Reactions near the Burning Surface of Double-Base Propellants

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An experimental study of the heat of reaction for the flameless combustion of M-2 double-base propellant at pressures from 0.3 to 200 psia has been performed using differential scanning calorimetry and thermogravimetric analysis. The heat of reaction varies from 280 cal/g at 0.3 psia to 580 cal/g at 100 psia with abrupt changes occurring near 2 psia, 20 psia, and 100 psia. The jumps in heat of reaction occur at pressures corresponding to jumps in the burning rate. These jumps are correlated to successive discrete gas-phase reactions which exist a few hundred microns above the deflagrating surface and move toward it with increase in the ambient pressures. Based on these results and the usual construction of a DSC, it is concluded that the DSC is inadequate for condensed-phase measurements of double-base propellants. Comparison of DSC and TGA data shows that the vaporization of pure nitroglycerine occurs near the onset of significant heating and that no heating occurs before weight loss begins, implying that pure "condensed phase" contributions are minor for M-2 double-base propellant.

I. Introduction

DESPITE the extensive efforts to comprehend the mechanism of combustion of solid propellants, there is no generally acceptable theory describing the burning process. The relative contribution of condensed phase reactions at various pressures is still undefined. Some contributors to the combustion literature feel that condensed-phase reactions contribute very little.[1,2] Recently, however, Waesche and Wenograd[3-5] have suggested that condensed-phase reactions may be the controlling factor in the combustion of ammonium perchlorate propellants at pressures below atmospheric where they associate the phenomena of "flameless combustion" with condensed-phase reactions. They used the differential scanning calorimeter (DSC), which measures the heat effect of a reaction as a function of absolute temperature, to investigate the reaction kinetics of ammonium perchlorate propellants at low pressures. Waesche states that the DSC is applicable in the acquisition of reaction kinetics data for condensed-phase processes because the placement of the sensing elements in the base of the sample holders is such that only condensed-phase enthalpy changes are measured, and the gaseous reaction products are swept away by the steady purge stream. Sammons[6] also used the DSC for ammonium perchlorate studies at atmospheric pressure and concluded that condensed-phase or surface heat release should be included in a combustion model. Pliukhin[7] states that the heat necessary for the flameless burning of double-base propellant is supplied almost completely by the condensed phase.

The previous use of the DSC in obtaining condensed-phase data for ammonium perchlorate propellants and the lack of experimental heat-of-reaction data in the low-pressure range for double-base propellants prompted the investigations leading to this paper. However, results indicate that the DSC is inadequate for measurements of condensed-phase heats of reaction for double-base propellants because of gaseous and/or heterogeneous reactions which occur very near and at the surface and cannot be swept away by the purge gas stream.

Since there seem to be many different definitions of the terms, a heterogeneous reaction will be defined to mean a reaction involving the interaction of decomposition gases with a condensed phase and a condensed-phase reaction will be defined as one which involves only condensed-phase reactants and products. Throughout this paper the term double-base propellant refers to standard M-2 propellant.

II. Apparatus

A Perkin-Elmer Corporation Differential Scanning Calorimeter Model DSC-1 was the primary instrument used in this investigation. In the DSC a sample material and a reference material in separate containers are heated at a programed temperature rise rate. A recording is made of the differential power required to keep the sample increasing in temperature at the same rate as the reference material. Integration of this recording provides the total enthalpy change for any chemical reactions in the sample. The sample and reference materials are encapsulated in small aluminum pans, 6 mm in diameter and 0.2 mm thick, and the pans placed in two small cups approximately 7 mm i.d. and 2 mm deep. A platinum resistance thermometer and heating element are in contact with the bottom of the sample-holding cups. The low thermal mass of such a system provides for rapid and accurate response to chemical heat generation.

As available from the manufacturer, the instrument is capable of measurements at atmospheric pressure and below. To allow for measurements above atmospheric pressure, the complete sample holder assembly and its cover were mounted inside an 8-in.-diam spherical steel pressure vessel (Fig. 1). Inert gas purge capability for all pressures was maintained by a system of needle valves and flowmeters. Additional descriptive information on these high-pressure modifications are applicability of the DSC to propellant studies is given in Ref. 8.

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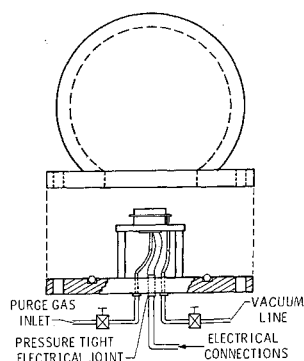† Associate Professor of Mechanical Engineering.

Fig. 1 DSC pressure vessel modification.

A Perkin-Elmer Model TGS-1 thermogravimetric analysis system (TGA) is used for weight loss vs temperature measurements at atmospheric pressure and below. It provides a record of μg level weight changes in a sample as a function of temperature from ambient to 1000°C. It utilizes a Cahn "RG" electrobalance which is mounted in a glass vacuum chamber, permitting control of the atmosphere around the sample suspended from the balance beam of the electrobalance into a furnace below it. The Cahn electrobalance provides a sensitivity of 0.0001 mg. The furnace consists of a platinum resistance heating element wrapped around the outside of a ceramic cylinder 9.4 mm in diameter. The sample is suspended in a sample pan inside the heated ceramic cylinder. The location of the furnace within the chamber permits close coupling of heat source and sample to permit rapid scanning without information loss. The low thermal mass of the furnace allows rapid programed temperature rise rates at 11 selected linear rates from 0.3 to 320 °C/min. The furnace acts as a heater and as a temperature sensor. In the temperature sensing mode, it forms one side of a bridge circuit. The other side of the bridge circuit is driven by the output signal from the temperature programmer. An error signal proportional to the temperature error is developed and fed into an amplifier. In the heating mode, the amplifier output is connected to the heater by means of an electronic system which provides 60-Hz power pulses designed to correct the temperature error.

III. Sample Preparation and Test Procedure

Two methods of sample preparation were used for the DSC experiments. The first method, described by Rogers and Morris,[9] consisted of mixing a measured amount of finely powered propellant with a measured quantity of Convalex-10 polyphenyl ether pump oil (Consolidated Vacuum Corporation), on a glass microscope slide. Mixtures were limited to 10% or less by wt of propellant to prevent self-heating effects. A number 28 nickel wire ring slightly less than 6 mm in diameter was placed in the bottom of a sample pan, provided with the DSC, and a small drop of mix was placed inside of the ring. The pan was then covered with the disk-type lid, pierced 8 to 10 times with a hypodermic needle to allow gaseous products to escape, and crimped onto the pan with the crimping tool provided by the manufacturer. Sample sizes of approximately 15 mg of mix could usually be handled without the liquid oozing out. Temperature scan rates of 20°C/min and sensitivity settings of 8 to 16 mcal/sec for full-scale deflection produced curves which remained on scale for the pressure range tested. The polyphenyl ether was tested in pure form and found to be inert over the pressure and temperature range of interest. Similar tests were performed using 1 to 2 mg of pure powdered M-2 propellant in the sample holder and the same trends in the results were obtained; however, data scatter was greater. The polyphenyl ether provides a more uniform environment and better reproducibility of results.

The second type of sample was prepared by cutting flat disks from a cylindrical rod of propellant 3 mm in diameter. Disks 0.6 to 0.7 mm thick provided weights of 16 and 22 mg. Each disk was then placed in a sample pan, covered with a pierced lid, and the assembly crimped to enclose the sample disk of propellant completely. Maximum sensitivity settings of 2 to 4 mcal/sec for full-scale deflection were used with this type sample.

Experimental procedures were in accordance with the operating instructions provided by the manufacturer except that argon was used as the pressurizing and purge gas because of its low thermal conductivity and resultant lower heat loss to the surroundings. Since the purge gas system is common to the sample and reference holders, and any difference in heat transfer is compensated for by the instrument electronics, the system accuracy is maintained.

For the TGA measurements, disks were cut from the cylindrical rods of propellant also. A prime factor in sample preparation was to maintain the best possible thermal contact with the sample pan to give sharp and reproducible results. Disks approximately 0.2 mm thick produced samples of 7 to 8 mg which fall in the optimum range of the instrument of 0.5 to 10 mg. TGA sample pans are roughly the same size as the DSC sample pans but no lids were required since prevention of radiation heat loss from samples was not a factor in weight-loss measurements. Experimental procedures were in accordance with the TGA operating instructions provided by the manufacturer and again argon was used as the purge and environmental gas.

IV. Experimental Results

Typical recorder outputs for the powdered propellant in polyphenyl ether samples are shown in Fig. 2. The first detectable indication of exothermic reaction occurred between 160°C and 170°C for the 20°C per min heating rate. The resulting bell-shaped curves were similar in shape for all pressures with slightly sharper peaks at the higher pressures. The curves are almost symmetrical about the peaks with a tendency for the high-temperature side of the bell to be slightly shorter. Some slight trial-and-error adjustment of the purge-gas flow rate and baseline slope was usually sufficient to insure returning to the baseline. The data were quite reproducible for the range of mixtures used, that is, 5 to 10% by wt of propellant in polyphenyl ether. The area under the curve bounded by a baseline drawn tangent to the lower edges of the bell was measured with a mechanical planimeter. The planimeter was then used to measure the area of a rectangle which was one-half of the chart in width, and in length equal to 1 min of run time. (For example, if the chart speed was 10 cm/min, the rectangle was 10 cm long.) A direct measure of the heat of reaction in calories was then given by

$$\text{Calories} = \frac{(\text{area of sample peak}) \ (\text{range setting}) \ (60)}{(\text{area of rectangle}) \ (1000)}$$

This was then divided by the weight of propellant in the sample to get the heat of reaction in calories per gram. The heats of
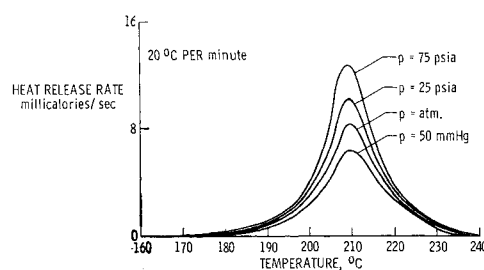

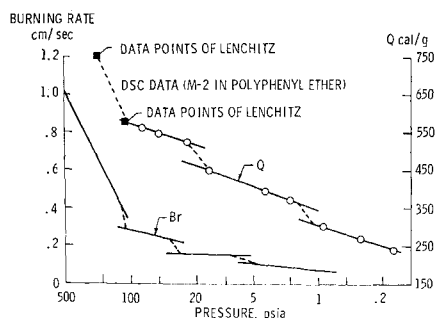Fig. 2 DSC thermograms of M-2 propellant.

Fig. 3   Heat of reaction and burning rate of M-2 propellant.

reaction were calculated and plotted as a function of pressure in Fig. 3. The variation of burning rate with pressure for M-2 propellant from Thompson and Suh[10] is also shown on Fig. 3. The heat of reaction continued to vary with pressure down to the limit of the equipment at 0.3 psia, as would be expected from a gaseous or heterogeneous surface reaction. Abrupt changes occur in the heat of reaction and burning rate in three pressure regions near 2 psia, 20 psia, and 100 psia.

In the maximum sensitivity runs using the nominal 20 mg disk samples of pure propellant, the first recognizable heat generation, indicated by departure from the baseline, occurred at approximately 140°C for a heating rate of 10°C/min. This exothermic indication continued to increase gradually as shown in Fig. 4. At approximately 165°C the established trend in the exothermic direction dropped slightly and then resumed its increase. This appears to be an endotherm on top of an established exothermic rate. If the main power switch was cut off prior to 165°C, the propellant sample holder assembly was found to be clean. But, if the temperature was allowed to increase beyond this point, a small amount of brown oily residue was always found on the bottom side of the dome-shaped cover over the sample holder cup and around the outside of the sample holder cup. These phenomena consistently occurred at 165°C for all pressures.

A disk sample was then used in the TGA at the same heating rate of 10°C per min. In the TGA results, as shown in Fig. 5, the first detectable weight loss always occurred at temperatures lower than the first detectable heat generation. The weight loss rate increased smoothly up to 165°C where a definite "knee" in the curve consistently occurred, for all pressures within the TGA limitations of 10 mm of mercury up to atmospheric pressure, and then the rate of weight loss increased rapidly.

The brown oily liquid which appeared if the temperature was allowed to increase past 165°C was apparently vaporizing from the propellant causing the endothermic dip on the DSC curve and the sudden increase in rate of weight loss on the TGA curve. A sample of this liquid was collected for an infrared analysis. The resulting spectrum is shown in Fig. 6. When compared to the spectrum of nitroglycerine from Pristera,[11] also shown on Fig. 6, the spectrum of the brown oily liquid was almost identical with all peaks occurring at the same wavelengths.
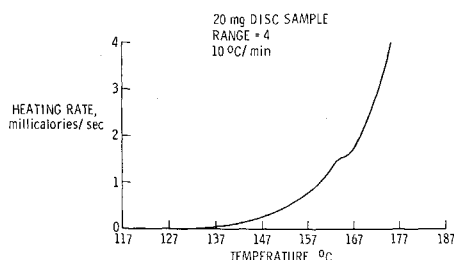

Fig. 4   DSC endothermic anomaly indicating vaporization of nitroglycerine.
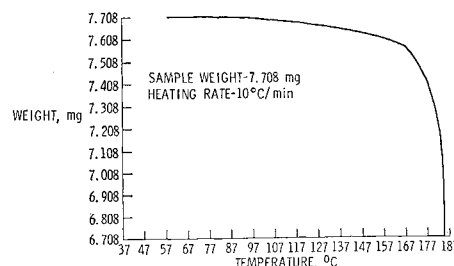

Fig. 5   TGA thermogram of M-2 propellant.

V.   Discussion

One of the most interesting results obtained was the jumps in the heat of reaction curve. These jumps agree with the data of Suh and Clary[12] shown in Fig. 7. The slopes of the curves in Fig. 7 are roughly parallel from 2.4 to 14.7 psia and a slope change occurs between 14.7 and 64 psia. From 65 psia to 115 psia the slopes are again roughly parallel and another change in slope occurs between 115 and 165 psia. The abrupt changes in burning rate seem to occur over a wide range of initial temperatures and appear to be more significant at higher initial temperatures, as indicated by the divergence of the curves in the jump regions at higher initial temperatures.

Thompson and Suh,[10] using synchronized high-speed motion-picture photography and microthermocouples embedded in the propellant, have identified distinct gas phase reaction zones near the surface as illustrated in Fig. 8. These distinct zones approach the burning surface as the ambient pressure is increased. At certain discrete ambient pressures within the range of pressures for which these zones exist, the heat of reaction and burning rate undergo a series of abrupt changes or jumps as shown in Fig. 3. In view of these results, it may be concluded that the DSC measurements also include the gas phase reactions and heterogeneous reactions, if the latter exist, in addition to condensed phase reactions. Examination of the purge gas flow path of the DSC shown in Fig. 9 indicates that the possibility of any gaseous reactants or products being swept away is very low.

The fact that weight loss, as indicated by TGA measurements, always begins before heat generation implies that gaseous decomposition products or reaction products are evolved in the heat-producing reactions and that pure condensed-phase reactions, which do not produce gases, are either insignificant or are not detectable by the DSC because they occur at the same temperatures at which the gas-producing reactions occur for double-base propellants.
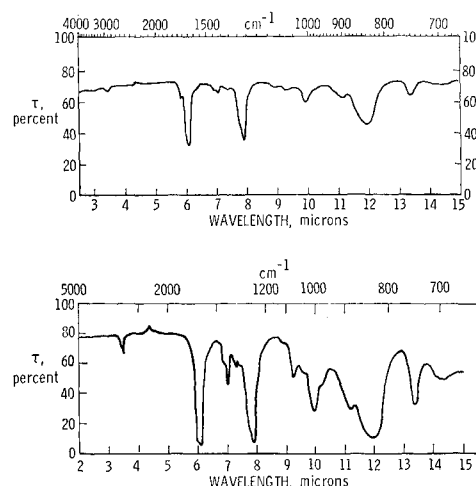

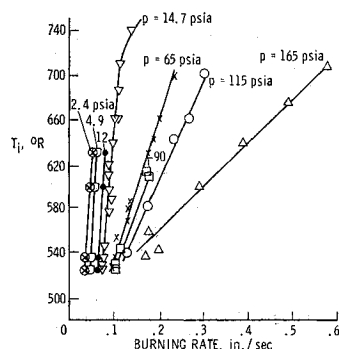**Fig. 6   IR spectra of oil liquid residue and nitroglycerine.**

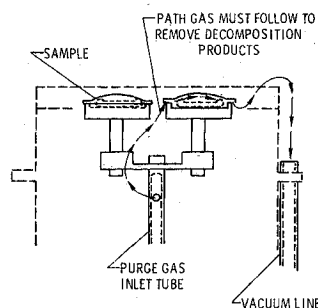**Fig. 7 Burning rate vs initial temperature of M-2 propellant.**

The abrupt changes which occur in the 2 psia and 20 psia regions are in the "flameless combustion" region. A visible flame appears at the 100 psia change. The fact that no visible flame occurs is thus not a justification for ruling out gas-phase reactions. The vaporization of nitroglycerine seems to occur prior to significant heat generation, again implying that reactions are gaseous or heterogeneous rather than condensed-phase reactions.

The accuracy of the DSC measurements has been verified by the closed bomb calorimeter measurements of Lenchitz[13] (data obtained at Picatinny Arsenal, Dover, N. J.) shown in Fig. 3. It should be noted that Lenchitz's results fall on the same line as the DSC measurements and that a closed bomb calorimeter measures all the reactions occurring within the bomb.

These experimental results do not, of course, prove that there are no condensed-phase reactions or tell whether or not they affect the burning rate to some extent. Indeed, it is expected that before any significant decomposition of the propellant can take place, some of the long chain molecules of nitrocellulose break, creating shorter chains. Such reactions may be either endothermic or exothermic depending on what kinds of molecules are formed after the chain breaking. Thus, it is our conclusion that the DSC measurements cannot provide the information on pure condensed-phase reactions alone.

Furthermore, there are internal surfaces in the propellant due to voids and impurities which provide possible internal reaction sites. In fact, such internal surface reactions involving decomposition gases may contribute more toward internal heating of the propellant than condensed phase reactions.

VI.   Conclusions

The flameless heat of reaction of a double-base propellant has been measured using a differential scanning calorimeter and found to vary with pressure down to 0.3 psia. However, the variation is not continuous. At certain distinct ambient
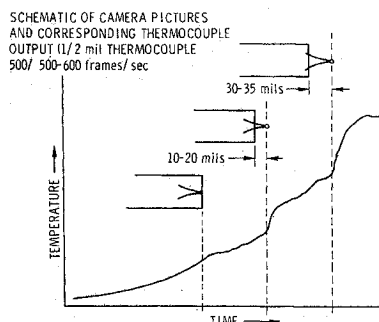

Fig. 8   Temperature jumps near surface.

Fig. 9   DSC purge gas flow path.

pressures, the heat of reaction and burning rate undergo a series of abrupt changes or jumps due to gas-phase reactions which exist very near the burning surface. Such reactions make the differential scanning calorimeter inadequate for separating the condensed phase contribution from the overall heat of reaction.

Comparison of thermogravimetric analysis and differential scanning calorimeter measurements at the same pressures detected the evolution of gases and the vaporization of nitroglycerine prior to the beginning of significant heat generation. These facts and the variation in heat of reaction with pressure at all pressures tested imply that the heat necessary for flameless burning is not supplied almost completely by the condensed phase, as suggested by others.

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