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The enthalpies of combustion and formation of *n*-propylcyclohexane and six methylethylcyclohexanes†

W. D. GOOD

Bartlesville Petroleum Research Center, Bureau of Mines,
U.S. Department of the Interior, Bartlesville, Oklahoma, U.S.A.

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The enthalpies of combustion of *n*-propylcyclohexane and six isomeric methylethylcyclohexanes were determined by oxygen-bomb combustion calorimetry. The following values are reported for the standard enthalpy of combustion, $\Delta H_c^\circ(298.15\ \mathrm{K})/\mathrm{kcal\ mol^{-1}}$, of these compounds in the liquid state: *n*-propylcyclohexane, (−1404.54±0.22); 1-methyl-1-ethylcyclohexane, (−1403.89±0.22); 1-methyl-*cis*-2-ethylcyclohexane, (−1404.84±0.22); 1-methyl-*trans*-2-ethylcyclohexane, (−1403.87±0.20); 1-methyl-*cis*-3-ethylcyclohexane, (−1402.33±0.26); 1-methyl-*cis*-4-ethylcyclohexane, (−1404.18±0.24); and 1-methyl-*trans*-4-ethylcyclohexane, (−1402.39±0.20). Enthalpies of formation in the liquid state were derived and compared with those predicted by the Allen correlation procedure.

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) that were largely produced by Johnson, Prosen, Rossini, and co-workers of the National Bureau of Standards. Cyclohexane,(2,3) methylcyclohexane,(3) ethylcyclohexane,(3) *n*-propylcyclohexane,(3) *n*-butylcyclohexane,(3) *n*-decylcyclohexane,(4) and seven dimethylcyclohexanes(5) have been studied by these workers. Enthalpies of combustion for six additional cyclohexanes, all with methylethyl substitution, are presented in this report. *n*-Propylcyclohexane was included so that values resulting from this research could be tied to those previously determined for the cyclohexanes.

2. Experimental

MATERIALS

The seven 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.

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TABLE 1. Compound description

Compound	Impurity, moles per cent
n-Propylcyclohexane	0.06±0.05 [a]
1-Methyl-1-ethylcyclohexane	(0.15±0.10) [b]
1-Methyl-*cis*-2-ethylcyclohexane	(0.15±0.10) [b]
1-Methyl-*trans*-2-ethylcyclohexane	(0.15±0.10) [b]
1-Methyl-*cis*-3-ethylcyclohexane	0.01±0.01 [c]
1-Methyl-*cis*-4-ethylcyclohexane	0.005±0.005 [c]
1-Methyl-*trans*-4-ethylcyclohexane	0.018±0.004 [d]

[a] Evaluated from time-temperature freezing behavior.

[b] These materials were not successfully crystallized. Purity estimated by analogy with isomers subjected to similar synthesis and purification.

[c] Evaluated from gas–liquid chromatographic measurements.

[d] Evaluated from calorimetric study of melting temperature as a function of fraction melted.

National Bureau of Standards sample 39i, benzoic acid, was used for calibration. Its energy of combustion is (-26.434 ± 0.003) kJ g^{-1} under certificate conditions. Conversion to standard conditions(6) gives (-6313.02 ± 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 $CH_{1.894}$. $\Delta E_c^\circ/M$ for this material was $(-10984.3_0 \pm 0.1_5)$ 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

All results reported are based on the 1961 International Atomic Weights(7) and fundamental constants(8) and the definitions: 0 °C≙273.15 K and 1 cal = 4.184 J. The laboratory standards of mass and electrical resistance were calibrated by the National Bureau of Standards.

For reducing apparent masses in air to masses and converting the energy of the actual bomb process to that of the isothermal process and reducing to standard states,(6) the values of table 2 were used for density ρ, specific heat capacity c_p, and

TABLE 2. Physical properties for correction of results

Compound	$\frac{\rho}{\mathrm{g\,cm^{-3}}}$	$\frac{c_p}{\mathrm{cal\,K^{-1}\,g^{-1}}}$	$\frac{(\partial E/\partial P)_T}{\mathrm{cal\,atm^{-1}\,g^{-1}}}$
n-Propylcyclohexane	0.7897	(0.44)	(−0.0068)
1-Methyl-1-ethylcyclohexane	0.805	(0.44)	(−0.0068)
1-Methyl-*cis*-2-ethylcyclohexane	0.809	(0.44)	(−0.0068)
1-Methyl-*trans*-2-ethylcyclohexane	0.796	(0.44)	(−0.0068)
1-Methyl-*cis*-3-ethylcyclohexane	0.784	(0.44)	(−0.0068)
1-Methyl-*cis*-4-ethylcyclohexane	0.795	(0.44)	(−0.0068)
1-Methyl-*trans*-4-ethylcyclohexane	0.778	(0.44)	(−0.0068)

$(\partial E/\partial P)_T$. The value for density of *n*-propylcyclohexane is from reference 1. Densities of the other compounds were determined by weighing sealed ampoules of known volume. The values of c_p and $(\partial E/\partial P)_T$ are estimates.

CALIBRATION

A set of calibration experiments with benzoic acid was interspersed within the series with the hydrocarbons. The result of the eight experiments was $\varepsilon(\text{calor}) = (4004.61 \pm 0.13)$ cal K^{-1} (mean and standard deviation).

APPARATUS AND PROCEDURES

Experimental procedures used for the combustion calorimetry of hydrocarbons were recently described.(2,9) Rotating-bomb calorimeter BMR II(10) and platinum-lined bomb Pt-3b,(11) 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(2,12) of borosilicate glass confined the volatile liquid samples.

CARBON DIOXIDE RECOVERY

Carbon dioxide was recovered from the combustion products of all experiments. A summary of the carbon dioxide recoveries is given 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 was detected.

TABLE 3. Carbon dioxide recovery

Compound	Per cent recovery [a]
Benzoic acid	100.002±0.004
n-Propylcyclohexane	99.994±0.005
1-Methyl-1-ethylcyclohexane	100.002±0.005
1-Methyl-*cis*-2-ethylcyclohexane	100.000±0.004
1-Methyl-*trans*-2-ethylcyclohexane	99.999±0.003
1-Methyl-*cis*-3-ethylcyclohexane	99.995±0.009
1-Methyl-*cis*-4-ethylcyclohexane	100.001±0.006
1-Methyl-*trans*-4-ethylcyclohexane	100.007±0.002

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

3. Results

CALORIMETRIC RESULTS

Results of typical combustion experiments for each compound are summarized in table 4. It is impractical to list summaries for all experiments, but values of $\Delta E_c^\circ/M$,

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† atm = 101 325 N m^{-2}.

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

	n-Propyl-cyclohexane	1-Methyl-1-ethyl-cyclohexane	1-Methyl-*cis*-2-ethyl-cyclohexane	1-Methyl-*trans*-2-ethyl-cyclohexane	1-Methyl-*cis*-3-ethyl-cyclohexane	1-Methyl-*cis*-4-ethyl-cyclohexane	1-Methyl-*trans*-4-ethyl-cyclohexane
m' (compd)/g	0.697 626	0.688 555	0.710 428	0.682 286	0.675 133	0.690 380	0.673 573
m''(oil)/g	0.024 810	0.033 474	0.039 517	0.040 223	0.047 875	0.033 810	0.050 475
m''' (fuse)/g	0.001 408	0.001 472	0.001 179	0.001 607	0.001 368	0.001 218	0.001 306
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr.}/K$	2.00170	2.00013	2.07797	2.00097	1.99983	2.00576	2.00281
ε(calor)$(-\Delta t_c)$/cal	−8016.02	−8009.76	−8321.48	−8013.12	−8008.54	−8032.29	−8020.47
ε(cont)$(-\Delta t_c)$/cal [b]	−10.15	−10.14	−10.70	−10.29	−10.15	−10.32	−10.30
ΔE_{ign}/cal	0.51	0.55	0.73	0.31	0.53	0.61	0.45
$\Delta E_{dec}(HNO_3)$/cal	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\Delta E_{(\text{corr. to std. states})}$/cal [c]	2.35	2.35	2.46	2.36	2.36	2.36	2.36
$-m''\Delta E_c^\circ/M$ (oil)/cal	272.52	367.69	434.07	441.82	525.87	371.38	554.43
$-m'''\Delta E_c^\circ/M$ (fuse)/cal	5.70	5.96	4.77	6.51	5.54	4.93	5.29
$m'\Delta E^\circ/M$ (compd)/cal	−7745.09	−7643.35	−7890.15	−7572.41	−7484.39	−7663.33	−7468.24
$\Delta E_c^\circ/M$ (compd)/cal g^{-1}	−11102.04	−11100.54	−11106.16	−11098.55	−11085.78	−11100.15	−11087.46

[a] Symbols and abbreviations of Hubbard *et al.*,$^{(6)}$ except as noted.

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

[c] Items 81 to 85, 87 to 89, 93, and 94 of computation form of Hubbard *et al.*$^{(6)}$

TABLE 5. Summary of experimental results

	Values of $(\Delta E_c^\circ/M)$/cal g^{-1} at 298.15 K						
	n-Propyl-cyclohexane	1-Methyl-1-ethyl-cyclohexane	1-Methyl-*cis*-2-ethyl-cyclohexane	1-Methyl-*trans*-2-ethyl-cyclohexane	1-Methyl-*cis*-3-ethyl-cyclohexane	1-Methyl-*cis*-4-ethyl-cyclohexane	1-Methyl-*trans*-4-ethyl-cyclohexane
	−11102.04	−11100.54	−11106.16	−11098.55	−11085.78	−11100.15	−11089.49
	−11104.15	−11100.82	−11107.75	−11098.49	−11088.93	−11099.89	−11087.46
	−11104.78	−11098.26	−11106.40	−11099.79	−11085.63	−11101.96	−11087.57
	−11106.35	−11098.27	−11107.52	−11099.66	−11086.72	−11103.93	−11086.29
	−11104.43	−11099.96	−11109.63	−11098.58	−11086.19	−11103.55	−11087.54
	−11104.55	−11098.15	−11106.93	−11099.57	−11086.00	−11100.34	−11086.11
	−11105.92	−11098.46	−11105.96	−11099.05	−11091.52	−11103.37	−11088.41
	−11103.71	−11100.14	−11104.70	−11100.15	−11085.28	−11099.89	−11087.28
Mean	−11104.48	−11099.31	−11106.87	−11099.22	−11087.00	−11101.62	−11087.51
Std. dev.	0.47	0.40	0.52	0.23	0.76	0.63	0.38

TABLE 6. Molar values (liquid state) at 298.15 K of cyclohexane derivatives

	n-Propyl-cyclohexane	1-Methyl-1-ethyl-cyclohexane	1-Methyl-*cis*-2-ethyl-cyclohexane	1-Methyl-*trans*-2-ethyl-cyclohexane	1-Methyl-*cis*-3-ethyl-cyclohexane	1-Methyl-*cis*-4-ethyl-cyclohexane	1-Methyl-*trans*-4-ethyl-cyclohexane
ΔE_c°/kcal mol^{-1}	−1401.87 ±0.22	−1401.22 ±0.22	−1402.17 ±0.22	−1401.21 ±0.20	−1399.66 ±0.26	−1401.51 ±0.24	−1399.73 ±0.20
ΔH_c°/kcal mol^{-1}	−1404.54 ±0.22	−1403.89 ±0.22	−1404.84 ±0.22	−1403.87 ±0.20	−1402.33 ±0.26	−1404.18 ±0.24	−1402.39 ±0.20
ΔH_f°/kcal mol^{-1}	−56.76 ±0.26	−57.41 ±0.24	−56.46 ±0.26	−57.43 ±0.24	−58.97 ±0.30	−57.12 ±0.28	−58.90 ±0.24

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 a gram of sample as the measure of the amount of reaction. Equation (1) represents the combustion reaction:

$$C_9H_{18}(l)+13.5\,O_2(g) = 9CO_2(g)+9H_2O(l). \qquad (1)$$

Table 6 gives derived molar values of the 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. The molar values of ΔE_c° and ΔH_c° refer to equation (1). The molar values of ΔH_f° refer to equation (2):

$$9C(c,\text{graphite})+9H_2(g) = C_9H_{18}(l). \qquad (2)$$

The uncertainties given in table 6 are the "uncertainty interval."(13) The enthalpies of formation of gaseous CO_2 and liquid water were taken to be −94.051 and −68.315 kcal mol^{-1}, respectively.(14) Uncertainties assigned to gaseous carbon dioxide(15) and liquid water(16) were 0.011 and 0.010 kcal mol^{-1}, respectively.

4. Discussion

COMPARISON WITH PREVIOUS WORK

n-Propylcyclohexane was the only compound studied that had been studied previously. Johnson *et al.*(3) found that $\Delta H_c^\circ(25^\circ\,C) = (-1404.34\pm0.27)$ kcal mol^{-1}. Agreement with the result of this research, (-1404.54 ± 0.22) kcal mol^{-1}, is well within the combined uncertainties of the two measurements.

ALLEN CORRELATION PROCEDURE

The only modern procedure for correlation that has been applied to the liquid cyclohexanes is that of Allen.(17) Values of the enthalpies of formation of the liquid predicted by the Allen method are tabulated alongside the experimental values in table 7. Although values predicted by the Allen method sometimes differ from experimental values by slightly more than estimated uncertainties in the experimental values, agreement is generally quite good.

TABLE 7. Comparison of calculated and experimental enthalpies of formation

	$-\Delta H_f^\circ(l, 298.15\,K)$/kcal mol^{-1} Allen method	This research
n-Propylcyclohexane	56.98	56.76±0.26
1-Methyl-1-ethylcyclohexane	57.00	57.41±0.24
1-Methyl-*cis*-2-ethylcyclohexane	56.97	56.46±0.26
1-Methyl-*trans*-2-ethylcyclohexane	58.00	57.43±0.24
1-Methyl-*cis*-3-ethylcyclohexane	58.56	58.97±0.30
1-Methyl-*cis*-4-ethylcyclohexane	56.97	57.12±0.28
1-Methyl-*trans*-4-ethylcyclohexane	58.56	58.90±0.24

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