Radiation-induced Reaction in an Aqueous Benzoic Acid Solution. I. Dose and Dose Rate Dependencies of Salicylic Acid, and of Biphenyldicarboxylic Acids

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Reactive species such as hydrogen atoms and hydroxyl radicals, and so-called "molecular" products hydrogen and hydrogen peroxide from water are yielded by the actions of ionizing radiation on aqueous solutions. Hydrogen atoms and hydroxyl radicals in these species react rapidly with many solutes dissolved in solutions. The reaction of many organic compounds with these reactive species has been studied by a number of workers.

The radiation-induced reaction of an aqueous benzoic acid solution was studied first by Weiss[1] using X-rays, and recently by Downes[2] using very weak Co-60 gamma rays source. Little attention had been paid by earlier workers to the effect of dissolving oxygen occurring in the reactions when solutions of organic compounds were irradiated by ionizing radiations. The presence of molecular oxygen during irradiation, however, would lead not only to the quantitative differences in the efficiency of the oxidative process but also to some qualitative differences in the reaction products.

In the present work, the radiation-induced reaction of an aqueous benzoic acid solution with, and without, molecular oxygen has been studied and does and dose rate dependencies of the yield of salicylic acid, and of biphenyldicarboxylic acids produced have been examined at high dose and high dose rate, using 10 kc. Co-60 source of the Japan Atomic Energy Research Institute[3].

Experimental

Materials. — Benzoic acid used in this work, obtained from a commercial source, was purified by recrystallization four times from ethanol, m. p. 122°C (uncorrected). Demineralized water was used to prepare a benzoic acid solution. Nitrogen to remove the oxygen contained in sample solutions was purified by letting it bubble through slightly acidified vanadyl sulfate solution[4]. Bomb oxygen was used without further purification.

Preparation of Solutions.—Solutions were 0.300% with regard to benzoic acid, and the pH was not specially adjusted. In order to prepare an oxygen free solution, oxygen contained in the solution was driven off by letting purified nitrogen bubble through for two hours. After this treatment, the concentration of oxygen in the solution is estimated to be lower than 1.9×10^{-5} mol./l.[5] Solutions were charged in 30 ml. test tubes, fitted with glass stoppers. The irradiation vessels were cleaned with cleaning solution, rinsed several times, and then washed with distilled water.

Saturation of oxygen during the irradiation was held by continuous bubbling of bomb oxygen in the sample solution. ($[O_2]$ was measured to be 1.2×10^{-3} mol./l.)[5]

Irradiation. — Both solutions with and without molecular oxygen were irradiated with gamma rays from 10 kc. Co-60 source with absorbed dose from 6.2×10^5 to 1.1×10^7 r and with dose rate from 2.7×10^4 to 3.9×10^5 r/hr. at room temperature. Dose rates were measured by means of both ferrous—ferric[6] and ceric-cerous[7] dosimeters, and the amount of energy absorbed in the solutions was calculated using *G*-values of Fe^{2+} oxidized to Fe^{3+} being 15.5 and of Ce^{4+} reduced to Ce^{3+} being 2.45.

Determination of Salicylic Acid. — The determination of salicylic acid was carried out by colourimetry. After adjusting the pH of the irradiation solution which, if necessary, was filtered off, between 2.5 and 2.8 by means of 50% acetic acid—3% ammonium acetate buffer, an adequate of 1% ferric chloride solution was added to give salicylic acid complex. The absorbance of salicylic acid complex was measured spectrophotometrically at 530 mμ.

Determination of Biphenyldicarboxylic Acids.—Irradiation in the absence of oxygen gave biphenyldicarboxylic acids as precipitate. The precipitate including three isomers of biphenyldicarboxylic acids was separated from the solution using the ultracentrifuge. The collected precipitate was dried for five hours at 80~85°C. Yields of biphenyldicarboxylic acids were determined gravimetrically. Biphenyldicarboxylic acids did not precipitate in the case of irradiation with oxygen.

1) J. Weiss, H. Leobl and G. Stein, *J. Chem. Soc.*, **1951**, 405.
2) A. M. Downes, *Auster. J. Chem.*, **2**, 155 (1958).
3) A. Danno et al., The 7th Hot Laboratories and Equipment Conference, Cleveland (1959), pp. 349~360.
4) L. Meites and J. Meites, *Anal. Chem.*, **20**, 984 (1948).
5) H. Hotta, A. Terakawa and S. Ōno, This Bulletin, 33, 442 (1960).
6) G. R. A. Johnson and J. Weiss, *Proc. Roy. Soc.*, **A240**, 189 (1957).
7) For example, T. Rigg, G. Stein and J. Weiss, ibid., **A211**, 375 (1952).

Results and Discussion

Aqueous solutions of benzoic acid were irradiated with Co-60 gamma rays at a fixed absorbed dose of 3.8×10^5 r by varying dose rate from 2.7×10^4 to 3.9×10^5 r/hr. The yield of salcylic acid produced is plotted against the dose rate in Figs. 1 and 2, in which Fig. 1 shows the case of oxygen saturated solutions and Fig. 2 the case of oxygen free solutions. As is shown in these figures, the yield of salicylic acid is decreasing with increasing dose rate in both systems. The yield of salicylic acid in the presence of oxygen was about ten times greater than that in the absence of oxygen.

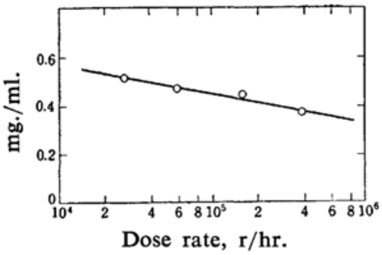


Fig. 1. Yields of salicylic acid produced in oxygen saturated solutions against dose rate. Dose is constant, 3.8×10^6 r.

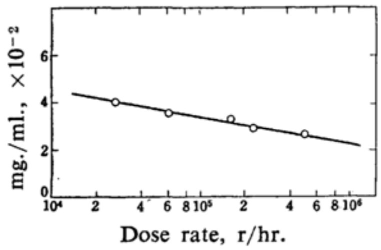


Fig. 2. Yields of salicylic acid produced in oxygen free solutions against dose rate. Dose is constant, 3.8×10^6 r.

Dose dependence of the yield of salicylic acid by a varying absorbed dose from 6.2×10^5 to 1.1×10^7 r at a fixed dose rate of 1.6×10^5 r/hr. is shown in Figs. 3 and 4, where Fig. 3 shows the system of oxygen saturated and Fig. 4 shows the system of oxygen free solution. Two curves show the same trend that the yield of salicylic acid at high dose is not linearly increasing with the absorbed dose, but gradually increases to approach some constant value. Salicylic acid was produced in both with, and without, molecular oxygen solutions, but biphenyldicarboxylic acids were not observed in the oxygen saturated solutions.

Absorbed dose and dose rate dependencies of yields of biphenyldicarboxylic acids were also studied. Figure 5 shows the plot of yields of biphenyldicarboxylic acids against dose rate.

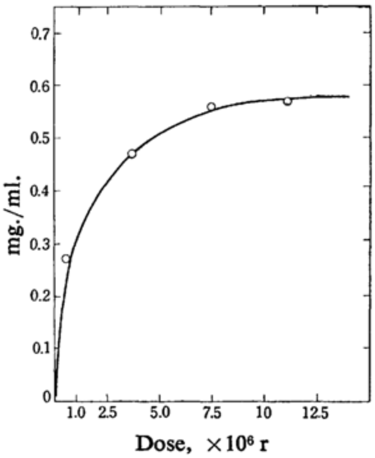


Fig. 3. Yields of salicylic acid produced in oxygen saturated solutions against dose. Dose rate is constant, 1.6×10^5 r/hr.

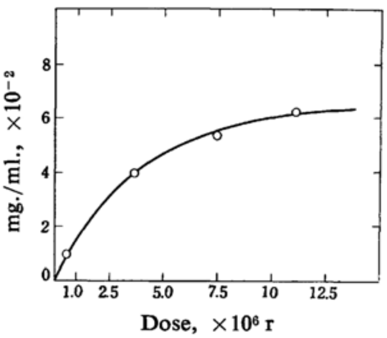


Fig. 4. Yields of salicylic acid produced in oxygen free solutions against dose. Dose rate is constant, 1.6×10^5 r/hr.

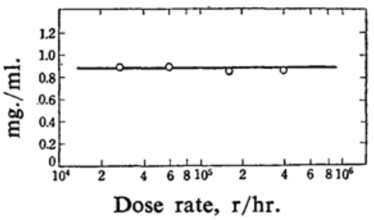


Fig. 5. Yields of biphenyldicarboxylic acid produced in oxygen free solutions against dose rate. Dose is constant, 3.8×10^6 r.

In this case, the absorbed dose was constant at 3.8×10^6 r. The yield of the dimer was constant independently of dose rates and $G=0.94$ was obtained. Figure 6 shows yields of biphenyldicarboxylic acids against the absorbed dose, which were produced when irradiation was carried out at a fixed dose rate of 1.6×10^5 r/hr. As is shown in this figure, yields of biphenyldicarboxylic acids have a linear relationship with the absorbed dose. This relationship is quite different from that of the

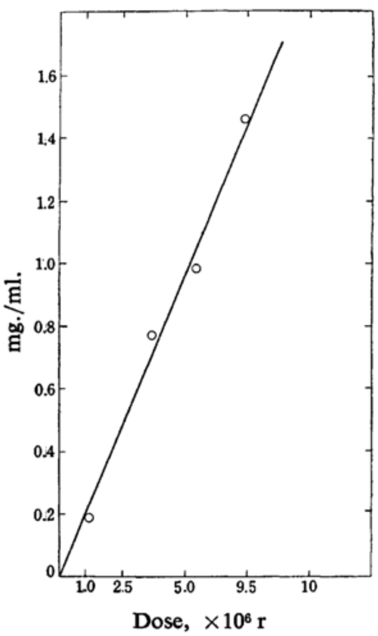


Fig. 6. Yields of biphenyldicarboxylic acid produced in oxygen free solutions against dose. Dose rate is constant, 1.6×10^5 r/hr.

yield of salicylic acid as is shown in Figs. 3 and 4.

Basing on the above results, the mechanism of the radiation-induced reaction in an aqueous solution of benzoic acid is assumed as follows.

In the present experiment, the concentration of benzoic acid was 3.0 mg./ml. of solution. At this relatively low concentration, the direct-hit effects of benzoic acid by gamma rays can be neglected. Water is decomposed by ionizing radiation into hydrogen atom, hydroxyl radical, hydrogen peroxide and hydrogen[8].

$$H_2O \rightsquigarrow H\cdot,\ HO\cdot,\ H_2O_2,\ H_2 \quad (1)$$

Accordingly, the radiation-induced reaction in a dilute aqueous solution is assumed to be initiated by reactive species such as the hydrogen atom and/or the hydroxyl radical produced from the radiolytic decomposition of water.

When water containing molecular oxygen was irradiated, the hydrogen atom produced according to Eq. 1 reacts rapidly with dissolving oxygen giving the hydroperoxy radical[9].

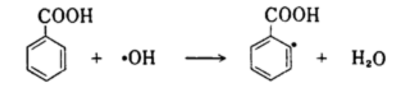
$$H\cdot + O_2 \rightarrow HO_2\cdot \quad (2)$$

Owing to this reaction, the concentration of hydrogen atom in the presence of oxygen may be considerably lower than that in the absence of oxygen.

If this fact is taken into consideration, radiation-induced reaction in an aqueous solution containing molecular oxygen must be initiated by the hydroxyl radical and/or the hydroperoxy radical formed according to Eq. 2. However, it should be noticed that the hydroperoxy radical is assumed to have less oxidizing power than the hydroxyl radical on thermodynamic grounds because the bond dissociation energy of hydrogen peroxide, $D(H-O_2H)$, calculated to be 90 kcal./mol., is smaller than that of water, $D(H-OH)$, calculated to be 118 kcal./mol.[10]

Therefore, the hydroperoxy radical appears to be unreactive directly towards benzoic acid. From these reasons, it would be reasonable to consider that the disappearance of benzoic acid in an aqueous solution is initiated by hydrogen-abstraction with the hydroxyl radical produced from radiolytic decomposition of water.

Dehydrogenation of ring hydrogen of benzoic acid, giving hydroxycarbonylphenyl radical as an intermediate, can be followed by a two reaction process: first, the reaction of this radical with hydroxyl radical to form salicylic acid which shows the hydroxylation of ortho-position of benzoic acid, and second, the dimerization of these radicals to produce biphenyldicarboxylic acid as follows.



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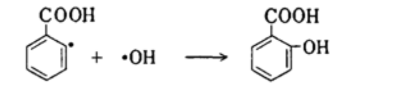

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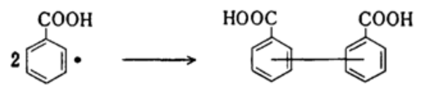


(5)

Biphenyldicarboxylic acids including all kinds of their isomers are insoluble in water giving a pale yellow precipitate and consequently do not suffer from further reaction. The yield of these acids is independent on the dose rate as is shown in Fig. 5, and has a first order relationship with the absorbed dose in the range of the present work (up to 1.1×10^7 r) as is shown in Fig. 6. These results signify that the formation of hydroxycarbonylphenyl radical produced as an intermediate according to Eq. 3 is linearly dependent on the absorbed dose.

8) A. O. Allen and H. A. Schwarz, Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, **29**, 30 (1958).

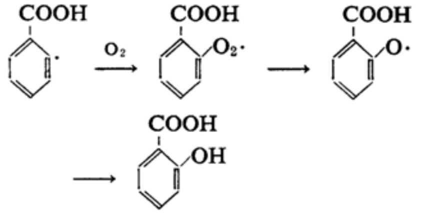
9) P. Riesz and E. J. Hart, *J. Phys. Chem.*, **63**, 858 (1959).

10) J. Weiss, *Internat. J. Appl. Radiation Isotopes*, **6**, 52 (1959).

Hydroxylation of benzoic acid takes place in all possible positions. Accordingly, three isomers of hydroxybenzoic acid may be formed. In the present work, the yield of only isomer, *o*-hydroxybenzoic acid, i. e. salicylic acid, was determined. The yield of salicylic acid at high dose does not show a linear relationship with absorbed dose, but increases gradually with increasing absorbed dose as is shown in Figs. 3 and 4. On the other hand, it is evident from the experimental results of Weiss[1] that the yield of the acid at the low dose (up to 5×10^4 E. U. in his work) has a linear relationship with the absorbed dose. It would seem, therefore, that the trend of the dose-yield curve of salicylic acid at the high dose in the present work may suggest further hydroxylation of salicylic acid to give di-hydroxybenzoic acids and the formation of these acids being more and more remarkable with increasing absorbed dose.

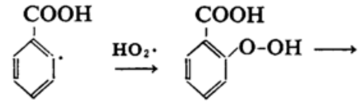
When irradiation of an aqueous solution containing molecular oxygen was carried out, hydroxylation of benzoic acid increased remarkably in comparison with that of the molecular oxygen free solution and the dimerization of hydrocarbonylphenyl radical did not occur. Therefore, the mechanism in this case must be mentioned compared to the different mechanism described above.

If a sufficient amount of molecular oxygen exists in an aqueous solution, it reacts easily with the hydroxycarbonylphenyl radical, as well as the hydrogen, and this reaction results finally in the formation of salicylic acid.



(6)

Consequently, the dimerization of the hydroxycarbonylphenyl radical was suppressed. Concerning the formation of salicylic acid in the presence of molecular oxygen, there is the possibility also of the reaction,



(7)

which can also lead to the eventual formation of salicylic acid. The contribution of this reaction is assumed to be small, because the concentration of oxygen is greater than that of hydroperoxy radical, provided that the reaction rate of the reaction 6 is of the same order as that of 7.

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