Thermochimica Acta, 54 (1982) 141–146
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

CALORIMETRIC VALUES OF COMPOSITE SOLID PROPELLANTS

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(Received 30 September 1981)

ABSTRACT

The calorimetric values of composite solid propellant based on polystyrene, polyphenolformaldehyde, poly(vinyl chloride) and carboxy-terminated polybutadiene were determined using combustion calorimetry in order to assess the uncertainities in their measurements. The dependence of the calorimetric values on various propellant composition was obtained. The stoichiometry of oxidizer and fuel in the propellant for complete combustion obtained experimentally were compared with the theoretical stoichiometry calculated based on the oxidizer decomposition.

INTRODUCTION

It is well known that energetics of propellants play a very vital role in the selection of their formulation and performance. A scan of the literature reveals that not much attention has been paid to obtaining reliable calorimetric data. In addition, the values available are on homogeneous propellants [1–5] and very few values have been reported for composite solid propellants [6–9].

In the present work an attempt has been made to determine the calorimetric values of composite solid propellants based on polystyrene (PS), polyphenolformaldehyde (PPF), poly(vinyl chloride) (PVC) and carboxy-terminated polybutadiene (CTPB) as binders with a view to assessing the uncertainties in enthalpy measurements and obtaining their dependence on the propellant composition.

EXPERIMENTAL

Calorimetric procedure

A bomb calorimeter (Toshniwal India) was used in the present work. The jacket temperature of the bomb calorimeter was maintained constant by circulating thermostated water. The Beckmann thermometer was replaced by a ten junction teflon coated (o.d. = 0.01 in. Omega U.S.A.) chromel–alumel thermocouple, one end of which was kept in a Dewar flask filled with water whose temperature was precisely

known and the other junction was kept in the bucket. The temperature of the cold junction (in Dewar) was maintained in such a manner that it was 0.2–0.5°C lower than the initial temperature of the bucket. This enabled the thermocouple output to be adjusted such that it could be traced on the chart recorder up to a maximum rise of 2.5°C in the bucket when the sample was fired. The time–temperature trace could, thus, give an accuracy of 0.005°C for the temperature measurement and 2.4 s on the time axis. The strip chart recorder was obtained from Omniscribe Digital Electronics, Bombay. The exact handling of the experiment was conducted according to the manufacturer's manual and the procedure described elsewhere [10]. A typical temperature–time plot is shown in Fig. 1. The corrected temperature rise (ΔT) was obtained by following the procedure given in Rossini's book [10].

The water equivalent was calculated by using the following equation and combusting NBS standard benzoic acid samples in the form of pellets supplied by the Parr Co., USA.

$$Q = \frac{W_1 \Delta H_1 + W_2 \Delta H_2 + W_3 \Delta H_3 + W_4 \Delta H_4}{\Delta T} - W$$

where

Q = water equivalent of the calorimeter, cal °C^{-1}
W = amount of water in the bucket + bomb
W_1 = weight of benzoic acid taken for the experiment
ΔH_1 = heat of combustion of benzoic acid = 6319 cal g^{-1}
W_2 = weight of ignition wire burnt
ΔH_2 = heat of combustion of ignition wire = 1433.08 cal g^{-1}
W_3 = weight of cotton burnt
ΔH_3 = heat of combustion of cotton = 4179.8032 cal g^{-1}
W_4 = weight of HNO_3 formed
ΔH_4 = heat of formation of HNO_3 = 223.68 cal g^{-1}

The reproducibility in the functioning of the calorimeter was checked from the

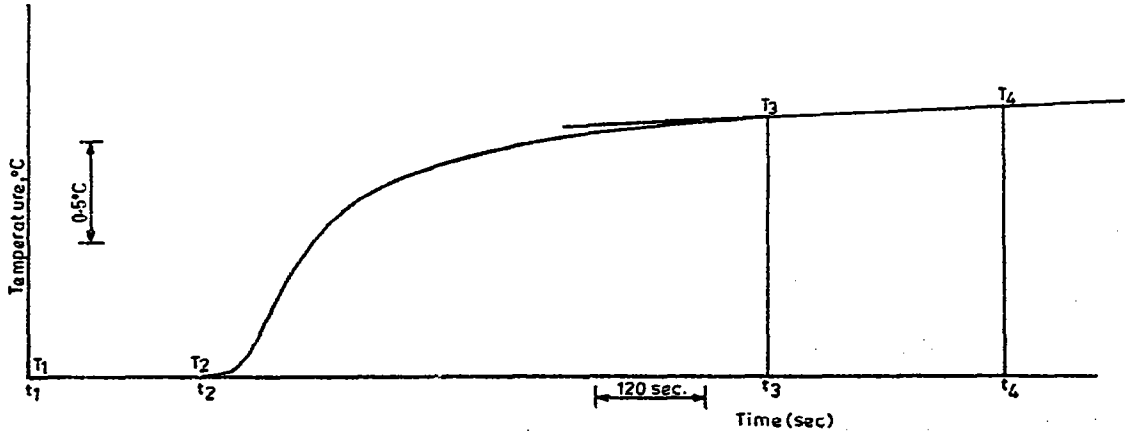

Fig. 1. A typical temperature–time plot.

water equivalent obtained (Table 1) by burning benzoic acid in several runs. The reproducibility in the measurement was 99.91%.

Calorimetric value of the propellant samples was calculated using the equation

$$(W+Q)\,\Delta T = W_1\,\Delta H_1 + W_2\,\Delta H_2$$

$$\Delta H_1 = \frac{(W+Q)\,\Delta T - W_2\,\Delta H_2}{W_1}$$

where

W = weight of water taken in the bucket + bomb
Q = water equivalent of the calorimeter
ΔT = corrected temperature rise
W_1 = weight of the propellant taken for experiment
ΔH_1 = calorimetric value of propellant
W_2 = weight of the ignition wire burnt
ΔH_2 = heat of combustion of ignition wire

Corrected temperature (ΔT) for the propellant sample was obtained using the same method as for the benzoic acid sample. All weighings for calorimetric experiments were done to an accuracy of one hundredth of a milligram using a Mettler balance.

Preparation of the propellants

The viscous pre polymers of the various binders PS [11], PPF [12], PVC [13] and CTPB [14] were prepared as described elsewhere. Ammonium perchlorate (particle size $53 \approx 105$ μm) based propellants were prepared by the usual method [11].

TABLE 1

Water equivalent of the calorimeter from benzoic acid combustion

Sample	Water equivalent (Q) (cal deg^{-1})	Average value of water equivalent (Q) (cal deg^{-1})	Standard mean deviation	Error (%)
Benzoic acid	516.0736	515.380	±0.455	0.088
Benzoic acid	515.1291			
Benzoic acid	514.9225			
Benzoic acid	515.7158			
Benzoic acid	514.9772			
Benzoic acid	515.4739			

RESULTS AND DISCUSSION

Calorimetric values of the propellants are presented in Tables 2 and 3. The average error was found to be 0.5% but the error values range from 0.1 to 0.9% for various samples. This error is much higher than that obtained for the benzoic acid sample, where the error is only 0.09%. The higher error in the heats of combustion of the propellants may be because of the composite nature of the samples and therefore depends very much on how the homogeneous mixing of the ingredients is achieved.

The plot of ΔH_c as a function of oxidizer loading is shown in Fig. 2.

The propellants were cast only up to 85% AP loading. When the AP loading is increased more than 85% the propellant could not be cast and the resultant material had very poor mechanical properties and often crumbled with the slightest pressure.

Stoichiometric calculations were made based on the available oxygen in AP according to the equation

$$4\,NH_4ClO_4 \rightarrow 2\,N_2 + 4\,HCl + 6\,H_2O + 5\,O_2$$

The calculations were made only for PS, PPF and PVC propellants. The CTPB based propellant was not included in this calculation because it contained aluminum powder and therefore could not be compared with other non-aluminised propellant systems. The results of the stoichiometric calculations are presented in Table 4. The experimental stoichiometry was determined from Fig. 2. For the PS and PPF propellants a maximum in the calorimetric value was obtained at 80% while the PVC propellant did not show any maximum up to 85% and ΔH_c values continuously increased up to 85% of AP loading.

Table 4 shows that the theoretical stoichiometry is higher than the experimental. The possible explanation for the same is as follows: in the stoichiometry calculation, only the oxidation due to oxygen produced from AP was considered, but in addition to oxygen, HCl is also produced. Since HCl is also an oxidizer it will also oxidize the binder.

The explanation for the anomoly in the case of PVC is not known at present. However, it may be pointed out that PVC on decomposition produces HCl by itself.

TABLE 2

Calorimetric values of the propellants

Composition (wt.%)		Calorimetric value (cal g^{-1})		
AP	Binder	PS/AP	PPF/AP	PVC/AP
70	30	1022.6±8.8	1123.1±7.0	1014.4±7.0
72	28			1052.0±7.4
75	25	1140 ±3.0	1232.5±7.7	1196.8±4.5
78	22			1294.0±5.9
80	20	1394.7±5.7	1428.5±2.0	1358.5±6.0
85	15	1232.1±3.5	1286.2±8.3	1483.0±2.0

TABLE 3

Calorimetric values of aluminised CTPB propellants

Composition (wt.%)							Calorimetric value (cal g^{-1})
AP	CTPB	Al	DOA	MAPO	GY	Lecithin	CTPB/AP/Al
58.1	18.8	18	2.7	1.1	0.80	0.50	1000.4 ± 5.5
62	15.7	18	2.3	0.90	0.70	0.40	1284.7 ± 8.0
64	14.0	18	2.0	0.90	0.70	0.40	1411 ± 5.0
65	13.2	18	1.8	0.90	0.70	0.40	1485.6 ± 7.4
66	12.3	18	1.7	0.90	0.70	0.40	1594.4 ± 5.5
67	11.5	18	1.5	0.90	0.70	0.40	1674.9 ± 6.9

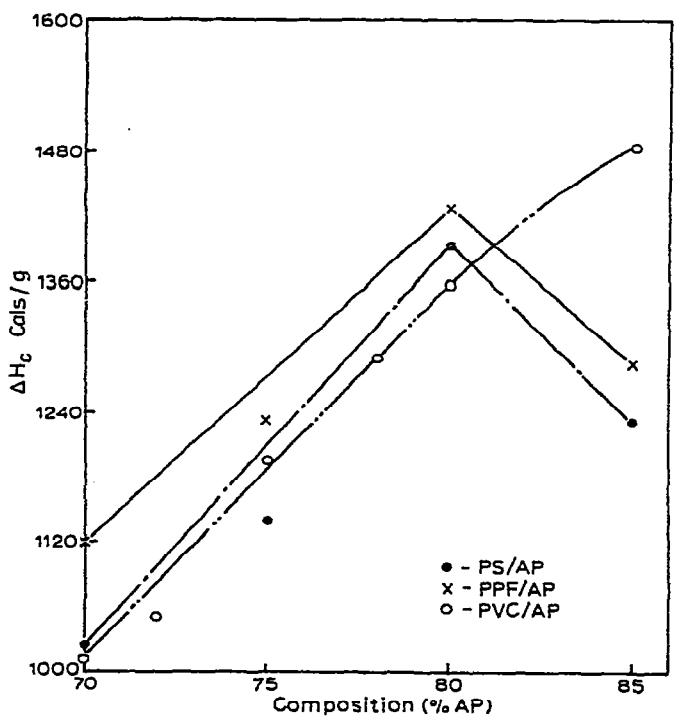

Fig. 2. Plot of ΔH_c as a function of oxidiser loading.

TABLE 4

Comparison of theoretical and experimental stoichiometric percent of AP values

Propellant system	Stoichiometric percent of AP	
	Theoretical	Experimental
PS/AP	90.03%	80%
PPF/AP	88.1%	80%
PVC/AP	84.0%	>85%

REFERENCES

1 J. Reinhard, W.E. Stump and J.S. Davidson, U.S. Pat. 3,767,489 (1973).
2 E. Edward, S. Gorden and S.H. Hayes, Br. Pat. 1,423,337 (1976).
3 Nitrochemie GmbH, Br. Pat. 1,498,171 (1978)
4 Nitrochemie GmbH, Br. Pat. 1,498,172 (1978).
5 J.S. Stack, U.S. Pat. 3,954,667 (1976).
6 J.P. Diebold and J.B. Eldrige, U.S. Pat. 3,702,354 (1972).
7 C.R. Meculloch, B.K. Moy and T.C. Randle, U.S. Pat. 3,725,154 (1973).
8 H.L. Girdhar and A.J. Arora, J. Technol., 17 (1979) 299.
9 R.P. Rastogi, K. Kishore and Gurdip Singh, AIAA J., 12 (1974) 9.
10 F.D. Rossini, Experimental Thermochemistry, Vol. 1, Interscience, New York, 1956.
11 K. Kishore, V.R. Pai Verneker and G. Prasad, Combust. Sci. Technol., 19 (1979) 107.
12 R.P. Rastogi and C.V. Ouseph, Combust. Flame, 9 (1965) 417.
13 K. Kishore, V.R. Pai Verneker, K.R. Shubha and S. Sankaralingam, Combust. Flame, in press.
14 K. Kishore, V.R. Pai Verneker and M.R. Sunita, AIAA J., 18 (1980) 104–105.