BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1003—1004 (1973)

The Formation of β-Glycine in the Thermal Decomposition of a Solid Complex of Aminomalonic Acid with Glycine

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(Recived September 5, 1972)

In a previous paper,[1] we reported that aminomalonic acid reacted with glycine to form a solid complex with a 1 : 1 molar ratio on crystallization from an aqueous solution, and that the solid complex decarboxylated at a higher temperature and at a slower rate than did aminomalonic acid, as was established by means of the DTA–TGA of the solid complex at a heating rate of 1°C/min in air. Moreover, it was found, by the aid of X-ray analysis, that an unstable unknown substance was formed, together with α- and γ-glycine, in the course of the thermal decomposition of the solid complex, and that this substance changed to either α- or γ-glycine above 150°C. At the stage where this substance is formed, however, the coexistence of a remaining solid complex and the α- and γ-glycine produced made it difficult for us to study the unstable substance. Here, an investigation was carried out into the conditions for the formation of the unstable unknown substance and on its formation mechanism.

Experimental

To a mixture of 1.19 g of a recrystallized aminomalonic acid and 0.75 g of glycine of a reagent grade, was added 30 ml of pure water and then 30 ml of methanol. The resulting solution was kept overnight in a refrigerator (7—8°C) to yield scaly crystals. The yield was 1.90 g (90%). Found: C, 30.86%; H, 5.36%. Calcd for $C_5H_{10}O_6N_2$ (aminomalonic acid : glycine = 1 : 1) : C, 30.93%; H, 5.15%. The X-ray diffraction pattern, the infrared spectrum, and the DTA-TGA of this substance agreed well with those of the crystalline powder[1] obtained by the concentration of an aqueous solution.

The solid complex was decomposed in a Riken-type sample dryer. The infrared spectra were observed with a Nihon Bunko Grating Infrared Spectrometer, type DS-402G, by means of the Nujol-mull method. X-ray analysis was carried out with the same apparatus as had previously been reported.[1] In order to represent the amount of the decomposition products semi-quantitatively, the ratio of the height of diffraction peak was used. Also, a sample holder was used throughout this work.

Results and Discussion

The unstable unknown substance changed either α- or γ-glycine at temperatures above 150°C.[1] On the assumption that the unknown substance may be formed in a large amount at a lower temperature, thermal decomposition was carried out at a temperature in the neighborhood of 122°C.

The decarboxylation proceeded extremely slowly and required about 45 hours for completion. The product in this period was only an unknown sudstance in many cases, but in some cases a small amount of α- and γ-glycine was also formed at the completion of the reaction. On further heating, the intensity of the dif-

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[1] T. Kinugasa, J. Nishijo, G. Hashizume, and I. Imanishi, This Bulletin, **44**, 2035 (1971).

Table 1. Decomposition products of solid complex and aminomalonic acid

Reactant	Reaction temperature (°C)	Reaction time (hours)	Fraction of decomposition (%)	Decomposition products	Relative amount of product[a]
Complex	122±1	25	70	unknown	0.51
		45	100	unknown	1.00
		90	100	unknown γ-glycine α-glycine	0.13 0.93 0.16
Aminomalonic acid	115±1	4	100	γ-glycine	

a) The ratio of the height of the diffraction peak due to each product in the reaction mixture to the height of the diffraction peak due to each compound alone at the respective diffraction angles.
α-glycine: at 29.3 (2θ), unknown: at 17.9 (2θ), γ-glycine: at 21.8 (2θ).

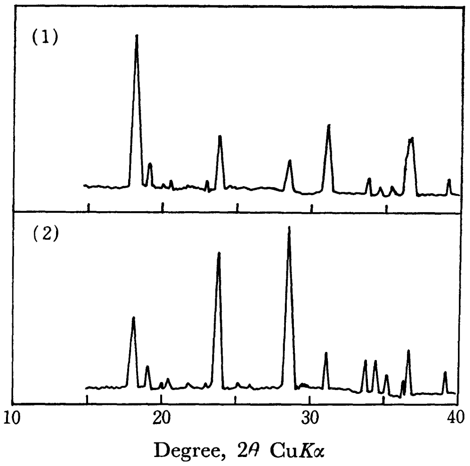

Fig. 1. X-ray diffraction patterns of (1) β-glycine and (2) the unknown.

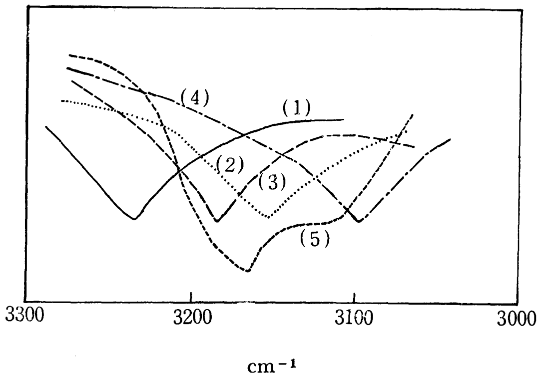

Fig. 2. Infrared spectra.
(1): complex. (2): α-glycine. (3): β-glycine. (4): γ-glycine. (5): aminomalonic acid.

fraction peak of the unknown substance decreased and γ-glycine was formed in a large amount, accompanied by the formation of a small amount of α-glycine. The infrared spectrum of the unknown substance differs slightly from that of α- or γ-glycine. These properties resemble those of β-glycine. The X-ray diffraction pattern of the unknown substance was compared with that of β-glycine which had been prepared according to Iitaka method[2] (Fig. 1). Although different in the relative intensities of the diffraction peaks, they agree with each other in the angles of the diffraction peaks. It was thus proved that the unknown substance produced in the thermal decomposition of the solid complex was β-glycine. The difference between them in the relative intensities of the diffraction peaks may result from the difference in the orientation of the crystals which is caused according to the method of preparation.

The formation mechanism of β-glycine, the most unstable among three polymorphic forms of glycine, will be discussed below. When aminomalonic acid decomposed slowly at the temperature in the neighborhood of 115°C, not β- but γ-glycine was detected in the decomposition product (Table 1). This is consistent with the findings that, as was reported previously,[3] aminomalonic acid decarboxylates, with the disintegration of the crystal lattice to amorphous glycine, and that the amorphous glycine crystallizes to γ-glycine, which is the most stable against the thermal processes.

On the other hand, scarcely no thermal change due to the crystallization of the decomposition products was in the decarboxylation of the solid complex.[1] This fact suggests that the decarboxylation of the complex occurs with no disintegration, but with only a slight displacement of the crystal lattice. Moreover, the observation that the crystal lattice is not disintegrated may be explained as follows. Since each stretching vibration of NH_3^+ in the aminomalonic acid and α-glycine is observed near 3165 cm^{-1} and 3154 cm^{-1} respectively and near 3233 cm^{-1} in the complex, the intermolecular hydrogen bond has been formed between aminomalonic acid and glycine by forming the solid complex (Fig. 2). Hence, when the solid complex decarboxylates at a low temperature and at a very slow rate, the intermolecular hydrogen bond may remain to some extent, and the disintegration of the crystal lattice of the complex may not occur. Therefore, the formation of an unstable compound such as β-glycine may be possible.

The authors wish to thank Professor Isamu Imanishi and Dr. Genzo Hashizume for their advice and interest.

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[2] Y. Iitaka, *Acta Crystallogr.*, **13**, 35 (1960).

[3] T. Kinugasa, J. Nishijo, and G. Hashizume, *Nippon Kagaku Zasshi*, **70**, 584 (1969).