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Radiation Chemistry of Dicarboxylic Acids in the Solid State. I. Radiolysis of Malonic Acid in the Solid State

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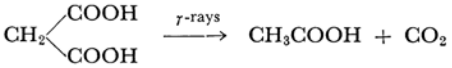
The radiolysis of solid malonic acid by ^{60}Co γ-rays has been studied *in vacuo* at -196°C, -78°C, and room temperature. All the products were measured after dissolving the irradiated malonic acid in water. The main products were carbon dioxide with $G=4.4$ and acetic acid with $G=4.5$, as was determined by the reverse isotope dilution analysis. The yields of the other products (hydrogen, carbon monoxide, methane, ethane and carbonyl compounds) were very low. These facts revealed that the following reaction takes place selectively:



$$CH_2\begin{cases}COOH\\COOH\end{cases} \xrightarrow{\gamma\text{-rays}} CH_3COOH + CO_2$$

The mechanism of the reaction is discussed with reference to the results of product analyses and ESR.

The radiation-induced reactions of monocarboxylic acids have been studied extensively in many laboratories.1-4) These studies have revealed that the most radiation-senstive bond in carboxylic acids is the C-carboxyl bond. Carbon dioxide and the saturated hydrocarbon with one carbon atom less than the original acids were found to be the main products in radiolysis. However, the bond rupture is not very specific, and other products, such as carbon monoxide, hydrogen, and water, were also produced. With regard to the reaction mechanism, work with deuterated and tritiated acetic acid showed that carbon dioxide is formed by a radical process rather than by a molecular process.3)

In contrast to monocarboxylic acids, there have been few studies on the radiation-chemical reaction of dicarboxylic acids. Molin *et al.*5) studied ESR and gaseous products in the radiolysis of dicarboxylic acids. However, none of the products except for carbon dioxide were determined in his work.

In this study, we aimed at the elucidation of the reaction mechanism on the radiolysis of malonic acid, by comparing the results of product analyses with the ESR spectra of irradiated malonic acid.6,7)

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1) W. L. Whitehead, C. Goodman and I. A. Breger, *J. Chim. phys.*, **48**, 184 (1951).

2) A. S. Newton, *J. Chem. Phys.*, **26**, 1764 (1957).

3) J. G. Burr, *J. Phys. Chem.*, **61**, 1481 (1957).

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5) Yu. N. Molin, I. I. Cheidze, N. Ya. Buben and V. V. Voevodskii, *Zhur. Strukt. Khim.*, **2**, 293 (1961).

6) H. M. McConell, C. Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).

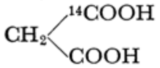
7) N. Tamura, M. A. Collins and D. H. Whiffen, *Trans. Faraday Soc.*, **62**, 2434 (1966).

Experimental

Material. Commercially-available malonic acid was used after repeated recrystallizations from water.

Gamma-Irradiation. Solid malonic acid was sealed in a vacuum in a tube with a break-off seal. The samples were irradiated by the ^{60}Co source of 16000 Ci at the Japan Atomic Energy Research Institute. Irradiation at low temperatures was carried out by placing the samples in a Dewar vessel filled with dry ice or liquid nitrogen. The absorbed dose was determined by means of Fricke dosimetry.

Analysis. *Gaseous Products.* The break-off seal of the tube containing the irradiated samples was cut in a vacuum system, and the irradiated malonic acid was dissolved by introducing water into the tube. A part of the gas evolved by this treatment was analyzed mass-spectrometrically with a CEC Model 103C spectrometer. In particular, carbon dioxide was collected as barium carbonate in a barium hydroxide solution and weighed.

Acetic Acid. Reverse isotope dilution analysis was used for the determination of acetic acid, using $CH_3{}^{14}COOH$. $CH_3{}^{14}COOH$ was synthesized from  $CH_2\langle{}^{14}COOH \atop COOH$ which had been provided by the Radio Isotope School of the Japan Atomic Energy Research Institute.

After irradiated malonic acid had been dissolved in a sodium hydroxide solution, which contained known amount of labeled acetic acid, in a vacuum, the pH was adjusted to 9.0. Analysis was then carried out according to the diagram shown in Chart 1. The separation of acetic acid from malonic acid was carried out by the repeated precipitation of malonic acid with lanthanum(III) nitrate. The solubility of lanthanum(III) malonate is much smaller than that of lanthanum(III) acetate.

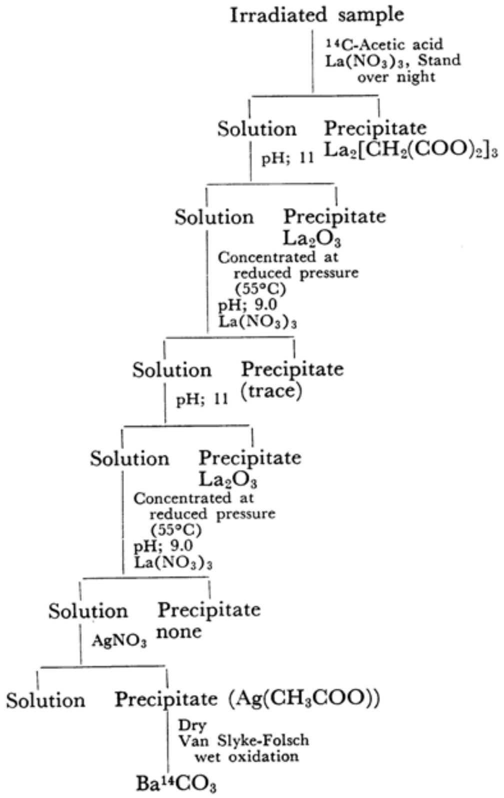


Chart 1. Procedure for the reverse isotope dilution analysis of acetic acid.

The specific activity of barium carbonate was measured with a liquid scintillation counter according to the method of Richmond.[8]

Radical Concentration. The surviving radical concentration was determined by means of ESR at room temperature. In order to eliminate the error caused by the uncertainty as to the position of the sample in the cavity of the spectrometer, the small glass tube containing the sample was inserted into the other tube, the position of which had been strictly fixed in advance. By using this method, the Q of the cavity in each sample of the irradiated malonic acid varied almost not at all, although a slight deviation was observed in the standard samples (DPPH in a benzene solution). The accuracy of the method was checked with samples of solid DPPH dispersed in solid malonic acid or in solid sodium carbonate. The ESR measurements gave the reproducible results for the relative concentration of the free radical. However, the absolute concentration was in error by 30%.

Aldehyde and Ketone. The yield of carbonyl compounds was determined by the method of Johnson and Scholes.[9]

Results and Discussion

Products. In the radiation chemistry of solid substances, some consideration must always be given to gaseous products, because the irradiated

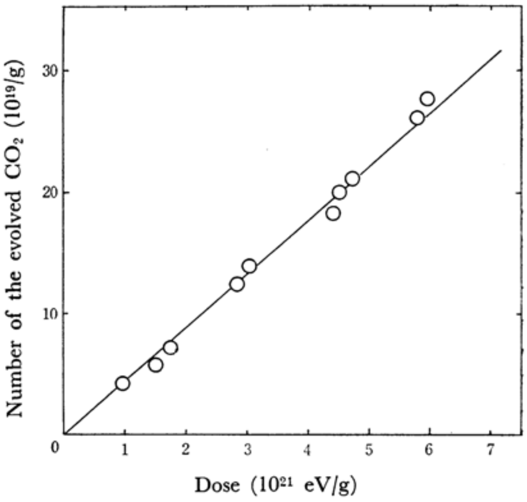


Fig. 1. Relation between absorbed radiation dose and the yield of carbon dioxide from γ-ray-irradiated malonic acid.

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[8] D. G. Ott, C. R. Richmond, T. T. Trujillo and H. Foreman, *Nucleonics,* **17,** 106 (1959).

[9] G. R. A. Johnson and G. Scholes, *Analyst,* **79,** 217 (1954).

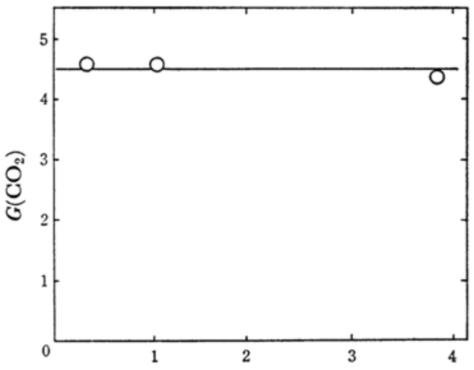

Fig. 2. Dose rate dependence of $G(CO_2)$ in the radiolysis of malonic acid.

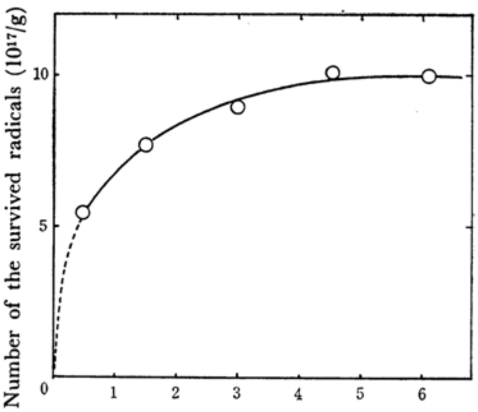

Fig. 3. Relation between the amount of survived radicals and absorbed radiation dose.

solid substances usually give two kinds of gaseous products; one is the gas evolved during irradiation, and the other is the gas evolved by dissolving the irradiated solid substances in a solvent.

In the case of solid malonic acid, both the gases consisted mainly of carbon dioxide and contained only a small quantity of carbon monoxide, methane, ethane, and hydrogen. A small difference in the composition of the two gases was observed. Gases other than carbon dioxide were less in the gas evolved when the irradiated malonic acid was dissolved in water. The ratio of the quantities of these gases varied depending on the crystal size and the absorbed radiation dose. However, the summed quantity of carbon dioxide in both the gases was proportional to the absorbed radiation dose, as may be seen in Fig. 1. From Fig. 1, $G(CO_2)$ is found to be 4.4. As is seen in Fig. 2, $G(CO_2)$ is dose-rate independent.

As to the origin of the gas evolved by dissolving the irradiated solid substances, the followings have been proposed:

1) By the decomposition of the non-radical intermediate produced in the irradiated crystals,[10]
2) By the reaction of surviving radicals trapped in the irradiated crystals,[11] and
3) By releasing the gas trapped in the irradiated crystals.[12]

In order to examine the radical origin of the gas evolved by dissolving the irradiated malonic acid in water, the yields of the surviving radicals were examined. The relation between the quantities of the surviving radicals and the absorbed dose is shown in Fig. 3.

The quantity of radicals reaches a limitting value at a high absorbed dose. The amounts of the radicals in the irradiated crystals are found to be smaller by a factor of 10^{-2} than those of the gaseous products evolved when the irradiated malonic acid is dissolved in water, so the gas produced secondarily cannot be ascribed to the surviving radicals. When the irradiated malonic acid was dissolved in organic solvents, such as dry pyridine, alcohol, ether, and tetrahydrofuran, no change in the product composition was observed. In the infrared spectra of the irradiated malonic acid, no new absorption bands except for those of acetic acid were observed. The isotopic ratio, $^{12}C/^{13}C$, of the carbon dioxide evolved during irradiation agreed with that of the carbon dioxide evolved by dissolving the irradiated malonic acid in water.

These results imply that the gas produced secondarily cannot be attributed to the non-radical intermediate. It is conceivable that the gas produced secondarily originates from the gas trapped in the crystals.

The *G* values of the products from the γ-ray-irradiated malonic acid are summarized in Table 1.

The main products are carbon dioxide and acetic acid—the corresponding decarboxylated compound. The *G* value of carbon dioxide was equal to that of acetic acid. In contrast to carbon dioxide and acetic acid, the yields of the other products, such as carbon monoxide, hydrogen, methane, and ethane, were very low, lower by an

TABLE 1. *G* VALUES FOR THE PRODUCTS FROM THE γ-RAY-IRRADIATED MALONIC ACID

Product	*G* value
CH_3COOH	4.5
CO_2	4.4
H_2	$<10^{-2}$
CO	$\sim5\times10^{-2}$
CH_4	$\sim4\times10^{-2}$
C_2H_6	$\sim2\times10^{-2}$
Aldehyde and ketone	$\sim2\times10^{-2}$

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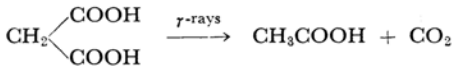
[10] A. Sugimori, This Bulletin, **39**, 2583 (1966).

[11] G. Meshitsuka, K. Shinodo, A. Minegishi, H. Suguro and Y. Shinozuka, *ibid.*, **37**, 928 (1964).

[12] G. Henning, R. Lees and N. S. Matheson, *J. Chem. Phys.*, **21**, 664 (1953).

order of two than those of carbon dioxide and acetic acid. These facts indicate that the γ-irradiation preferentially brings about the following reaction:



$$CH_2\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow{\gamma\text{-rays}} CH_3COOH + CO_2 \quad (1)$$

The specificity of the radiation-induced reaction is characteristic of malonic acid. In the radiolysis of monocarboxylic acids, the formation of considerable amounts of carbon monoxide, hydrogen, and water has been reported.[1-4] In the case of malonic acid, it is significant that the yield of hydrogen produced by the γ-irradiation is very poor.

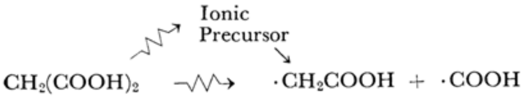
ESR study revealed that the free radical, $\cdot CH(COOH)_2$, is stable;[6,7] this would predict the easy elimination of the hydrogen atom during γ-irradiation. However, we observed a poor yield of hydrogen, which might be formed in the course of the hydrogen abstraction from C–H or O–H by the hydrogen atom. This indicates that the radiation energy absorbed by a malonic acid molecule is consumed selectively by the rupture of the C-carboxyl bond—the weakest bond in the molecule.

Analogous results were obtained in the radiolysis of cyanoacetic acid, which is easily decarboxylated by heat. In its radiolysis, the yields of the gaseous products other than carbon dioxide are again very low, as is shown in Table 2.

TABLE 2. *G* VALUES FOR THE GASEOUS PRODUCTS FROM THE γ-RAY-IRRADIATED CYANOACETIC ACID

Product	*G* value
CO_2	4.6
H_2	$<10^{-2}$
CO	$<10^{-2}$
HCN	$\sim 5\times10^{-2}$

Reaction Mechanism of the Radiation-Induced Decomposition of Malonic Acid. ESR study of the irradiated malonic acid[6,7] has revealed that the primarily-produced free radical is $\cdot CH_2COOH$, whereas the $\cdot CH(COOH)_2$ radical was not observed in the irradiation at 77°K. In the cases of ethylmalonic, *n*-propylmalonic, and *n*-butylmalonic acid, the ESR spectra presumably due to the anion radicals of the parent acids were observed. Although in the case of malonic acid the spectra of the anion radical were not confirmed, the existence of such an ionic precursor is possible. Therefore, the first step of the reaction is:



$$CH_2(COOH)_2 \rightsquigarrow \text{Ionic Precursor} \rightsquigarrow \cdot CH_2COOH + \cdot COOH \quad (2)$$

The radicals formed in Eq. (2) can give carbon dioxide and acetic acid by two different processes. One is the mechanism similar to that proposed by Burr[3] for the radiation-induced decomposition of acetic acid:

$$\cdot CH_2COOH + \cdot COOH \rightarrow CH_3COOH + CO_2 \quad (3)$$

The other is the sequence of reactions:

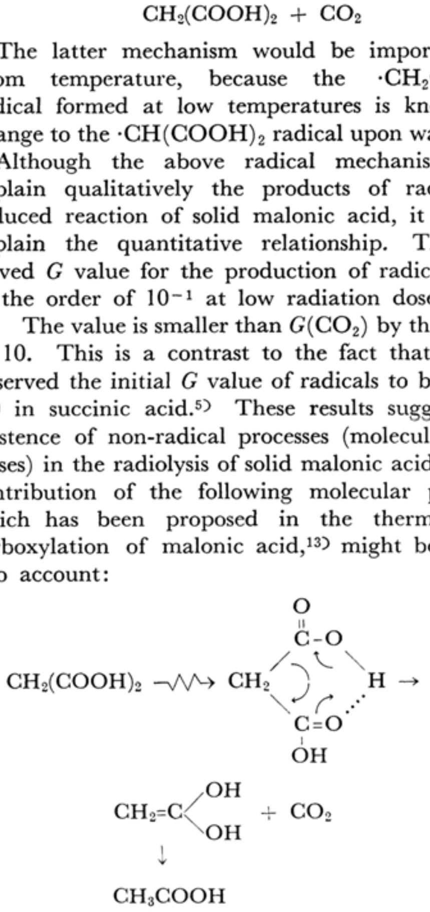
i) the hydrogen abstraction of $\cdot CH_2COOH$ from a neighboring malonic acid molecule,
ii) a radical-radical reaction similar to Eq. (3):

$$\cdot CH_2COOH + CH_2(COOH)_2 \rightarrow CH_3COOH + \cdot CH(COOH)_2 \quad (4)$$

$$\cdot CH(COOH)_2 + \cdot COOH \rightarrow CH_2(COOH)_2 + CO_2 \quad (5)$$

The latter mechanism would be important at room temperature, because the $\cdot CH_2COOH$ radical formed at low temperatures is known to change to the $\cdot CH(COOH)_2$ radical upon warming.

Although the above radical mechanism can explain qualitatively the products of radiation-induced reaction of solid malonic acid, it cannot explain the quantitative relationship. The observed *G* value for the production of radicals was of the order of 10^{-1} at low radiation doses (Fig. 3). The value is smaller than $G(CO_2)$ by the factor of 10. This is a contrast to the fact that Molin observed the initial *G* value of radicals to be 5.9—8.0 in succinic acid.[5] These results suggest the existence of non-radical processes (molecular processes) in the radiolysis of solid malonic acid. The contribution of the following molecular process, which has been proposed in the thermal decarboxylation of malonic acid,[13] might be taken into account:



(6)

The contribution of such a molecular process is favored by the fact that cyanoacetic acid, which easily decomposes to give carbon dioxide on heating, also gave carbon dioxide selectively when it was exposed to γ-irradiation. Although the observed temperature dependence (Table 3) is not in accord with this mechanism, we cannot expect temperature dependence in such a molecular process;

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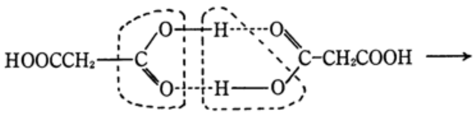
[13] See J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," Benjamin Inc., New York (1964), p. 524.

therefore, it may be considered that a part of the radiolytic decarboxylation proceeds *via* this molecular mechanism.

TABLE 3. TEMPERATURE DEPENDENCE OF $G(CO_2)$ IN THE RADIOLYSIS OF MALONIC ACID

Temperature	G value
Room temperature	4.4
− 78°C	2.3
−196°C	1.7

As to the mechanism of the radiolysis of malonic acid, Molin proposed the following scheme:[5)]



$$HOOCCH_2\cdot + CO_2 + H_2O + O{=}C\text{-}CH_2COOH$$

This mechanism was based on his observation of the formation of water. However, we could not observe the formation of water in the radiolysis of the malonic acid recrystallized from ethanol. Indeed, the stoichiometry of the products and the absence of carbonyl compounds which would react with 2, 4-dinitrophenylhydrazine makes the radiolytical formation of water unlikely. In our experiment, however, water was also detected in the radiolysis of the malonic acid recrystallized from water. Therefore, the water observed by Molin may have originated from the water trapped in the crystals before irradiation.

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