The Heats of Dilution of Aqueous Solutions of Glycine at 25°

BY JULIAN M. STURTEVANT

In connection with other calorimetric work in progress in this Laboratory it became necessary to determine the heats of dilution of aqueous solutions of glycine at 25°. Glycine which had been carefully purified by Owen[1] was used after being dried for several days at 100°. The calorimeter and experimental procedure have been described[2] elsewhere. The specific heat data for glycine solutions given by Gucker, Ford and Moser,[3] and the value for the specific heat of water at 25° due to Osborne, Stimson and Ginnings[4] were used in the calculations.

The experimental data are summarized in Table I. Values of the relative apparent molal heat content, $\Phi_H - \Phi_H^0$, were obtained by extrapolation of the experiments with the 1.1407 M and 0.9670 M solutions to infinite dilution, assuming linearity with the first power of the molality in dilute solutions. These values are plotted in Fig. 1 against the molality of the glycine. The smooth curve in this plot is given by the expression

TABLE I

THE HEATS OF DILUTION OF AQUEOUS SOLUTIONS OF GLYCINE AT 25°

Initial molality	Final molality	Heat of dilution int. joules per mole	Deviation from Eq. (1) Joules per mole	Microvolts
1.1407	0.0366	401.1	+6.7	+0.04
1.1407	.0496	384.4	−3.9	− .03
1.1407	.0967	369.5	+3.0	+ .05
1.1407	.1660	335.0	−0.8	− .02
0.4316	.0361	156.8	−9.0	− .05
.8291	.0700	285.7	−0.1	0
.8291	.0805	279.3	−1.7	−0.02
.9670	.0253	354.6	+5.4	+ .02
.9670	.0378	335.5	−7.8	− .05
.9670	.0434	338.2	−2.5	− .02
.9670	.0577	335.5	+1.6	+ .02
.9670	.0724	323.7	−3.4	− .04
		Mean	±3.8	± .03

$$\Phi_H - \Phi_H^0 = \frac{-485m}{1 + 0.395m} - 23.7m^2 \qquad (1)$$

The experimental values show an average deviation from this curve of ±4 joules per mole. Values of the heats of dilution, Φ_H (final) − Φ_H (initial), calculated from this equation show an average deviation from the experimental values corresponding to an error in the temperature change measurements of ±0.03 microvolt (approximately 40 microdegrees), which is about the error to be expected with the temperature measuring device used.

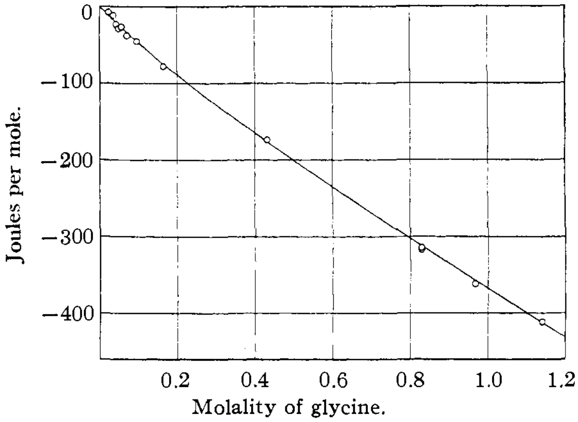

Fig. 1.—Relative apparent molal heat content of glycine solutions at 25°.

The last five runs were made under conditions designed to ensure the exclusion of carbon dioxide from the solutions. It is seen that these runs are consistent with the others in which no special precautions were taken beyond employing boiled, distilled water which had been cooled in an atmosphere of tank nitrogen.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

RECEIVED APRIL 4, 1940

---

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

[2] Sturtevant, *J. Phys. Chem.*, in press; THIS JOURNAL, **62**, 584 (1940).

[3] Gucker, Ford and Moser, *J. Phys. Chem.*, **43**, 153 (1939).

[4] Osborne, Stimson and Ginnings, *Bur. Standards J. Research*, **23**, 197 (1939).

Quantum Yield in Chloroacetic Acid

BY LLOYD B. THOMAS

Rudberg[1] has determined the quantum yield for the hydrolysis of monochloroacetic acid to be 1.05 chloride ions produced per absorbed quantum of λ 2537 and offered this in support of the Einstein Law of Photochemical Equivalence. This system has since been widely used as a standard actinometer for photochemical reactions. Harris and Kaminsky[2] have used their "precision actinometer" to check Rudberg's value and obtained a quantum yield of 1.07 with an accuracy within 5.5%. Smith, Leighton and Leighton[3] have repeated the determination with the startling result that the quantum yield at 25° is 0.315. It seems important that this value be checked.

---

[1] Rudberg, *Z. Physik*, **24**, 247 (1924).

[2] Harris and Kaminsky, THIS JOURNAL, **57**, 1158 (1935).

[3] Smith, Leighton and Leighton, *ibid.*, **61**, 2299 (1939).

We have used the chloroacetic acid actinometer together with three thermopiles, two quartz-cadmium photocells, and two Bureau of Standards lamps in an attempt to make an accurate determination of the light flux from a true resonance type source of λ 2537.[4] The thermopiles were of the vacuum quartz type, two constructed with the Bi–Ag couple and one with the Bi–Bi 5% Sn couple. Two had platinum black receivers and one carbon black. These were used in two ways. First, the flux of λ 2537 was measured directly by placing the thermopiles with the elements 6 cm. below the exit window and alternately freezing out with liquid air and resupplying mercury vapor to the resonance lamp. Second, the thermopiles were used to calibrate the photocells using a Hg–He discharge tube from which the fraction of energy emitted at λ 2537 was estimated by filters and spectrograms to be 85% and which had a much greater intensity than the resonance lamp so would give larger thermopile deflections. At least 99% of the deflection with the photocells when using the Hg–He discharge tube was due to λ 2537 as judged by interposing a Corning 986 Corex Red-Purple filter between the source and the photocells on the one hand, and between the source and the spectrograph on the other. The photocell reading was reduced to 2.7% by the filter (5 mm.) and the time of exposure of the spectrum plate had to be increased about thirty times to give the same darkening of the 2537 line. The transmission of this filter according to the curve given by the makers is about 3% at 2537 Å. The resonance lamp gives 99.9% of its line energy at 2537 Å. judging from a series of spectrograms ranging in exposure from one-fourth to two hundred and fifty seconds. The above estimates neglect the possibility of the presence of some radiation at λ 1849. This is absorbed strongly in air and is shown not to be present in appreciable amount by the fact that the intensities from the He–Hg discharge tube as measured by the photocell obeyed closely the inverse square law up to 80 cm. in air, the largest distance tried.

The average of ten determinations involving various combinations of the above instruments gave 5.93×10^{12} quanta per sq. cm. per second at 6 cm. from the resonance lamp exit window, per unit photocell current. A photocell was used at all times with the resonance lamp as a check on the constancy of its intensity. The mean deviation among these ten values was 5% from the above value. Exposures were made in a quartz cylindrical vessel 8 mm. in thickness placed 6 cm. below the exit window. The vessel was filled with 1 *M* acid and exposed for periods of about five hours. During exposure the intensity of the lamp was followed with the photocell. Exposed and unexposed samples were run consecutively for chloride ion by electrometric titration with standard silver nitrate using the calomel and silver–silver chloride electrodes. The e. m. f. *vs.* volume of silver nitrate curves were plotted together and the amount of chloroacetic acid hydrolyzed by the light was read from the difference along the volume axis between the two curves at the inflection point. Microburets were used and the above differences amounted to about 0.6 ml. of 0.000864 *N* silver nitrate. The normality of the silver nitrate checked well against standard potassium chloride solution by the titration method used.

The quantum yields at 26° on the two samples run were 0.332 and 0.352. The average of these, 0.342, is to be compared to the value 0.33, read from the curve of Smith, Leighton and Leighton for 26°. The agreement is within the errors of measurement in either experiment.

CHEMISTRY LABORATORY
THE UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI

RECEIVED MAY 6, 1940

---

[4] Described at A. C. S. meeting, Cincinnati, Ohio, April 9, 1940.

NEW COMPOUNDS

DIMETHYLETHYLPHENYLAMMONIUM BROMIDE

Dimethylaniline was allowed to react with ethyl bromide in the cold for a few days. The product recrystallized from absolute alcohol and ethyl acetate gave fine glistening needles which sublimed at 193–194° (uncor.) and turned slightly blue on standing, presumably through oxidation. This substance has already been mentioned[1] as formed from dimethylaniline and ethyl bromide but no analysis or statement of its properties has been given.

Anal. Calcd. for $C_{10}H_{16}NBr$: C, 52.18; H, 7.01; N, 6.09; Br, 34.71. Found: C, 52.42; H, 7.16.

This work was done at the suggestion and under the direction of Dr. Alexander E. Knoll of Columbia University. The carbon and hydrogen analysis was performed in Dr. Knoll's laboratory by Mr. S. Gottlieb.

---

[1] *Gazz. chim. ital.*, **42**, 425–437 (1912).

929 WEST END AVENUE
NEW YORK, N. Y.
ARTHUR KANT

RECEIVED APRIL 16, 1940

BENZAL-2,4,6-TRIBROMOANILINE

Benzal-2,4,6-tribromoaniline was prepared by heating equivalent parts of benzaldehyde and 2,4,6-tribromoaniline; m. p. 94–95° after two crystallizations from alcohol.

Anal. Calcd. for $C_{13}H_8NBr_3$: Br, 57.3. Found: Br, 57.1.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
W. S. EMERSON
F. C. UHLE

RECEIVED MAY 1, 1940

ACETYLENIC CYCLOHEXANE DERIVATIVES

1 - (3 - Methyl - 1 - pentyn - 3 - ol) - 2 - methylcyclohexanol.—To the Grignard reagent prepared from 24 g. of magnesium, 115 g. of ethyl bromide and 200 ml. of anhydrous ether was added with stirring a solution of 69 g. (0.5 mole) of 1-ethynyl-2-methylcyclohexanol[1] in 100 ml. of anhydrous ether as rapidly as possible without loss of ether. The solution was stirred for one hour after all the

---

[1] Cook and Lawrence, *J. Chem. Soc.*, 58 (1938).