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The Role of Reaction Sites in the Radiolysis of Solid Succinic Acid

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The main gaseous products in the radiolysis of solid succinic acid are CO_2, CO, and H_2. It was found that the $G(CO+H_2)$ from the powder is much higher than that from the single crystal, while there is no difference in $G(CO_2)$ between the powder and the single crystal, indicating that CO_2 is produced homogeneously in the solid. The clear difference in the $G(CO+H_2)$ between the powder and the single crystal cannot be attributed to the analytical procedure, the secondary reaction of CO, or the presence of H_2O as an impurity. It may be due to the difference in the primary process of the radiolysis. It is conceivable that the mobile active entity formed by the γ-irradiation of the crystal migrates to the special reaction sites and produces CO and H_2. The difference in $G(CO+H_2)$ may also be due to the different numbers of the sites between the powder and the single crystal. It is discussed whether the mobile entity is a cation, an electron, or an exciton.

We have previously studied the radiolysis in the solid state in order to elucidate the primary process of radiolysis in the solid state and in order to obtain information about reaction kinetics in the solid state. In the previous studies, some peculiar phenomena in solid-state radiolysis have been reported.[1,2] The formation of the exciton may play an important role in the radiolysis of solid isobutane, while it plays only a minor role in the liquid phase.[1] When solid isobutane is γ-irradiated, an isobutyl radical is formed in the crystalline state, while a tertiary butyl radical is formed in the glassy state.[2] This result cannot be

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[1] a) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **42**, 1164 (1969). b) T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, *ibid.*, **43**, 1017 (1970). c) T. Miyazaki, T. Yamada, T. Wakayama, K. Fueki, and Z. Kuri, *ibid.*, **44**, 934 (1971).

[2] a) T. Miyazaki, T. Wakayama, K. Fueki, and Z. Kuri, This Bulletin, **42**, 2086 (1969). b) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 3584 (1970).

explained by the ordinary theory of a unimolecular reaction in the gas phase.

In a previous communication, the preliminary findings on the effect of crystal size on the radiolysis of succinic acid have been reported. In this work we will study this effect in more detail in order to get a better understudying of solid-state radiolysis.

Experimental

The succinic acid was supplied by the Katayama Chemical Co. and was more than 99.8% pure. The acid was in the form of a single crystal 0.5—1.0 cm long, and its melting point was 185°C. The single crystal was ground into powder with an agate mortar. The diameter of the powder was measured with a microscope and found to be about 2×10^5 Å.

After the samples of the single crystal or the powder had been degassing for more than 3 hours on a vacuum line, they were irradiated with γ-rays from Co-60 at a dose rate of 4.4×10^{19} eV/g hr. After irradiation, the sample was melted at 185°C, and then the gaseous products were analyzed as follows: the gaseous products (mixtures of CO and H_2) not condensable at the temperature of liquid nitrogen were analyzed by a gas burette connected to a Toepler 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

Gaseous Products in the Radiolysis of Solid Succinic Acid. The main gaseous products in the radiolysis of solid succinic acid are shown in Table 1. When succinic acid is γ-irradiated at -196°C in the powdered form or in the single crystal, the $G(CO+H_2)$ values are about 0.3 and 0.04 respectively at a dose of 6.6×10^{20} eV/g. The fact that the $G(CO+H_2)$ value is different from the previously-reported value[3] may be due to the difference in dose between the two cases. On the contrary, there is no clear difference in the yield of CO_2 between the powder and the single crystal. The yield of CO is about four times that of H_2. It should be noted that the $G(CO+H_2)$ value from the powder is much higher than that from the single crystal.

TABLE 1. RADIOLYSIS OF SOLID SUCCINIC ACID

State	Irrad. Temp.	Method of Analysis	$G(CO+H_2)$	$G(CO_2)$
Powder	-196°C	Melting	$0.20^{a)}+0.11^{b)}$	2.01
Powder	-196°C	Melting	$0.20^{a)}+0.10^{b)}$	1.90
Single Crystal	-196°C	Melting	0.06	1.89
Single Crystal	-196°C	Melting	0.02	1.60
Powder	-196°C	Dissolved in ethanol	0.24	
Single Crystal	-196°C	Dissolved in ethanol	0	
Powder	30°C	Melting	0.92	4.92
Single Crystal	30°C	Melting	0.24	4.60

a) Yield before melting the sample
b) Yield after melting the sample
Dose: 6.6×10^{20} eV/g

The possibility that the difference in $G(CO+H_2)$ value may be attributed to thermal decomposition during the analysis can be excluded for the following two reasons. First, two-thirds of the total yields of $CO+H_2$ could be measured at room temperature without melting the irradiated powder at 185°C, and the yields are much higher than the total yields from the single crystal. Second, when the CO and H_2 were measured after the γ-irradiated sample had been dissolved in ethanol at room temperature, the clear difference in $G(CO+H_2)$ value between the powder and the single crystal was also observed.

Does the CO produced in the single crystal react with the trapped radicals to result in the low yield of CO, while CO in the powder diffuses to the surface without the reaction? The yields of $CO+H_2$ trapped in the powder at the irradiation temperature of -196°C and 30°C are 0.1 and 0.5 respectively. These values are higher than the total yields from the single crystal at each temperature. The difference in $G(CO+H_2)$ value between the powder and the single crystal cannot be ascribed to this cause.

Therefore, the difference in $G(CO+H_2)$ may represent the difference in the yields of products in the radiolysis of succinic acid.

Effect of H_2O on the Radiolysis of Succinic Acid. Solid succinic acid contains a small amount of water in its crystal. When a solid succinic acid is melted at 185—190°C, the water is vaporized from the acid; then the vapor pressure of water can be measured after the sample has been rapidly cooled to room temperature. In order to examine whether or not water was produced by the thermal decomposition of succinic acid at 185—190°C, the samples were held at this temperature for different times and then the amounts of water were measured. As is shown in Table 2, the amounts of water do not depend upon the time the substances are kept at 185—190°C; therefore, they represent the amounts of water present in the crystal as an impurity.

TABLE 2. AMOUNTS OF H_2O AS AN IMPURITY IN THE SUCCINIC ACID

State	Time held at 185—190°C	H_2O (mol%)
Single Crystal	0.3 hr	10
Single Crystal	1.5 hr	8
Single Crystal	3.0 hr	13
Powder	0.3 hr	13

Since the water usually acts as an effective cation scavenger in the radiolysis, there is a possibility that the amount of water in the powder is smaller than that in the crystal and that the difference in $G(CO+H_2)$ value between the powder and the single crystal is due to this effect. Table 2 shows, however, that the amount of water in the powder is approximately equal to that in the single crystal. When the polycrystalline sample from which water has been completely removed

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[3] T. Miyazaki, S. Okada, T. Wakayama, K. Fueki, and Z. Kuri, This Bulletin, **43**, 1907 (1970).

Table 3. Effect of H_2O on the radiolysis of succinic acid at $-196°C$

State	$G(CO+H_2)$	$G(CO_2)$
Sample A	0.22	2.01
Sample B	0.19	1.83
Powder	0.31	1.96

Sample A: Polycrystal, from which H_2O is removed completely by melting the powder.
Sample B: Polycrystal, from which H_2O is removed completely by melting the single crystal.
Dose: 6.6×10^{20} eV/g

by melting and degassing, is γ-irradiated, the yield of $CO+H_2$ is rather smaller than that from the powder (Table 3). Therefore, the difference in $G(CO+H_2)$ value between the powder and the single crystal cannot be ascribed to the effect of water, but must be ascribed to a difference in the physical state, such as the surface area or the defects in the crystal.

Effect of Total Dose. The dependence of gaseous products on the total dose is shown in Figs. 1 and 2. The rate of the production of $CO+H_2$ decreases gradually with an increase in the dose, while the yield of CO_2 increases linearly with an increase in the dose. These results suggest that the mechanism of the formation of CO and H_2 differs from that of CO_2. 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 $CO+H_2$. The yields of $CO+H_2$ in the radiolysis of the single crystal at $-196°C$ seem to be negligibly small at a low dose. This is because the analysis of a small amount of $CO+H_2$ with Toepler pump is very difficult. On the contrary, CO_2 may be produced homogeneously in the crystal.

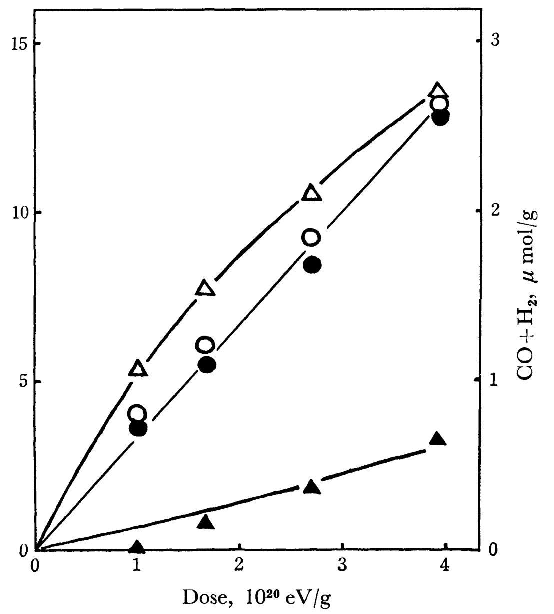

Fig. 1. Yield of gaseous products in the radiolysis of solid succinic acid at $-196°C$ against the total dose.
△: Yields of $CO+H_2$ from succinic acid in the powder.
▲: Yields of $CO+H_2$ from succinic acid in the single crystal.
○: Yields of CO_2 from succinic acid in the powder.
●: Yields of CO_2 from succinic acid in the single crystal.

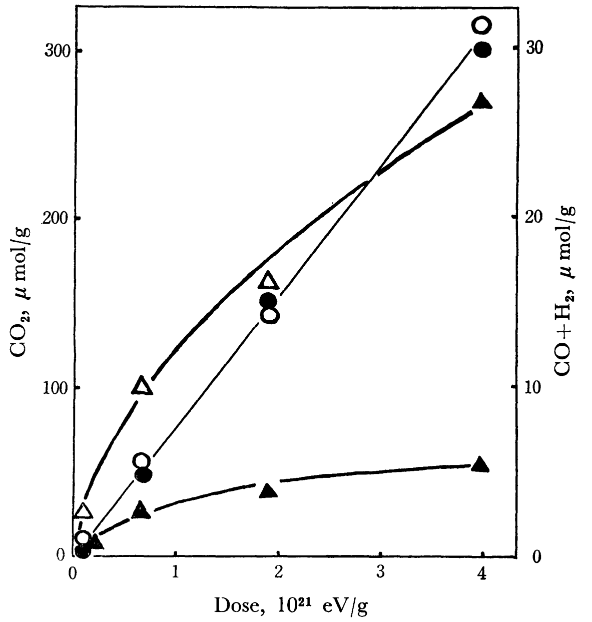

Fig. 2. Yields of gaseous products in the radiolysis of solid succinic acid at room temperature against the total dose.
△: Yields of $CO+H_2$ from succinic acid in the powder.
▲: Yields of $CO+H_2$ from succinic acid in the single crystal.
○: Yields of CO_2 from succinic acid in the powder.
●: Yields of CO_2 from succinic acid in the single crystal.

Yield Measured at Room Temperature without Melting. A fraction of the gaseous products can be measured at room temperature without melting the irradiated sample; the measurable yields depend upon the storage time at room temperature (Fig. 3). When the powdered succinic acid is irradiated at $-196°C$, the

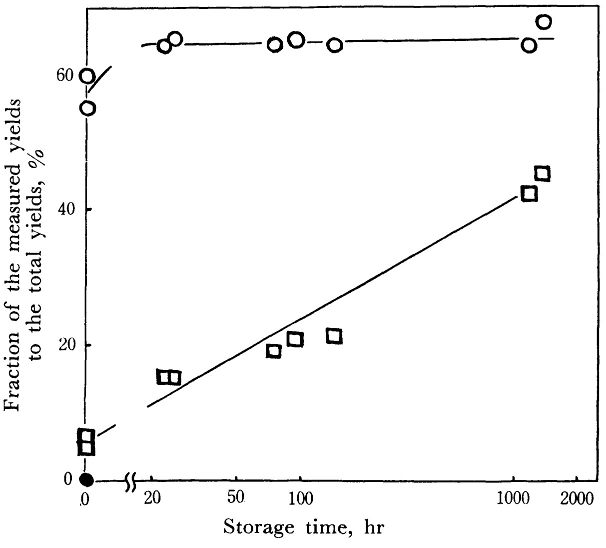

Fig. 3. Effect of storage time on the yields measured at room temperature before melting the irradiated sample.
○: Yields of $CO+H_2$ measured at room temperature before melting the irradiated sample.
□: Yields of CO_2 measured at room temperature before melting the irradiated sample.

$CO+H_2$ cannot be measured at -196°C, but two-thirds of the total yield can be measured immediately after warming up to room temperature. The measurable amount of $CO+H_2$ does not increase even if the sample is stored for longer than 1000 hr at room temperature. On the contrary, the amount of CO_2 measurable at room temperature gradually increases with the passage of the storage time. As will be discussed in the next section, the gaseous products may be formed mainly by warming the irradiated sample to room temperature. Two-thirds of CO and H_2 may be formed at some sites such as the surface and may come out easily from the crystal. The residue may be formed at another type of site, such as defects of the crystal, and be tightly trapped in the crystal. The results indicate that CO_2 may be formed uniformly in the crystal and may gradually diffuse to the surface during storage at room temperature.

Mechanism of Reaction. Since the effect of reaction sites on the radiolysis has not been reported previously, and since our information about the solid-state kinetics of molecular compounds is very scanty at present, it is not possible to explain this effect in a satisfactory way. We will discuss here a possible mechanism for this effect. Several investigators have proposed the following mechanism for explaining the ESR results on succinic acid:[4)]

$$\begin{aligned}&HOOCCH_2CH_2COOH \rightsquigarrow\\&\quad HOOCCH_2CH_2COOH^+ + e^- &(1)\\&HOOCCH_2CH_2COOH^+ + HOOCCH_2CH_2COOH \rightarrow\\&\quad HOOCCH_2CH_2COO\cdot + HOOCCH_2CH_2COOH_2{}^+ &(2)\\&HOOCCH_2CH_2COO\cdot \rightarrow HOOCCH_2CH_3\cdot + CO_2 &(3)\\&e^- + HOOCCH_2CH_2COOH \rightarrow\\&\qquad\qquad HOOCCH_2CH_2COOH^- &(4)\\&HOOCCH_2CH_2COOH^- \rightarrow HOOCCH_2CH_2 + CO_2{}^- &(5)\\&HOOCCH_2CH_2\cdot + HOOCCH_2CH_2COOH \rightarrow\\&\quad HOOCCH_2CH_3 + HOOCCH_2\dot{C}HCOOH &(6)\\&HOOCCH_2CH_2\cdot \rightarrow HOO\dot{C}CHCH_3 &(7)\end{aligned}$$

Reactions (1), (2), and (4) take place at -196°C by γ-irradiation. Reactions (3), (5), (6), and (7) represent the reactions which occur when the irradiated sample is warmed from -196°C to room temperature. The facts that CO_2 is the main gaseous product in the radiolysis of succinic acid and that it is formed homogeneously in the crystal can be explained by the above reaction mechanism.

On the other hand, it is conceivable that CO and H_2 may be produced when the mobile active entity formed by γ-irradiation migrates to the reaction sites, such as the surface and defects in the crystal. We will now discuss whether the mobile entity is a cation, an electron, or an exciton.

(a) Cation: A crystal of succinic acid is a monoclinic plate; its structure was determined by Broadley *et al.* (Fig. 4).[5)] Two nearest neighbor molecules of succinic acid are tightly combined by two hydrogen bonds between their carboxyl groups. Once a succinic acid cation is formed in reaction (1), its proton may be transferred easily to the second molecule by a quantum-tunneling process in a hydrogen bond (reaction (2)).[6)] It is, however, difficult for the proton transfer to the third molecule to occur by this process, since there is no hydrogen bond between the protonated second molecule and the third molecule which is not depicted in Fig. 4.

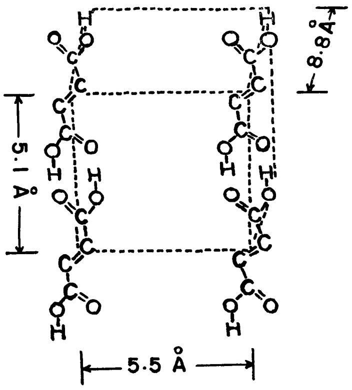

Fig. 4. Structure of the crystal of succinic acid in the unit cell.

The interaction between the protonated second molecule and the third molecule can roughly expressed by a charge-induced dipole interaction:

$$E = -\frac{e^2\alpha}{2r^4} \tag{I}$$

where E is the energy of interaction, and r, the distance between a charge and an induced dipole. α is the effective polarizability and is taken as 2×19^{-24} cc for a carbonyl group. Assuming that the charge of the protonated second molecule is localized on the oxygen atom, the distance (r) between the charge and a carbonyl group of the third molecule is 3.14 Å. From Eq. (I), we get $E\sim-1$ Kcal, which is rather less than the energy of the hydrogen bond, suggesting that the ion-molecule reaction would not occur easily.

Since water is an effective proton scavenger in the radiolysis, the fact that water does not affect the yields of CO and H_2 suggests that the proton does not move in the crystal.

(b) Electron: When 2-methyltetrahydrofuran (MTHF) glass containing a small amount of succinic acid is γ-irradiated at -196°C, the electrons are completely captured by the acid.[7)] Since the efficiency of electron capture by maleic acid (HOOCCHCH-COOH) is 5—10 times as great as that of biphenyl in MTHF glass at -196°C,[8)] succinic acid also may cap-

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[4)] R. N. Schwartz, M. W. Hanna, and B. K. Bales *J. Chem. Phys.*, **51**, 4336 (1969). The related papers on ESR studies are cited therein.

[5)] J. S. Broadley, D. W. J. Cruickshank, J. D. Morrison, J. M. Robertson, and H. M. M. Shearer, *Proc. Roy. Soc.* (London), **A251**, 441 (1959).

[6)] I. Miyagawa, N. Tamura, and J. W. Cook, *J. Chem. Phys.*, **51**, 3520 (1969).

[7)] T. Suzuki, T. Miyazaki, A. Torikai, K. Fueki, and Z. Kuri, unpublished results.

[8)] A. Torikai, T. Suzuki, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, (1971) **75**, 482 (1971).

ture electrons efficiently in the solid state.

Since the absorption spectrum of the succinic-acid anion is not observed in the visible region, it is expected that the acid may possess a high electron affinity and that the anion, once it is formed, does not release an electron easily. Therefore, it seems that an electron does not move a long distance in the crystal of succinic acid.

(c) Exciton: In the previous studies of the radiolysis of solid isobutane,[1)] it has been suggested that an exciton may play an important role in the solid-state radiolysis and that it will migrate to a distance of 20—30 Å. Since all the molecules of succinic acid in the crystal are combined by hydrogen bonds in one direction, an exciton, if it is formed, can migrate to a farther distance in the succinic acid than in saturated hydrocarbons. If it is supposed that the exciton migrates to the surface of succinic acid and is ionized there (reaction (9)), CO and H_2 may be formed by the neutralization of the succinic-acid ion by warming the sample up to room temperature (reaction (10)). This opinion is based on the findings that CO and H_2 are not observed at −196°C, and that CO is not adsorbed on the surface of succinic acid at −196°C. The reaction scheme may be represented as follows:

$$\mathrm{HOOCCH_2CH_2COOH} \rightsquigarrow (\mathrm{HOOCCH_2CH_2COOH})_n{}^* \quad \text{(in the crystal)} \qquad (8)$$

$$(\mathrm{HOOCCH_2CH_2COOH})_n{}^* \rightarrow \mathrm{HOOCCH_2CH_2COOH^+} + \mathrm{HOOCCH_2CH_2COOH^-} \quad \text{(at the surface)} \qquad (9)$$

$$\mathrm{HOOCCH_2CH_2COOH^+} + \mathrm{HOOCCH_2CH_2COOH} \rightarrow \mathrm{HOOCCH_2CH_2COO\cdot} + \mathrm{HOOCCH_2CH_2COOH_2{}^+} \qquad (2)$$

$$\mathrm{HOOCCH_2CH_2COOH_2{}^+} + \mathrm{HOOCCH_2CH_2COOH^-} \rightarrow \mathrm{CO},\ \mathrm{H_2},\ \text{other products} \quad \text{(warming up to room temperature)} \qquad (10)$$

where $(\mathrm{HOOCCH_2CH_2COOH})_n{}^*$ is an exciton. The possibility that the exciton state in the solid may correspond to the superexcited state and be related to the ionization of the solid has also been suggested for the radiolysis of solid isobutane.[1c)]

The authors wish to express their appreciation to Dr. Machio Iwasaki of the Government Industrial Research Institute of Nagoya for many fruitful discussions, and to Dr. Nobuo Tagusagawa of Nagoya University for his measurement of the crystal size of the powder.