

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XIII. The Heat Capacities and Entropies of *n*-Tetradecane and the Hydroxybenzoic Acids. The Relative Free Energies of Some Benzenoid Position Isomers

BY GEORGE S. PARKS AND DONALD W. LIGHT

This investigation was carried out with the dual purpose of further testing some of the empirical entropy relationships developed recently by Parks and Huffman¹ and of utilizing Keffler and Guthrie's precise combustion values² for the three hydroxybenzoic acids in a study of the relative thermodynamic stability of some benzenoid position isomers.

Materials

n-Tetradecane (C₁₄H₃₀).—A quantity of *n*-tetradecane, obtained from the Eastman Kodak Co., was subjected to ten fractional crystallizations in our laboratory. The final product melted at 5.5°, which is also the value given in the "International Critical Tables."

o-, *m*- and *p*-Hydroxybenzoic Acids (C₇H₆O₃).—These three acids were likewise obtained from the Eastman Kodak Co. Their respective melting points were 157, 200 and 212°. The samples yielded no appreciable ash on burning and, as small amounts of solid organic impurities would have only a negligible influence on our ensuing heat capacity values, the only purification deemed necessary was to keep them in a vacuum over phosphorus pentoxide for several days before using.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and also the fusion data for *n*-tetradecane. The apparatus and details of experimental procedure have been fully described in other places.³ In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%.

The specific heats, expressed in terms of the 15° calorie⁴ and with all weights reduced to a vacuum basis, appear in Table I. They are also represented graphically in Fig. 1, where it is apparent that the values for the three hydroxybenzoic acids conform approximately to the same curve. Only one heat capacity value is given in

the literature⁵ for any of these substances within the temperature range of this study: that of Bartoli and Stracciati for *n*-tetradecane at 290°K. This result is 4.4% below our present curve.

TABLE I
SPECIFIC HEATS PER GRAM OF SUBSTANCE

<i>n</i> -Tetradecane: Crystals					
T, °K.	C _p	T, °K.	C _p	T, °K.	C _p
93.3	0.180	151.1	0.250	200.9	0.311
98.8	.188	164.0	.263	204.5	.312
105.3	.196	174.8	.277	213.6	.323
109.4	.201	184.4	.292	222.8	.337
121.1	.216	197.4	.300	231.4	.348
133.2	.230	194.2	.320	235.8	.357
139.4	.238				
Liquid					
280.6	0.517	286.3	0.521	290.6	0.523
284.4	.520				
<i>o</i> -Hydroxybenzoic Acid: Crystals					
96.0	0.1112	152.6	0.1550	224.1	0.2168
104.8	.1184	166.7	.1668	250.8	.2393
116.5	.1275	173.9	.1729	276.5	.2624
125.8	.1343	195.0	.1909	284.9	.2697
134.8	.1413	201.5	.1975	288.6	.2755
144.4	.1487				
<i>m</i> -Hydroxybenzoic Acid: Crystals					
94.4	0.1087	147.2	0.1506	231.5	0.2218
101.1	.1148	161.1	.1624	255.7	.2414
107.8	.1200	168.3	.1679	278.9	.2627
122.1	.1311	200.7	.1952	285.3	.2676
130.9	.1378	225.9	.2164	288.4	.2723
139.2	.1440				
<i>p</i> -Hydroxybenzoic Acid: Crystals					
94.9	0.1074	145.0	0.1486	228.6	0.2202
101.9	.1139	163.8	.1638	250.9	.2383
107.6	.1187	170.1	.1692	256.2	.2442
114.3	.1232	191.9	.1906	276.5	.2618
123.1	.1313	198.4	.1936	280.9	.2680
131.0	.1369	222.6	.2149	283.8	.2686

Two determinations of the heat of fusion of *n*-tetradecane were carried out. The first, which was quite satisfactory, gave 53.55 cal. per gram. The second, which unfortunately involved a rather large correction for the heat exchange with the jacket of the calorimeter, yielded 52.88 cal. As a final value we have taken 53.33 cal. per gram

(1) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932, p. 209.

(2) Keffler and Guthrie, *J. Phys. Chem.*, **31**, 65 (1927).

(3) Parks, *THIS JOURNAL*, **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

(4) The factor 0.2390 has been used in converting the joule to the 15° calorie.

(5) Landolt-Börnstein-Roth-Scheel, "Tabellen," Verlag Julius Springer, Berlin, 1923, p. 1272.

at 278.6°K. The specific heat curve for this compound also discloses a small maximum or "hump" in the neighborhood of 194°K. This hump rises about 6% above a strictly linear curve and corresponds to an energy effect of 0.22 cal. per gram or 43.6 cal. per mole.

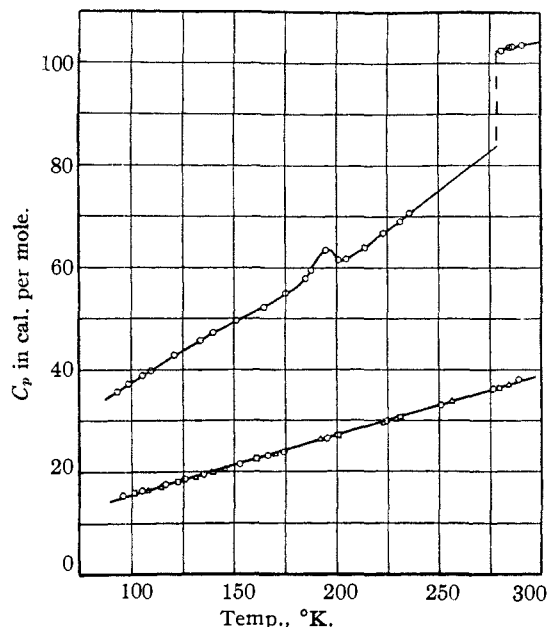


Fig. 1.—The upper curve represents the molal heat capacity of *n*-tetradecane, crystals and liquid. The lower curve represents the molal heat capacity of the hydroxybenzoic acids (circles refer to the ortho, squares to the meta, and triangles to the para acid).

Discussion

Entropies of the Compounds.—Using the data contained in the preceding section in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for these four compounds. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman⁶ for estimating the entropy increases for the crystals (Line 1 in the data of Table II) from 0 to 90°K. The various entropy increments from 90 to 298.1°K., which

TABLE II
ENTROPIES OF THE COMPOUNDS PER MOLE

	C ₁₄ H ₃₀	C ₆ H ₄ (OH)CO ₂ H		
		<i>ortho</i>	<i>meta</i>	<i>para</i>
Crystals (0–90°K.)	28.74	13.70	13.50	13.23
Crystals (above 90°K.)	60.72	28.90	28.78	28.79
Fusion	37.94
Liquid	7.00
<i>S</i> ₂₉₈	134.4	42.6	42.3	42.0

(6) Kelley, Parks and Huffman. *J. Phys. Chem.*, **33**, 1802 (1929).

appear in Lines 2, 3 and 4 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree are given in the last line.

These experimental values for *S*₂₉₈ can now be compared with the values predicted with the aid of the empirical rules developed by Parks and Huffman.¹ For liquid *n*-tetradecane the predicted value is 132.8 E. U. or only 1.2% below the experimental result. For the hydroxybenzoic acids the predicted value is 40.8 E. U., which is respectively 4.2, 3.5 and 2.9% below our present results for the ortho, meta and para compounds. On the whole this agreement is quite satisfactory.

The Free Energies of the Hydroxybenzoic Acids.—We have also calculated the free energies of the hydroxybenzoic acids by means of the third law of thermodynamics and the fundamental equation, $\Delta F = \Delta H - T\Delta S$. The absence of a combustion value for *n*-tetradecane precludes such a calculation in its case at the present time, although we expect that an investigation now being initiated in this Laboratory will furnish us with many precise combustion values for compounds of this type within the next few years.

The essential data are given in Table III. For obtaining the values of ΔH_{298} we have used the heats of combustion determined for these acids by Keffer and Guthrie² in conjunction with the values 68,310 cal. and 94,240 cal. for the heats of combustion of hydrogen and graphitic carbon, respectively. The thermochemical measurements of Keffer and Guthrie were obviously carried out with extreme care and the three combustion values are probably reliable for comparative purposes to within 100 calories, although the studies by Verkade and Coops⁷ and others on the heat of combustion of the ortho acid indicate that the absolute uncertainty may be as much as 400 calories. The ΔS_{298} values represent simply the differences between the *S*₂₉₈ for each acid and the corresponding values for the entropies of the elements contained therein. For this purpose we have used the following atomic entropies: C (graph.), 1.36 E. U.; $\frac{1}{2}$ H₂, 15.615 E. U.; and $\frac{1}{2}$ O₂, 24.52 E. U. The value for graphite is that given in the succeeding paper by Jacobs and Parks.⁸ The other two values are those found by Giaque⁹ and by Giaque and Johnston.¹⁰

(7) Verkade and Coops, *J. Phys. Chem.*, **34**, 2549 (1930).

(8) Jacobs and Parks, *THIS JOURNAL*, **56**, 1513 (1934).

(9) Giaque, *ibid.*, **52**, 4825 (1930).

(10) Giaque and Johnston, *ibid.*, **51**, 2300 (1929).

The molal free energies of formation from the elements appear in the last line of the table. The absolute error in these values may be as great as 700 calories, but for comparative purposes they are probably reliable to within 250 calories.

TABLE III

THERMAL DATA AT 298.1°K. FOR THE HYDROXYBENZOIC ACIDS

The 15° Cal. is used throughout and all weights have been reduced to a vacuum basis.

Compound	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
Heat of combustion at const. pressure	722,570	722,720	721,830
ΔH_{298}	-142,040	-141,890	-142,780
ΔS_{298} (in E. U.)	-134.2	-134.5	-134.8
ΔF_{298}°	-101,810	-101,570	-102,370

Our thermal data indicate that in the case of these benzenoid position isomers the heats of formation, entropies of formation and free energies lie very close together. While the apparent order

of increasing thermodynamic stability (*i. e.*, decreasing ΔF_{298}°) is here (1) meta, (2) ortho and (3) para, the small difference between the values for the first two compounds is really within the experimental error.

Summary

1. The specific heats of *n*-tetradecane and of the ortho, meta and para hydroxybenzoic acids have been measured over a wide range of temperatures. The heat of fusion of *n*-tetradecane has also been determined.
2. The entropies of the four compounds have been calculated from these heat capacity data.
3. The free energies of formation of the three hydroxybenzoic acids have also been calculated and have been found to lie extremely close to one another.

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Thermal Data on Organic Compounds. XIV. Some Heat Capacity, Entropy and Free Energy Data for Cyclic Substances

BY CHARLES J. JACOBS AND GEORGE S. PARKS

From *a priori* considerations as well as from the published experimental data it appears that a cyclic molecule possesses at ordinary temperatures considerably less intramolecular vibrational energy than the corresponding aliphatic or straight-chain molecule. As a consequence the molal entropy of the cyclic compound should be appreciably lower. This has been found true in the case of cyclohexane and *n*-hexane where S_{298} for the former is 49.2 E. U. per mole as against 70.8 E. U. for the latter.¹ In the past, however, the thermal data available for cyclic compounds outside of the class of the benzene derivatives have been quite scanty; and accordingly the present investigation was carried out to increase our information on ring compounds, both of the carbocyclic and heterocyclic types. In this connection we have studied cyclopentane, thiophene, dioxane, pyrene and graphite.

Materials

Cyclopentane (C₅H₁₀).—The cyclopentane was kindly prepared for us by Mr. Robert Kemp, working under the

(1) Parks, Huffman and Thomas, *THIS JOURNAL*, **52**, 1038 (1930); Huffman, Parks and Barmore, *ibid.*, **53**, 3884 (1931).

direction of Professor C. R. Noller. Commercial dicyclopentadiene was first purified by fractional distillation under reduced pressure at 85–87° and then depolymerized, by heating at 180–200°, to yield cyclopentadiene. The latter was immediately reduced by hydrogen with the aid of a platinum oxide catalyst. The resulting cyclopentane was then filtered to remove the catalyst, washed with sulfuric acid, dried with anhydrous potassium carbonate, and distilled twice through a 1-meter column packed with copper rings. The final product boiled sharply at 49.5° at 767 mm. It was extremely pure, as was proven by the sharpness of the melting process and transitions in the course of the ensuing heat capacity measurements.

Thiophene (C₄H₄S).—A 100-g. sample of Eastman synthetic thiophene was fractionally distilled in our laboratory, and the middle half of the resulting distillate was employed in the present measurements. This material in the crystalline condition at low temperatures showed a considerable premelting effect as the melting point was approached and its purity could hardly be adjudged as satisfactory.

1,4-Dioxane (C₄H₈O₂).—A high-grade Eastman material was subjected to eight fractional crystallizations. The final product had a sharp melting point at 11.1°, as measured with a mercury thermometer which had been calibrated by the United States Bureau of Standards.

Pyrene (C₁₆H₁₀).—Two samples of purified pyrene were employed in the present study. The first sample was prepared from a good German material by successive frac-