just about the same as the ones reported above.

TABLE IV

n	$S_{20,m}$
0	0.0597
2	− .0419
4	.0360
6	− .0326
8	.0302
10	− .0284

Summary

A model of the potential for rotation about the ethylenic double bond is presented and the possibilities for two types of isomerization reactions are discussed. One is an adiabatic reaction which has essentially the "normal" properties for first order reactions. The other is a non-adiabatic reaction which has a very small frequency factor. It is shown that this small factor arises from two causes: (1) the interaction between the two potential surfaces concerned is rather small; (2) only a few of the states in the final potential are available to the molecules in the initial potential. Absolute reaction rate expressions are given for the rates of these reactions and the calculated rate constants for the isomerization of maleic dimethyl ester and butene-2 (which react by the non-adiabatic mechanism) are in satisfactory agreement with experimental values.

The possibility for tunneling is considered and it is concluded that there is vanishingly small probability for this process.

PRINCETON, NEW JERSEY RECEIVED AUGUST 7, 1940

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

Thermal Data. XIV. The Heat Capacities and Entropies of Some Compounds Having the Peptide Bond

BY HUGH M. HUFFMAN

The peptide bond is of primary importance in the structure of proteins. As the initial step in an investigation of the energetics of this bond we have determined the heat capacities of glycylglycine, alanylglycine, leucylglycine, hippuric acid and hippurylglycine. These data have been utilized to calculate the entropies of these compounds.

Experimental

In principle the method of Nernst was employed with an aneroid calorimeter to determine the "true" specific heat. The details of the method have been described elsewhere[1] so that only a brief account need be given. In brief it consists of supplying, electrically, a measured amount of energy to the gold calorimeter containing the substance under investigation. To ensure rapid attainment of thermal equilibrium, the substance is pressed into dense pellets, about 2 mm. thick, and spaced along the centrally located thermocouple well by means of thin gold disks which are in good thermal contact with the walls of the calorimeter. The electrical measurements of current and voltage are made on a "White" double potentiometer by the proper use of accurately calibrated resistances. Time measurements are made by means of a calibrated stop watch. The temperature measurements are made by means of the White potentiometer in conjunction with a single junction copper–constantan thermocouple. This couple is periodically standardized against one of the couples calibrated in the investigation of Giauque, Johnston and Kelley.[2]

Materials.—The *dl*-alanylglycine was a commercial product obtained from Hoffmann–LaRoche. Nitrogen determinations by micro Kjeldahls gave 99.7% of theoretical. The ash content was less than 0.1%.

The *dl*-leucylglycine was given to us by K. Linderstrøm-Lang; according to his analytical data he found 100.1% of the theoretical carboxyl groups and 99.6% of the theoretical amino groups. Nitrogen analyses by micro Kjeldahls gave 99.8% of theoretical.

The hippuric acid, hippurylglycine and glycylglycine were "Analytically Pure" products obtained from the Amino Acid Manufacturers and were guaranteed to be not less than 99.5% pure.

The heat capacity data in terms of the defined conventional calorie (1 calorie = 4.1833 int. j.) are given in Table I. The entropies of these compounds have been calculated by a graphical integration of a plot of C_p against ln T over the experimental range and by the extrapolation method of Parks, Kelley and Huffman[3] from 0 to 90°K. The molal entropies of these compounds are given in Table II. We estimate that the accuracy of the experimentally determined quantities is 1% or better. It is not possible to make a reliable estimate of the uncertainty in the extra-

(1) Parks, THIS JOURNAL, **47**, 338 (1925).

(2) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

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

polated portion of the entropy because of the differences in composition and structure between these compounds and those which were utilized in obtaining the empirical extrapolation formula. Nevertheless we believe that when these data are utilized in conjunction with data obtained in the same way on similar compounds the absolute errors will tend to cancel.

TABLE I

HEAT CAPACITY PER GRAM OF SUBSTANCE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		dl-Alanylglycine			
84.7	0.1254	129.9	0.1670	219.6	0.2385
89.5	.1300	145.5	.1798	237.9	.2516
95.7	.1358	159.4	.1899	260.0	.2694
102.5	.1433	159.6	.1899	276.1	.2816
104.0	.1448	179.9	.2061	284.4	.2876
110.3	.1512	200.2	.2222	290.8	.2924
111.0	.1523	220.3	.2378	296.4	.2973
120.4	.1596				
		Hippuric acid			
84.8	0.1075	145.1	0.1562	260.2	0.2519
89.6	.1111	160.0	.1680	275.8	.2658
95.6	.1160	174.7	.1798	281.1	.2707
103.1	.1228	190.2	.1936	287.7	.2761
111.0	.1292	205.7	.2058	293.3	.2814
120.1	.1369	220.2	.2186	298.4	.2859
129.6	.1440	240.4	.2348		
		Glycylglycine			
86.7	0.1239	136.0	0.1734	244.1	0.2555
91.8	.1292	155.4	.1894	257.6	.2650
97.9	.1355	172.8	.2040	276.2	.2784
103.2	.1417	190.4	.2168	280.3	.2818
110.4	.1486	209.5	.2308	287.2	.2877
117.2	.1561	223.5	.2403	293.9	.2927
		dl-Leucylglycine			
85.7	0.1216	160.4	0.2015	240.2	0.2731
90.8	.1278	170.0	.2102	250.6	.2820
97.6	.1365	179.7	.2189	261.0	.2916
105.9	.1463	189.2	.2279	276.6	.3056
113.7	.1550	200.0	.2375	283.4	.3121
130.9	.1732	209.7	.2466	290.5	.3184
140.6	.1829	220.4	.2556	297.1	.3246
150.4	.1920	230.3	.2626		
		Hippurylglycine			
84.7	0.1066	147.2	0.1622	228.7	0.2236
87.7	.1088	156.4	.1682	241.5	.2337
93.6	.1136	160.7	.1707	253.7	.2438
94.6	.1152	173.6	.1805	262.2	.2508
100.3	.1201	180.7	.1854	265.7	.2534
102.8	.1223	185.9	.1896	277.3	.2638
112.2	.1304	198.0	.1991	281.7	.2673
122.7	.1414	205.9	.2052	287.2	.2716
133.1	.1513	216.7	.2140	296.7	.2808
134.1	.1520				

TABLE II

ENTROPIES OF THE COMPOUNDS

Cal. degree^{-1} mole^{-1}

Substance	S_{90}	$\Delta S_{90\text{-}298.1}$	$S_{298.1}$
dl-Alanylglycine	15.84	35.15	51.0
Hippuric acid	18.48	38.72	57.2
Glycylglycine	13.60	31.80	45.4
dl-Leucylglycine	19.71	45.50	67.2
Hippurylglycine	24.14	51.04	75.2

Summary

1. The experimentally determined heat capacities of *dl*-alanylglycine, glycylglycine, *dl*-leucylglycine, hippuric acid and hippurylglycine have been presented.

2. The entropies of the five peptides at 298.1°K. have been calculated.

PASADENA, CALIFORNIA RECEIVED NOVEMBER 18, 1940

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Interaction of Ions and Dipolar Ions. II. The Solubility of Silver Iodate and Lead Iodate in Glycine and in Alanine Solutions[1]

BY R. M. KEEFER AND H. G. REIBER

In a previous communication[2] it was shown that the solubility of barium iodate and calcium iodate at 25° in aqueous glycine or alanine solutions could be expressed by equations of the type

$$\frac{1}{Z_1Z_2}\log\frac{S}{S_\infty} = 0.505\left(\frac{78.54}{D_d}\right)^{3/2}\frac{\sqrt{\mu}}{1+A\sqrt{\mu}} + 0.0625\frac{R^2}{a}[R^\pm] \quad (1)$$

where Z_1 and Z_2 are the valences of the ions; D_d is the dielectric constant of the amino acid solution; A, R, and a are constants; and $[R^\pm]$ is the molality of the dipolar ions. The solubility of silver iodate or of lead iodate in glycine or in alanine solutions is much larger than could be pre-

(1) Presented at the Detroit Meeting of the American Chemical Society, September, 1940.

(2) Keefer, Reiber and Bisson, THIS JOURNAL, **62**, 2951 (1940). The following corrections should be made in Part 1. The ordinates of Figs. 1 and 2 should be divided by two. The ordinates of Fig. 3 should read 0.01 and 0.02 instead of 0.05 and 0.10. The values of $\Delta\left(\frac{1}{Z_1Z_2}\log S\right)$ in Table IV should be multiplied by 10^{-4}.