linear equation is obtained of the form

$$y = a + bx_1 + cx_2 \qquad (3)$$

where $a = A$, $c = -C$, and $b = (A \times C - B)$.

The constants of linear Equation 3 were evaluated by multilinear least squares regression. This method of linearization was used because it permits explicit solution of Equation 2 for either log P or t. The Antoine constants are listed in Table III together with several statistical parameters showing the goodness of fit of the equations to the experimental data. The maximum error of 3.6% was obtained for hexadecanol, one of the two alcohols which appeared to contain detectable trace impurities. However, this maximum error is well within the expected maximum error for the Antoine equation which is reported to be about 5% (*12*).

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LITERATURE CITED

(1) Biddiscombe, D.P., Collerson, R.R., Handley, R., Harrington, G., Martin, J.F., Sprake, C., *J. Chem. Soc.* **1963**, p. 1954.
(2) Brunel, R.F., Crenshaw, J.L., Tobin, E., *J. Am. Chem. Soc.* **43**, 561 (1921).
(3) Butler, J., Ramchandani, C.N., Thompson, D., *J. Chem. Soc.* 138, 280 (1935).
(4) Carley, J.F., Bertelsen, L.W., *Ind. Eng. Chem.* 41, 2806 (1949).
(5) Dreisbach, R.R., Martin, R.A., *Ibid.*, **41**, 2875 (1949).
(6) Dreisbach, R.R., Schrader, S.A., *Ibid.*, **41**, 2879 (1949).
(7) Hovorka, F., Lankelma, H.P., Stanford, S.C., *J. Am. Chem. Soc.* **60**, 820 (1938).
(8) Kemme, H.R., Kreps, S.I., unpublished data.
(9) Lenth, C.W., *J. Am. Chem. Soc.* **55**, 3283 (1933).
(10) Li, C.M.J., Rossini, F., J. Chem. Eng. Data **6**, 268 (1961).
(11) Rose, A., Papahronis, B.T., Williams, E., *Ibid.*, **3**, 216 (1958).
(12) Reid, R.C., Sherwood, T.K., "The Properties of Gases and Liquids," p. 135, McGraw-Hill, New York, 1966.
(13) Smyth, C.P., Engel, E.W., *J. Am. Chem. Soc.* **51**, 2646 (1929).
(14) Winslow, D.H., "A Correlation of Vapor Pressure, Temperature and Carbon Numbers of Homologous Series," M.S. thesis, Newark College of Engineering, Newark, N.J., 1965.

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Enthalpies of Combustion of Toluene, Benzene, Cyclohexane, Cyclohexene, Methylcyclopentane, 1-Methylcyclopentene, and *n*-Hexane

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The enthalpies of combustion of toluene, benzene, cyclohexane, cyclohexene, methylcyclopentane, 1-methylcyclopentene, and *n*-hexane were measured in a bomb calorimeter. Values, in kilocalories per mole based on the mass of sample, for the enthalpies of combustion, $\Delta Hc^\circ_{298.15}$, of the liquid hydrocarbons in gaseous oxygen to form gaseous carbon dioxide and liquid water are toluene, −934.49 ± 0.12; benzene, −780.95 ± 0.10; cyclohexane, −936.87 ± 0.13; cyclohexene, −896.75 ± 0.12; methylcyclopentane, −941.28 ± 0.14; 1-methylcyclopentene, −897.17 ± 0.13; and *n*-hexane, −995.03 ± 0.13. Values of the enthalpy of formation of the liquids were derived. They were compared to existing hydrocarbon data and can be used to check the internal consistency of the existing selections of data for the several families of hydrocarbons. The best means of measuring the amount of reaction in combustion calorimetry were reconsidered. Both sample mass and carbon dioxide recovery were used as measures of the amount of reaction. A new carbon dioxide absorbent was used and was superior to older absorbents.

THE BUREAU OF MINES is conducting thermodynamic studies at the Bartlesville Petroleum Research Center on selected hydrocarbons under American Petroleum Institute Research Project 62, "Thermodynamics of Hydrocarbons from Petroleum." In this project, research in combustion calorimetry is being done to extend and improve the existing thermochemical data for the hydrocarbons (*1*) largely produced by Johnson, Prosen, Rossini, and coworkers of the National Bureau of Standards.

The work on hydrocarbons by the National Bureau of Standards was planned carefully. Series of measurements on isomeric families of compounds gave highly accurate values of the heats of isomerization. Other studies gave precise values of the $-CH_2-$ increment to the enthalpy of formation, and values for larger families of compounds were made internally consistent by studying single isomers from each of several smaller families in one carefully planned series of experiments. For example, all the alkanes were interrelated by studying the *n*-alkanes. The internal consistency of the enthalpies of formation of the alkanes probably would not be improved now by repeated studies.

The method of calibration differed from that used by Johnson, Prosen, Rossini, and collaborators. Earlier calibration was done with electrical energy, but later benzoic acid combustion was the means of calibration. For many good reasons (*4*), today most precision combustion calorimetry uses benzoic acid calibration. It is possible, however, that changes over the years have introduced lack of agreement between families of compounds. The principal reason for the research reported here was to check the consistency of the values for the alkanes, benzenes, cyclohexanes, cyclohexenes, and cyclopentenes.

Whether sample mass or carbon dioxide recovery is the best means of measuring the amount of reaction in combustion calorimetry has been debated for years. Results of this research show that comparable accuracy can be achieved by either method if careful attention is given to experimental detail; however, the use of sample mass is giving more precise results in this laboratory.

Two series of experimental measurements are reported. In the first, a lengthy group of measurements on toluene investigated sample mass and carbon dioxide mass as means of measuring the amount of reaction. In the second series, six C_6 hydrocarbons from six different families were studied to check the interrelation of existing enthalpy-of-combustion values.

EXPERIMENTAL

Procedures. The basic procedures used in combustion calorimetric research by this laboratory have been described (*6, 8, 9*). Only details pertinent to current research are reported here.

Materials. The purity of the sample of toluene (API Research Project 44), used earlier for low-temperature calorimetric research (*22*) in this laboratory, was determined by calorimetric studies of the melting point as a function of the fraction melted as 99.999 mole %.

The six C_6 hydrocarbons were samples of API research hydrocarbons purified and made available by the API Research Project 58B from the Carnegie-Mellon University (Table I).

The sample of benzoic acid used for calibration was National Bureau of Standards Sample 39I. The material had a heat of combustion of 26.434 ± 0.003 absolute kilojoules per gram under certificate conditions. Conversion to standard conditions (*10*) gives −6313.02 ± 0.72 cal. per gram for $\Delta Ec°/M$, the energy of the idealized combustion reaction.

The auxiliary oil, sample designation USBM-P3a, had the empirical formula $CH_{1.894}$. A recent redetermination of this formula favors this composition over the $CH_{1.891}$ formerly used. The most recent determination of $\Delta Ec°/M$ for this material gave $-10{,}984.3_0 \pm 0.1_5$ cal. per gram (mean and standard deviation), a value that has held remarkably constant for 15 years.

For the cotton thread fuse empirical formula $CH_{1.774}O_{0.887}$, $\Delta Ec°/M$ was −4050 cal. per gram.

For reducing weights in air to weights in vacuo and for correcting to standard states, the values summarized in Table II, all for 298.15° K., were used for density, ρ, specific heat, c_p, and $(\partial E/\partial P)_T$ for the substances. Values of density and specific heat are from the literature and from unpublished measurements of this laborabory or, in parentheses, estimated by analogy with structurally similar substances. Values of $(\partial E/\partial P)_T$ were calculated from the temperature dependence of density by using the approximation, $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$.

Calorimetric Apparatus. The rotating-bomb calorimeter, laboratory designation BMR II (*6*), and platinum-lined bomb Pt-3B (*5*), internal volume 0.349_4 liter, have been described. Rotation of the bomb was not necessary for combustion experiments with hydrocarbons.

The 16-gram platinum crucibles used as sample holders were 22 mm. in diameter and 25 mm. deep. A massive platinum baffle (*9*) covered the crucible in all experiments except benzoic acid calibration experiments.

Ampoule Technique. Borosilicate glass ampoules were filled with the hydrocarbon samples. The filling method has been described (*7*). Mass of the individual ampoules was from 25 to 35 mg. Light borosilicate glass ampoules such as these fuse almost completely, seldom occlude carbon, and never discolor during the combustion reaction as soft-glass ampoules do (*11, 16*).

Table I. Compound Description

	Impurity, Mole %
Benzene (B)	0.017 ± 0.015
Cyclohexane (B)	0.009 ± 0.006
Cyclohexene	0.022 ± 0.020
Methylcyclopentane (C)	0.01 ± 0.01
1-Methylcyclopentene	0.11 ± 0.08
n-Hexane (B)	0.015 ± 0.010

Table II. Physical Properties at 298.15° K.

	ρ, G./Ml.	c_p, Cal./Deg./G.	$(\partial E/\partial P)_T$, Cal./Atm./G.
Toluene	0.8623	0.408	−0.00663
Benzene	0.87370	0.416	−0.00768
Cyclohexane	0.77389	0.444	−0.00678
Cyclohexene	0.80609	0.434	−0.00702
Methylcyclopentane	0.74394	0.451	−0.00671
1-Methylcyclopentene	0.7752	(0.449)	(−0.00721)
n-Hexane	0.65481	0.541	−0.00660
Benzoic acid	1.320	0.289	−0.00278
Auxiliary oil	0.87	(0.53)	(−0.0061)
Fuse	1.5	(0.4)	(−0.007)

A variation of the original sealing technique was used. In some instances, the sealing of the 0.2- to 0.4-mm. capillary by passage through a small oxyhydrogen flame is accompanied by traces of decomposition. These hydrocarbons exhibited this tendency. When this decomposition occurs, a clean seal often can be obtained by breaking the capillary about 5 mm. from the bulb, touching a small piece of ice to the side of the bulb away from the capillary, and then touching the capillary to the oxyhydrogen flame. Ampoules can be sealed by this method without measurable loss of glass. Agreement of sample mass with mass calculated from carbon dioxide recovery also demonstrates that this sealing technique can be used without introducing significant amounts of air or water.

The samples of toluene, benzene, cyclohexane, methylcyclopentane, and *n*-hexane were dried by a vapor pass over freshly activated molecular sieve before the ampoules were filled. The cyclohexene and 1-methylcyclopentene were dried by a liquid contact with calcium hydride.

Calibration. Two sets of calibration experiments were done. A set interspersed within the toluene experiments gave $\mathcal{E}(\text{calor.}) = 4004.9_4 \pm 0.1_1$ cal. per deg. (mean and standard deviation for 11 experiments). A second set distributed among the combustion experiments with the C_6 compounds gave $\mathcal{E}(\text{calor.}) = 4004.9_2 \pm 0.1_0$ cal. per deg. (mean and standard deviation for nine experiments).

Measurement of Amount of Reaction. The mass of combustible substance placed in the bomb has been the classical measure of the amount of reaction in combustion calorimetry. This measure has been used by this laboratory because present methods for measuring the mass of a pure or well-defined combustible are believed adequate. However, carbon dioxide often has been recovered as a confirmation of sample purity, and the absence of carbon monoxide or other products of incomplete combustion is proved by either qualitative or quantitative tests. Experiments are rejected whenever soot is deposited on the bomb walls or crucible.

The oxygen purification train and the carbon dioxide recovery system used in this laboratory and those described by Prosen and Rossini (*16*) are essentially identical. The carbon dioxide absorption tubes described by Prosen and Rossini (*17*) have been modified by replacing the tapered joints with ball-and-socket joints, easing somewhat the cleaning of the joints and the assembly of the system.

Determining amounts of reaction by measuring carbon dioxide recovery never has given the precision obtained by measuring the mass of sample, despite repeated attempts by several investigators in this laboratory. Excellent arguments for using carbon dioxide recovery have been outlined by Prosen (*14*) and Rossini (*18*). In carbon dioxide analysis the difficulty in weighing precisely the relatively large and massive absorption tubes probably has not been emphasized adequately. As the contents of an Ascarite absorption tube are spent by repeated absorption and flushing, the change in physical appearance of the contents also might pose a question as to whether the chemistry of the absorption process is understood completely.

During the combustion experiments with toluene, carbon dioxide was recovered by two methods. For five experiments with toluene and five experiments with benzoic acid, carbon dioxide was recovered in Ascarite absorption tubes by the method evolved by Prosen and Rossini (*16, 17, 20*). For six experiments with toluene and five experiments with benzoic acid, carbon dioxide was recovered by using anhydrous lithium hydroxide.

For the experiments with anhydrous lithium hydroxide as the absorbent, the absorption tubes were cleaned and were filled about two thirds with anhydrous lithium hydroxide. A thin layer of asbestos was placed on top of the anhydrous lithium hydroxide, and the remainder of the tube was filled with commercial anhydrous magnesium perchlorate. In the earlier experiments a glass wool plug was placed in the bottom of the tubes, but this procedure was abandoned in later experiments to allow the anhydrous lithium hydroxide to fill the side arm. This procedure gives a better defined edge to the anhydrous lithium hydroxide, and any overflow of carbon dioxide from the first absorber is quickly indicated.

A factor for obtaining the mass of carbon dioxide from the change in weight of the absorption tube has been calculated as outlined by Rossini (*20*). Opinions conflict as to the chemical reaction occurring when magnesium perchlorate takes up water and about the composition of the commercial "anhydrous" magnesium perchlorate. Factors were calculated for three possible reactions:

$$CO_2 + 2LiOH + \tfrac{1}{3}Mg(ClO_4)_2 = Li_2CO_3 + \tfrac{1}{3}[Mg(ClO_4)_2\cdot 3H_2O] \qquad (1)$$

$$CO_2 + 2LiOH + \tfrac{1}{6}\,Mg(ClO_4)_2 = Li_2CO_3 + \tfrac{1}{6}\,[Mg(ClO_4)_2\cdot 6H_2O] \qquad (2)$$

$$CO_2 + 2LiOH + \tfrac{1}{3}Mg(ClO_4)_2\cdot 3H_2O = Li_2CO_3 + \tfrac{1}{3}[Mg(ClO_4)_2\cdot 6H_2O] \qquad (3)$$

Reaction 2 is the sum of Reactions 1 and 3. The volume changes are +0.427, +0.362, and +0.297 ml. per gram of CO_2 for Reactions 1, 2, and 3, respectively. This volume change was calculated by using these densities (gram per ml. at 25° C.): LiOH, 1.46; Li_2CO_3, 2.11; $Mg(ClO_4)_2$, 2.60; $Mg(ClO_4)_2\cdot 3H_2O$, 2.044; and $Mg(ClO_4)_2\cdot 6H_2O$, 1.970. This increase in volume displaces helium. At 25° C. and 730 mm., the density of helium is 0.000157 gram per ml.; at 25° C. and 760 mm., its density is 0.000164 gram per ml. Rounding the density to 0.00016 introduces an uncertainty of, at most, 4 p.p.m. During all experiments, the air density varied at most 0.040 mg. per ml., from 1.14_0 to 1.18_0 mg. per ml. The correction for buoyancy on the weights can be taken as 0.00116/8.4 or −0.00014 gram per gram of CO_2 with an error of, at most, 5 p.p.m. The final overall factors are 0.99993, 0.99992, and 0.99991 for Reactions 1, 2, and 3, respectively. The mean of the first two factors, 0.99992_5, was used. The uncertainty is about 1 part in 100,000 because of variations in air density and pressure of helium. A further uncertainty of about 5 parts in 10,000 stems from uncertainty in the density of lithium hydroxide.

Table III. Carbon Dioxide Recovery

	Ascarite	Lithium Hydroxide
Benzoic acid	99.994 ± 0.004[a] (5)[b]	100.002 ± 0.003 (5)[b]
Toluene	99.993 ± 0.009 (5)	99.987 ± 0.013 (6)

[a] Average deviation from mean. [b] Number of experiments.

Table IV. Carbon Dioxide Recovery

	Single-Pan Balance	Two-Pan Balance
Benzoic acid (7)[a]	99.998 ± 0.008[b]	100.001 ± 0.009[b]
Benzene (7)	99.997 ± 0.010	99.995 [illegible] 0.011
Cyclohexane (8)	100.000 ± 0.011	100.005 ± 0.010
Cyclohexene (7)	99.995 ± 0.005	99.996 ± 0.007
Methylcyclopentane (8)	99.992 ± 0.012	99.990 ± 0.012
1-Methylcyclopentene (8)	99.994 ± 0.008	99.993 ± 0.010
n-Hexane (9)	99.998 ± 0.008	100.003 ± 0.010

[a] Number of experiments. [b] Percentage recovery with average deviation from mean.

Values of 1.46 and 2.54 grams per ml. were found. Flotation experiments in chloroform and chloroform-benzene mixtures indicate that 1.46 is more nearly correct, and this value was used in the above calculations. Carbon dioxide recoveries by using the two different absorbents are summarized in Table III. Per cent recoveries listed in Table III were calculated from the masses of the combustibles. In this series of experiments, the absorption tubes were weighed with a single-pan balance.

As an absorbent, anhydrous lithium hydroxide proved as good as or better than Ascarite, and is much easier to handle. The spent material is easily removed from the tubes, which are not so prone to plugging.

Anhydrous lithium hydroxide alone was employed in the second series of experiments when the C_6 hydrocarbons were studied. The absorption tubes were weighed on both single- and two-pan balances to determine accuracy in using the single-pan balance. Carbon dioxide recoveries are summarized in Table IV.

Units of Measurements and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (*2*) and the 1963 fundamental constants and definitions of the thermodynamic temperature scale and calorie (*3*). The laboratory standards of mass and resistance had been calibrated by the National Bureau of Standards.

Reduction to Standard States. Rigorous reduction to standard states was done for each experiment following the procedure of Hubbard, Scott, and Waddington (*10*). Computation was done by means of the computer program developed by C. Howard Shomate, U.S. Naval Ordnance Test Station, China Lake, Calif.

CALORIMETRIC RESULTS

Typical calorimetric experiments with all seven compounds are summarized in Table V. The results for all experiments are summarized in Table VI. Values of $\Delta Ec°/M$ refer to the idealized combustion reaction (*4*).

$$C_aH_b(\text{liq}) + (a + b/4)O_2(g) = aCO_2(g) + b/2\ H_2O(\text{liq}) \qquad (4)$$

The numerical data of Tables V and VI refer to the gram of sample as the unit of measure.

Another set of data was obtained from the carbon dioxide recoveries. The auxiliary oil and fuse were assumed to burn completely, and the sample mass was derived from the carbon dioxide recovery through the stoichiometry of the combustion reaction. This computation gave the values of $\Delta Ec°/M$ given in Table VII. The values of standard deviation of the mean derived from the carbon dioxide recovery are about twice those derived from sample mass;

Table V. Summary of Typical Calorimetric Experiments[a]

	Toluene	Benzene	Cyclohexane	Cyclohexene	Methylcyclo-pentane	1-Methylcyclo-pentene	n-Hexane
m' (compound), g.	0.731820	0.773889	0.682561	0.691820	0.681149	0.710960	0.673561
m'' (oil), g.	0.054996	0.026492	0.038936	0.044146	0.037945	0.025131	0.023180
m''' (fuse), g.	0.000970	0.001151	0.001020	0.000960	0.001052	0.000951	0.001039
n^i (H_2O), mole	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c = t_f - t_i + \Delta t_{cor.}$, deg.	2.00144	2.00236	1.99980	2.00300	2.00234	2.00417	2.00077
ε(calor.)($-\Delta t_c$), cal.	−8015.65	−8019.29	−8009.04	−8021.85	−8019.23	−8026.56	−8012.91
ε(cont.)($-\Delta t_c$), cal.[b]	−9.76	−9.81	−9.74	−9.75	−9.76	−9.78	−9.85
$\Delta E_{ign.}$, cal.	0.99	0.51	0.56	0.39	0.59	0.63	0.73
$\Delta E_{dec.}$ (HNO_3), cal.	0.02	0.03	0.05	0.00	0.00	0.00	0.00
$\Delta E_{(cor.\ to\ std.\ states)}$, cal.[c]	3.72	4.02	2.34	2.79	2.33	2.79	1.88
$-m'' \Delta Ec°/M$ (oil), cal.	604.09	291.00	427.68	484.91	416.80	276.05	254.62
$-m''' \Delta Ec°/M$ (fuse), cal.	3.93	4.66	4.13	3.89	4.26	3.85	4.21
$m' \Delta Ec°/M$ (compound), cal.	−7412.66	−7728.88	−7584.02	−7539.62	−7605.01	−7753.02	−7761.32
$\Delta Ec°/M$ (compound), cal./g.	−10,129.07	−9987.06	−11,111.12	−10,898.24	−11,164.97	−10,905.00	−11,522.81

[a] Symbols and abbreviations those of Hubbard *et al.* (*10*) except as noted. [b] ε^i(cont.)$(t^i - 25) + \varepsilon^f$(cont.)$(25° - t^f + \Delta t_{corr.})$. [c] Items 81–85, 87–90, 93, and 94 of computation form of Hubbard *et al.* (*10*).

Table VI. Summary of Experimental Results

Values of $\Delta Ec°/M$, in cal. per gram at 25° C.

	Toluene	Benzene	Cyclohexane	Cyclohexene	Methyl-cyclopentane	1-Methyl-cyclopentene	n-Hexane
	−10,129.07	−9987.06	−11,111.12	−10,898.24	−11,164.97	−10,905.00	−11,522.81
	−10,128.95	−9985.90	−11,112.06	−10,899.21	−11,162.71	−10,904.54	−11,522.27
	−10,128.23	−9986.08	−11,110.51	−10,898.98	−11,164.69	−10,902.25	−11,522.65
	−10,128.40	−9985.36	−11,109.72	−10,898.54	−11,162.34	−10,904.57	−11,521.81
	−10,128.80	−9986.22	−11,110.98	−10,898,02	−11,163.63	−10,902.45	−11,522.55
	−10,129.24	−9986.78	−11,111.66	−10,897.80	−11,162.68	−10,903.06	−11,520.85
	−10,128.73	−9985.18	−11,109.27	−10,898.92	−11,160.82	−10,903.17	−11,522.02
	−10,128.76		−11,109.38	−10,898.00	−11,161.78	−10,903.06	−11,521.97
	−10,129.40						−11,522.21
	−10,130.06						
	−10,129.16						
Mean	−10,128.98	−9986.08	−11,110.59	−10,898.46	−11,162.95	−10,903.51	−11,522.13
Std. dev.	0.15	0.15	0.37	0.19	0.50	0.37	0.19

Table VII. $\Delta Ec°/M$ Calculated from Carbon Dioxide Recovery

Values of $\Delta Ec°/M$, in cal. per gram at 25° C.

	$\Delta Ec°/M$ (with Std. Dev.)
Toluene	−10,130.03 ± 0.14
Benzene	−9,986.37 ± 0.43
Cyclohexane	−11,110.65 ± 0.70
Cyclohexene	−10,898.98 ± 0.41
Methylcyclopentane	−11,163.82 ± 0.63
1-Methylcyclopentene	−10,904.15 ± 0.52
n-Hexane	−11,522.35 ± 0.55

however, the values of standard deviation of the mean are well within the 0.01% generally representing precise combustion calorimetry.

Molal values of $\Delta Ec°$ and $\Delta Hc°$ are given in Table VIII along with some other recent literature values. Except for the values for 1-methylcyclopentene, agreement of values is within the assigned "uncertainty interval" (*18*).

DERIVED RESULTS

Values of the enthalpies of combustion derived from the mass of sample and current best values (*23*) of the enthalpies of formation of gaseous carbon dioxide and liquid water were combined to derive values of the enthalpy of formation according to the generalized equation:

$$aC(c, \text{graphite}) + b/2\ H_2(g) = C_aH_b(\text{liq}) \qquad (5)$$

The results are given in Table IX. Uncertainties expressed are the "uncertainty interval" (*18*). Uncertainties attached to liquid water and gaseous carbon dioxide were 0.010 (*19*) and 0.011 (*21*) kcal. per mole, respectively.

DISCUSSION

The enthalpies of combustion of toluene, benzene, cyclohexane, and n-hexane agree with the literature values as shown in Table VIII, but corresponding values of cyclohexene, 1-methylcyclopentene, and methylcyclopentane differ. While the values for cyclohexene and methylcyclopentane agree with the literature values just within their assigned uncertainties, the values for 1-methylcyclopentene are in disagreement. The literature values for these last three compounds rest on benzoic acid calibration (*12*, *13*), whereas for the other four compounds showing good agreement, the literature values are based on electrical calibration.

No attempt was made to select "best values" from this research. If the data are to be correlated with data relying on the mass of CO_2 as the measure of the amount of reaction, the values of this research dependent upon the mass of CO_2 possibly should be used. Data of this research indicate that the values for the cyclohexenes, cyclopentenes, and cyclopentanes need adjustment for correlations.

NOMENCLATURE

∂ = differential operator
T = temperature
m = mass, grams
n = number of moles

Table VIII. Summary of Molal Values at 298.15° K. (Kcal. per Mole)

	$-\Delta Ec^\circ$ (Sample Mass)	$-\Delta Ec^\circ$ (CO_2 Mass)	ΔHc° (Sample Mass)	$-\Delta Hc^\circ$ (CO_2 Mass)	$-\Delta Hc^\circ$ (Literature)
Toluene	933.30 ± 0.12	933.40 ± 0.12	934.49 ± 0.12	934.59 ± 0.12	934.50 ± 0.12 (*15*)
Benzene	780.06 ± 0.10	780.08 ± 0.12	780.95 ± 0.10	780.97 ± 0.12	780.98 ± 0.10 (*15*)
Cyclohexane	935.10 ± 0.13	935.10 ± 0.13	936.87 ± 0.13	936.88 ± 0.17	936.88 ± 0.17 (*12*)
Cyclohexene	895.27 ± 0.12	895.32 ± 0.13	896.75 ± 0.12	896.80 ± 0.13	896.62 ± 0.13 (*13*)
Methylcyclopentane	939.50 ± 0.14	939.57 ± 0.16	941.28 ± 0.14	941.35 ± 0.16	941.14 ± 0.18 (*12*)
1-Methylcyclopentene	895.69 ± 0.13	895.74 ± 0.14	897.17 ± 0.13	897.22 ± 0.14	896.85 ± 0.14 (*13*)
n-Hexane	992.96 ± 0.13	992.98 ± 0.16	995.03 ± 0.13	995.05 ± 0.16	994.99 ± 0.20 (*17*)

Table IX. Enthalpy of Formation of Liquid Hydrocarbons at 298.15° K., Kcal. per Mole (with Uncertainty Interval)

	$\Delta Hf^\circ_{298.15}$
Toluene	2.87 ± 0.15
Benzene	11.70 ± 0.13
Cyclohexane	−37.32 ± 0.16
Cyclohexene	−9.13 ± 0.14
Methylcyclopentane	32.92 ± 0.17
1-Methylcyclopentene	−8.71 ± 0.15
n-Hexane	−47.48 ± 0.16

P = pressure, atm.
$\mathcal{E}$(calor.) = heat equivalent of calorimeter, cal./deg.
$\mathcal{E}$(cont.) = heat equivalent of contents, cal./deg.
$\Delta E_{\text{dec.}}$ = energy of decomposition, cal.
$\Delta E_{\text{ign.}}$ = electrical ignition energy, cal.
$\Delta E_{\text{cor. to std. states}}$ = energy for reduction to standard states, cal.
$\Delta Ec^\circ/M$ = standard energy of idealized combustion reaction, cal./gram
ΔEc° = standard energy of idealized combustion reaction, kcal./mole
ΔHc° = standard enthalpy of combustion, kcal./mole
ΔHf° (l) = standard enthalpy of formation of liquid, kcal./mole

Superscripts

i = initial state
f = final state

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LITERATURE CITED

(1) American Petroleum Institute Research Project 44, Chemical Thermodynamics Properties Center, Texas A&M University, College Station, Tex., "Selected Values of Properties of Hydrocarbons and Related Compounds" (loose-leaf sheets, extant 1968).
(2) Cameron, A.E., Wichers, E., *J. Am. Chem. Soc.* **84**, 4175 (1962).
(3) Cohen, E.R., DuMond, J.W.M., *Rev. Mod. Phys.* **37**, 537 (1965).
(4) Coops, J., Jessup, R.S., van Nes, K., "Experimental Thermochemistry," F.D. Rossini, Ed., Chap. 3, pp. 27–58, Interscience, New York, 1956.
(5) Good, W.D., Douslin, D.R., Scott, D.W., George, A., Lacina, J.L., Dawson, J.P., Waddington, G., *J. Phys. Chem.* **63**, 1133 (1959).
(6) Good, W.D., Scott, D.W., Waddington, G., *Ibid.*, **60**, 1080 (1956).
(7) Guthrie, G.B., Scott, D.W., Hubbard, W.N., Katz, C., McCullough, J.P., Gross, M.E., Williamson, K.D., Waddington, G., *J. Am. Chem. Soc.* **74**, 4662 (1952).
(8) Hubbard, W.N., Frow, F.R., Waddington, G., *J. Phys. Chem.* **65**, 1326 (1961).
(9) Hubbard, W.N., Katz, C., Waddington, G., *Ibid.*, **58**, 142 (1954).
(10) Hubbard, W.N., Scott, D.W., Waddington, G., "Experimental Thermochemistry," F.D. Rossini, Ed., Chap. 5, pp. 75–128, Interscience, New York, 1956.
(11) Jessup, R.S., *J. Res. Natl. Bur. Std.* **18**, 115 (1937).
(12) Johnson, W.H., Prosen, E.J., Rossini, F.D., *Ibid.*, **36**, 463 (1946).
(13) Labbauf, A., Rossini, F.D., *J. Phys. Chem.* **65**, 476 (1961).
(14) Prosen, E.J., "Experimental Thermochemistry," F.D. Rossini, Ed., Chap. 6, pp. 129–48, Interscience, New York, 1956.
(15) Prosen, E.J., Gilmont, R., Rossini, F.D., *J. Res. Natl. Bur. Std.* **34**, 65 (1945).
(16) Prosen, E.J., Rossini, F.D., *Ibid.*, **27**, 289 (1941).
(17) *Ibid.*, **33**, 255 (1944).
(18) Rossini, F.D., "Experimental Thermochemistry," F.D. Rossini, Ed., pp. 11–13, 297–320, Interscience, New York, 1956.
(19) Rossini, F.D., *J. Res. Natl. Bur. Std.* **6**, 1 (1931).
(20) *Ibid.*, p. 37.
(21) Rossini, F.D., Jessup, R.S., *J. Res. Natl. Bur. Std.* **21**, 491 (1938).
(22) Scott, D.W., Guthrie, G.B., Messerly, J.F., Todd, S.S., Berg, W.T., Hossenlopp, I.A., McCullough, J.P., *J. Phys. Chem.* **66**, 911 (1962).
(23) Wagman, D.D., Evans, W.H., Halow, I., Parker, V.B., Bailey, S. M., Schumm, R.H., "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Std. (U. S.) Tech. Note **270-1** (1965).

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