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"EFFECT OF CRYSTALLINE CONDITION ON THE RADIOLYSIS OF SOLID SUCCINIC ACID"

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ABSTRACT

Gaseous products in the radiolysis of solid succinic acid have been measured by the revised analytical method proposed recently (Int J Radiat Phys Chem., 1974, 6, 271). $G(CO + H_2)$ from powder is much higher than that from the single crystal and decreases with an increase of dose, suggesting that CO and/or H_2 are produced at some active sites in the crystal. On the contrary, $G(CO_2)$ is not affected by the crystalline condition and the dose, suggesting that CO_2 is produced homogeneously in the crystal.

INTRODUCTION

Radiolysis of solid succinic acid have been studied by several investigators[1-5]. Gaseous products are CO_2, CO, and H_2. Miyazaki et al.[3-4] 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 Bartoníček et al.[2] have made a comment upon this observation. 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.[3-4] 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. Bartoníček et al. proposed another technique of sample sublimation in vacuo at 150°C.

In this study we have reexamined the radiolysis of solid succinic acid by using the analytical method proposed by Bartoníček et al.[2] and confirmed the previous observation of Miyazaki et al.[3-4].

EXPERIMENTAL

The succinic acid, supplied by the J. T. Baker Co. with a purity of more than 99.6%, was recrystallized from aqueous solution. The acid was in the form of a single crystal 0.5 – 1.0 cm long. The single crystal was ground into powder with an agate mortar.

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

The gases from the irradiated samples were released by sample sublimation in vacuo at $150 \pm 4°C$. The gaseous products (mixture of CO and H_2) 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, while 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

The dependence of gaseous products on the dose is shown in Figure 1. The yields of $CO + H_2$ from the powdered samples are clearly much higher than those from the single crystals. Since we have adopted the analytical procedure proposed by Bartoníček et al.[2], the possibility of thermal decomposition can be omitted. The blank test shows that the formation of CO and H_2 from nonirradiated sample during the analytical process can be neglected. Therefore, the difference in the amounts of $CO + H_2$ 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.[3-4] $G(CO + H_2)$ at the dose of 5.5×10^{20} eV/g are 0.81 and 0.28 for the powder and the single crystal respectively, which are approximately the same values as those reported previously (0.92 and 0.24 for the powder and the single crystal respectively)[3] It is noted that $G(CO + H_2)$ obtained by Bartoníček et al. are $0.15 \sim 0.38$[2] and 0.63[1], suggesting that $G(CO + H_2)$ may depend upon the experimental conditions even in their experiments.

Present values from the powder are higher than those of Ref.[2]. One important difference between the two groups is that Bartoníček et al. made the powder by the recrystallization, while we made the powder by using an agate mortar. They kept the sample at 100°C after they obtained the powder. If CO and H_2 are produced at the special reaction sites, such as the active surface and defects, in the solid succinic acid, it may be probable that the process of the preparation of the powder may influence the yields of CO and H_2. The rate of production of $CO + H_2$ decreases gradually with an increase in the dose (Figure 1). If it is supposed that CO and H_2 are produced at special active sites of the crystal, the sites may be gradually consumed with an increase in the dose, resulting in a decrease in the rate of the formation of $CO + H_2$.

On the contrary, CO_2 is formed linearly with an increase in the dose. $G(CO_2)$ 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[1-5]. It is conceivable that CO_2 is produced homogeneously in the crystal.

Further study on the formation of CO and H_2 are now in progress.

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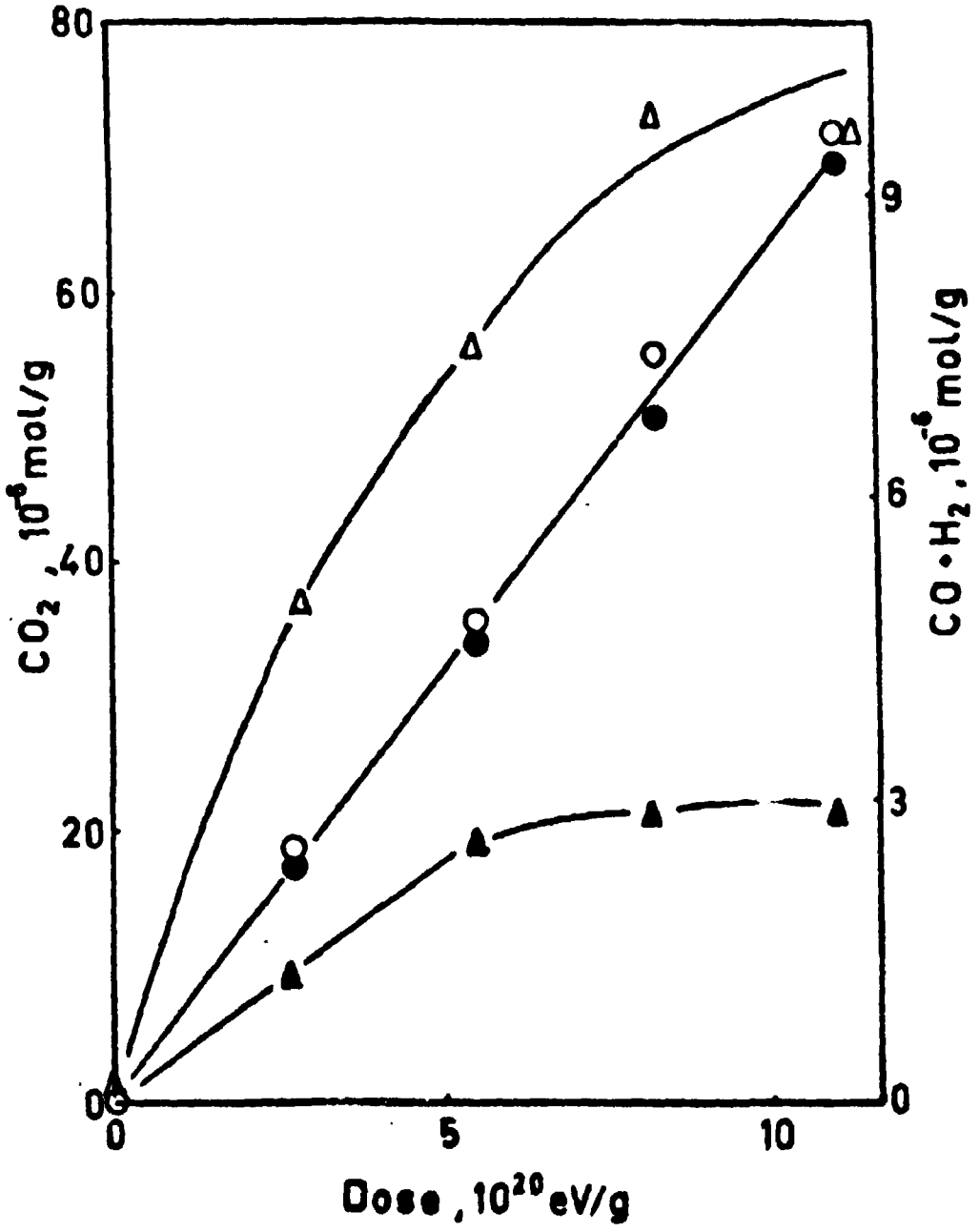

Figure 1 – Yield of gaseous products in the radiolysis of solid succinic acid at room temperature against the total dose.

Δ : Yields of $CO + H_2$ from the powder.

▲ : Yields of $CO + H_2$ from the single crystal.

○ : Yields of CO_2 from the powder.

● : Yields of CO_2 from the single crystal.

RESUMO

Os produtos gasosos na radiólise do ácido succínico têm sido medidos pelo método analítico proposto recentemente (Int J. Radiat. Phys. Chem., 6, 271, 1974). O valor de $G(CO + H_2)$ das amostras em pó é muito maior que o das amostras na forma de cristal e decresce com o aumento de dose, indicando que CO e/ou H_2 são produzidos em alguns sitios ativos no cristal Ao contrário, o valor de $G(CO_2)$, não é afetado pela forma cristalina e nem pela dose, indicando que CO_2 é produzido homogeneamente no cristal

REFERENCES

1. BARTONIČEK, B Gamma radiolysis of solid succinic acid. *Int. J. radiat. Phys., Chem.*, Oxford, 5:361-9, 1973.

2. _____ & PEJŠA, R. On the use of solid succinic acid for dosimetric purposes. *Int. J. radiat. Phys. Chem.*, Oxford, 6:271-4, 1974.

3. MIYAZAKI, T.; FUJITANI, Y.; WAKAYAMA, T.; FUEKI, K. & KURI, Z. The role of reaction sites in the radiolysis of solid succinic acid. *Bull. chem. Soc. Japan*, Tokyo, 44:984-8, 1971.

4. _____; OKADA, S.; WAKAYAMA, T.; FUEKI, K. & KURI, Z. Effect of crystal size on the radiolysis of solid succinic acid. *Bull. chem. Soc. Japan*, Tokyo, 43:1907, 1970.

5. MOLIN, Y. N.; CHKHEIDZE, I. I.; BUBEN, N. Y. & VOEVODSKII, V. V. EPR spectra of irradiated decarboxylic acids. *J. struct. Chem.*, New York, 2:279-85, 1961.