

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. X. The Heats of Combustion and Free Energies, at 25°, of Some Organic Compounds Concerned in Carbohydrate Metabolism

BY HUGH M. HUFFMAN AND SIDNEY W. FOX

In the study of certain reactions of intermediary metabolism, a knowledge of the energetics involved is of interest. For this reason we are presenting the free energies of several compounds which are concerned in carbohydrate metabolism.

Utilizing data presented in this paper and available from other sources we have calculated the standard free energies of formation of fumaric acid, maleic acid, succinic acid, α -dextrose, β -dextrose, and α -dextrose monohydrate.

The experimental part of this paper is concerned with the determination of the heats of combustion of four of the compounds listed above.

Calorimetric Method

The calorimetric method has been described in previous publications.¹ Since no important changes have been made, only the essential details will be given. All of the combustions were made in a Parr bomb having a volume of 0.380 liter and with an initial oxygen pressure of 30 atmospheres and with 1 ml. of water in the bomb. The platinum wire technique^{1a} was used exclusively. The heat capacity of the bomb was controlled carefully throughout the course of the investigation by frequent calibration with Bureau of Standards benzoic acid standard sample no. 39e, having for its isothermal heat of combustion, $-\Delta U_B/m$, at 25° the value of 26,419 N.B.S. international joules.²

The unit of energy used throughout this paper is the defined conventional calorie which is derived from the international joule by multiplying by the factor 1.0004/4.185. The methods of calculation, the corrections and the symbols are those given by Stiehler and Huffman.^{1b} The molecular weights used are based on the 1937 table of atomic weights. All of the thermal data are given for the isothermal process at 25° and for true mass.

Preparation, Purification, and Heats of Combustion of the Compounds

Fumaric Acid.—Samples (a) and (b) were prepared from Eastman practical fumaric acid by 2 and 3 crystallizations

(1) (a) Huffman and Ellis, *THIS JOURNAL*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935).

(2) Jessup and Green, *Bur. Standards J. Research*, **10**, 552 (1933).

from water in the usual manner. Sample (c) was prepared originally by Professor J. B. Conant of Harvard University and was used in the heat capacity investigation of Parks and Huffman.³ For this investigation it was subjected to two additional crystallizations from water. Titration of sample (c) with sodium hydroxide gave the theoretical value.

Maleic Acid.—Sample (a) was prepared originally by Professor J. B. Conant from maleic anhydride and was used by Parks and Huffman³ for heat capacity measurements. For this investigation it was twice recrystallized from 50% aqueous solutions.

Sample (b) was obtained by four crystallizations of Pfanstiehl c. p. maleic acid. This sample gave low combustion values.

Samples (c) and (d) were prepared from Eastman maleic anhydride. Two portions of this material were each subjected to three fractional distillations giving final products boiling at 200° and having boiling ranges of 0.3 and 0.1°, respectively. The first distillate was dissolved in ten parts of water and evaporated to dryness over sodium hydroxide (c). The second distillate was dissolved in three parts of water and evaporated to dryness over phosphorus pentoxide (d). The ash content was completely negligible.

α -Dextrose.—The method of Hudson and Dale⁴ was used to purify and convert glucose, from two different sources, into α -dextrose. A preparation obtained using Pfanstiehl c. p. glucose as the starting material was washed with boiling absolute alcohol. This treatment apparently caused mutarotation, as this material had an initial specific rotation of 62°, sample (a). A portion of this sample was again converted to the α -form and was washed twice by shaking with about 5 volumes of 80% ethanol followed by rapid filtration to give sample (b). Sample (c) was prepared from Kahlbaum dextrose in the same manner as sample (b). In this case it was necessary to use norite to decolorize.

Sample (d) was made from Pfanstiehl c. p. dextrose by dissolving in one-sixth its weight of hot water. This concentrated solution was then allowed to cool slowly to 75° with continuous stirring. Under these conditions the stable crystalline modification is anhydrous α -dextrose. The mass thus obtained was transferred to a suction filter in an air-bath at 80°. No visible filtration took place but in about one hour the mass was superficially dry.

Bureau of Standards dextrose (standard sample no. 41) was used without further purification, sample (e).

The initial specific optical rotation was determined on samples b, c, d and e giving for $[\alpha]_D^{25}$ 113, 112, 109 and 110°, respectively. The ash determination on each of these samples showed that this factor was entirely negligible.

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

(4) Hudson and Dale, *ibid.*, **39**, 324 (1917).

TABLE I
 THE EXPERIMENTAL DATA AT 25°

Sample	P ₂ O ₅ vac.	Desiccation Vac. 80°	Oven 100°	True mass	Total heat evolved, cal.	Cal. from HNO ₃	Cal. from oil	Cal. from paper and Et	-ΔU _B /m cal. g. ⁻¹	Devia- tion, cal.
Fumaric acid (a)	480			2.29218	6330.6	0.1		16.8	2754.4	-0.4
Fumaric acid (b)			140	2.31668	6400.0	1.2		17.1	2754.7	- .1
Fumaric acid (b)			72	2.38677	6593.1	1.5		17.8	2754.3	- .5
Fumaric acid (c)	192		72	2.29353	6336.9	1.1		18.3	2654.5	- .3
Fumaric acid (c)			120	2.29090	6329.3	0.1		18.3	2754.8	.0
Fumaric acid (c)			120	2.28978	6327.8	1.1		16.6	2755.8	1.0
Fumaric acid (c)			214	2.29292	6335.2	0.8		17.0	2755.2	0.4
Mean									2754.8	± .4
Maleic acid ^a (a)	31			2.08685	5865.3	.2		17.2	2802.3	+ .5
Maleic acid (c)	78			2.25235	6327.0	.1		17.5	2801.3	- .5
Maleic acid (c)	80			2.25444	6333.6	.1		17.8	2801.5	- .3
Maleic acid (c)	82			2.25321	6335.3	5.6		17.3	2801.6	- .2
Maleic acid (d)	6	1		2.26002	6351.1	0.8		17.0	2802.3	.5
Maleic acid (d)		44		2.24466	6308.0	.8		17.7	2802.0	.2
Mean									2801.8	± .4
α-d-Glucose (b)	800	160		1.67761	6259.6	.1		17.8	3720.6	.6
α-d-Glucose (b)	800	160		1.66565	6213.1	.1		16.8	3720.0	.0
α-d-Glucose (b)		90	47	1.45337	5973.3	.1	549.4	17.9	3719.6	- .4
α-d-Glucose (b)			265	1.67959	6267.5	.2		17.8	3720.8	.8
α-d-Glucose (d)		100		1.69517	6324.5	.3		17.1	3720.6	.6
α-d-Glucose (d)		100		1.68041	6454.2	.2	184.5	17.9	3720.3	.3
α-d-Glucose (d)			48	1.69472	6322.1	.1		18.4	3719.6	- .4
α-d-Glucose (d)			48	1.69574	6323.3	.1		16.8	3719.0	-1.0
α-d-Glucose (e)		88		1.69946	6339.8	.1		18.1	3719.8	-0.2
Mean									3720.0	± .5
α-d-Glucose hydrate (a)				1.84726	6462.1	.1	223.5	17.9	3367.5	- .2
α-d-Glucose hydrate (a)				1.85043	6454.9	.1	203.0	20.8	3367.3	- .4
α-d-Glucose hydrate (a)				1.84829	6442.1	.1	199.2	17.2	3368.3	.6
Mean									3367.7	± .4

^a For maleic acid the time of desiccation was in days and the temperature *in vacuo* was 50°.

α-Dextrose Hydrate

Pfanstiehl dextrose was purified and converted to α-dextrose in the manner previously described. It was covered with 80% ethanol, allowed to stand for nine days, the ethanol filtered off and the crystalline material dried in the air of the room. The specific rotation of this material, based on the weight of hydrate, was 101°. The ash content was negligible.

In addition to the combustion value for this material it was necessary to determine the exact state of hydration. The following procedure was carried out. Five samples of the air-dried material were placed in bottles and weighed to the nearest 0.01 mg. The bottles were transferred to the balance case and allowed to stand open for a period of three months. During this period the samples decreased in mass by 0.22 to 0.30 mg. The crystalline samples were then made into pellets and the above procedure repeated. At the end of this period three of the samples were used for combustion measurements and a fourth to determine the state of hydration. The water was determined by drying *in vacuo* at 70° for five days followed by a short period in air at 100°. The loss in weight during this treatment was equivalent to 100.21% of theoretical, based on the final mass of anhydrous dextrose. The experimentally determined masses of the combustion samples were corrected for this excess mass on the assumption that the

extra water acted merely as an inert impurity. This correction amounts to about 0.02% of the final combustion value. Due to difficulties inherent in the water determination the absolute uncertainty in the case of hydrates may be somewhat larger than in the case of unhydrated substances.

The experimental results of the combustions on these four compounds are given in Table I. In addition to the experimental values we have also calculated the quantities $-\Delta U_B$, $-\Delta U_R$, $-\Delta H_R$ and $-\Delta H_f^\circ$ which we have defined previously.^{1b} For the sake of completeness we have also included in this table values for certain of the quantities for succinic acid⁵ and β-dextrose. In the case of the values of $-\Delta U_B$ the uncertainty assigned is the precision uncertainty.⁶ The absolute accuracy in all cases is about 0.025% except that in the case of the hydrate it may be greater due to uncertainty in regard to the exact amount of water in the hydrated samples. In calculating $-\Delta U_R$ we have arbitrarily allowed

(5) Huffman, *THIS JOURNAL*, **60**, 1171 (1938).

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

for a 10% uncertainty in the Washburn correction. We have not estimated the accuracy of the values of $-\Delta H_f^\circ$ because the uncertainty in the value for the heat of formation of carbon dioxide is not definitely known. In calculating $-\Delta H_f^\circ$ we have used the values of $-68,313^7$ for the heat of formation of water and $-94,240^8$ for the heat of formation of carbon dioxide from graphite both at 25° .

Discussion of the Results

Glucose has been burned by Stohmann⁹ and his co-workers and also by Emery and Benedict.¹⁰ The published results of these investigators do not include enough information to permit a recalculation of their data for precise comparison with our results. However, we have applied approximate corrections and find that their results are higher than ours by several tenths of a per cent.

Fumaric and maleic acids have been burned by a number of workers,¹¹ again the information is not complete enough to permit an accurate recalculation of their data. In the case of the investigations carried out in Roth's laboratory we have made approximate corrections and find that their values for fumaric and maleic acids are about 0.05 and 0.5%, respectively, higher than the values reported by us.

We are not aware of any combustion data on α -dextrose monohydrate. However, the heats of solution of the hydrated and anhydrous forms have been measured by Hendricks, Steinbach, LeRoy and Moseley,¹² and Hendricks, Dorsey, LeRoy and Moseley.¹³ From their data we have calculated for the reaction α -dextrose(s) + $H_2O(l) = \alpha$ -dextrose hydrate(s), $\Delta H = -2470$ cal.; this is to be compared with $\Delta H = -2850$ cal. calculated from our combustion data. This is fair agreement considering the uncertainty involved in the combustion of hydrates.

We have also attempted to obtain the heat of combustion of β -dextrose; unfortunately the re-

sults were not completely satisfactory. However, concordant results on two different samples gave a value of $\Delta H_R = -671.09$ kcal. Again using the solution data of the above authors^{12,13} for α -dextrose and β -dextrose we have calculated $\Delta H_R = -671.08$ kcal. This is in excellent agreement with our tentative combustion value. Nevertheless we should like to point out that this need not be the correct value as the solution data may have been complicated by the same sorts of irregularities which we encountered in our combustion measurements. We do feel, though, that it is probably very near to the true value.

The Free Energies of the Compounds

The entropies of fumaric acid, maleic acid and succinic acid have been reported by Parks and Huffman.³ The entropy of glucose has been calculated by Parks, Kelley and Huffman¹⁴ from the heat capacity data of Simon.¹⁵ The latter author does not state explicitly that his measurements were made on α -dextrose; however, since this is the form of glucose usually obtained we feel fairly certain that this was the substance used. The values for the heats of formation are those given in Table II.

Since entropy values are not available for α -dextrose hydrate and β -dextrose we have calculated the values of ΔF° from the solubility data in conjunction with the ΔF° value for α -dextrose. Jackson and Silsbee¹⁶ have determined the solubility of α -dextrose and α -dextrose hydrate in water at several temperatures. The anhydrous form is unstable at 25° ; nevertheless we have extrapolated the solubility data to this temperature and have calculated that the mole ratio of α -dextrose is 0.162, at the same temperature the mole ratio of α -dextrose hydrate is 0.095. From these data, assuming the formation of perfect solutions, we have calculated for the reaction α -dextrose(s) + $H_2O(l) = \alpha$ -dextrose hydrate(s), $\Delta F = -320$ cal. When this is combined with the ΔF° of α -dextrose and that of water, $-56,720$ cal.,¹⁷ we find for α -dextrose hydrate $\Delta F^\circ = -275,760$ cal.

Hudson and Yanovsky¹⁸ have determined the instantaneous solubilities of α - and β -dextrose in 80° alcohol. Using these data Parks and

(7) Rossini, *Bur. Standards J. Research*, **6**, 34 (1931).

(8) Huffman, Fox and Ellis, *THIS JOURNAL*, **59**, 2149 (1937).

(9) Stohmann, *Z. physik. Chem.*, **6**, 334 (1890); Stohmann and Langbein, *J. prakt. Chem.*, [2] **45**, 305 (1892).

(10) Emery and Benedict, *Am. J. Physiol.*, **23**, 301 (1911).

(11) (a) Stohmann, Kleber and Langbein, *J. prakt. Chem.*, [2] **40**, 202 (1889) (9); (b) Roth, "Landolt-Börnstein, Tabellen," 1923; (c) Reyer, "Landolt-Börnstein Tabellen," 1923; (d) Languinine, *Ann. chim. phys.*, [6] **23**, 179 (1891); (e) Ossipov, *J. soc. chim. russe*, **22**, 317 (1890).

(12) Hendricks, Steinbach, LeRoy and Moseley, *THIS JOURNAL*, **56**, 99 (1934).

(13) Hendricks, Dorsey, LeRoy and Moseley, *J. Phys. Chem.*, **34**, 418 (1930).

(14) Parks, Kelley and Huffman, *THIS JOURNAL*, **51**, 1969 (1929).

(15) Simon, *Ann. Physik*, **68**, 258 (1922).

(16) Jackson and Silsbee, *Bur. Standards Sci. Papers*, No. 437 (22).

(17) Giaque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

(18) Hudson and Yanovsky, *THIS JOURNAL*, **39**, 1013 (1917).

TABLE II
 SUMMARY OF DERIVED DATA AT 25°

Substance	Formula	Mol. wt.	Density	$-\Delta U_B$ kcal. mole ⁻¹	$-\Delta U_R$ kcal. mole ⁻¹	$-\Delta H_R$ kcal. mole ⁻¹	$-\Delta H_f^\circ$ kcal. mole ⁻¹	$d \Delta U_R/dT$ mole ⁻¹ , cal.
Fumaric acid	C ₄ H ₄ O ₄	116.071	1.635	319.75 ± 0.05 ^a	319.30 ± 0.09 ^b	318.71	194.88	-14
Maleic acid	C ₄ H ₄ O ₄	116.071	1.59	325.21 ± .04	324.73 ± .09	324.14	189.45	-15
α - <i>D</i> -Glucose	C ₆ H ₁₂ O ₆	180.154	1.544	670.17 ± .07	669.58 ± .13	669.58	305.73	-65
α - <i>D</i> -Glucose hyd.	C ₆ H ₁₄ O ₇	198.169	1.56	667.37 ± .12	666.73 ± .18	666.73	376.90	-71
β - <i>D</i> -Glucose	C ₆ H ₁₂ O ₆	180.154	1.54	(671.67) ^c	(671.08) ^c	(671.08) ^c	(304.23) ^c	-65
Succinic acid	C ₄ H ₆ O ₄	118.087	1.56	356.99 ± .04	356.54 ± .08	356.24	225.66	-27

^a These values are the precision uncertainties. ^b These values include an allowance for a 10% uncertainty in the Washburn correction. ^c These values calculated from solution data.

Huffman¹⁹ have calculated for the reaction α -dextrose(s) = β -dextrose(s) at 25°, $\Delta F = 400$ cal. This leads to a value for β -dextrose(s) of $\Delta F^\circ = -218,320$ cal. The values of the free energies of these six compounds and the other essential data are collected in Table III. For the entropies of the elements we have used for C, H₂ and

O₂ the values 1.36,²⁰ 31.23,²¹ and 49.03²² e. u. per mole, respectively.

Using the calculated values of ΔF° and ΔH_f° for α -dextrose hydrate and β -dextrose in conjunction with the equation $\Delta F = \Delta H - T\Delta S$ we have calculated ΔS and S for these two substances. The entropy values thus calculated have been included in Table III.

TABLE III

THERMAL DATA AT 298.1°K.

Substance	$\Delta H_{298.1}^\circ$ kcal.	$S_{298.1}$ ke. u.	$\Delta S_{298.1}$ e. u.	$\Delta F_{298.1}^\circ$ kcal.
Fumaric acid	-194.88	39.7	-126.3	-157.23
Maleic acid	-189.45	38.1	-127.9	-151.32
Succinic acid	-225.66	42.0	-155.2	-179.36
α - <i>D</i> -Glucose	-305.73	50.7	-291.9	-218.72
α - <i>D</i> -Glucose (hyd.) ^a	(-376.52)	(60.4)	(-338.0)	(-275.76)
β - <i>D</i> -Glucose ^a	(-304.23)	(54.4)	(-288.2)	(-218.32)

^a The data for these two substances are calculated from solution data as described in the text.

(19) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York City, 1932, p. 179.

Summary

1. The experimentally determined heats of combustion at 25° of fumaric acid, maleic acid, α -dextrose and α -dextrose hydrate are presented.

2. Using the data of this paper and certain other data the free energies of formation at 25° of fumaric acid, maleic acid, succinic acid, α -dextrose, β -dextrose and α -dextrose hydrate have been calculated.

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

(21) Giauque, *ibid.*, **52**, 4816 (1930).

(22) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

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The Ionic Dissociation of Sodium Triphenylmethyl

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It has been shown¹ that the sodium derivatives of certain free radicals may behave as electrolytes in solution. Bent² has taken advantage of this fact in calculating the electron affinity of triphenylmethyl in his studies of the strength of bonds in organic compounds. In order to make this calculation, he was forced to assume a value for the ionization constant of sodium triphenylmethyl, since no direct measurements were available. The value used was 10⁻⁴, but the state-

ment was made that this value is somewhat uncertain, and that the true value is probably considerably lower than this.³

Subsequent to the publication of this calculation, Kraus and Fuoss⁴ discovered a relationship between the dissociation constants of weakly dissociated salts in solvents of low dielectric constant and a parameter a which is roughly proportional to the distance of closest approach of the ions in solution. If we assume from crystal

(1) (a) A. W. Schlenk and E. Marcus, *Ber.*, **47**, 1664 (1914); (b) C. A. Kraus and W. H. Kahler, *THIS JOURNAL*, **55**, 3541 (1933).

(2) H. E. Bent, *ibid.*, **52**, 1498 (1930).

(3) See footnote 14; H. E. Bent and R. G. Gould, *ibid.*, **57**, 1218 (1935).

(4) C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 1022 (1933).