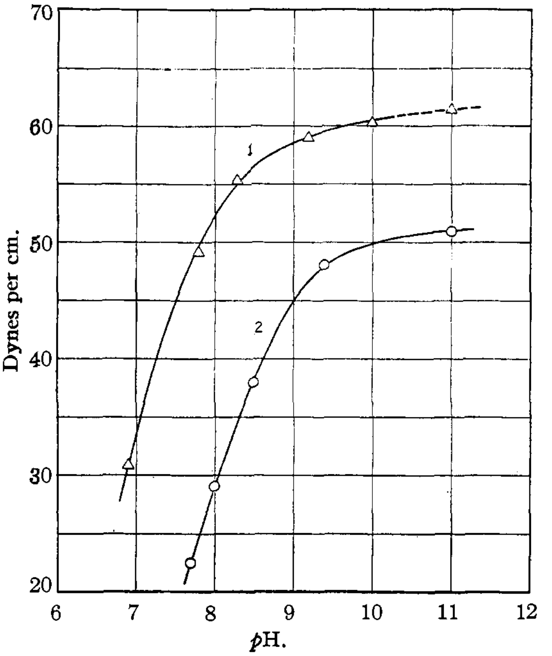

Fig. 5.—Equilibrium surface tension of sodium laurate solutions in 0.001 *N* buffers. Curve 1 is for 0.001 *N* laurate. Curve 2 is for 0.005 *N* laurate.

grossly retard the speed of stable orientation of molecules in the surface region, so that the speed of transport of solute from the bulk of the solution to the surface region is no longer the principal factor determining the time effect in the surface tension.

Summary

The fall with time of the surface tension of aqueous solutions of sodium laurate has been measured by the method of sessile bubbles at 25°. The range of soap concentration was from 0.001 *N* to 0.07 *N*, and of *p*H from 7 to 11. At *p*H 11 and concentrations less than the critical concentrations for micelle formation the surface tension falls gradually for several hours. The equilibrium surface tension depends upon the concentration. The time effect largely disappears in micellar solutions. With decreasing *p*H the equilibrium surface tension and the time required to attain it diminish markedly. This result is thought due to the possibility of closer packing of fatty acid molecules than ions in the surface film and the more rapid diffusion of non-ionized molecules into the surface region.

ITHACA, NEW YORK RECEIVED AUGUST 6, 1940

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Calorimetric Investigations of Organic Reactions. III. The Heats of Ionization of Glycine at 25°[1]

BY JULIAN M. STURTEVANT

The only data concerning the heats of ionization of amino acids at present available are those determined from the temperature coefficients of the ionization constants.[2] While it is probable that the ionization constants themselves are quite reliable, the temperature coefficients are small, so that the per cent. errors in the heats of ionization may be large. For example, in the case of the acid ionization of glycine, measured by Owen,[3] errors in the values of log K_A of ±0.5 per cent. could, in the most unfavorable case, cause an error of 25% in the temperature coefficient and the heat of ionization. The per cent. error to be expected in the heat of the basic ionization of glycine as determined by electromotive force measurements is considerably smaller, partly because the temperature coefficient of the ionization constant is larger and partly because the basic constants themselves are smaller and can therefore be determined with greater accuracy.

The present paper reports some calorimetric measurements of the heats of neutralization of glycine by hydrochloric acid and sodium hydroxide. The interpretation of the calorimetric data is complicated by various medium effects, but it is believed that reliable values for the ionization heats are obtained.

Experimental Part

The calorimetric measurements were made in the apparatus described elsewhere.[4] In the present experiments, varying amounts of hydrochloric acid or sodium hydroxide contained in the dilution cup were allowed to react with varying

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[1] Part of the material in this paper was presented at the Cincinnati meeting of the American Chemical Society, April, 1940.

[2] See the review by Harned and Owen, *Chem. Rev.*, **25**, 31 (1939).

[3] Owen, THIS JOURNAL, **56**, 24 (1934).

[4] Sturtevant, *J. Phys. Chem.*, in press.

amounts of glycine dissolved in pure water in the calorimeter. In the sodium hydroxide experiments, precautions described previously[5] were taken to prevent contamination by atmospheric carbon dioxide.

The stock hydrochloric acid was made up from Baker analyzed material, and was standardized gravimetrically, its concentration being known to better than ±0.05%. The preparation and analysis of the stock sodium hydroxide solution has already been described.[5] The glycine was part of the sample used in some dilution experiments,[6] and was kindly furnished by Dr. B. B. Owen[3] of this Laboratory. At the completion of the experiments it was found that the glycine lost 0.02% of its weight after six days at 100–105° and atmospheric pressure. It was therefore concluded that the moisture content was negligible.

Corrections for the change of the vapor pressure of the solvent during the dilution have been applied.

Experiments with Hydrochloric Acid.—In the experiments with hydrochloric acid, the process of which the heat effect was measured consisted in the addition of n_1 moles of m_1' molal hydrochloric acid to n_2 moles of m_2' molal glycine zwitterion,[7] to form n_3 moles of glycine hydrochloride at a molality of m_3

$$n_1\text{HCl}(m_1') + n_2\text{Z}^{\pm}(m_2') = n_3\text{Z}\cdot\text{HCl}(m_3) + (n_1 - n_3)\text{HCl}(m_1 - m_3) + (n_2 - n_3)\text{Z}^{\pm}(m_2 - m_3);\ \ \Delta q \qquad (1)$$

The values of m_3, $m_1 - m_3$, $m_2 - m_3$ can be calculated from the values of m_1, m_2, the final molalities of HCl and $\text{Z}^{\pm}$ if no reaction had taken place, by means of the ionization constant. The ionization process may be represented by the equation

$$\text{ZH}^+ = \text{Z}^{\pm} + \text{H}^+;\ \ \Delta H_{\text{A}} \qquad (2)$$

The thermodynamic ionization constant is

$$K_{\text{A}} = k_{\text{A}}\frac{\gamma_{\text{Z}^{\pm}}\gamma_{\text{H}^+}}{\gamma_{\text{ZH}^+}} \equiv k_{\text{A}}\gamma_{\text{A}}^2 \qquad (3)$$

where the γ's are activity coefficients and k_{A} is the apparent ionization constant given by

$$k_{\text{A}} = \frac{(m_1 - m_3)(m_2 - m_3)}{m_3} \qquad (4)$$

The value of K_{A} reported by Owen,[3] 0.00447 at 25°, has been used. The only values for the activity ratio γ_{A} available are those determined by Harned and Owen[8] for 0.1 molal glycine solutions:

$$\log \gamma_{\text{A}} = 0.055\,\mu = 0.055m_1 \qquad (5)$$

These values have been employed although the glycine concentrations used varied from 0.02 to 0.3 molal. However, it will be shown later that the results are insensitive to the value of the ionization constant, and that, in fact, a value for the constant can be calculated from the calorimetric data which is in fair agreement with the e. m. f. value, and which gives essentially the same values for the heat of ionization.

The observed heat effect includes the heat of the dilution of the hydrochloric acid by the water in the glycine solution and of the dilution of the glycine by the water in the hydrochloric acid. We therefore deduct the dilution heats

$$n_1\text{HCl}(m_1') = n_1\text{HCl}(m_1);\ \ n_1\Delta H_1 \qquad (6)$$

$$n_2\text{Z}^{\pm}(m_2') = n_2\text{Z}^{\pm}(m_2);\ \ n_2\Delta H_2 \qquad (7)$$

to obtain the heat of the hypothetical process

$$n_1\text{HCl}(m_1) + n_2\text{Z}^{\pm}(m_2) = n_3\text{Z}\cdot\text{HCl}(m_3) + (n_1 - n_3)\text{HCl}(m_1 - m_3) + (n_2 - n_3)\text{Z}^{\pm}(m_2 - m_3);\ \ \Delta q - n_1\Delta H_1 - n_2\Delta H_2 \qquad (8)$$

The values of ΔH_1 [9] and ΔH_2 [6] were interpolated in previously published results.

If we assume that Z·HCl is completely ionized to ZH^+ and Cl^-, it follows that

$$\Delta H_{\text{A}} = -\frac{1}{n_3}\Delta q + \frac{n_1}{n_3}\Delta H_1 + \frac{n_2}{n_3}\Delta H_2 \qquad (9)$$

However, this ΔH_{A} is probably not to be identified with ΔH_{A}^0, the heat of ionization of one mole of $\text{Z}\cdot\text{H}^+$ at infinite dilution, since various medium effects are doubtless operative at finite concentrations, and since an excess of HCl and $\text{Z}^{\pm}$ are present. No fully satisfactory method of deducing the value of ΔH_{A}^0 has been developed in the present case. It is found that ΔH_{A} as calculated by equation (9) can with fair accuracy be represented as a linear function of the ionic strength, m_1, and the extrapolated value at $m_1 = 0$ has been taken as the appropriate value of ΔH_{A}^0. However, it is felt that the deviations of the individual values of ΔH_{A} from the straight line are larger than the experimental accuracy of the data warrant, presumably because of the presence of further unidentified medium effects. Because of this fact rather complete experimental data will be reported, so that attempts by others to develop a more satisfactory interpretation may be made.

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(5) Sturtevant, THIS JOURNAL, **62**, 2276 (1940).

(6) Sturtevant, *ibid.*, **62**, 1879 (1940).

(7) It can be shown that at concentrations of glycine above about 0.005 molal in pure water only about 0.04% of the glycine is in the form of positive and negative amino acid ions. It is therefore a sufficiently good approximation to consider the glycine as being entirely zwitterionic. A more detailed discussion of this point, in connection with the heat of dilution of glycine, will be presented in a forthcoming communication.

(8) Harned and Owen, THIS JOURNAL, **52**, 5091 (1930).

(9) Sturtevant, *ibid.*, **62**, 584 (1940).

TABLE I

HEAT OF REACTION OF GLYCINE WITH HYDROCHLORIC ACID IN WATER AT APPROXIMATELY 25°
Concentration of Hydrochloric Acid, m_1', = 3.3369 molal in Runs 1–6, 3.3292 in Runs 7–13.

Run	Moles of HCl n_1	Moles of glycine n_2	Ionic strength m_1	Initial molality of glycine m_2'	Final total molality of glycine m_2	Initial temp., °C.	Heat capac. of final soln., joules (int.) per g. per °C.	Observed temp. rise, °C.	Observed heat effect, Δq joules (int.)	Heat of diln. of HCl $n_1 \Delta H_1$, joules (int.)	Heat of diln. of glycine, $n_2 \Delta H_2$ joules (int.)	Corrected heat effect $\Delta q - n_1 \Delta H_1 - n_2 \Delta H_2$ joules (int.)
1	0.02639	0.01795	0.2012	0.1456	0.1369	25.03	4.105	0.2479	−149.48	−80.21	+0.07	− 69.34
2	.01148	.01383	.0986	.1223	.1187	24.97	4.130	.1430	− 77.63	−37.36	.02	− 40.29
3	.002076	.02973	.0174	.2502	.2489	25.05	4.112	.02799	− 15.64	− 7.42	.01	− 8.23
4	.02650	.04110	.2030	.3354	.3149	24.89	4.086	.3106	−187.89	−80.29	.32	−107.92
5	.01665	.01121	.1237	.0865	.0833	24.92	4.136	.1528	− 94.42	−53.09	.02	− 41.35
6	.01151	.005316	.0948	.0451	.0438	24.92	4.154	.1017	− 57.28	−37.50	.00	− 19.78
7	.02199	.02202	.1815	.1923	.1818	24.74	4.114	.2578	−145.32	−67.22	.10	− 78.20
8	.01266	.01268	.0935	.0964	.0936	24.82	4.148	.1325	− 82.55	−41.18	.02	− 41.39
9	.008261	.008265	.0637	.0650	.0638	24.96	4.159	.08815	− 52.78	−27.67	.00	− 25.11
10	.01102	.02204	.0808	.1655	.1615	25.03	4.123	.1251	− 78.41	−36.36	.04	− 42.09
11	.02772	.002901	.2105	.0235	.0220	25.15	4.116	.1584	− 95.38	−83.78	.00	− 11.60
12	.02971	.004757	.2326	.0400	.0372	25.01	4.119	.1844	−108.23	−88.53	.01	− 19.74
13	.01919	.01251	.1532	.1047	.0999	25.00	4.127	.1854	−107.35	−59.93	.03	− 47.45

TABLE II

HEAT OF THE ACID IONIZATION OF GLYCINE AT 25°

Run	$k_A \times 10^3$	Molality of ZHCl m_3	Moles of ZHCl n_3	Heat of ionization, ΔH_A, joules (int.) per mole	ΔH_A (25°)	ΔH_A Calcd. by Eq. (11)	Deviation, joules per mole		ΔH_A calcd. by successive approximations
							Expected	Observed	
1	4.25	0.1292	0.01695	4091	4095	4145	± 9	− 50	4099
2	4.36	.0867	.01011	3987	3983	4016	11	− 33	3984
3	4.45	.0171	.002037	4038	4044	3913	49	+131	4033
4	4.24	.1960	.02559	4218	4204	4148	6	+ 56	4208
5	4.32	.0763	.01027	4026	4016	4047	11	− 31	4021
6	4.35	.0406	.004922	4019	4009	4011	21	− 2	4014
7	4.26	.1559	.01888	4142	4109	4120	7	− 11	4115
8	4.36	.0754	.01021	4052	4027	4009	12	+ 18	4034
9	4.40	.0490	.006358	3950	3945	3972	18	− 28	3947
10	4.38	.0768	.01048	4017	4021	3993	12	− 28	4025
11	4.24	.0215	.002838	4089	4108	4157	39	− 49	4108
12	4.21	.0365	.004657	4233	4234	4185	23	+ 49	4243
13	4.30	.0932	.01168	4064	4064	4085	11	− 21	4068
						Mean	±18	± 39	

It should be emphasized that it is not likely that any revision in the interpretation of the data will produce a large change in the value assigned to ΔH_A^0.

It has been shown by Lambert and Gillespie,[10] in the case of the neutralization of strong acids by strong bases, that heats of ionization should be calculated to constant concentration. In the present case attempts to do this by correcting the HCl and $Z^{\pm}$ concentrations to m_3 have led to values of ΔH_A which could not be brought into reasonable correlation with any of the variables.

The experimental data are summarized in Table I. The heat capacities of the final solutions were measured as previously described[4]; since these heat capacities were used to evaluate the heats of reaction, the initial temperature is to be taken as the temperature of the reaction. These heat capacities may not be very precise since it was not convenient to hold constant the amount of gold foil and vaseline used in sealing the dilution cup. The corrected heat effects listed in the last column were obtained by deducting the hydrochloric acid and glycine dilution heats from the observed heat.

Table II summarizes the calculation of the ionization heats. Using the ionization constants listed in the second column, the molalities and numbers of moles in the third and fourth columns are readily calculated. The quantities in the fifth column are the negative of the figures in the last column of Table I divided by n_3. These quantities have been corrected to 25° using the

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[10] Lambert and Gillespie, THIS JOURNAL, 53, 2632 (1931).

temperature coefficient found by Owen[3] for the heat of ionization.

Three different temperature intervals are involved in calculating ΔH_A: the temperature rise due to the reaction, the part of this rise due to the dilution effects, and the temperature rise during the heat capacity determination. If we leave out of consideration the very small glycine dilution heats, and assign an uncertainty of ± 0.10 microvolt (120 microdegrees) to each of the first two temperature intervals, and ±0.05 to the last interval, we find that the expected uncertainty in ΔH_A is

$$\delta(\Delta H_A) = \pm 0.05\frac{C}{n_3}\sqrt{8 + \left(\frac{\Delta\mu_1}{\Delta\mu_2}\right)^2} \qquad (10)$$

where C is the total heat capacity (solution plus calorimeter) in joules per microvolt, $\Delta\mu_1$ is the observed temperature rise in microvolts minus that due to the hydrochloric acid dilution, and $\Delta\mu_2$ is the temperature rise in the heat capacity determination. Values of $\delta(\Delta H_A)$ calculated in this way are listed in the eighth column of Table II.

The values of ΔH_A were fitted to a linear equation in the ionic strength by the method of least squares, the individual values being weighted in proportion to the reciprocal of the expected deviation. The equation obtained is

$$\Delta H_A = 3891 + 1264\, m_1 \qquad (11)$$

Comparison of the eighth and ninth columns of Table II shows that the deviations of the observed ΔH_A from this equation average about twice as large as the expected deviations. It seems probable that this discrepancy indicates that the interpretation of the experimental data is not complete.

A method of successive approximations may be employed to calculate values of ΔH_A which are independent of the e. m. f. values of k_A. An approximate value of ΔH_A is obtained from the runs in which a large excess of acid or glycine was used, since for these runs $n_3 \approx n_2$ or n_1, respectively. This ΔH_A is used with the data for the runs for which $n_2/n_1 = 1$ to calculate k_A, it being assumed that k_A is constant over the whole concentration range involved. The value obtained in this way is $k_A = 0.00354$. This k_A is employed in the remaining ten runs to calculate ΔH_A, the values obtained being used to determine the coefficients in an equation of the form of equation (11). The data in runs having $n_2/n_1 \approx 1$ (runs 1, 2, 5, 7, 8, 9) are then utilized to calculate a new k_A, the result being 0.00436 (average deviation from the mean = ±0.00039). This value of k_A leads to the ΔH_A given in the last column of Table II. It is seen that these values agree closely with those obtained using the k_A derived from e. m. f. data. The closeness of the agreement found is somewhat fortuitous, though a considerably different value of k_A would not seriously alter the ΔH_A.

Experiments with Sodium Hydroxide.—The treatment of the data obtained with sodium hydroxide is entirely analogous to that given above, if we take as the ionization process

$$\text{ZOH}^- = \text{Z}^\pm + \text{OH}^-;\ \Delta H_B \qquad (12)$$

for which

$$K_B = \frac{(m_1 - m_3)(m_2 - m_3)}{m_3}\,\frac{\gamma_{Z^\pm}\,\gamma_{OH^-}}{\gamma_{ZOH^-}} \equiv k_B\gamma_B^2 \qquad (13)$$

instead of employing the alternative scheme in which K_B is replaced by K_W/K_{A_2}, K_{A_2} being the second dissociation constant of the dibasic acid ZH^+. In equation (13), m_1, m_2 are, respectively, the final concentrations of alkali and glycine if no reaction had occurred, and m_3 is the concentration of sodium glycinate formed. As in the previous case, the value $K_B = 0.000060$ given by Owen[3] was used in the calculations. In the present case the results are so insensitive to the value of the ionization constant that the apparent constant may be set equal to the thermodynamic constant.

Table III gives a summary of the experimental results. One run has been omitted because the dilution cup leaked, and another because it showed a very large deviation from the other runs, the reason for the deviation being unknown.

The calculation of the ionization heats is summarized in Table IV. The quantities in each column have a significance entirely analogous to those in the corresponding column of Table II. In calculating the expected deviations, an uncertainty of ±0.05 microvolt has been assigned to each of the temperature intervals involved. As before it is found that the deviations from the least squared equation

$$\Delta H_B = 11{,}591 - 466\, m_1 \qquad (14)$$

are somewhat larger than the expected deviations.

If we consider ZH^+ as a dibasic acid, then its ionization heats are related to ΔH_A and ΔH_B as follows

$$\Delta H_{A_1} = \Delta H_A;\ \Delta H_{A_2} = \Delta H_W - \Delta H_B$$

If we take for ΔH_W the value 56,050 joules per mole given by Lambert and Gillespie,[10] we obtain $\Delta H^0_{A_2} = 44{,}460$ joules per mole.

TABLE III

HEAT OF REACTION OF GLYCINE WITH SODIUM HYDROXIDE AT APPROXIMATELY 25°

Concentration of Sodium Hydroxide, $m_1' = 4.1826$

Run	Moles of NaOH n_1	Moles of glycine n_2	Ionic strength m_1	Initial molality of glycine m_2'	Final total molality of glycine m_2	Initial temp., °C.	Heat capac. of final soln., joules (int.) per g. per °C.	Observed temp. rise, °C.	Observed heat effect, Δq joules (int.)	Heat of diln. of NaOH, $n_1 \Delta H_1$, joules (int.)	Heat of diln. of glycine, $n_2 \Delta H_2$, joules (int.)	Corrected heat effect $\Delta q - n_1 \Delta H_1 - n_2 \Delta H_2$, joules (int.)
1	0.006019	0.004891	0.0454	0.0373	0.0369	24.99	4.169	0.08983	− 54.89	+ 1.72	0	− 56.61
2	.008051	.008052	.0645	.0656	.0645	25.02	4.158	.1514	− 87.52	2.60	0	− 90.12
3	.01345	.01346	.1046	.1073	.1047	25.04	4.149	.2458	−146.35	5.03	+0.02	−151.40
4	.001214	.001228	.00879	.00891	.00889	24.97	4.163	.02046	− 13.00	0.15	0	− 13.15
5	.03488	.004549	.2549	.0354	.0333	25.02	4.123	.05863	− 36.72	15.59	+0.01	− 52.32
6	.03062	.001016	.2180	.00764	.00724	25.01	4.139	−.00297	+ 1.895	13.49	0	− 11.60
7	.002204	.03481	.0156	.2477	.2468	25.00	4.115	.03866	− 25.10	0.38	+0.01	− 25.49
8	.006108	.02426	.0474	.1904	.1882	25.01	4.129	.1146	− 68.36	1.76	.02	− 70.14

TABLE IV

HEAT OF THE BASIC IONIZATION OF GLYCINE AT 25°

Run	Molality of sodium glycinate m_3	Moles of sodium glycinate n_3	Heat of ionization, ΔH_B, joules (int.) per mole	ΔH_B (25°)	ΔH_B calcd. by Eq. (14)	Deviation, joules per mole Expected	Observed
1	0.0367	0.004858	11652	11651	11570	±21	+ 81
2	.0626	.007807	11544	11545	11561	18	− 16
3	.1021	.01313	11527	11530	11542	18	− 12
4	.00814	.001124	11701	11698	11587	56	+111
5	.0332	.004548	11504	11506	11472	22	+ 34
6	.00724	.001016	11416	11417	11489	62	− 72
7	.0156	.002204	11567	11567	11584	32	− 17
8	.0474	.006105	11489	11490	11569	19	− 79
					Mean	±31	± 53

It is interesting to present the heat data in the form of a thermal titration curve. If we plot the heat of partially neutralizing one gram of glycine from its isoelectric *p*H (6.1) to another *p*H as a function of the latter *p*H, we obtain an S-shaped curve reminiscent of ordinary titration curves (Fig. 1). Since the *p*H's of the solutions were not measured, and since the calculation of *p*H values involves several uncertainties, it has seemed best for the present purposes to use hydrogen ion concentrations rather than activities. Taking the value $-\log K_W = 14.00$, we then have

$pH \approx -\log (m_1 - m_3)$ for the experiments with HCl

$pH \approx 14.00 + \log (m_1 - m_3)$ for the experiments with NaOH

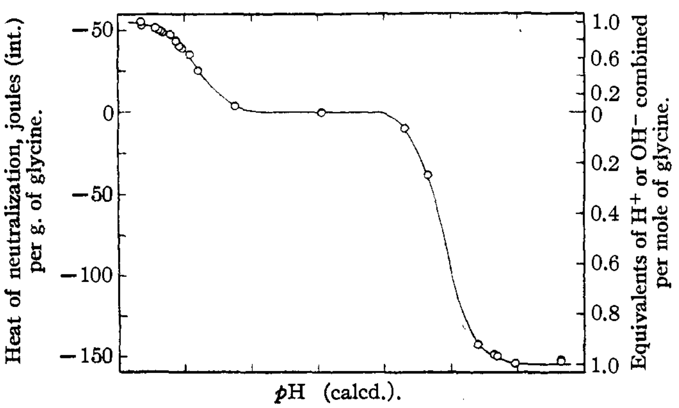

Fig. 1.—Thermal titration curve for glycine at 25°. The solid line is the calculated dissociation curve (vertical scale distorted). The calorimetric data are represented by circles.

For comparison with the calorimetric data, the solid curve in Fig. 1 is a calculated titration curve. The vertical scale in this plot has been adjusted so that it is proportional to the heat of neutralization on both the acidic and basic sides. This curve is a plot of m_3/m_2 as a function of the (calculated) *p*H. While these calculated *p*H values are probably considerably in error, the comparison between the ordinary and thermal titration curves is valid since the same *p*H values are used in both cases. The fact that the calorimetric points do not coincide with the titration curve is perhaps to be attributed to the incomplete evaluation of the various medium effects in operation. In order to improve this situation, it might be advantageous to perform future experiments of this type in the presence of a neutral salt, such as potassium chloride, added in sufficient amount to make the ionic strengths of the final solutions constant.

Comparison with Previous Results.—Both ΔH^0_A and ΔH^0_B were determined by Owen[3] by the e. m. f. method. The values obtained by him are given in Table V, together with values calculated by other workers from his data. The values of ΔH_A and ΔH_B at zero ionic strength found in this research are also given in the table for comparison. The agreement in the case of ΔH^0_A is probably within the accuracy of the e. m. f. data. The excellent agreement in the case of ΔH^0_B is, of course, fortuitous, though, as pointed out above, one would expect better agreement in this case.

TABLE V

IONIZATION HEATS OF GLYCINE AT 25°

			Calculated from Owen's e. m. f. data by		
		Owen[3]	Harned and Owen[2]	Everett and Wynne-Jones[b]	This Research
ΔH^0_A	joules per mole	4848	4915	4602	3891
	calories[a] per mole	1159	1175	1100	930
ΔH^0_B	joules per mole	11570	11570	11710	11591
	calories[a] per mole	2765	2765	2800	2771

[a] One calorie = 4.1833 international joules.

[b] Everett and Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

The application of the calorimeter developed by the author to these amino acid reactions has been carried out at the suggestion of Professor Edwin J. Cohn of the Harvard Medical School.

Summary

Calorimetric measurements of the heats of neutralization of glycine by hydrochloric acid and sodium hydroxide at 25° are reported. The results of these measurements are interpreted to yield values of the acidic and basic ionization heats which are in satisfactory agreement with the less accurate values deduced from electromotive force measurements.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 24, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 83]

Studies in Organo-Silicon Synthesis. III. Two-Stage Wurtz Reactions with Silicon Halides

BY WALTER C. SCHUMB AND CHARLES M. SAFFER, JR.[1]

In the first paper of this series[2] it was shown that hexaaryldisilanes are not formed from hexachlorodisilane and hexachlorodisiloxane in the Wurtz reaction with aryl halides and sodium. Instead the Si–Si or Si–O–Si bond was invariably broken, leading to the formation of the tetrasubstituted monosilanes. In an attempt to elucidate the mechanism of the general reaction, the Wurtz reactions between hexachlorodisilane and hexabromodisiloxane with chlorobenzene and sodium have been carried out in two stages. The intermediate sodium compound was first prepared from chlorobenzene and sodium. Then the silicon halide was allowed to react with it. Although some tetraphenylsilane resulted, the main products of the two reactions were hexaphenyldisilane and hexaphenyldisiloxane, respectively. These two latter compounds had been prepared previously from the same silicon halides only by a special use of the Grignard reagent.[3] These results seem to indicate that in the ordinary one-stage Wurtz reaction the energy liberated in the system by the formation of sodium phenyl is enough to rupture the Si–Si and Si–O–Si bonds. When this energy is evolved and dissipated before the silicon halide is added, no bond fission occurs. The presence of some tetraphenylsilane in both reactions is explained by the incomplete conversion of the chlorobenzene to phenylsodium.

To test the further substitution of sodium compounds for the Grignard reagent in organo-silicon synthesis, the reaction between excess silicon tetrachloride and phenylsodium was carried out. The products were the same as those obtained when phenylmagnesium bromide was used. Benzylsodium was condensed with hexachlorodisilane and the hitherto unreported hexabenzyldisilane was obtained. In order to establish its identity more completely, this compound also was prepared from benzylmagnesium chloride and Si_2Cl_6 by the Grignard reaction, since previous work[3] had proved that hexasubstituted disilanes are readily prepared by this method. The resulting

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(1) Present address: Converse Memorial Laboratory, Harvard University, Cambridge, Mass.

(2) Schumb, Ackerman and Saffer, THIS JOURNAL, **60**, 2486 (1938).

(3) Schumb and Saffer, *ibid.*, **61**, 363 (1939).