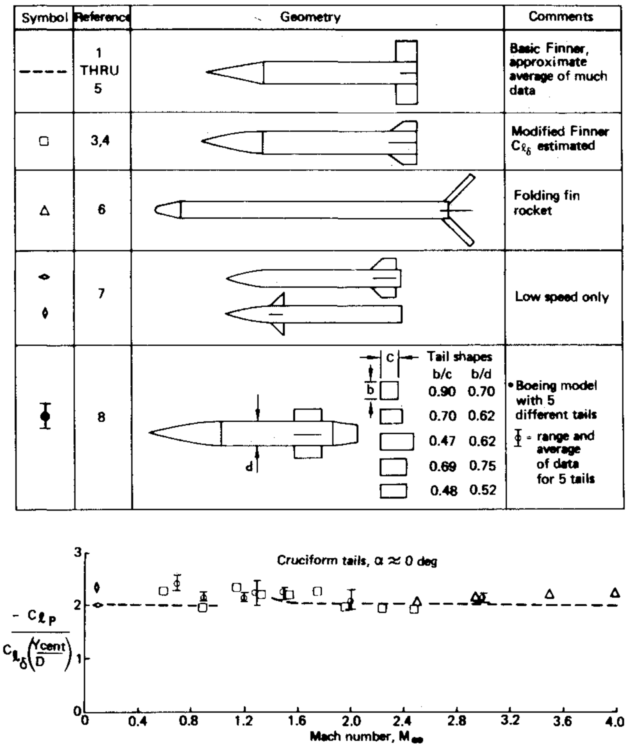

Fig. 1 Correlation of roll damping data for cruciform-tailed missiles.

configurations. This term is intended to account for differences in tail geometry and the ratio of body diameter to tail span. To obtain C_{ℓ_p} from Fig. 1, C_{ℓ_δ} must be known. Theoretial methods[10] and much experimental data are available for predicting this coefficient. Figure 1 is valid only for a missile with a single set of cruciform fins. If canards or wings are located ahead of a tail, large roll damping interference effects may occur between the forward and aft surfaces.[2]

Use of Eq. (1) to predict roll damping, within the limitations discussed above, should be adequate for most engineering purposes. Figure 1 should be updated as additional experimental data become available.

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A Calorimetric Bomb for Determining Heats of Combustion of Hypergolic Propellants

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Introduction

IN connection with our studies on hypergolic hybrid propellant systems,[1-3] it was found desirable to have an idea of the actual experimental values of their heats of combustion. A survey of the literature showed that, although a variety of bomb calorimeters[4,5] are available for measuring the heat of combustion values of solid fuels in gaseous oxygen, no suitable device exists so far for determining these values using a liquid oxidizer instead of oxygen. The apparatus described by Rastogi and Kishore[6] gives values very much lower than expected. Herein we report the design and operation of an improved bomb-calorimetric device for measuring the heats of combustion of hypergolic hybrid and biliquid propellant systems.

Experimental

Bomb Calorimetric Device

The usual pressure bomb assembly for the calorimetric measurements has been modified as shown in Fig. 1. The liquid oxidizer is placed in a specially designed duck-shaped glass vessel. The glass duck is supported by two loops of a stainless steel (SS) wire hanger around the pegs at the sides so that it is able to rotate freely. The hanger in turn is fixed by means of a screw to the lid of the bomb. The fuse wire usually meant for igniting the fuel is used for keeping the glass duck in the upright position, instead.

To start with, a known amount of the liquid oxidizer (HNO_3) is placed in the glass duck which is then fixed onto the hanger and supported by the fuse wire in the upright position. The fuel is placed in the SS cup. The bomb is then carefully closed and kept in an isothermal static-bomb calorimeter while connected to the firing unit. After the initial temperature has been noted, the firing switch is pressed, which results in the snapping of the fuse wire. The duck inverts and pours the entire oxidizer onto the fuel causing instantaneous ignition of the fuel. The rise in temperature is then noted and the heat of combustion is calculated[7] from the rise in temperature and water equivalent data. The water equivalent of the calorimeter was determined by the usual procedure in oxygen using AR-grade benzoic acid. The experiments were repeated for each fuel, varying the amount of the oxidizer close to

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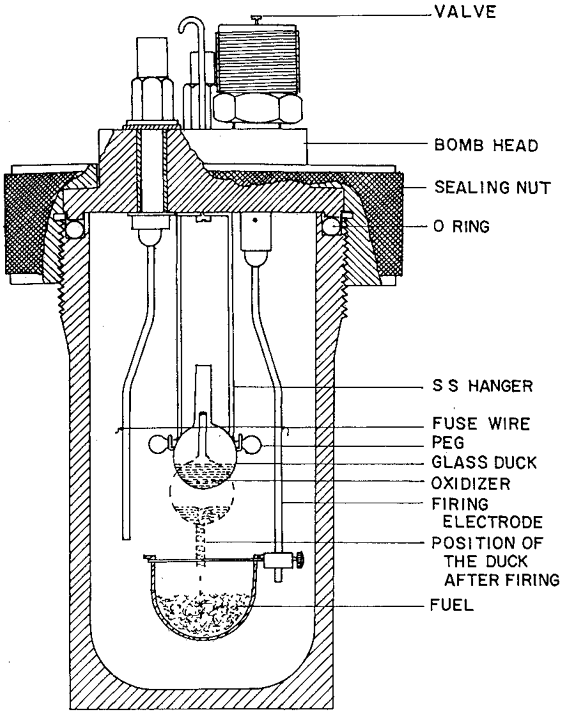

Fig. 1 **Combustion bomb for hypergolic propellants.**

stoichiometry. An average of a minimum of three values was taken for each oxidizer/fuel (O/F) ratio.

Materials

The mono-thiocarbonohydrazones were synthesized and purified as reported earlier.[8] The phenylhydrazones and p-hydroxylbenzaldehydedimethylhydrazone were prepared following the procedures described earlier.[3,9] Monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) were supplied by M/S Aldrich Chemical Co., U.S.A.

The oxidizers, white fuming nitric acid (WFNA) and red fuming nitric acid (RFNA), were prepared in the laboratory following standard procedures.[10] The white fuming nitric acid was distilled off from a 3:1 mixture of fuming nitric acid and concentrated sulphuric acid under reduced pressure. On analysis, the composition of the WFNA was found to be HNO_3, 99.82%; NO_2, 0.14%; and H_2O less than 0.1%. Nitrogen dioxide was prepared by heating dried lead nitrate at 350°C in a slow stream of oxygen and condensing the vapour of NO_2. The red fuming nitric acid was prepared by mixing calculated amounts of WFNA and liquid NO_2. The actual concentration of NO_2 in the acid was determined by chemical analysis.[11]

Results and Discussion

The heats of combustion of various fuels obtained using anydrous nitric acid as oxidizer are reported in Table 1. Also

Table 1 Heats of combustion with WFNA as oxidizer

No.	Compound	O/F[a] I = M II = S	Heat of combustion, kcal/g Observed	 Calculated
1	Benzaldehydethiocarbono-hydrazone $C_6H_5CH{:}NNHC{:}SNHNH_2$	3.5 3.1	4.77 4.18	6.08
2	p-Dimethylaminobenzaldehyde-thiocarbonohydrazone $N(CH_3)_2C_6H_4CH{:}NNHC{:}SNHNH_2$	4.0 3.65	5.10 4.78	6.54
3	p-chlorobenzaldehydethio-carbonohydrazone $ClC_6H_4CH{:}NNHC{:}SNHNH_2$	3.0 2.65	2.67 2.42	5.10
4	2-Furaldehydethiocarbonohydrazone $O-CH=CH-CH=C-CH{:}NNHC{:}SNHNH_2$	3.5 2.5	4.73 3.72	5.08
5	Formaldehydethiocarbonohydrazone $CH_2NHNHC{:}SNHNH$	3.0 2.15	4.26 3.68	4.37
6	Acetonethiocarbonohydrazone $(CH_3)_2CNHNHC{:}SNHNH$	3.5 2.75	5.43 4.89	5.60
7	Cyclohexanonethiocarbonohydrazone $(CH_2)_5CNHNHC{:}SNHNH$	3.35 3.25	5.51 5.27	6.34
8	Monomethylhydrazine CH_3NHNH_2	2.81 2.73	5.79 5.49	6.47
9	Unsymmetrical dimethylhydrazine $(CH_3)_2NNH_2$	3.55 3.36	3.99 3.94	7.49
		3.74[b]	4.34	

[a] M = O/F ratio corresponding to maximum heat liberation; S = O/F stoichiometric ratio. [b] Oxidizer used, RFNA-20% NO_2.

Table 2 Comparison of heat of combustion data

Fuel	Heat of combuston, kcal/g	
	Present method	Earlier method[6]
p-Dimethylaminobenzaldehyde-phenylhydrazone	4.52	2.25[9,13]
Furfuraldehydephenylyrazone	5.07	2.16[9,13]
p-Hydroxybenzaldehydedimethyl-hydrazone	4.95	2.16[9,13]
mono-Acetonethiocarbonohydrazone	5.43	2.18

shown are the theoretical heats of combustion of the thiocarbonohydrazones with nitric acid as oxidizer. These theoretical values were calculated from the heat of formation data which in turn were determined from the heats of combustion in oxygen.[12] In the calculations CO_2, N_2 and $H_2SO_4xH_2O$ were assumed to be the products of combustion. In each case, it is found that the maximum heat is liberated when the amount of the oxidizer is slightly more than stoichiometric requirement. In general, the observed heats of combustion of the hybrid systems are in the range of 4 to 6 kcal/g of the fuel. When some solid fuels such as formaldehyde-, acetone- and 2-furadehyde-thiocarbonohydrazones are used, the observed heat of combustion is nearly 97% of the theoretical value, indicating the excellent performance of the device when appropriate propellants are chosen. In other cases, the observed values are somewhat lower than those calculated by assuming complete combustion with HNO_3, using the heats of formation data of the respective fuels. The poor realization of the heat of combustion in these cases could mean incompatibility of the propellants, as a result of which the combustion is incomplete, under these conditions. Usually a small amount of solid/liquid residue was observed in the cup after combustion in such cases. It is also possible, however, that products other than those assumed for calculating the theoretical heat of combustion values, are formed.

In the thiocarbonohydrazones-WFNA systems, it is generally observed that the realization of heat of combustion in aliphatic carbonyl derivatives is higher than the aromatic aldehyde analogs. A comparison of the heat of combustion data shows that they vary with the functional group on the benzene ring in aromatic alehyde derivatives, in the order

$$(CH_3)_2N- > H > Cl$$

The electron-releasing groups appear to facilitate the combustion. When NO_2, a strong electron-withdrawing group, is substituted in the benzene ring the system becomes nonhypergolic. The heats of combustion of the other derivatives are found to be in the order

Formaldehyde < 2 – Furaldehyde < Acetone < Cyclohexanone

which is to be expected on the basis of their theoretical values. However, it is to be noted that the percentage realization of heat does not follow the above order. Of hypergolic biliquid propellant systems, the UDMH-WFNA system gives significantly lower heat of combustion than the theoretical value. This value is improved slightly when RFNA is used as oxidizer instead. The reason for this is not very clear. It could arguably be the incomplete combustion. However, the realization of the heat of combustion in the case of MMH-WFNA system is about 90%.

A comparison of the experimental values of the heat of combustion determined by the present method and those obtained[9,13] using the apparatus described by Rastogi and Kishore is made in Table 2. It is obvious that the present device is far superior. Furthermore, because of its simplicity of operation this device could be conveniently applied in studies relating to the measurements of heats of solution, hydrolysis, neutralization, etc.

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Charging of a Manned Maneuvering Unit in the Shuttle Wake

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Introduction

WHEN the Space Shuttle flies in polar orbit, it will encounter the aurora at times. The aurora is produced by

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