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The enthalpies of combustion and formation of 1,8-dimethylnaphthalene, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, and 2,7-dimethylnaphthalene, [a,b]

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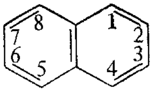
The enthalpies of combustion of 1,8-dimethylnaphthalene, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, and 2,7-dimethylnaphthalene were measured by precision oxygen-bomb calorimetry. The following values, based on the mass of carbon dioxide produced, are reported for the standard enthalpy of combustion, $\Delta H_c^\circ(298.15\ \mathrm{K})/\mathrm{kcal_{th}\ mol^{-1}}$, of these compounds in the crystalline state: 1,8-dimethylnaphthalene, $-(1544.70 \pm 0.25)$; 2,3-dimethylnaphthalene, $-(1537.95 \pm 0.21)$; 2,6-dimethylnaphthalene, $-(1537.14 \pm 0.38)$; and 2,7-dimethylnaphthalene, $-(1537.21 \pm 0.23)$.† None of these values would have been predictable within experimental uncertainty, and a predicted value for 1,8-dimethylnaphthalene probably would have been different by 7 $\mathrm{kcal_{th}\ mol^{-1}}$ from the experimental value.

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 turned to multi-ring hydrocarbons and their alkyl derivatives. Enthalpies of combustion of indan and seven alkyl indans have been reported,(1) and the enthalpies of combustion of four dimethylnaphthalenes are presented in this report. No earlier literature values for the dimethylnaphthalenes exist.



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

[b] Contribution No. 201 from the energy relationships laboratory of the Bartlesville Energy Research Center.

† Throughout this paper $\mathrm{cal_{th}} = 4.184\ \mathrm{J}$; atm = 101.325 kPa.

2. Experimental

MATERIALS

Samples of 1,8-dimethylnaphthalene, 2,6-dimethylnaphthalene, and 2,7-dimethylnaphthalene were prepared and purified by the American Petroleum Institute Research Project on the Synthesis of Petroleum-Related Hydrocarbons under the direction of Professor E. J. Eisenbraun of Oklahoma State University. Low-temperature properties and some vapor pressures have been measured at this center. Study of the melting temperature as a function of fraction melted showed the purity of 1,8-dimethylnaphthalene to be 99.993 moles per cent and that of 2,7-dimethylnaphthalene to be 99.95 moles per cent. The study of 2,6-dimethylnaphthalene was complicated by solid solution of an impurity, but the purity was estimated to be about 99.9 moles per cent. The commercially obtained sample of 2,3-dimethylnaphthalene had been treated by vacuum sublimation and zone refining. Purity was estimated to be >99.9 moles per cent by the supplier.

National Bureau of Standards Sample 39i benzoic acid was used for calibration. Its specific energy of combustion is $-(26.434 \pm 0.003)\,\mathrm{kJ\,g^{-1}}$ under certificate conditions. Conversion to standard conditions(2) gives $-(6313.02 \pm 0.72)\,\mathrm{cal_{th}\,g^{-1}}$ for $\Delta E_c^\circ/M$, the specific energy of the idealized combustion reaction.

For the polyester film, empirical formula $C_{10}H_8O_4$, used to confine the sample, $\Delta E_c^\circ/M$ was $-(5473.8_9 \pm 0.2_8)\,\mathrm{cal_{th}\,g^{-1}}$ (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 $-4050\,\mathrm{cal_{th}\,g^{-1}}$.

APPARATUS AND PROCEDURES

Experimental procedures used for the combustion calorimetry of hydrocarbons were recently described.(3) Rotating-bomb calorimeter BMR II(4) and platinum-lined bomb Pt-3b,(5) internal volume $0.349_4\,\mathrm{dm^3}$, were used. The bomb was not rotated. For every experiment, $1\,\mathrm{cm^3}$ of water was added to the bomb, and it was flushed and charged to 30 atm with pure oxygen. Because the oxygen used was quite pure, the amount of HNO_3 formed was negligible. Each experiment was started at 296.15 K, and because the masses of combustibles were properly chosen, the final temperatures were very nearly 298.15 K. Pellets were prepared from the compounds, and they were confined beneath polyester disks to inhibit sublimation from the platinum crucible used for the combustion reaction.(1)

CALIBRATION

A set of benzoic acid calibration experiments was interspersed within the series of experiments with the dimethylnaphthalenes. The result of the eight experiments was $\varepsilon(\mathrm{calor}) = (4005.67 \pm 0.12)\,\mathrm{cal_{th}\,K^{-1}}$ (mean and standard deviation).

UNITS OF MEASUREMENTS AND AUXILIARY QUANTITIES

The experimental results reported are based on the 1961 atomic weights.(6) The laboratory standards of mass and resistance were calibrated by the National Bureau of Standards.

TABLE 1. Physical properties at 298.15 K
($\mathrm{cal_{th}} = 4.184$ J; atm = 101.325 kPa)

	ρ / $\mathrm{g\,cm^{-3}}$	$(\partial E/\partial p)_T$ / $\mathrm{cal_{th}\,atm^{-1}\,g^{-1}}$	c_p / $\mathrm{cal_{th}\,K^{-1}\,g^{-1}}$
1,8-Dimethylnaphthalene	1.14	(− 0.006)[a]	0.37
2,3-Dimethylnaphthalene	1.13	(− 0.006)	(0.34)
2,6-Dimethylnaphthalene	1.13	(− 0.006)	0.31
2,7-Dimethylnaphthalene	1.15	(− 0.006)	0.31

[a] Values in parentheses are estimates.

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,(2) the values in table 1 were used for density ρ, specific heat capacity c_p, and $(\partial E/\partial p)_T$. Values of density were calculated from the dimensions of weighed pellets. Values of c_p for 1,8-dimethylnaphthalene, 2,6-dimethylnaphthalene, and 2,7-dimethylnaphthalene are measurements of the low-temperature calorimetry group of this research center. The value of c_p for 2,3-dimethylnaphthalene and all values of $(\partial E/\partial p)_T$ are estimates (in parentheses).

CARBON DIOXIDE RECOVERY

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

TABLE 2. Carbon dioxide recovery

Compound	Number of experiments	Per cent recovery[a]	Compound	Number of experiments	Per cent recovery[a]
Benzoic acid	8	100.014 ± 0.005	2,6-Dimethylnaphthalene	8	99.966 ± 0.017
1,8-Dimethylnaphthalene	7	99.966 ± 0.019	2,7-Dimethylnaphthalene	8	99.998 ± 0.007
2,3-Dimethylnaphthalene	7	99.990 ± 0.012			

[a] Mean and standard deviation.

3. Results

Results for typical calorimetric experiments for each compound are listed in table 3. Because the samples of dimethylnaphthalenes had brief exposure to the laboratory (50 per cent relative humidity) and because materials that have been zone-refined in glass tubes may contain small amounts of glass that has been pulled away from the tube walls during crystallization, the mass of sample was calculated indirectly from the mass of carbon dioxide produced. It is impractical to summarize results of all

TABLE 3. Summary of typical calorimetric experiments at 298.15 K[a] ($\mathrm{cal_{th}} = 4.184$ J)

	1,8-Dimethyl-naphthalene	2,3-Dimethyl-naphthalene	2,6-Dimethyl-naphthalene	2,7-Dimethyl-naphthalene
m'(compound)/g	0.806 811	0.808 562	0.809 549	0.810 216
m''(dry polyester)/g	0.011 633	0.011 650	0.011 650	0.011 378
m'''(fuse)/g	0.001 984	0.001 883	0.001 908	0.001 506
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{\mathrm{corr}})/\mathrm{K}$	2.00598	2.00153	2.00295	2.00412
$\varepsilon(\mathrm{calor})(-\Delta t_c)/\mathrm{cal_{th}}$	−8035.30	−8017.48	−8023.16	−8027.85
$\varepsilon(\mathrm{cont})(-\Delta t_c)/\mathrm{cal_{th}}$ [b]	−8.89	−8.84	−8.90	−8.95
$\Delta E_{\mathrm{ign}}/\mathrm{cal_{th}}$	0.51	0.51	0.59	0.51
$\Delta E_{\mathrm{dec}}(\mathrm{HNO_3})/\mathrm{cal_{th}}$	0.00	0.00	0.00	0.00
$\Delta E_{(\mathrm{corr\ to\ std\ states})}/\mathrm{cal_{th}}$	4.32	4.33	4.34	4.34
$\{-m''(\Delta E_c^\circ/M)(\mathrm{dry\ polyester})\}/\mathrm{cal_{th}}$	63.68	63.77	63.77	62.28
$\{-m'''(\Delta E_c^\circ/M)(\mathrm{fuse})\}/\mathrm{cal_{th}}$	8.04	7.63	7.73	6.10
$\{m'(\Delta E_c^\circ/M)(\mathrm{compound})\}/\mathrm{cal_{th}}$	−7967.64	−7950.08	−7955.65	−7963.57
$\{(\Delta E_c^\circ/M)(\mathrm{compound})\}/\mathrm{cal_{th}\,g^{-1}}$	−9875.47	−9832.37	−9827.23	−9828.95

[a] The symbols and abbreviations of this table are those of reference 2 except as noted.

[b] $\varepsilon^i(\mathrm{cont})(t_i - 298.15\ \mathrm{K}) + \varepsilon^f(\mathrm{cont})(298.15\ \mathrm{K} - t_f + \Delta t_{\mathrm{corr}})$.

[c] Items 81 to 85, 87 to 90, 93, and 94 of the computation form of reference 2.

experiments, but values of $\Delta E_c^\circ/M$, the energy of the idealized combustion reaction, for all experiments are given in table 4.

The equation:

$$C_{12}H_{12}(c)+15O_2(g) = 12CO_2(g)+6H_2O(l), \qquad (1)$$

represents the combustion reaction for the dimethylnaphthalenes, and all values of $\Delta E_c^\circ/M$, tables 1 and 2, refer to this equation. Derived values of the molar energy of the combustion reaction ΔE_c°, the standard enthalpy of combustion ΔH_c°, and the standard enthalpy of formation ΔH_f° of the crystalline compounds are given in table 5.

TABLE 4. Summary of experimental results at 298.15 K ($\mathrm{cal_{th}} = 4.184$ J)

	1,8-Dimethyl-naphthalene	2,3-Dimethyl-naphthalene	2,6-Dimethyl-naphthalene	2,7-Dimethyl-naphthalene
		$\{\Delta E_c^\circ/M\}/\mathrm{cal_{th}\,g^{-1}}$		
	−9877.48	−9832.37	−9831.84	−9828.34
	−9875.47	−9832.20	−9830.88	−9827.18
	−9874.63	−9833.57	−9824.66	−9826.85
	−9874.59	−9832.88	−9823.98	−9827.18
	−9877.57	−9833.33	−9825.51	−9827.10
	−9875.63	−9833.38	−9827.12	−9828.95
	−9876.79	−9831.82	−9827.23	−9829.49
			−9829.65	−9829.40
Mean:	−9876.02	−9832.79	−9827.60	−9828.06
Standard deviation:	0.48	0.26	1.03	0.39

TABLE 5. Derived molar values for crystalline compounds at 298.15 K
($\mathrm{cal_{th}} = 4.184$ J)

	ΔE_c° $\mathrm{kcal_{th}\ mol^{-1}}$	ΔH_c° $\mathrm{kcal_{th}\ mol^{-1}}$	ΔH_f° $\mathrm{kcal_{th}\ mol^{-1}}$
1,8-Dimethylnaphthalene	-1542.92 ± 0.25	-1544.70 ± 0.25	6.19 ± 0.29
2,3-Dimethylnaphthalene	-1536.17 ± 0.21	-1537.95 ± 0.21	-0.56 ± 0.26
2,6-Dimethylnaphthalene	-1535.36 ± 0.38	-1537.14 ± 0.38	-1.37 ± 0.40
2,7-Dimethylnaphthalene	-1535.43 ± 0.23	-1537.21 ± 0.23	-1.30 ± 0.27

The values of ΔE_c° and ΔH_c° refer to equation (1). The values of ΔH_c° refer to the equation:

$$12\mathrm{C(c, graphite)} + 6\mathrm{H_2(g)} = \mathrm{C_{12}H_{12}(c)}. \tag{2}$$

The uncertainties given in table 5 are the "uncertainty intervals".(7) The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be -94.051 and -68.315 $\mathrm{kcal_{th}\ mol^{-1}}$, respectively.(8) Uncertainties assigned to gaseous CO_2,(9) and liquid H_2O,(16) were 0.011 and 0.010 $\mathrm{kcal_{th}\ mol^{-1}}$, respectively.

4. Discussion

Comparison of molar enthalpies of formation of the four compounds would be more certain if it were possible to compare them in the ideal gaseous state, but enthalpies of sublimation are not yet available. Comparison of molar enthalpies of formation in the solid crystalline state is possible, and this comparison should be somewhat informative because the compounds are isomeric and the molecular dimensions are not vastly different; therefore, the enthalpies of sublimation should not be greatly different.

The molar enthalpies of formation of crystalline 2,6-dimethylnaphthalene and 2,7-dimethylnaphthalene are about the same, and the molar enthalpy of formation of 2,3-dimethylnaphthalene is about 0.8 $\mathrm{kcal_{th}\ mol^{-1}}$ more positive because of the familiar "*ortho*" effect. The value of the enthalpy of formation of 1,8-dimethylnaphthalene is about 7.5 $\mathrm{kcal_{th}\ mol^{-1}}$ more positive than those for 2,6-dimethylnaphthalene and 2,7-dimethylnaphthalene because of the proximity and interference of the methyl groups and/or non-coplanarity of the ring system with the resulting loss in resonance energy. A similar effect has been observed(11) in the dimethylphenanthrenes, the dimethylbenzo(c)phenanthrenes, and the dimethylbenzanthracenes.

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