THE DEFLAGRATION OF HYDRAZINE PERCHLORATE (1)

by

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I. ABSTRACT

Hydrazine perchlorate, like ammonium perchlorate, is a molecule containing within itself the elements of a fuel and an oxidizer. It should, therefore, like ammonium perchlorate, be capable of self-deflagration. This paper describes studies of hydrazine perchlorate deflagration and of various properties of hydrazine perchlorate pertinent to the question of its self-deflagration.

It has been found that hydrazine perchlorate will deflagrate reproducibly if a few per cent of fuel is present. Deflagration rates have been measured photographically with cylindrical strands pressed to 95-98% crystal density for ambient pressures from 0.26 to 7.7 atmospheres. A liquid layer was observed at the surface in these experiments. Steady deflagration could not be attained outside these pressure limits. Deflagration experiments were also performed with hydrazine perchlorate-catalyst mixtures.

In addition to the above experiments, vaporization rate measurements, measurements of the temperature profile of a deflagration wave at one atmosphere by means of fine thermocouples, and spectroscopic measurements of the flame temperature above a deflagrating strand were also made.

The temperature profile measurements indicate temperatures as high as 450°C in the condensed phase and are consistent with little heat release in the condensed phase. The vaporization measurements are consistent with a dissociative vaporization of hydrazine perchlorate. The flame temperature found was 2275 ± 50°K in satisfactory agreement with the value of 2224°K calculated on the basis of thermodynamic equilibrium in the products.

The above results are discussed in terms of the mechanism of the deflagration process.

II. INTRODUCTION

We are engaged in a general program of research whose goal is the understanding of the factors that govern the nature of the deflagration of composite solid propellants. Our efforts have been devoted to studies of the oxidizer alone, ever since early observations that ammonium perchlorate deflagrated as a monopropellant at rates comparable to those found for propellant formulations containing it (2). Earlier work in this laboratory dealt with the self-deflagration of ammonium perchlorate (3). We report here on studies with the related, but more energetic, material--hydrazine perchlorate.

Hydrazine perchlorate is a white crystalline solid melting at 140-142°C. It forms a hemihydrate which can readily be dehydrated at 64.5°C under vacuum. It has been reported (4) that dry hydrazine perchlorate can be detonated by shock or friction and that it has a shock sensitivity comparable to that of initiating explosives. We have observed the usual percautions in handling this material and have experienced explosions with it only under extreme conditions, i.e., in certain deflagration experiments. However, it is a very energetic material and must be handled with great care.

The thermal decomposition of hydrazine perchlorate has been investigated and ammonium perchlorate found to be a major product (5).

We know of no studies of the self-deflagration of hydrazine perchlorate. The results reported here are concerned with studies of pure hydrazine perchlorate and hydrazine perchlorate containing small amounts of additives.

III. EXPERIMENTAL PART

A. Preparation of Hydrazine Perchlorate

Hydrazine perchlorate was prepared by titrating a solution of 85% hydrazine hydrate to a pH of 3.2 with 48% perchloric acid. This yielded a stock solution which could be stored indefinitely. Hydrazine perchlorate was precipitated by pouring a volume of this solution into five volumes of isopropanol at 0°C. The hydrazine perchlorate was filtered, washed with cold isopropanol and vacuum dried at 80°C.

The material was analyzed iodometrically (6). Purities > 99%, as indicated by the analysis, were obtained. The melting point was 142-143°C.

B. Processing of Hydrazine Perchlorate

The hydrazine perchlorate used for the deflagration measurements was prepared in the form of small spherical particles of fairly uniform size distribution by means of a melt-shot apparatus copied from one in the literature. In this apparatus, solid hydrazine perchlorate is fed into a spinning aluminum dish maintained at a temperature above the melting point of hydrazine perchlorate and fitted with a small lateral hole in the side which permitted the ejection of the molten spheres which cool as they fly through the air. It was found that 160°C was a satisfactory temperature for the dish. With the dish spinning at 2400 RPM the particle sizes of the spheres obtained, as determined by microscopic examination of a random selection, varied from 50-300μ. Analysis of material prepared in this way indicated that no decomposition occurred during the shotting process.

C. Strand Preparation

Strands were either tamped or pressed. Tamped strands were prepared by pouring small increments of material into a tube and tamping each increment gently with a Teflon rod. Pressed strands were prepared in a steel mold by means of a hydraulic press. Pressures of ~ 40,000 psi gave strands of 95-98% of crystal density which was considered adequate. Pressing operations were performed remotely.

The mixtures of hydrazine perchlorate and the fuels or catalysts were prepared by mixing the hydrazine perchlorate shot with the finely-ground other ingredients in an ordinary vee mixer for several hours. The uniform deflagration rates observed with the various mixtures attest to the homogeneity of strands prepared in this way.

D. Sublimation Experiments

The sublimation experiments were performed with a conventional cold-finger vacuum sublimation apparatus, with a removable cold finger. The apparatus was evacuated by an oil pump to about 5 microns, lowered into a thermostat and the timer started.

Two sublimation apparatuses were used. At first a fairly small one with a cross sectional area of 0.5 cm^2 was used to keep the amount of hydrazine perchlorate required down to about 0.5 g. Subsequently a larger apparatus having a cross-sectional area of 4.90 cm^2 was used with amounts of hydrazine perchlorate of the order of 1.5 - 2.0 g.

At the conclusion of the experiment the sublimate was carefully removed from the cold finger and weighed. The weight of the residue was found by weighing the outer tube, washing out the residue and re-weighing the tube. The analyses were performed by iodometry.

E. The Flame Temperature Measurements

A tungsten ribbon filament lamp that had been calibrated by the National Bureau of Standards for the temperature range 1100 - 2300°C was used for these measurements, which were performed in the conventional manner (7).

IV. RESULTS

The experiments performed in this program are grouped into (a) experiments in which vaporization rates of pure hydrazine perchlorate were measured; (b) deflagration rate measurements; (c) temperature profile measurements; and (d) flame temperature measurements.

A. Vaporization Rate Measurements

These experiments were performed in the glass sublimation apparatuses described in the Experimental Part. The surface area of the liquid was quite undisturbed by bubbles during these experiments and its magnitude was constant during an experiment. The temperature of the liquid was assumed to be that of the bath in which the apparatus was immersed. The results are given in Table I.

TABLE I

Vaporization Rates of Hydrazine Perchlorate

Temp. (°K)	Area (cm^2)	Duration (sec)	Weights in Grams Charged	Sublimed	Residue	% recov.	% Hydrazine Perchlorate in Sublimate	Residue	10^6 × Rate of Vaporization (g/cm^2-sec)
453	4.90	18,900	1.56	0.22	1.32	99	99.8	99.4	2.38
463	0.50	21,240	0.244	0.073	0.163	97			6.85
473	4.90	18,900	1.70	0.54	1.14	99	95.0	99.0	5.84
492	0.50	2,220	0.239	0.036	0.200	99			32.4
508	4.90	2,400	1.65	0.83	0.79	98	99.0	100.0	70.5

The relation between vaporization rate and vapor pressure is given by $g = \alpha P \sqrt{\frac{M}{2\pi RT}}$ (8).

g = vaporization rate in g cm^{-2} sec^{-1}

α = evaporization coefficient

P = vapor pressure in dynes cm^{-2}

M = molecular weight of vaporizing species

T = absolute temperature

R = gas constant in ergs $mole^{-1}$ deg^{-1}

This expression can be written,

$$g \sqrt{T} = \alpha \sqrt{\frac{M}{2\pi R}} \; P$$

For many liquids α has been found to be unity. However a very low value for this quantity has been calculated (9) for ammonium chloride and, since very few species that are chemically similar to hydrazine perchlorate have been investigated, we do not feel justified in assigning a value of unity for α in the present case.

It is of interest to see how the parameter $g\sqrt{T}$ varies with T. Since it is proportional to P, we would expect a Clausius-Clapeyron relationship to hold, if α were constant, and in Fig. 1 we plot $\log\left(g\sqrt{T}\right)$ vs 1/T. The data are fairly linear and the line in Fig. 1, which was drawn visually, corresponds to the equation:

$$\log_{10}\left(g\sqrt{T}\right) = 10.0 - \frac{6475}{T}$$

The slope of the line is a measure of the heat of vaporization ΔH_v and leads to a value of 29.6 kcal/mole for this quantity. The corresponding value for ammonium perchlorate is 29 kcal/mole (10). It is of interest to compare the above value for ΔH_v to that calculated for the vaporization process. If we consider that hydrazine perchlorate vaporizes with dissociation, as is believed to be true for ammonium perchlorate, the equilibrium is

$$N_2H_5ClO_{4(l)} \rightleftharpoons N_2H_{4(g)} + HClO_{4(g)}$$

The enthalpy change for this process would be $2\Delta H_v$ or 59.2 kcal/mole. The heat of formation of crystalline hydrazine perchlorate is -42.5 kcal/mole (11) and a value of 3.84 kcal/mole has been reported for the heat of fusion (12). The heat of formation for the liquid is thus -38.7 kcal/mole. The values for gaseous perchloric acid and gaseous hydrazine are -1.1 (13) and 22.75 kcal/mole (14) respectively. These values yield 60.4 kcal/mole as the enthalpy change in the above equilibrium. The agreement with the experimental value supports our belief that the vaporization rates are proportional to the vapor pressure and that the vaporization process is dissociative.

B. Deflagration Rate Measurements

Deflagration rates were measured from motion picture records of the deflagration experiments. The lengths of strands used were in the range of 1.5 - 2.0 cm. In all cases the linear deflagration rate was determined from the slope of the curve of length deflagrated vs. time. These curves were all linear, i.e., the deflagration rates were constant over the length of the strand. In all the deflagration experiments a molten layer could be seen at the surface of the deflagrating strand. Gas evolution within the layer was so vigorous that the liquid layer never appeared transparent but rather like a foam. The liquid-solid interface was distinct however and the rate measurements were made by measuring the regression rate of this interface.

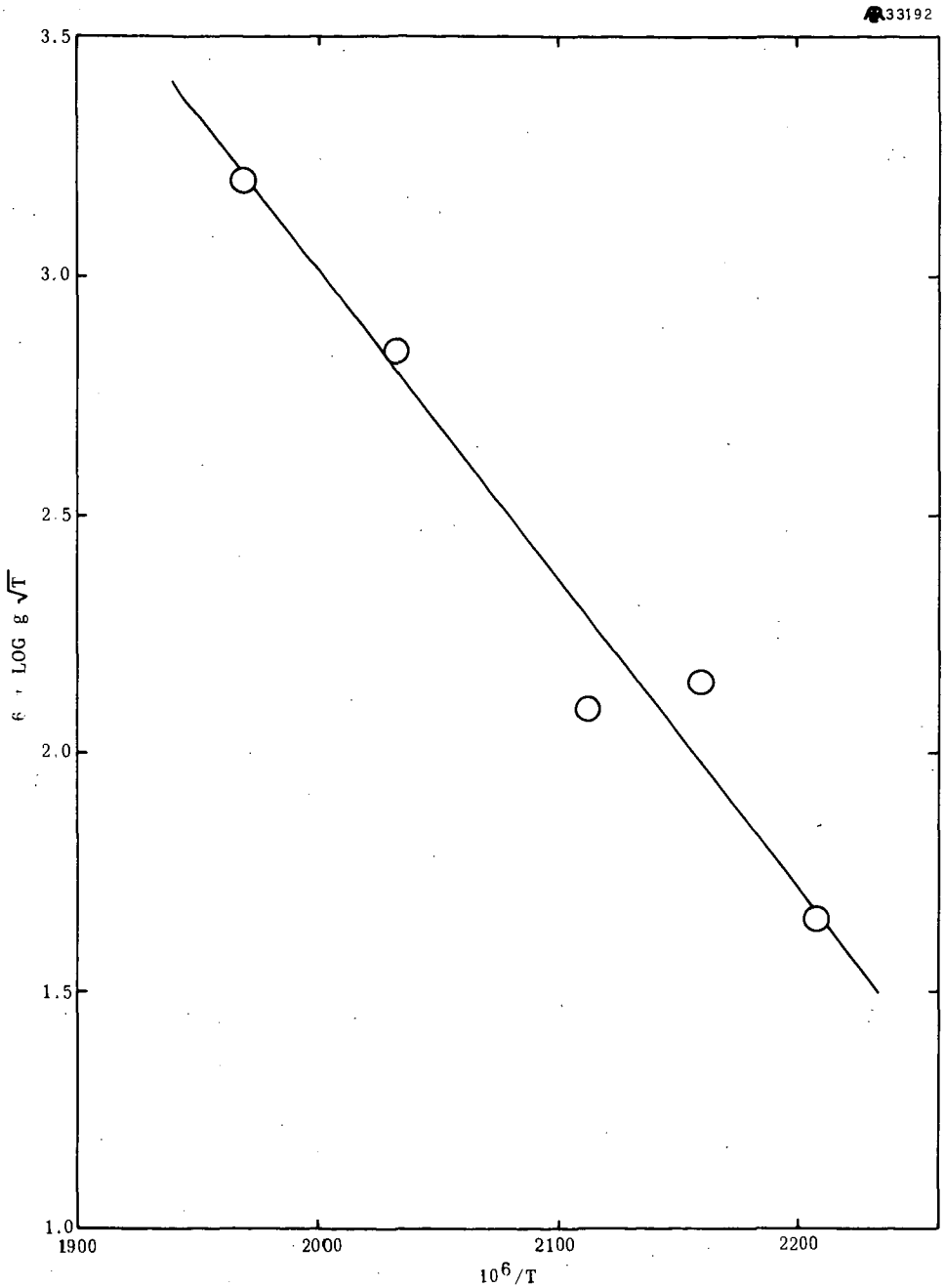


Figure 1. The Rate of Vaporization of Hydrazine Perchlorate.

1. The Deflagration of Pure Hydrazine Perchlorate

The behavior of pure hydrazine perchlorate, i.e., material containing no additives, was unreproducible. Smooth deflagration of tamped (ρ = 1.1 - 1.3 g/cc) and pressed(ρ = 1.8 - 1.9)g/cc strands of hydrazine perchlorate was attained for pressures from 0.25 to 4.3 atmospheres but at a subsequent time strands prepared and ignited in the same way did not propagate deflagration. When this was observed, experiments were performed with strands preheated to 50°C. Smooth deflagration was attained at two, four and six atmospheres but these results too were not reproducible at a later date.

2. The Deflagration of Hydrazine Perchlorate-Additive Mixtures

a. Fuel Additives

In the case of ammonium perchlorate, it has been found (15) that at pressures below that at which pure ammonium perchlorate will sustain deflagration, ammonium perchlorate-fuel mixtures containing of the order of 5% fuel do deflagrate smoothly. Paraformaldehyde was the most effective of the fuel additives in promoting deflagration and for that reason experiments were performed with mixtures of hydrazine perchlorate and various formaldehyde polymers.

Experiments with paraformaldehyde were unsuccessful because it was found that when these additives were mixed with hydrazine perchlorate the mixture became yellow and the consistency changed from that of the original powders to that of a dough. S-trioxane, a more stable formaldehyde polymer than paraformaldehyde, gave a less reactive mixture than paraformaldehyde, but the results were still unsatisfactory. Del-rin*, a stabilized formaldehyde polymer, proved even less reactive than S-trioxane. Magnesium oxide was added to hydrazine perchlorate-Del-rin mixtures on the theory that acidity in the hydrazine perchlorate might be responsible for the reaction occurring. It was found that mixtures of 94.5% hydrazine perchlorate - 0.5% MgO - 5% Del-rin were stable and a series of experiments was performed with this mixture.

Other fuel-type additives were effective in promoting the deflagration of hydrazine perchlorate. Experiments have been performed with thiourea and naphthalene. The results of the deflagration experiments for preheated pure hydrazine perchlorate and for the hydrazine perchlorate-fuel mixtures are summarized in Table II and Fig. 2. The strands used were all pressed to about 95% of the crystal density, i.e., to a density of about 1.85 g/cc.

* DuPont trade name

TABLE II

Deflagration Rates for Hydrazine Perchlorate

No.	Composition	ρ (g/cc)	P (atm)	$\dot{r}$ (cm/sec)	$\dot{m}$ (g/cm^2-sec)
1	5% Del-Rin 0.5% MgO	1.87	0.26	0.01-0.02	0.02-0.04
2	5% Del-Rin 0.5% MgO	1.85	0.52	0.11	0.21
3	pure HP preheated to 69°C	1.87	1.0	0.24	0.45
4	5% Del-Rin 0.5% MgO	1.85	1.0	0.22	0.41
5	5% Del-Rin 0.5% MgO	1.85	1.0	0.22	0.41
6	2% Thiourea	1.86	1.0	0.17	0.32
7	5% Naphthalene	1.83	1.0	0.21	0.38
8	20% Thiourea	1.79	1.0	0.18	0.32
9	preheated to 50°C	1.91	2.0	0.52	0.98
10	5% Del-Rin 0.5% MgO	1.85	3.0	0.56	1.0
11	5% Del-Rin 0.5% MgO	1.85	4.3	0.90	1.67
12	preheated to 50°C	1.91	6.0	1.29	2.48
13	5% Del-Rin 0.5% MgO	1.85	7.0	1.39	2.5
14	5% Thiourea	1.82	7.7	1.73	3.18
15	10% Thiourea	1.81	7.7	1.21	3.1

Deflagration rates are given for pressures ranging from 0.26 atmospheres to 7.7 atmospheres. The experiment at 0.26 atmospheres yielded a curve of length-deflagrated vs. time that was somewhat concave upward. The rate cited is thus a rather crude value but is of interest because of the low pressure. All the other rates were constant. Attempts to measure rates at higher pressures than 7.7 atmospheres resulted either in a complete lack of ignition or in a deflagration that proceeded down the sides of the strands leaving a central unburned core.

Fig. 2 shows that all the data fall fairly well around a single line, $\dot{r} = 0.22\ P$, where $\dot{r}$ is in cm/sec and P is in atmospheres.

b. The Effects of Catalysts

It has been found that copper chromite, potassium dichromate, and magnesium oxide promote the deflagration of hydrazine perchlorate. Since none of these additives has any fuel content, they must be considered to be catalysts. The results of experiments with these additive species are shown in Table III. Experiments were performed both with pressed ($\rho \approx 1.9$ g/cc) and tamped ($\rho \approx 1.1$ g/cc) strands.

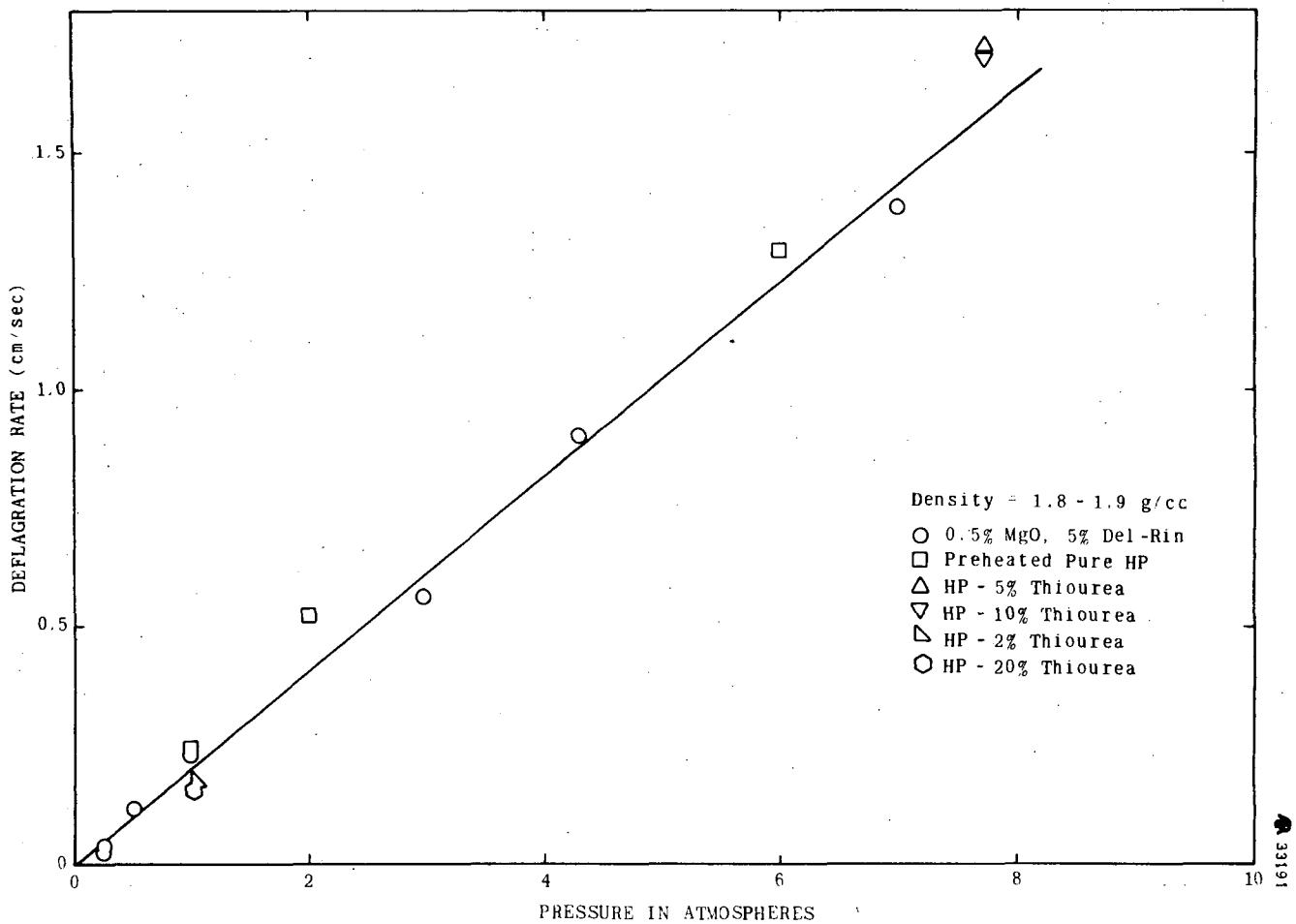


Figure 2. The Rate of Deflagration of Hydrazine Perchlorate With Small Amount of Fuel.

TABLE III

The Effect of Catalysts on the Deflagration of Hydrazine Perchlorate

No.	Composition (% of additives)	ρ (g/cc)	P (atm)	$\dot{r}$ (cm/sec)	$\dot{m}$ (g/cm^2/sec)
1	2.5% $CuCrO_2$	1.13	1	did not deflagrate	
2	5% $CuCrO_2$	1.10	1	1.20	1.32
3	5% $CuCrO_2$	1.93	1	0.71	1.37
4	5% $CuCrO_2$	1.95	0.52	0.36	0.69
4a	5% $CuCrO_2$	1.93	2	exploded	
5	2.5% $K_2Cr_2O_7$	1.17	1	did not deflagrate	
6	5% $K_2Cr_2O_7$	1.19	1	0.75	0.89
7	2% MgO	1.90	1	0.26	0.50
8	5% MgO	1.91	1	0.21	0.59
9	10% MgO	1.89	1	0.35	0.66
10	20% MgO	1.86	1	partial deflagration	
11	2% CaO	1.31	1	0.12	0.16

It may be noted that for copper chromite and potassium dichromate a minimum of around 5% catalyst was necessary in order to attain steady deflagration; however when deflagration did occur the rate was high compared to the case for fuel-promoted deflagration. It may be noted too, table entries 2 and 3, that for strands containing 5% copper chromite but having different densities, the mass deflagration rates agree well while the linear rates do not. It thus seems satisfactory to compare mass rates for strands of different densities. A comparison of this type shows that potassium dichromate is a powerful catalyst but not as powerful as copper chromite.

Magnesium oxide exerts quite a different effect than do the above catalysts. Thus less of it, 2%, is required to promote steady deflagration, but it is not capable of producing as spectacular a rate as copper chromite or potassium dichromate, even in amounts as great as 10%.

The effect of calcium oxide was briefly examined since it is chemically similar to magnesium oxide. A tamped strand deflagrated at 1 atmosphere to give a somewhat lower rate, i.e., as compared to the curve of Fig. 2. Calcium oxide is quite deliquescent and there were indications in this experiment of some moisture absorption.

In a side experiment to see if there was any generality to the effect of magnesium oxide, a tamped strand of hydrazine nitrate containing 2% magnesium oxide was found to deflagrate steadily at 0.04 cm/sec (ρ = 0.93 g/cc, $\dot{m}$ = 0.037 g/cc sec) while pure hydrazine nitrate would not propagate deflagration.

3. The Temperature Profile Measurements

Temperature profiles of the deflagration wave have been made using thermocouples of 0.0005-inch Pt - Pt, 10% Rh wires joined in a fused bead of approximately 0.001-inch diameter. The voltage changes were recorded by a Visicorder which registers voltage changes by the deflection of a light point on a moving film. The deflagration rates were measured simultaneously so that it was possible to convert temperature-time records to temperature-distance records. The turbulence of the liquid layer as observed in the deflagration rate measurements indicated that one could not expect a smooth temperature-time record. Figures 3 and 4 illustrate the type of record obtained. There are some irregularities in the curves, but the data are not too erratic for analysis.

Fig. 3 shows tracings of the records obtained at 0.5 atmospheres with a pressed strand of 94.5% hydrazine perchlorate, 5% Del-Rin, 0.5% Magnesium Oxide, ρ = 1.85 g/cc and Fig. 4 shows the tracing of the record obtained for a tamped strand of the same composition, ρ = 1.24 g/cc, at one atmosphere. In Fig. 5 and 6 are shown the experimental data converted to a temperature-distance function by means of the measured deflagration rates.

The solid curves in Figs. 5 and 6 are the theoretical curves obtained for indicated values of thermal diffusivity of the solid. The following treatment has been applied. The temperature gradient within the zone bounded by the deflagrating surface on the one hand and ambient temperature on the other can be written

$$k \frac{d^2T}{dx^2} - c\rho r \frac{dT}{dx} + q_c = 0$$

where

k = coefficient of heat conduction

c = specific heat

ρ = density

q_c = heat produced within the zone

T = temperature at point x

r = deflagration rate

If $q_c = 0$, the above on integration yields

$$\ln \frac{T_2 - T_u}{T_1 - T_u} = \frac{r}{K} \quad (x_2 - x_1)$$

where $K = \frac{k}{cp}$ = thermal diffusivity, T_2 and T_1 are the temperatures at point x_2 and x_1, and T_u is the ambient temperature.

It is possible to evaluate K for the particular experimental data and to fit a T - x curve to the points. As Figs. 5 and 6 show, the values for K that give the best fits are 0.0012 cm^2/sec for the pressed (ρ = 1.85 g/cc) strand and 0.0018 cm^2/sec for the tamped (ρ = 1.24 g/cc) strand. These values can be compared to the value of 0.00285 cm^2/sec which can be calculated for ammonium perchlorate of crystal density, from reported values (16) of heat capacity and thermal conductivity. The values found here thus appear to be of the right order of magnitude.

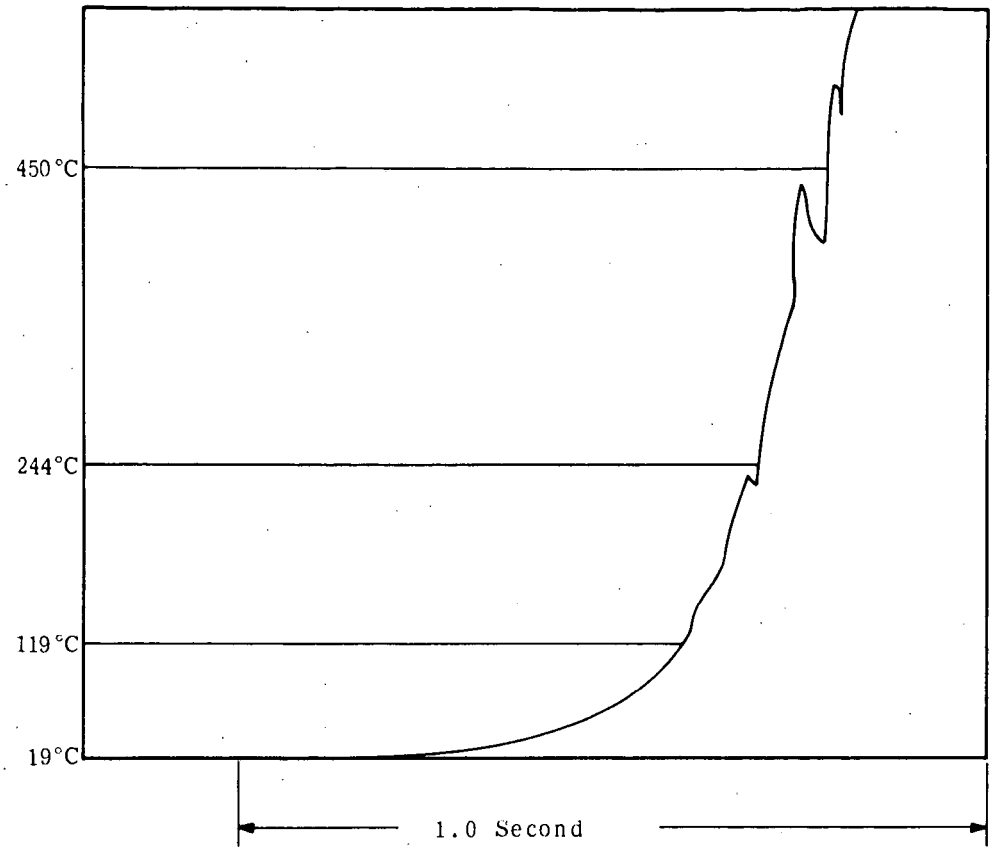
The curves of Figs. 5 and 6 fit the data fairly well. Thus Fig. 5 gives no indication of heat release in the condensed phase below 450° C. Fig. 6 shows the same result at least to 400° C. It may be further noted that at 0.5 atm, for the pressed strand, Fig. 5, the condensed phase reaction zone was about 0.5 mm thick while at one atmosphere, for the tamped strand, it was about 0.3 mm thick.

4. Temperature Profiles for Catalyzed Strands

Fig. 7 shows the temperature-time records of a hydrazine perchlorate-2% MgO strand at one atmosphere. The distinctive feature is the thickness of the reaction zone ~1.6 mm. This may be compared to Fig. 4 for the hydrazine perchlorate-5% Del-Rin-0.5% MgO strand where ambient pressure was also one atmosphere but the zone thickness was about 0.3 mm.

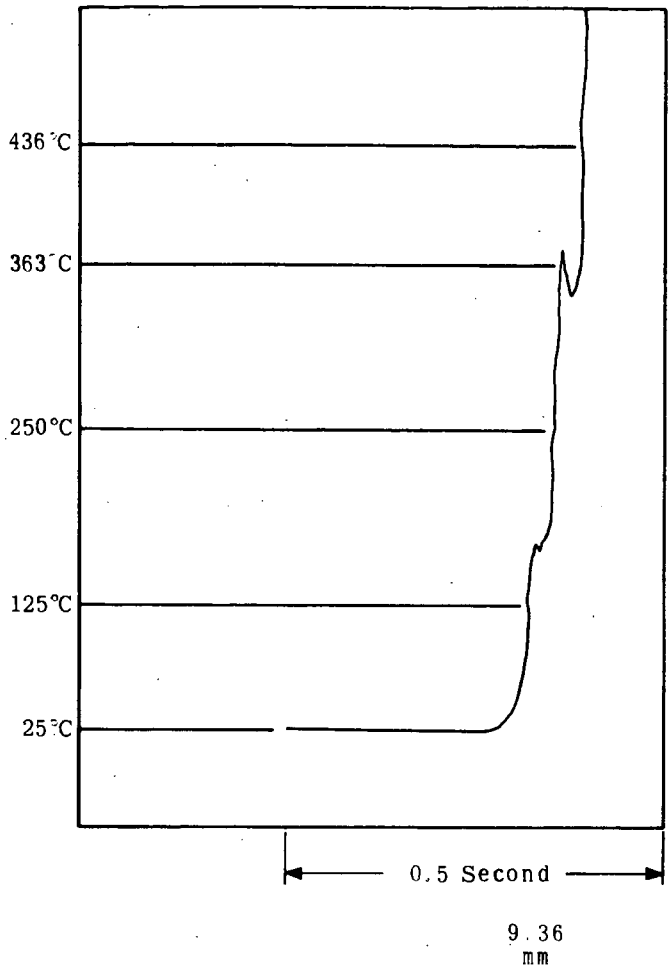
5. Flame Temperature Measurements

Thermodynamic calculations of the nature of the products of hydrazine perchlorate self-deflagration at a series of processes were performed by an IBM-7090 computer program. The results are shown in Table IV. The calculations were made assuming constant-pressure adiabatic combustion to give equilibrium products. As Table IV shows the flame temperature at 1 atmosphere is 2245.5° K; this is about 800° higher than that for ammonium perchlorate (2b).



Strand Composition: 94.5% Hydrazine Perchlorate
5% Del-Rin, 0.5% Magnesium Oxide
Density = 1.85 g/cc
Pressure = 0.5 Atmosphere
Deflagration Rate = 0.09 cm/sec

Figure 3. Tracing of Thermocouple Record of Hydrazine Perchlorate Deflagration Wave.



Strand Composition: 94.5% Hydrazine Perchlorate
5% Del-Rin, 0.5% Magnesium Oxide
Density = 1.24 g/cc
Pressure = 1 Atmosphere
Deflagration Rate = 0.30 cm/sec

Figure 4. Tracing of Thermocouple Record of Hydrazine Perchlorate Deflagration Wave.

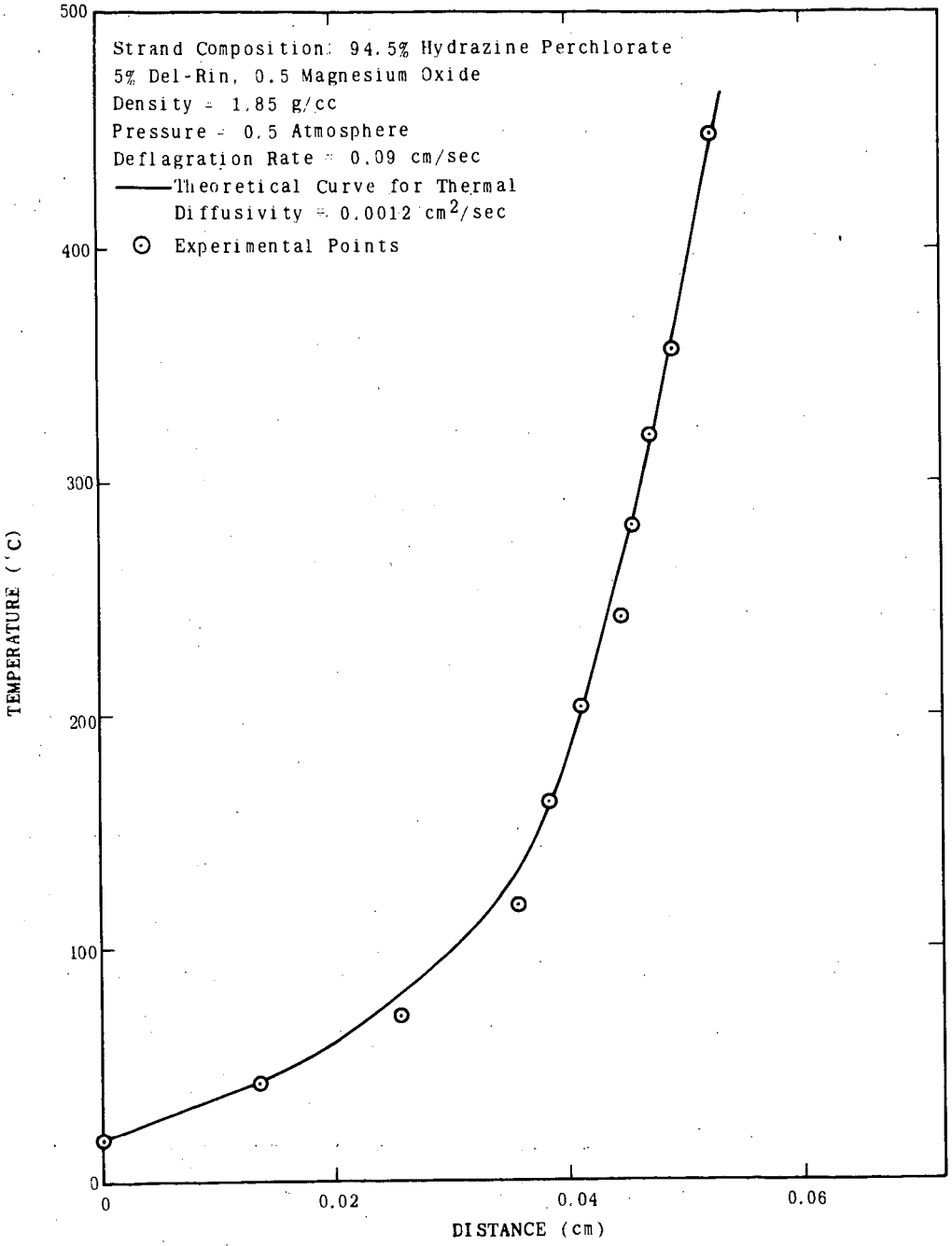


Figure 5. Temperature Profile of a Hydrazine Perchlorate Deflagration Wave.

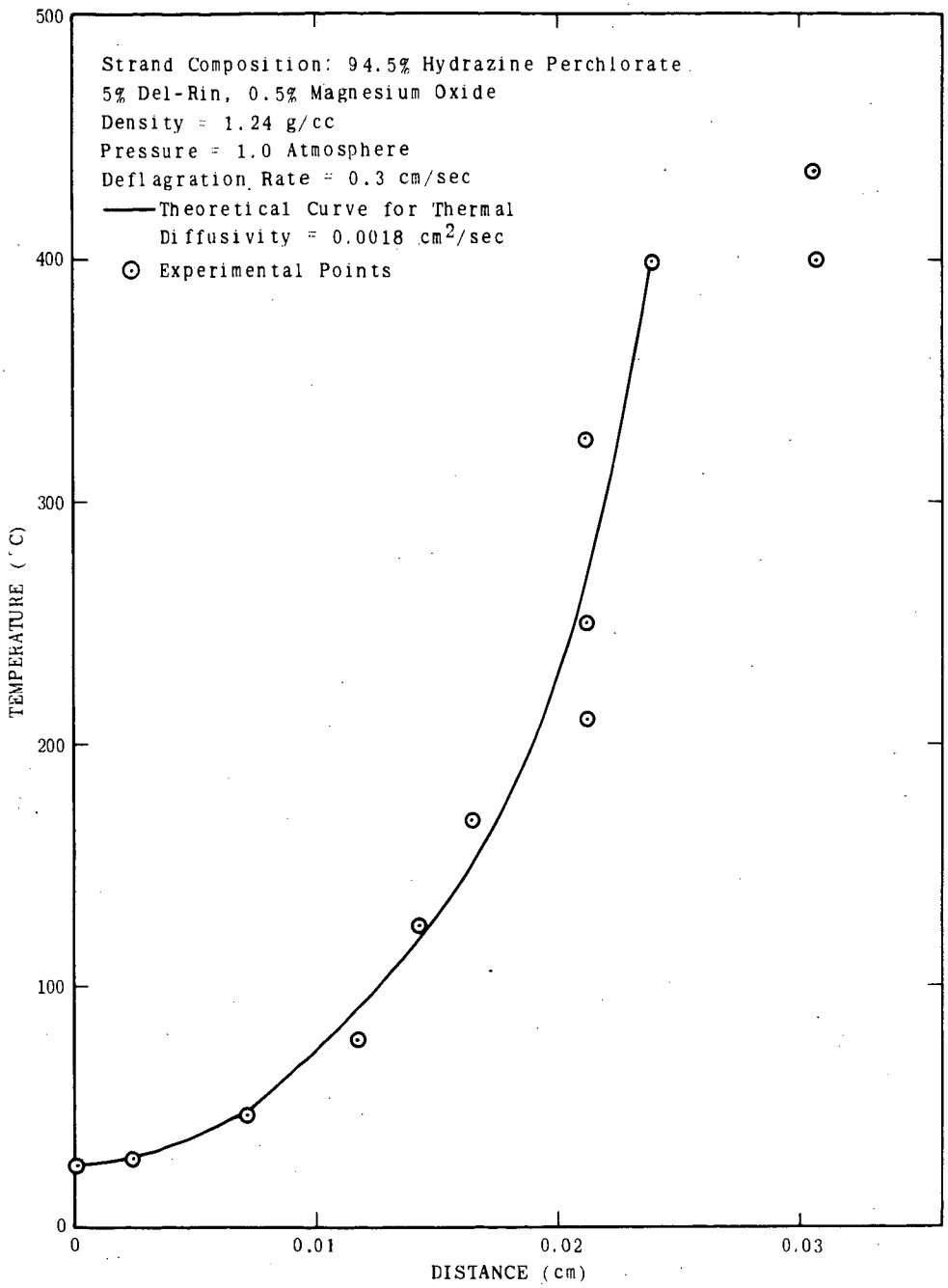
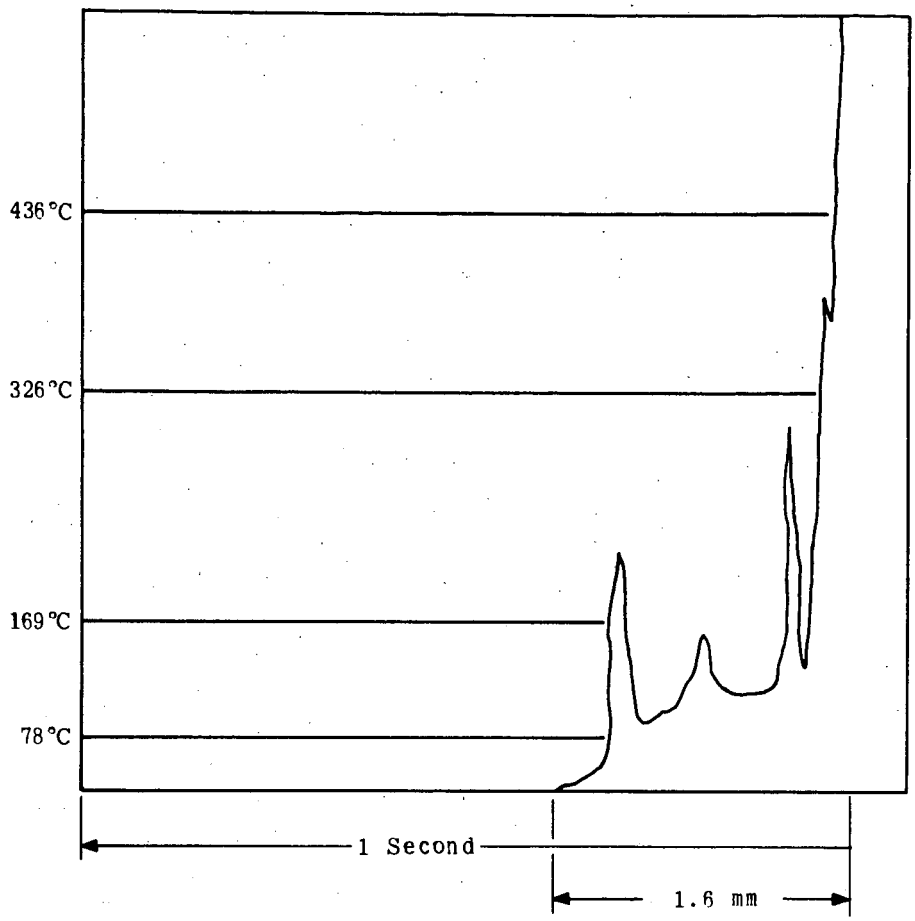


Figure 6. Temperature Profile of a Hydrazine Perchlorate Deflagration Wave.



Strand Composition: 98% Hydrazine Perchlorate
2% Magnesium Oxide
Density = 1.05 g/cc
Pressure = 1 Atmosphere
Deflagration Rate = 0.46 cm/sec

Figure 7. Tracing of Thermocouple Record of Hydrazine Perchlorate Deflagration Wave.

TABLE IV.

HYDRAZINE PERCHLORATE

Constant-pressure adiabatic combustion. Initial temperature 25° C

(ΔH_f = -42.5 kcal/mole)

P (atm) →	1	10	68.05	100
T (°K)	2245.5	2291.6	2318.7	2323.2
Total moles per 100 gm	3.815	3.798	3.787	3.784
Species (Moles/100 gm) ↓				
H	1.008×10^{-3}	2.606×10^{-4}	0.766×10^{-4}	5.949×10^{-5}
O	5.871×10^{-3}	2.456×10^{-3}	1.103×10^{-3}	9.341×10^{-4}
N	0	0	0	0
Cl	0.940×10^{-1}	6.146×10^{-2}	4.112×10^{-2}	3.774×10^{-2}
H_2	5.369×10^{-3}	2.204×10^{-3}	0.982×10^{-3}	8.313×10^{-4}
H_2O	1.526	1.523	1.524	1.525
HCl	0.659	0.688	0.699	0.700
O_2	0.705	0.715	0.719	0.720
OH	4.872×10^{-2}	3.262×10^{-2}	2.231×10^{-2}	2.060×10^{-2}
N_2	0.741	0.740	0.739	0.739
NO	2.606×10^{-2}	2.889×10^{-2}	3.062×10^{-2}	3.090×10^{-2}
NO_2	2.698×10^{-5}	0.898×10^{-4}	2.410×10^{-4}	2.933×10^{-4}
N_2O	0	2.354×10^{-6}	6.512×10^{-6}	0.796×10^{-5}
Cl_2	7.932×10^{-4}	2.588×10^{-3}	6.764×10^{-3}	0.816×10^{-2}

The stoichiometry corresponds closely to

$$N_2H_5ClO_4 \rightarrow N_2 + HCl + 2H_2O + O_2$$

Since it has been found that the self-deflagration of ammonium perchlorate does not lead to the products calculated on the basis of thermodynamic equilibrium, we felt it desirable to measure the flame temperature for hydrazine perchlorate. A flame temperature appreciably different from that calculated would indicate a non-equilibrium distribution of products which would require investigation.

Preliminary experiments were performed in which lengths of one mil platinum wire were stretched through the center of tamped strands of hydrazine perchlorate. Examination of the wire after deflagration showed that the passage of the flame had melted it. The melting point of platinum is 2042° K and the heat loss by radiation was estimated at about 40° K. This placed the flame temperature at somewhere above 2082° K.

Flame temperature measurements by the sodium line reversal method were made with hydrazine perchlorate strands containing 2% thiourea and 2% sodium chloride. It was found that this amount of sodium chloride was necessary to achieve a sufficient intensity of emission of the sodium D line for these experiments. It may be pointed out that in oxygen-rich, chlorine-containing flames, as this one is, the concentration of sodium atoms is decreased because the equilibrium

$$H + NaCl \rightleftharpoons HCl + Na$$

is shifted to the left because the hydrogen atom concentration is so low.

Thermodynamic calculations for the composition containing 2% thiourea and 2% sodium chloride were made and the theoretical flame temperature was found to be 2224° K. A series of measurements by the sodium line reversal method gave a figure of 2275 ± 50° K for the flame temperature. This is close enough agreement so that we feel that thermodynamic equilibrium is achieved in the flame and the reaction products are as written above. This differs markedly from the results with ammonium perchlorate where a substantial fraction of the nitrogen was present as oxides of nitrogen even at elevated pressures (3).

V. DISCUSSION

A. A General Description of the Hydrazine Perchlorate Deflagration Process

Let us first assemble a description of the deflagration process for hydrazine perchlorate from the above results. It is a process characterized by the formation of a molten zone which is quite turbulent and foamy; it is a very erratic process, particularly for the pure material and it is subject to very potent catalysis by copper chromite and potassium dichromate and to moderate catalysis by magnesium oxide. The process is comparatively reproducible in the presence of small amounts of fuel, and the rate obtained is apparently not dependent on the nature of the fuel but only on the ambient pressure. It is expressible by $\dot{r} = 0.22P$ where $\dot{r}$ is in cm/sec and P in atmospheres. This corresponds to a rate, at one atmosphere, some 15 times that calculated by extrapolation for ammonium perchlorate (3). However the process is unstable at pressures above about 7 atmospheres and steady deflagration cannot be attained above this pressure.

The temperature profile in uncatalyzed strands is such as to indicate little heat production in the condensed phase, and a liquid layer thickness of 0.3 mm at one atmosphere and 0.56 mm at half an atmosphere. This layer is much thicker for magnesium oxide-catalyzed strands.

Finally, from the measured flame temperature, we conclude that thermodynamic equilibrium is attained in the deflagration products.

B. The Mechanism of Deflagration Hydrazine Perchlorate

One approach to the consideration of the mechanism of hydrazine perchlorate deflagration is to consider whether it fits the classification of a vaporization type process like ammonium perchlorate, i.e., where the material vaporizes without decomposition and exothermic gas-phase reactions occur with resultant heat transfer to the condensed phase. The alternative to a process of this type is one wherein heat production occurs in the molten zone as a result of condensed phase reactions.

Here it is of interest to consider the vaporization rate measurements. The data obtained corresponded to the expression

$$\log_{10}(g\sqrt{T}) = 10.0 - \frac{6475}{T}$$

In the temperature profiles of the deflagration experiments both at one atmosphere, Fig. 6, and one-half atmosphere, Fig. 5, temperatures of the order of 450°C were attained. Insertion of this temperature in the above expression yields a vaporization rate of 0.4 gm/cm^2 -sec. The deflagration rate found at one atmosphere was 0.36 gm/cm^2 -sec while that at half an atmosphere was 0.18 gm/cm^2-sec. The vaporization rate measurements are thus not inconsistent with a vaporization-type mechanism for hydrazine perchlorate deflagration.

If this is considered as one point in favor of a vaporization-type mechanism, a second point in favor of it is the observation that the shape of the temperature profile in the condensed phase was that expected for the case where there is no heat release in the condensed phase. A third point consistent with this picture is the increase of deflagration rate with pressure, a relation that can be explained on the basis that, as the pressure is increased, the exothermic gas-phase reactions occur ever closer to the condensed phase resulting in a higher rate of heat transfer.

The main features of our results which are inconsistent with the above picture are the very erratic nature of the deflagration of pure hydrazine perchlorate and the turbulent behavior of the molten zone. It is difficult to see how, for example, small amount of impurities could affect the vaporization process from the turbulent molten layer. In other words if the deflagration were dependent on vaporization it appears that it should be more reproducible. Contrariwise, if condensed phase reactions are important, then the presence of small amounts of impurities which could catalyze these reactions could easily be important in deciding whether deflagration occurred or not. The turbulent, foaming appearance of the molten zone also suggests that gas evolution, i.e., reaction, is occurring within the body of the molten liquid.

The most plausible description of the process is one in which the mechanism is predominantly a vaporization process but where there is a small (because the temperature profile does not show it) but necessary contribution from condensed-phase reaction.

We feel that the erratic deflagration behavior of pure hydrazine perchlorate is attributable to the presence or absence of small amount of impurities that catalyzed the condensed-phase process, which implies that

when the condensed phase process did not occur, deflagration would not propagate. The function of the fuels then would be to allow exothermic oxidation-reduction reactions to occur in the condensed-phase that would likewise promote deflagration. The fact that the deflagration rates observed depended only on ambient pressure, irrespective of whether the strand was pure hydrazine perchlorate, whether it was preheated, or what the nature of the fuel was, suggests that although a condensed-phase reaction is a sine qua non for stable deflagration, the actual rate is determined by the ambient pressure.

We attribute the effects of copper chromite, potassium dichromate and magnesium oxide to catalysis of condensed-phase reactions, of the catalysis of the pyrolysis reaction by species of this type (12).

Finally we consider the apparent upper pressure limit of deflagration occurring at about seven atmospheres. A similar phenomenon was observed for ammonium perchlorate at pressures near 2000 psi. This was found to be due to convective cooling and was eliminated by alteration of the strand geometry or by wrapping the strand with asbestos. It does not appear that convective cooling is occurring here, since cessation of deflagration occurs even when the material is contained within a glass tube, which should minimize convective effects. At present we can only conclude that at pressures of the order of seven atmospheres, the liquid layer becomes too thin to support the contribution of condensed-phase reaction necessary for stable deflagration and it is for this reason that the upper limit is observed.

VI. REFERENCES

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