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The enthalpies of combustion and formation of *n*-propylcyclopentane and five methylethylcyclopentanes†‡

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The enthalpies of combustion of *n*-propylcyclopentane and five isomeric methylethylcyclopentanes were determined by oxygen-bomb combustion calorimetry. The following values, based on the mass of sample, are reported for the standard enthalpy of combustion ΔH°_c/(298.15 K)/kcal mol^{-1} of these compounds in the liquid state: *n*-propylcyclopentane, $-(1253.82 \pm 0.18)$; 1-methyl-1-ethylcyclopentane, $-(1252.62 \pm 0.22)$; 1-methyl-*cis*-2-ethylcyclopentane, $-(1253.32 \pm 0.22)$; 1-methyl-*trans*-2-ethylcyclopentane, $-(1252.30 \pm 0.20)$; 1-methyl-*cis*-3-ethylcyclopentane, $-(1252.47 \pm 0.22)$; and 1-methyl-*trans*-3-ethylcyclopentane, $-(1252.09 \pm 0.20)$. Enthalpies of formation in the liquid state are derived. A comparison of the enthalpies of combustion of the alkyl cyclopentanes and alkyl cyclohexanes is made.

1. Introduction

The Bureau of Mines is studying the thermodynamic properties of selected hydrocarbons under American Petroleum Institute Research Project 62: "Thermodynamics of Hydrocarbons from Petroleum". Through the research in combustion calorimetry, which is part of this project, the Bureau is extending and improving the existing thermochemical data for the hydrocarbons.(1–5) Cyclopentane,(6), methylcyclopentane,(2, 6) ethylcyclopentane,(6) propylcyclopentane,(6) *n*-decylcyclopentane,(7) and five dimethylcyclopentanes(8) have been studied. Enthalpies of combustion of the five methylethylcyclopentanes are presented in this report. *n*-Propylcyclopentane was included so that values resulting from this research could be tied to those previously determined for the cyclopentanes.

2. Experimental

MATERIALS

The six hydrocarbon samples were purified by the American Petroleum Institute Research Project 58B at Carnegie–Mellon University, A. J. Streiff, Director. Sample descriptions given by API Project 58B are listed in table 1.

[†] This investigation was part of American Petroleum Institute Research Project 62, "Thermodynamics of Hydrocarbons from Petroleum," which the Bureau of Mines conducts at Bartlesville, Okla.

[‡] Contribution No. 181 from the thermodynamics laboratory of the Bartlesville Petroleum Research Center.

TABLE 1. Compound description

Compound	Moles per cent of impurity
n-Propylcyclopentane	0.19 ± 0.10
1-Methyl-1-ethylcyclopentane	0.09 ± 0.08
1-Methyl-*cis*-2-ethylcyclopentane	0.057 ± 0.005
1-Methyl-*trans*-2-ethylcyclopentane	0.04 ± 0.02
1-Methyl-*cis*-3-ethylcyclopentane	0.3[a]
1-Methyl-*trans*-3-ethylcyclopentane	1.0[b]

[a] Principal impurity is the *trans* isomer.
[b] Principal impurity is the *cis* isomer.

National Bureau of Standards sample 39i benzoic acid was used for calibration. Its specific energy of combustion is $-(26.434 \pm 0.003)$ kJ g^{-1} under certificate conditions. Conversion to standard conditions(9) gives $-(6313.02 \pm 0.72)$ cal g^{-1} for $\Delta E_c^\circ/M$, the energy of the idealized combustion reaction.

The auxiliary oil, sample designation USBM–P3a, had the empirical formula $CH_{1.894}$. For this material $\Delta E_c^\circ/M = -(10984.3_0 \pm 0.1_5)$ cal g^{-1} (mean and standard deviation). For the cotton thread fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta E_c^\circ/M$ was -4050 cal g^{-1}.

UNITS OF MEASUREMENTS AND AUXILIARY QUANTITIES

The experimental results reported are based on the 1961 atomic weights(10) and the definitions: 0 °C ≙ 273.15 K and 1 cal = 4.184 J.(11)

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,(9) the values in table 2 were used for density ρ, specific heat capacity c_P, and $(\partial E/\partial P)_T$.

TABLE 2. Physical properties at 298.15 K

Compound	ρ / g cm^{-3}	$(\partial E/\partial P)_T$ / cal atm^{-1} g^{-1}	c_P / cal K^{-1} g^{-1}
n-Propylcyclopentane	0.77225	−0.0098	(0.46)
1-Methyl-1-ethylcyclopentane	0.776	(−0.0098)	(0.46)
1-Methyl-*cis*-2-ethylcyclopentane	0.781	(−0.0098)	(0.46)
1-Methyl-*trans*-2-ethylcyclopentane	0.765	(−0.0098)	(0.46)
1-Methyl-*cis*-3-ethylcyclopentane	0.760	(−0.0098)	(0.46)
1-Methyl-*trans*-3-ethylcyclopentane	0.758	(−0.0098)	(0.46)

Values of the density of *n*-propylcyclopentane and of the temperature dependence of density from which $(\partial E/\partial P)_T$ was derived are from reference 1. All other values of density are measurements of this laboratory. All other values of $(\partial E/\partial P)_T$ and heat capacity are estimates (in parentheses).

CALIBRATION

A set of calibration experiments with benzoic acid was interspersed within the series with the hydrocarbons. The result of the eight experiments was $\varepsilon(\text{calor}) = (4004.80 \pm 0.14)$ cal K^{-1} (mean and standard deviation).

APPARATUS AND PROCEDURES

Experimental procedures used for the combustion calorimetry of hydrocarbons were recently described.(2, 3) Rotating-bomb calorimeter BMR II(12) and platinum-lined bomb Pt–3b,(13) internal volume 0.349_4 dm^3, were used. Rotation of the bomb was not necessary. For every experiment 1 cm^3 of water was added to the bomb, and it was flushed and charged to 30 atm† with pure oxygen. Because of the purity of the oxygen used in the experiments, the formation of nitric acid was negligible. Each experiment was started at 23 °C, and because the masses of combustibles were properly chosen, the final temperatures were very nearly 25 °C. Fragile flexible ampoules(2, 14) of borosilicate glass confined the volatile liquid samples.

CARBON DIOXIDE RECOVERY

Carbon dioxide was recovered from the combustion products of all experiments. The carbon dioxide recoveries are summarized in table 3. Anhydrous lithium hydroxide was used as the absorbent.(2) The combustion products were checked for carbon monoxide and other products of incomplete combustion, but none were detected.

TABLE 3. Carbon dioxide recovery

Compound	Per cent recovery[a]
Benzoic acid	100.009 ± 0.002
n-Propylcyclopentane	100.011 ± 0.004
1-Methyl-1-ethylcyclopentane	100.006 ± 0.004
1-Methyl-*cis*-2-ethylcyclopentane	100.006 ± 0.002
1-Methyl-*trans*-2-ethylcyclopentane	100.011 ± 0.004
1-Methyl-*cis*-3-ethylcyclopentane	100.013 ± 0.004
1-Methyl-*trans*-3-ethylcyclopentane	99.998 ± 0.003

[a] Standard deviation from the mean based on eight experiments with each compound.

3. Results

CALORIMETRIC RESULTS

Results of typical combustion experiments for each compound are listed in table 4. It is impractical to list summaries for all experiments, but values of $\Delta E_c^\circ/M$, the energy of the idealized combustion reaction, for all experiments are given in table 5. All values of $\Delta E_c^\circ/M$ in tables 4 and 5 refer to the reaction of one gram of sample.

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† atm = 101 325 N m^{-2}.

TABLE 4. Summary of typical calorimetric experiments at 298.15 K[a]

	n-Propyl-cyclopentane	1-Methyl-1-ethyl-cyclopentane	1-Methyl-*cis*-2-ethyl-cyclopentane	1-Methyl-*trans*-2-ethyl-cyclopentane	1-Methyl-*cis*-3-ethyl-cyclopentane	1-Methyl-*trans*-3-ethyl-cyclopentane
m'(compound)/g	0.667 222	0.660 638	0.665 305	0.662 905	0.641 557	0.648 719
m''(oil)/g	0.052 220	0.060 516	0.054 969	0.057 182	0.079 944	0.072 646
m'''(fuse)/g	0.001 293	0.001 374	0.001 361	0.001 386	0.001 102	0.001 333
$n^{\mathrm{i}}(\mathrm{H_2O})$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{\mathrm{corr}})/\mathrm{K}$	2.00071	2.00344	2.00198	2.00021	2.00312	2.00263
ε(calor)$(-\Delta t_c)$/cal	−8012.41	−8023.33	−8017.47	−8010.39	−8022.03	−8020.10
ε(cont)$(-\Delta t_c)$/cal[b]	−10.31	−10.33	−10.33	−10.31	−10.34	−10.32
ΔE_{ign}/cal	0.59	0.61	0.45	0.61	0.49	0.53
$\Delta E_{\mathrm{dec}}(\mathrm{HNO_3})$/cal	0.00	0.00	0.00	0.00	0.00	0.00
ΔE(corr to std. states)/cal[c]	2.28	2.29	2.28	2.28	2.29	2.29
$-m''\Delta E_c^\circ/M$(oil)/cal	573.60	664.73	603.80	628.10	878.13	797.96
$-m'''\Delta E_c^\circ/M$(fuse)/cal	5.24	5.56	5.51	5.61	4.46	5.40
$m'\Delta E_c^\circ/M$(compound)/cal	−7441.01	−7360.47	−7415.76	−7384.10	−7147.00	−7224.24
$\Delta E_c^\circ/M$(compound)/cal g^{-1}	−11152.23	−11141.46	−11146.41	−11139.00	−11140.09	−11136.16

[a] The symbols and abbreviations of this table are those of reference 9 except as noted.

[b] $\varepsilon^{\mathrm{i}}(\mathrm{cont})(t_i - 25\ {}^\circ\mathrm{C}) + \varepsilon^{\mathrm{f}}(\mathrm{cont})(25\ {}^\circ\mathrm{C} - t_f + \Delta t_{\mathrm{corr}})$.

[c] Items 81 to 85, 87 to 90, 93, and 94 of the computation form of reference 9.

TABLE 5. Summary of experimental results. Values of $(\Delta E_c^\circ/M)/\mathrm{cal\ g^{-1}}$ at 298.15 K

	n-Propyl-cyclopentane	1-Methyl-1-ethyl-cyclopentane	1-Methyl-*cis*-2-ethyl-cyclopentane	1-Methyl-*trans*-2-ethyl-cyclopentane	1-Methyl-*cis*-3-ethyl-cyclopentane	1-Methyl-*trans*-3-ethyl-cyclopentane
	−11152.23	−11142.11	−11149.20	−11139.00	−11142.16	−11137.71
	−11151.28	−11141.66	−11149.23	−11140.17	−11141.27	−11136.57
	−11152.69	−11142.08	−11149.85	−11137.92	−11140.32	−11136.77
	−11152.16	−11144.71	−11147.52	−11140.46	−11142.25	−11134.85
	−11151.01	−11139.40	−11145.27	−11136.93	−11139.08	−11136.94
	−11151.23	−11140.83	−11146.62	−11136.32	−11138.57	−11135.64
	−11153.50	−11138.95	−11147.06	−11139.63	−11140.09	−11138.55
	−11152.45	−11141.46	−11146.41	−11137.89	−11136.98	−11136.16
Mean:	−11152.07	−11141.40	−11147.65	−11138.54	−11140.09	−11136.65
Standard deviation:	0.30	0.63	0.57	0.54	0.59	0.41

TABLE 6. Derived molar values at 298.15 K

	ΔE_c°(l)/kcal mol^{-1}	ΔH_c°(l)/kcal mol^{-1}	ΔH_f°(l)/kcal mol^{-1}
n-Propylcyclopentane	−1251.45 ± 0.18	−1253.82 ± 0.18	−45.11 ± 0.22
1-Methyl-1-ethylcyclopentane	−1250.25 ± 0.22	−1252.62 ± 0.22	−46.31 ± 0.24
1-Methyl-*cis*-2-ethylcyclopentane	−1250.95 ± 0.22	−1253.32 ± 0.22	−45.61 ± 0.24
1-Methyl-*trans*-2-ethylcyclopentane	−1249.93 ± 0.20	−1252.30 ± 0.20	−46.63 ± 0.24
1-Methyl-*cis*-3-ethylcyclopentane	−1250.10 ± 0.22	−1252.47 ± 0.22	−46.46 ± 0.24
1-Methyl-*trans*-3-ethylcyclopentane	−1249.72 ± 0.20	−1252.09 ± 0.20	−46.84 ± 0.22

Equation (1) represents the combustion reaction:

$$C_8H_{16}(l) + 12O_2(g) = 8CO_2(g) + 8H_2O(l). \qquad (1)$$

Derived values of the molar energy of the idealized combustion reaction ΔE_c°, the standard enthalpy of combustion ΔH_c°, and the standard enthalpy of formation ΔH_f°, of the liquid hydrocarbons are given in table 6. The values of ΔE_c° and ΔH_c° refer to equation (1). The values of ΔH_f° refer to equation (2):

$$8C(c, \text{graphite}) + 8H_2(g) = C_8H_{16}(l). \qquad (2)$$

The uncertainties given in table 6 are the "uncertainty interval".(15) The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be −94.051 and −68.315 kcal mol^{-1}, respectively.(16) Uncertainties assigned to gaseous carbon dioxide(17) and liquid water (18) were 0.011 and 0.010 kcal mol^{-1}, respectively.

4. Discussion

n-Propylcyclopentane was the only compound that had been studied previously. Johnson *et al.* found that ΔH_c°(25 °C) = −(1253.74 ± 0.28) kcal mol^{-1}. Agreement with the result of this research, −(1253.82 ± 0.18) kcal mol^{-1}, is well within the combined uncertainties of the two measurements.

TABLE 7. Comparison of similar cyclohexanes and cyclopentanes

Substituent group(s)	ΔH_c°(298.15, l)/kcal mol^{-1}		Methylene increment/kcal mol^{-1}
	-Cyclohexane (A)	-Cyclopentane (B)	(A) − (B)
n-Propyl-	1404.54 ± 0.22[a]	1253.82 ± 0.18[b]	150.72 ± 0.28
Ethyl-	1248.23 ± 0.35[c]	1097.50 ± 0.22[e]	150.73 ± 0.41
1-Methyl-1-ethyl-	1403.89 ± 0.22[a]	1252.62 ± 0.22[b]	151.27 ± 0.31
1, 1-Dimethyl-	1246.55 ± 0.45[d]	1095.44 ± 0.25[e]	151.21 ± 0.51
1-Methyl-*cis*-2-ethyl-	1404.84 ± 0.22[a]	1253.32 ± 0.22[b]	151.52 ± 0.31
1, *cis*-2-Dimethyl-	1248.31 ± 0.43[d]	1097.06 ± 0.30[e]	151.25 ± 0.52
1-Methyl-*trans*-2-ethyl-	1403.87 ± 0.20[a]	1252.30 ± 0.20[b]	151.57 ± 0.28
1, *trans*-2-Dimethyl-	1246.77 ± 0.44[d]	1095.64 ± 0.27[e]	151.13 ± 0.52
1-Methyl-*cis*-3-ethyl-	1402.33 ± 0.26[a]	1252.47 ± 0.22[b]	149.86 ± 0.34
1, *cis*-3-Dimethyl-	1245.66 ± 0.41[d]	1096.39 ± 0.33[e]	149.27 ± 0.53

[a] From reference 5.
[b] This research.
[c] From reference 6.
[d] From reference 20.
[e] From reference 8.

Correlation methods for the enthalpies of combustion of the cyclic liquid hydrocarbons are not completely developed, and the one somewhat successful method(19) applies only to compounds with completely staggered carbon skeletons. However, a suggestive correlation is shown in table 7 between the enthalpies of combustion of the C_3-cyclopentanes of this research, the C_3-cyclohexanes,(5) the C_2-cyclopentanes,(6,8) and the C_2-cyclohexanes.(6,20) The constancy of the methylene increment is well within experimental uncertainty.

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