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EFFECT OF CRYSTALLINE CONDITION ON RADIOLYSIS OF SOLID SUCCINIC ACID

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Abstract—The γ-radiolysis of solid succinic acid is reexamined by the analysis of gaseous products. G(CO) from the powder is much higher than that from the single crystal. The large difference in G(CO) between the powder and the single crystal cannot be attributed to thermal decomposition during the analytical procedure, but to the difference of the yields in the radiolysis. G(CO) from the powder decreases upon annealing the sample.

INTRODUCTION

RADIATION chemistry of solid organic substances contains some interesting phenomena which are characteristic of the solid phase and cannot be explained by applying the mechanism in the gas or liquid phases to the solid phase. Radiolysis of solid succinic acid have been studied by several investigators.[1–4] Gaseous products are CO_2, CO, and H_2. Miyazaki *et al.*[2] found that $G(CO + H_2)$ from a powdered sample is much higher than the yield from a single crystal, while $G(CO_2)$ is independent of the crystalline condition. They considered that CO and/or H_2 are formed at some active sites, such as the surface and defects, in the crystal.

Recently Bartoniček *et al.* have made a comment in this Journal[4] that they did not find any difference on $G(CO + H_2)$ between the powder and the single crystal. It was mentioned that Miyazaki *et al.*[2] used a wrong technique for releasing gases from the irradiated sample: they melted the sample at 185°C, a temperature at which thermal decomposition could possibly occur. Bartoniček *et al.* proposed another analytical technique of sample sublimation *in vacuo* at 150°C[4].

In this study we have reexamined the radiolysis of solid succinic acid by using the analytical method proposed by Bartoniček *et al.*[4] and confirmed the previous observation by Miyazaki *et al.*[2]

EXPERIMENTAL

The succinic acid, supplied by the J. T. Baker Co., with a purity of more than 99.6 mol %, was recrystallized from aqueous solution. The acid was in the form of a single crystal 0.5–1.0 cm long. The powder was made by several methods, which will be explained in a later section.

After the samples of the single crystal or the powder had been degassed for more than 3 h on a vacuum line, they were irradiated at room temperature with γ-rays from ^{60}Co of 9000 Ci at a dose rate of 3.4×10^{19} eV g^{-1} h^{-1}.

The gases from the irradiated samples were released by sample sublimation *in vacuo* at 150 ± 4°C. The gaseous products not condensable at the temperature of liquid nitrogen were analyzed by a gas burette connected to a Tepler pump and a cupric oxide furnace kept at 240°C. Mass spectrometric analysis indicated that these gaseous products consist mainly of CO, the amount of which is larger by one order of magnitude than that of H_2. Therefore the gaseous product not condensable at liquid nitrogen temperature is described in this paper as CO gas, though a small amount of H_2 may be present in this gaseous product. Another gaseous product (CO_2) not condensable at the temperature of dry ice was measured by means of the gas burette alone.

RESULTS AND DISCUSSION

Effect of dose on the formation of CO *and* CO_2

The dose dependence of gaseous products in the radiolysis of succinic acid is shown in Fig. 1. The powder was made by grinding the single crystal with an agate mortar. The yields of CO from the powdered sample are clearly much higher than those from the single crystal. Since CO was analyzed by the method of sample sublimation *in vacuo* at 150°C, the possibility of thermal decomposition can be omitted[4]. The blank test shows

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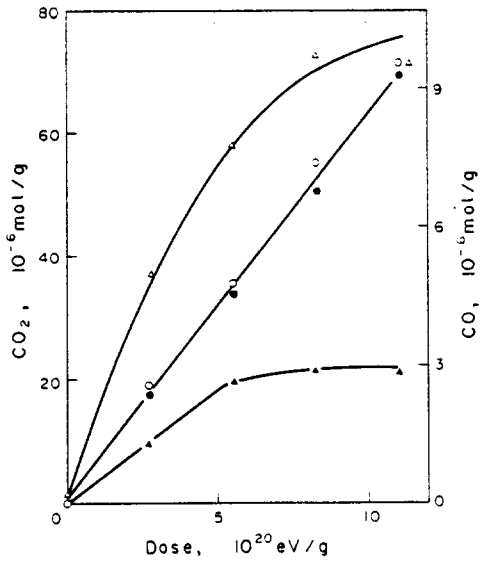

FIG. 1. Yields of gaseous products in the radiolysis of solid succinic acid at room temperature against the total dose. △: Yields of CO from powder. ▲: Yields of CO from single crystal. ○: Yields of CO_2 from powder. ●: Yields of CO_2 from single crystal.

that the formation of CO from the nonirradiated sample during the analytical process can be neglected. Therefore the difference in the amounts of CO between the powder and the single crystal represents the difference of the yields in the radiolysis and confirms the previous results obtained by Miyazaki *et al.*[2] G(CO) at the dose of 5.5×10^{20} eV g^{-1} are 0.85 and 0.28 for the powder and the single crystal, respectively. These values are approximately the same as those reported previously; 0.92 and 0.24 for the powder and the single crystal respectively[2b]. $G(CO_2)$ are 3.9 and 3.7 for the powder and the single crystal, respectively. These values are consistent with the reported values by several investigators[1-4].

The rate of production of CO decreases gradually with an increase in the dose, while CO_2 is formed linearly with an increase in the dose. As described in the later section, if it is supposed that CO is produced at special active sites of the crystal, the site may be gradually consumed with an increase in the dose, resulting in a decrease in the rate of the formation of CO.

Present value of G(CO) from the powder is much higher than that of ref. 4. The experimental procedure of the present work has two differences from that of Bartoniček *et al.* One is that we made the powder by grinding with an agate mortar, while they made the powder by recrystallization from aqueous solution. Another is that they kept the sample at 100°C after they obtained the powder. The former difference suggests the possibility that when the powder is made by grinding in the air with the mortar, the oxidation of succinic acid might take place. The formation of oxides or peroxides in the powder might increase the formation of CO in the radiolysis of the powdered sample. The latter difference suggests the possibility that the storage of the sample at 100°C might cause the annealing of the crystal. The annealing of the sample might decrease G(CO) in the powdered sample. Therefore, these two possibilities will be discussed in the following sections.

Effect of air on G(CO) of powder

In order to examine the effect of air on G(CO) in the radiolysis of powdered succinic acid, the powders are obtained by several methods, which exclude the air. G(CO) of five kinds of powders are compared in Table I. Powder 1 is obtained by grinding the single crystal with an agate mortar in air. Powder 2 is obtained by grinding the single crystal with an agate mortar in nitrogen gas. The contact of the air with the powder 2 is excluded during the entire procedure of sample preparation on a vacuum line. Powder 3 is obtained by rapid sublimation of the powder 1 at 150°C on a vacuum line. Powder 4 is obtained by rapid sublimation of a single crystal at 150°C on a vacuum line. When an

TABLE I. EFFECT OF CRYSTALLINE CONDITIONS ON G(CO) IN THE RADIOLYSIS OF SUCCINIC ACID AT ROOM TEMPERATURE[a]

State of solid	G(CO)	Method of production of solid
Single crystal	0.28	Crystallization from aqueous solution
Powder 1	0.85	Grinding with an agate mortar in air
Powder 2	0.71	Grinding with an agate mortar in N_2 gas
Powder 3	0.91	Sublimation of powder 1 into vacuum
Powder 4	0.94	Sublimation of single crystal into vacuum
Powder 5	0.81	Reprecipitation from benzene

[a]A dose is 5.5×10^{20} eV g^{-1}. G(CO) of powder 1 is an average of five runs. Other G(CO) are averages of two runs.

aqueous solution of succinic acid is poured rapidly into benzene, a powdered succinic acid (powder 5) is obtained by the reprecipitation from benzene. G(CO) of powders 2–5 are 0.71–0.91, which are approximately equal to G(CO) of powder 1 and much higher than G(CO) of single crystal (Table I). Since the air is excluded in the process of the formation of the powders 2–4, a large difference of G(CO) between the powder and the single crystal is not due to the oxide or peroxide, but to the difference of the two crystalline conditions.

Effect of annealing on G(CO)

Powder 1 and single crystal were stored in air at 100°C or 130°C before γ-irradiation. The effect of storage time on G(CO) is shown in Fig. 2. When the storage time increases, G(CO) of the powder decreases gradually at 100°C and rapidly at 130°C. On the contrary, little effect of the storage time has been observed on G(CO) of the single crystal. A slight increase of the G(CO) may be due to the occurrence of partial sublimation of the single crystal (cf. powder 4 in Table I). The decrease of G(CO) of the powder in Fig. 2 may be explained by the hypothesis that CO may be formed at some active sites in the crystal. The storage of the sample at high temperature may cause the annealing of the solids. The annealing of the powder may remove the active sites, in which CO may be formed preferentially. Thus G(CO) of the powder may decrease upon the annealing.

Since the number of the active site in the powder may be much higher than that in the single crystal, G(CO) of the powder may be much higher than that of single crystal. The results obtained here are merely phenomenological and the more exact works on the heterogeneous character of the solid radiation chemistry may be desirable in future.

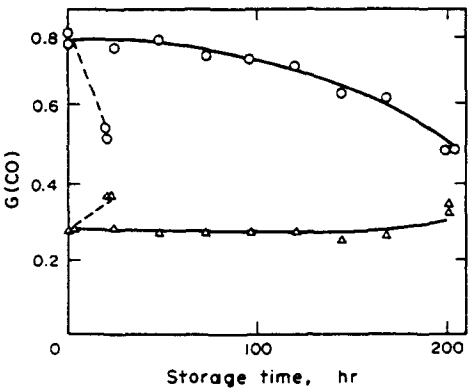

FIG. 2. Effect of annealing on G(CO). O—O: Powder 1 at 100°C. O---O: Powder 1 at 130°C. Δ—Δ: Single crystal at 100°C. Δ---Δ: Single crystal at 130°C. G(CO) of powder 1 is a little smaller than the value in Table I. This is because the results in Fig. 2 are obtained from the same lot of powder 1, while the value in Table I is an average of different lots of powder 1.

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