arylation of phosphorus oxychloride with a consequent shift to the right of the equilibrium proposed in the introductory portion of this paper.

Summary

The composition of the product obtained when phenol is allowed to react with phosphorus oxychloride in the presence of pyridine is influenced by the mole ratios of the constituents and by the subsequent temperature treatment. Increases in mole ratios of pyridine to phosphorus oxychloride and of phenol to phosphorus oxychloride bring about more complete arylation. A complex equilibrium is established with the result that ammonolysis gives mixtures of phenyl diamidophosphate, diphenyl amidophosphate and triphenyl phosphate. In view of the fact that the phenyl esters of amido- and diamidophosphoric acids are readily separable, this procedure is recommended for their preparation.

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The Heat Capacities and Entropies of Three Disaccharides

BY ADOLPH G. ANDERSON[1] AND GEBHARD STEGEMAN

During recent years a program has been carried out in this Laboratory to secure thermal data on biologically important compounds. As part of this project, the heat capacities of three disaccharides have been measured from 60 to 298°K.

Method and Apparatus.—The method and apparatus were similar to those used by Gibson and Giauque.[2] This particular assembly has been described by Haas and Stegeman,[3] and only changes in design will be mentioned here.

Calorimeter.—The calorimeter used in this investigation was made from a thin copper cylinder of about 130-ml. capacity, closed at the ends by thin copper plates. Eight radial copper vanes were soldered into position between the inside surface of the cylinder and a small central brass tube. Into this central tube a heating element could be placed with a snug fit. This heating element consists of a thin brass tube on which was wound a constantan wire of 140 ohms resistance. The very small change of resistance with the temperature during a measurement makes the estimation of the energy input a less tedious task than before. Three measurements of the heating current were usually made to guard against a potential change in the operating battery. The resistance of the heater was always measured before and after a determination and the constancy of the heating current appeared to indicate that no contact potentials of any consequence were developed during the operation. The heat capacity of the calorimeter was about 13 cal. at 298°K.

The temperature change of the calorimeter was determined by measuring the resistance of a gold wire containing about 0.1% of silver. This double silk-covered wire of no. 36 B. and S. gage was wound on the outside of the calorimeter and baked on with Bakelite lacquer. It had a resistance of about 400 ohms at room temperature. The ends of the calorimeter were plated with gold and the wire was covered with gold leaf. The whole arrangement gave a very satisfactory performance.

The Dewar flask holding the cooling liquid was enclosed in a brass cylinder closed at both ends. By the use of a Cenco Hypervac pump, liquid nitrogen could be evaporated sufficiently rapidly to reach a temperature between 55 and 60°K.

All electrical measurements were made on a White double potentiometer of 100,000 microvolts range, using a Leeds and Northrup type H. S. galvanometer. The galvanometer sensitivity varied between the following limits: 0.0016 ohm, or 0.0010°K., per mm. scale deflection at 60°K.; 0.0124 ohm, or 0.0087°K., per mm. scale deflection at 298°K. The scale was read to 0.1 mm. A Weston unsaturated standard cell, certified by the Bureau of Standards, was used as a reference.

Calibration of the Calorimeter.—The temperature scale from 60 to 90°K. was established by the use of a copper–constantan thermocouple,[4] previously compared with a thermocouple standardized against a hydrogen gas thermometer by Giauque, Buffington and Schulze.[5] The temperature scale from 90 to 298°K. had been established previously by the use of a copper–constantan thermocouple standardized by the Bureau of Standards. A comparison of the two thermocouples showed them to be in agreement at 90°K. and also at higher temperatures. It was estimated by the Bureau of Standards that the thermocouple was correct to ±2.0 microvolts which corresponds to ±0.1°K. at 90°K. and to ±0.05°K. at 298°K.

As a check on the standardization of the calorimeter, the heat capacity of naphthalene was measured at intervals from 70 to 298°K. Typical results taken from curves are compared with published data[6] in the table below.

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(1) From a thesis submitted by A. G. Anderson in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

(3) Haas and Stegeman, *ibid.*, **58**, 879 (1936).

(4) This thermocouple was made available through the kindness of Dr. C. Travis Anderson, United States Bureau of Mines.

(5) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

(6) Huffman, Parks and Daniels, *ibid.*, **52**, 1547 (1930); Southard and Brickwedde, *ibid.*, **55**, 4378 (1933).

°K.	Huffman, Parks and Daniels	Southard and Brickwedde	This investigation
290	38.0	38.7	38.4
235	30.0	30.2	30.1
75		11.9	12.0

Preparation of Samples.—The sources of the samples and the methods employed in their purification have been mentioned previously,[7] but a supplementary microanalysis of the two lactose samples was made in addition.[8]

	Analyses, % H	Analyses, % C	Theoretical, % H	Theoretical, % C
α-Lactose monohydrate	6.76	40.25	6.71	40.00
β-Lactose	6.50	42.31	6.48	42.10

Some uncertainty regarding the composition of the monohydrate existed at the time of its preparation, but the results of the analysis do not appear to indicate any dehydration resulting from the drying process.

Heat Capacity Determination.—In Table I are listed the results of heat capacity measurements on the compounds investigated. The unit of energy used is the defined conventional calorie, related to the international joule by the expression, 1 cal. = 4.1833 int. joules.[9]

Calculated Values.—The molal entropy of each sugar was evaluated graphically from 90 to 298°K. from the heat capacity data. The extrapolation method of Kelley, Parks and Huffman[10] was used in estimating the molal entropy from 0 to 90°K. This was possible because the curves calculated using the standard heat capacity data for aliphatic compounds coincided with the experimental curves from 60 to 90°K.

TABLE I

T, °K.	C_p, cal. K°	T, °K.	C_p, cal. K°	T, °K.	C_p, cal. K°
MOLAL HEAT CAPACITY OF α-LACTOSE MONOHYDRATE Mol. wt., 360.314; wt. of sample *in vacuo*, 88.517 g.					
61.33	21.98	148.30	54.86	239.02	85.49
65.15	23.63	156.90	57.62	246.02	87.94
69.70	25.49	164.04	59.95	252.92	90.65
75.00	27.71	171.85	62.61	257.99	92.06
81.74	30.37	180.61	65.50	261.72	93.30
86.85	32.48	187.39	68.53	268.21	96.65
91.73	34.64	195.39	70.63	274.33	97.14
96.55	36.12	204.15	73.70	279.56	99.26
103.74	38.63	213.01	76.21	284.21	100.74
109.42	40.61	214.48	77.22	289.17	102.57
115.57	42.97	219.77	79.07	292.91	103.59
122.23	45.58	222.39	79.93	293.35	104.10
129.51	48.12	227.86	81.62	297.42	105.06
140.75	52.11	231.69	82.65		
MOLAL HEAT CAPACITY OF β-LACTOSE Mol. wt., 342.298; wt. of sample *in vacuo*, 113.11 g.					
65.51	22.14	138.72	47.70	217.62	73.62
72.89	25.03	149.22	50.86	225.97	75.81
78.88	27.29	157.75	53.80	235.29	78.62
87.84	30.58	164.86	56.28	243.97	81.35
95.54	33.19	173.35	58.90	252.86	84.53
104.51	36.22	183.05	61.23	262.76	86.95
114.32	39.58	190.47	63.68	270.93	89.60
121.77	42.02	201.24	67.43	280.11	92.89
129.98	44.61	208.73	69.97	289.44	95.55
MOLAL HEAT CAPACITY OF β-MALTOSE MONOHYDRATE Mol. wt., 360.314; wt. of sample *in vacuo*, 65.168 g.					
61.11	21.93	164.95	61.76	235.25	86.44
66.32	24.08	173.05	64.32	241.24	88.19
70.40	25.64	183.48	67.96	242.20	88.33
75.33	27.95	190.22	70.59	249.92	90.74
82.13	30.87	194.08	70.94	257.63	94.09
91.23	34.62	201.11	73.66	259.14	95.02
100.90	38.47	201.99	74.02	264.28	96.34
103.47	39.39	210.45	76.62	269.17	97.64
113.36	42.84	211.69	77.94	272.03	98.89
121.67	46.27	216.41	78.97	276.73	100.51
133.00	49.97	218.75	80.23	283.58	102.75
147.93	55.81	223.44	82.13	289.40	104.94
155.83	58.38	229.13	83.20	296.27	107.72

The entropy of formation from the elements of each compound was calculated by the use of the values 1.36, 15.615, and 24.515, representing the entropy of carbon, hydrogen, and oxygen, respectively. Values for ΔH, obtained by Clarke and Stegeman,[7] were used to calculate the free energy of formation of each of the compounds. The results of these calculations are found in Table II.

TABLE II

	E. u./mole
ENTROPY OF α-LACTOSE MONOHYDRATE	
0–90°K. (extrapolation)	24.2
90–298.16°K. (graphical)	74.88
$S_{298.16°K.}$	99.1
ENTROPY OF β-LACTOSE	
0–90°K. (extrapolation)	22.6
90–298.16°K. (graphical)	69.73
$S_{298.16°K.}$	92.3
ENTROPY OF β-MALTOSE MONOHYDRATE	
0–90°K. (extrapolation)	24.2
90–298.16°K. (graphical)	75.59
$S_{298.16°K.}$	99.8

SUMMARY OF DERIVED DATA

Compound	$\Delta S_{298.16°K.}$	$\Delta H^\circ_{298.16°K.}$ cal./mole	$\Delta F^\circ_{209.16°K.}$ cal./mole
α-Lactose monohydrate	−586.2	−592,900	−418,200
β-Lactose	−537.2	−533,800	−373,700
β-Maltose monohydrate	−585.5	−587,000	−412,600

Discussion of Results.—In the heat capacity determinations, the average deviation of the

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(7) Clarke and Stegeman, THIS JOURNAL, **61**, 1726 (1939).

(8) This analysis was kindly made by Dr. W. R. Kirner of the Coal Research Laboratory of the Carnegie Institute of Technology.

(9) Technical News Bull., Bur. of Standards, No. 156 (1930).

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

individual measurements from a smooth curve drawn through the plotted data was 0.3%. The values of the entropy for each of the compounds have the usual uncertainty arising from the extrapolated portion of the heat capacity curve.

The molal entropy of β-lactose at 298.16°K. was found to be lower by 4.3 e. u. than the value previously determined in this Laboratory.[11] This discrepancy is caused by errors in the calibration of the calorimeter thermometer, as a result of a poor reference scale for the lower temperatures.

Summary

1. The heat capacity has been measured for three disaccharides from 60 to 298°K.

2. From these and other data, the entropy and free energy of formation at 298.16°K. have been calculated for each sugar.

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(11) Furtsch and Stegeman, THIS JOURNAL, 58, 881 (1936).

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The Heat Capacities and Entropies of Two Monosaccharides

BY GEORGE W. JACK[1,2] AND GEBHARD STEGEMAN

In this paper are presented heat capacity data from 60° to 298°K., for *l*-sorbose and α-*d*-galactose. From these and other thermal data the entropies and free energies of formation have been computed. The case of *l*-sorbose is of particular interest in that it displays a transition of the type shown by ammonium chloride.

Preparation of Materials.—The *l*-sorbose was obtained from the Chas. Pfizer Chemical Co. This sugar was used without special preparation other than drying to constant weight. Combustion studies in this Laboratory[3] have shown that the particular sample of *l*-sorbose used required no further treatment.

The α-*d*-galactose used was obtained from the Pfanstiehl Chemical Co. and was purified in a manner similar to that described by Hudson and Yanovsky.[4] This consisted in solution of the sugar in pure water, filtration to remove insoluble impurities, and reduction of the water by evaporation *in vacuo* to the amount required for the proper water–alcohol mixture to ensure the presence of the desired solid isomer. The water–alcohol mixture was formed by adding the proper quantity of anhydrous ethyl alcohol. The precipitated sugar was allowed to stand in the alcohol solution for one week; it was then filtered, and vacuum dried over anhydrous calcium chloride at 45°.

The initial and final rotations of the purified α-*d*-galactose were $[\alpha]^{20}_D$ 80.3° and $[\alpha]^{20}_D$ 144.0°, respectively. These compare favorably with Hudson's values[4] of 80.5 and 144.0°.

The Heat Capacity Measurements.—The apparatus and method have been described.[5] In the region of transition of *l*-sorbose, numerous measurements of the heat capacities were made in order to determine as accurately as possible the shape of the heat capacity–temperature

TABLE I

MOLAL HEAT CAPACITIES OF α-*d*-GALACTOSE

T, °K.	C_p, cal./°K.	*T*, °K.	C_p, cal./°K.
63.92	11.32	185.77	32.93
68.52	12.17	194.63	34.71
74.03	13.42	195.08	34.97
79.42	14.54	201.46	35.60
86.81	16.08	204.82	36.52
93.86	17.42	213.78	38.11
103.48	19.20	226.39	39.88
113.18	20.98	234.71	41.21
124.08	22.79	243.69	42.71
133.16	24.44	253.78	44.74
142.40	26.08	263.88	46.55
152.41	27.76	272.54	48.41
161.33	29.18	280.37	49.43
169.45	30.54	288.28	50.26
176.06	31.57	296.86	52.71

TABLE II

MOLAL HEAT CAPACITIES OF *l*-SORBOSE

T, °K.	C_p, cal./°K.	*T*, °K.	C_p, cal./°K.
64.02	11.48	194.30	44.25
69.51	12.56	196.11	48.91
76.03	13.99	198.30	75.36
82.39	15.29	198.70	98.10
88.36	16.55	198.83	122.49
99.00	18.58	200.03	125.03
105.04	19.74	200.98	56.28
115.51	21.85	202.27	39.48
124.17	23.48	204.86	39.39
132.36	25.27	207.74	39.75
141.29	27.37	213.96	40.30
151.59	29.48	224.44	42.36
160.10	31.26	235.18	43.97
170.95	34.07	245.68	45.53
181.93	37.01	257.47	47.84
182.70	37.38	268.04	49.80
187.59	39.40	276.05	51.13
190.45	41.34	284.02	52.12
192.50	42.61	292.85	53.76
192.92	42.84	295.86	54.64
193.34	43.02		

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(1) From a thesis presented to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The author is indebted to the Buhl Foundation of Pittsburgh for a grant which facilitated this work.

(3) Clarke and Stegeman, THIS JOURNAL, 61, 1726 (1939).

(4) Hudson and Yanovsky, *ibid.*, 39, 1013 (1917).

(5) Anderson and Stegeman, *ibid.*, 63, 2119 (1941).