Radiation-induced Reaction in an Aqueous Benzoic Acid Solution. II. Determination of Products by Isotope Dilution Method

By Akihisa SAKUMOTO and Gen-ichi TSUCHIHASHI

(Received August 3, 1960)

In the preceding paper*, dose and dose rate dependencies of the yield of salicylic acid, and of biphenyldicarboxylic acids were studied in the presence or the absence of molecular oxygen when aqueous solutions of benzoic acid were irradiated with Co-60 gamma rays. In the presence of molecular oxygen, the yield of salicylic acid was greater than that in the absence of molecular oxygen and biphenyldicarboxylic acids was not produced, whereas in the absence of melecular oxygen the main products were biphenyldicarboxylic acids. In the preceding paper, the isomers of hydroxybenzoic and biphenyldicarboxylic acids produced in the solution could not be identified.

The determination of 2-, 3- and 4-hydroxybenzoic acid and biphenyl as reaction products was carried out by Weiss and his collaborators

---

* Part I: A. Sakumoto and G. Tsuchihashi, This Bulletin, 34, 660 (1961).

using paper chromatography[1]. Recently, Downes separated the isomers of monohydroxybenzoic acids from benzoic acid, and the isomers of dihydroxybenzoic acids from salicylic acid as reaction products by radioactive assay and radiochromatography[2].

In the present work, an isotope dilution method was applied in order to determine the reaction products in the radiolysis of aqueous solutions of benzoic acid (carboxyl-^{14}C) in the presence or the absence of molecular oxygen. From the results obtained, a mechanism of the radiation-induced reaction will be discussed.

Experimental

Materials.—Benzoic acid (carboxyl-^{14}C) was synthesized from phenylmagnesium bromide and $^{14}CO_2$ by Grignard reaction[3]. This acid was purified by recrystallization from ethanol-water to give a constant specific activity. The specific activity of the acid was 2.289×10^{-2} mc./mol.

Each isomer of biphenyldicarboxylic acid used for the carrier of the isotope dilution method was synthesized according to the method cited in the literatures[4,5]. Each compound was purified by recrystallization except 4,4′-biphenyldicarboxylic acid which was purified by precipitation four times from dilute alkaline solution of it. The melting points** of the isomers were as follows: 2,2′-, 228.0~228.5°C; 3,3′-, 356~357°C. 4,4′-Biphenyldicarboxylic acid did not melt.

Commercial grade 2-, 3-, 4-hydroxybenzoic acid and 2,3-, 2,4-, 2,5-, 2,6-dihydroxybenzoic acid were also purified by recrystallization. The melting points** of the isomers were as follows; 2-, 157~158.5°C; 3-, 200~200.5°C; 4-, 213~213.5°C; 2,3-, 205~206°C; 2,4-, 212.5~213°C; 2,5-, 199~200°C; 2,6-, 149~151°C.

Preparation of Solution. — The preparation of 0.300% aqueous benzoic acid (carboxyl-^{14}C) solution was carried out by dissolving it in demineralized water. The pH of the solution was not specially adjusted. The irradiation samples of both oxygen free and saturated solution were prepared as described in the preceding paper.

Irradiations.—The irradiation vessels and method have been described in the preceding paper. In the present work, irradiations were carried out at the dose rate of 1.6×10^5 r/hr. and the absorbed dose of 4.0×10^6 r in the presence of molecular oxygen and at the dose rate of 1.7×10^5 r/hr. and the absorbed dose of 4.3×10^6 r in the absence of molecular oxygen at room temperature. The measurement of the absorbed dose was carried out according to the method as described in Part I.

Radioactive Assay of Irradiation Products. — Determination of the yield of irradiation products was carried out as follows. An adequate of analyzing carrier which was weighed accurately was added to an aliquot of irradiated solution, and then dissolved. After the solution was cooled to precipitate the added carrier, the precipitate was filtered off and purified several times by recrystallization to offer a constant counting rate after oxidation to barium carbonate.

Purification of 4,4′-biphenyldicarboxylic acid, being insoluble in ordinary organic solvents, was carried out by dissolving it in dilute sodium hydroxide and reprecipitating it by adding dilute hydrochloric acid.

The isotope dilution method was also applied in order to determine unreacted benzoic acid (carboxyl-^{14}C) left in the solution after irradiation. After the addition of non-active benzoic acid, the purification of the acid was carried out by recrystallization six time from ethanol-water and then by sublimation three or five times.

Each sample purified was oxidized according to the Van Slyke-Folch oxidation method[6]. Carbon dioxide liberated after oxidation of a purified sample was absorbed by 0.74 N sodium hydroxide solution and then precipitated as barium carbonate by adding 17.6% barium chloride-2.5% ammonium chloride solution.

The resulting barium carbonate was filtered off, washed with ethanol and dried. The specific activity of barium carbonate was measured at infinite thickness by a Tracerlab. T. G. C.-14 counter.

Results

Isomers of hydroxybenzoic acid and biphenyldicarboxylic acid were assayed as products when

TABLE I. YIELDS OF PRODUCTS IN OXYGEN FREE SOLUTION OF BENZOIC ACID (CARBOXYL-^{14}C) IRRADIATED WITH Co-60 GAMMA RAYS

Product	Weight mg./ml.	Yield %	*G*-Value
2-Hydroxybenzoic acid	0.040	1.3	0.066
3-Hydroxybenzoic acid	0.047	1.6	0.077
4-Hydroxybenzoic acid	0.056	1.9	0.092
2,2′-Biphenyldicarboxylic acid	0.41	14	0.38
3,3′-Biphenyldicarboxylic acid	0.072	2.4	0.068
4,4′-Biphenyldicarboxylic acid	0.30	10	0.28
Benzoic acid*	1.86	62	
−Benzoic acid**	1.14	38	1.88

Dose, 4.3×10^6 r, dose rate, 1.7×10^5 r/hr.

* Unchanged benzoic acid (carboxyl-^{14}C) in the irradiated solution.

** The disappearance of benzoic acid (carboxyl-^{14}C), calculated from the amount of unchanged benzoic acid (carboxyl-^{14}C).

---

[1] J. Weiss, H. Loeble and G. Stein, *J. Chem. Soc.*, **1951**, 405.

[2] A. M. Downes, *Austr. J. Chem.*, **2**, 154 (1951).

[3] W. G. Dauben and P. E. Yankwich, *Anal. Chem.*, **19**, 828 (1947).

[4] "Organic Syntheses", Coll. Vol. I (1948), p. 222.

[5] F. Ullman and O. Löwenthal, *Ann.*, 332, 72 (1904).

** The melting point of each compound is uncorrected.

[6] D. D. Van Slyke and H. Folch, *J. Biol. Chem.*, 136, 509 (1940).

an aqueous solution of benzoic acid (carboxyl-^{14}C) irradiated in oxygen free solution. Results obtained are summarized in Table I shown as the yield and *G*-value of each reaction product. In Table I, benzoic acid indicates unchanged benzoic acid (carboxyl-^{14}C) which is left in the irradiated solution. *G*-Value of the disappearance of benzoic acid (carboxyl-^{14}C) shown as (-benzoic acid) in Table I, calculated from the amount of unchanged benzoic acid (carboxyl-^{14}C), is 1.88. The ratio of produced hydroxybenzoic acids and biphenyldicarboxylic acids is approximately 1 : 3. The *G*-value ratio of each hydroxybenzoic acid and each biphenyldicarboxylic acid will be discussed in the following section.

When irradiation was carried out in the presence of oxygen, the yield of products was quantitatively and qualitatively different from those in the absence of oxygen. 2, 3-, 2, 4,- 2, 5- and 2, 6-Dihydroxy benzoic acid are produced in place of isomers of biphenyldicarboxylic acid. The total amount of dihydroxy benzoic acids is 0.31 as *G*-value, being about one fifth of mono-hydroxybenzoic acids. Table II shows the yield and *G*-value of products in the oxygen saturated solution. In this case, *G*-value of 2, 2′-biphenyldicarboxylic acid, the most abundant isomer in the irradiation of oxygen free solution, was estimated to be lower than 0.0003. Therefore, a noticeable amount of isomers of biphenyldicarboxylic acid was not observed in an oxygen saturated solution.

TABLE II. YIELDS OF PRODUCTS IN OXYGEN SATURATED SOLUTION OF BENZOIC ACID (CARBOXYL-^{14}C) IRRADIATED WITH Co-60 GAMMA RAYS

Product	Weight mg./ml.	Yield %	*G*-value
2-Hydroxybenzoic acid	0.45	15	0.79
3-Hydroxybenzoic acid	0.16	5.4	0.29
4-Hydroxybenzoic acid	0.37	12	0.65
2, 3-Dihydroxy-benzoic acid	0.072	2.4	0.12
2, 4-Dihydroxy-benzoic acid	0.056	1.9	0.088
2, 5-Dihydroxy-benzoic acid	0.060	2.0	0.096
2, 6-Dihydroxy-benzoic acid	0.0036	0.12	0.0057
Benzoic acid*	1.31	61	
−Benzoic acid**	1.19	39	2.12
2, 2′-Biphenyl-dicarboxylic acid	2.9×10^{-4}		0.0003

Dose, 4.0×10^6 r, dose rate, 1.6×10^5 r/hr.

* Unchanged benzoic acid (carboxyl-^{14}C) in the irradiated solution.

** The disappearance of benzoic acid (carboxyl-^{14}C) calculated from the amount of unchanged benzoic acid (carboxyl-^{14}C).

Discussion

The mechanism of radiation-induced reaction of an aqueous solution of organic compound has been studied by a number of workers. The primary process of the reaction is assumed to be radiolytic decomposition of water. Recently, Burton and his collaborators proposed the following *G*-values for the species$^{7)}$.

$$H_2O \rightsquigarrow H\cdot,\ HO\cdot,\ H_2,\ H_2O_2 \qquad (1)$$
$$G = 3.70 \quad 2.93 \quad 0.39 \quad 0.78$$

These values will be used in the following discussion.

From the present results of radioactive assay, some information about the initial step of the radiation-induced reaction is obtained. As is shown in Tables I and II, *G*-values of the disappearence of benzoic acid were 2.12 in the presence of molecular oxygen and 1.88 in the absence of molecular oxygen. These values agree fairly well with each other in spite of irradiation conditions being different.

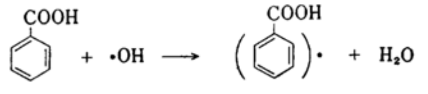
This agreement signifies that dissolving oxygen does not affect the initial step of the decomposition of benzoic acid. It would be, therefore, reasonable to consider that in both cases the initial stage of the reaction is initiated by the attack of the same radical on the benzoic acid molecule.

Hydrogen atom in the reactive species produced from water reacts easily with dissolving oxygen forming hydroperoxy radical in the presence of oxygen.

$$H\cdot + O_2 \rightarrow HO_2\cdot \qquad (2)$$

If the decomposition of benzoic acid is initiated by the hydrogen atom, it is impossible to explain the *G*-value of the decomposition of benzoic acid being almost of the same value regardless of the dissolving of oxygen. Consequently, a hydroxyl radical must be considered to be the only radical which can attack benzoic acid.

Based on the above reasons, the disappearence of benzoic acid in an aqueous solution is considered to be initiated by hydrogen-abstraction of hydroxyl radical as is proposed in the previous paper:



(3)

The concentration of hydroxycarbonylphenyl radical as an intermediate in the reaction must

---

7) K. C. Kurien, P. V. Phung and M. Burton, *Radiation Research*, 11, 283 (1959).

TABLE III. G-VALUE OF INTERMEDIATE RADICAL

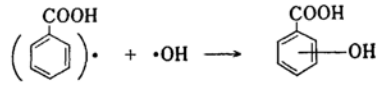
Condition	Hydroxyl radical: Used for hydrogen-abstraction	Hydroxyl radical: Used for combination with H. C. P. radical	Total	H. C. P. radical[*1]
Oxygen free	G(H)[*2]$+2G$(B)[*3]$=1.7$	G(H)$=0.24$	1.94	G(H)$+2G$(B)$=1.7$
Oxygen saturated	G(H)$+2G$(D)[*4]$=2.3$	zero	2.3	G(H)$+G$(D)$=2.0$

[*1] H. C. P. radical is hydroxycarbonylphenyl radical
[*2] The total G-value of hydroxybenzoic acids
[*3] The total G-value of biphenyldicarboxylic acids
[*4] The total G-value of dihydroxybenzoic acids
The G-value of hydroxyl radical produced in the primary process is 2.92[7].

be of the same value in both cases, because the G-value of hydroxyl radical produced primarily from radiolytic decomposition of water is constant of 2.93 regardless of whether with or without oxygen.

In spite of the constant G-value of the disappearance of benzoic acid, the products of the reaction in the presence of oxygen were quite different from those in the absence of oxygen. In the former case hydroxybenzoic acids were the predominant products, whereas biphenyldicarboxylic acids were the main products in the latter case.

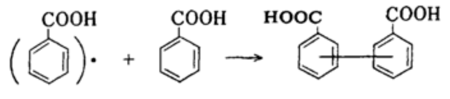
In the absence of oxygen, the total G-value of biphenyldicarboxylic acid as main product was 0.73, whereas that of hydroxybenzoic acid was 0.24. Hydroxybenzoic acid may be produced by the combination reaction of hydroxyl radical with hydroxycarbonylphenyl radical:



(4)

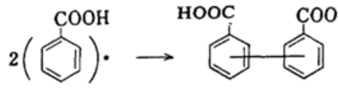
In this case, the amount of hydroxyl radical concerned in the hydroxylation of benzoic acid might be two fold of the amount of hydroxybenzoic acid, and so the G-value of this radical participating in the reaction will be calculated to be 0.48, and subsequently, the G-value of hydroxycarbonylphenyl radical produced in the reaction as an intermediate might be 0.24.

On the other hand, there are two possibilities of the formation of biphenyldicarboxylic acids from hydroxycarbonylphenyl radical. If biphenyldicarboxylic acids are produced by the substitution reaction of hydroxycarbonylphenyl radical as in the following,



(5)

the disappearance of benzoic acid in this case would be considerably greater than that in the presence of oxygen as mentioned below. It is because the same yield of hydroxycarbonylphenyl radical is proposed in both cases. Accordingly, the formation of biphenyldicarboxylic acids can be attributed to the dimerization of hydroxycarbonylphenyl radical.

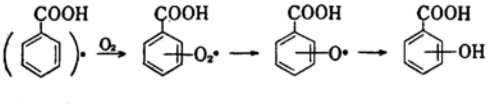


(6)

In this case, the amount of hydroxycarbonylphenyl radical converted into biphenyldicarboxylic acids is two times as much as that of biphenyldicarboxylic acid. If the predominant process of the reaction is the dimerization of hydroxycarbonylphenyl radicals, the total amount of hydroxycarbonylphenyl radical is 1.70 as calculated in Table III.

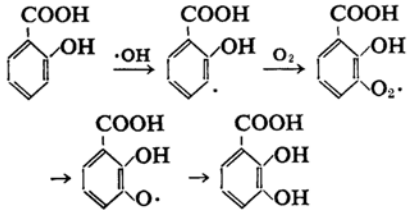
In the presence of molecular oxygen, hydroxybenzoic acids were predominant products. Noticeable amount of biphenyldicarboxylic acid was not observed. The G-value of 2,2′-biphenyldicarboxylic acid, the most abundant isomer in the absence of molecular oxygen, was reduced to the value of 0.0003. Therefore, it would be unlikely that hydroxybenzoic acid in the presence of molecular oxygen is produced by the combination reaction of hydroxycarbonylphenyl radical with a hydroxyl radical, because the formation of hydroxybenzoic acid by this type of the reaction would be, without fail, accompanying the formation of biphenyldicarboxylic acid as in the case of oxygen free solution.

Hydroxycarbonylphenyl radical produced according to Eq. 3 reacts easily with dissolving oxygen to give a hydroxycarbonylphenylperoxy radical. It is, in general, considered that aromatic peroxide is very unstable. Consequently, the peroxy radical would decompose spontaneously into the phenoxy radical and then the reaction results finally in the formation of monohydroxybenzoic acid as is shown in the following:



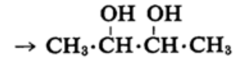
(7)

The formation of dihydroxybenzoic acids as minor products may be also explained by the same sequence starting from mono-hydroxybenzoic acid instead of benzoic acid. For example, the following sequence is given for 2, 3-dihydroxybenzoic acid:

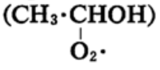

(8)

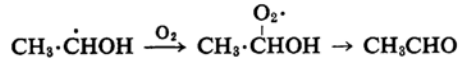
The above mechanism is supported by the radiation-induced reaction of an aqueous ethanol solution by Weiss and collaborators[8]. They found butane-2, 3-diol as main products in the irradiation of an oxygen free solution,

$$CH_3{\cdot}CH_2OH \xrightarrow{HO\cdot} CH_3{\cdot}\dot{C}HOH$$



$$\rightarrow CH_3{\cdot}\overset{OH}{CH}{\cdot}\overset{OH}{CH}{\cdot}CH_3$$

but, in the presence of oxygen, the dimerization of these radicals was completely suppressed, and acetaldehyde was formed as a predominant product. In this case, they proposed the formation of the peroxy radical  $(CH_3{\cdot}\underset{O_2\cdot}{CHOH})$ as an intermediate in the reaction.



$$CH_3{\cdot}\dot{C}HOH \xrightarrow{O_2} CH_3{\cdot}\overset{O_2\cdot}{C}HOH \rightarrow CH_3CHO$$

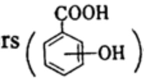
Table III shows the *G*-value of intermediate radicals produced in systems both with and without molecular oxygen. Based on the mechanism given by Eqs. 3, 7 and 8, the *G*-values of hydroxyl and hydroxycarbonylphenyl radicals as an intermediate in the presence of oxygen are calculated to be 2.3 and 2.0, respectively, as is shown in the Table III. The total *G*-value of reacting hydroxyl radical is close to that of hydroxyl radical produced in the primary process (1). Accordingly, it is likely that the most of the hydroxyl radicals formed in the primary process of the reaction react with benzoic acid giving the reaction products. The *G*-value of both hydroxyl and hydroxycarbonylphenyl radicals estimated here are greater in the presence of oxygen than in its absence.

There remain, therefore, some possibilities of the formation of hydroxyl radicals from hydroperoxy radicals produced according to Eq. 2 as follows:

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (9)$$

$$H_2O_2 \rightarrow 2HO\cdot \qquad (10)$$

Some information for the orientation of the hydroxycarbonylphenyl radical is obtained from the experimental values. *G*-Value of 2-, 3- and 4-hydroxycarbonylphenyl radical produced in the absence of oxygen are calculated to be 0.83, 0.21 and 0.65, respectively, basing on the yields of products summerized in Table I. Thus, the *G*-value ratio of 2-: 3-: 4-hyroxycarbonylphenyl radical is 1:0.26:0.79.

On the other hand, *G*-values of hydroxybenzoic acid, in the presence of oxygen, were 0.79, 0.29 and 0.65 for 2-, 3-, 4-isomer, respectively. In this case, the present authors can not predict any *G*-values of intermediate hydroxy, hydroxycarbonylphenyl radical isomers . produced from mono-hydroxybenzoic acids. If the formation of dihydroxybenzoic acid, being much smaller than that of mono-hydroxybenzoic acid, might be neglected, the *G*-value ratio calculated as 1:0.37:0.82 for 2-: 3-: 4-hydroxycarbonylphenyl radical in the presence of molecular oxygen agrees fairly well with that in the absence of molecular oxygen. The easiness of the abstraction of ring hydrogen of benzoic acid by hydroxyl radical is shown, basing on the *G*-value ratio of 2-, 3- and 4-hydroxycarbonylphenyl radical, in the following.

ortho > para > meta

It seems also likely that this agreement supports the above postulate that the reaction is initiated by hydrogen-abstraction reaction of hydroxyl radical without regard to dissolving oxygen.

The ratio of hydroxybenzoic acids obtained by Weiss and his collaborators was approximately 5:2:10 for 2-: 3-: 4-hydroxybenzoic acid in the solution containing molecular oxygen, whereas the ratio was 6:4:10 under the condition of with insufficient quantity of available oxygen. In their results, the para-isomer was major component[1]. On the other hand, the ratio of mono-hydroxybenzoic acids obtained by Downes was approximately 9:5:4 for 2-: 3-: 4-hydroxybenzoic acid[2]. In this case, the ortho-isomer was a major component as well as in the present results, although a different ratio was obtained. These different ratios of products may be attributed rather to the different analytical method, the radiation energies or the experimental conditions such as temperature or concentration than to the different dose rate.

We wish to express our thanks to Professor K. Kimura for his kind guidance and Dr. A. Danno for his many helpful discussions.

Division of Radiation Applications
Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken

---

[8] G. G. Jayson, G. Scholes and J. Weiss, *J. Chem. Soc.*, **1957**, 1358.