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Radiation Chemistry of Dicarboxylic Acids in the Solid State. II. C-13 Isotope Effects in the Radiation-induced Decarboxylation of Malonic and Several Aliphatic Dicarboxylic Acids

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The C-13 isotope effects in the radiation-induced decarboxylation of several dicarboxylic acids were investigated. Malonic acid showed a C-13 isotope effect of about 2%; this is much greater than those of monocarboxylic acids. The greater isotope effect of malonic acid is attributed to the intramolecular competition of the C-carboxyl bond rupture. Succinic, adipic, and pimeric acid, in which the intramolecular interaction of two carboxyl groups can be expected, gave large isotope-effect values, whereas glutaric and sebatic acid, in which such an effect may be expected to be small, showed lower isotope effects. Analogously, maleic acid (cis isomer) showed a larger isotope effect than did fumaric acid (trans isomer).

In a previous paper,[1] we reported that the radiation-induced reaction of malonic acid in the solid state is very specific:

$$CH_2(COOH)_2 \xrightarrow{\gamma\text{-rays}} CH_3COOH + CO_2$$

Carbon dioxide, with the G value of 4.4, and acetic acid, with the G value of 4.5, were the main products; all the other products were formed in very small yields. Since this reaction is the same as that found in thermal reaction, and since the thermal decarboxylation of malonic acid has been extensively studied,[2] especially from the view point of the carbon isotope effect, we considered that the study of the C-13 isotope effect in the radiation-induced decarboxylation in comparison with that in

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[1] A. Hosaka, A. Sugimori, T. Genka and G. Tsuchihashi, This Bulletin, **40**, 1799 (1967).

[2] J. Bigeleisen and M. Wolfsberg, "Advances in Chemical Physics," Vol. 1, Interscience Publishers, New York (1958), p. 15. References are therein.

the thermal reaction would be useful in the elucidation of the mechanism of the C-carboxyl bond rupture in the radiolysis of malonic acid.

In the present study, the C-13 isotope effects of malonic acid and several aliphatic dicarboxylic acids were studied in connection with the results of the analyses of the products of the radiation-induced reaction.

Experimental

Samples. Commercially-available aliphatic carboxylic acids (cyanoacetic, crotonic, malonic, succinic, glutaric, adipic, sebatic, maleic and fumaric acid) were used after repeated recrystallizations from water. Phenylmalonic acid was synthesized from phenyl acetic acid.

Gamma-Irradiation. Samples were irradiated in the same way as has been described elsewhere.[1)]

Analyses of the Products and the Determination of the C-13 Isotope Effect. In a vacuum system, the irradiated acids were dissolved in cold water (in the case of water-soluble acids: cyanoacetic, crotonic, malonic, glutaric, maleic, and phenylmalonic acid) or hot water (in the case of less water-soluble acids: succinic, adipic, pimeric, sebatic, and fumaric acid.) The methods of analyzing the gaseous products have been described previously.[1)] For the determination of the isotope effect, the carbon dioxide evolved was collected in a barium hydroxide solution after it had passed through a dry-ice trap (for the elimination of less volatile impurities which might affect the mass spectrometric determination of the C-13 isotope effect). The barium carbonate samples were then reconverted into carbon dioxide using NaCl+HCl in a vacuum system. The $^{12}CO_2/^{13}CO_2$ ratio was obtained from the ratio of the ion currents for $m/e=44$ and 45 after applying a suitable correction for the contribution of $^{12}C^{16}O^{17}O$ to the $m/e=45$ peak. Mass spectrometric analyses were carried out mainly with a CEC Model 103C mass spectrometer. Some samples were analyzed by the double scanning method using an Atlas Mass Spectrometer for purposes of comparison and checking. The values obtained with the two spectrometers agreed within the limits of standard error.

The isotope effect was evaluated by comparing the isotope abundance of the radiolytically-produced carbon dioxide with that of the standard carbon dioxide produced by the wet oxidation (Van Slyke-Folsch method[3)]) of the corresponding intact acid. The abundance of C-13 agreed in all the carbon dioxide used as a standard. This ensured that none of the acid employed had an abnormal isotope abundance in the molecules.

Results

The results of the isotope effects in the radiolytic decarboxylation of malonic acid are shown in Table 1.

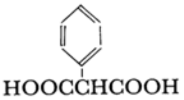
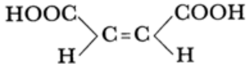
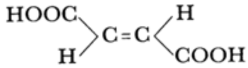
TABLE 1. TEMPERATURE DEPENDENCE OF THE ISOTOPE EFFECT IN THE RADIATION-INDUCED DECARBOXYLATION OF MALONIC ACID IN THE SOLID STATE

Irradiation temperature	Observed isotope effect $\frac{^{12}CO_2}{^{13}CO_2}\cdot\frac{\alpha}{1-\alpha}$
20°C (Room temperature)	1.019 ± 0.002
-78°C	1.017 ± 0.002
-196°C	1.017 ± 0.002

The values are expressed as the ratios of the $^{12}CO_2/^{13}CO_2$ in radiolytically-produced carbon dioxide to the $^{12}CO_2/^{13}CO_2$ in the carbon dioxide obtained by the complete oxidation of the intact acid. The latter gives the abundance of ^{12}C to ^{13}C: $(1-\alpha)/\alpha$ (where α is equal to the atom fraction of ^{13}C in naturally-occurring carbon). Table 1 shows that the isotope effect is independent of the irradiation temperature.

Table 2 shows the isotope effects observed in the radiation-induced decarboxylation of several solid monocarboxylic acids and dicarboxylic acids.

TABLE 2. ^{13}C-ISOTOPE EFFECTS IN THE RADIATION-INDUCED DECARBOXYLATION OF SEVERAL CARBOXYLIC ACIDS IN THE SOLID STATE

Acid	Observed isotope effect $\frac{^{12}CO_2}{^{13}CO_2}\cdot\frac{\alpha}{1-\alpha}$
	1.021 ± 0.003
$NCCH_2COOH$	1.006 ± 0.003
$CH_3CH{=}CHCOOH$	1.007 ± 0.003
$HOOC(CH_2)_2COOH$	1.013 ± 0.003
$HOOC(CH_2)_3COOH$	1.006 ± 0.003
$HOOC(CH_2)_4COOH$	1.020 ± 0.003
$HOOC(CH_2)_5COOH$	1.020 ± 0.003
$HOOC(CH_2)_8COOH$	1.007 ± 0.003
 $\begin{matrix}HOOC & & COOH\\ & C=C & \\ H & & H\end{matrix}$	1.024 ± 0.003
 $\begin{matrix}HOOC & & H\\ & C=C & \\ H & & COOH\end{matrix}$	1.011 ± 0.003

Substituted malonic acid, such as phenylmalonic acid, showed an isotope effect comparable to that of malonic acid. On the other hand, monocarboxylic acids, such as cyanoacetic and crotonic acid, showed much smaller isotope effects than did malonic and phenylmalonic acid; the isotope effects in cyanoacetic acid are equal to those in crotonic acid.

The effect of an increase in the carbon chain between two carboxyl groups can be seen in the series from malonic ($(CH_2)_1$ acid) to sebatic ($(CH_2)_8$ acid) acid. A successive decrease in the

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3) D. D. Van Slyke and H. Folsch, *J. Biol. Chem.*, **136**, 509 (1940).

^{13}C-isotope effect was observed in succinic and glutaric acid. Although sebatic acid gave a low value of the isotope effect, adipic ($(CH_2)_4$ acid) and pimeric ($(CH_2)_5$ acid) acid showed abnormally large isotope effects.

A comparison of the geometrical isomer, fumaric, and maleic acid cited in the last two columns in Table 2, shows an interesting feature: maleic acid (cis isomer) shows a larger isotope effect than fumaric acid (trans isomer). These facts will be discussed below in terms of the intramolecular interaction of two carboxyl groups.

The gaseous products from the γ-ray-irradiated dicarboxylic acids were also examined. The main gaseous products were carbon dioxide and hydrogen. A small amount of hydrocarbon was also detected. The relations of the yields of carbon dioxide and hydrogen to the length of the carbon chain between the two carboxyl groups are shown in Fig. 1.

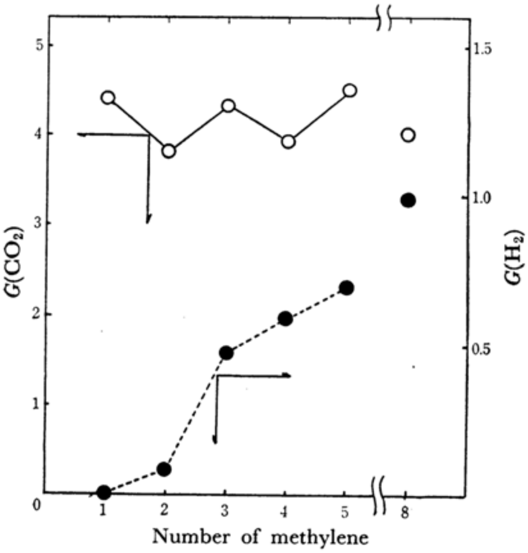


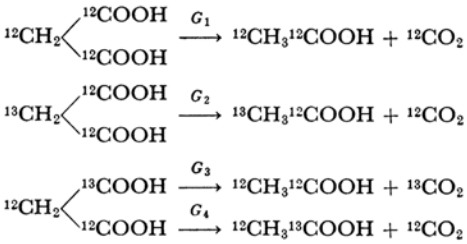
Fig. 1. Relation between the number of methylene and $G(CO_2)$ and $G(H_2)$ in the radiolysis of dicarboxylic acids.
—○— $G(CO_2)$ --●-- $G(H_2)$

One feature is that the formation of carbon dioxide changes in a zigzag manner. The $G(CO_2)$ value for dicarboxylic acid with an odd carbon number is greater than those of neighboring acids with even carbon numbers. This zigzag change in $G(CO_2)$ is similar to that observed in the monocarboxylic acid series.[4]

In contrast with the relatively constant $G(CO)_2$, the G values of hydrogen were very low for malonic and succinic acid and then increased steadily with an increase in the carbon chain. However, $G(H_2)$ is much inferior to $G(CO_2)$ in the lower dicarboxylic acids.

Discussion

The kinetic treatment of the C-13 isotope effect in the thermal decarboxylation of malonic acid was given by Bigeleisen.[2] By replacing the rate constants with G values, the following scheme can be devised for the radiation-induced decarboxylation of malonic acid:



$$^{12}CH_2\begin{cases}^{12}COOH\\ ^{12}COOH\end{cases} \xrightarrow{G_1} {}^{12}CH_3{}^{12}COOH + {}^{12}CO_2 \quad (1)$$

$$^{13}CH_2\begin{cases}^{12}COOH\\ ^{12}COOH\end{cases} \xrightarrow{G_2} {}^{13}CH_3{}^{12}COOH + {}^{12}CO_2 \quad (2)$$

$$^{12}CH_2\begin{cases}^{13}COOH \xrightarrow{G_3} {}^{12}CH_3{}^{12}COOH + {}^{13}CO_2 \quad (3)\\ ^{12}COOH \xrightarrow{G_4} {}^{12}CH_3{}^{13}COOH + {}^{12}CO_2 \quad (4)\end{cases}$$

where G_1—G_4 refer to the G values of the corresponding reactions. At the low conversion (below 1% of conversion) where our study was employed, the observed $^{13}CO_2/^{12}CO_2$ value should be expressed as:

$$\frac{^{13}CO_2}{^{12}CO_2} = \frac{G_3M_3}{G_1M_1 + G_2M_2 + G_4M_3} \quad (5)$$

where M_1, M_2 and M_3 are molar fractions of $^{12}CH_2\begin{smallmatrix}^{12}COOH\\ ^{12}COOH\end{smallmatrix}$, $^{13}CH_2\begin{smallmatrix}^{12}COOH\\ ^{12}COOH\end{smallmatrix}$ and $^{12}CH_2\begin{smallmatrix}^{13}COOH\\ ^{12}COOH\end{smallmatrix}$ respectively. By employing α (the atom fraction of ^{13}C occurring in the normal malonic acid used), M_1, M_2, and M_3 are found to be:

$$\begin{aligned} M_1 &= 1 - 3\alpha \\ M_2 &= \alpha \\ M_3 &= 2\alpha \end{aligned} \quad (6)$$

By substituting these values into Eq. (5) and by making approximations, $G_4 \simeq G_3 \simeq G_1/2$ and $G_1 \simeq G_2$, we obtain;

$$\frac{^{13}CO_2}{^{12}CO_2} = \frac{2\alpha G_3/G_1}{1 - 3\alpha + \alpha + \alpha} \quad (7)$$

Then,

$$\frac{G_1}{2G_3} = \frac{\alpha}{1-\alpha} \cdot \frac{^{12}CO_2}{^{13}CO_2} \quad (8)$$

The right side of Eq. (8) is the observed isotope effect. We can see that the values of the isotope effects shown in Tables 1 and 2 express the difference between the G values of Reaction (1) and Reaction (3)×2. This is the intermolecular isotope effect. The corresponding value of the intermolecular isotope effect in the thermal decomposition of malonic acid has also been determined. It is dependent on the temperature; the value of $(^{12}CO_2/^{13}CO_2)\cdot(\alpha/(1-\alpha)) = 1.034$ was given for the decomposition at 137°C.[5] The value for the radiation-induced reaction is 1.019; this value is

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[4] R. H. Johnsen, *J. Phys. Chem.*, **63**, 2041 (1959).

[5] J. G. Lindsay, A. N. Bourns and H. G. Thode, *Can. J. Chem.*, **30**, 163 (1952).

smaller by one-half than that for thermal decomposition at 137°C. However, the isotope effect of the radiation-induced decarboxylation of malonic acid is much larger than those of monocarboxylic acids (cyanoacetic and crotonic acid).

If the existence of another carboxyl group does not affect the C-carboxyl splitting, the isotope effect of malonic acid must be the same as that of monocarboxylic acids. Therefore, some intramolecular selection concernig the splitting of the C-carboxyl bond in malonic acid is to be expected. In other words, the difference in G_3 and G_4 is important in the case of malonic acid. This situation indicates that the absorbed energy of radiation does not cause any spontaneous bond cleavage, and that some quasi-equilibrium will be attained before decomposition. In such a case, Bigeleisen's theoretical evaluation of the intramolecular isotope effect of malonic acid²⁾ is considered to be useful. He gave the value of 1.020 for the effect, which is independent of the temperature. If we adopt $G_4/G_3=1.020$ and rewrite Eq. (8), we obtain:

$$\frac{{}^{12}CO_2}{{}^{13}CO_2}\cdot\frac{\alpha}{1-\alpha}=\frac{2G_3}{G_3+G_4}\cdot\frac{G_1}{G_3+G_4} \qquad (9)$$

Then,

$$\frac{G_1}{G_3+G_4}=1.009$$

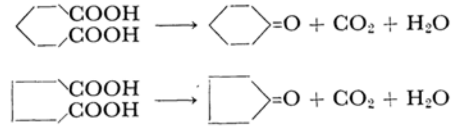
The value is approximately equal to the isotope effect in monocarboxylic acids. This is considered to be reasonable. This evaluation also supports the idea that the bond rupture is not at random and that the weaker ${}^{12}C$-${}^{12}COOH$ bond is preferentially broken through a kind of intermediate (excited molecule), the lifetime of which is long enough to make the absorbed radiation energy spread over the whole malonic acid molecule. From the value of the isotope effect in the radiation-induced reaction, we might give 1000°C for the effective temperature of the intermediate.⁶⁾ The specific radiation-induced reaction of malonic acid reported previously¹⁾ (the C–H bond rupture is two orders smaller than the C–COOH bond rupture) can be understood by this quasi-equilibrated excited state.

In succinic acid and glutaric acid, the existence of methylene groups between two carboxyl groups prevents the complete interaction (energy exchange) between two carboxyl groups in one molecule. This lowers the intramolecular isotope effects in such compounds. The decrease in energy exchange between the carboxyl group and the methylene group which is apart from the carboxyl group results in the C–H bond rupture in higher homologues of dicarboxylic acid. In sebatic acid, which has eight methylene groups between two carboxyl groups, the intramolecular interaction of two carboxyl groups cannot be expected; in fact, the isotope effect was observed to be the same as that in monocarboxylic acids.

From the findings on the isotope effect and on the $G(H_2)$ of dicarboxylic acids, energy exchange between two carboxyl groups has been found to be effective for one and two methylenes.

Analoguous results were obtained in the ESR study of the X-ray-irradiated substituted malonic acids. Tamura, Collins, and Whiffen⁷⁾ observed not the free radical, $CH_3CH_2\dot{C}HCH(COOH)_2$ but the free radical, $CH_3\dot{C}HCH_2CH(COOH)_2$, in the low temperature irradiation of *n*-propylmalonic acid. This indicates that the protecting effect of the carboxyl group can operate over two methylene groups.

The abnormally high isotope effects in adipic and pimeric acid are due to the intramolecular interaction of two carboxyl groups, not through the methylene chain but through the proximity of the two carboxyl groups as a result of the formation of a five or six-membered ring. Such interaction is possible because the thermal reaction of these compounds is known to be a decarboxylated ring closure:⁸⁾



In these compounds, the molecule takes a straight-chain structure in crystals,⁹⁾ but carboxyl groups are apt to react intramolecularly to form cyclic compounds when the molecule is brought to a highly energetic state. The explanation in terms of the intramolecular interaction as a result of the proximity of two carboxyl groups is consistent with the fact that, in the case of adipic and pimeric acid, the increase in the isotope effect is not accompanied by a decrease in the G value of hydrogen. The difference of isotope effect in fumaric and maleic acid can be interpreted in this way. The cis dicarboxyl structure, in which the greater intramolecular interaction of two carboxyl groups is to be expected, showed a greater isotope effect than the trans dicarboxyl structure.

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6) The effective temperature was evaluated by extrapolating the value of isotope effect in the figure shown in Ref. 2, p. 71.

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

8) See J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," Benjamin Inc., New York (1964), p. 551.

9) J. D. Morrison and J. M. Robertson, *J. Chem. Soc.*, **1949**, 987.