dehydes and the corresponding methyl ketones are similar. It is also evident that the position of their long-wave bands in alkaline solution is influenced by the presence of methoxy groups on the benzene ring. The effect on the *p*-hydroxyaldehydes is as follows: With no methoxy group the absorption maximum is at 336, with one it is at 353 and with two methoxy groups it is at 370 mμ. The corresponding wave lengths for the methyl ketones are 328, 348 and 362 mμ, respectively. The positions of the long-wave bands of other ketones are given in Table I. Replacement of the methyl ketones with other alkyl radicals does not have much effect on the position of the maximum unless additional chromophoric groups are introduced (*cf.* acetovanillone and 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione).

The position of the long-wave bands of the corresponding acids (*p*-hydroxybenzoic, vanillic and syringic) is not so greatly affected by methoxy groups, the maxima of alkaline solution being at 280, 298 and 300 mμ. For the simple phenols (phenol, guaiacol and 1,3-pyrogallol dimethyl ether) the effect is small (see Table I).

The behavior of the *p*-hydroxyaldehydes and *p*-hydroxyketones in alkaline solution is similar to that of *p*-nitrophenol. Alkaline solutions of the latter are yellow as the displacement of the long-wave band is greater, maxima absorption being at 400 mμ.

Summary

1. The ultraviolet absorption bands of phenolic compounds in absolute ethyl alcohol solution are displaced in the direction of longer wave lengths when the solutions are made alkaline. Usually the intensity of absorption of the long-wave band is increased.

2. The displacement and increase in intensity of the long-wave band is greatest for *p*-hydroxyaldehydes and *p*-hydroxyketones.

3. The position of the long-wave bands of alkaline solutions of *p*-hydroxyaldehydes and *p*-hydroxyketones is influenced by the presence of methoxy groups on the benzene ring.

4. The behavior of the *p*-hydroxyaldehydes and *p*-hydroxyketones in alkaline solution is similar to that of *p*-nitrophenol.

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[CONTRIBUTION NO. 591 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Solubilities of Four Amino Butyric Acids and the Densities of Aqueous Solutions of the Acids at 25°[1]

BY L. S. MASON

The solubilities of β-amino-*n*-butyric acid and γ-aminobutyric acid have not been determined heretofore. There are variations in the values of the solubilities of α-amino-isobutyric acid and α-amino-*n*-butyric acid reported by others.[2,3] The densities of various concentrations of aqueous solutions of these compounds have not been available previously. A knowledge of these properties was of importance in connection with a study of the heats of dilution of aqueous solutions of these four acids.[4] The latter investigation is a part of a systematic study[5,6] of the heats of dilution of solutions of various amino acids in progress in this Laboratory.

The chief criterion of purity chosen for these materials was that a sample of an acid have essentially a constant solubility when saturated aqueous solutions were formed successively from the residue from each preceding solution. This method of "constant solubility" has been found to be the most sensitive criterion of purity for compounds of this type.[2]

Materials

A quantity of glycine was purified at the same time for another purpose from a Merck and Company product. The α-amino-isobutyric and the α-amino-*n*-butyric acids were obtained from Eastman Kodak Company. The β-amino-*n*-butyric and the γ-aminobutyric acids were from the University of Illinois. The usual methods of purification were employed, with variations of conditions and solvents indicated by variations in the behavior of the compounds. All of the purified materials were ashed in a muffle furnace. In the case of the α-acids, the ash was less than 0.01%, and less than 0.02% for the β- and γ-acids. Formol titration was performed on the α-acids and the β-acid, using a Beckman *p*H-meter equipped with glass and calomel electrodes. In the case of the α-butyric acids, the percentage purity was determinable by formol titration with an error of 0.2–0.3%, and in the case of the β-acid with an error of about 1.0%.

The Solubilities.—The solids were equilibrated with water in a thermostat at 25 ± 0.02°, usually

(1) The generous support of the Buhl Foundation in this study is acknowledged.

(2) E. J. Cohn, T. L. McMeekin, J. T. Edsall and J. H. Weare, THIS JOURNAL, **56**, 2270 (1934).

(3) P. K. Smith and E. R. B. Smith, *J. Biol. Chem.*, **121**, 607 (1937).

(4) L. S. Mason and A. L. Robinson, THIS JOURNAL, **69**, 889 (1947).

(5) W. E. Wallace, W. F. Offutt and A. L. Robinson, *ibid.*, **65**, 347 (1943).

(6) H. A. Benesi, L. S. Mason and A. L. Robinson, *ibid.*, **68**, 1755 (1946).

for forty-eight hours, with stirring. Saturation and filtration were performed in the same unit. A glass tube, 15 cm. by 1 cm. diameter, with a stopcock at one end, was equipped with a reciprocating stirrer. A circle of filter paper, 4 mm. in diameter, was placed over the opening in the stopcock and held in place by a metal ring. Five to seven grams of amino acid was placed in the tube with just sufficient water so that 1 to 2 g. of saturated solution could be removed. A tared weighing bottle was attached to the delivery tube from the stopcock and arranged so that by opening the stopcock and applying suction the solution could be filtered from the saturation mixture directly into the weighing bottle while the entire unit was immersed in the thermostat.

After the first saturated solution was removed, more water was added and the system equilibrated and filtered again. In this way three or four samples of saturated solutions were extracted from the same portion of original solid. The solutions were evaporated at room temperature in a vacuum desiccator, then dried to constant weight. In the case of the α-amino acids, drying was done in a 110° oven at atmospheric pressure. The β- and γ-acids were dried at 80° and 0.5 mm. in a vacuum oven. All samples were dried to constant weight. In some selected cases a small amount of water was added to the dried samples and the drying repeated. The same constant weights were observed.

The Densities.—The solutions used for determination of the heats of dilution were prepared by volume. In order to convert the molarities of the solutions to molalities, the densities of the solutions were required. The densities of solutions of the four amino butyric acids were measured over a range of concentrations, using calibrated 10-ml. pycnometers at 25°.

Density determinations were made in duplicate and the solutions at each concentration were prepared from the original solids.

Results

The results of the solubility determinations are given in Table I. The solubility values for glycine and α-amino-isobutyric acid agree quite well with values of other investigators given for comparison.[2] The present value for α-amino-*n*-butyric acid is considerably lower than one comparison value[3] and somewhat lower than the other value listed.[2] The values of successive extractions in this experiment are quite consistent, however, and should represent a pure material. In the table are shown typical data for α-amino-*n*-butyric acid, illustrating the solubility behavior before and after purification. The precision of the values for the β-acid and the γ-acid leave a great deal to be desired. However, it is felt that the scattering of the values represents variations due to experimental difficulties rather than impure materials.

TABLE I

THE SOLUBILITIES OF GLYCINE AND AMINO BUTYRIC ACIDS AT 25°

Solubilities are expressed in grams per 1000 g. of water.

Amino acid		Extractions: First	Second	Third	Fourth	Mean	Values from other studies[b]
Glycine	(1)	249.8	250.2	...[a]			
	(2)	249.7	250.9	250.9		250.3	250.0[2]
α-Amino-isobutyric	(1)	153.1	153.1	153.2			158.4[2]
	(2)	152.3	152.4	152.7		152.8	158.4[3]
α-Amino-*n*-butyric before purif.	(1)	261.5	251.3	217.7			
	(2)	255.0	247.0	218.0			
After purification	(1)	210.2	210.5	210.0			215.9[2]
	(2)	211.0	211.1	210.0		210.5	230.5[3]
β-Amino-*n*-butyric	(1)	1249	1257	1259			
	(2)	1255	1250	...[a]		1250	
γ-Amino-*n*-butyric	(1)	1310	1290	1288	1304	1300	

[a] Insufficient solid remained for satisfactory determination. [b] Additional solubility values are tabulated in "Proteins, Amino Acids and Peptides," E. J. Cohn and J. T. Edsall, Reinhold Publishing Corporation, New York, N. Y., 1943, p. 199.

In the case of the β- and γ-acids the following factors contribute to the uncertainties of the results. The very high solubilities of these acids necessitate a large ratio of the amounts of solid and water first placed in the extraction apparatus, in order that sufficient solid remain for the successive extractions. This complicates attainment of equilibrium conditions. The sirupy saturated solutions are difficult to filter, evaporate and dry. Uncertainties are introduced by small variations due to evaporation during suction filtration and

TABLE II

THE DENSITIES OF AQUEOUS SOLUTIONS OF AMINO BUTYRIC ACIDS

Concentration moles/liter	Measured density	$\delta \times 10^4$ (eq. − meas.)	Concentration (moles/1000 g. H_2O)
	α-Amino-isobutyric acid		
0.1014	0.9997	0	0.1025
.3780	1.0064	+4	.3907
.9505	1.0219	−4	1.0287
1.330	1.0312[a]	+1	1.488
	α-Amino-*n*-butyric acid		
0.5506	1.0122	−1	0.5764
1.0474	1.0258	−1	1.1411
1.3144	1.0326	−6	1.4651
1.800	1.0456[a]	+6	2.0944
	β-Amino-*n*-butyric acid		
0.1000	0.9996	+1	0.1011
.1990	1.0024	−1	.2027
.3960	1.0075	0	.4096
.7880	1.0179	−1	.8413
	γ-Amino-*n*-butyric acid		
0.1000	1.0002	−2	0.1010
.1990	1.0030	0	.2025
.3960	1.0084	+3	.4091
.7880	1.0207	−4	.8391

[a] Density for saturated solution from ref. 2.

by bumping and spattering during evaporation and drying. If evaporation is conducted too slowly the mixture may form a crust over the surface or form a dense mass in the bottom of the weighing bottle which is very difficult to dry. The mean values are probably valid, however, to about 10 g. per 1000 g. of water.

The density determinations are summarized in Table II. In all four cases the density appears to be a linear function of concentration, in the case of the α-acids up to saturation, in the case of the β- and γ-acids up to about 0.8 M, the highest concentration measured. The densities were plotted against molarity and the best straight line was drawn through the experimental points for each case. The densities were expressed from these graphs by the equations

α-Amino-isobutyric acid $d^{25} = 0.9971 + 0.0257\ M$
α-Amino-n-butyric acid $d^{25} = 0.9971 + 0.0273\ M$
β-Amino-n-butyric acid $d^{25} = 0.9971 + 0.0263\ M$
γ-Aminobutyric acid $d^{25} = 0.9971 + 0.0294\ M$

In the third column of the table are shown the deviations of the values calculated by the equations from the measured values.

Summary

The solubilities in water at 25° of glycine, α-amino-isobutyric acid, α-amino-n-butyric acid, β-amino-n-butyric acid and γ-aminobutyric acid have been measured. The solubilities remained essentially constant when successive saturated solutions were formed from the same portions of solid samples.

The densities of aqueous solutions of the four amino butyric acids at 25° were measured. Densities appear to be linear with respect to molarities in each case.

PITTSBURGH, PENNA. RECEIVED JUNE 17, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Reactions of Furan Compounds. VII. Thermal Interconversion of 2,3-Dihydrofuran and Cyclopropane Aldehyde[1]

BY CHRISTOPHER L. WILSON

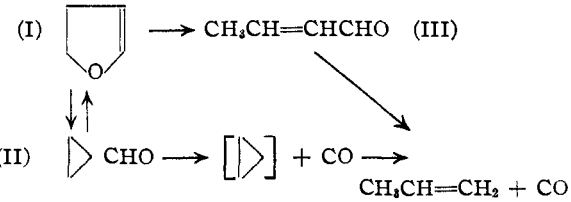
To explain the formation of cyclopropane aldehyde (II), in the pyrolytic decomposition of certain tetrahydrofuran compounds it was suggested in Part IV of this series[2] that the aldehyde resulted by rearrangement of 2,3-dihydrofuran (I). The rearrangement has now been established by experiments with pure 2,3-dihydrofuran made in quantity for the first time.

Cyclopropanealdehyde was just detectable after passing the dihydrofuran vapor through a tube filled with broken glass and heated to 375°. The contact time was 54 sec. The amount of aldehyde formed increased with temperature but the yield calculated on consumed dihydrofuran decreased and, instead, crotonaldehyde, carbon monoxide and propylene were formed. At 550° carbon monoxide and propylene constituted practically the entire product.

Contact materials of recognized catalytic activity had no appreciable accelerating influence on aldehyde formation. A nickel–copper catalyst, for example, gave no aldehyde at all but, instead, propane and carbon monoxide probably by ring fission first to n-butaldehyde. It is also possible that cyclopropanealdehyde and cyclopropane might have intervened. There was little, if any, reduction to tetrahydrofuran even when hydrogen was also admitted. An activated alumina which is effective in the rearrangement of ethylene oxides to aldehydes[3] caused complete destruction even at 200°. With aluminum silicate some cyclopropanealdehyde was obtained at 450° but the yield was lower than when only glass contact material was employed.

Using a glass filling for the reaction tube the effect of change of temperature on the formation of various products is given in the diagram. The increased formation of gases at the higher temperatures reduced the contact time which to some extent offset the effect of increased temperature.

The results are explained by supposing three consecutive reactions (I) → (II) → (III) → CO, C_3H_6. Attempts to establish this sequence further by experiments at 500° with (II) and (III) showed, however, that the true picture may not be so simple. Cyclopropanealdehyde (II) on heating gave a little 2,3-dihydrofuran in addition to crotonaldehyde, carbon monoxide and propylene, establishing the reversibility of the first step.



REACTION SCHEME AT 500°

Crotonaldehyde decomposed as expected into carbon monoxide and propylene. The ratio of these two gases by volume was 1.7:1 whereas from cyclopropane aldehyde the ratio was 1.1:1. It is not known why this ratio differs from unity

(1) This and the following paper were reported at the Atlantic City meeting of the American Chemical Society in April, 1947.
(2) Wilson, *J. Chem. Soc.*, 58 (1945).
(3) Ipatiev and Leontovitch, *Ber.*, **36**, 2017 (1903).