[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XX. Modern Combustion Data for Two Methylnonanes, Methyl Ethyl Ketone, Thiophene and Six Cycloparaffins

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In a continuation of the thermochemical studies initiated by Richardson and Parks[2] in this Laboratory, we have recently measured very accurately the heats of combustion of 2-methylnonane, 5-methylnonane, methyl ethyl ketone, thiophene, and six cycloparaffins, *viz.*, methylcyclopentane, ethylcyclopentane, cyclohexane, methylcyclohexane, *n*-heptylcyclohexane and *n*-dodecylcyclohexane. These thermochemical results will be summarized in the present paper. In subsequent publications they will be combined with the proper entropy data to yield values for the free energies of the several compounds.

Apparatus and Method

The apparatus and general method were essentially the same as in the previous study of Richardson and Parks. Three cylinders of oxygen were used in this investigation and with each a new series of calibrations of the calorimeter, involving five to eight combustions, was carried out with standard benzoic acid (sample 39e) supplied by the United States Bureau of Standards. For the "standard" conditions of our calorimeter the three series of calibrations yielded the mean results 3211.4 (±0.2) cal., 3211.2 (±0.5) cal., and 3211.3 (±0.2) cal. for the energy equivalent per degree at 25.0°. These values are in excellent agreement with the result (3211.3 ± 0.4 cal.) reported previously.

The combustions were made with the bomb filled with oxygen to a pressure of 30 atm. at 23° and, except in the case of thiophene, with 1 ml. of water initially in the bomb. In general, most of the air originally in the bomb was washed out by two preliminary fillings with oxygen to a pressure of 5 atm. and thus the correction for nitric acid formation was kept down to about 1 calorie in a total of approximately 6000 calories.

In the case of thiophene, however, this washing out was omitted because we found that the air originally in the bomb was very essential as a catalyst for the complete oxidation of the sulfur to sulfuric acid. After each combustion of this substance we analyzed for both nitric acid and nitrous acid and corrected for the small heat effects of these according to the procedure of Huffman and Ellis.[3] In this work with thiophene appropriate corrections were also made on the standard energy equivalent of our calorimetric system (a) for the omission of the 1 ml. of water usually placed within the bomb, (b) for the absence of any vaporization of this water during the average temperature rise of 2°, and (c) for the small amount of water vapor condensed from the air initially in the bomb by the sulfuric acid produced. The sulfuric acid corresponded approximately to the concentration $H_2SO_4 \cdot 1.70H_2O$ and hence for comparative purposes our experimental combustions were always corrected to this exact composition by means of Table III in the paper of Huffman and Ellis.

Because of their volatility all these compounds, save the dodecylcyclohexane, were sealed into thin-walled capsules of soft glass, which in general had volumes of 0.5 to 0.8 ml. and weighed 0.065 to 0.085 g. empty. These capsules were flattened or collapsed on opposite sides so that, when practically filled with the sample to be burned, they would withstand the deformation produced by the oxygen pressure within the bomb. The capsules were made so light because it was found that when they weighed more than 0.100 g. they tended to explode on ignition and the liquid therein was thrown about the bomb with incomplete combustion as a result. Under our conditions the thin glass fused quietly to allow smooth combustion from the liquid surface. As a "promoter" in these combustions about 0.02 g. of *n*-hexadecane was placed within the combustion crucible and always in part on an upturned flat side of the glass capsule so that the ignition took place mainly from above. Hexadecane was chosen for this purpose because of its very small volatility at room temperature and its high, precisely known heat of combustion (11,283 cal. $g.^{-1}$ in air[2]). Its preliminary ignition was always accomplished with the platinum wire and cotton string system described by Richardson and Parks.

Units.—The unit of energy used 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. The molecular weights are based on the 1939 table of atomic weights.[4]

Materials

The various substances studied had been prepared and purified with great care and were exceptionally high grade. After due allowance is made for the effect of dissolved air in these liquids, the impurities, except possibly in the case of the heptylcyclohexane, should produce no error in the combustion results greater than 0.01%.

Methylnonanes.—The samples of 2-methylnonane and 5-methylnonane were prepared in the Research Laboratory of the Ethyl Gasoline Corporation. Their preparation and properties have been fully described by Calingaert and Soroos.[5]

***n*-Heptylcyclohexane and *n*-Dodecylcyclohexane.**—These substances were prepared in the Chemical Laboratory of Stanford University by Dr. Simon Kinsman, working with Prof. C. R. Noller. The preparations were made

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[1] Du Pont Fellow, 1939–1940.

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

[3] Huffman and Ellis, *ibid.*, **57**, 41 (1935).

[4] Baxter, Guichard, Hönigschmid and Whytlaw-Gray, **61**, 223 (1939).

[5] Calingaert and Soroos, *ibid.*, **58**, 635 (1936).

from highly purified intermediates by Grignard syntheses, followed by careful drying and fractional distillations under reduced pressure. Part of these samples were first used in heat capacity measurements at low temperatures and in this connection their fusion behavior was carefully noted.

The *n*-dodecylcyclohexane melted sharply at 12.5° and from its fusion curve we have estimated its purity at 98.8 mole %. Undoubtedly the remaining 1.2% represents for the most part closely related hydrocarbons which produce no appreciable error in the heat of combustion. The *n*-heptylcyclohexane melted at −41.2° but with considerable premelting. Our estimate of its purity was 97.1 mole %. In view of this rather low figure the material was carefully tested for impurities, such as halogens, which might produce an appreciable error in our combustion value. These tests indicated not more than 0.003% chlorine (by weight). Moreover, microanalyses on these two compounds yielded results for carbon and hydrogen corresponding to the theoretical compositions within the limits of experimental error (about 0.1%).

Methyl Ethyl Ketone.—This material was specially prepared for our low temperature specific heat measurements by the Shell Development Company. The fusion behavior indicated a purity of 99.74 mole %. As several months elapsed after our specific heat studies, we again dried and redistilled this material in two batches, just before the combustions, using as drying agents calcium sulfate and calcium oxide, respectively. These two samples yielded identical combustion results within the limits of experimental error.

Methylcyclopentane, Ethylcyclopentane, Cyclohexane, Methylcyclohexane and Thiophene.—All five compounds were specially prepared for this study in the Research Laboratory of the Shell Development Co. Three purity requirements were set up for these preparations: first, that the sample should be free of any elements not present in the molecular formula of the compound; second, that its only permissible impurities should be isomers or closely related homologs; and third, that its absolute purity should be greater than 98 mole %. Careful syntheses and extensive chemical purifications were relied on to meet these first and second requirements and repeated fractional distillations in a Podbielniak column to meet the third. The final criterion of purity adopted was that all portions of the distillate, on refractionation of a "pure" sample, should be of the same refractive index (within ±0.00003) as the charge to the still.

In the case of the ethylcyclopentane three different syntheses were employed before all these requirements were completely met. The second of these preparations, however, contained only 0.012% chlorine and we made a number of combustions with this as well as with the "pure" third sample. Counting this small chlorine content as inert material, we obtained practically identical heats of combustion for these two samples.

For cyclohexane three fractional crystallizations were employed in addition to the foregoing purification methods. The final product melted very sharply at 6.35°.

Table I contains the refractive indices and densities at 20° of the "pure" samples of these five compounds.

TABLE I

REFRACTIVE INDICES AND DENSITIES

Substance	n^{20}_D	d^{20}_4
Methylcyclopentane	1.4095	0.7482
Ethylcyclopentane	1.4196	.7665
Cyclohexane	1.4262	.7785
Methylcyclohexane	1.4230	.7694
Thiophene	1.5283	1.0638

The Heats of Combustion and Derived Data

After considerable preliminary work on the method of burning with the glass capsules, about sixty precise combustion determinations were made upon these ten compounds. These combustions ordinarily involved gaseous carbon dioxide and liquid water as end-products but in the special case of thiophene the water was replaced by sulfuric acid at the concentration $H_2SO_4 \cdot 1.7H_2O$.

Table II contains a summary of our experimental combustion data together with some important thermal data calculated therefrom. The number of combustions made on each particular compound is given in the fifth column. The resulting mean values for the energy evolved in the isothermal bomb process per g. at 25.0°, represented by the term $-\Delta U_B/m$, and the mean deviations of the individual combustions from these mean values, represented by 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.[6] The energy evolved in this hypothetical standard process is designated in the table 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, $-\Delta H_f^\circ$, the heat of formation of the compounds from the elements (gaseous hydrogen, graphitic carbon and rhombic sulfur) was then calculated from $-\Delta H_R$ by use of 68,318 cal.[7] and 94,030 cal.[8] for the heats of formation of water and carbon dioxide, respectively, and in the case of thiophene by the value $\Delta H = -135{,}010$ cal.[3] for the process

$$S(\text{rhombic}) + 2.7H_2O(l) + 3/2O_2(g) = H_2SO_4 \cdot 1.7H_2O \quad (1)$$

In the calculation of the quantity $-\Delta U_R$ from the tabulated $-\Delta U_B/m$ values a correction of +0.02% was made in all cases for the air dis-

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

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

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

TABLE II

SUMMARY OF EXPERIMENTAL AND DERIVED DATA

All substances are liquid and all weights are reduced to a vacuum basis

Substance	Formula	Mol. wt.	Density	No. of combns.	$-\Delta U_B/m$ and Δ cal. g.$^{-1}$	$-\Delta U_R$ kcal. mole^{-1}	$-\Delta H_R$ kcal. mole^{-1}	$-\Delta H_f^\circ$ kcal. mole^{-1}
2-Methylnonane	$C_{10}H_{22}$	142.278	0.725	5	11,344.6±2.4	1614.00±0.56	1617.26	74.54
5-Methylnonane	$C_{10}H_{22}$	142.278	.729	5	11,347.9±1.8	1614.46±0.38	1617.72	74.08
Methylcyclopentane	C_6H_{12}	84.157	.745	6	11,153.8±3.3	938.58±0.40	940.36	33.73
Ethylcyclopentane	C_7H_{14}	98.183	.763	10	11,147.6±2.7	1094.40±0.37	1096.47	39.97
Cyclohexane	C_6H_{12}	84.157	.775	5	11,106.8±1.5	934.62±0.31	936.40	37.69
Methylcyclohexane	C_7H_{14}	98.183	.766	5	11,086.0±2.9	1088.35±0.45	1090.42	46.02
n-Heptylcyclohexane	$C_{13}H_{26}$	182.341	.810	5	11,088.6±0.8	2021.71±0.55	2025.56	84.96
n-Dodecylcyclohexane	$C_{18}H_{36}$	252.472	.822	5	11,108.5±1.7	2804.30±0.84	2809.63	112.63
Methyl ethyl ketone	C_4H_8O	72.105	.805	9	8,068.6±2.3[a]	581.70±0.20	582.59	66.80
Thiophene	C_4H_4S	84.132	1.060	3	7,915.1±2.5	665.91±0.60	667.39	−19.62

[a] This is the mean of the six combustions made on the unboiled samples.

solved in the liquid sample when weighed. This is the correction worked out from the available solubility data by Richardson and Parks to allow for the air dissolved in other liquid hydrocarbons. Whether the same figure should be applied to methyl ethyl ketone, which is considerably more polar, seemed perhaps questionable. Accordingly, we first made six combustions on the two preparations of this substance containing dissolved air and then three more combustions on samples of the same materials which, just prior to weighing, had been boiled under reduced pressure. For $-\Delta U_B/m$ the mean value for these first six combustions, corrected by +0.02%, was 8070.2 (±2.3) cal., while the last three air-free samples yielded a mean of 8071.1 (±0.9) cal. This agreement is highly satisfactory, and therefore we have used 8070.6 cal. as a final mean for this substance in computing $-\Delta U_R$.

The uncertainties attached to the tabulated values of $-\Delta U_R$ have been calculated by use of the "precision error" described by Rossini.[9] This includes not only the "reaction error" for the combustion of the particular compound but also our "calibration error" averaging 0.014%, an "assigned error" of 0.023% on the standardizing substance, and an arbitrary allowance for a 10% uncertainty in the Washburn correction.

Previous Work.—The literature contains no earlier combustion values for five of these compounds. Zubow made determinations on methylcyclopentane, cyclohexane, methylcyclohexane and methyl ethyl ketone. His values, as revised by Swietoslawski,[10] differ from our present data by −0.23%, +0.01%, +0.16% and −0.04%, respectively. More modern combustion results for cyclohexane, obtained by Richards and Barry (revision by Swietoslawski and Bobinska[11]) and by Roth and von Auwers,[12] exceed our present value by 0.41 and 0.10%, respectively. Berthelot's very early result[12] for thiophene apparently differs from ours by +0.54% and that of Thomsen by −0.68%.

Acknowledgment.—Before concluding, we wish to thank Dr. George Calingaert for the gift of the methylnonane samples and the Shell Development Co. for the preparation of six of these ten compounds as well as for financial assistance in this research during the summer of 1939.

Summary

1. A bomb calorimeter has been calibrated and then used for precise measurements of the heats of combustion of the following ten substances at 25° and constant volume: 2-methylnonane, 5-methylnonane, methylcyclopentane, ethylcyclopentane, cyclohexane, methylcyclohexane, *n*-heptylcyclohexane, *n*-dodecylcyclohexane, methyl ethyl ketone and thiophene.

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

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RECEIVED MARCH 11, 1940

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[9] Rossini, *Chem. Rev.*, **18**, 252 (1936).

[10] Swietoslawski, THIS JOURNAL, **42**, 1092 (1920).

[11] Swietoslawski and Bobinska, *ibid.*, **49**, 2476 (1927).

[12] Landolt–Börnstein–Roth–Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 1587.