*Hydroxyl Radicals in the γ-Radiolysis of Aqueous Benzene Solutions**

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The results of studies of the γ-irradiation of aqueous gelatin solutions[1,2] suggest that hydroxyl radicals play an important role in the radiation induced crosslinking of high polymers in aqueous solutions.[3] With dilute aqueous solutions it is ordinarily true that only water absorbs the incident energy. The dissociation of the water leads to the production of hydroxyl radicals, which then attack the solute. The hydroxyl radical can abstract hydrogen atoms from solutes such as organic polymers to produce polymer radicals. This process can be considered an oxidation of the polymer solute. In an oxygen-free solution, hydrogen atoms may also abstract hydrogen from the polymer solute. The polymer radicals produced may then combine with each other to produce crosslinks. However, experiments in this laboratory suggest that hydrogen atoms[*1]

$$RH + OH^{\cdot} \rightarrow R^{\cdot} + H_2O$$

$$RH + H^{\cdot} \rightarrow R^{\cdot} + H_2$$

$$R^{\cdot} + R^{\cdot} \rightarrow R - R$$

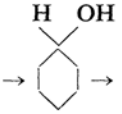
are quite ineffective, although hydroxyl radicals promote crosslinking considerably.[2,3] Hydrogen atoms apparently preferably combine to produce hydrogen molecules. If hydrogen atoms can be changed to hydroxyl radicals, an increase in the extent of crosslinking is to expected.

Dainton et al. have shown that nitrous oxide is capable of reacting with the 'basic form' of the hydrogen atom produced by the γ-radiolysis of water to produce hydroxyl radicals and nitrogen.[4,5] The occurrence of such a reaction should increase the yield of crosslinking. The present author has, accordingly, studied the effect of nitrous oxide on

$$N_2O + H^{\cdot} \rightarrow OH^{\cdot} + N_2$$

the γ-radiolysis of an aqueous benzene solution. Benzene was used instead of a polymeric substance in order to simplify the analysis of the experimental results.

Previous studies[7-10] of the oxidation of benzene in oxygen-free aqueous solutions by γ-irradiation have been interpreted in terms of the following sequence of reactions:

$PhH + OH^{\cdot} \rightarrow$  $\rightarrow Ph^{\cdot} + H_2O$

$$PhH + H^{\cdot} \rightarrow PhH_2 \rightarrow \text{Polymer}$$

$$Ph^{\cdot} + Ph^{\cdot} \rightarrow Ph_2$$

$$Ph^{\cdot} + OH^{\cdot} \rightarrow PhOH$$

In aerated solutions the following reaction also occurs:

$$Ph^{\cdot} + O_2 + H_2O \rightarrow PhOH + H_2O_2$$

This schema shows that the oxidation of benzene is effected by hydroxyl radicals, but not by hydrogen atoms. Therefore, the yield of hydroxyl radicals is estimated from the yield of the oxidized products, namely, phenol and biphenyl, from benzene. The production of a small amount of oxygen by the primary action of γ-rays on water and nitrous oxide merely results in an increase in the yield of phenol. The total yields of biphenyl and phenol from benzene in the presence of nitrous oxide should equal the radical yields of water upon radiolysis, provided that nitrous oxide does in fact change all the hydrogen atoms into hydroxyl radicals. According to Allen,[11] the radical yields (G_H and G_{OH} for ^{60}Co-gamma rays) for irradiated water are 2.85 ± 0.15 and 2.4 respectively in neutral solutions.

Hydrogen peroxide also reacts with hydrogen atoms to give hydroxyl radicals.[9] Therefore, hydrogen peroxide can also be used to study the effect of hydroxyl radicals in the oxidation of

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[1] Y. Tomoda and M. Tsuda, *Tokyo Kogyo Shikensho Hokoku*, **55**, 490 (1960).

[2] Y. Tomoda and M. Tsuda, *J. Polymer Sci.*, **54**, 321 (1961).

[3] Y. Tomoda and M. Tsuda, *Nature*, **190**, 905 (1961).

[*1] The hydrogen atoms described here may be better represented by solvated electrons.

[4] F. S. Dainton and D. B. Peterson, *Nature*, **186** 878 (1960).

[5] F. S. Dainton and S. A. Sills, ibid., **186**, 879 (1960).

[6] Chemical Society of Japan, "Kagaku-Benran," Maruzen Co., Ltd.. Tokyo (1958), p. 572.

[7] G. Stein and J. Weise, *J. Chem. Soc.*, **1949**, 3245.

[8] J. H. Baxendale and D. Smithies, *J. Chem. Phys.*, **23**, 604 (1955).

[9] P. V. Phung and M. Burton, *Radiation Research*, **7**, 199 (1957).

[10] J. H. Baxendale and D. Smithies, *J. Chem. Soc.*, **1959**, 779.

[11] A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co. Inc., Princeton (1961), p. 46.

organic compounds. However, in this case it is also necessary to consider the possibility

$$H_2O_2 + H^\cdot \rightarrow OH^\cdot + H_2O$$

of the consumption of hydroxyl radicals by hydrogen peroxide (reaction 1), which will compete with reaction 2. However, it is known

$$OH^\cdot + H_2O_2 \rightarrow H_2O + HO_2 \qquad (1)$$

$$PhH + OH^\cdot \rightarrow PH^\cdot + H_2O \qquad (2)$$

that, at a high concentration of hydrogen peroxide, the decomposition of the peroxide proceeds through a chain-reaction mechanism,[12] and that hence, the production of oxygen does not result in the consumption of any hydroxyl radicals at all.

Experimental

A 3000 curie ^{60}Co source was used for all irradiations. The dose rate, which was measured with a Fricke Dosimeter, was 1.98×10^5 rads/hr.

Fifty grams of water were weighed into a 100 ml. ampoule, and oxygen was completely removed by passing nitrogen gas through the water for 30 min. After the addition of 2 ml. of benzene, the ampoule was sealed. In the case of the nitrous oxide solutions, flushing with nitrogen for 30 min. was followed by passing nitrous oxide through the water for 30 min. at 3∼5°C, prior to the addition of the 2 ml. of benzene. Hydrogen peroxide solutions were prepared by the addition of 10 ml. of an 8.91 mol./l. aqueous hydrogen peroxide solution which had been acidified with sulfuric acid to give the final solution, with a pH of 3, in order to prevent the spontaneous decomposition of the hydrogen peroxide.[13] The ampoules were vigorously agitated for 10 min. immediately before γ-irradiation in order to ensure the saturation of the solution with benzene. All irradiations were carried out at 25°C by a time scale.

Biphenyl was analyzed according to the method of Phung and Burton.[9] Phenol was analyzed by the method of Baxendale et al.[8,14,15] Phenol was extracted from the sample with ether after biphenyl and benzene had first been removed by extraction with *n*-hexane, and it was determined spectrometrically using an absorption at 273.5 mμ. A correction was applied for the distribution of phenol between water and *n*-hexane. With samples containing hydrogen peroxide, correction must be made for the absorption by hydrogen peroxide at 273.5 mμ. The contribution by hydrogen peroxide to the absorption at 273.5 mμ was calculated from the absorption at 247 mμ. (Biphenyl, which also absorbs at 247 mμ, was removed by extraction with *n*-hexane prior to the spectrometric analysis.)

Results

G-Values were calculated from the gradient of the lines Fig. 1 and Fig. 2.

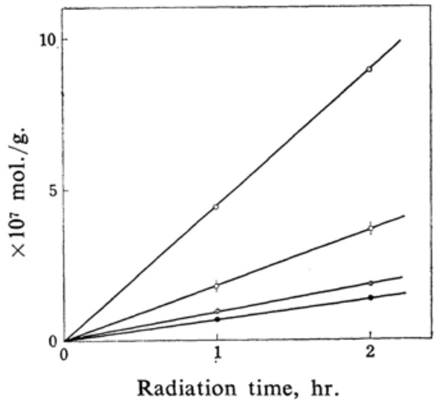

Fig. 1. Ordinate: Amounts of phenol and biphenyl produced in one gram of water (mole).

Phenol $\begin{cases} N_2 & ● \\ N_2O & ⌽ \end{cases}$ Biphenyl $\begin{cases} N_2 & ⦶ \\ N_2O & ○ \end{cases}$

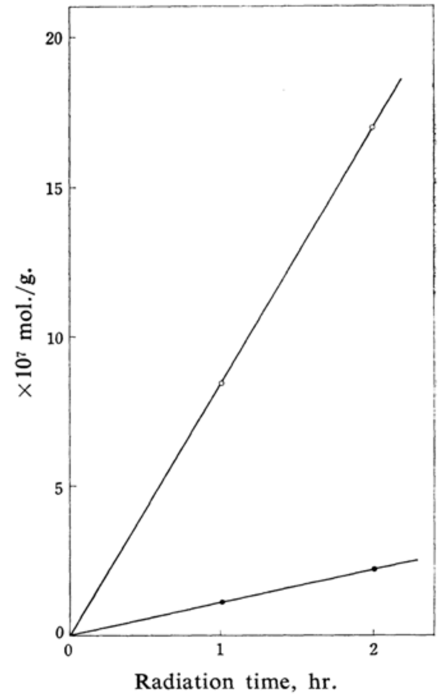

Fig. 2. Ordinate: Amounts of phenol and biphenyl produced in one gram of water containing hydrogen peroxide (mole).
Phenol ○ Biphenyl ●

TABLE I. CONDITIONS AND *G* VALUES

Condition	$G(Ph_2)$	$G(PhOH)$
Nitrogen	0.45	0.35
Nitrous oxide	2.15	0.90
Hydrogen peroxide	0.55	4.11

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[12] Ref. 11, p. 102.

[13] Y. Shibata, "Muki-Kagaku Zensho II-1-1," Maruzen Co., Ltd., Tokyo, (1951), p. 238.

[14] J. H. Baxendale and J. Magee, *Discussions Faraday Soc.*, **14**, 160 (1953).

[15] J. Goodman and J. Steigman, *J. Phys. Chem.*, **62**, 1020 (1958).

TABLE II

	$G(Ph_2)$	$G_1(PhOH)$	$G_2(PhOH)$	$G(PhOH)$[a]	$G((OH)PhH^{\cdot})$[b]
N_2	0.45	0.23	0.12	0.35	1.48
N_2O	2.15	0.78	0.12	0.90	5.98
H_2O_2	0.55	0.28	3.83	4.11	5.49

a) $G(PhOH)=G_1(PhOH)+G_2(PhOH)$

b) $G((OH)PhH^{\cdot})=2G(Ph_2)+2G_1(PhOH)+G_2(PhOH)$

The yield of biphenyl for oxygen-free (N_2-saturated) benzene solutions agrees with the value obtained by Baxendale and Smithies[8], but it is smaller than that reported by Phung and Burton.[9] The yield of phenol reported for oxygen-free benzene solutions is substantially in accordance with other reports.[8,9]

Discussion

The 'basic form' of the hydrogen atom produced by the dissociation of irradiated water seems to be a solvated electron, e_{aq}^-, and it preferably reacts with nitrous oxide[16] and hydrogen peroxide.[17-21]

$$e_{aq}^- + N_2O \rightarrow N_2 + H_2O_2^- \rightarrow N_2 + OH^{\cdot} + OH^-$$

$$e_{aq}^- + H_2O_2 \rightarrow H_2O_2^- \rightarrow OH^{\cdot} + OH^-$$

Under the present experimental conditions, the concentration ratio $[H_2O_2]/[H^+]$ was about 10^3 (pH $\sim$3), and the ratio of the rate constants for the $H_2O_2+e_{aq}^-$ and $H^+ + e_{aq}^-$ reactions is about 1/2.[20] Therefore, the production of the acidic form of the hydrogen atom, H, should be negligible in the present case.

In nitrous oxide solutions the yield of hydroxyl radicals should be $2(G(Ph_2)+G(PhOH))=6.10$, which is larger than the expected value of 5.25 ± 0.15 (the sum of G_H and G_{OH}).[11] The discrepancy may be partly due to the oxygen produced by the decomposition of water and nitrous oxide.

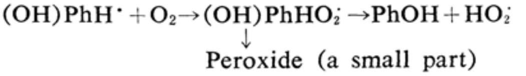
In hydrogen peroxide solutions the yield of hydroxyl radicals should be $2G(Ph_2)+G(PhOH)=5.21$ because of the presence of the large amount of oxygen produced by the radiolysis of hydrogen peroxide.

Recently, Dorfman et al. reported the production of hydroxycyclohexadienyl radicals in the process of the radiolysis of an aqueous benzene solution.[22] The discussion of our data in terms of their mechanism may be necessary. They proposed the following sequence of reactions:

$$PhH + OH^{\cdot} \rightarrow (OH) \leftarrow PhH^{\cdot}$$

$$2(OH)PhH^{\cdot} \rightarrow ((OH)PhH)_2 \rightarrow Ph_2$$

$$2(OH)PhH^{\cdot} \rightarrow PhOH + (OH)PhH_2 \qquad (3)$$



$$\begin{array}{l}(OH)PhH^{\cdot} + O_2 \rightarrow \underset{\substack{\downarrow \\ \text{Peroxide (a small part)}}}{(OH)PhHO_2^{\cdot}} \rightarrow PhOH + HO_2^{\cdot}\end{array} \qquad (4)$$

$(OH)PhH_2$ may change to $PhH+H_2O$. In deaerated solutions,[22] $G(Ph_2)$ $\sim$0.5 and $G(PhOH)$ $\sim$0.23. The distribution of hydroxycyclohexadienyl radicals between biphenyl and phenol seems to be about 2:1. This ratio of distribution was applied to our data (Table II). $G_1(PhOH)$ is the yield of phenol produced by reaction 3, $G_2(PhOH)$ is that by reaction 4, and $G(PhOH)$ is the experimental result. $G((OH)PhH^{\cdot})$ should equal the radical yield of water, (G_H+G_{OH}).

In oxygen-free solutions our result for $G((OH)PhH^{\cdot})$ agrees with that obtained by Dorfman et al.[22]

According to Allen,[11] G_H in an atmosphere with a high concentration of oxygen is larger by 0.1 in G value than the ordinary value. Therefore, $G((OH)PhH^{\cdot})$ should be 5.35 ± 0.15 in hydrogen peroxide solutions; the experimental result agrees with this expected value.

In nitrous oxide solutions the same value of $G_2(PhOH)$ as in deaerated solutions was applied. The value of $G((OH)PhH^{\cdot})$ is 10% larger than the expected value.

Summary

Some experiments have been made in order to prove the hypothesis that the hydroxyl radical plays an important role in the oxidation of organic compounds by γ-radiolysis in aqueous solutions. Nitrous oxide and hydrogen peroxide have been found to be capable of converting radiation-induced hydrogen atoms (or their stoichiometrically-equivalent

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[16] F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc.*, **A267**, 443 (1962).

[17] P. E. Riesz and B. E. Burr, *Radiation Research*, **16**, 663 (1962).

[18] N. F. Barr and A. O. Allen, *J. Phys. Chem.*, **63**, 928 (1959).

[19] E. Hayon and A. O. Allen, ibid., **65**, 2181 (1961).

[20] G. Czapski and A. O. Allen, ibid., **66**, 262 (1962).

[21] W. M. Garrison, B. M. Weeks and S. Cole, *Nature*, **193**, 129 (1962).

[22] L. M. Dorfman, R. E. Bühler and I. A. Taub, *J. Chem. Phys.*, **36**, 549, 3051 (1962).

species) into hydroxyl radicals. In the γ-radiolysis of aqueous benzene solutions in the presence of nitrous oxide or hydrogen peroxide, the yield of the oxidation products from benzene has been found to equal, as had been expected, the sum of the yields of hydrogen atoms and hydroxyl radicals from water.

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