Technical Notes

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Enthalpies of Combustion of Ramjet Fuels

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Nomenclature

c_p = specific heat capacity, $\mathrm{cal}_{th}\ \mathrm{g}^{-1}$
cal_{th} = thermochemical calories = 4.184 absolute joules
E = internal energy
ΔE_c° = standard molar energy of idealized combustion reaction, $\mathrm{kcal\ mol}^{-1}$
$\Delta E_c^\circ/M$ = standard energy of idealized combustion reaction, $\mathrm{cal}_{th}\mathrm{g}^{-1}$
H = enthalpy
ΔH_c° = standard molar enthalpy of combustion, $\mathrm{kcal\ mol}^{-1}$
ΔH_f° = standard molar enthalpy of formation, $\mathrm{kcal\ mol}^{-1}$
P = pressure, atm
T = temperature, K
t = temperature, °C
∂ = differential operator
ρ = density, $\mathrm{g\ cm}^{3}$

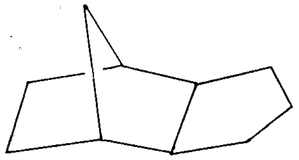
Introduction

IN cooperation with the Air Force Office of Scientific Research, this laboratory has studied compounds with high enthalpies of combustion per unit mass[1,2] and per unit volume.[3,4] This report gives the details of experimental measurements of the enthalpies of combustion of four hydrocarbon liquids being evaluated as ramjet fuels; the four liquids have high enthalpies of combustion per unit volume.

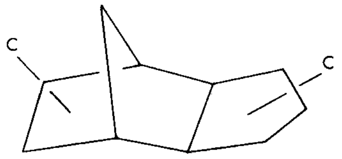
Materials

All four fuels studied are liquids. Carbon skeletons of three parent molecules are shown in Fig. 1. RJ-4 is a mixture of the *exo-* and *endo-* isomers of tetrahydrodi(methylcyclopentadiene), and RJ-4-I is the *exo-* form alone. Both the *exo-* and *endo-* forms have two methyl groups per molecule. The location of the methyl groups is uncertain, and several different dimethyl isomers are known to exist in both the *exo-* and *endo-* forms. JP-9 is a blend of 10.3 wt.% methylcyclohexane, 68.4 wt.% of *exo*-THDC, and 21.2 wt.% of the hydrogenated dimers of norbornadiene whose empirical formula is $C_{14}H_{18}$. Carbon skeletons of typical isomers are shown in Fig. 2. The empirical formula for the blend is $C_{10.529}H_{16.202}$. *exo*-THDC, RJ-4, and RJ-4-I were provided by G.W. Burdette, Development Dept., Naval Weapons Center, China Lake, Calif. The JP-9 sample was obtained from J. McCoy, Fuels Branch, Fuels and Lubrication Division, Air Force Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio; it is from Sun Oil Co. Batch 24. All materials were used as received.

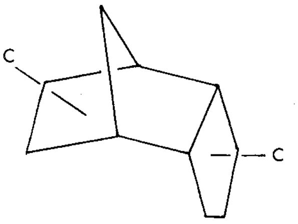
Carbon dioxide was recovered from the combustion products of typical calorimetric experiments with all four fuels. Quantitative carbon dioxide recovery is a good indication that combustion was complete, that the sample was dry, and that sample combustion was understood. A summary of carbon dioxide recovery is given in Table 1. The value for JP-9 is noticeably lower than the recoveries from the other three fuels, perhaps because the empirical formula of the blend is not exactly known.



exo-Tetrahydrodicyclopentadiene $(C_{10}H_{16})$

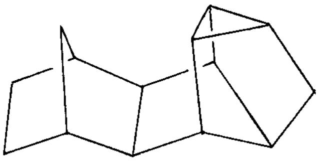


exo-Tetrahydrodi(methylcyclopentadiene) $(C_{12}H_{20})$



endo-Tetrahydrodi(methylcyclopentadiene) $(C_{12}H_{20})$

Fig. 1 Carbon skeletons of hydrocarbon fuels.



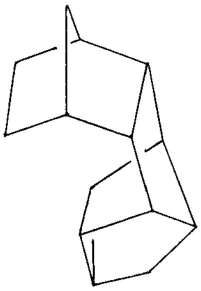


Fig. 2 Carbon skeletons of typical isomers of hydrogenated dimer of norbornadiene.

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National Bureau of Standards benzoic acid sample 39i was used for calibration. Its certified energy of combustion, $-(26434 \pm 3)$ J g^{-1}, was converted to standard conditions[5] giving $-(6313.02 \pm 0.72)$ cal g^{-1} for $\Delta E_c^\circ/M$, the specific energy of the idealized combustion reaction. Previous combustion experiments on the auxiliary oil, laboratory designation TKL 66, gave a value for $\Delta E_c^\circ/M$ of $-(11004.41 \pm 0.42)$ cal g^{-1}. For the cotton thread fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta E_c^\circ/M = -4050$ cal g^{-1}.

Apparatus and Procedure

Experimental procedures used for the combustion calorimetry of hydrocarbons by this laboratory have been described.[6,7] Rotating-bomb calorimeter BMR II[8] and platinum-lined bomb Pt-3b,[9] internal volume 0.349_4 dm^3, were used without bomb rotation. For each experiment, 1 cm^3 of water was added to the bomb, and the bomb was flushed and charged to 30 atm (3040 kPa) with pure oxygen. Because the oxygen was pure, nitric acid formation was negligible. Each experiment was started at 296.15 K, and the final temperatures were very nearly 298.15 K. Fragile flexible ampoules[6,10] of borosilicate glass confined the liquid samples. In filling ampoules with JP-9, the apparatus was charged with enough methylcyclohexane to provide its saturation vapor pressure before introducing the sample in order to minimize the evaporation of that component from the fuel.

Units of Measurement and Auxiliary Quantities

The results are based on the 1961 atomic weights[11] and the 1963 definition of the thermochemical calorie (cal = 4.184 J).[12] The reference temperature is 298.15 K (25°C). For reducing weights in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,[5] the values in Table 2 were used for density ρ, specific heat capacity c_p, and $(\partial E/\partial P)_T$. The values of density were obtained from the mass of material contained by ampoules of known volume. Values of c_p were from differential scanning calorimetry. Values of $(\partial E/\partial P)_T$ are estimates.

Table 1 Carbon dioxide recovery

Fuel	No. of Experiments	Percent recovery[a]
exo-THDC	6	99.99_1
RJ-4	6	99.98_3
RJ-4-I	3	99.96_2
JP-9	4	99.63_0

[a] Mean value.

Table 2 Physical properties at 298.15 K[a] (cal_{th} = 4.184 J; atm = 101.325 kPa)

Fuel	ρ, g cm^{-3}	$(\partial E/\partial P)_T$, cal_{th} atm^{-1} g^{-1}	c_p, cal_{th} K^{-1} g^{-1}
exo-THDC	0.939	(−0.003)	0.415
RJ-4	0.920	(−0.003)	0.441
RJ-4-I	0.917	(−0.003)	0.441
JP-9	0.946	(−0.003)	0.393

[a] Values in parentheses are estimates.

Calibration

One set of calibration experiments wth benzoic acid was run concurrently with the series of experiments with *exo*-THDC and RJ-4. The calibration result was ϵ(calor) $= (4008.11 \pm 0.20)$ cal_{th} K^{-1} (mean and standard deviation of the mean). A second set of calibration experiments was run concurrently with the series of experiments with RJ-4-I and JP-9. The calibration result was ϵ(calor) $= (4007.02 \pm 0.26)$ cal_{th} K^{-1} (mean and standard deviation of the mean).

Calorimetric Results

Results of typical experiments with the four fuels are summarized in Table 3. Values of $\Delta E_c^\circ/M$, the specific energy of the idealized combustion reaction, for all experiments are given in Table 4; all values refer to the reaction of unit mass of sample. The idealized combustion and formation reactions for *exo*-THDC are represented by Eqs. (1) and (2), respectively:

$$C_{10}H_{16}(l) + 14O_2(g) = 10CO_2(g) + 8H_2O(l) \tag{1}$$

$$10C(c,graphite) + 8H_2(g) = C_{10}H_{16}(l) \tag{2}$$

The idealized combustion and formation reactions for RJ-4 and RJ-4-I are represented by Eqs. (3) and (4), respectively:

$$C_{12}H_{20}(l) + 17O_2(g) = 12CO_2(g) + 10H_2O(l) \tag{3}$$

$$12C(c,graphite) + 10H_2(g) = C_{12}H_{20}(l) \tag{4}$$

The reader should be reminded that RJ-4 and RJ-4-I are mixtures of isomers. The idealized combustion reaction for JP-9 is represented by Eq. (5):

$$C_{10.529}H_{16.202}(l) + 14.579O_2(g) = 10.529CO_2(g) + 8.101H_2O(l) \tag{5}$$

Derived Results

Derived values of the standard molar energy of the idealized combustion reaction, ΔE_c°, the standard molar enthalpy of combustion, ΔH_c°, and the standard molar enthalpy of formation, ΔH_f° (*exo*-THDC, RJ-4, and RJ-4-I only), of the fuels in the liquid state are given in Table 5. Values of ΔE_c° and ΔH_c° refer to Eqs. (1), (3), and (5); the

Table 3 Summary of typical calorimetric experiments at 298.15 K[a] (cal_{th} = 4.184 J)

	exo-THDC	RJ-4	RJ-4-I	JP-9
m'(fuel)/g	0.693077	0.671733	0.661629	0.675054
m''(auxiliary substance)/g	0.056663	0.071059	0.081998	0.073573
m'''(fuse)/g	0.001316	0.001200	0.001250	0.001078
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535
$\Delta T_c/K = (T_f - T_i + \Delta T_{corr})/K$	2.00216	2.00052	2.00235	1.99890
$\epsilon(calor)(-\Delta T_c)/cal_{th}$	−8024.89	−8018.33	−8023.45	−8009.63
$\epsilon(cont)(-\Delta T_c)/cal_{th}$[b]	−10.20	−10.19	−10.19	−10.15
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18
$\Delta E_{(corr\ to\ std\ states)}/cal_{th}$[c]	3.02	2.90	2.91	3.09
$\{-m''(\Delta E_c^\circ/M)(auxiliary\ substance)\}/cal_{th}$	623.54	781.96	902.33	809.63
$\{-m'''(\Delta E_c^\circ/M)(fuse)\}/cal_{th}$	5.33	4.86	5.06	4.36
$\{m'(\Delta E_c^\circ/M)(fuel)\}/cal_{th}$	−7403.02	−7238.62	−7123.16	−7202.52
$\{(\Delta E_c^\circ/M)(fuel)\}/cal_{th}\,g^{-1}$	−10681.37	−10776.04	−10766.10	−10669.55

[a] The symbols and abbreviations of this table are those of Ref. 5 except as noted. [b] $\epsilon^i(cont)(T_i - 298.15\ K) + \epsilon^f(cont)\ (298.15\ K - T_f + \Delta T_{corr})$. [c] Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Ref. 5.

Table 4 Summary of experimental results at 298.15 K ($\mathrm{cal}_{th} = 4.184$ J)

	$(\Delta E_c^\circ/M)/\mathrm{cal}_{th}\ \mathrm{g}^{-1}$			
	exo-THDC	RJ-4	RJ-4-I	JP-9
	−10685.70	−10776.90	−10764.86	−10672.39
	81.04	74.78	64.27	68.70
	79.84	76.04	66.10	69.55
	83.59	76.14	63.12	66.80
	81.37	77.91	62.46	70.40
	−10680.53	−10772.28	−10762.78	−10668.28
Mean	−10682.01	−10775.68	−10763.93	−10669.35
Standard deviation of the mean	0.90	0.80	0.57	0.78

Table 5 Derived molar values for the liquid state at 298.15 K ($\mathrm{cal}_{th} = 4.184$ J)

Fuel	ΔE_c°, $\mathrm{kcal}_{th}\ \mathrm{mol}^{-1}$	ΔH_c°, $\mathrm{kcal}_{th}\ \mathrm{mol}^{-1}$	ΔH_f°, $\mathrm{kcal}_{th}\ \mathrm{mol}^{-1}$
exo-THDC	−1455.31 ± 0.33	−1457.68 ± 0.33	−29.35 ± 0.35
RJ-4	−1770.37 ± 0.37	−1773.33 ± 0.37	−38.43 ± 0.40
RJ-4-I	−1768.44 ± 0.36	−1771.40 ± 0.36	−40.36 ± 0.39
JP-9	−1523.55 ± 0.34	−1525.95 ± 0.34	------------

values of ΔH_f° refer to Eqs. (2) and (4). The uncertainties given in Table 5 are the "uncertainty intervals."[13] The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be -94.051 and -68.315 $\mathrm{kcal}_{th}\ \mathrm{mol}^{-1}$, respectively.[14] Uncertainties assigned to the respective values were 0.011 $\mathrm{kcal}_{th}\ \mathrm{mol}^{-1}$ for CO_2[15] and 0.010 $\mathrm{kcal}_{th}\ \mathrm{mol}^{-1}$ for $H_2O(l)$.[16]

The values of enthalpy of combustion given in Tables 3-5 are the "gross" heats of combustion for which the reaction products are gaseous carbon dioxide and liquid water. For combustion yielding gaseous carbon dioxide and gaseous water, the values of the "net" heat of combustion are: *exo*-THDC, $-(10081.5 \pm 2.3)$ cal g^{-1}; RJ-4, $-(10153.1 \pm 2.3)$ cal g^{-1}; RJ-4-I, $-(10141.7 \pm 2.2)$ cal g^{-1}; and JP-9, $-(10089.5 \pm 2.4)$ cal g^{-1}.

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Artificially Thickening a Smooth-Wall Turbulent Boundary Layer

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Introduction

THE ability to thicken a turbulent boundary layer artificially gives the investigator a way to obtain thick layers in short wind tunnel distances, and thus expand the experimental operating domain of a wind tunnel without the high cost of increasing the length of the test surface. One must prove, however, that the thickened boundary layer has the

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