in methyl chloride is 66 kcal.,[27] about 50 kcal. will be required to form the two free radicals from *t*-butyl chloride. There can be very little reduction of this value by effects such as solvation. Assuming as before that every sufficiently energetic collision results in the formation of a free radical (no steric factor in the kinetic equation) and that the radical so formed instantaneously reacts with toluene to form the product without energy requirements, using a collision factor of 1×10^{13}, and equation (24), the rate is calculated to be $K = 1 \times 10^{-23}$ mole per mole per second. Compared to the determined rate of 1×10^{-5} mole per mole per second, this rate is prohibitively slow.

It might be assumed that the reaction proceeds through a chain mechanism. Chain lengths in solution are usually less than 1000. One case of 50,000 is reported.[28] Assuming then even a chain length of 100,000, the rate of our reaction on a free radical mechanism is 1×10^{-18} mole per mole per second, a factor of 10^{13} slower than the experimental.

In reactions in a medium such as toluene it is generally recognized that the maximum possible concentration of a reaction intermediate, such as a carbonium ion or a simple alkyl free radical, must necessarily be very small. In many hypothetical mechanisms employing these intermediates the attempt is made to overcome this difficulty by assuming that they have only transitory existence. The above calculations show that this assumption cannot overcome the difficulty, as they give the maximum possible rate at which the intermediates can be formed and assume that this rate is the rate of the total reaction, that is, that the intermediate reacts instantaneously and completely as soon as formed to produce the final products.

Summary

A more refined apparatus has been made for and more precise measurements have been made of the reaction of *t*-butyl chloride and toluene as catalyzed by hydrogen fluoride.

The effect of four promoters, water, methanol, diethyl ether and hexamethylacetone, has been studied. It was found that the rate of the reaction increased with the increasing concentration of the promoter, but that all promoters gave essentially the same effect at the same molar concentration.

It was found necessary to modify the equations used by Sprauer and Simons to correlate the rate measurements in any one experiment, but their equations and theory are essentially confirmed.

The amphoteric medium effect as it contributes to the mechanism of the reaction is substantiated by these measurements and by the effects of the promoters. It is also shown to be reasonable on the basis of other investigations.

A one-step, condensed phase, catalyzed, and promoted reaction as the essential factor in the mechanism is shown to be satisfactory from kinetic considerations and reasonable from energy considerations. Mechanisms utilizing ions or free radicals as intermediates are shown to be untenable from energy considerations.

State College, Pa. Received October 30, 1944

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[27] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 49.

[28] E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, London, 1939, p. 262.

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 986]

The X-Ray Investigation of Copper *dl*-α-Aminobutyrate

By A. J. Stosick

As part of the program of investigation of amino acids and proteins undertaken in these Laboratories, it has been of interest to find an improved method of determining the detailed atomic configurations of amino acids by X-rays. At the suggestion of Professor Pauling, crystalline nickel and copper salts of several of the amino acids were prepared, with the hope that the heavy metal atoms in the crystals would in most cases determine the phases of the structure factors. This would enable the investigation to reach the stage of Fourier projections more quickly than for crystals of the amino acids themselves, since the coördinates of the heavy metal atoms very likely would be determined easily. In two cases, those of copper *dl*-α-aminobutyrate, to be reported in this paper, and of nickel glycine dihydrate, to be reported in a subsequent paper, these expectations were realized. The proposed method of attack however has its own inherent disadvantage. Final adjustment of parameters utilizing a comparison between calculated and estimated values for the *F*'s is necessarily more difficult because of the preponderant contribution of the heavy atoms to the *F*'s of all but special classes of reflections.

Since the work on copper *dl*-α-aminobutyrate, begun in 1939, cannot be continued at present, the results which have been obtained are presented here. The *x* and *z* parameters of all atoms have been determined, and little doubt remains as to the nature of the bonds in the molecules or the packing of the molecules in the crystal.

Crystals of copper *dl*-α-aminobutyrate were prepared by placing an excess of cupric oxide or cupric carbonate in a warm aqueous solution of *dl*-α-aminobutyric acid, removing the excess solid by filtration, and allowing the somewhat elongated dark blue plate-like crystals to form either by slow evaporation or by slow cooling. The direction of elongation of the crystals corresponds to the crystallographic *b* axis of the monoclinic unit cell.

Single crystal diffraction patterns were obtained by the Laue, rotation, oscillation, and equi-inclination Weissenberg methods. For the rotation and oscillation photographs about the *b* and *c* axes copper K radiation filtered by nickel foil was used, while unfiltered copper K radiation was used for the equi-inclination Weissenberg photographs of the reciprocal lattice layers *h0l*, *h1l*, *h2l* and *h3l*.

The following monoclinic unit cell was found to satisfy the observed reflections

$a = 11.09 \pm 0.02$ Å. $\beta' = 87°51'$
$b = 5.06 \pm .01$ Å. $C_{2h}^5 - P\frac{2_1}{c}$
$c = 9.45 \pm .02$ Å. $Z = 2$

These dimensions were obtained (with use of the wave length value λCuKα = 1.539 Å.) from the layer line spacings and from the positions of equatorial reflections on a rotation photograph for which the *b* axis of the crystal was the rotation axis. The measured density of 1.70 ± 0.02 corresponds to 2.01 molecules of copper *dl*-α-aminobutyrate per unit cell. The missing reflections suggest as the probable space group C_{2h}^5–$P\frac{2_1}{c}$, and, assuming this space group to be the correct one, the copper atoms must be placed in one of the sets of twofold centrosymmetric special positions. The pair chosen was $00\frac{1}{2}$ and $0\frac{1}{2}0$.

The intensities of more than one hundred *h0l* reflections were estimated visually from Weissenberg photographs for which packs of five films were used.[1] The exposures of photographs taken in this way vary in a geometrical progression; the intensity ratio of successive films was determined previously by other means. No corrections were made on the estimated intensities for either absorption or extinction. Although the crystal was quite small (0.10 mm. × 0.20 mm. × 0.38 mm.) and was rotated about its longest dimension, absorption corrections for the other dimensions would be appreciable; approximate calculations indicate that CuKα is absorbed to the extent of 26% by 0.10 mm., and to the extent of 46% by 0.20 mm. of the crystal. From the estimated intensities the estimated values of F^2_{h0l} and $|F_{h0l}|$ were calculated by correcting for the Lorentz and polarization factors.

The projected Patterson function, $p(x,z)$, was calculated with use of Beevers–Lipson strips with a tabular interval of $^1/_{60}$ cycle; the results of this calculation appear in Fig. 1. One unit cell is shown; for greater clarity only one of the two molecules in the unit cell is shown, only zero and positive contours are drawn, and only a few contours are drawn around metal atom positions. Because of the presence of the heavy metal atom the only significant peaks correspond to projected interatomic distance vectors with a metal atom at one end of the vector, and hence the Patterson projection has much of the appearance of the corresponding Fourier projection.

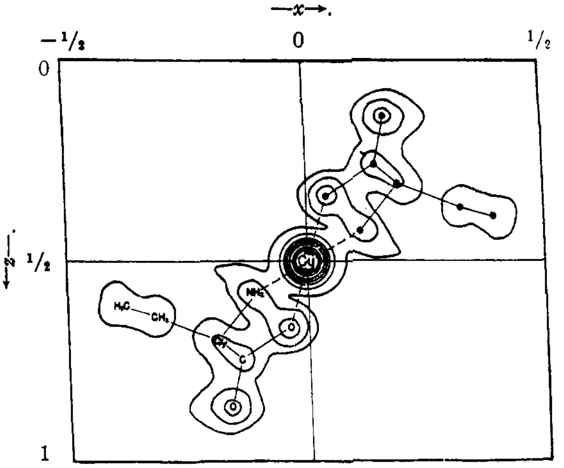

Fig. 1.—Patterson projection $p(x,z)$ showing one of the two molecules in the unit cell.

Using the parameters found from $p(x,z)$ the signs of the *h0l* structure factors were calculated, and the Fourier projection $\rho(x,z)$ (Fig. 2) was made. Only zero and positive contours are shown in the drawing, which embraces one unit cell, and for clarity numerous contours around the positions of the copper atoms have been deleted. The *h0l* structure factors were recalculated for the parameters obtained from $\rho(x,z)$, and from a comparison of $F_{\text{est.}}$ and $F_{\text{calcd.}}$ a scale factor and a temperature factor were determined. In Table I are tabulated the values of $|F_{\text{est.}}|$ on the revised scale and $F'_{\text{calcd.}}$ including the temperature

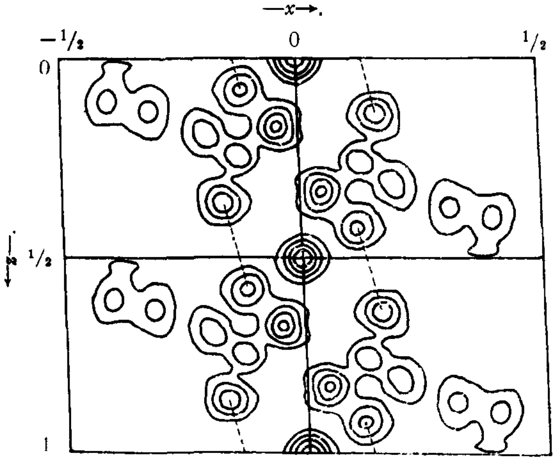

Fig. 2.—Fourier projection $\rho(x,z)$.

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[1] J. J. De Lange, J. M. Robertson and J. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

TABLE I

COMPARISON OF OBSERVED AND CALCULATED F VALUES FOR COPPER *dl*-α-AMINOBUTYRATE

$h0l$	$\lvert F_{\text{est.}}\rvert$	$F'_{\text{calcd.}}$	$h0l$	$\lvert F_{\text{est.}}\rvert$	$F'_{\text{calcd.}}$	$h0l$	$\lvert F_{\text{est.}}\rvert$	$F'_{\text{calcd.}}$
002	14.1	12.9	408	18.5	17.8	804	28.8	32.9
004	<1.9	0.5	4.0.10	13.1	15.6	806	3.2	−0.1
006	31.6	28.4	$40\bar{2}$	<1.9	6.3	808	8.6	8.1
008	20.8	19.0	$40\bar{4}$	43.5	46.0	$80\bar{2}$	29.4	28.1
0.0.10	6.4	9.4	$40\bar{6}$	51.8	48.0	$80\bar{4}$	27.2	24.4
100	80.6	114.4	$40\bar{8}$	<2.9	0.9	$80\bar{6}$	<2.9	3.4
102	53.5	54.4	$4.0.\overline{10}$	12.8	8.4	$80\bar{8}$	11.4	13.6
104	33.3	40.0	500	40.0	38.4	900	13.1	12.6
106	44.8	40.2	502	39.6	44.1	902	15.0	15.5
108	10.2	4.5	504	<2.2	−1.5	904	23.4	28.0
1.0.10	3.2	0.9	506	26.9	27.7	906	<2.9	7.1
$10\bar{2}$	20.2	−10.6	508	22.7	18.4	908	6.1	9.8
$10\bar{4}$	29.8	32.2	5.0.10	9.3	13.0	$90\bar{2}$	22.4	23.8
$10\bar{6}$	23.7	27.8	$50\bar{2}$	8.0	14.0	$90\bar{4}$	19.5	19.4
$10\bar{8}$	24.6	17.5	$50\bar{4}$	40.9	38.0	$90\bar{6}$	<2.9	1.3
$1.0.\overline{10}$	11.2	9.8	$50\bar{6}$	41.6	31.1	$90\bar{8}$	6.1	8.1
200	29.1	38.7	$50\bar{8}$	<2.9	1.8	10.0.0	17.0	17.2
202	37.7	36.2	$5.0.\overline{10}$	12.2	14.0	10.0.2	29.2	29.0
204	33.9	40.6	600	44.8	42.2	10.0.4	10.9	13.4
206	46.7	46.2	602	27.8	31.0	10.0.6	<2.6	2.6
208	7.7	11.3	604	4.5	−4.6	10.0.8	2.6	8.5
2.0.10	<2.9	1.8	606	23.1	28.5	$10.0.\bar{2}$	5.1	5.9
$20\bar{2}$	53.4	58.4	608	25.3	22.3	$10.0.\bar{4}$	10.6	9.4
$20\bar{4}$	32.0	42.6	6.0.10	<2.2	1.2	$10.0.\bar{6}$	9.0	9.7
$20\bar{6}$	9.6	3.2	$60\bar{2}$	13.5	17.0	11.0.0	<2.9	0.8
$20\bar{8}$	21.8	12.4	$60\bar{4}$	37.1	33.0	11.0.2	23.7	23.7
$2.0.\overline{10}$	21.8	21.6	$60\bar{6}$	25.9	19.7	11.0.4	12.5	14.0
300	15.1	19.0	$60\bar{8}$	10.9	12.9	11.0.6	8.3	11.3
302	76.8	75.2	$6.0.\overline{10}$	7.4	7.7	$11.0.\bar{2}$	4.2	4.3
304	35.2	37.2	700	33.0	34.5	$11.0.\bar{4}$	12.5	13.2
306	32.0	28.6	702	28.2	26.0	$11.0.\bar{6}$	8.0	12.8
308	13.4	13.5	704	4.2	9.3	12.0.0	<2.6	4.7
3.0.10	7.4	10.3	706	6.4	9.2	12.0.2	8.0	9.1
$30\bar{2}$	16.0	21.7	708	21.4	23.8	12.0.4	<2.2	3.6
$30\bar{4}$	25.0	23.6	7.0.10	<1.9	4.7	12.0.6	8.6	12.9
$30\bar{6}$	33.6	27.0	$70\bar{2}$	30.4	31.8	12.0.2	14.1	18.5
$30\bar{8}$	17.6	19.6	$70\bar{4}$	35.8	31.2	12.0.4	4.2	5.6
$3.0.\overline{10}$	17.6	18.0	$70\bar{6}$	<2.9	1.2	13.0.0	3.2	5.7
400	9.9	2.1	$70\bar{8}$	13.1	12.8	13.0.2	6.1	8.5
402	56.6	60.5	$7.0.\overline{10}$	5.4	5.2	13.0.4	5.1	7.7
404	25.3	24.4	800	16.6	14.9	$13.0.\bar{2}$	9.0	13.0
406	29.4	28.7	802	28.2	26.1	14.0.0	<1.6	2.5

TABLE II

	Cu	O_1	O_2	N	C_1	C_2	C_3	C_4
x	0	0.049	0.166	0.124	0.126	0.200	0.316	0.400
z	$^1/_2$	0.327	0.141	0.424	0.251	0.316	0.374	0.400

factor exp.$(-2.9 \sin^2\theta/\lambda^2)$. The x and z parameters obtained from $\rho(x,z)$ are presented in Table II.

Discussion of the Structure.—An interesting feature of the structure is the coördination of the amino nitrogen and the carboxyl oxygen atoms around the copper atoms. This coördination is presumably square, and is necessarily coplanar, since the copper atoms are at centers of symmetry. Assuming the Cu–N and Cu–O bonds to have the covalent values of 2.02 Å. and 1.98 Å., respectively, a calculation indicates that the coördination plane is tipped with respect to the basal plane by a rotation of 28° about the N–Cu–N line and by a rotation of 39° about the O–Cu–O line.

In Figure 2 broken lines have been drawn to indicate hydrogen bonds which presumably exist between amino nitrogen atoms and carboxyl oxygen atoms. These hydrogen bonds hold the crystal together in the y and z directions, whereas only van der Waals forces are operative in the x direction. The crystals available were too small to permit reliable observation as to whether or not the crystals show marked cleavage parallel to the (100) planes, but it was observed that slight pressure reduces a crystal to a mass of thin flakes.

Acknowledgment.—To author wishes to acknowledge his indebtedness to Professor Linus

Pauling for having suggested this problem and for his constructive criticism of the manuscript.

Summary

The unit cell, the probable space group, and the x and z atomic parameters for the monoclinic crystals of copper *dl*-α-aminobutyrate have been determined by X-ray diffraction methods. The Patterson projection $p(x,z)$ has the appearance of the Fourier projection $\rho(x,z)$, because of the presence of the heavy copper atoms in the special centrosymmetric positions of the probable space group C_{2h}^5–$P\frac{2_1}{c}$. Although the y parameters have not been determined the existence has been shown of coplanar coördination of carboxyl oxygen atoms and amino nitrogen atoms around the copper atoms, and the presence of oxygen-to-nitrogen hydrogen bonds in the x and z plane is evident.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 15, 1944

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 987]

The Crystal Structure of Nickel Glycine Dihydrate

BY A. J. STOSICK

Introduction.—As a part of the program of protein and amino acid research undertaken in these laboratories, the crystal structure of the dihydrated nickel salt of glycine has been determined by X-ray methods. The investigation, which was begun in the fall of 1939, was substantially completed by the spring of 1941, when the assumption of other duties by the author caused the work to be discontinued. It is the purpose of this paper to present the results of the investigation, since there is little likelihood that the investigation will be resumed in order to refine the parameters.

The purpose of investigating nickel glycine dihydrate was twofold: first, to make a comparison of the structure of the glycine residue in the salt with that for glycine itself as determined by Albrecht and Corey[1]; and second, to determine whether the presence of the metal atom facilitates the structure determination. The use of a metal as an aid in determining the structure of complex organic substances has been discussed previously.[2,3]

The crystals used in this investigation were prepared by placing an excess of nickel carbonate in a warm aqueous solution of glycine. The solution was then filtered and the solvent was allowed to evaporate slowly. The crystals have previously been reported by Bruni.[4] Accurate optical goniometry was not possible with the crystals although superficially their faces were well defined. After a preliminary coarse optical orientation the final adjustment of the crystal orientation was made by means of preliminary X-ray photographs. The faces appearing on the crystals appear to be those for the planes $\{100\}$, $\{\bar{1}00\}$, $\{011\}$, $\{01\bar{1}\}$, $\{0\bar{1}1\}$, and $\{0\bar{1}\bar{1}\}$, but this identification has not been confirmed.

The Unit Cell and Space Group.—A cursory optical examination showed that the crystals are anisotropic, and suggested that they exhibit monoclinic symmetry. Examination of Laue, rotation and equi-inclination Weissenberg photographs of the crystals led to the following monoclinic unit cell and probable space group

$a = 7.60 \pm 0.02$ Å. $\beta' = 63°25'$
$b = 6.60 \pm .02$ Å. $Z = 2$
$c = 9.63 \pm .02$ Å. $C_{2h}^5 - P\frac{2_1}{c}$

The length of the b axis was calculated from the spacings of layer lines on a b axis rotation photograph. The lengths of the a and c axes were determined from the spacings of equatorial reflections on the same photograph. The acute monoclinic angle β' was also determined from equatorial reflections on this same photograph; four different sets of reflections gave values differing by a maximum of only 0°8′. The density of the crystals, measured by the flotation method, was found to be 1.86 g./cc. This density corresponds to 1.99 molecules of the formula $Ni(NH_2CH_2CO_2)_2 \cdot 2H_2O$ in each unit cell, and if the indicated space group is correct the metal atoms must be located at centers of symmetry.

The space group assigned to the crystals C_{2h}^5–$P\frac{2_1}{c}$, is consistent with the many absences noted on Weissenberg photographs of the reciprocal lattice layers $h0l$, $h1l$, $h2l$, $hk0$ and $0kl$. No reflections were observed which required any other space group for the crystals.

The Structure Determination.—The intensities of the $h0l$, $0kl$ and $hk0$ reflections were visually estimated from Weissenberg photographs taken with unfiltered copper K radiation. In addition Weissenberg photographs of the $h0l$ reflections were taken using filtered molybdenum K radiation.

No corrections were made for absorption or extinction; the shape of the crystals (slightly elongated rhombohedra with b normal to the direction

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(1) G. Albrecht and R. B. Corey, THIS JOURNAL, **61**, 1087 (1939).

(2) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936); J. M. Robertson and I. Woodward, *ibid.*, 219 (1937).

(3) A. J. Stosick, THIS JOURNAL, **67**, 362 (1945).

(4) Bruni, *Atti della Reale Accademia dei Lincei*, [5] **13**, II, 27; cf. Beilstein also