistent results. In the last report, all the data obtained as of that date were tabulated and it was tentatively concluded that the flame temperature was significantly below the theoretical value of 1600° K. During the present period, further measurements were carried out to precisely establish the flame temperature value. These data together with the earlier reliable Ch-Al data are tabulated in Table I. The average of the observed values is $1345 \pm 20^{\circ}$ K. The thermocouple bead will be at a lower temperature than the flame due to radiation heat loss. This radiation correction is $24 - 58^{\circ}$ K, depending on the amount of surface oxidation of the bead (1). Hence, the HDP flame temperature is $1385 + 35^{\circ}$ K at 28 atm.

Additional flame temperature measurements at 55 atm have yielded a value of over 1500°K. The precise value is not yet firmly established, but it definitely appears that the flame temperature rises with pressure. A closer approach to thermodynamic equilibrium seems to be attained at higher pressures. Further experiments are planned along these lines.

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TABLE I

Flame Temperature Measurements for HDP at 28 atm Using Fine Chromel-Alumel Thermocouples

Run	<u>T</u> observed (°K)	
16	1355	
17	1355	
18	1325	
19	1370	
20	1310	
21	1365	
22	1365	
23	1325	
ave. = 1345° K ± 20° K		
	+ 40° K ± 15° K (radiation correction)	
	1385° K ± 35° K	

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B. Temperature Profile Measurements of HDP

The thermocouple output records plus the deflagration velocity can be used to obtain the thickness of the heated condensed zone and the thermal diffusivity of the oxidizer. For two experiments in which the records were useful for this purpose the thickness of the heated condensed phase was found to be 550 ± 80 microns (at 28 atm). The thickness of the corresponding zone for hydrazine perchlorate (containing 5% Del-Rin and 0.5% MgO) is 500 microns at 0.5 atm and 300 microns at 1 atm (2). The deflagration rate of HDP at 28 atm is comparable to that of HP in the 0.5 to 1 atm range.

The thermal diffusivity of deflagrating HDP has been measured in the following way. From the thermocouple output records mentioned above, distance - temperature plots were constructed. These temperature profiles of the HDP deflagration wave are described by the heat balance equation;

$$\lambda \quad \frac{d^2T}{dx^2} - Cp \ p \ r \quad \frac{dT}{dx} + Q(x) = 0$$

where

λ = coefficient of heat conduction Cp = specific heat ρ = density r = deflagration rate Q(x) = heat produced at point x due to chemical reaction.

Considering the zone in which Q(x) = 0 and integrating from ambient temperature, T_{u} , $(x = -\infty)$ to some T and x,

$$\frac{\mathrm{d}\mathbf{T}}{\mathrm{d}\mathbf{x}} = \frac{\mathbf{T} - \mathbf{T}_{\mathbf{u}}}{\eta}$$

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where $\eta = \frac{\lambda}{Cp \ pr}$, has the dimensions of distance, and is the subtangent of the temperature curve at the point (T,x). Thus, η is readily obtained by drawing a tangent to the temperature profile curve and measuring the subtangent (see ref. 3). In this way the thermal diffusivity of HDP $(p = 2.1 \ g/cc)$ was determined to be $.0015 \pm .0005 \ cm^2/sec$. For comparison, the corresponding values for HP are $.0012 - .0018 \ cm^2/sec$ (at 0.5 and 1 atm)(2), and for ammonium perchlorate, $.0015 \ cm^2/sec$ (at 200°C, determined by an independent method (4)).

The thermal diffusivity and the thickness of the heated condensed zone were obtained from experiments that were not specifically designed to yield that information with maximum precision. Hence, no approximate figure can be cited for the surface temperature; but the experimental records show no indication of chemical reaction in the condensed phase up to the melting point of HDP, 190° C.

C. Deflagration Rate Measurements of HDP

The measurements of deflagration rate of HDP as a function of pressure were extended to 330 atm. The data are given in Table II and shown in Figure 1. Shown in the same figure is the curve for ammonium perchlorate (5). The two oxidizers show very similar deflagration behavior over the pressure range 22 to 300 atm. The mass burning rate would be nearly identical to the linear since the density of the HDP strands was carefully controlled. In Figure 2, the deflagration rate as a function of pressure is shown as a log-log plot. The pressure exponent is seen to change drastically from low to high pressure.

The lower pressure limit (6 atm) of the present data may not represent the true lower limit for HDP. The present results were obtained with strands of 8 mm diameter, fitted into Pyrex tubes. From the measured thermal diffusivity of HDP and the deflagration rate at 6 atm, the characteristic parameter, η , can be calculated to be 600 microns. At 28 atm, this parameter is approximately one-eighth of the width of the combustion wave (measured from the point where the temperature shows a perceptible rise above ambient to the flame front). The wave width at 6 atm then should be approximately 5 mm. Ordinarily, the quenching diameter is several times the wave width, thus it is surprising that HDP will deflagrate

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TABLE II

Deflagration Rate Data for HDP

r (cm/sec)	<u>P</u> atm
.03	6.1
.02	6.1
.05	11.2
.145	21.4
.21	28.2
• 3 ¹ 4	35•4
•H4	42.2
.47	49.4
•43	49.0
.56	56.1
.62	62.9
•75	70.1
.85	90.7
•94	111
1.10	135
1.26	216
1.27	265
1.4	328

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Figure 1. Linear Deflagration Pate of Hydrazine Diperchlorate and Ammonium Perchlorate as a Function of Pressure.

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Figure 2. Log-Log Plot of Linear Deflagration Rate of HDP Versus Pressure.

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at 6 atm in an 8 mm diameter tube. The deflagration at 6 atm is in fact very erratic and unstable and sometimes ceases before the entire strand is consumed. It is expected that the use of larger diameter tubes would allow measurements to be made below 6 atm.

IV. PLANS FOR FUTURE WORK

The flame temperatures of deflagrating HDP at pressures above 28 atm will be measured to determine the variation of flame temperature with pressure. Fine thermocouples will be used to measure the temperature profile through the HDP combustion wave, more carefully than has been done to date. It is also planned to measure the profile of HDP containing catalysts. Condensed phase chemical reactions brought about by the catalyst should show up in this way.

A few high pressure deflagration rate experiments are planned to more firmly establish the r vs. P curve in the upper regime. An attempt will be made to burn HDP at pressures below 6 atm using larger diameter strands. We plan also to measure quenching diameters as a function of pressure for HDP.

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