[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Heats of Combustion and of Formation of the Nine Isomeric Heptanes in the Liquid State

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While there exist in the literature reliable values for the heats of combustion and of formation of all the *n*-alkanes including *n*-dodecane,[2] and a few still higher,[3] the corresponding quantities for the branched isomers have until recently been unavailable. Precise values for isobutane and for the pentanes have been reported by Rossini, and by Knowlton and Rossini,[4] and for the isomeric hexanes the energies of isomerization are now available.[5] The data obtained for the hexanes indicated the desirability of further information to be obtained from compounds of increasingly complex structure.

In 1938, through the coöperation of the Standard Oil Company of California, specially prepared synthetic specimens of the eight branched heptanes were made available to this Laboratory for measurements of their heats of combustion. The results of this work are presented here.

Experimental

Materials.—The series of eight branched-chain heptanes was prepared synthetically by the Research and Development Department of the Standard Oil Company of California, essentially by the method of Edgar, Calingaert and Marker.[6] The final steps in the preparation of each involved refluxing over sodium followed by fractionation through a column having the efficiency of thirty-eight theoretical plates.

Two samples of the *n*-heptane were used. One was obtained from the Eastman Kodak Company and purified in this Laboratory by prolonged shaking with concentrated sulfuric acid, washing, drying, refluxing over sodium-potassium alloy, followed by fractionation. The other was kindly supplied to us by the National Bureau of Standards as was also a sample of 2,2,3-trimethylbutane, for purposes of comparison. In addition one sample of 3,3-dimethylpentane was made available through the courtesy of Dr. George Calingaert of the Ethyl Gasoline Corporation. This latter compound as received showed evidence of containing a small trace of unsaturated material and was subjected to the same purification as the *n*-heptane described above.

The physical properties shown by these compounds as they were used for combustions are recorded in tabular form. The refractive indices were read on a Pulfrich refractometer and the boiling points determined in an apparatus like that designed by Mair,[7] with the use of a Pt-resistance thermometer calibrated by the National Bureau of Standards. Small pressure corrections were obtained from the work of Shepard, Henne and Midgley.[8] Excellent agreement was observed between the constants as determined by us and those most recently reported for *n*-heptane and 2,2,3-trimethylbutane by the National Bureau of Standards.[2,9]

Apparatus.—The precision adiabatic calorimeter has been described previously.[10] It was calibrated by measuring the heat developed in the combustion of benzoic acid (Std. sample 39e Natl. Bureau of Standards).

The average of seven runs gave a calorimeter constant of 2607.3 cal. deg.$^{-1}$ with an arithmetical mean deviation of ±0.22, a maximum deviation of 0.40, and a standard deviation of ±0.11.[11] No allowance was made here for the uncertainty in the value assigned to the standard benzoic acid. The energy unit used is the arbitrary calorie obtained by multiplying the international joule by the factor 4.1833.

Procedure.—The samples were contained in thin, flattened glass ampoules and were ignited by the use of iron wire.

The weight of hydrocarbon taken varied from 0.40–0.60 g. It was not feasible to flush the bomb repeatedly with oxygen, due to breakage of the ampoules, hence the nitric acid correction ranged variously between 1.5–10.0 calories.

The ampoules were filled by repeated evacuation, hence the samples contained only a small amount of air, less than the equilibrium amount. The construction of the bomb used, a Parr double-valve model, unfortunately precluded the use of the most desirable technique in which the amount of substance burned is determined by the weight of combustion products rather than the weight of the original sample.

The stock samples from which the ampoules were filled were kept over sodium or sodium-potassium alloy. In a few instances attempts were made to dry them further with phosphorus pentoxide. Several samples were dehydrated by cooling to the temperature of solid carbon dioxide and filtering through glass wool in a closed glass system. Samples of the same hydrocarbon treated by these different methods gave combustion values which

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[2] R. S. Jessup, *J. Research Natl. Bur. Standards*, **18**, 115 (1937); Rossini, *ibid.*, **6**, 37 (1931); **7**, 329 (1931); **12**, 735 (1934).

[3] Richardson and Parks, THIS JOURNAL, **61**, 3543 (1939).

[4] Rossini, *J. Research Natl. Bur. Standards*, **15**, 357 (1935); Knowlton and Rossini, *ibid.*, **22**, 415 (1939).

[5] Rossini and Prosen, THIS JOURNAL, **62**, 2250 (1940).

[6] Edgar, Calingaert and Marker, *ibid.*, **51**, 1483 (1929).

[7] Mair, *J. Research Natl. Bur. Standards*, **9**, 457 (1932).

[8] Shepard, Henne and Midgley, THIS JOURNAL, **53**, 1948 (1931).

[9] Smith, *J. Research Natl. Bur. Standards*, **26**, 129 (1941).

[10] Hughes, Corruccini and Gilbert, THIS JOURNAL, **61**, 2639 (1939).

[11] Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

TABLE I

THERMOCHEMICAL DATA FOR THE ISOMERIC HEPTANES AT 25° IN THE LIQUID STATE

Compound	B. p., °C. (corr.)	n^{20}_{D}	$-\Delta U_B/m$, cal. g.$^{-1}$	$-\Delta H_R$, kcal. mole^{-1}	Relative energy cont. E^0 (isomer)-E^0 (*n*-heptane) liq., cal./mole	Molal heat of formation $-\Delta H_{f298}$
n-Heptane (E. K. Co.)	98.45	1.38772	11463.8 ± 1.6[e]			
n-Heptane (Bur. Stds.)	98.42	1.38764	11464.0 ± 1.7	1150.77	0	−53,987
3-Ethylpentane	93.37	1.39327	11462.1 ± 1.0	1150.57	− 190	−54,178
2-Methylhexane	90.08	1.38478	11451.5 ± 1.0	1149.51	−1250	−55,239
3-Methylhexane[a]	91.96	1.38857	11458.8 ± 2.7	1150.25	− 520	−54,410
3-Methylhexane[b]			11447.2 ± 1.0			
2,3-Dimethylpentane	89.78	1.39202	11447.0 ± 0.3	1149.06	−1700	−55,690
2,4-Dimethylpentane	90.49	1.38167	11434.2 ± 0.7	1147.78	−2985	−56,972
2,2-Dimethylpentane	79.25	1.38209	11425.0 ± 0.9	1146.86	−3910	−57,894
3,3-Dimethylpentane	85.97	1.39094	11408.9 ± 0.7			
3,3-Dimethylpentane (Ethyl Gas Corp.)	85.85	1.39094	11433.8 ± 0.8	1147.74	−3025	−57,013
2,2,3-Trimethylbutane (St. Oil)[c]			11431.9 ± 1.7			
2,2,3-Trimethylbutane (St. Oil)[d]	80.91	1.38939	11421.0 ± 0.8			
2,2,3-Trimethylbutane (Bur. Stds.)	80.88	1.38947	11436.1 ± 1.2	1147.97	−2800	−56,783

[a] Measurements made 1939 by Albert Hughes, S. O. Fellow 1938–39. [b] Measurements made 1940 by George F. Davies. [c] Measurements made 1940 (July). [d] Measurements made 1940 (Nov.). [e] Arithmetical deviation from the mean.

could not be statistically differentiated. Standard conditions were maintained in the bomb as recommended by Washburn,[12] as to oxygen pressure (30 atm.) and volume of water added (1 ml.). The starting temperature was in each case 25° and the energy change of the isothermal process was calculated from the temperature rise and heat capacity of the products. Any run showing evidence of carbon formation was rejected. In a number of runs the combustion products were tested for the presence of carbon monoxide with negative results.

Molecular weights were calculated on the basis of the 1941 table of atomic weights.

Results and Discussion

Summarized results for the series are shown in Table I. Good agreement is shown between the purified Eastman Kodak Company sample and that from the Bureau of Standards. The mean value for this compound agrees very well with that obtained by Jessup.[2] The final results are recorded in each case as $-\Delta U_B/m$, cal. g.$^{-1}$, which is the isothermal heat of the bomb reaction using Washburn's notation,[12] and $-\Delta H_R$, kcal. mole^{-1}, which is the isothermal heat of combustion per mole of liquid hydrocarbon at 25° at constant pressure, all reactants and products being at the standard pressure of 1 atmosphere. For changing the conditions from those of the bomb reaction to the standard state at constant volume a correction of −0.026% was used.

From the values for $-\Delta H_R$, the molal heat of formation of each heptane may be found by introducing the heat of formation of carbon dioxide gas (−94,029.9 cal./mole at 25°) and for liquid water (−68,318.1 cal./mole).[13] The energies of isomerization may also be obtained directly from the heats of combustion, and are shown in the table. Acceptance of the heats of combustion as they stand leads to a probable deviation in these energies of ± 200–300 cal., but this is perhaps too optimistic. They are in reasonable accord with similar quantities calculated for the hexanes.[5]

Detailed calculations of free energy or exhaustive conclusions concerning energy relationships are hampered by discrepant data obtained for three of the isomers. In 1939 upon receipt of the 3-methylhexane from the donor laboratory a heat of combustion of 11,458.8 ± 2.7 cal./g. was obtained by Albert Hughes. Approximately a year later repetition gave a value with less deviation approximately 10 cal. lower (Notes *a* and *b*, Table I). Similarly the 2,2,3-trimethylbutane gave a value about 10 cal. lower than it had five months earlier. This behavior was not observed in any of the other isomers and indicated the possibility of contamination subsequent to receipt by us, or absorption of water. Efforts to remove water which might have caused the lowering brought no change in the heat of combustion.

In the case of the latter compound a check sample was very kindly furnished by the National Bureau of Standards, for which values are reported in the table. While there is no quantitative evi-

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

(13) Rossini, *ibid.*, **22**, 407 (1939).

dence to support it, belief is held that the higher values obtained on the samples just after their receipt may reasonably be selected as more representative, and weighted preference be given them.

The results obtained on the original 3,3-dimethylpentane were seriously out of line. The b. p. was somewhat high, also. Another sample of this compound was obtained from the Ethyl Gasoline Corporation. This sample as received showed the presence of traces of unsaturated material. It was subjected to rigorous purification but final fractionation was carried out in a different still from that used for the other isomers. The results are therefore not strictly comparable.

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Special thanks are due Dr. F. D. Rossini of the Bureau of Standards for assistance without which the project could not have been completed.

Summary

1. Isothermal heats of combustion at 25° have been reported for the nine isomeric heptanes.
2. From these are calculated the energies of isomerization for the heptanes in liquid form.
3. The heats of formation at 25° have been calculated and tabulated.

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Current-Voltage Curves of Mercurous and Mercuric Salts at the Dropping Mercury Electrode

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It is claimed[2] that the concentration of dissolved mercury salts cannot be determined polarographically. In the present paper it is shown that the concentration of both mercurous and mercuric salts can be determined with the dropping electrode, while a few experiments revealed that these salts yield well-defined diffusion currents at a platinum micro-wire electrode. It was of interest to subject the various current–voltage (c. v.) curves to a physico-chemical analysis. When in equilibrium with the surrounding mercurous ion solution the potential of a mercury electrode is given by

$$\pi = C + RT/2F \ln [\mathrm{Hg_2}]_0^{++} \qquad (1)$$

in which the subscript zero denotes the concentration (or better the activity) of the mercurous ions at the surface of the dropping electrode. The equation of the polarographic wave then should be given by[3]

$$\pi = \pi_0 + RT/2F \ln (i_d - i) \qquad (2)$$

i_d denoting the diffusion current of the mercurous ions.

When a solution of a mercuric salt is electrolyzed at the dropping electrode, the interaction between mercury and the mercuric ions has to be considered

$$\mathrm{Hg} + \mathrm{Hg^{++}} \rightleftarrows \mathrm{Hg_2^{++}} \qquad (3)$$

The equilibrium constant of this reaction $[\mathrm{Hg_2^{++}}]/[\mathrm{Hg^{++}}] = K$ was first determined by Ogg,[4] who shook solutions of mercuric nitrate with mercury until equilibrium was attained. He reported an average value for K of 120. Carter and Robinson[5] determined the oxidation potential of mercurous–mercuric perchlorate solutions at a platinum electrode. From the value obtained and the normal potential of the mercury–mercurous ion electrode they calculated a value of K of 81. In the experimental part it is shown that equilibrium between mercury and mercuric ions (eq. 3) is established very rapidly at the dropping electrode. Consequently, the c. v. curve of a mercuric salt (strong electrolyte) should practically coincide with that of an equimolecular mer-

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(1) From the experimental part of a thesis submitted by C. S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the Doctor's degree (1940).

(2) H. Hohn, "Chemische Analysen mit dem Polarographen," Julius Springer, Berlin, 1937.

(3) Comp. I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

(4) A. Ogg, *Z. physik. Chem.*, **27**, 293 (1898).

(5) S. R. Carter and R. Robinson, *J. Chem. Soc.*, 207 (1927).