A Liquid Chromatographic Study of the Radiolysis of Aqueous Solutions of *p*-Bromophenol[1]

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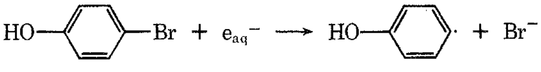
The potentialities of using liquid chromatographic methods to examine radiation chemical effects in aqueous systems has been explored using the radiolysis of *p*-bromophenol as a test system. It is shown that one can readily follow both the consumption of the starting material and the formation of products with sufficient accuracy that detailed measurements of the dependence of the reaction on various kinetic parameters are possible. Hydrated electrons are found to react quantitatively with *p*-bromophenol to produce *p*-hydroxyphenyl radicals. In the absence of a scavenger for these radicals they add to the parent molecule to produce 2-bromo-5,4′-dihydroxybiphenyl and 5-bromo-2,4′-dihydroxybiphenyl with the initial yields at millimolar solute concentrations being estimated as 1.3 and 1.0, respectively. A very pronounced dose dependence in the formation of these products is, however, observed as a result of very rapid tertiary reactions of the *p*-hydroxyphenyl radical which result in the production of terphenyls. Addition of a suitable source of hydrogen to the system results in the conversion of *p*-hydroxyphenyl radical to phenol. The yield of phenol at a *p*-bromophenol concentration of 5×10^{-4} M and high concentrations of isopropyl alcohol is 2.8. Measurements of the dependence of the phenol yield on the concentration of added alcohol indicate that abstraction of H from the alcohol is 2.4 times slower than the addition to *p*-bromophenol. By comparison with the known rate for the addition reaction a rate constant of 3×10^7 M^{-1} sec^{-1} for the abstraction process is obtained. The experiments described in this paper were carried out on solutions containing solutes in the concentration range 10^{-4}–10^{-2} M and products were measured in the region of 10^{-6}–10^{-4} M. In appropriate systems measurements can be carried out on components present at concentrations as low as 10^{-8} M. The availability of rapid ultrasensitive analytical methods of the type used here obviously makes possible many types of studies which heretofore could be carried out only with difficulty or not at all.

The recent development of very sensitive high-speed liquid chromatographic methods[2] has opened many possibilities for studying product formation in the radiolysis of dilute aqueous solutions of organic compounds. In liquid chromatography component separation is, in many cases, comparable to that attained in gas chromatographic analysis and detectors are now available which, in instances where the material being examined has an appropriately high extinction coefficient, reduce the sensitivity levels to below the micromolar level so that product formation can be studied at exceedingly low dose levels. We have undertaken an investigation of product formation in the radiolysis of *p*-bromophenol solutions in order to examine some of the potentialities of the liquid chromatographic approach. An aromatic system was chosen because all aromatic products will have relatively high extinction coefficients at the 254-nm wavelength of a convenient commercially available optical detector. *p*-Bromophenol has previously been the subject of a number of steady-state investigations which show that e_{aq}^- reacts to form Br^- quantitatively.[3,4] Presumably *p*-hydroxyphenyl radical is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produced as a complementary intermediate but measurements of its yield have not, as yet, been made. Pulse radiolysis investigations have shown that this radical reacts extremely rapidly with the parent compound.[5] Classical elution and thin-layer chromatographic methods have been applied to characterize certain of the products from both the radiolysis and photolysis as substituted biphenyls[6,7] but no detailed quantitative study of product formation has been undertaken. The results of our study are presented here in some detail in order to demonstrate the excellent promise of the application of liquid chromatographic methods to kinetic investigations on aqueous systems. These studies, of course, provide further information on the radiolysis of *p*-bromophenol solutions. The reaction of e_{aq}^- with *p*-bromophenol is shown to be an excellent source of the *p*-hydroxyphenyl radical for studies of the reaction kinetics of this latter species.

Experimental Section

An high-speed liquid chromatographic apparatus assembled in our laboratory, which is suitable for analysis of dilute aqueous solutions, is described in detail elsewhere.[8] The principal components are a Model 709 Laboratory Data Control solvent delivery system (Milton Roy con-

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(1) Supported in part by the U. S. Atomic Energy Commission.

(2) "Modern Practice of Liquid Chromatography," J. J. Kirkland, Ed., Wiley, New York, N. Y., 1971.

(3) F. A. Peter and P. Neta, *J. Phys. Chem.*, **76**, 630 (1972).

(4) M. Anbar, Z. B. Alfassi, and H. Bregman-Reisler, *J. Amer. Chem. Soc.*, **89**, 1263 (1967).

(5) B. Cercek and M. Kongshaug, *J. Phys. Chem.*, **74**, 4319 (1970).

(6) (a) M. Namiki, T. Komiya, S. Kawakishi, and H. Aoki, *Chem. Commun.*, 311 (1970); (b) T. Komiya, S. Kawakishi, H. Aoki, and M. Namiki, *Agr. Biol. Chem.*, **34**, 349 (1970); (c) *ibid.*, **35**, 1558 (1971).

(7) H. I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, **88**, 3269 (1966).

trolled volume minipump equipped with a pulse dampener), dual chromatographic columns for analysis and reference streams, and a Model 1205 Laboratory Data Control uv monitor. This monitor has a volume of 8 μl and a path length of 10 mm. Samples were introduced onto the column through a Teflon sealed valve using an injection loop of 0.19 ml.

The output of the uv monitor corresponds to a signal of 10 mV for an optical absorbance of 0.02. Using an RC filter with a time constant of 10 sec in the output of the uv monitor we have found it possible to spread an absorbance of 0.002 full scale (*i.e.*, 1 mV output) on a 10-in. recorder with, under optimum conditions, a short-term noise level of $\sim$0.1 in. (0.01 mV). This noise corresponds to an absorbance of 2×10^{-5} and the long-term drift on a well-conditioned column is comparable. For a compound with an extinction coefficient of 10^4 M^{-1} cm^{-1} the potentially available sensitivity is, therefore, $\sim 2 \times 10^{-9}$ M provided the peak width can be maintained comparable to the injection volume. For a product with a radiation chemical yield (G) of 3 molecules/100 eV, a product concentration at this level corresponds to a dose of $\sim$1 rad (6.24×10^{13} eV/g) so it is seen that for products which have appropriately high extinction coefficients the system can, indeed, be made very sensitive. In the present work the sensitivities are appreciably less (phenol and *p*-bromophenol, for example, have extinction coefficients of about 520 and 350 M^{-1} cm^{-1} at 254 nm although the extinction coefficients at the maxima of 270 and 280 nm are larger by a factor of $\sim$3). We have not attempted to push the present studies to any ultimate level.

The chromatographic columns used in this work consisted of a 0.5–2 m length of ⅛-in. No. 316 stainless steel tubing (2.1 mm i.d.). Most studies were carried out with columns packed with Corasil/C_{18}, a packing material supplied by Waters Associates which consists of 37–50 μ superficially porous silicous particles with octadecyl groups permanently bonded to the surface. These columns were found to be particularly useful for analyzing the substituted biphenyls and terphenyls. In some of the later studies, where consumption of *p*-bromophenol was to be measured, Du Pont Strong Anion Exchange Chromatographic Packing was used to separate the various radiation-produced products from the *p*-bromophenol. This material permits regulation of retention time by adjustment of pH and ionic strength. Over the short term, column stability is sufficiently good that peak height is a good measure of concentration for a given component provided one does not exceed column capacity and artificially broaden the peak. In fact, over moderate changes, peak height is in many ways a better measure of concentration in that it tends to be invariant with flow rate whereas peak area is, of course, inversely dependent on the flow. Most of the results obtained here were from comparison of peak heights with reference samples run under identical chromatographic conditions, usually on the same day. Intercomparison under different chromatographic conditions can, of course, be done only in terms of peak area. All chromatographic data were collected under isothermal conditions using distilled water, aqueous methanol, or an appropriately buffered aqueous solution as eluent.

Certain of the peaks were collected as they came off the column and examined with a Cary 14 spectrophotometer. A semimicro cell with a 10-mm path length was used and permitted the examination of 0.6 ml of solution.

Reference compounds and other chemicals were used as received from various suppliers. The compounds used were *p*-bromophenol and hydroquinone (Eastman Organic Chemical), resorcinol, catechol and methanol (Baker Analyzed Reagent), 4-bromoresorcinol (Aldrich), isopropyl alcohol (Fisher Certified Grade), ethylene (Philips Research Grade), nitrogen (Union Carbide High Purity Grade), and nitrous oxide (Matheson). Buffers were solutions of KH_2PO_4 (Baker Analyzed Reagent) adjusted to a pH of 7.0 with KOH (Baker Analyzed Reagent). Water was triply distilled.

Irradiations were carried out in ^{60}Co γ-ray sources at absorbed dose rates of 6.16×10^{16} or 8.60×10^{17} eV g^{-1} min^{-1}. Most of these studies involved absorbed doses in the range of 6×10^{16}–1×10^{19} eV g^{-1}. Solutions of *p*-bromophenol were purged of oxygen by bubbling with either nitrogen, ethylene, or nitrous oxide at atmospheric pressure prior to irradiation. Irradiated samples were introduced into the liquid chromatograph approximately 1 min after completion of the irradiation.

Results and Discussion

Resolution of Products. In the present study separation of phenol, the dihydroxybenzenes, the parent *p*-bromophenol, and phenolic biphenyls and terphenyls is of principal interest. All of these compounds are well separated on the nonpolar column described in the Experimental Section. The relative retention times of benzene, phenol, and a number of their derivatives are tabulated in ref 8. The monocyclic compounds had well-defined Gaussian shape peaks with peak widths from 1 to 4 times the sample size of 0.19 ml. Under the chromatographic conditions used to examine the monocyclic phenols the higher molecular weight products produced from *p*-bromophenol eluted at very long times and had very wide band widths. Higher molecular weight products appeared as well-defined peaks and were resolved from *p*-bromophenol and other monocyclic aromatic compounds by eluting at $\sim$1 ml/min with 25–40% methanol at a somewhat elevated temperature. Under these conditions the lower molecular weight products were only partly resolved. In general it was not found practical to attempt to analyze for all products in a single chromatogram. Rather, attention was focused on a group of products which eluted in a particular region and conditions adjusted to optimize their resolution.

Consumption of p-Bromophenol. In a given series of experiments peak heights are, in general, reproducible to $\sim$1% so that it is readily possible to determine the yield for the consumption of a particular component with reasonable accuracy in the region of $\sim$20% conversion. Chromatographic separation of the reactant from the products, of course, avoids interference from the latter's absorption which is a problem in the conventional spectrophotometric approach. We can cite, for example, the results of an experiment with 1.4×10^{-4} M *p*-bromophenol (N_2O saturated) irradiated with a dose of 4×10^{18} eV/g. The chromatographic experiment showed that the *p*-bromophenol concentration was reduced to 39% of its initial value. Other products which eluted in the same region had an integrated absorption about equal to that of the remaining *p*-bromophenol. The uv absorption spectrum of the irradiated sample showed, however, a considerable absorption at all wavelengths below 350 nm (*p*-bromophenol which

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(8) K. Bhatia, *Anal. Chem.*, in press.

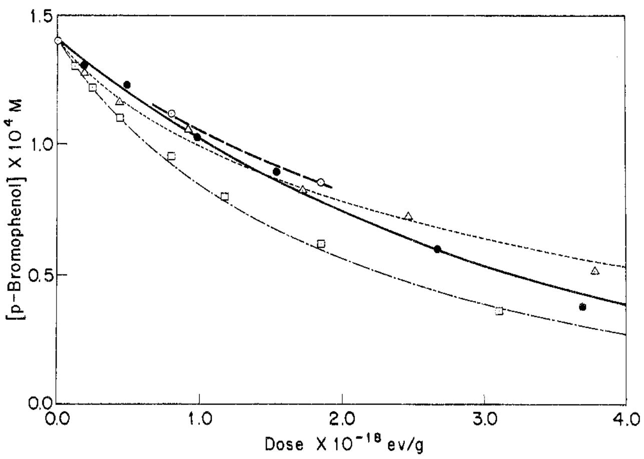

Figure 1. Consumption of *p*-bromophenol in phosphate buffer at pH 7: □, nitrogen purged; △, saturated with N_2O; ●, saturated with C_2H_4; and O containing 10^{-2} *M* isopropyl alcohol and purged with N_2. Curves are calculated by numerical integration of eq I as described in the text.

has a strong maximum at 280 nm does not absorb appreciably above 300 nm) and an increase over the original solution by a factor of 4 at the wavelength of the detector. One obviously cannot obtain significant quantitative analytical data solely from the spectrophotometric results.

Typical reactant consumption curves are given in Figure 1 for 1.4×10^{-4} *M* solutions of *p*-bromophenol buffered to pH 7 with 10^{-3} *M* phosphate and saturated with N_2, N_2O, or C_2H_4. The slopes determined in the region of ~25% consumption correspond to radiation chemical yields for loss of *p*-bromophenol of 2.2, 3.0, and 3.7 molecules/100 eV respectively for the C_2H_4, N_2O, and N_2 saturated solutions. There is, however, considerable curvature to the plots and it is obvious that these values represent only very rough lower limits to initial yields. Examination of the highly irradiated solutions under a variety of column conditions shows that there is no interference with the *p*-bromophenol determinations from impurities and/or other products. We are, of course, primarily interested in determining the initial yields for purposes of comparing them with the yields of radicals produced from the water. The problem of determining these yields from the observed data becomes one of properly taking into account the effect of buildup of product as the reaction progresses.

A simple solution to the above problem is obtained for the case where the rate constant for reaction of the intermediate with the product (k_P) is equal to that for reaction with the initial reactant. In this case it is easily shown that one expects an exponential decrease with dose in the concentration of the reactant.[9] The initial slope is given by $[S]_0 \ln 2/D_{1/2}$ where $D_{1/2}$ is the dose for 50% reaction as determined from a semilogarithmic plot of the data and $[S]_0$ is the original concentration of the solute of interest. In the actual experiment a qualitative indication as to whether the product is more or less reactive than the reactant is obtained from the sign of the curvature of such logarithmic plots. A logarithmic plot of the data on C_2H_4 saturated solutions (the data of Figure 1) shows only a slight negative curvature at the highest doses and gives a $D_{1/2}$ of 2.3×10^{18} eV/g. This value corresponds to an initial radiation chemical yield of 2.6. Logarithmic plots of the other data show marked positive curvature and the initial yields can only be estimated to be greater than 4.1 and 3.3 for the N_2 and N_2O saturated solutions.

If it is assumed that the concentration of reactive product is equal to the loss in concentration of reactant and that the relative rate constants for the competing reactions are describable by a single ratio k_P/k_1 the differential equation describing the change in *p*-bromophenol concentration ([BrPhOH]) with dose is

$$-\frac{d[\mathrm{BrPhOH}]}{dD} = \frac{10G_i}{N}\,\frac{1}{1 + \dfrac{k_P([\mathrm{BrPhOH}]_0 - [\mathrm{BrPhOH}])}{k_1[\mathrm{BrPhOH}]}} \qquad \text{(I)}$$

In eq I $10G_i/N$ is the change of concentration per unit dose at zero dose, D is the dose in eV/g, and G_i is the initial radiation chemical yield in molecules per 100 eV absorbed energy, and N Avogadro's number (the factor 10 is introduced to convert eV/g to units of 100 eV/l.). Integration of this equation does not give an expression of the form $[\mathrm{BrPhOH}] = f(D)$[10] and numerical integration methods are indicated. We have conveniently carried out such integrations on a Hewlett-Packard calculator-plotter using a Runge-Kutta routine. Equation I is obviously an over simplification in that it does not take into account tertiary and higher order reactions or the buildup of product which is not produced from the reactant being investigated. It is, however, a reasonable approximation and is useful in attempting to obtain information on the initial yields. In an approach such as used here two parameters are important: the initial slope and the ratio of the rate constants. One finds that the corrections to the yields at low conversions are not unduly sensitive to the rate constant ratio so that one can proceed by successive approximations after first adjusting this ratio to fit the curvature at high conversions. Curves obtained in this way are given in Figure 1. The initial slopes correspond to radiation chemical yields of 2.65, 4.2, and 5.3 for the C_2H_4, N_2O, and N_2 saturated solutions. The first of these values is quite well known since the semilogarithmic plots show k_P/k_1 to be slightly less than 1 (0.95 was used in calculating the curve). The other two values are somewhat problematical since, in order to fit the data, they require values for k_P/k_1 which seem excessively high (respectively, 4.0 and 2.0).

The simplest case to discuss is that for solutions saturated with C_2H_4 [0.0043 *M*]. The ethylene serves both to remove the H atoms and OH radicals and also prevent secondary reactions of the *p*-hydroxyphenyl radical so that the *p*-bromophenol should be consumed principally by the reactions of the hydrated electrons (the rate constant for this reaction is $6 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$).[3,4] At a *p*-bromophenol concentration of 1.4×10^{-4} *M* the yield for attack on the solute by hydrated electrons is expected to be 2.62 by comparison with the yields observed in the case of CH_3Cl solutions[11] and with other measurements at low solute concentrations (2.63 ± 0.07; see ref 11). The initial yield observed here agrees extremely well. Since bromide ion is

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(9) E. N. Weber and R. H. Schuler, *J. Amer. Chem. Soc.*, **74**, 4415 (1972).

(10) Equation I can be integrated to give an integral of the form *D* = *f*(BrPhOH). Methods similar to those used by D. Perner and R. H. Schuler (*J. Phys. Chem.*, **70**, 2224 (1966)) in treating the radiolysis of HI solutions can be used to construct a plot of [BrPhOH] = *f*(*D*). However, with currently available computational tools it is much more convenient to carry out integrations of kinetic expressions such as I by numerical methods such as those used by I. Mani and R. J. Hanrahan (*J. Phys. Chem.*, **70**, 2233 (1966)) in treating the HI problem.

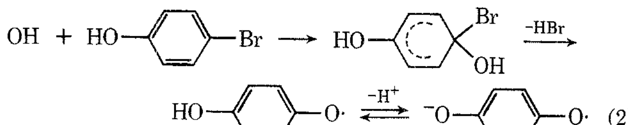
(11) T. I. Balkas, J. H. Fendler, and R. H. Schuler, *J. Phys. Chem.*, **74**, 4497 (1970).

produced with an identical yield[3] it is clear that hydrated electrons react with *p*-bromophenol essentially entirely according to reaction 1. One set of experiments was performed with unbuffered solutions 10^{-3} M in *p*-bromophenol and saturated with ethylene. The results were comparable to those of Figure 1 and the initial yield found to be 2.8. A slightly higher yield (~3.0) is expected since ~20% of the H atoms and OH radicals will escape scavenging by the ethylene but the difference is within the errors involved in interpreting the data.

Two experiments were done on isopropyl alcohol containing solutions and the results are also given in Figure 1. In this case the principal products which can interfere with the initial reaction are phenol (see below), acetone, and hydrogen peroxide. The rate constant for the reaction of e_{aq}^- with phenol is low and the principal problem is the buildup of acetone and hydrogen peroxide both of which have rate constants for reaction with e_{aq}^- a factor ~2 greater than that for *p*-bromophenol.[12] Taking into account the relative yields of these products the effective rate constant ratio to be used in eq 1 is 1.74. The dashed curve in Figure 1 was calculated based on this ratio and an initial yield of 2.65 and constitutes an *a priori* prediction of the dependence of *p*-bromophenol concentration on dose for this case. The agreement is seen to be excellent. These results show that in dilute solution *p*-bromophenol does not react to any significant extent with isopropyl alcohol radicals either by addition or by an electron transfer process.

The yield of 4.2 for consumption of *p*-bromophenol from N_2O saturated solutions is considerably less than the yield expected if all the H atoms ($G(H) = 0.6$) and OH radicals ($G(OH) = 6.0$) react irreversibly with the *p*-bromophenol. The rate constant for OH attack on *p*-bromophenol is very high (7×10^9 M^{-1} sec^{-1})[12] so that one can rule out the competitive reaction of OH with radiation produced product as the principal source of the curvature exhibited in Figure 1. Since OH adds to the aromatic ring to form hydroxycyclohexadienyl type radicals (at least initially) the low initial yields observed would seem to require secondary processes that somehow reverse the loss of *p*-bromophenol which results from the addition process.

There are, of course, four different types of addition sites in this molecule. Addition at the bromine position undoubtedly results in loss of Br^- *via* a dehydrohalogenation process.



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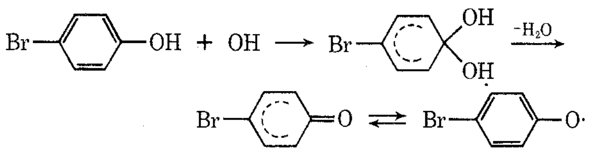
In situ esr experiments,[13] in fact, show that benzosemiquinone radical anion is produced from OH attack in this system. The experiments of Peter and Neta,[3] where a Br^- yield of 3.5 was observed in the absence of OH scavenger, indicate that about 20% of the OH radicals result in Br^- formation and this would seem to be a reasonable contribution for reaction 2. Such reaction must, of course, result in the irreversible destruction of *p*-bromophenol. Attack of OH at the other positions can lead to the formation of the *p*-bromophenoxyl radical *via* loss of water from the addition product. A first-order decay of the dihydroxycyclohexadienyl intermediate with a period of ~100 μsec has been observed in pulse radiolysis experiments on *p*-bromophenol and has been identified with loss of water.[14] Such a process follows quite reasonably if addition occurs at the OH position. Addition of OH at the other positions



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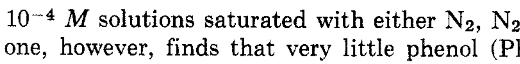
can, however, also lead to the same radical *via* ionization of the original phenolic group followed by charge transfer to the added OH group and subsequent loss of OH^-. It seems likely that the *p*-bromophenoxyl radical produced from these reactions is readily reduced to *p*-bromophenol by reaction with other radiation produced product. If so, the loss of *p*-bromophenol resulting from OH attack obviously need not be quantitative. The high curvature of the data for N_2O solutions in Figure 1 can be readily explained by a rapidly increasing importance of these reduction reactions as the irradiation progresses. A complete quantitative treatment of this system requires detailed and as yet unavailable information on the relative importance of the different reactions. Except for the small contribution of reaction 2, the reactions of OH with the aromatic ring do not directly involve the presence of Br on the ring. The complications involving the reactions of OH in phenolic systems can be better studied by examining phenol itself and will not be discussed here further in any detail.

The N_2 purged system shows complications similar to those in the N_2O system. Since, as we will show below, the *p*-hydroxyphenyl radical produced in reaction 1 reacts rapidly with a second molecule of *p*-bromophenol we expect the initial yield for reactant consumption to be $2G(e_{aq}^-)$ plus the contributions from the reaction of H and OH. The latter can be estimated as approximately one-half the yield from the N_2O saturated system or 2.1. A total initial yield of ~8 is therefore expected whereas the experimental value is considerably lower (only 5.3). In this case product buildup rapidly interferes with the secondary reaction of the *p*-hydroxyphenyl radical with *p*-bromophenol and the initial slope of data such as those given in Figure 1 can easily be severely underestimated. It is seen that for both the N_2 and N_2O saturated cases the secondary chemical reactions are sufficiently complicated that when the loss of the reactant is being examined it is difficult to draw detailed quantitative conclusions at the conversion levels required to make significant observations.

Production of p-Hydroxyphenyl Radical. From the above it would appear that reaction 1 should be an excellent source of the *p*-hydroxyphenyl radical. Reaction of this radical with any source of hydrogen present in the system is expected to produce phenol. In the irradiation of 4.7×10^{-4} M solutions saturated with either N_2, N_2O, or C_2H_4 one, however, finds that very little phenol (PhOH) is produced at dose levels sufficient to consume only a small fraction (<5%) of the *p*-bromophenol ($G(PhOH) < 0.05$). Neither the hydrated electron nor OH radical ap-



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[12] M. Anbar and P. Neta, *Int. J. Appl. Rad. Isotopes*, **18**, 493 (1967).

[13] Experiments of the type described by K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, **75**, 1186 (1971).

[14] E. J. Land and M. Ebert, *Trans. Faraday Soc.*, **63**, 1181 (1967).

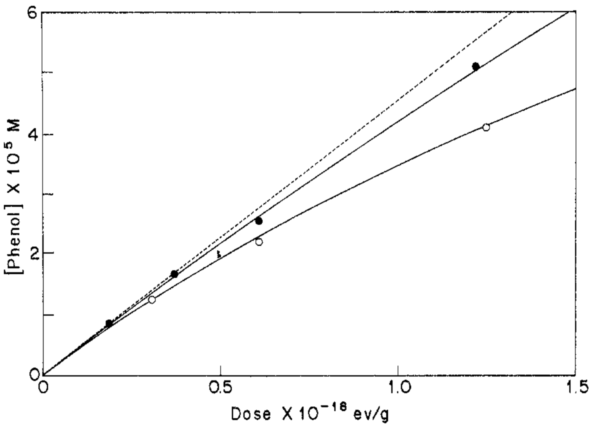


Figure 2. Production of phenol from 1.4 (○) and 4.7 (●) × 10^{-4} *M* pH 7 solutions of *p*-bromophenol containing a 300-fold higher concentration of isopropyl alcohol. Curves are calculated by integration of the right-hand side of eq I using kinetic parameters identical with those used to compute the curves of Figure 1. The dashed line corresponds to an initial yield of 2.75 for phenol production.

pears to be a direct source of phenol. In the case of N_2 purged systems some phenol is produced at higher doses but is attributable to reaction of the *p*-hydroxyphenyl radical with radiation produced product. Irradiation of isopropyl alcohol containing solutions shows a large yield of phenol which presumably results from reaction 4. Competitive studies described below show that an alcohol concentration of ~300 times that of *p*-bromophenol is sufficient to scavenge ~99% of the initial radicals. Yield–dose plots for phenol production from isopropyl alcohol containing solutions are given in Figure 2. The data obtained at 1.4 × 10^{-4} *M* *p*-bromophenol (and isopropyl alcohol 0.04 *M*) exhibit a slight dependence of yield on dose which is related to the curvature of the plot in Figure 1. Taking $d[PhOH]/dD = -d[BrPhOH]/dD$ one can carry out a numerical integration of the right-hand side of eq I to obtain the dose dependence of the phenol concentration. The lower curve of Figure 2 is calculated with parameters identical with those used in Figure 1 and the agreement is seen to be excellent, *i.e.*, in this system the *p*-bromophenol consumed appears entirely as phenol. At a *p*-bromophenol concentration of 4.7 × 10^{-4} *M* (and the isopropyl alcohol concentration increased proportionately to 0.13 *M*) the buildup of product interferes less at a given dose and an almost linear yield–dose plot is observed. One can estimate by trial integrations that for this solution irradiated to a dose of 1.2 × 10^{18} eV/g the observed yield should be 9.5% low as the result of the interfering secondary reactions. Correcting the yield observed by this factor one obtains an initial slope which corresponds to a phenol production yield of 2.75. The correction for the secondary reactions is small and believed to be known to within the overall experimental error of the measurement which is estimated to be ~2%. The upper solid curve is calculated from an integration of eq I on the basis of this initial yield. If we apply a 1% correction for inefficiency of scavenging by isopropyl alcohol the *p*-hydroxyphenyl radical yield resulting from electron attack on 5 × 10^{-4} *M* *p*-bromophenol can be given as 2.78 ± 0.05. This value is slightly higher than that of 2.68 expected at this concentration from the generalizations from the methyl chloride study.[11]

The variation in yield observed over the factor of 3 change in *p*-bromophenol concentration is expected to be only 0.06 units.[11] The experimentally observed increase (0.10) is certainly small although the uncertainties in the determination of the initial yields, particularly at the lower concentration, introduce errors in the difference of the magnitude of the expected effect. Similar experiments at significantly higher *p*-bromophenol concentrations are precluded by the inordinately high concentrations of alcohol required to completely scavenge the *p*-hydroxyphenyl radicals.

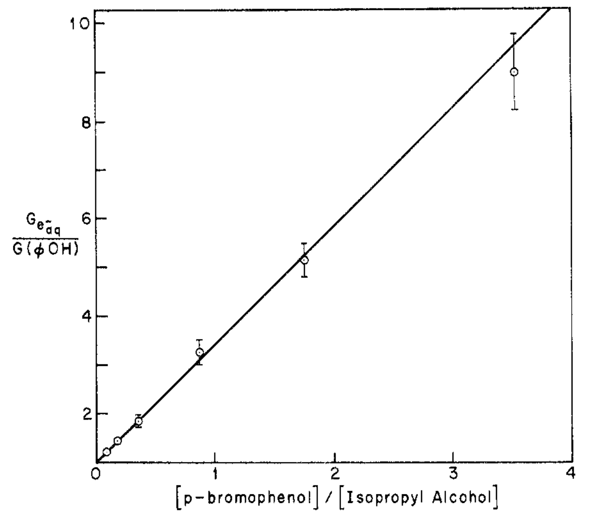
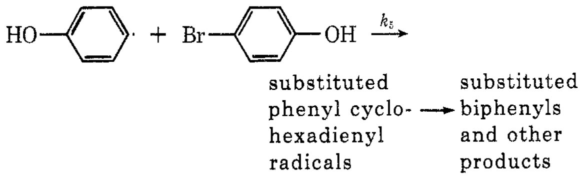


Figure 3. Competitive plot for the production of phenol from solutions containing added isopropyl alcohol (see eq II). The vertical bars represent error limits of ±0.3 × 10^{-6} *M* in the measurement of the phenol concentration. A ratio of 2.4 for the rate constants for addition of *p*-hydroxyphenyl to *p*-bromophenol and abstraction from the alcohol was calculated from the slope of the linear relationship.

Competitive Scavenging of the p-Hydroxyphenyl Radical. In the absence of a hydrogen source the *p*-hydroxyphenyl radical is rapidly removed from the system by addition to *p*-bromophenol and ultimately produces products other than phenol. The competition between reac-



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tions 4 and 5 can be readily carried out by determining the dependence of the yield for phenol production on the relative concentration of the hydrogen donor. This competition is described by

$$\frac{G(e_{aq}^-)}{G(PhOH)} = 1 + \frac{k_5}{k_4}\frac{[BrPhOH]}{[RH]} \qquad (II)$$

where the yield of hydrated electrons is identified with the limiting yield at infinite scavenger concentration, *i.e.*, 2.8. Data for competition between isopropyl alcohol and *p*-bromophenol (the latter at 4.7 × 10^{-4} *M*) are given in Figure 3. The rate constant ratio k_5/k_4 determined from the slope of the linear dependence given in this figure is 2.4 ± 0.2. Cercek and Kongshaug[5] have measured the absolute rate constant for the addition reaction to be 7 × 10^7 M^{-1} sec^{-1}. From this value the absolute rate constant for the abstraction of hydrogen from isopropyl alcohol by *p*-hydroxyphenyl radical is calculated to be 3 × 10^7 M^{-1}

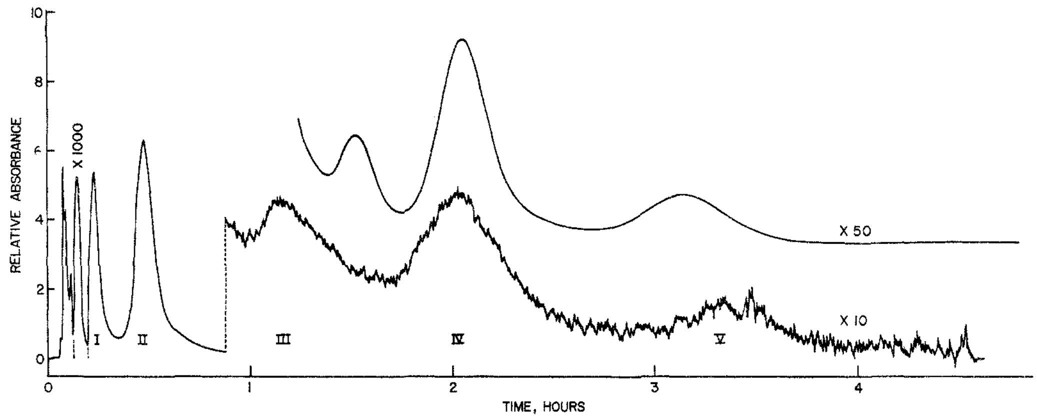
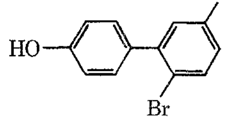


Figure 4. Chromatographic analysis of the substituted biphenyl and terphenyl products: lower trace from a solution of 10^{-2} *M* *p*-bromophenol (nitrogen purged) irradiated to a dose of 5×10^{19} eV/g; upper trace from a solution 5×10^{-2} *M* irradiated to a dose of 10^{20} eV/g. The eluents used were 25 and 40% methanol in water. Chromatograms were recorded at an attenuation of 200 unless indicated otherwise. The *p*-bromophenol peak was recorded at X1000 and the peaks to the left of this are phenol and other low molecular weight products. Peaks identified as I and II are identifiable with the substituted biphenyls similarly labeled in the text. Peaks III, IV, and V are assignable as substituted terphenyls with the structure of IV being given in the text. The noise level in the lower recording is about ten times poorer than that obtained under optimum conditions.

sec^{-1}. These high reaction rates make it impractical to directly examine for *p*-hydroxyphenyl radical by steady-state esr methods since the observation time ($\sim 10^{-4}$ sec) in such experiments would require experiments to be carried out at concentrations below 10^{-4} *M*.

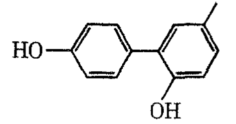
Other Low Molecular Weight Products. Two components in addition to phenol are observed at elution times shorter than that of *p*-bromophenol. The first, which is not significantly separated from the solvent peak, is attributable to quinone and/or hydroquinone.[8] Under the chromatographic conditions used, hydroquinone is partially oxidized to quinone and cannot be quantitatively determined. The upper limit for the formation of hydroquinone is estimated as 0.4 and that for quinone as 0.1. Peter and Neta's results on bromide production indicate that the yield for debromination of *p*-bromophenol by OH radicals is ~ 0.5. The second component has an elution volume $\sim 90\%$ of that of *p*-bromophenol and was not resolved from the starting material sufficiently well and hence quantitative measurements were not possible. The peak is very probably a mixture of 4-bromoresorcinol and 4-bromocatechol. The retention time was, in fact, shown to be comparable to that of 4-bromoresorcinol. Other products are either produced in low yield or have very low extinction coefficients.

Identification of the Addition Products. The substituted phenylcyclohexadienyl radicals produced in reaction 5 will, in part, disproportionate or be oxidized by other means to form the corresponding substituted biphenyls. Only addition at the 2 or 3 position, however, can result simply in the formation of a derivative of biphenyl so that only two such derivatives are expected, *i.e.*



I

and



II

Both I and II have been isolated in previous experiments and identified by comparison of the nmr spectra of their methyl ethers with authentic samples.[6a,b] These compounds have very large extinction coefficients (>5 × 10^3

Figure 5. Absorption spectra of (from top to bottom) *p*-bromophenol, the *p*-bromophenol fraction recovered from the irradiated sample, and central cuts from Peaks I and II of Figure 4. The spectra are displaced upward by an absorbance of 0.4 indicated by the tick marks on the left. The *p*-bromophenol from the irradiated sample was taken as a broad cut and shows the presence of a component which absorbs below 320 nm. Peaks I and II are seen to be free of any significant contribution from *p*-bromophenol.

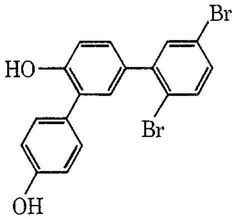
TABLE I: Spectral Data on Chromatographic Peaks I, II, and IV

λ_{max}, nm		Extinction coefficients, M^{-1} cm^{-1}	
Present work	ref 6[a]	Present work	ref 6[a]
Peak I. 2-Bromo-5,4′-dihydroxybiphenyl			
230	230	12,200	11,400
253	252	(5,800)[b]	5,800
284	284	2,200	2,300
Peak II. 5-Bromo-2,4′-dihydroxybiphenyl			
203		54,000	
223	224	25,500	22,400
254	259	(14,800)[b]	14,800
295	295	7,600	7,000
Peak IV. 5-Bromo-2,4′,4′′-trihydroxy-*m*-terphenyl[c]			
232	223	27,000	29,500
253	256	(28,000)[b]	28,000
298	295	11,600	12,800

[a] Values reported by Namiki, *et al.*, (ref 6) for authentic methyl ether derivatives of I, 2-bromo-5,4′-dihydroxbiphenyl; II, 5-bromo-2,4′-dihydroxybiphenyl; and IV, 5-bromo-2,4′,4′′-trihydroxy-*m*-terphenyl. It has been shown in ref 6b that the parent compound and its methyl ether have essentially the same absorption spectrum. [b] Assumed, other extinction coefficients normalized to these values. [c] The three other isomers of this terphenyl reported in ref 6 have extinction coefficients of 34,000, 13,200, and 11,200 M^{-1} cm^{-1} at 254 nm.

M^{-1} cm^{-1}) at 254 nm and it is expected that they should be readily observable in an appropriate chromatographic experiment. As is illustrated in Figure 4 we find for a 10^{-2} M solution of *p*-bromophenol irradiated to a dose of 5 × 10^{19} eV/g two large peaks (labeled I and II) with retention volumes ~1.6 and 3.2 times that of the *p*-bromophenol. Samples of 0.6 ml taken at the center of each of these peaks were examined spectrophotometrically. Comparison of the absorption spectra given in Figure 5 with the data reported by Komiya, *et al.*,[6b] (see Table I) allows identification of peaks I and II as 2-bromo-5,4′-dihydroxybiphenyl and 5-bromo-2,4′-dihydroxybiphenyl, respectively. Saturation of the solution with N_2O reduces the intensity of peaks I and II by an amount equal to the fractional scavenging of e_{aq}^- by the N_2O. A comparison at 10^{-3} M *p*-bromophenol of N_2 and N_2O saturated solution ($[N_2O]$ = 0.02 M) showed that >95% of peak II was essentially eliminated by the competitive reaction of e_{aq}^- with the N_2O. These products do not appear to be (nor are they expected to be) produced by the reactions of OH. No other products from OH reaction with retention volumes greater than that of *p*-bromophenol were detected in these experiments.

Three additional peaks labeled III, IV, and V also appear in the chromatogram at longer retention times. At the dose levels employed in the experiments illustrated in Figure 4 tertiary reactions involving the substituted biphenyls are important (see below) and it seems likely that these peaks all represent substituted terphenyls produced in such tertiary reactions. Eight derivatives of terphenyl are possible products of the reaction of *p*-hydroxyphenyl radical with I and II. The absorption spectra of the methyl ethers of four have been reported by Namiki, *et al.*[6a,c] Using the 0–0.1 A scale expansion slide wire of the Cary 14 spectrophotometer we were able to obtain the spectrum of peak IV in Figure 4 from the 0.05 M sample irradiated to a dose of 10^{20} eV/g. The data are reported in Table I. As is evident from Table I, peak IV is assignable to 5-bromo-2,4′,4′′-trihydroxy-*m*-terphenyl (IV). Product IV would be produced by addition at the 3′ position of II. We have not attempted to identify the other peaks. It is pointed out that the initial addition reaction (reaction II) produces a cyclohexadienyl radical which is not capable of further direct reaction with *p*-bromophenol. As a result the terphenyl products must be produced by tertiary reactions rather than by a chain of addition events in which the product radical simply adds to another *p*-bromophenol. These terphenyls are, therefore, a trivial result of the buildup of product and have nothing to do with the initial reactions in the *p*-bromophenol system.



IV

Dose Dependence for the Formation of Substituted Biphenyls. The buildup of 5-bromo-2,4′-dihydroxybiphenyl (peak II) with dose is illustrated in Figure 6 for three concentrations of *p*-bromophenol. At the highest concentration the production of this biphenyl is essentially linear with dose and the slope should represent the initial yield. Although we did not have a reference sample available the sensitivity of the detector could be estimated from the extinction coefficients given by Namiki, *et al.*[6a] In taking the chromatogram of Figure 4 the entire peak (9.14 ml) was collected and found from the spectrophotometric measurement to contain 1.2 × 10^{-7} M 5-bromo-2,4′-dihydroxybiphenyl. The concentration in chromatographic sample (0.189 ml) was 48.5 times greater. This measurement allowed the chromatographic sensitivity to be determined as 2.7 × 10^{-7} M/unit peak height (unit peak height = absorbance of 0.0002). The initial slope for the formation of this product was then determined in the region of 10^{18} eV/g for the solution 0.05 M in *p*-bromophenol. The slope corresponds to G(5-bromo-2,4′-dihydroxybiphenyl) = 1.6. Such a yield represents 47% of the hydrated electrons which should be scavenged by the *p*-bromophenol at this concentration ($G(e_{aq}^-)$ = 3.4 at $k[S]$ = 3 × 10^8 sec^{-1}).[11] The accuracy here is primarily limited by the available information on the extinction coefficient which is estimated to be good only to ~20%.

The yield of 2-bromo-5,4′-dihydroxybiphenyl can be estimated from the above by comparing the relative areas of peaks I and II. The ratio of the heights of peaks I and II does not depend on dose in any obvious way so that it is believed proper to make a comparison at the relatively high dose of Figure 4. Correcting the relative peak areas of 0.35:1 for the relative extinction coefficients at 254 mμ of 0.39:1 (Table I) one finds that the yield of I is 0.79 that of II. From this ratio G(2-bromo-5,4′-dihydroxybiphenyl) is 1.3. In the initial stages compounds I and II account for essentially all (*i.e.*, 85 ± 20%) of the *p*-hydroxyphenyl radicals produced in reaction 1 so that addition must occur predominantly at the positions ortho and meta to the hydroxyl group of *p*-bromophenol. The cyclohexadienyl type radicals produced in reaction 5 (or products formed from them) ultimately must be almost quantitatively oxidized in the subsequent reactions. It was pointed out earlier that in the absence of scavenger the *p*-bromo-

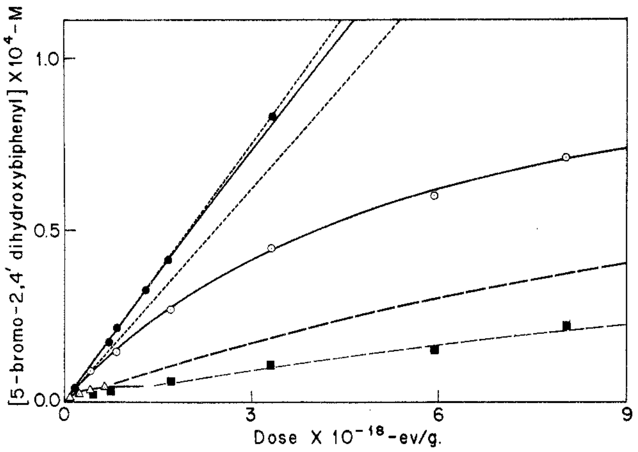
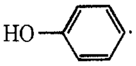


Figure 6. Production of 5-bromo-2,4′-dihydroxybiphenyl in nitrogen purged solutions as a function of dose. Initial *p*-bromophenol concentrations were (●) 4.7 × 10^{-2}, (○) 2 × 10^{-3}, and (△) 10^{-4} *M*. Data (■) for solutions containing 2.5 × 10^{-3} *M* *p*-bromophenol and 1.2 × 10^{-2} *M* isopropyl alcohol are also given. The solid curves were calculated by integration of eq III. The initial slopes (given by the dashed lines) correspond to yields, respectively, of 1.6 and 1.3 at the highest and the lower two *p*-bromophenol concentrations. The heavy dashed line corresponds to the yields predicted for the alcohol containing solutions. The experimentally observed yields are lower indicating that in the alcohol containing system the intermediate radicals are less efficiently oxidized by the secondary reactions than in the alcohol free system.

phenoxyl radical resulting from OH attack appears to be reduced to a considerable extent back to *p*-bromophenol. The high yield of substituted biphenyls noted here appears to result from a complementary oxidation of the phenyl cyclohexadienyl radicals formed in reaction 5. The similarity in the yields of I and II indicates very little selectivity in the addition reaction (reaction II).

A comparison of the relative areas of peaks IV and II in the lower curve of Figure 4, together with the appropriate extinction coefficients (Table I), shows that peak IV corresponds to a yield of ~5% of that of II. The extinction coefficients at 254 nm of the other substituted terphenyls expected to be formed are about the same or lower than that of IV (lower by a factor of ~3 in certain instances; see footnote *c* in Table I) so it is possible that the smaller peaks in the chromatogram actually correspond to comparable amounts of product. Since IV is the end product of only one out of ten possible reaction paths it is reasonable to estimate the total amount of terphenyl product to be 20–30% of II. At the dose involved this particular experiment, however, only ~20% of the *p*-bromophenol has been consumed. Since the relative concentrations of biphenyl product is low relative to *p*-bromophenol a high yield of terphenyl product implies that the *p*-hydroxyphenyl radical reacts considerably more rapidly with I and II than with *p*-bromophenol itself. This tentative conclusion appears to be substantiated by the kinetic treatment of the dose dependence given below.

The data of Figure 6 show that at concentrations of *p*-bromophenol in the region of millimolar and less, the rate of formation of product II decreases with dose in the region of 10^{18} eV/g and higher. At such high doses the *p*-hydroxyphenyl radical can react with any of the products including the biphenyls, the molecular H_2O_2, and the products of the OH reactions. The yield of *p*-hydroxyphenyl radical will itself decrease because of reactions of e_{aq}^- with radiation produced product as has been illustrated in Figure 2. A complete kinetic treatment of this complex situation is obviously very difficult and requires a considerable amount of data not yet available. Since it appears that *p*-hydroxyphenyl radical reacts considerably more rapidly with the biphenyl derivatives than with *p*-bromophenol we will treat the dose dependence as a consequence of the simple competition between reaction 5 and 6. If we assume that the fraction of reaction 5 that results in the formation of II is f_{II} and that the rate constants for the removal of both I and II by reaction 6 are identical then


+ substituted biphenyls $\xrightarrow{k_6}$ substituted terphenyls (6)

$$\frac{d[Br(PhOH)_2]_{II}}{dD} = \frac{10G(HOPh\cdot)}{N} f_{II} \left[1 - \frac{k_6[Br(PhOH)_2]_{II}}{f_{II}k_5[BrPhOH]}\right] \Bigg/ \left[1 + \frac{k_6[Br(PhOH)_2]_{II}}{f_{II}k_5[BrPhOH]}\right] \quad (III)$$

In eq III $G(HOPh\cdot)$ is the yield of *p*-hydroxyphenyl radicals which, from the above results, should be approximated by

$$G(HOPh\cdot) = G(e_{aq})^- \frac{1}{1 + \dfrac{k_p([BrPhOH]_0 - [BrPhOH])}{k_1[BrPhOH]}} \quad (IV)$$

The quantity $(10G(HOPh\cdot)_0/N)f_{II}$ can be determined from the initial slope in the absence of added solute (see above) and the ratio of rate constants k_6/k_5 by appropriately fitting the dose dependence. The solid curves in Figure 6 were obtained by numerical integrations of eq III, for three concentrations of *p*-bromophenol. A relatively high rate constant for reaction 6 (~3 × 10^8 M^{-1} sec^{-1}) is indicated by the pronounced curvature of the results at 2 × 10^{-3} *M* and is in accord with a high yield for formation of terphenyl products in secondary processes as noted above.

While the treatment given here greatly oversimplifies the actual situation it does show that competition with radiation produced product should not be important at high concentrations of *p*-bromophenol (>10^{-2} *M* for doses ~10^{18} eV/g). For the experiments at 2 × 10^{-3} *M* *p*-bromophenol the measurements at even the lowest doses used here are slightly affected by product buildup. Approximate, but reasonably accurate, corrections for the dose dependence can be estimated from the calculations. By applying these corrections to the measured yields the initial slope is found to be ~20% lower than that at 5 × 10^{-2} *M*. An effect of this magnitude is expected from the concentration dependence for scavenging electrons from within the spurs.[11] For experiments at 10^{-4} *M* the dose dependence is so severe that no reasonable estimates of the initial yield can be obtained from the experimental measurements.

Effect of Scavengers on the Biphenyl Products. Addition of a solute that reacts with *p*-hydroxyphenyl radical such as isopropyl alcohol causes a pronounced decrease in

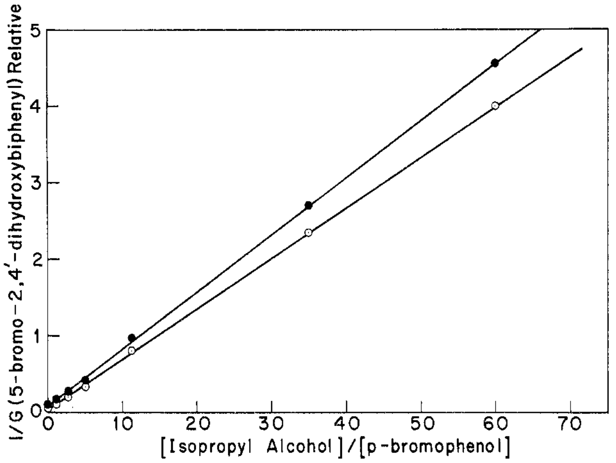


Figure 7. Competitive plot of the dependence of the yield of 5-bromo-2,4′-dihydroxybiphenyl on the ratio of the concentrations of isopropyl alcohol and *p*-bromophenol (see eq VI) ●, observed at a dose of 9 × 10^{18} eV/g; ○, from calculated initial yields. The ratio of k_4/k_5 calculated from the slope-intercept ratio of the lower plot is 1.3. Although the dependence on [RH]/[BrPhOH] seems to follow simple competitive kinetics the rate constant ratio appears to be anomalously high because of changes in the radical termination process.

the formation of the biphenyl products. For example, the yield of 5-bromo-2,4′-dihydroxybiphenyl from a solution 2 × 10^{-3} *M* in *p*-bromophenol and 0.1 *M* isopropyl alcohol is only 2% of that in the absence of the alcohol. Appropriate modification of eq III to take into account the competitive effect of reaction 4 gives

$$\frac{d[\mathrm{Br(PhOH)_2}]_{\mathrm{II}}}{dD} = \frac{10G(\mathrm{HOPh}\cdot)}{N} f_{\mathrm{II}}\left[1 - \frac{k_6[\mathrm{Br(PhOH)_2}]_{\mathrm{II}}}{f_{\mathrm{II}}k_5[\mathrm{BrPhOH}]}\right] \Bigg/ \left[1 + \frac{k_4[\mathrm{RH}]}{k_5[\mathrm{BrPhOH}]} + \frac{k_6[\mathrm{Br(OH)_2}]_{\mathrm{II}}}{f_{\mathrm{II}}k_5[\mathrm{BrPhOH}]}\right] \quad \mathrm{(V)}$$

The competition can be expressed in terms of the initial yields as

$$G_{\mathrm{i}}[\mathrm{Br(PhOH)_2}]_{\mathrm{II}} = G(\mathrm{e_{aq}}^-)f_{\mathrm{II}}\frac{1}{1 + \dfrac{k_4[\mathrm{RH}]}{k_5[\mathrm{BrPhOH}]}} \quad \mathrm{(VI)}$$

where k_5 is the rate constant for reaction of the *p*-hydroxyphenyl radical with the *p*-bromophenol. It would appear that, in principle, the rate constant ratio k_4/k_5 should be determinable from measurements of the slopes and intercepts of plots of $1/G_{\mathrm{i}}[\mathrm{Br(PhOH)_2}]_{\mathrm{II}}$ *vs.* [RH]/[BrPhOH]. For a number of reasons it is attractive to attempt to measure the relative rate constants for the reaction of *p*-hydroxyphenyl radical with various solutes based on their effect in reducing the formation of the substituted biphenyls. In contrast to the measurements of phenol production, competitive experiments can be carried out at relatively high scavenger concentrations since one can quantitatively measure small concentrations of the substituted biphenyls. One can also examine substances such as ethylene which give no easily measurable product. Only measurements of the relative yields in the presence and absence of a scavenger are required for the determination of k_4/k_5 from eq VI so that knowledge of the extinction coefficients or the absolute calibration of the apparatus is not involved.

Competitive experiments were carried out with isopropyl alcohol and the results are given in Figure 7. With correction of the experimentally observed data (the solid circles) to zero dose by factors determined from appropriate trial integrations of eq V, the open circles of Figure 7 were obtained. From the slope and intercept an apparent value of 1.3 was obtained for k_4/k_5. This value is considerably higher than that of 0.42 given above from measurements on phenol production. The discrepancy is far outside the errors involved in the interpretation of the data in terms of the initial slopes. On reflection it is obvious that the difficulty lies in the importance of the term f_{II} in eq VI. Basically the efficiency for the oxidation of the phenyl cyclohexadienyl radicals produced in reaction 5 is dependent on the nature of the radical termination process. Addition of the alcohol results in the replacement of the easily reduced *p*-bromophenoxyl radicals (see above) by isopropyl alcohol radicals. This change apparently causes a decrease in the efficiency of the disproportionation or other oxidation processes that result in the production of compounds I and II from the radicals. This effect is also seen in Figure 6 where the heavy dashed curve gives the dose dependence for the formation of II in a system containing isopropyl alcohol which is predicted from the parameters determined in the alcohol free system and the value of k_4/k_5 determined from the phenol production measurements. The experimentally observed yields are considerably lower and can be accounted for if f_{II} is reduced to 0.30 (the light dashed curve). Further experiments are in order to examine the effects of changes in the termination processes on f_{II} since if this can be elucidated the approach outlined here should provide ready access to a large amount of comparative rate information on the reactions of aromatic radicals.