Effect of Crystal Size on the Radiolysis of Solid Succinic Acid

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Recently we studied the radiolysis of hydrocarbons in the solid state and proposed that the formation of the exciton may play an important role in the radiolysis.[1,2] In the present work we have studied the radiolysis of crystalline succinic acid ($HOOCCH_2CH_2COOH$) at 77°K. The γ-irradiation of the acid was performed at 77°K in the form of a single crystal of 0.5—1.0 cm long or the powdered form. After irradiation, the sample was melted at 185°C, and then the gaseous products were analyzed as follows: the gaseous products (a mixture 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 gaseuous product (CO_2) not condensable at the temperature of dry ice was measured by means of the gas burette alone.

The yield of $CO+H_2$ is plotted against the total dose in Fig. 1. The $G(CO+H_2)$ from the powder and the single crystal are about 0.5 and 0.1 respectively at a dose of 4.6×10^6 rad. There is no difference in the yield of CO_2 between the powder and the single crystal; in both cases it is about 1.9 G-unit. It should be noted that the $G(CO+H_2)$ from the powder is much higher than that from the single crystal. In order to examine whether the difference in $G(CO+H_2)$ can be attributed to the analytical procedure, the CO and H_2 were measured after the γ-irradiated sample had been dissolved in ethanol at room temperature without melting the sample at 185°C. The clear difference in $G(CO+H_2)$ between the powder and the single crystal was also observed in this case. In the radiolysis of succinic acid in the powdered form, the $G(CO)$ and $G(H_2)$ were about 0.4 and 0.1 respectively. Most of the CO and H_2 could be measured without melting the irradiated sample, while most of the CO_2 was not measurable until the sample had melted. The results indicate that CO and H_2 may be produced at the surface of the crystal and that $G(CO+H_2)$ may depend upon the surface area or the size of the crystal. It is conceivable that the mobile active entity formed by the γ-irradiation of the crystal migrates to its surface and produces CO and H_2.

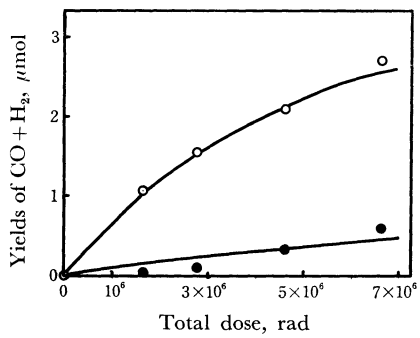

Fig. 1. Yields of $CO+H_2$ in the radiolysis of solid succinic at 77°K against the total dose.
dose rate: 3.0×10^5 rad/hr. Yields are expressed as 10^{-6} mol of products from 1 g of γ-irradiated succinic acid.
○: Yields from succinic acid in the powdered form.
●: Yields from succinic acid in the single crystal.

Since the effect of crystal size on the radiolysis has not been reported previously, it is not possible at present to discuss fully whether the mobile entity is a hole, an electron, or an exciton. It is expected, from an ESR study[3] of γ-irradiated succinic acid, that holes and electrons may be trapped in the crystal by the hydride-ion-transfer reaction and the electron-capture reaction:

$$HOOCCH_2CH_2COOH \rightsquigarrow HOOCCH_2CH_2COOH^+ + e^- \quad (1)$$

$$HOOCCH_2CH_2COOH^+ + HOOCCH_2CH_2COOH \longrightarrow HOOCCH_2CH_2COO\cdot + HOOCH_2CH_2COOH_2^+ \quad (2)$$

$$HOOCCH_2CH_2COO\cdot \longrightarrow HOOCCH_2CH_2\cdot + CO_2 \quad (3)$$

$$e^- + HOOCCH_2CH_2COOH \longrightarrow HOOCCH_2CH_2COOH^- \quad (4)$$

$$HOOCCH_2CH_2COOH^- \longrightarrow HOOCCH_2CH_3 + CO_2^- \quad (5)$$

Further studies of the effect of crystal size on the radiolysis are now in progress.

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)

2) a) T. Miyazaki, T. Wakayama, K. Fueki and Z. Kuri, *ibid.*, **42**, 2086 (1969). b) T. Wakayama, T. Miyazaki, K. Fueki and Z. Kuri, *J. Phys. Chem.*, submitted for publication.

3) R. N. Schwartz, M. W. Hanna and B. L. Bales, *J. Chem. Phys.*, **51**, 4336 (1969).