computational capability available. No attempt has been made to justify the many assumptions and simplifications involved, for they may differ in other systems; rather the intent has been to convey an approach that has proved to be useful in such problems encountered over the past several years.

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Performance Parameters of Some New Hybrid Hypergols

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Introduction

THE hypergolic nature of thiocarbonohydrazones, the solid derivatives of thiocarbonohydrazide with various carbonyl compounds, on coming into contact with fuming nitric acid, was discovered recently in the authors' laboratory.[1] The short ignition delays of some of these systems, measured using a drop-tester-type device, indicate the potential use of the thiocarbonohydrazones (TCH) as hypergolic hybrid rocket fuels. In addition to short ignition delays, these materials have other desirable fuel properties that include high stability toward aerial oxidation, nonhygroscopic nature, high melting/decomposition temperatures,[2] etc. All of these aspects led to the evaluation of such performance parameters as specific impulse, characteristic velocity, flame temperature, etc., of propellant systems comprising of TCH as solid fuels and anhydrous nitric acid (HNO_3) as liquid oxidizer. In doing so, however, it was realized that the thermochemical data of the various TCH needed for evaluation of the performance parameters are not reported in the literature. Therefore, the present study was undertaken to determine experimentally the heat of combustion and formation data and to evaluate the theoretical performance parameters of the various TCH-HNO_3 systems as hybrid propellants.

Experimental

Materials

Monothiocarbonohydrazones were synthesized by reacting thiocarbonohydrazide with various aldehydes and ketones, taken in 1:1 mole ratio and characterized as reported earlier.[1,3] For preparing bis-acetonethiocarbonohydrazone, thiocarbonohydrazide was refluxed with excess of acetone and the material precipitated was recrystallized using ice-cold petroleum ether.[4]

Heat of Combustion

Measurements of the heat of combustion (calorific value) were carried out using a conventional constant volume (300 ml) isothermal static bomb-calorimeter under constant pressure (30 atm) of oxygen. The water equivalent of the calorimeter was determined by combusting Analar-grade ben-

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zoic acid. To determine the heat of combustion, the sample thiocarbonohydrazone was pelletized and weighed, and wrapped with a known amount of surgical cotton to effect complete combustion. Appropriate corrections were applied for the heats of combustion of fuse wire and cotton. The average deviation in the heat of combustion values was on the order of ± 30 cal/g.

The Huffman-Ellis[5] method was adopted to evaluate the heats of combustion of various TCH. No water was taken in the bomb initially and $H_2SO_4 \cdot xH_2O$ was assumed to be the product of combustion, where $x+1$ moles of water were produced during combustion. The standard heats of formation were evaluated assuming idealized combustion and taking into account the heat of formation of $H_2SO_4 \cdot xH_2O$ actually formed.[5] A sample calculation of the standard heat of formation of formaldehydethiocarbonohydrazone ($C_2H_6N_4S$) is given in Table 1. The heat of combustion and formation of various TCH are given in Table 2.

Performance Calculation

The performance parameters were calculated using input data such as heat of formation of the fuel and oxidizer, composition of the propellant, chamber pressure and temperature, etc., on a DEC system 1090 computer, making use of the NASA-SP273 program. The chamber pressure Pc in hybrid rockets being of the order of 25-40 atm, was fixed at 30 atm in the present study. The parameters were evaluated by both equilibrium flow and frozen flow conditions at various oxidizer/fuel (O/F) ratios and exit pressures. However, for realistic considerations of hybrid systems, the parameters are reported at exit pressure $P=0.5$ atm, i.e., at expansion ratio Pc/P equal to 60 assuming equilibrium flow conditions.

Results and Discussion

The heat of formation data presented in Table 2 show that many of the TCH reported herein are endothermic or weakly exothermic compounds. This is significant from an energy point of view. However, it may, be pointed out that measurement of heats of combustion of compounds containing sulfur involves several difficulties. Although rotating bomb-calorimeters have been recommended for very high precision work, the Huffman-Ellis[5] method using static bomb-calorimeters has been reported[6] to yield moderately accurate values when used in carefully planned comparative measurements. Perhaps this method is appropriate for the present study, since, in evaluating the heats of formation, only heat of dilution of H_2SO_4 by the theoretically formed water is taken into ac-

Table 1 Sample calculation of the standard heat of formation

Molecular weight	118.16
Sample weight	0.3127 g
Total calories to calorimeter	1808 cal
Total correction	384.7 cal
Molar heat of combustion at contant volume (ΔE_c)	537.82 kcal
Mean value	537.04 kcal
Idealized combustion equation	

$$C_2H_6N_4S_{(s)} + 5O_{2(g)} \rightarrow 2CO_{2(g)} + 2N_{2(g)} + H_2SO_4 \cdot 2H_2O_{(l)}$$
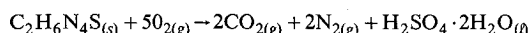
Molar heat of combustion at constant pressure (ΔH_c)	537.63 kcal
Standard heat of formation at constant volume (ΔE_f)	

$$[2\Delta E_f(CO_2) + 3\Delta E_f(H_2O) + \Delta E_f(H_2SO_4 \cdot 2H_2O)] - \Delta E_c$$

$$+11.55 \text{ kcal/mole}$$

Similarly,

Standard heat of formation at constant pressure (ΔH_f)	$+8.57$ kcal/mole

Table 2 Heat of combustion and formation of thiocarbonohydrazones, kcal/mole

No.	Thiocarbonohydrazone	$-\Delta E_C$	$-\Delta H_C$	ΔE_f	ΔH_f
1	Benzaldehyde $C_6H_5CH:NNHC:SNHNH_2$	1238.0	1239.2	+10.6	+6.5
2	p-Dimethylaminobenzaldehyde $p\text{-}(CH_3)_2NC_6H_4CH:NNHC:SNHNH_2$	1622.5	1624.1	+37.0	+31.0
3	2-Formaldehyde $C_4H_3OCH:NNHC:SNHNH_2$	963.4	964.0	−7.6	−11.3
4	Formaldehyde $CH_2NHNHC:SNHNH$	537.0	537.6	+11.6	+8.6
5	Acetone $(CH_3)_2CNHNHC:SNHNN$	855.2	856.4	+4.0	−0.2
6	Cyclohexanone $(CH_2)_5CNHNHC:SNHNH$	1234.9	1236.7	−34.5	−39.8
7	Bis-Acetone $(CH_3)_2C:NNHC:SNHN:C(CH_3)_2$	1266.8	1268.6	−3.6	−7.9

Table 3 Theoretical performance parameters of various thiocarbonohydrazones-HNO_3 systems

Parameter	Fuel No.[a]						
	1	2	3	4	5	6	7
Optimum oxidizer/fuel ratio	2.8	2.8	2.5	1.9	2.5	3.1	2.8
Specific impulse, I_{sp},s	245.5	250.3	240.9	238.9	246.7	246.3	249.0
Vacuum specific impulse, I_{vac},s	267.9	272.7	262.3	260.3	269.0	269.2	271.0
Combustion chamber temperature, T, K	3061.0	3081.0	3012.0	2945.0	3002.0	2985.0	3040.0
Mean molecular weight, M, g/mole	28.53	27.41	28.80	28.50	27.52	27.69	27.03
Characteristic velocity, C^*, m/s	1490.0	1526.0	1469.0	1458.0	1500.0	1493.0	1523.0

[a]Fuel numbers as reported in Table 2.
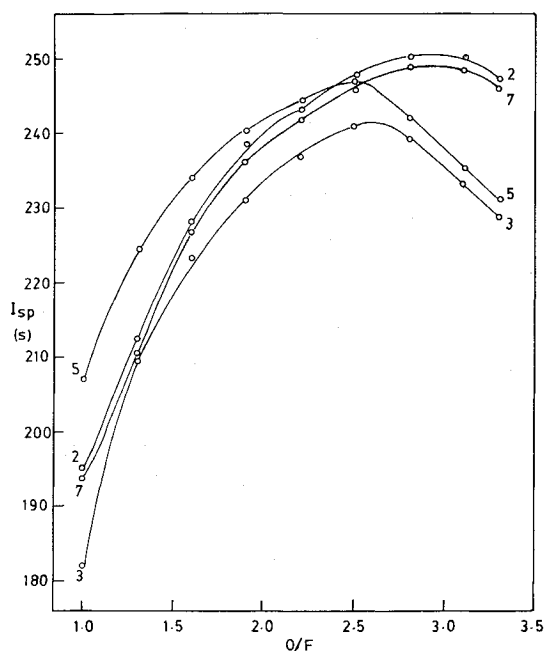
Fig. 1 Variation of specific impulse with mixture ratio of HNO_3,-TCH systems (see Table 2).
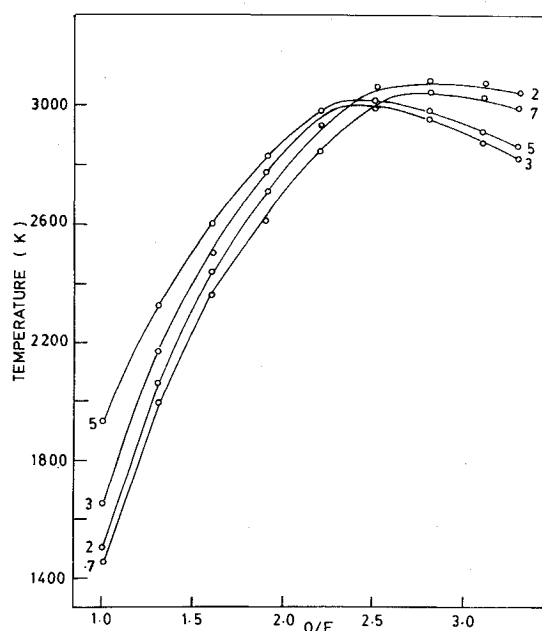
Fig. 2 Variation of chamber temperature with mixture ratio of HNO_3-TCH systems (see Table 2).

count. The adequacy of the method is further apparent by the closeness of the experimental and calculated values of heats of combustion using HNO_3 at the oxidizer,[7] wherein the heats of formation data derived by this method were used.

The important parameters of the various TCH-HNO_3 propellant systems are present in Table 3. The values reported are obtained at optimum O/F ratio, assuming equilibrium flow conditions. The plots of specific impulse (I_{sp}) against the O/F ratio presented in Fig. 1 show that I_{sp} increases rapidly with O/F ratio and then begins to decrease passing through a maxi-

mum which lies on the fuel-rich side of the stoichiometric ratio. The optimum I_{sp} obtained is in the range of 240-250 s, without using any metallic ingredients. These values may be compared with those obtained in the often-used hypergolic biliquid system, such as unsymmetrical dimethylhydrazine (UDMH)-HNO_3 (272.4 s),[8] a hybrid system R005-RFNA (250 s), or a nonhypergolic hybrid, rubber-RFNA (260 s) system.[9] These values of specific impulse are, however, reported at $Pc/P=68.05$, i.e. for expansion from 68.05 to 1 atm.

Another promising feature of these systems is evident by their flame temperatures. The nature of the plots of chamber temperature with O/F ratio, presented in Fig. 2, is closely similar to that of the specific impulse plots. The flame temperatures calculated at chamber pressure, 30 atm, are quite high, being on the order of 3000 K and comparable to those obtained with potential systems such as UDMH-HNO$_3$.[8]

As expected, the performance parameters of the various TCH-HNO$_3$ systems are of the same order. However, a close inspection of the data reveals that the p-dimethylaminobenzaldehyde derivative-HNO$_3$ system yields the highest I_{sp} and flame temperature among the various systems based upon mono-TCH. The reason for this could be the relatively low average molecular weight of its combustion products. Having the highest formula weight, it has the lowest percentage of sulphur, consequently, it will produce the lowest amount of sulfur-containing products; thereby reducing the average molecular weight. A similar conclusion may be drawn by comparing the performance parameters of the mono- and bis-acetone thiocarbonohydrazones-HNO$_3$ systems. The apparently superior parameters of the bis-derivative-HNO$_3$ system could be attributed to the relatively smaller percentage of sulfur that the bis-derivative has, as compared to the monoanalog.

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Combustion Related to Solid-Fuel Ramjets

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Introduction

AS the second stage of a medium- or long-range missile, the solid-fuel ramjet (SFRJ) is a viable alternative to a rocket. The combustion process in a SFRJ is similar to that in hybrid

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rockets, with the exception that the freestream contains a relatively low oxidizer in the SFRJ. Bartel and Rannie[1] introduced the concept of SFRJ and modeled the combustion process both experimentally and theoretically. The regression rate data on tubular carbon block in a turbulent airstream exhibited the familiar dependence on the mass flux G as $G^{0.8}$. Boaz and Netzer[2] carried out experimental investigations in a range of chamber pressure p with PMMA as the fuel. They obtained the regression rate law as, $\dot{r} = cp^{0.51}G^{0.41}T^{0.34}$. Schadow et al.[3] obtained radial and axial profiles of the temperature and species concentration in this setup. The airstream was heated to 550 K to simulate the actual condition in a ramjet. The experimental results of Schadow et al.[3] were reproduced by the theoretical model of Netzer.[4,5] Mady el al.[6] investigated the effect of port flow rate and bypass flow rates on the combustion mechanism and efficiency. When the airflow was totally through the fuel port, the regression rate could be expressed in the form, $\dot{r} = 0.0043p^{0.29}G^{0.38}$; but when part of the airflow was bypassed, the expression changed to $\dot{r} = 0.0016 p^{0.42}G^{0.003}$. The heat-transfer mechanism has been argued to be convection dominated in the former case, but radiation dominated in the latter. Subsequent work by Hewett and Netzer[7] showed that the expression obtained for the case with bypass airflow could have been in error.

The convective theory of boundary-layer combustion of Marxman et al.[8] yields a burning rate expression of the type $\dot{r} = a_0 G^n p^m B^{0.23}$. The index n would be 0.8 for turbulent flow and 0.5 for laminar flow in the port of the fuel grain. Although most of the hybrid rocket results are indeed correlated in the form of $G^{0.8}$, it has been contended that it could as well be 0.5. The results on the SFRJ indicate values closer to 0.5 than to 0.8. The pressure sensitivity of the regression rate is weak as given by the theory and arises through chemical kinetics and radiation effects. But, experiments using SFRJ seem to indicate a stronger dependence. The present work is aimed at enriching the experimental data in this area and examining these aspects of the SFRJ.

Experimental

The setup used for the present experiments is shown schematically in Fig. 1. The airflow from the blower is taken through a control valve, a "flow straightner," and a calibrated venturimeter to the combustion chamber containing the tubular fuel blocks. Preliminary experiments showed that a diaphragm at the inlet with a resulting recirculation zone is essential for stabilizing the flame. In the present work, the weight loss method is adopted to derive the fuel regression data. A number of blocks with the same initial diameter (40 mm i.d.) are burned through different burn times and the corresponding weight losses are measured. The ignition was through a solid propellant piece glued on the inner surface of the fuel blocks. Quenching was effected by purging with nitrogen.

Initial attempts with blocks of pure fuel-like rubber and polyester were in vain since both ignition and sustanance of
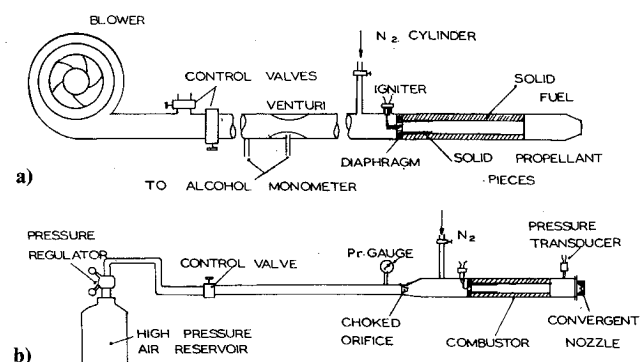

Fig. 1   Experimental setup: a) low pressure; b) high pressure.