

Decomposition Pathways of *p*-Bromophenol on γ -Irradiation in Aqueous Systems[†]

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In order to elucidate the radiolysis mechanism of *p*-bromophenol, quantitative determination of the radiolysis products was carried out by gas chromatography and polarography. $G(-p\cdot\text{BP})$ and $G(\text{Br}^-)$ were 3.86 and 2.58 at neutral pH, and 1.09 and 0.26 at pH 1.0, respectively. This, together with the radical scavenger effects indicated that hydrated electrons contribute principally to the degradation of *p*-bromophenol through debromination, followed by the formation of dimer and trimer products by phenylation of the resulting *p*-hydroxyphenyl radical. This chain-like reaction may cause the difference ($G\text{-value}=1.28$) between $G(-p\cdot\text{BP})$ and $G(\text{Br}^-)$. The contribution of OH radicals to $G(-p\cdot\text{BP})$ is known to be small as compared with other aromatic compounds, because of the poor yield of hydroxylated products such as hydroquinone, 4-bromocatechol and 4-bromoresorcinol.

Radiolysis of phenolic compounds in aqueous system has been investigated for phenol,^{1,2)} 4-nitrophenol,^{3,4)} hydroquinone,⁵⁾ 4-hydroxybenzoic acid.⁶⁾ The results indicate that these compounds are generally decomposed through the formation of a hydroxycyclohexadienyl radical by the attack of OH radicals arising from water radiolysis on the aromatic ring. Regarding the radiolysis of halogenophenols, little is known except for the study by Anbar *et al.*⁷⁾ In connection with the radiation-enhanced bactericidal activity of halogenophenols,^{8,9)} we have attempted the isolation and identification of the main radiolysis products of *p*-bromophenol^{10~12)} and have identified two new asymmetric diphenols, 3-bromo-6,4'-dihydroxybiphenyl and 2-bromo-5,4'-dihydroxybiphenyl, as the main products and hydroquinone, 4-bromocatechol and four new terphenyls as minor products. This paper deals with the quantitative determination of the main radiolysis products of *p*-bromophenol using gas chromatographic and polarographic methods to elucidate the role of each active

species from water radiolysis.

MATERIALS AND METHODS

Materials and irradiation. All reagents used were of guaranteed grade. Triply distilled water was used for the preparation of irradiating solutions. Irradiations were carried out at room temperature with γ -rays from a Co^{60} source of 4000 Ci. The dose rate was 6.9×10^4 , 1.6×10^5 or 1.86×10^5 rad/hr. Except where otherwise noted, *p*-bromophenol was irradiated at a concentration of 5 mM and the pH was adjusted to 5.0 or 7.0 with 20 mM phosphate buffer and to 1.0, 2.0 or 3.0 with sulfuric acid. The solutions were irradiated after deaeration by bubbling with purified nitrogen gas.

IR, Mass and NMR spectra. IR, Mass and NMR spectra were measured with a JASCO Model IR-E as KBr disks, with a Hitachi mass spectrometer RMU-6D and with a JMN-4H-100 NMR unit, respectively.

Gas chromatography. Quantitative measurements of *p*-bromophenol and radiolysis products such as hydroquinone, 4-bromocatechol, 4-bromoresorcinol and the dimer products were undertaken by gas chromatography (glc); a gas chromatograph model JEG-1100 equipped with FID and a dual stainless steel column was used (1 m \times 3 mm, 8% silicon DC QF-1 on 80~100 mesh Gaschrom Q; Carrier gas N_2 , 0.5 kg/cm², oven temp. 100~300°C programed at 6°C/min; Inject temp. 300°C, detection temp. 300°C). The irradiated

[†] Radiation Chemistry of Halogenophenols in Aqueous Solution. Part III. Part II, see Reference 11).

solution of *p*-bromophenol was extracted with ether and the concentrate was subjected to glc using biphenyl as an internal standard. In the case of such radiolysis products as hydroquinone, 4-bromocatechol and 4-bromoresorcinol, glc was done after silylation of the ether extracts with 25% bis (trimethyl silyl) acetamide (BSA) in acetonitrile containing phenanthrene as an internal standard.

Quantitative measurement of Br^- . The amount of Br^- formed in *p*-bromophenol solution by γ -irradiation was measured by polarography with a Yanagimoto PA 102 Polarograph. The capillary flow rate was $m = 3.20$ mg/sec and the mercury dropping time was $t = 2.55$ sec, $m^{2/3} \cdot t^{1/6} = 2.54$.

RESULTS

Decomposition of p-bromophenol and formation of Br^- and the dimer with increasing irradiation dose

As shown in Fig. 1, *p*-bromophenol decomposed in a linear manner with increasing dose up to 5×10^5 rad, with a linear production of Br^- . The initial G-values for the decomposition of *p*-bromophenol and the formation of Br^- were calculated to be 3.86 and 2.58, respectively. In addition, as shown in Fig. 3, the amount of the dimer product increased almost linearly up to 2.0×10^5 rad and the initial G-value was calculated to be 0.80.

Effects of pH on the decomposition of p-bromophenol and the formation of Br^- and the dimer products

To elucidate the roles of hydrated electrons and hydrogen radicals in the radiolysis of *p*-bromophenol, the effects of pH during irradiation on the decomposition of *p*-bromophenol, as well as on the formation of Br^- and the dimer products, were examined. Deoxygenated aqueous solutions of 5 mM *p*-bromophenol were irradiated with 5×10^5 rad at various pH values below 7.0. As shown in Fig. 2, both the decomposition of *p*-bromophenol and the formation of Br^- remained unchanged at neutral pH between 5.0 and 7.0 with $G(-p\text{-BP}) = 3.86$ and $G(\text{Br}^-) = 2.58$, but they decreased with decreasing pH below 5.0 to 1.09 and 0.26, respectively. A marked decrease in the yield with decrease in pH below 3.0 was also ob-

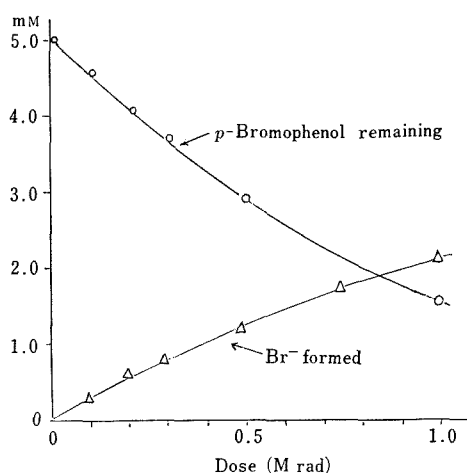


FIG. 1. Changes in the Amounts of *p*-Bromophenol Remaining and Br^- Formed with Increasing Irradiation Dose.

Dose rate; 0.69 and 1.6×10^5 rad/hr.

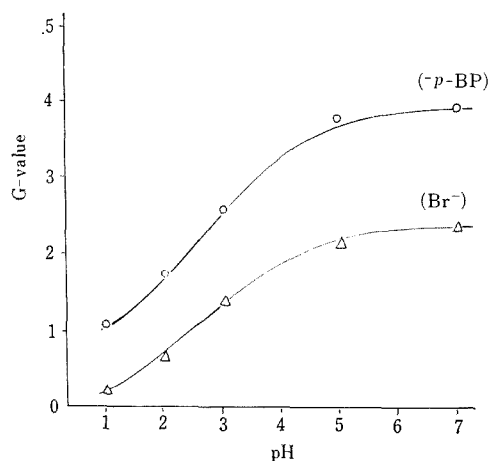


FIG. 2. The Effects of pH on *p*-Bromophenol Decomposition and Br^- Formation in γ -Irradiated *p*-Bromophenol Solution.

Dose rate; 0.69 and 1.6×10^5 rad/hr
Total dose; 5.0×10^5 rad.

served in the case of dimer formation as illustrated in Fig. 4, where $G(\text{dimer})$ was 0.43 at pH 7.0 and decreased to 0.022 at pH 1.0.

Effects of additives on the radiolysis of p-bromophenol in aqueous solution

The effects of $\text{N}_2\text{O}^{13)}$ and $\text{air}^{14)}$ were investigated on the decomposition of *p*-bromophenol and the formation of Br^- . As shown in Table

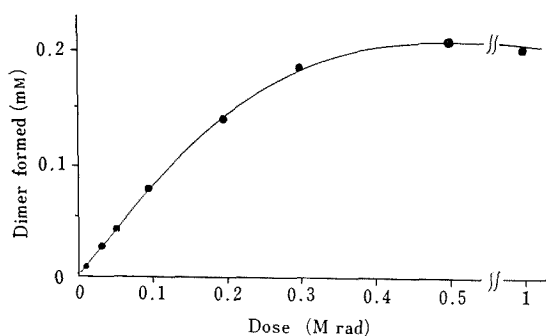


FIG. 3. Dimer Formation in γ -Irradiated *p*-Bromophenol Solution.

Dose rate; 1.6×10^5 rad/hr.

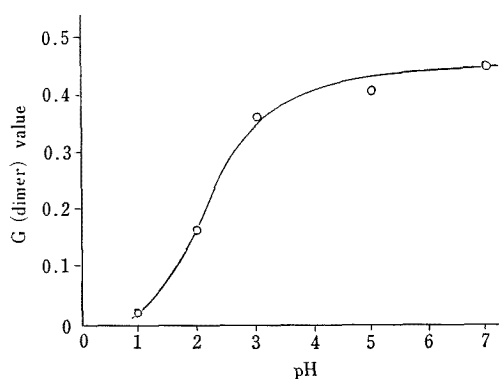


FIG. 4. The Effect of pH on Dimer Formation in γ -Irradiated *p*-Bromophenol Solution.

Dose rate; 1.86×10^5 rad/hr
Total dose; 5.0×10^5 rad.

I, $G(-p\text{-BP})$ decreased significantly to 1.93 when saturated with N_2O while it increased markedly to 4.18 in the presence of air. On the other hand, $G(\text{Br}^-)$ apparently decreased with increasing N_2O concentration up to about

10 mM, as shown in Fig. 5, but it did not change in the presence of air (Table I).

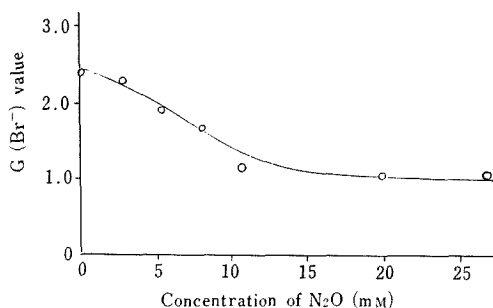


FIG. 5. Effect of N_2O on Br^- Formation in γ -Irradiated *p*-Bromophenol Solution.

5 mM *p*-bromophenol (*in vacuo*) in phosphate buffer (pH 7.0) was γ -irradiated in the presence of N_2O .
Dose rate; 6.9×10^4 rad/hr
Total dose; 5.0×10^5 rad.

On the other hand, scavengers of OH radicals, $\text{HCOONa}^{15)}$ and *t*-BuOH,¹⁵⁾ had almost no effect upon the decomposition of *p*-bromophenol and the liberation of Br^- , as shown in Table I. The addition of 2 mM and 20 mM $\text{HCOONa}^{16)}$ and 1 M *t*-BuOH did not significantly change the $G(-p\text{-BP})$ and $G(\text{Br}^-)$ values. The effects of N_2O and $\text{KCNS}^{15)}$ scavengers of hydrated electrons and OH radicals, respectively, on the formation of the dimer products were also investigated and the results are summarized in Table I. It was demonstrated that $G(\text{dimer})$ was markedly decreased from 0.423 to 0.065 in N_2O , while it increased slightly to 0.442 in the presence of 10 mM KCNS .

Identification and quantitative measurements of some hydroxylated products in irradiated

TABLE I. EFFECTS OF VARIOUS ADDITIVES ON THE γ -RADIOLYSIS OF *p*-BROMOPHENOL IN AQUEOUS SYSTEMS

Additives	$G(p\text{-BP})$	$G(\text{Br}^-)$	$G(\text{dimer})$	$G(\text{Hy})$	$G(4\text{-BC})$	$G(4\text{-BR})$
N_2	3.86	2.58	0.423	0.049	0.020	0.011
N_2O	1.93	1.06	0.065	0.052	0.743	0.260
$\text{KCNS}(10 \text{ mM})$	3.94		0.442	none	none	none
pH 1	1.09	0.26	0.022			
$\text{HCOONa}(2 \text{ mM})$	3.15	2.62				
$\text{HCOONa}(20 \text{ mM})$	3.18	2.64				
<i>t</i> -BuOH(1 M)	3.18	2.58				
Air	4.15	2.48				

p-BP, *p*-Bromophenol; Hy, Hydroquinone; 4-BC, 4-Bromocatechol; 4-BR, 4-Bromoresorcinol.

solutions of *p*-bromophenol were done by glc. The peaks observed at retention times of 7.50, 10.0 and 10.5 min in Fig. 6 correspond to hydroquinone, 4-bromocatechol and 4-bromoresorcinol, respectively, on comparison with authentic samples. The formation of 4-bromoresorcinol was also demonstrated from the mass spectrum ($M^+ = 332$ and 334, relative abundance %, *ca* 1:1) of the TMS derivative isolated by glc and moreover by agreement with the TMS derivative of 4-bromocatechol in respect to molecular weight. The effects of N_2O and KCNS on the yields of these hydroxylated products are given in Table I; their yields were calculated to be 0.049, 0.020 and 0.011, respectively, at 5.0×10^5 rad. As shown in Fig. 6,

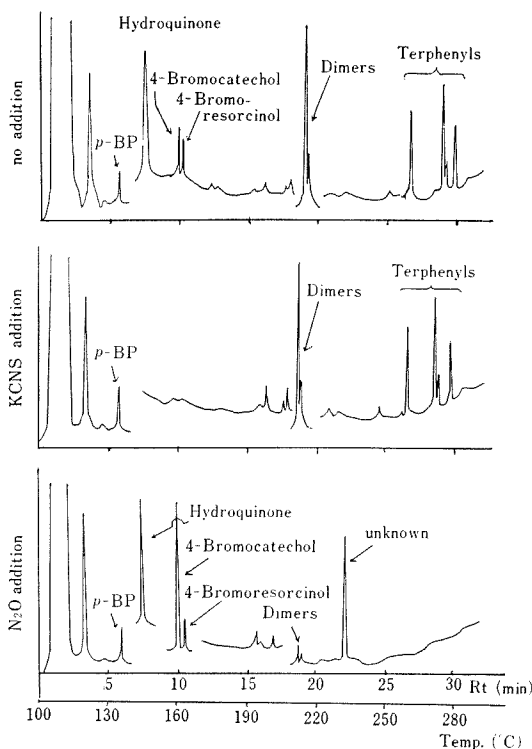


FIG. 6. Gas Chromatograms of the Silyl Ethers of γ -Irradiated *p*-Bromophenol Products.

formation of these three hydroxylated products was abolished by 10 mM KCNS, but increased markedly on the addition of N_2O together with the formation of an unknown product ($Rt = 22.0$ min).

Reaction of *p*-bromophenol with Fenton's reagent¹⁷⁾

Fifty ml of 3% hydrogen peroxide and 50 ml of 0.1 M ferrous sulphate were added simultaneously to 250 ml of 50 mM *p*-bromophenol solution, pH 2.0. The reaction mixture was concentrated and subjected to gradient elution chromatography on a silica gel column with benzene-ethyl acetate to give two main crude fractions, named F_p-1 and F_p-2 , in yields of 950 mg and 38 mg, respectively. On gas chromatography of the silylated reaction mixture, three peaks appeared at retention times of 7.50, 10.0 and 10.5 min (yield ratio; 1:12:3 from the peak areas). The peaks having retention times of 7.50 and 10.0 min corresponded to F_p-1 and F_p-2 , respectively, and were assigned to 4-bromocatechol and hydroquinone, respectively, on the basis of IR, Mass and NMR spectra.

DISCUSSION

From the results presented in Fig. 1, the radiolysis of *p*-bromophenol in deaerated aqueous solution proceeds with a comparatively high decomposition yield of *p*-bromophenol ($G = 3.86$) along with the formation of a considerable amount of Br^- ($G = 2.58$). The $G(p\text{-BP})$ value is higher than any of the G -values for the active species produced by the radiolysis of water, that is, $G(OH) = 2.59$, $G(e_{aq}^-) = 2.58$ and $G(H) = 0.55$,¹⁸⁾ while the $G(Br^-)$ value corresponded well to the $G(OH)$ and $G(e_{aq}^-)$ values. The difference between the above G -values suggests that some other radiolytic pathways exist besides the liberation of Br^- from *p*-bromophenol. Here, the liberation of Br^- was clearly demonstrated to be caused principally by the action of hydrated electrons, but not OH or H radicals, because the $G(Br^-)$ value fell to zero at pH 1.0, where hydrated electrons were converted into H radicals¹⁹⁾ and the difference in the $G(Br^-)$ values at pH 7.0 and pH 1.0 coincided well with the $G(e_{aq}^-)$ value. The following scavenger effects also support this view; that is, $G(Br^-)$ decreased with increase in N_2O concentration

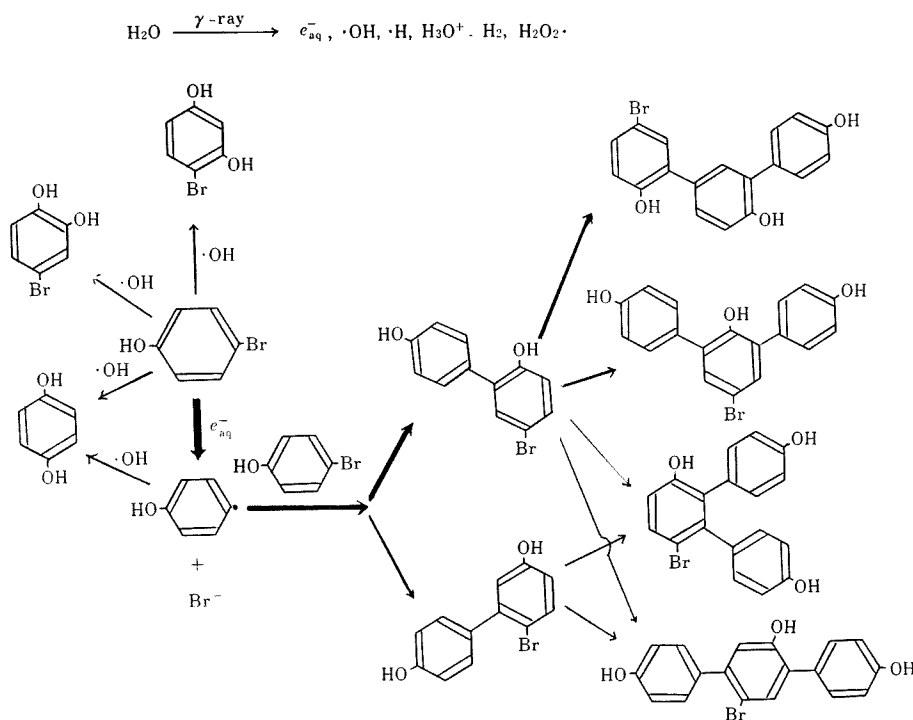
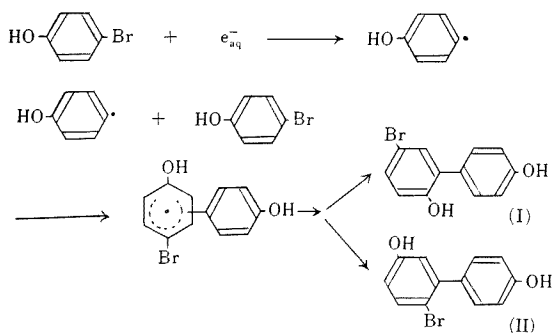


FIG. 7. Decomposition Pathways of *p*-Bromophenol in Aqueous Solutions on γ -Irradiation.

(Fig. 5), while the addition of OH radical scavengers, HCOONa or *t*-BuOH, did not affect it.

On the other hand, the results shown in Figs. 3, 4, 5 and Table I, demonstrate that the dimer products previously reported¹⁰) were formed predominantly at neutral pH and did not form at pH 1.0 or in the presence of N₂O at pH 7.0, though the yield was not much affected by KCNS. Thus it is reasonable to suppose that hydrated electrons are the sole factor contributing to dimer formation, and the process may be pictured as follows,

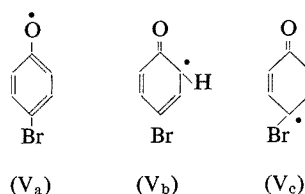


Namely the reaction of *p*-bromophenol with hydrated electrons may produce an intermediate, *p*-hydroxyphenyl radical,²⁰⁾ which will then attack the positions *ortho* or *meta* to the hydroxyl group of unreacted *p*-bromophenol molecules to give the two asymmetric dimers (I and II). It was also concluded that the decomposition of *p*-bromophenol is caused mainly by the debromination process mentioned above and decomposition due to the attack of OH and H radicals might not account for more than 1.0 in the G-value, because $G(-p\text{-BP})$ at pH 1.0 was about 1.0.

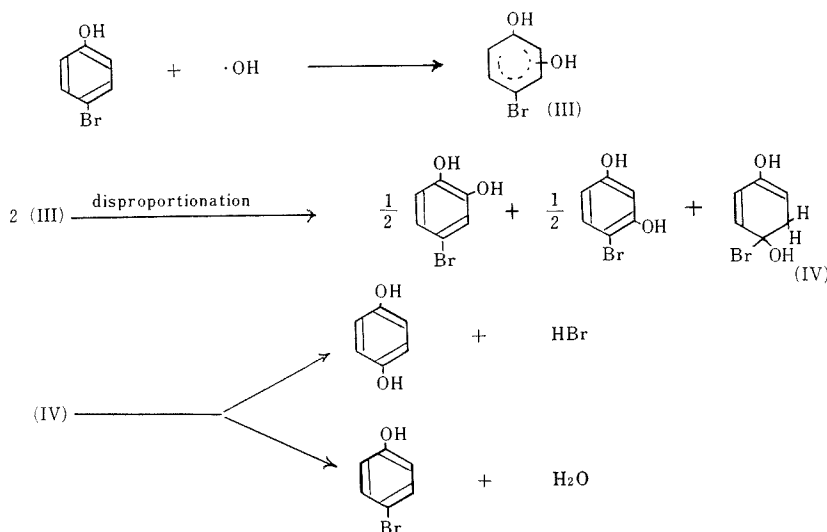
On the other hand, the hydroxylated products of *p*-bromophenol, such as 4-bromocatechol, 4-bromoresorcinol and hydroquinone are known to be formed with G-values of 0.020, 0.011 and 0.049, respectively. It should be noted that in the radiolysis, hydroquinone was predominant among these products, while the model system for hydroxyl radical reaction involving Fenton's reagent gave 4-bromocatechol as a major product. However, the observed yields of hydroxylated products were as

small as 0.08 in the total G-value, as expected from stoichiometrical aspects, based on the OH radical yield. Generally, in the radiolysis of aromatic compounds in aqueous systems, the reaction of OH radicals occurs preferentially to give hydroxylated products. For example, the radiolysis of 4-nitrophenol gives 4-nitrocatechol and 4-aminophenol with G-values of 2.95 and 1.1, respectively,³⁾ and it is to see that the radiolysis process of *p*-bromophenol is significantly different from that of 4-nitrophenol. As for the action of OH radicals on *p*-bromophenol, Fenton's reagent gave 4-bromocatechol, 4-bromoresorcinol and hydroquinone in a yield ratio of 12:3:1; that is, ortho addition was more favorable than para addition followed by debromination in the case of OH radical reaction. From these results, the process of formation of the hydroxylated products can be postulated as follows,

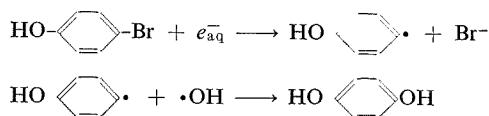
phenoxy radical^{1,12)} with canonical forms (V_a, b and c), produced by the addition of OH radical to the nucleus followed by liberation of H₂O.²⁾ 4-Bromocatechol and hydroquinone may be formed successively by attack of OH radical on the phenoxy radical.



Furthermore, from the yield ratio (0.743:0.26:0.052) of 4-bromocatechol, 4-bromoresorcinol and hydroquinone in the presence of N₂O, the major pathway of formation of hydroquinone may be considered to be as follows,

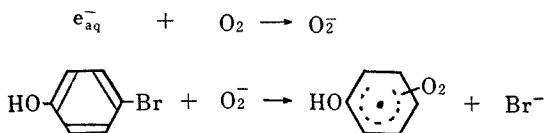


The intermediate hydroxyhexadienyl radical produced by the action of OH radicals on *p*-bromophenol would yield 4-bromocatechol, 4-bromoresorcinol and preferentially hydroquinone, mainly by disproportionation. In this case, hydroquinone may be formed by the elimination of hydrogen bromide through the intermediate *p*-hydroxy substituted form (IV). A second route may proceed through the



Another interesting fact is that a similar level of $G(\text{Br}^-)=2.48$ with a considerably higher value of $G(-p.\text{BP})=4.15$ was observed in the case of aerobic radiolysis as compared to the values for anaerobic irradiation. In this case,

the reaction of hydrated electrons with *p*-bromophenol may be eliminated by the faster reaction of oxygen with e_{aq}^- to form O_2^- .¹⁴⁾ Thus, the mechanism of Br^- liberation in the presence of O_2 can be explained well by introducing the idea of "electron transfer."



As shown in the above equation, the electron on super oxide O_2^- , will transferred to the bromine atom of *p*-bromophenol to give Br^- .

In conclusion, it was demonstrated that the radiolysis of *p*-bromophenol in deaerated aqueous solutions proceeded characteristically by the reaction of hydrated electrons causing debromination followed by the formation of oligomer products, as shown in Fig. 7.

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