J. Chem. Thermodynamics **1970**, 2, 237–244

The enthalpies of combustion and formation of the isomeric pentanes†‡

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(*Received 2 October 1969*)

The enthalpies of combustion of the three isomeric pentanes were measured by oxygen-bomb combustion calorimetry. The following values, based on the mass of carbon dioxide produced, are reported for the standard enthalpy of combustion $\Delta H_c^\circ(298.15\ \mathrm{K})/\mathrm{kcal\ mol^{-1}}$ of these compounds in the liquid state: *n*-pentane, $-(838.69 \pm 0.16)$; 2-methylbutane, $-(837.57 \pm 0.20)$; 2,2-dimethylpropane, $-(834.71 \pm 0.14)$. These results were compared with modern values obtained by flame calorimetry. Older experimental results were reviewed, and "best values" of the enthalpies of combustion were selected. These selected values were compared with the enthalpies of combustion predicted by modern correlative procedures.

1. Introduction

The Bureau of Mines is conducting thermodynamic studies on selected hydrocarbons under American Petroleum Institute Research Project 62, "Thermodynamics of Hydrocarbons from Petroleum." An experimental goal of this program is the provision of basic thermodynamic data for a limited number of carefully selected "key" compounds. The accuracy of the data for the key compounds is important; from them, the properties for many other compounds can be calculated by correlation.

A recent flame calorimetric determination of the enthalpies of combustion of the isomeric pentanes(1) indicated that the older experimental enthalpy of combustion results(2–4) for the pentanes are not completely reliable. Pilcher and Chadwick noted that their experimental results(1) did not agree with earlier results(2,4) based upon the amount of water formed in the combustion reaction. The flame calorimetric results of Rossini on *n*-butane(4) and 2-methylpropane(5) based on the water formed were later amended by Prosen, Maron, and Rossini(6) by (0.56 ± 0.23) and $(0.97 \pm 0.19)\ \mathrm{kcal\ mol^{-1}}$, respectively.

A corroborative determination of the enthalpies of combustion of the pentanes by a different experimental procedure was desirable, and this paper reports the results of that investigation. This is the first study of all three pentanes by bomb calorimetry under a single calibration series.

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† 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. 174 from the thermodynamics laboratory of the Bartlesville Petroleum Research Center.

2. Experimental work

APPARATUS AND PROCEDURES

Experimental measurements of the enthalpy of combustion followed procedures recently reported.(7,8) The rotating-bomb calorimeter BMR II(9) and platinum-lined bomb Pt-3b,(10) internal volume 0.349_4 dm^3, have been described. The bomb was not rotated. Water (1 cm^3) was added to the bomb, and the bomb was flushed and charged to 30 atm† with pure oxygen. Formation of nitric acid was minimized by use of pure oxygen. Each experiment was started at 23 °C, and because of the masses of combustibles chosen, the final temperatures were nearly 25 °C. All experiments with *n*-pentane employed fragile glass ampoules with flexible walls.(11) Only seven complete combustion reactions were obtained in 16 attempts. Because of its high volatility, 2,2-dimethylpropane was confined in rigid ampoules.(12) Seven complete combustion reactions were obtained in seven attempts. The first experiments with 2-methylbutane employed flexible ampoules. Only four successful reactions were obtained in 11 attempts, so rigid ampoules were tried. Three successful reactions then occurred in four attempts.

When rigid ampoules are used, it is necessary to leave a small vapor space inside the ampoule, and the precise determination of the mass of sample is impossible. For this reason, the mass of carbon dioxide produced in the combustion experiments was used as a measure of the amount of reaction rather than the mass of sample. Anhydrous lithium hydroxide was used as absorbent for the carbon dioxide.(8) The combustion products were analyzed for carbon monoxide or other products of incomplete combustion, but none were detected.

MATERIALS

The pentanes were samples of API research hydrocarbons purified and made available by American Petroleum Institute Research Project 58B at Carnegie-Mellon University, A. J. Streiff, Director. Sample designations and impurities given by API Project 58B are listed in table 1.

TABLE 1. Compound description

Compound	Moles per cent of impurity
n-Pentane (B)	0.05 ± 0.04
2-Methylbutane	0.05 ± 0.04
2,2-Dimethylpropane (B)	0.003 ± 0.002

The auxiliary oil, sample designation USBM-P3a, had the empirical formula $CH_{1.894}$, and $\Delta E_c^\circ/M$ 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}.

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† atm = 101 325 N m^{-2}.

CALIBRATION

The calorimeter was calibrated with benzoic acid, NBS Sample 39i, which has an energy of combustion of $-(26.434 \pm 0.003)$ kJ g^{-1} under certificate conditions. Conversion to standard conditions(15) gives $-(6313.02 \pm 0.72)$ cal g^{-1} for $\Delta E_c^\circ/M$, the energy of the idealized combustion reaction. The energy equivalent of the calorimetric system ε(calor) was (4004.80 ± 0.12) cal K^{-1} (mean and standard deviation for seven calibration experiments).

UNITS OF MEASUREMENT AND AUXILIARY QUANTITIES

The experimental results reported are based on the 1961 atomic weights(13) and the 1963 definitions of the thermodynamic temperature scale and of the thermochemical calorie (cal = 4.184 J).(14)

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,(15) 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-Pentane	0.621 05	−0.017	0.55_4
2-Methylbutane	0.617 15	−0.019 [a]	0.54_6
2,2-Dimethylpropane	0.585 25	(—) [b]	0.54_8

[a] Used only for experiments in flexible ampoules.

[b] Value not needed since all experiments were with rigid ampoules.

Values of density are from the API Research Project 44 tables.(16) Values of $(\partial E/\partial P)_T$ were calculated from the temperature dependence of density by use of the approximation, $(\partial E/\partial P)_T = -T(\partial V/\partial T)_p$. The values of heat capacity are from the literature.(17–19)

3. Calorimetric results

Typical combustion experiments for the pentanes are summarized in table 3. It is impractical to list summaries for all experiments, but values of $\Delta E_c^\circ/M$ for all experiments are tabulated in table 4. Standard deviations of the mean are given. All values of $\Delta E_c^\circ/M$ refer to unit mass of sample, but the sample mass was calculated indirectly(8) from the mass of carbon dioxide. For this calculation the molecular weight of CO_2 was taken to be 44.00995, and the molecular weight of C_5H_{12} was taken to be 72.15139. The values of $\Delta E_c^\circ/M$ (tables 3 and 4) refer to equation (1):

$$C_5H_{12}(l) + 8O_2(g) = 5CO_2(g) + 6H_2O(l). \qquad (1)$$

TABLE 3. Summary of typical calorimetric experiments at 298.15 K [a]

	n-Pentane	2-Methyl-butane	2,2-Dimethyl-propane
m'(compound)/g	0.623 026	0.649 038	0.605 130
m''(oil)/g	0.071 685	0.045 604	0.094 703
m'''(fuse)/g	0.001 421	0.001 309	0.001 076
$n_i(H_2O)$/mol	0.055 35	0.055 35	0.055 35
$\Delta t_c = (t_f - t_i + \Delta t_{corr})$/K	2.000 69	2.001 33	2.002 90
ε(calor)($-\Delta t_c$)/cal	−8012.36	−8014.94	−8021.23
ε(cont)($-\Delta t_c$)/cal [b]	−10.44	−10.43	−10.47
ΔE_{ign}/cal	0.49	0.57	0.80
$\Delta E_{dec}(HNO_3)$/cal	0.10	0.00	0.10
$\Delta E_{(corr\ to\ std\ states)}$/cal [c]	1.65	1.59	1.98
$-m''\Delta E_c^\circ/M$(oil)/cal	787.41	500.92	1040.24
$-m'''\Delta E_c^\circ/M$(fuse)/cal	5.75	5.30	4.36
$m'\Delta E_c^\circ/M$(compound)/cal	−7227.40	−7516.99	−6984.22
$\Delta E_c^\circ/M$(compound)/cal g^{-1}	−11 600.42	−11 581.71	−11 541.65

[a] The symbols and abbreviations of this table are those of reference 15 except as noted.

[b] ε_i(cont)(t_i−25 °C) + ε_f(cont)(25 °C$-t_f+\Delta t_{corr}$).

[c] Items 81–85, 87–90, 93, and 94 of the computation form of reference 15.

TABLE 4. Summary of experimental results. Values of $\Delta E^\circ/M$ at 298.15 K

	$(\Delta E_c^\circ/M)$/cal g^{-1}		
	n-Pentane	2-Methyl-butane	2,2-Dimethyl-propane
	−11 600.42	−11 581.71	−11 543.99
	−11 600.84	−11 588.93	−11 541.65
	−11 597.10	−11 583.07	−11 543.04
	−11 602.01	−11 582.14	−11 545.19
	−11 599.71	−11 581.78	−11 543.99
	−11 595.71	−11 582.08	−11 544.24
	−11 599.64	−11 587.12	−11 547.21
Mean:	−11 599.34	−11 583.82	−11 544.18
Standard deviation:	0.83	1.11	0.66

4. Selection of values of the enthalpy of vaporization

Many of the earlier investigations on the pentanes were gas phase studies. To compare results of the earlier investigations with those of the present, it is necessary to select values of the enthalpy of vaporization. Values of the enthalpies of vaporization of

TABLE 5. Enthalpy of vaporization ΔH_v at 298.15 K

Compound	ΔH_v/cal mol^{-1}	ΔH_v°/cal mol^{-1}
n-Pentane	6316.4	6389 ± 10
2-Methylbutane	5937	6029 ± 11
2,2-Dimethylpropane	5221	5351 ± 14

n-pentane[(20)] and 2-methylbutane[(21)] are from the literature. The value for neopentane is from unpublished measurements of the Vapor-flow Calorimetry Research Group of this laboratory. Values of enthalpy of vaporization to the real gas at 298.15 K, ΔH_v(298.15 K), and calculated values of the enthalpy of vaporization to the ideal gas at 298.15 K, ΔH_v°(298.15 K), are tabulated in table 5.

5. Derived results

The derived molar values for the pentanes are given in table 6. Values of ΔE_c^c (298.15 K), the energy of the idealized combustion reaction, and ΔH_c°(298.15 K), the standard enthalpy of combustion, refer to equation (1). The values of the enthalpies of formation of the liquid or gas refer to equation (2):

$$5\ C(c,\ \text{graphite}) + 6H_2(g) = C_5H_{12}(l\ \text{or}\ g). \tag{2}$$

TABLE 6. Derived molar values at 298.15 K

Compound	$\Delta E_c^\circ(l)$ / kcal mol^{-1}	$\Delta H_c^\circ(l)$ / kcal mol^{-1}	$\Delta H_f^\circ(l)$ / kcal mol^{-1}
n-Pentane	−836.91 ± 0.16	−838.69 ± 0.16	−41.46 ± 0.18
2-Methylbutane	−835.79 ± 0.20	−837.57 ± 0.20	−42.58 ± 0.20
2,2-Dimethylpropane	−832.93 ± 0.14	−834.71 ± 0.14	−45.44 ± 0.16
Compound	ΔH_v° / kcal mol^{-1}	$\Delta H_c^\circ(g)$ / kcal mol^{-1}	$\Delta H_f^\circ(g)$ / kcal mol^{-1}
n-Pentane	6.39 ± 0.01	−845.08 ± 0.16	−35.07 ± 0.18
2-Methylbutane	6.03 ± 0.01	−843.60 ± 0.20	−36.55 ± 0.20
2,2-Dimethylpropane	5.35 ± 0.01	−840.06 ± 0.14	−40.09 ± 0.16

Uncertainties expressed are the "uncertainty interval."[(22)] 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.[(23)] Uncertainties assigned to gaseous carbon dioxide[(24)] and liquid water[(25)] were 0.011 and 0.010 kcal mol^{-1}, respectively.

6. Discussion

COMPARISON OF RESULTS WITH EARLIER INVESTIGATIONS

The only direct comparison of the combustion calorimetry results is with the work of Prosen and Rossini[(3)] who measured the enthalpy of combustion of liquid *n*-pentane, ΔH_c°(298.15 K) = −(838.71 ± 0.18) kcal mol^{-1}, in excellent agreement with the result of this research. The value of Prosen and Rossini for *n*-pentane and the values of the enthalpies of combustion of all the pentanes from this research were converted to the enthalpies of combustion in the ideal gaseous state using values of ΔH°_v (298.15 K) from table 6.

These values of the enthalpy of combustion of the ideal gas may be compared with the results of several other investigations (table 7).

TABLE 7. Enthalpies of combustion of ideal gas at 298.15 K

	ΔH°_c/kcal mol^{-1}		
	n-Pentane	2-Methylbutane	2,2-Dimethylpropane
Rossini, 1934(4)	845.27 ± 0.22 [a]	—	—
Prosen and Rossini, 1944(3)	845.10 ± 0.18 [b]	—	—
Knowlton and Rossini, 1939(2)	—	843.38 ± 0.15 [b]	840.59 ± 0.22 [a]
Pilcher and Chadwick, 1967(1)	844.99 ± 0.23 [b]	843.31 ± 0.22 [b]	839.88 ± 0.23 [b]
This research	845.08 ± 0.16 [b]	843.60 ± 0.20 [b]	840.06 ± 0.14 [b]

[a] Based on mass of water formed.

[b] Based on mass of carbon dioxide formed.

SELECTION OF BEST VALUES OF ENTHALPIES OF COMBUSTION AND FORMATION

All values of the enthalpy of combustion of the ideal gas that had been derived from the mass of CO_2 produced, table 7, were combined by weighting them inversely as the squares of their uncertainty intervals. The values of Rossini(4) for *n*-pentane and of Knowlton and Rossini(2) for 2,2-dimethylpropane, based on the amount of water formed, were rejected. The selected values of the enthalpy of combustion of the ideal gas were combined with values of the enthalpies of vaporization from table 6 in order to calculate the enthalpies of combustion of the liquid. The selected values of the enthalpies of combustion were combined with values of the enthalpies of formation of gaseous carbon dioxide(23) and liquid water(23) to calculate selected values of the enthalpy of formation. The selection of "best values" of the enthalpies of combustion and formation is given in table 8.

TABLE 8. Selected molar values at 298.15 K

Compound	$\Delta H^\circ_c(l)$ / kcal mol^{-1}	$\Delta H^\circ_c(g)$ / kcal mol^{-1}	$\Delta H^\circ_f(l)$ / kcal mol^{-1}	$\Delta H^\circ_f(g)$ / kcal mol^{-1}
n-Pentane	−838.68 ± 0.11	−845.07 ± 0.11	−41.47 ± 0.14	−35.08 ± 0.14
2-Methylbutane	−837.39 ± 0.11	−843.42 ± 0.11	−42.76 ± 0.14	−36.73 ± 0.14
2,2-Dimethylpropane	−834.66 ± 0.12	−840.01 ± 0.12	−45.49 ± 0.15	−40.14 ± 0.15

COMPARISON WITH ALLEN CORRELATION PROCEDURE

One of the more successful methods for the correlation of values of the enthalpies of formation of the hydrocarbons is that of Allen.(26) The values of the enthalpies of formation of the gaseous pentanes predicted by the Allen method are compared with the experimental values of this research and with the "selected values" (table 8) in table 9. The agreement between the predicted values and the selected values is a considerable improvement over the older selected values.(16) The agreement between the experimental values of this research and the Allen procedure is remarkable.

TABLE 9. Comparison with Allen correlation method

Compound	$\Delta H_f^\circ(298.15\ \mathrm{K})/\mathrm{kcal\ mol^{-1}}$		
	This research	Selected value	Allen method
n-Pentane	−35.07	−35.08	−35.08
2-Methylbutane	−36.55	−36.73	−36.47
2,2-Dimethylpropane	−40.09	−40.14	−40.07

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