Discussion

The values in Table I are slightly higher than the average of previously reported data. Our data also show a small, but persistent, difference in the solubilities of the samples. The larger solubility of samples 3 and 4 is most likely due to the more perfect development of these crystals resulting from the slower rate of precipitation used in their preparation.

Considering the temperature difference the data of Table II are in good agreement with those of Huybrechts and Ramelot[2b] and Pleissner.[3]

Acknowledgment.—The authors wish to express their sincere gratitude to Mr. Mathew J. Kelly, who did practically all the necessary machine work in the construction of the apparatus.

Summary

1. Using large volumes of solvent and four different samples the solubility of lead sulfate in water at 20° has been found to be 43.5 ± 0.1 mg. per liter.

2. Data have been obtained for the solubility of lead sulfate in dilute sulfuric acid solutions at 20°.

[3] Pleissner, *Arb. Kais. Gesundheitsamt*, **26**, 384 (1907).

ELKINS, WEST VIRGINIA

RECEIVED APRIL 10, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE INSTITUTE OF PHYSICAL CHEMISTRY OF THE TECHNISCHE HOCHSCHULE OF BRAUNSCHWEIG]

Thermal Data on Organic Compounds. XII. The Heats of Combustion of Nine Hydrocarbons

BY HILDEGARD BANSE AND GEORGE S. PARKS[1]

In the calculation of the free energy of formation of an organic compound by means of the third law of thermodynamics and the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$, the heat of combustion of the compound in question enters as a very important quantity. In fact, at the present time it is frequently the most serious source of error in the resulting free energy value, as most of the available combustion data for organic compounds were determined prior to 1900 at a time when calorimetric methods and the purification of such substances had not reached so high a standard as at present. For this reason there is now a very urgent need for new combustion determinations on organic compounds.

In this paper we shall present combustion values which we have recently obtained for the following nine hydrocarbons: diisobutylene, *n*-octane, *n*-dodecane, durene, isodurene, prehnitene, pentamethylbenzene, hexamethylbenzene and dibenzyl.

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Materials

Diisobutylene.—This sample was from the material prepared for the specific heat measurements of Parks and Huffman[2] by Dr. H. E. Buc of the Standard Oil Development Company. As the recent studies of Whitmore[3] and his collaborators indicate, it was probably a mixture of two closely related olefin isomers but for the present measurements this fact is relatively unimportant because without doubt such isomers have practically identical heats of combustion.

***n*-Octane and *n*-Dodecane.**—These samples constituted part of the extremely pure materials prepared by Shepard, Henne and Midgley, and for a full description of their preparation and properties the reader is referred to the recent paper[4] by these investigators.

Durene, Isodurene, Prehnitene, Pentamethylbenzene and Hexamethylbenzene.—These five hydrocarbons were kindly given to us by Professor Lee Irvin Smith of the University of Minnesota. Details concerning them will not be given here, as their preparation and properties have been fully described elsewhere.[5] It is sufficient for us to say in this connection that all of these materials were of extremely satisfactory purity for our measurements.

Dibenzyl.—The dibenzyl was carefully prepared for us by Mr. John D. Ferry. C. P. material, obtained from the Eastman Kodak Company, was subjected to four fractional crystallizations from ethyl alcohol. The final product, freed of alcohol and dried over phosphorus pentoxide, melted at 51.3°.

Experimental Results

The heats of combustion of these nine hydrocarbons were determined by burning them in a platinum-lined bomb at an oxygen pressure of 35 atmospheres. The bomb was immersed in a non-adiabatic water calorimeter, and the temperature rise during the combustion was measured by means of a calibrated Beckmann thermometer. The complete apparatus, the details of experimental procedure and the calculation of the results have been fully described by Roth and his collaborators in other places.[6]

The samples of crystalline substances (durene, pentamethylbenzene, hexamethylbenzene and dibenzyl) were placed in the platinum combustion crucible in the form of pellets or, in a few determinations, as a fused solid formed by a preliminary melting of a mass of small crystals in the bottom of the crucible. In no cases did the volatility of these solids constitute a serious problem. On the other hand, the samples of the liquid hydrocarbons, with the exception of the first determination on diisobutylene, were always placed directly in the combustion crucible and this was then covered with a lid of "cellon" (*i. e.*, heavy cellophane) to prevent evaporation prior to ignition.[7] In the case of diisobutylene the first determination was made upon a liquid sample contained in a small glass bulb, which was broken in ignition by the burning of an external, auxiliary sample of vaseline.

The various experimental values for the heats of combustion per gram (weighed in air) of the nine hydrocarbons are given in Table I. These are based upon the calorimetric standard of Professor Roth's laboratory:[8]

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(2) Parks and Huffman, THIS JOURNAL, **52**, 4381 (1930).

(3) Whitmore and Church, *ibid.*, **54**, 3710 (1932).

(4) Shepard, Henne and Midgley, *ibid.*, **53**, 1948 (1931).

(5) Smith and Lux, *ibid.*, **51**, 2994 (1929); Smith and MacDougall, *ibid.*, **51**, 3001 (1929).

(6) (a) Abderhalden, "Handbuch der biologischen Arbeitsmethoden," Urban and Schwarzenberg, Vienna, 1928, Abt. II-2, pp. 1645–1690; (b) Roth, "Physikalisch-chemische Übungen," Leopold Voss, Leipzig, 1928, pp. 71–77 and 86–94; (c) Roth, "Thermochemie" (Sammlung Göschen), de Gruyter and Co., Berlin, 1932, pp. 22–31 and 72–87.

(7) Roth and Wallasch, *Ann.*, **407**, 134 (1915).

(8) Roth, Doepke and Banse, *Z. physik. Chem.*, **133**, 431 (1928).

TABLE I

EXPERIMENTAL COMBUSTION VALUES AT CONSTANT VOLUME AND 19°

(In 15°-calories per gram of substance, weighed in air)

Substance	1st result	2d result	3d result	4th result	Final mean
Diisobutylene	11,298	11,280	(11,257)	11,288	11,289
n-Octane	11,448	11,468	11,435	....	11,450
Durene	10,344	10,346	10,352	....	10,347
Isodurene	10,363	10,355	10,355	....	10,358
Prehnitene	10,379	10,377	10,385	....	10,380
Pentamethylbenzene	10,441	10,444	10,440	....	10,442
Hexamethylbenzene	(10,485)	10,511	10,513	10,506	10,510
n-Dodecane	11,339	11,367	11,350	11,343	11,350
Dibenzyl	9,928	(9,907)	9,922	9,920	9,923

6323 15°-calories for the combustion of one gram of benzoic acid (weighed in air). For each substance at least three concordant determinations were made, and the mean of these appears in the last column. The occasional determinations which involved the production of appreciable carbon, or other evidence of incomplete combustion, have been entirely omitted in the preparation of this table. A few other determinations (those inclosed in parentheses) proved to be somewhat low and discordant and these have also been dropped from consideration on the presumption of incomplete combustion. In view of the accuracy of the measurements and the unusual purity of the materials, it then seems safe to conclude that the error in these final mean values is less than 0.1% in all cases, except possibly that of *n*-octane.

TABLE II

DERIVED COMBUSTION DATA AT 19°

(The 15°-cal. is used throughout and all weights have been reduced to a vacuum basis)

Formula	Substance	Molecular weight	Standardized heat of combustion per gram	Heat of combustion per mole at constant volume	Heat of combustion per mole at constant pressure
C_8H_{16}	Diisobutylene (l)	112.13	11,273	1,264,100	1,266,400
C_8H_{18}	*n*-Octane (l)	114.14	11,434	1,305,100	1,307,700
$C_{10}H_{14}$	Durene (s)	134.11	10,337	1,386,300	1,388,300
$C_{10}H_{14}$	Isodurene (l)	134.11	10,348	1,387,800	1,389,800
$C_{10}H_{14}$	Prehnitene (l)	134.11	10,370	1,390,700	1,392,800
$C_{11}H_{16}$	Pentamethylbenzene (s)	148.13	10,432	1,545,300	1,547,600
$C_{12}H_{18}$	Hexamethylbenzene (s)	162.14	10,500	1,702,500	1,705,100
$C_{12}H_{26}$	*n*-Dodecane (l)	170.21	11,335	1,929,300	1,933,100
$C_{14}H_{14}$	Dibenzyl (s)	182.11	9,914	1,805,400	1,807,400

Some important derived data are presented in Table II. Column 4 contains our mean combustion values per gram, calculated for weighings in vacuum and referred to the "international" calorimetric standard.[9] The product of these values and the corresponding molecular weights

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(9) The so-called international calorimetric standard is based upon a value of 6324 15°-calories for the combustion, at constant volume, of one gram of benzoic acid (weighed in air). This value is only 0.016% higher than that (6323) recently suggested by Roth as the most probable one for benzoic acid.

(Column 3) next yields the molal heats of combustion at constant volume, as given in the fifth column. From these last data the corresponding molal heats of combustion at constant pressure may be readily calculated.

Except in the case of *n*-octane, the literature[10] contains only meager combustion data for comparison with our present results. For *n*-octane our value is only 0.01% above the earlier one reported by Roth but about 0.53% above that of Richards and Jesse. It is also 0.20% higher than a recent unpublished result obtained at the United States Bureau of Standards.[11] In the early days of combustion calorimetry Stohmann and his collaborators made determinations upon durene, pentamethylbenzene, hexamethylbenzene and dibenzyl. These results are higher than ours by 0.39, 0.41, 0.41 and 0.18%, respectively. On the other hand, Malbot's determination for diisobutylene, made in 1889, is fully 1.1% below the value reported in Table II.

In passing, two features of our data in Table II are worthy of brief notice. The first pertains to the effect of a CH_2 increment. The difference between the molal heats at constant pressure for *n*-dodecane and *n*-octane is 625,400 or 156,350 cal. per CH_2 increment. This result agrees remarkably well with that (156,300) obtained recently by Verkade[12] and his collaborators in their extensive studies of the heats of combustion of various series of normal aliphatic compounds.

The second feature concerns the relations of the three tetramethylbenzenes. Of course durene (1,2,4,5-methyl) is a solid at room temperature, but from the recent study of Ferry and Thomas[13] we estimate that its molal heat of fusion at 19° is about 4700 cal. Hence, adding this quantity to the experimental value given in Table II, we find 1,393,000 cal. for the heat of combustion (at constant pressure) of the hypothetical liquid durene. This value is only 0.02% above that found for prehnitene (1,2,3,4) and 0.23% above that found for isodurene (1,2,3,5). Thus it is apparent that the heats of combustion of these position isomers are practically identical within the limits of experimental error.

Before concluding, we desire to thank Professor Walther A. Roth, in whose laboratory these measurements have been made, for his encouragement and valuable advice throughout the course of our investigation.

Summary

Accurate values have been obtained for the heats of combustion of nine hydrocarbons.

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RECEIVED APRIL 17, 1933
PUBLISHED AUGUST 5, 1933

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[10] Landolt–Börnstein–Roth–Scheel, "Tabellen," Julius Springer, Berlin, 1923, pp. 1288–1290.

[11] Private communication to the authors by Dr. Graham Edgar of the Ethyl Gasoline Corporation.

[12] Verkade and Coops, *Rec. trav. chim.*, **46**, 911 (1927); Verkade, Coops and Hartman, *ibid.*, **45**, 585 (1926).

[13] Ferry and Thomas, *J. Phys. Chem.*, **37**, 253 (1933).