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Solid Complex Formation of Aminomalonic Acid with Glycine[1]

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It was found by X-ray analysis that aminomalonic acid forms a solid complex with glycine in a molar ratio of 1 : 1 on crystallization from an aqueous solution. DTA-TGA of the solid complex at a heating rate of 1.0°C/min in air showed that the solid complex decarboxylates at higher temperature, but more slowly than aminomalonic acid and that both endothermic and following exothermic peaks which were distinctly observed in the region of decarboxylation of aminomalonic acid at temperatures 108—140°C are only slightly observed at 168—175°C. Activation energies in the thermal decomposition of aminomalonic acid and the solid complex, caluculated from themogravimetric curves, were 69.4 kcal/mol and 21.3 kcal/mol, respectively. The results indicate that aminomalonic acid is thermally more stabilized than the acid itself by forming the solid complex with glycine.

The authors reported[2] the results of differential thermal analysis of aminomalonic acid. Crystals were obtained by distilling off the solvent from a saturated aqueous solution of aminomalonic acid on a water bath at 25°C under a pressure of 10 mmHg. When the concentration process for each mother liquid was repeated seven or eight times, no further crystallization occurred easily with concentration, and a viscous residue remained, which turned into crystalline powder on being allowed to stand in air. Results of elementary analysis were: H, 5.60; C, 31.21%. Calculated values for aminomalonic acid and glycine are: H, 4.20; C, 30.26% and H, 6.67; C, 32.00%, respectively. Thus, it seems that a fair amount of glycine was contained in these crystals. On heating of aminomalonic acid with micro melting point apparatus,[3] decomposition took place accompanied with bubbling but no such phenomenon was observed for the crystalline powder. It seems that aminomalonic acid can form a solid complex with glycine on crystallization from an aqueous solution. The present study was carried out to confirm this supposition.

Experimental

Materials. Aminomalonic acid purified by recrystallization and glycine (Merck Co.) were dissolved in water with the molar ratio of 1 : 1 and the solvent was distilled off on a water bath at 25°C under a reduced pressure of 3—5 mmHg to leave a viscous residue. When this was allowed to stand in air, crystalline powder was obtained. These crystalline powder was obtained. These crystals are designated as AM_1–G_1 hereafter (AM: aminomalonic acid, G: glycine, the subscripts refer to the molar ratio). They were dried at 50°C for 5 hr., pulverized thoroughly in an agate mortar, and used for further experiments. Samples of different molar ratios were also prepared according to the same procedure.

Analysis. X-ray analysis was carried out with an X-ray diffractometer, Rigaku Denki Geigerflex, using Ni filtered CuK_α radiation. IR spectra were measured with a Nihon Bunko Grating Infrared Spectrometer, type DS-402G, by means of the KBr-pellet method. DTA-TGA was carried out by using the same apparatus as reported.[2] Samples of 200—500 meshes were used for measurements.

Determination of the contents of aminomalonic acid and γ-glycine. Aminomalonic acid was mixed with AM_1–G_1 to obtain samples with various weight ratios of aminomalonic acid to AM_1–G_1. The intensity [(half width) × (height)] of diffraction peaks due to aminomalonic acid at 24.1° (2θ) in these samples was measured to obtain a calibration curve used for the determination of aminomalonic acid content. Conditions of measurements were: 40 kV-1.5 mA, full-scale 400 count/sec, scanning speed 0.5°(2θ)/min, chart speed 20 mm/min. γ-Glycine was added to obtain the samples with various weight ratios of γ-glycine to AM_1–G_1. A calibration curve obtained with these samples, employing the height of diffraction peak due to γ-glycine at 21.8 (2θ) as peak intensity, was used for the determination of γ-glycine content. The conditions were the same as in the case of aminomalonic acid except for 40 kV-1.0 mA and 40 mm/min of chart speed.

Results and Discussion

The Complex Formation. X-ray diffraction patterns of aminomalonic acid, α-, β-, γ-glycine are

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2) T. Kinugasa, J. Nishijo, and G. Hashizume, *Nippon Kagaku Zasshi*, **90**, 584 (1969).

3) Yanagimoto melting point apparatus.

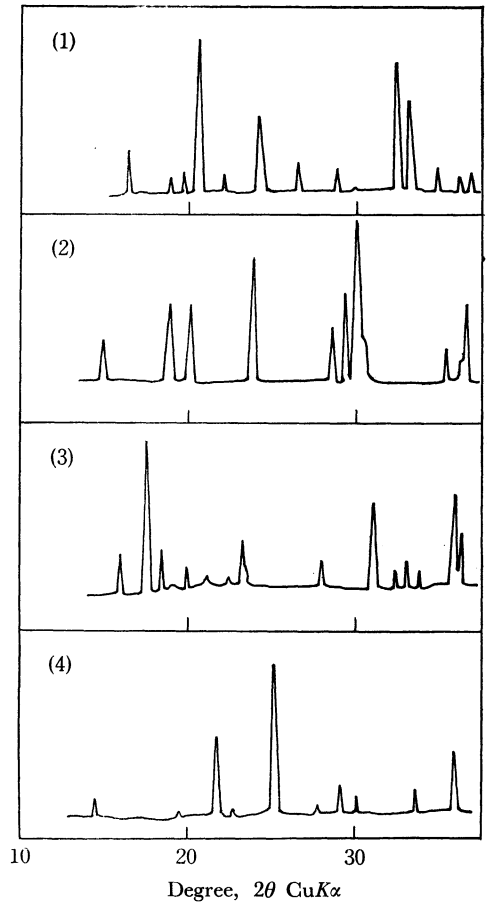

Fig. 1. X-ray diffraction patterns.
(1) Aminomalonic acid (2) α-glycine (3) β-glycine
(4) γ-glycine

shown in Fig. 1. The samples having ratios of aminomalonic acid to glycine 1 : 1, 1 : 2, 2 : 1, prepared according to method described in the experimental section, are shown in Fig. 2.

AM_1–G_1 gave a new diffraction pattern differing from each component, *viz.*, aminomalonic acid and glycine (α-, β-, γ-). AM_2–G_1 gave diffraction patterns of AM_1–G_1 and aminomalonic acid, whereas AM_1–G_2 gave those of AM_1–G_1 and γ-glycine. AM_4–G_3 and AM_5–G_4 also gave diffraction patterns of AM_1–G_1 and aminomalonic acid, while AM_3–G_4 and AM_4–G_5 gave those of AM_1–G_1 and γ-glycine.

TABLE 1. QUANTITATIVE DETERMINATION OF AMINOMALONIC ACID (IN AM_2–G_1, AM_4–G_3, AND AM_5–G_4) AND γ-GLYCINE (IN AM_1–G_2, AM_3–G_4, AND AM_4–G_5) BY X-RAY ANALYSIS

	Calcd %		Found %	
	AM	γ-Gly	AM	γ-Gly
AM_2–G_1	38.0		39.5	
AM_4–G_5	17.0		17.4	
AM_5–G_4	13.3		11.8	
AM_1–G_2		27.9		28.0
AM_3–G_4		11.6		11.5
AM_4–G_5		8.8		7.5

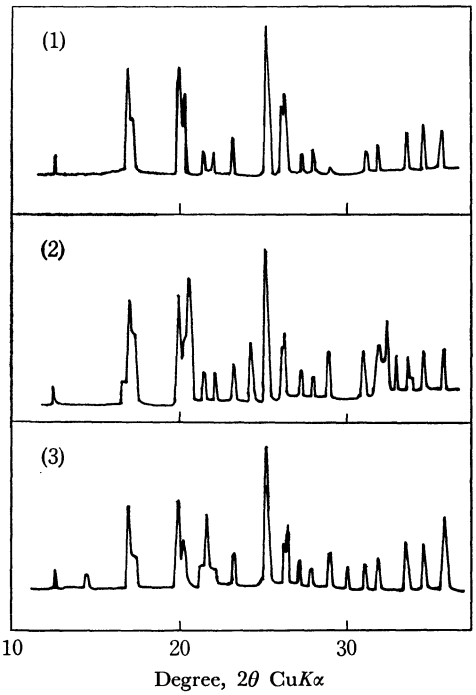

Fig. 2. X-ray diffraction patterns of AM_1–G_1 (1), AM_2–G_1 (2), and AM_1–G_2 (3).

The amount of aminomalonic acid was determined by means of calibration curves for AM_2–G_1, AM_4–G_3, and AM_5–G_4, and that of γ-glycine for AM_1–G_2, AM_3–G_4, and AM_4–G_5. The weight percentages of excess aminomalonic acid and γ-glycine, calculated by assuming that the crystals showing diffraction patterns of AM_1–G_1 are formed by the equimolar mixture of aminomalonic acid and glycine, agreed with the experimental values. The results are shown Table 1. Accordingly, it was confirmed that aminomalonic acid can form a solid complex with glycine in a molar ratio of 1 : 1 and the solid complex shows the diffraction patterns of AM_1–G_1. The diffraction angles and relative intensities are given in Table 2.

The infrared absorption spectra of the equimolar mechanical mixture of aminomalonic acid and γ-glycine (I), and AM_1–G_1(II) are shown in Fig. 3. Each absorption band in (I) could be assigned to those of aminomalonic acid and γ-glycine, whereas the absorption bands observed in (II) were different from

TABLE 2. X-RAY DIFFRACTION DATA OF AM_1–G_1

2θ(°)	$H/H°$	2θ(°)	$H/H°$
12.65	7	26.58	28
16.90	54	27.51	5
17.27	15	28.22	11
19.95	50	29.03	4
20.34	17	30.90	8
21.57	5	31.92	13
22.22	5	33.70	27
23.41	23	34.80	21
25.32	100	35.88	25
26.38	32	39.58	6

θ=Bragg angles. $H/H°$=relative height of diffraction peak.

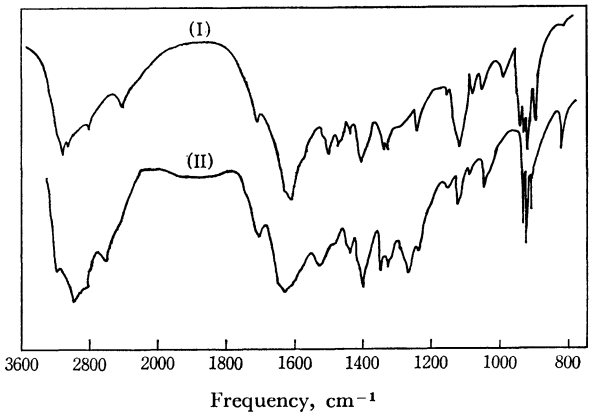

Fig. 3. Infrared spectra of equimolar mechanical mixture of aminomalonic acid and γ-glycine (I), and AM_1–G_1 (II).

those in (I). This indicates that there is an interaction between the molecules of aminomalonic acid and glycine.

Differential Thermal Analysis and Thermogravimetric Analysis. The solid line in Fig. 4 shows DTA–TGA curves of AM_1–G_1 in air. The amount of sample was 81.5 mg and the heating rate was 1.0°/min. For comparison, DTA–TGA curves of aminomalonic acid are shown by dotted lines. Conditions of measurements were the same as in AM_1–G_1 except for the sample amount, which was 50 mg in the present case. From the TGA curve of AM_1–G_1, the decarboxylation started at 115°C, the amount of carbon dioxide liberated did not reach the theoretical value until 170°C. In the DTA curve, endothermic and the succeeding exothermic peaks observed in the region of decarboxylation of aminomalonic acid, were slightly observed at temperatures 168°—175°C. An endothermic peak was also observed in the neighborhood of 185°C, which is supposed to be due to the transition of γ-glycine to α-glycine.

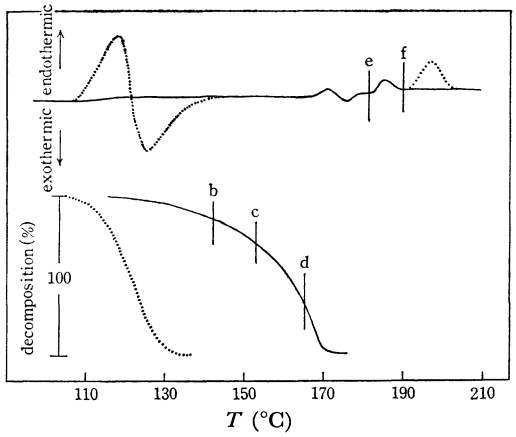

Fig. 4. DTA-TGA curves of AM_1-G_1 (solid lines) aminomalonic acid (dotted lines), in air.
Heating rate: 1.0°C/min. Sensivility: ±50 μV.
Reference: silica powder.

In order to examine the decarboxylation products of AM_1–G_1, samples were collected at the stages of b, c, d, e, and f in the DTA–TGA curves in Fig. 4 and X-ray analysis was carried out. The results are shown in Fig. 5. At stage b, the diffraction patterns of γ-glycine and several unknown diffraction peaks were observed along with those of AM_1–G_1. At stage c, γ-glycine, unknown material and α-glycine were observed in addition to the initials material, AM_1–G_1. The intensities of unknown diffraction peaks increased at c, but at stage d they disappeared and the diffraction peaks due to γ- and α-glycine were observed for AM_1–G_1. At e, diffraction peaks due to γ- and α-glycine were observed, and at f merely those due to α-glycine. Accordingly, the endothermic peak at about 185°C was due to the heat of transition from γ- to α-glycine. It shifted to the lower temperature side by 13°C as compared with that of aminomalonic acid. The unknown intermediate of decarboxylation is under investigation.

Activation Energies of Decarboxylation of AM_1–G_1 and Aminomalonic Acid. Coats and Redfern[4] derived

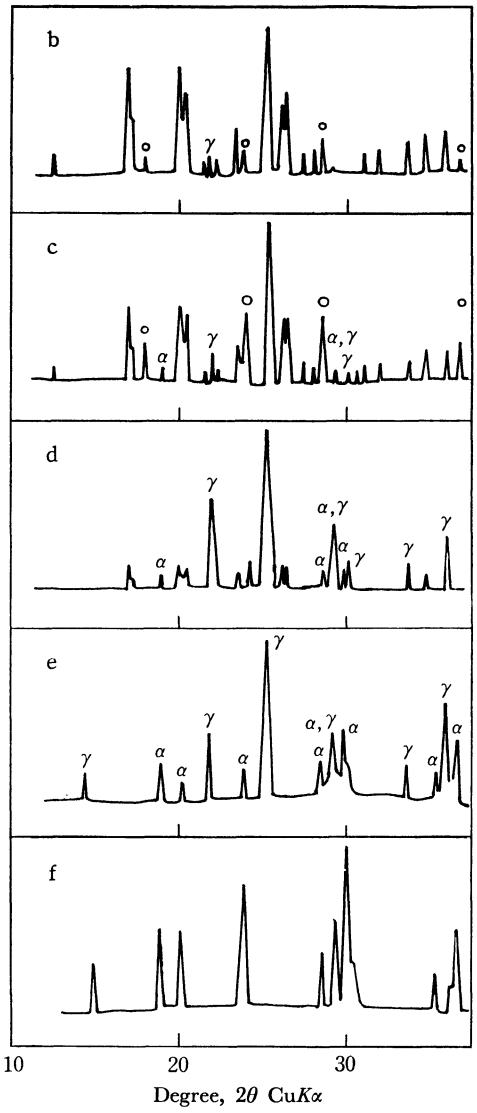

Fig. 5. X-ray diffraction patterns of decarboxylation products.
b, c, d, e, and f represent the places where the samples were collected in DTA-TGA curves of Fig. 6.
○: unknown material γ : γ-glycine α : α-glycine

4) A. W. Coats and J. P. Redfern, *Nature*, **201**, 68 (1964).

the following equations for the determination of activation energy of solid state reaction accompanied by weight decrease.

If $n \neq 1$,

$$\log_{10}\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3RT} \quad (1)$$

If $n=1$,

$$\log_{10}\left\{\frac{-\log(1-\alpha)}{T^2}\right\} = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3RT} \quad (2)$$

where α=fraction of decomposition, n=order of reaction, E=activation energy, A=frequency factor, $a=\mathrm{d}T/\mathrm{d}t$, T=absolute temperature,

Using equation (1) or (2), the activation energy of decarboxylation reaction of AM_1–G_1 and aminomalonic acid was obtained from the TGA curves (Fig. 4). Assuming that $n=0$, 1/2, 2/3, or 1 in the decomposition range of 17 to 65% for AM_1–G_1 and 12 to 60% for aminomalonic acid,

$\log_{10}\{1-(1-\alpha)^{1-n}/T^2(1-n)\}$ or $\log_{10}\{-\log(1-\alpha)/T^2\}$ was plotted against $1/T$. The linear relation was obtained at $n=0$ for AM_1–G_1 and at $n=1$ for aminomalonic acid (Figs. 6 and 7). The value of activation energy obtained was 21.3 kcal/mol for AM_1–G_1 and 69.4 kcal/mol for aminomalonic acid. Although AM_1–G_1 has a smaller activation energy than aminomalonic acid and is advantageous from the viewpoint of reaction rate, AM_1–G_1 reacts more slowly even at a higher temperature.

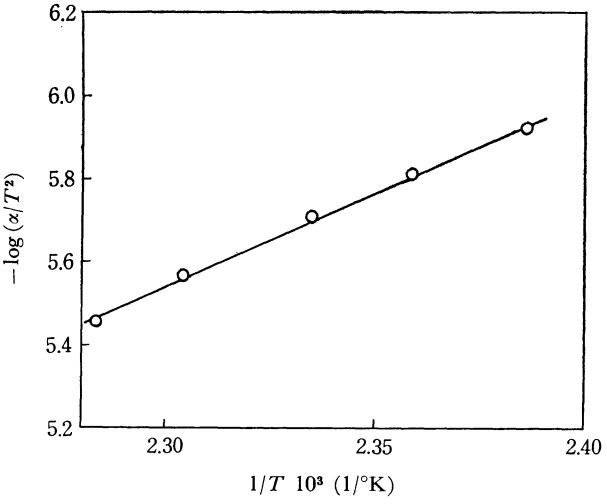

Fig. 6. Decarboxylation of AM_1-G_1. $n=0$.

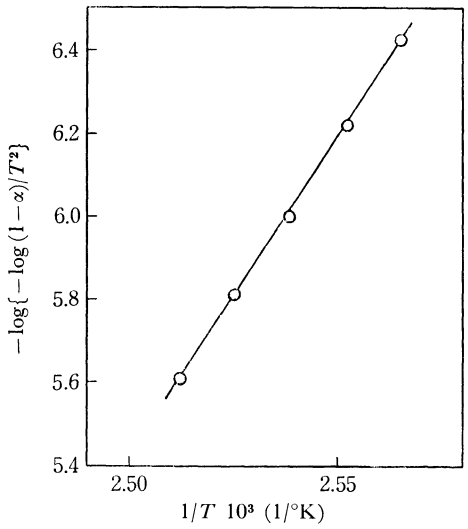

Fig. 7. Decarboxylation of aminomalonic acid. $n=1$

This indicates that the entropy term is effective in the depression of this reaction. This is attributed to the fact that, since the solid complex formed by the interaction of aminomalonic acid with glycine is thermally more stable than the crystals of aminomalonic acid alone, molecular motion is more restricted and the increase of entropy at the activated state was smaller in the solid complex than in the crystal of aminomalonic acid.

Conclusion

Aminomalonic acid can form an equimolar solid complex with glycine. In its crystalline state, aminomalonic acid is thermally stabilized due to its stronger interaction with glycine compared with the molecular interaction between aminomalonic acid molecules alone.