[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF STANFORD UNIVERSITY AND SAN JOSE STATE COLLEGE]

Thermal Data on Organic Compounds. XIX. Modern Combustion Data for Some Non-volatile Compounds Containing Carbon, Hydrogen and Oxygen

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The heat of combustion of an organic compound constitutes a very important quantity in the calculation of the free energy of formation of the compound by means of the third law of thermodynamics and the fundamental equation $\Delta F = \Delta H - T\Delta S$. Unfortunately, until very recently it has often been the most serious source of error in the resulting free energy value because most of the available combustion data were determined prior to 1900 when calorimetric methods and the purification of substances had not reached so high a standard as at present. For this reason there is now a very urgent need for new combustion data on organic compounds, and accordingly an extensive program of such thermochemical studies has been undertaken at Stanford University.

In this paper we shall summarize the data obtained in an investigation of the heats of combustion of β-methylnaphthalene, phthalic anhydride, phthalic acid, anthracene, phenanthrene, stilbene, pyrene, *n*-hexadecane, cetyl alcohol, 1,3,5-triphenylbenzene, and a sample of polyisobutylene.

Method and Apparatus

The bomb calorimeter was chosen as the type to be used in this investigation because it is best suited for work with solids or liquids of low volatility. After considerable preliminary experimentation our calorimetric apparatus was finally patterned very closely after that described by Huffman and Ellis[1] and our entire procedure became essentially the same as theirs. For this reason we shall forego here any detailed description of our calorimetry and merely present the important characteristics of the apparatus and one or two minor differences from the methods of Huffman.

Our "Parr bomb" had a capacity of 390 ml. Platinum wire was employed as the ignition medium to avoid the somewhat uncertain correction due to oxidation of the iron wire, which is so often used; and the electrical energy introduced in the ignition process was determined accurately by measurements of time, current, and voltage. A small piece of cotton string (instead of the filter paper in Huffman's procedure) was ignited by the platinum wire and this in turn ignited the sample of material under study, which had been placed in a platinum crucible. The heat of combustion of the string was found to be 4169 (±2) cal. per gram, weighed in air. Before each combustion 1 ml. of water was placed in the bomb, which was then filled with pure commercial oxygen to a pressure of 30 atm. at 22°.

In many of the experiments the air initially in the bomb was washed out by filling the bomb at least twice with oxygen to a pressure of 5 atm. and then allowing it to escape until the pressure was reduced to 1 atm. However, there was always present a small quantity of nitrogen within the bomb and the consequent nitric acid produced in the combustion process was titrated with $N/14.55$ sodium carbonate solution. The magnitude of the thermal correction for this nitric acid, calculated on the basis of an evolution of 14,550 cal. per mole of aqueous nitric acid formed, was about 10 calories if the air was not previously washed out and about 1 calorie if it was washed out.

Water for the calorimeter, ordinarily 2780 g., was weighed to 0.05 g. on a high capacity balance. The mass of the material to be burned was determined to 0.00001 g. on a Kuhlmann microchemical balance.

The temperature rise in the calorimeter was measured by a platinum resistance thermometer calibrated by the Bureau of Standards, a Mueller thermometer bridge, a high sensitivity galvanometer, and a lamp-and-scale reading device, all supplied by the Leeds and Northrup Co. The sensitivity of the system was such that a change of 0.00001 ohm (0.0001°) in the resistance of the thermometer caused the reflection from the galvanometer mirror to shift 2 mm. on the scale. The galvanometer was used as a null point instrument in conjunction with a chronograph precise to 0.1 second.

The corrected temperature rise was calculated by the method described by Dickinson.[2] From this temperature rise and the sum of the energies supplied the energy equivalent of the system at 25° was calculated in the calibration experiments; and conversely with the aid of this last quantity the various combustion results were subsequently derived.

Units.—The unit of energy throughout this paper is the defined conventional calorie which has been derived from the international joule by multiplying by the factor 1.0004/4.185. The unit of mass is the gram true mass which is derived from the weight in air against brass weights by use of a suitable correction factor for buoyancy. In cases where the density of the material in question was not available in the literature, we have made rough estimates from the mass and volume of the pelleted substances. The molecular weights used are based on the 1939 table of atomic weights.[3]

Calibration of the Calorimeter.—Benzoic acid (sample 39e) supplied by the United States Bureau of Standards was burned in the bomb, under approximately the standard calorimetric conditions of Washburn,[4] to determine the energy equivalent of the calorimeter at 25°. For this sample Jessup and Green[5] have obtained a combustion

(1) Huffman and Ellis, THIS JOURNAL, **57**, 41 (1935).

(2) Dickinson, *Bull. Bureau of Standards*, **11**, 189 (1914).

(3) Baxter, Guichard, Hönigschmid and Whytlaw-Gray, THIS JOURNAL, **61**, 223 (1939).

(4) Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

(5) Jessup and Green, *J. Research Nat. Bur. Standards*, **13**, 469 (1934).

value of 26,419 international joules (equal to 6315.3 cal.) per gram under these standard conditions.

TABLE I

CALIBRATIONS WITH OXYGEN CYLINDER 2

$\Delta\theta$, corr. rise °C.	True mass, benzoic acid, g.	Cal. from b. a.	Cal. from HNO_3	Cal. from string + *Elt*	Energy equiv., cal. per °C.	Dev. from mean, %
1.7932	0.90756	5731.4	9.3	17.4	3211.0	−0.009
1.7959	.90871	5738.6	9.8	19.9	3211.9	+ .019
1.7835	.90301	5702.7	9.9	15.1	3211.5	+ .006
1.7916	.90662	5725.5	9.5	17.0	3210.5	− .025
1.7399	.88080	5562.4	9.5	16.5	3211.9	+ .019
1.9722	.99918	6310.0	0.8	18.6	3211.3[a]	.000
1.9124	.96871	6117.6	1.2	18.0	3211.0[a]	− .009
				Mean	3211.3	± .012

[a] This calibration was made with 2.0 g. less water in the calorimeter and hence 2.0 cal. have been added to the experimental result to bring it up to the "standard" conditions for our calorimeter.

Three different cylinders of oxygen were used during the course of the present investigation and two other cylinders have been used in subsequent work in this Laboratory. With each cylinder of oxygen a series of calibrations of the calorimeter was carried out with the standard benzoic acid. Usually the individual runs in a series were made at different stages of pressure during the use of the cylinder and in this connection no significant changes appeared during the decrease of the oxygen pressure. Table I contains the details for seven calibrations with Cylinder 2, which was used in about 60% of the combustions in the present study. The other four series of calibrations were similarly concordant among themselves and yielded means in excellent agreement with that tabulated here.

Purification of the Compounds

Highest purity Eastman Kodak Co. chemicals were the starting materials in the preparation of all the samples except those of pyrene and polyisobutylene. They were further purified in our Laboratory by recrystallization from suitable solvents and subsequent drying in an electric oven. After such preparation all crystalline materials were kept in desiccators over "dehydrite" and, for at least three days prior to combustion determinations, in vacuum desiccators with frequent evacuation. Ash determinations were made on all substances but, except in the cases of phenanthrene and sample 3 of pyrene, the results were negligible. In these two cases suitable corrections were made in the combustion values.

β-Methylnaphthalene.—Two samples were prepared independently by three successive crystallizations from absolute ethyl alcohol.

Phthalic Anhydride.—Four samples were prepared as follows. (1) The material was crystallized once from a mixture of equal parts of pure benzene and petroleum ether and then sublimed before use. (2) One crystallization was made in this case from a 50–50 mixture of benzene and isooctane and this was followed by sublimation. (3) The third sample was subjected to one crystallization from "hexone"; the crystals were washed with benzene and then crystallized once from benzene. The product was then sublimed three times before using. (4) This sample was crystallized from "hexone," washed with benzene, then twice crystallized from benzene, and finally sublimed twice.

o-Phthalic Acid.—Two separate samples were prepared by three crystallizations from specially distilled water.

Anthracene.—The original Eastman Kodak Co. product was a muddy yellow. After three crystallizations from benzene the material was of a light yellow color.

Phenanthrene.—This sample was the product of three crystallizations from benzene; it had 0.007% ash content.

Stilbene.—This sample was prepared by crystallizing three times from benzene.

Pyrene.—From the material purified by Jacobs and Parks[6] three samples, all light green in color, were prepared for these combustion measurements. (1) This was the product of one crystallization from benzene followed by one from "hexone." (2) For this sample the procedure was reversed, benzene being used for the solvent after "hexone." (3) Another quantity of pyrene was subjected to three crystallizations from benzene. Ash determinations on this sample showed 0.016% non-combustible.

n-Hexadecane.—The Eastman Kodak Co. product (m. p. 16°) was used in its original form for sample 1. Sample 2 was prepared from some of this material by four crystallizations from a 50–50 mixture of *n*-propyl alcohol and methyl alcohol, followed by six crystallizations from ethylene dichloride. A careful qualitative test for chlorine in the final product (m. p. 17.0°) was negative.

Cetyl Alcohol.—Two samples were prepared. (1) The material (m. p. 48°) was recrystallized twice from methyl alcohol. In spite of being dried for several days in a vacuum desiccator, this sample had a pronounced odor and yielded combustion values averaging 0.071% lower than sample 2. As this indicated incomplete removal of the methyl alcohol, the data obtained for it have not been used in computing the final results in Table III. (2) This sample was prepared by two crystallizations from benzene as a solvent with subsequent drying.

1,3,5-Triphenylbenzene.—Four samples were prepared as follows. (1) This was the product of a crystallization from glacial acetic acid, followed by washing with ethyl alcohol and two crystallizations from ethyl alcohol. (2 and 3) These samples were crystallized three times from absolute ethyl alcohol. They were prepared separately at different stages of this study. (4) This material was twice crystallized from benzene.

Polyisobutylene.—This material was furnished in a very pure form by the Shell Development Company and was not subjected to any additional treatment before use. Its properties have been previously described by Ferry and Parks.[7] Its apparent molecular weight was about 4900, although of course it was a mixture of many polymers.

The Heats of Combustion and Derived Data

The experimental data for the combustions on the two samples of β-methylnaphthalene are presented in Table II. The energy evolved in the isothermal bomb process per g. at 25.0° is represented by $-\Delta U_B/m$ and the deviations of the

(6) Jacobs and Parks, THIS JOURNAL, **56**, 1513 (1934).
(7) Ferry and Parks, *J. Chem. Physics*, **4**, 70 (1936).

individual runs from the mean by Δ. The detailed experimental data for the remaining ten substances are essentially similar in character; they have been omitted here for reasons of spatial economy. Except in the case of cetyl alcohol previously cited, the different samples of any substance yielded extremely concordant combustion values.

TABLE II

THE EXPERIMENTAL DATA FOR β-METHYLNAPHTHALENE AT 25°

Sample	True mass, g.	Total heat evolved, cal.	Cal. from HNO_3	Cal. from string and *Elt*	$-\Delta U_B/m$, cal. g.$^{-1}$	Δ
1	0.58994	5766.1	10.7	15.3	9730.0	+2.0
1	.58946	5759.4	10.6	15.4	9726.5	−1.5
1	.59188	5783.8	10.0	15.0	9729.6	+1.6
1	.59176	5781.6	10.4	15.2	9726.9	−1.1
1	.59236	5788.3	10.7	15.5	9727.3	−0.7
2	.59251	5788.9	10.5	15.1	9726.9	−1.1
2	.59067	5774.2	11.1	14.8	9731.8	+3.8
2	.59076	5770.3	10.7	14.4	9725.1	−2.9
				Mean	9728.0	±1.8

Table III contains a summary of the experimental data for the heats of combustion of the eleven substances together with some important thermal data calculated therefrom. The number of combustions made in each particular case is given in the fifth column; the resulting mean values for $-\Delta U_B/m$ and the mean deviations (Δ) appear in the succeeding column. The values of the bomb process were then calculated per mole and corrected to the standard constant-volume process where the reactants and products are each at 1 atmosphere by means of the equations of Washburn.[4] The energy evolved in this hypothetical standard process is designated by the symbol $-\Delta U_R$. From this quantity $-\Delta H_R$, the heat evolved in the isobaric process at 1 atm., was obtained by addition of the proper work term. Finally, $-\Delta H^\circ_f$, the heat of formation of the compounds from the elements, was then calculated from $-\Delta H_R$ by use of 68,318 cal.[8] and 94,030 cal.[9] for the heats of formation of water and carbon dioxide, respectively.

The two liquids, *n*-hexadecane and polyisobutylene, were never evacuated in the vacuum desiccators and undoubtedly contained dissolved air. According to the solubility data in the "International Critical Tables"[10] and the more recent study of Frolich,[11] this dissolved air at saturation would amount to about 0.02% by weight; and therefore the values for $-\Delta U_R$ in Table III for these two substances have been arbitrarily increased by this percentage in the course of the calculation from the values of $-\Delta U_B/m$.

The uncertainties attached to the values of $-\Delta U_R$ have been calculated by use of the "precision error" described by Rossini.[12] This includes not only the "reaction error" for the combustion of the particular compound but also our "calibration error" of 0.012%, an "assigned error" (by Jessup and Green) of 0.023% on the standardizing substance, and an arbitrary allowance for a 10% uncertainty in the Washburn correction. In the cases of *n*-hexadecane and polyisobutylene an additional 20% uncertainty in the correction for air saturation was assumed.

TABLE III

SUMMARY OF EXPERIMENTAL AND DERIVED DATA AT 25°

Substance	Formula	Mol. wt.	Density	No. of comb.	$-\Delta U_B/m$ and Δ, cal. g.$^{-1}$	$-\Delta U_R$, kcal. mole^{-1}	$-\Delta H_R$, kcal. mole^{-1}	$-\Delta H^\circ_f$, kcal. mole^{-1}
β-Methylnaphthalene (s)	$C_{11}H_{10}$	142.19	1.029	8	9728.0 ± 1.8	1382.43 ± 0.52	1383.91	− 7.99
Phthalic anhydride (s)	$C_8H_4O_3$	148.11	1.527	10	5265.4 ± 2.6	779.04 ± .45	778.74	+110.14
Phthalic acid (s)	$C_8H_6O_4$	166.13	1.593	5	4642.9 ± 0.6	770.51 ± .32	770.21	+186.98
Anthracene (s)	$C_{14}H_{10}$	178.22	1.25	6	9451.0 ± .5	1683.27 ± .58	1684.75	− 16.94
Phenanthrene (s)	$C_{14}H_{10}$	178.22	1.025	4	9396. ± .9	1673.47 ± .61	1674.95	− 26.74
Stilbene (s)	$C_{14}H_{12}$	180.24	1.14	6	9754.1 ± 1.3	1757.02 ± .67	1758.80	− 32.47
Pyrene (s)	$C_{16}H_{10}$	202.24	1.25	11	9260.1 ± 3.4	1871.49 ± .84	1872.97	− 26.90
n-Hexadecane (l)	$C_{18}H_{34}$	226.44	0.775	9	11266.8 ± 1.9	2551.07 ± .97	2556.11	+109.78
Cetyl alcohol (s)	$C_{16}H_{34}O$	242.44	.90	7	10302.7 ± 2.0	2497.04 ± .90	2501.78	+164.11
Triphenylbenzene (s)	$C_{24}H_{18}$	306.39	1.206	12	9542.4 ± 3.2	2921.83 ± 1.27	2924.50	− 52.92
Polyisobutylene (l)	$(C_4H_8)_n$	n(56.105)	0.907	6	11175.8 ± 1.3	626.95 ± 0.23	628.14	+ 21.25

Previous Work

We have found no record of previous combustion measurements for β-methylnaphthalene, pyrene and polyisobutylene.

(8) Rossini, *J. Research Nat. Bur. Standards*, **22**, 407 (1939).

(9) Rossini and Jessup, *ibid.*, **21**, 491 (1938).

(10) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., p. 261.

(11) Frolich, Tauch, Hogan and Perr, *Ind. Eng. Chem.*, **23**, 548 (1931).

(12) Rossini, *Chem. Rev.*, **18**, 252 (1936).

For the remaining eight substances there are available in the literature a fair number of early values, mostly obtained around 1890, and a few really modern results. The early values[13] include determinations on all eight substances by Stohmann and his collaborators and a few results by Luginin and by Berthelot. Today it is practically impossible to translate these early data over to our modern standards. As published, they tend to run higher than our present results by amounts ranging up to 1.4%.

Coming to the modern data, where it is possible to put the heats of combustion on a better comparative basis with our new values, we find that Beckers'[14] results for cetyl alcohol and anthracene differ from ours by only −0.05 and +0.02%, respectively, the values of Verkade and Coops[15] for phthalic acid and phthalic anhydride exceed ours by 0.02 and 0.51%, and that of Swietoslawski[15] for phthalic anhydride is 0.04% above our result. In the case of stilbene Roth's value[13] exceeds the present result by 0.17%, that of Berner[16] by 0.07%. For phenanthrene other recent values[17] differ from that given here by −0.06 and +0.45%, and correspondingly for anthracene by +0.03 and +0.17%. For triphenylbenzene Professor Huffman at the California Institute of Technology has kindly made a pair of determinations on our original material with his own calorimetric apparatus. His mean result is 0.02% above that reported in this paper.

(13) Landolt–Börnstein–Roth–Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 1587.

(14) Beckers, *Bull. soc. chim. Belg.*, **40**, 518 (1931).

(15) Verkade and Coops, *Rec. trav. chim.*, **47**, 606 (1928).

(16) Berner, *Arch. Math. Naturvidenskab*, **39**, No. 6 (1926).

(17) Milone and Rossignoli, *Gazz. chim. ital.*, **62**, 644 (1932); Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935).

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Summary

1. A bomb calorimeter has been calibrated and then used for precise measurements of the heats of combustion of the following eleven substances at 25° and constant volume: β-methylnaphthalene, phthalic anhydride, phthalic acid, anthracene, phenanthrene, stilbene, pyrene, *n*-hexadecane, cetyl alcohol, triphenylbenzene and polyisobutylene.

2. From these experimental results the corresponding heats of combustion and heats of formation at constant pressure have been calculated.

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Raman Spectra of Acetylenes. II. Displacements and Depolarization Factors for Phenylacetylene and Derivatives of the Type $C_6H_5C{\equiv}CR$[1]

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As was indicated in the first paper of this series[2] (subsequently referred to as I) the line near 2200 cm.$^{-1}$ in disubstituted acetylenes is not single, but is split into two or more parts. To explain this doubling, Gredy[3] postulates the co-existence of two molecular forms each of which gives its own characteristic frequency. Kohlrausch, Pongratz and Seka[4] give some support to this hypothesis by the statement that more than one frequency, if only one molecular form is present, is difficult to understand. Badger[5] attributes the splitting to a Fermi resonance interaction between the fundamental in this region and an overtone of a frequency near 750 or 1100 cm.$^{-1}$, the latter of which should not appear in the Raman spectra. Glockler and Davis[6] accounted for the two lines in dimethylacetylene by supposing that one is due to a symmetrical, the other to an asymmetrical, vibration. If this is true for disubstituted acetylenes in general, the two frequencies in this region should have strikingly

(1) Much of the experimental work discussed in this paper was carried out at Lynchburg College.

(2) M. J. Murray and Forrest F. Cleveland, THIS JOURNAL, **60**, 2664 (1938).

(3) Blanche Gredy, Thèses, Paris, 1935.

(4) K. W. F. Kohlrausch, A. Pongratz and R. Seka, *Sitzber. Akad. Wiss. Wien.*, Abt. IIb, **146**, 218 (1937).

(5) R. M. Badger, *J. Chem. Phys.*, **5**, 178 (1937).

(6) G. Glockler and H. W. Davis, *ibid.*, **2**, 881 (1934).