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The enthalpies of combustion and formation of indan and seven alkylindans†‡

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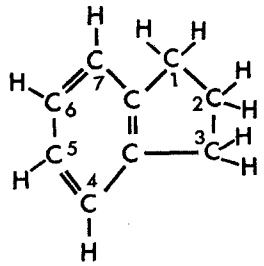
The enthalpies of combustion of indan and seven alkylindans were determined by oxygen-bomb combustion calorimetry. The following values, based on the mass of sample burned, are reported for the standard enthalpy of combustion $\Delta H^\circ_c(298.15\ \mathrm{K})$/kcal mol^{-1} of these compounds in the condensed state: indan(l), $-(1190.84 \pm 0.33)$; 1,1-dimethylindan(l), $-(1499.97 \pm 0.42)$; 4,6-dimethylindan(l), $-(1497.54 \pm 0.36)$; 4,7-dimethylindan(l), $-(1497.07 \pm 0.35)$; 1,1,4,6-tetramethylindan(l), $-(1805.99 \pm 0.65)$; 1,1,4,7-tetramethylindan(l), $-(1807.89 \pm 0.41)$; 1,1,4,6,7-pentamethylindan(c), $-(1958.01 \pm 0.48)$; and 1,1-dimethyl-6-*tert*-butylindan(l), $-(2120.57 \pm 0.58)$. Enthalpies of formation in the condensed state are derived.

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". Recent research in combustion calorimetry, a part of this project, has yielded values of the enthalpies of combustion of some highly branched nonanes,[1] the isomeric pentanes,[2] the methylethylcyclohexanes,[3] and the methylethylcyclopentanes.[4] Present studies are turning to multi-ring hydrocarbons and their alkyl derivatives. Enthalpies of combustion of indan and seven alkylindans are presented in this report.



Indan

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2. Experimental work

MATERIALS

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

TABLE 1. Compound description

Compound	Mole percentage of impurity
Indan	0.02 ± 0.02
1,1-Dimethylindan	0.10 ± 0.10
4,6-Dimethylindan	0.019 ± 0.002
4,7-Dimethylindan	0.014 ± 0.002
1,1,4,6-Tetramethylindan	0.065 ± 0.010
1,1,4,7-Tetramethylindan	0.11 ± 0.02
1,1,4,6,7-Pentamethylindan	0.11 ± 0.02
1,1-Dimethyl-6-*tert*-butylindan	0.047 ± 0.004

National Bureau of Standards sample 39i benzoic acid was used for calibration. Its specific energy of combustion is $-(26.434\pm0.003)$ kJ g^{-1} under certificate conditions. Conversion to standard conditions[5] gives $-(6313.02\pm0.72)$ cal g^{-1} for $\Delta E_c^\circ/M$, the specific energy of the idealized combustion reaction.

The auxiliary oil, sample designation USBM-P3a, had the empirical formula $CH_{1.894}$. For this material $\Delta E_c^\circ/M = -(10984.3_0\pm0.1_5)$ cal g^{-1} (mean and standard deviation). The value of $\Delta E_c^\circ/M$ for the polyester film, empirical formula $C_{10}H_8O_4$, was $-(5473.8_9\pm0.2_8)$ cal g^{-1} (mean and standard deviation) for the dry polyester. 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[6] and the following definitions: 0 °C ≙ 273.15 K and 1 cal = 4.184 J.[7] The laboratory standards of mass and resistance were calibrated by the National Bureau of Standards.

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}
Indan	0.960	(−0.007)	0.385
1,1-Dimethylindan	0.919	(−0.007)	0.408
4,6-Dimethylindan	0.944	(−0.007)	(0.41)
4,7-Dimethylindan	0.950	(−0.007)	(0.41)
1,1,4,6-Tetramethylindan	0.913	(−0.007)	(0.4)
1,1,4,7-Tetramethylindan	0.930	(−0.007)	(0.4)
1,1,4,6,7-Pentamethylindan	1.072	(−0.003)	(0.3)
1,1-Dimethyl-6-*tert*-butylindan	0.900	(−0.007)	(0.4)

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 $(\partial E/\partial p)_T$. Values of density are measurements of this laboratory. The heat capacity of indan was measured by Stull *et al.*,[8] and the heat capacity of 1,1-dimethylindan is an unpublished measurement of the low-temperature calorimetry group of this Laboratory. All other values of c_p and of $(\partial E/\partial p)_T$ are estimates (in parentheses).

CALIBRATION

A set of benzoic acid calibration experiments was interspersed within the series of combustion experiments with the alkyl indans. The result of the ten experiments was $\varepsilon(\text{calor}) = (4006.80 \pm 0.30)$ cal K^{-1} (mean and standard deviation).

APPARATUS AND PROCEDURES

Experimental procedures used for the combustion calorimetry of hydrocarbons were recently described.[1, 4, 9] Rotating-bomb calorimeter BMR II[10] and platinum-lined bomb Pt-3b,[11] internal volume 0.349_4 dm^3, were used. The bomb was not rotated. 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, the amount of HNO_3 formed 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. The seven liquid compounds were dried by means of a liquid phase contact with CaH_2 and confined in flexible ampoules of borosilicate glass.[9, 12] The single solid compound, 1,1,4,6,7-pentamethylindan, was not further dried. Pellets were pressed from this compound and placed inside the platinum crucible beneath a tightly fitting polyester disk.

CARBON DIOXIDE RECOVERY

Carbon dioxide was recovered from the combustion products of all experiments. Anhydrous lithium hydroxide was used as the absorbent.[9] The combustion products were checked for carbon monoxide and other products of incomplete combustion, but none were detected. The carbon dioxide recoveries are summarized in table 3.

TABLE 3. Carbon dioxide recovery

Compound	Per cent recovery [a]
Benzoic acid (10)[b]	100.003 ± 0.004
Indan (8)	99.996 ± 0.004
1,1-Dimethylindan (8)	99.990 ± 0.005
4,6-Dimethylindan (8)	100.001 ± 0.005
4,7-Dimethylindan (8)	99.998 ± 0.004
1,1,4,6-Tetramethylindan (8)	99.992 ± 0.005
1,1,4,7-Tetramethylindan (8)	99.991 ± 0.005
1,1,4,6,7-Pentamethylindan (9)	99.984 ± 0.004
1,1-Dimethyl-6-*tert*-butylindan (8)	99.997 ± 0.005

[a] Mean and standard deviation.
[b] Number of experiments.

† atm = 101 325 N m^{-2}.

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

	Indan	1,1-Dimethyl-indan	4,6-Dimethyl-indan	4,7-Dimethyl-indan	1,1,4,6-Tetra-methylindan	1,1,4,7-Tetra-methylindan	1,1,4,6,7-Penta-methylindan	1,1-Dimethyl--6-*tert*-butylindan
m'(compound)/g	0.725 863	0.683 606	0.717 743	0.692 641	0.699 069	0.692 229	0.765 835	0.647 489
m''(auxiliary)/g	0.065 013 [b]	0.092 617 [b]	0.061 365 [b]	0.085 599 [b]	0.071 809 [b]	0.077 363 [b]	0.011 999 [c]	0.112 932 [b]
m'''(fuse)/g	0.001 102	0.001 073	0.001 654	0.001 049	0.001 116	0.001 415	0.001 691	0.001 151
$n^i(H_2O)$/mol	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35
Δt_c/K $= (t_f - t_i + \Delta t_{corr})$/K	2.000 88	2.001 04	2.000 15	2.001 50	2.001 78	2.001 48	2.000 89	1.999 99
ε(calor)$(-\Delta t_c)$/cal	−8017.13	−8017.77	−8014.20	−8019.61	−8020.73	−8019.53	−8017.17	−8013.56
ε(cont)$(-\Delta t_c)$/cal [d]	−10.20	−10.24	−10.34	−10.25	−10.32	−10.24	−10.04	−10.30
ΔE_{ign}/cal	0.61	0.90	0.65	0.71	0.51	0.73	0.80	0.78
$\Delta E_{(corr\ to\ std\ states)}$/cal [e]	3.77	3.44	3.49	3.46	3.29	3.28	3.44	3.11
$-(m''\Delta E_c^\circ/M)$(auxiliary)/cal	714.13	1017.33	674.05	940.24	788.77	849.78	65.71	1240.48
$-(m'''\Delta E^\circ/M)$(fuse)/cal	4.46	4.34	6.70	4.25	4.52	5.73	6.85	4.66
$(m'\Delta E_c^\circ/M)$(compound)/cal	−7304.36	−7002.00	−7339.65	−7081.20	−7233.96	−7170.25	−7950.41	−6774.83
$(\Delta E_c^\circ/M)$(compound)/cal g^{-1}	−10 062.99	−10 242.73	−10 226.00	−10 223.48	−10 347.99	−10 358.21	−10 381.36	−10 463.23

[a] The symbols and abbreviations of this table are those of reference 5 except as noted.
[b] Paraffin oil.
[c] Polyester.
[d] ε^t(cont)$(t_i - 25\ °C) + \varepsilon^t$(cont)$(25\ °C - t_f + \Delta t_{corr})$.
[e] Items 81 to 85, 87 to 90, 93, and 94 of the computation form of reference 5.

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

	Indan	1,1-Dimethyl-indan	4,6-Dimethyl-indan	4,7-Dimethyl indan	1,1,4,6-Tetra-methylindan	1,1,4,7-Tetra-methylindan	1,1,4,6,7-Penta-methylindan	1,1-Dimethyl-6-*tert*-butylindan
	−10 061.60	−10 240.32	−10 228.42	−10 220.06	−10 344.60	−10 358.41	−10 380.59	−10 460.25
	−10 065.65	−10 242.73	−10 228.10	−10 223.48	−10 352.61	−10 356.33	−10 381.13	−10 466.13
	−10 062.63	−10 242.57	−10 225.44	−10 222.25	−10 348.62	−10 355.64	−10 380.84	−10 463.23
	−10 064.24	−10 245.40	−10 226.00	−10 223.46	−10 344.87	−10 358.21	−10 376.84	−10 462.96
	−10 062.99	−10 248.08	−10 224.97	−10 225.80	−10 342.42	−10 357.29	−10 383.97	−10 468.20
	−10 068.31	−10 241.06	−10 227.75	−10 221.38	−10 340.55	−10 355.88	−10 381.36	−10 461.43
	−10 059.38	−10 239.20	−10 222.64	−10 223.91	−10 347.99	−10 358.63	−10 385.04	−10 462.07
	−10 066.66	−10 245.96	−10 228.82	−10 226.08	−10 352.74	−10 361.17	−10 384.05	−10 467.61
							−10 382.36	
Mean:	−10 063.93	−10 243.16	−10 226.52	−10 223.30	−10 346.79	−10 357.69	−10 381.78	−10 463.98
Standard Deviation:	1.02	1.08	0.75	0.73	1.59	0.65	0.82	1.05

TABLE 6. Derived molar values at 298.15 K

Compound	State	ΔE_c° / kcal mol^{-1}	ΔH_c° / kcal mol^{-1}	ΔH_f° / kcal mol^{-1}
Indan	Liquid	−1189.36 ± 0.33	−1190.84 ± 0.33	2.80 ± 0.35
1,1-Dimethylindan	Liquid	−1497.90 ± 0.42	−1499.97 ± 0.42	−12.79 ± 0.45
4,6-Dimethylindan	Liquid	−1495.47 ± 0.36	−1497.54 ± 0.36	−15.23 ± 0.38
4,7-Dimethylindan	Liquid	−1495.00 ± 0.35	−1497.07 ± 0.35	−15.70 ± 0.38
1,1,4,6-Tetramethylindan	Liquid	−1803.33 ± 0.65	−1805.99 ± 0.65	−31.51 ± 0.67
1,1,4,7-Tetramethylindan	Liquid	−1805.23 ± 0.41	−1807.89 ± 0.41	−29.61 ± 0.44
1,1,4,6,7-Pentamethylindan	Crystalline	−1955.05 ± 0.48	−1958.01 ± 0.48	−41.85 ± 0.51
1,1-Dimethyl-6-*tert*-butylindan	Liquid	−2117.31 ± 0.58	−2120.57 ± 0.58	−41.66 ± 0.62

3. Results

CALORIMETRIC RESULTS

Results of typical combustion experiments for each compound are listed in table 4. It is impractical to list summaries of 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. Equation (1) represents the combustion reaction of the compounds:

$$C_aH_b(\text{l or c}) + (a + \tfrac{1}{4}b)O_2(\text{g}) = aCO_2(\text{g}) + \tfrac{1}{2}bH_2O(\text{l}). \quad (1)$$

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

$$a\text{C(c, graphite)} + \tfrac{1}{2}bH_2(\text{g}) = C_aH_b(\text{l or c}). \quad (2)$$

The uncertainties given in table 6 are the "uncertainty interval".[13] The enthalpies of formation of CO_2(g) and H_2O(l) were taken to be -94.051 and -68.315 kcal mol^{-1}, respectively.[14] Uncertainties assigned were 0.011 kcal mol^{-1} for CO_2(g),[15] and 0.010 kcal mol^{-1} for H_2O(l).[16]

4. Discussion

Indan was the only one of our compounds that had been studied previously. Stull *et al.*[8] found that $\Delta H_c^\circ(25\,^\circ\text{C}) = -(1190.63 \pm 0.47)$ kcal mol^{-1}. Agreement with the result of this research, $-(1190.84 \pm 0.33)$ kcal mol^{-1}, is well within the combined uncertainties of the two measurements.

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