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CALORIMETRIC STUDY OF THE ENERGY ON COMBUSTION OF AMMONIUM PERCHLORATE IN 11 ATM HELIUM

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ABSTRACT

The combustion of pure ammonium perchlorate in helium at 11 atm was studied using a newly constructed twin-type combustion calorimeter. The calorimeter has an error of around ±3% for the measurements of the combustion energy of benzoic acid in 11 atm oxygen. The samples of ammonium perchlorate were ignited with external heating in the helium atmospheres, and the heat evolution on combustion has been measured to be 1280 ± 55 cal g^{-1}.

INTRODUCTION

The mechanism of decomposition of ammonium perchlorate (AP) consists of the formation of NH_3 and $HClO_4$ molecules on the surface, their desorption into the gas phase, and their reaction there. These gas-phase reactions are exothermic and heat conducted to the AP results by a rise in temperature, accelerating decomposition, and deflagration[1]. This deflagration is of thermal origin, and easily occurs as the ambient gas pressure and the external heating rate are increased[2].

The combustion of AP at high pressures has been investigated intensively[3–5] to obtain a basic understanding of this process. The calorific value, however, of AP exploded in an inert gas atmosphere does not seem to have been reported so far.

The present paper reports a calorific value of AP combustion obtained in He at 11 atm using a new type of combustion calorimeter, of samples containing 17–24 mg.

EXPERIMENTAL

Materials

The sample of AP used was the same as that described in the latest report[2]. The benzoic acid was authorized at the National Research Institute for Pollution and Resources, Tokyo, having a combustion energy of 6321 cal g^{-1}. The low-density polyethylene (*d*, 0.92) was supplied without additives by Nippon Unicar Co., Tokyo.

Apparatus and procedure

The combustion calorimeter, a twin-type calorimeter with differential thermal method, was constructed in cooperation with Rigaku Denki Co., Tokyo. The schematic diagram is shown in Fig. 1.

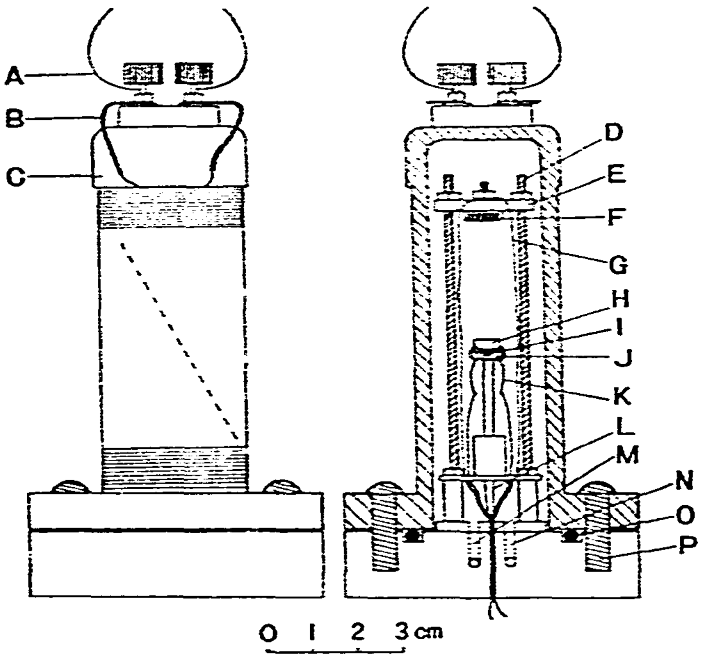

Fig. 1. Schematic diagram of the combustion calorimeter. A, lead wires for bridge circuit; B, resistance wire of Ni; C, aluminum pressure vessel; D, supporting rods; E, quartz glass disk; F, G, ignition heater and lead wire; H, sample holder; I, L, thermocouple and lead wire; J, K, sample heater and lead wire; M, gas inlet; N, gas outlet; O, Viton O-ring; P, bolts.

It consists of two cylindrical aluminum pressure vessels (25 mm i.d., 91 mm depth, 44.6 cm^3 int. volume) which are placed on the stainless-steel pedestals with O-ring seal. Various gas atmospheres may be charged in the vessels via the inlet of one of the vessels as the gas pipes connect each other, at a maximum pressure of 11 atm. These two aluminum vessels located at a distance of 37 mm to each other are mounted inside a cell (160 mm i.d., 160 mm depth). A covered vessel (300 × 300 × 320 mm), in which water is circulated at room temperature, is put on the cell. Helium gas is filled in the cell at 1 atm before the measurements are taken.

The surface of each aluminum vessel is plated with alumina for the insulation, and wound 67 times with a resistance wire of nickel at 1 mm intervals. The nickel wires (0.1 mm diam., 6.3 m length, resistance 75 Ω) constitute a bridge circuit which is applied at a constant voltage of 2 V. The potentials in the circuit resulting from the temperature changes on the surface of one of the vessels are amplified, and recorded on an electronic recorder at a full scale 5 mV.

In each vessel of the heat detector, a platinum sample holder (6 mm diam., 3 mm depth) mounted on a cylindrical ceramics is fitted with a platinum heater

(0.1 mm diam., resistance 5 Ω, potential 20 V) at the lower part of the holder. Platinum or aluminum sample cells (5 mm diam., 2.5 mm depth) were placed in the holders of the two detectors for the combustion experiments. A platinel (±) thermocouple is put in contact with the bottom of the holder in each detector to measure the temperature of a sample or to control the temperature-rise rate. A quartz glass disk above each holder is supported with two stainless-steel rods in order to confine the combustion zone to a rather limited space. A 12 Ω manganin heater (0.2 mm diam., potential 30 V) is fitted under the bottom of the disk in each detector to ignite a sample with a cotton thread at room temperature. The leading-in wires for the sample heaters and ignition heaters are of platinum.

Figure 2 shows a typical thermogram of the potential in the bridge circuit versus time, having a time constant of 5 min. If the equivalent heat is applied to the two sample holders for the ignition of a sample, the heat evolution on combustion, Q, is given by

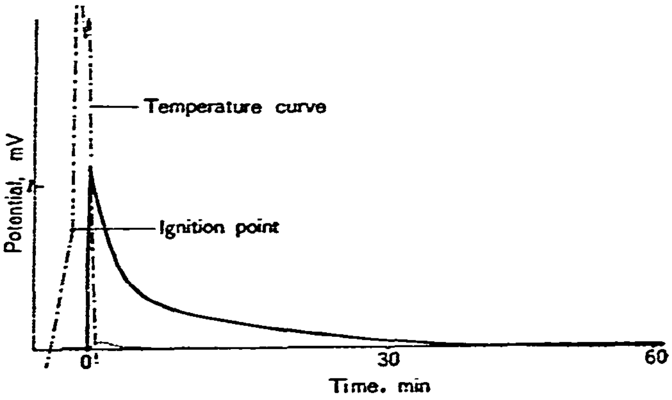

Fig. 2. Thermogram of combustion of polyethylene (~10 mg) in 11 atm O_2 at heating rate of 160 °C min^{-1}. Dotted curve, effect of error for blank run.

$$Q = C\int_0^\infty \frac{d}{dt}(T_s - T_r)dt + k\int_0^\infty (T_s - T_r)dt$$

where C is the heat capacity of the aluminum vessel, t the time, T_s and T_r the surface temperatures of the sample-side and reference-side detector, respectively, and k the coefficient of heat transfer. The first term of the right-hand side of the equation is zero when the surface temperatures of the two detectors are the same before and after the measurement. Thus, the heat evolution may be determined by integrating the total area under the thermogram. For the measurements of the heat evolution of samples, electrical calibration was carried out by heating the sample holder of the sample-side detector with 12.495 J sec^{-1} for a fixed time.

The potentials in the bridge circuit, being given a gain of 100, are integrated automatically for each 0.5 sec intervals by the integrator (constructed at Kuwano

Denki Co., Tokyo) and printed out. An error due to a slight shift of a baseline of thermogram is electrically corrected in the integrator. The effect of an error (shown with a dotted curve in Fig. 2), which was observed when the two sample holders were heated at a certain heating rate, was corrected by taking a separate blank run.

12 to 20 mg of pressed samples of benzoic acid were wrapped with a Japanese paper (almost pure cellulose), and ignited in a platinum cell at an oxygen pressure of 11 atm through a cotton thread suspended from the ignition heater with a 30 mm platinum wire. The samples of low-density polyethylene (10–18 mg) were placed in a platinum cell and ignited at a heating rate of 160°C min^{-1} in an atmosphere of oxygen at 11 atm. A helium atmosphere of 11 atm was employed for the combustion experiments of AP (loose powder) with a mass of 17–24 mg. The samples of AP were ignited at a heating rate of 155°C min^{-1} or 2000°C min^{-1} (mean) in a platinum or aluminum cell.

RESULTS AND DISCUSSION

The results of combustion studies on benzoic acid, polyethylene, and AP are presented in Tables 1 and 2. The combustion energies of Japanese paper and cotton thread were measured to be about 4.040 and 4.050 cal mg^{-1}, respectively. A combustion energy of low-density polyethylene has been reported[6] to be 11140 cal g^{-1}.

In these experiments, the residual products and gaseous or liquid state products remained after the combustion of samples were not evaluated for the correction of the combustion energies. It is noticed that this combustion calorimeter probably has an error of around ±3% from the measurements of the combustion energy of benzoic acid, even though the effect of possible errors of electrical calibrations and combustion products was taken into consideration.

The heat evolution on combustion of AP in He at 11 atm (ca. 1280 cal g^{-1}) is little influenced by the difference in sample cell or the external heating rate when the sample is heated rapidly. The ignition temperatures range from 464 to 507 °C, while the minimum ignition temperature of AP at 1 atm has been reported to be 427–430 °C by Galwey and Jacobs[7], and Kuratani[8]. Guirao and Williams[9] suggest that for deflagration of AP at pressures over 20 atm, equilibrium for a dissociative sublimation process is likely to exist at the interface between the gaseous and condensed phases. Thus, further study will be needed for the calorimetric study of combustion of AP to

TABLE 1

COMBUSTION OF BENZOIC ACID AND LOW-DENSITY POLYETHYLENE IN O_2 AT 11 atm

Sample	*No. of expt.*	*Comb. energy (cal mg^{-1})*
Benzoic acid	9	6.372±0.183
Low-density polyethylene	7	11.016±0.228

TABLE 2

COMBUSTION OF AMMONIUM PERCHLORATE IN He AT 11 atm
$Q = 1.280 \pm 0.055$ cal mg^{-1}.

No.	*Cell*	*Heat. rate (°C min^{-1})*	*Ignit. temp. (°C)*	*Weight (mg)*	*Comb. energy (cal mg^{-1})*	*Residue (mg)*
1	Pt	155	464	23.62	1.285	—
2	Pt	155	474	22.49	1.258	0.09
3	Pt	155	509	16.81	1.253	0.06
4	Pt	155	507	21.14	1.318	0.19
5	Pt	155	505	19.08	1.285	0.17
6	Pt	155	497	20.64	1.395	0.07
7	Pt	155	496	19.17	1.335	—
8	Pt	155	495	21.72	1.253	0.09
9	Pt	2000	501	18.98	1.253	—
10	Pt	2000	490	18.16	1.302	—
11	Pt	2000	479	18.15	1.253	0.05
12	Pt	2000	488	19.62	1.154	0
13	Al	2000	486	18.23	1.395	0.08
14	Al	2000	490	18.24	1.335	0.07
15	Al	2000	497	18.57	1.121	—

establish the effects on the sublimation during heating or deflagration, and on the pressure of various gas atmospheres.

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