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Solid Complex Formation of Malonic Acid with Glycine

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Synopsis. A solid complex in a molar ratio of 1 : 1 was inferred to be formed by means of an intermolecular hydrogen bond between the hydrogen atom of the -COOH of malonic acid and the $-COO^-$ of glycine.

As a part of a series of studies of the interaction of organic acid with amino acid, we previously reported[1] that oxalic acid forms a solid complex at a molar ratio of 1 : 1 with a large number of α-amino acids and also at a molar ratio of 1 : 2 with some of the α-amino acids. Therefore, it was presumed that the formation of the complexes was promoted by proton-transfer from the carboxyl group in oxalic acid to the carboxyl ion of amino acid in the case of the 1 : 1 complex and by the intermolecular hydrogen bond between two hydrogen atoms of the carboxyl groups in oxalic acid and the carboxyl ions of two molecules of amino acid in the case of the 1 : 2 complex. To investigate further the factors affecting the formation of a solid complex of organic acids with α-amino acid, we have chosen malonic acid, which is a weaker acid than oxalic acid and glycine, and studied it with respect to the formation of a solid complex between them.

Experimental

Preparation of the Solid Complex. A mixture of malonic acid (special-grade chemicals) and glycine (special-grade chemicals) in a molar ratio of 1 : 1 was dissolved into purified water. By evaporating the solvent at 60 °C under a pressure of 30—40 mmHg, a viscous residue was obtained. The residue gradually crystallized when left standing at room temperature. This substance will hereafter be called M_1-G_1, where M and G stand for malonic acid and glycine respectively where the subscripts refer to the molar ratio. The crystalline substance was dried at 60 °C for 10 hr, pulverized in an agate mortar, and then used as the sample. The same procedure was followed to prepare samples of different molar ratios.

Measurements. The X-ray analysis and DTA-TG were carried out using the apparatus previously reported.[1] The infrared absorption spectra were measured with a Hitachi spectrophotometer, Model EPI-G2. The Nujol-mull method was used in the measurements. The pH value was measured by means of a Toa Denpa HM-5A-type apparatus. The determination of malonic acid and glycine by X-ray diffractometry was carried out by the method reported previously.[1]

Results and Discussion

The X-ray diffraction patterns of malonic acid, γ-glycine, and M_1-G_1 are shown in Fig. 1. In the case of M_1-G_1, a new diffraction pattern, diffrent from those of the component, malonic acid, and glycine, was obtained. On the other hand, M_2-G_1, M_3-G_2, and M_4-G_3 gave patterns of M_1-G_1 and malonic acid, while

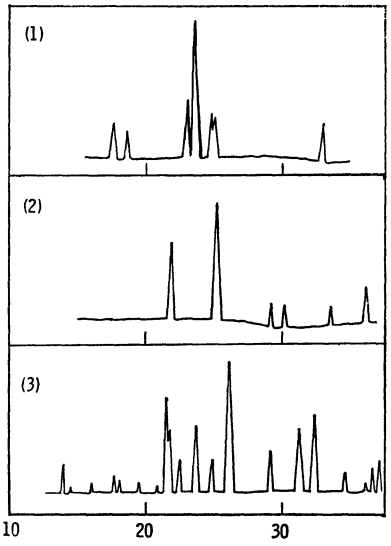

Fig. 1. X-Ray diffraction patterns of malonic acid (1), γ-glycine (2) and M_1-G_1 (3).

M_1-G_2, M_2-G_3, and M_3-G_4 gave those of M_1-G_1 and γ-glycine. The determination of the mole ratio of malonic acid to glycine in the complex was carried out by the method reported previously;[1] it was concluded that malonic acid reacts with glycine in a 1 : 1 molar ratio to produce a solid complex which gives the diffraction pattern of M_1-G_1.

The infrared spectrum of M_1-G_1 is shown in Fig. 2. For comparison, the infrared spectra of the components, malonic acid and glycine, are shown in Fig. 2. The infrared spectrum of M_1-G_1 is diffrent from the sum; this fact indicates the presence of an interaction between

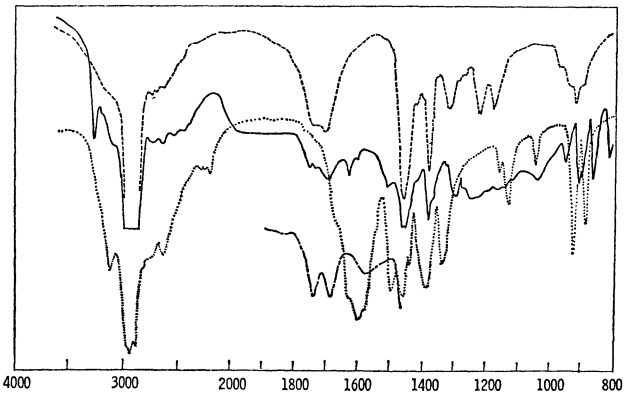

Fig. 2. Infrared absorption spectra of M_1-G_1 (——), malonic acid (----), γ-glycine (·····) and deuterated M_1-G_1 (————) in Nujol.

malonic acid and glycine. The absorption bands which are observed at 3250—2300 cm^{-1}, 1620 cm^{-1}, and 1510 cm^{-1} in M_1-G_1 shift toward lower wave numbers upon deuteration. Therefore, NH_3^+ is present in M_1-G_1. An absorption band assigned to COOH is observed in the region of 1750—1695 cm^{-1}, and it is inferred from the shape of the absorption band and the wave number that there exists a COOH group of a different type of intermolecular hydrogen bond in M_1-G_1. Also, an absorption band appearing near 1575 cm^{-1} in the deuterated M_1-G_1 seems to be assignable to $-COO^-$. The X-ray diffraction pattern of M_1-G_1 was identical with that of the deuterated M_1-G_1.

The DTA-TG of M_1-G_1 and malonic acid are shown in Fig. 3. In the case of malonic acid, a small endothermic peak due to a transition and a large endothermic peak due to fusion are observed near 92 °C and 132 °C respectively. Following this sharp endothermic peak, a broad endothermic change due to the decomposition of malonic acid into acetic acid and carbon dioxide was observed. Now, in the case of M_1-G_1, a sharp, large endothermic peak due to fusion and a small but sharp exothermic peak due to the crystallization of the dissolved glycine to α-glycine were observed near 113 and 145 °C respectively. The gradually increasing endothermic change shown by M_1-G_1 after fusion is similar to that shown by malonic acid alone and is considered to be the energy required for the decomposition of M_1-G_1 into glycine, acetic acid, and carbon dioxide. The slight exothermic change observed after the exothermic peak due to the crystallization to α-glycine indicates a possibility that glycine in part undergoes thermal polymerization in this temperature range.[2]

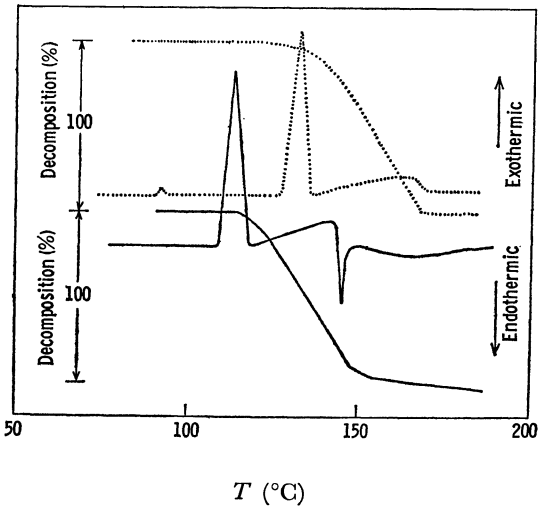

Fig. 3. DTA-TG curves of M_1-G_1 (——) and malonic acid (·····), in air. heating rate: 1.25 °C/min, sensivility: ±50 μV, reference: α-alumina powder.

The driving force in the formation of a solid complex of malonic acid with glycine was considered. The pK_1 and pK_2 of malonic acid are 2.76 and 5.29 respectively, whereas the pK_1 of glycine is 2.35.[3] Hence, the formation of the so-called salt in aqueous solution would not be extensive. The pH of an aqueous solution of mixture of malonic acid and glycine, 0.1 mol/l in respect to each component, was 2.60 at room temperature. The ratio of $G^{\pm}(NH_3^+CH_2COO^-)$ to $G^+(NH_3^+CH_2COOH)$ in the aqueous solution was determined by means of the following equation:

$$\frac{[G^{\pm}][H^+]}{[G^+]} = 10^{-2.35}, \quad \frac{[G^{\pm}]}{[G^+]} = 1.8$$

Therefore, G^+ is about one half of $G^{\pm}$. It is known that the shape of the infrared absorption band of -COOH in M_1-G_1 differs from that of -COOH in malonic acid alone, but is similar in wave number, that the stretching vibration of NH_3^+ is shifted toward the higher wave-number side compared with that of glycine alone, that M_1-G_1 undergoes a breakdown to malonic acid and γ-glycine upon treatment with methanol or ethanol and malonic acid dissolves in an organic solvent while γ-glycine remains undissolved. On the basis of these experimental results, it is difficult to consider that the proton of -COOH of malonic acid has transferred to the $-COO^-$ of glycine in M_1-G_1. It has, hence, been inferred that the solid complex is formed as a result of formations of an intermolecular hydrogen bond between the hydrogen atom of malonic acid and the $-COO^-$ of glycine.

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