Photocleavage of Phenoxyphenols and Bromophenols[1]

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Abstract: Flash photolysis of three bromophenols and five aryloxyphenols in water does not appear to involve the phenolic site directly—the hydrated electron, produced with other phenols, was not detected here. Under steady irradiation (2537 A) in water, the bromophenols yield dihydroxybenzenes and *sym*-dihydroxybiphenyls which derive from carbon–bromine bond cleavage. Flash spectroscopy indicates that the phenoxyphenols first give hydroxyphenoxy radicals, by shearing off the phenyl radical. Under steady irradiation, the phenoxyphenols yield dihydroxybenzenes, phenyldihydroxybenzenes, and in one case a tetrahydroxybiphenyl. These preferred bond cleavage processes turn out to be most plausible on thermochemical grounds. For the mechanism, it is suggested that photolysis in both series produces a radical pair, *e.g.*, eq 1 and 12. The radical pair, ($C_6H_5\cdot\cdot OC_6H_4OH$), may reorient within its solvent cage and then collapse to give selected phenyldihydroxybenzenes. Otherwise, this pair and the one formed from the bromophenols, ($Br\cdot\cdot C_6H_4OH$), may react directly with the solvent or break up (out of the cage) and then react.

Recent work has shown that the flash photolysis in water of phenolic compounds such as phenol, the cresols, the dihydroxybenzenes, the dihydroxybiphenyls, tyrosine, and methoxyphenol among others produces the hydrated electron.[3–5] Two families, the phenoxyphenols and the bromophenols, are different.[4] In order to understand this variable behavior, the transient products of photolysis and the products of steady irradiation of typical members of these two groups have been studied in detail.[4–6] Elsewhere we report on the phenols.[7] Here we report on the photochemistry of some aryloxyphenols and the bromophenols.[8]

Experimental Section and Results

The dihydroxybenzenes were used as purchased. The hydroxydiphenyl ethers and the bromophenols were recrystallized or redistilled before use. The sources of the compounds are given in Table I and in the table of R_f values of the companion paper.[7] Molecular extinction coefficients of some of the compounds at 2538 A have been given previously.[7]

Table I. R_f Values by Thin Layer Chromatography (Tlc)[a]

Compound	Source	Elution method 1	3	4	6	7
2-Bromophenol	*b*	7.0	4.8		6.3	8.0
3-Bromophenol	*b*	6.5	3.2		5.3	7.2
4-Bromophenol	*b*	6.2	2.6		5.4	7.3
2,3-Dihydroxybiphenyl	*c*	5.7		3.9	5.3	7.7
2,4-Dihydroxybiphenyl	*d*	4.7		1.9	3.0	5.2
2,5-Dihydroxybiphenyl	*b*	4.9		2.6	3.5	5.3
2,6-Dihydroxybiphenyl	*e*	6.0		4.9	4.7	6.7
3,4-Dihydroxybiphenyl	*b*	5.2		2.5	3.7	5.8
Diphenylene oxide	*f*	9.2	7.8	8.9	9.9	9.9

[a] For a more extensive list of R_f values and the tlc elution methods, see ref 7. The compounds were purchased or synthesized by methods given in the citations. [b] Purchased. [c] C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, **14**, 798 (1949). [d] C. M. Suter and P. G. Smith, *J. Am. Chem. Soc.*, **61**, 166 (1939). [e] This study. [f] M. Tomita, T. Nakano, and K. Hirai, *J. Pharm. Soc. Japan*, **74**, 934 (1954); *Chem. Abstr.*, **49**, 10964 (1955).

Stedronsky prepared 2,6-dihydroxybiphenyl for us. A mixture of 2,6-dimethoxybromobenzene[9a] (5.0 g, 0.023 mole), iodobenzene (9.4 g, 0.046 mole), and Baker precipitated copper powder (40 g) was heated for 15 hr at 250° in a sealed glass tube (*ca.* 15 ml). The solid residue was cooled, crushed, and extracted with ether. Work-up of the extract gave a reddish oil which was distilled at 115–122° (0.07 mm). The distillate was recrystallized to give colorless needles (from ethanol–water), mp 87–88°. A proton count of the methoxy (τ 6.42) to aryl protons was that expected for 2,6-dimethoxybiphenyl.

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.50; H, 6.54. Found: C, 78.74; H, 6.58.

The dimethoxybiphenyl was hydrolyzed with hydriodic acid to give 2,6-dihydroxybiphenyl, mp 118–119.5° (lit.[9b] mp 118.5–119.5°) from methanol–water.

The flash photolysis apparatus and technique has been described previously.[5] In this work, solute concentrations were chosen so that the optical density of the maximum absorption was *ca.* 1.0 in a 1-cm cell.

In the steady irradiation studies, we followed the general procedure given for the phenols.[7] The compounds were dissolved in water or cyclohexane (300 ml), then saturated with oxygen or flushed with nitrogen. A low-pressure mercury resonance lamp dipping into the solutions was our 2537-A source.[7] After irradiation, the solutions were acidified and extracted with ether. These extracts were evaporated and the residues

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(1) This work has been supported by the National Institutes of Health, U. S. Public Health Service.

(2) To whom inquiries should be addressed.

(3) L. I. Grossweiner, G. W. Swenson, and E. F. Zwicker, *Science*, **141**, 805 (1963).

(4) (a) L. I. Grossweiner and H. I. Joschek, Advances in Chemistry Series, No. 50, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1965, p 279. (b) H. I. Joschek and L. I. Grossweiner, *J. Am. Chem. Soc.*, **88**, 3261 (1966).

(5) (a) G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, **61**, 708 (1965); (b) L. I. Grossweiner and W. A. Mulac, *Radiation Res.*, **10**, 515 (1959); (c) L. I. Grossweiner and E. F. Zwicker, *J. Chem. Phys.*, **34**, 1417 (1961); *J. Phys. Chem.*, **67**, 549 (1963).

(6) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963).

(7) H. I. Joschek and S. I. Miller, *J. Am. Chem. Soc.*, **88**, 3273 (1966).

(8) (a) M. S. Kharasch, G. Stampa, and W. Nudenberg, *Science*, **116**, 309 (1952). (b) F. L. Bach, Abstracts of Papers Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 9S. This work is on an analogous system: the photolysis of diphenyl ether gives phenol, benzene, 2,3-dimethyl-2,3-butanediol, *o*- and *p*-phenylphenol. The mechanism suggested is analogous to ours. Flash spectra of diphenyl ether in our laboratory indicates that the hydrated electron and the phenoxyl radical are not produced. The quantum efficiency of the process must be low since the characteristic flash spectrum of the phenoxyl radical is not observed.[4]

(9) (a) H. Lettré and A. Jahn, *Ber.*, **85**, 350 (1952); (b) H. Budzikiewicz and W. Metlesics, *J. Org. Chem.*, **24**, 1125 (1959).

Table II. Products of the Steady Irradiation of the Hydroxybiphenyl Ethers (10^{-3} *M*) at 10–20°[a,b]

Irradiation products	2-Hydroxydiphenyl ether 3 hr, O_2–H_2O	3 hr, N_2–H_2O	2 hr, N_2–C_6H_{12}	3-Hydroxydiphenyl ether 3 hr, O_2–H_2O	14 hr, N_2–H_2O	23 hr, N_2–C_6H_{12}	4-Hydroxydiphenyl ether 0.5 hr, O_2–H_2O	3 hr, O_2–H_2O	3 hr, N_2–H_2O	3 hr, N_2–C_6H_{12}
Hydroquinone							−	+	+	Tr
Resorcinol				+	+	Tr				
Catechol	+	+	+							
3,3′,4,4′-Tetrahydroxybiphenyl		+								
2,3-Dihydroxybiphenyl	+	+	+							
2,4-Dihydroxybiphenyl				+	+					
2,5-Dihydroxybiphenyl							+	+	+	
2,6-Dihydroxybiphenyl				+	+					
3,4-Dihydroxybiphenyl	+	+	+							
Diphenylene oxide	−	−	−							
Phenol	−	−	−	−	−		−	−	−	
4,4′-Dihydroxybiphenyl	−	−	−	−	−		−	−	−	
2,4′-Dihydroxybiphenyl	−	−	−	−	−		−	−	−	
2,2′-Dihydroxybiphenyl	−	−	−	−	−		−	−	−	

[a] Of necessity, the tlc analyses were qualitative. If substantial quantities of a compound were present this is indicated by a plus (+); if very small amounts were found, trace (Tr) is used; compounds looked for but not found are labeled minus (−). Where there is a blank, this means that no special effort was made to check all of these compounds; the tlc plates were routinely examined, of course, for their presence. There were other products that could not be identified either because tlc reference compounds were unavailable or because our analyses were unsuitable. [b] Horizontal comparisons of relative amounts of products in a given run are meaningful in an approximate sense. Vertical comparisons are not so safe but might be made relative to a given compound.

were analyzed by thin layer chromatography (tlc). The elution methods have been described.[7] The R_f values of the reactants and possible products in Table I should be regarded as a supplement to the main list.[7]

Since our tlc technique was designed primarily for phenolic compounds, other products were not identified. It was apparent, however, that the product mixtures from the phenoxyphenols in water were "clean," that is, there was little darkening of the solution under irradiation. On the other hand, irradiation of the bromophenols produced large quantities of tarry products. In cyclohexane, the photolytic products from the hydroxydiphenyl ethers were highly contaminated with dark materials, so much so that only small amounts of products were available for examination (see Table II).

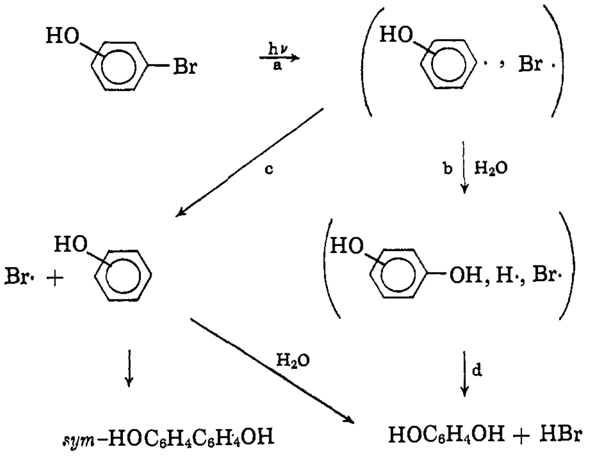
Bromophenols. The products of steady irradiation are given in Table III. 4-Bromophenol gave 4,4′-dihydroxybiphenyl and hydroquinone, 3-bromophenol gave resorcinol, and 3,3′-dihydroxybiphenyl and 2-bromophenol gave catechol and 2,2′-dihydroxybiphenyl. We also noticed that, on flash photolysis, the pH of the bromophenol solutions decreased from *ca.* 6.0 to *ca.* 3.9 after ten flashes; presumably hydrogen bromide was formed.

Table III. Products of the Steady Irradiation of the Bromophenols (2×10^{-3} *M*) in Deaerated Water at 10–20°[a,b]

Irradiation products	2-Bromo- 1.0 hr	10 hr	3-Bromo- 7.0 hr	4-Bromo- 1.0 hr	5.0 hr
2,4-Dihydroxybiphenyl	−	−	−	−	−
4,4′-Dihydroxybiphenyl	−	−	−	−	*
2,2′-Dihydroxybiphenyl	−	*	−		−
Hydroquinone	−	−	−	+	+
Catechol	+	+	−	−	−
Resorcinol	−	−	+	−	−
3,3′-Dihydroxybiphenyl			Tr		

[a] The meanings of the symbols used in this table are described in footnotes *a* and *b* of Table II, with the addition of an asterisk (*) to note the presence of a compound.

Previously it was noted that aromatic compounds, *e.g.*, phenol, whose ionization potentials were relatively low, were also likely to give up a hydrated electron on irradiation.[4a] Although the bromophenols have sufficiently low ionization potentials,[10] they do not give the electron.[4a] It is true that bromophenol has a relatively high scavenging rate for the hydrated electron, that is, *ca.* 2.7×10^9 M^{-1} sec^{-1} at *ca.* 25° or *ca.* 700 times that of phenol,[11] but this is not high enough to preclude observation of the hydrated electron by flash spectroscopy.[3,4] The fact that bond cleavage takes place according to eq 1 is plausible: although 113 kcal/mole (2537 A) may be accepted by the molecule, *ca.* 85 kcal/mole would be required to yield the electron[7] but only *ca.* 67 kcal/mole would be required to break the carbon–bromine bond.[12]



(1)

A proposed mechanism for the photolysis of bromophenols in water is given in eq 1. A radical pair is produced, initially with excess energy of *ca.* 46 kcal/

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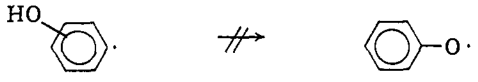
[10] G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

[11] M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964).

[12] Pertinent aspects of the thermochemistry in this paper are in the Appendix. All figures for bond dissociation energies or heats of formation will have the units kcal/mole.

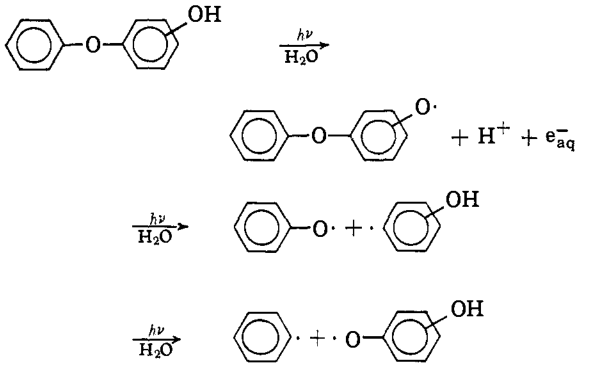
mole. One or other of the radicals then reacts with water and generates another radical pair as in step b. Besides the reactions in or near their solvent cage, the radicals also must separate as in c. The hydroxyphenyl radical may then "wait" until it collides favorably with a hydroxyphenyl radical, a water molecule, or possibly another radical pair. Among the possibilities we considered, the thermochemistry of the hydroxyphenyl radical reactions of eq 1 seems to be the most favorable.[12] Possible rearrangements of type 2 do not occur, first



(2)

because the phenoxyl radical could not be detected by flash photolysis and second because the typical coupling products of the phenoxyl radical were absent.[7] For each bromophenol, there was only one symmetric carbon–carbon dimer or dihydroxybenzene corresponding to the starting material.

Phenoxyphenols. At the outset, three possible photolytic paths might be considered for the phenoxyphenols



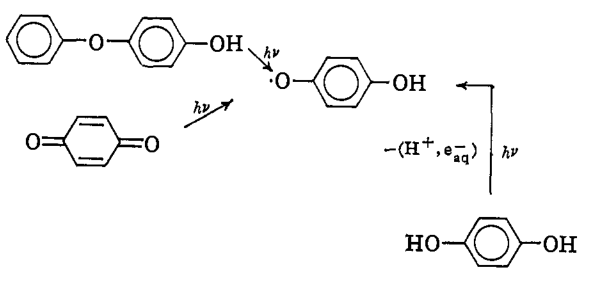
(3)

(4)

(5)

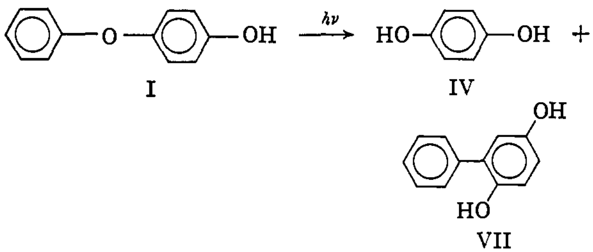
All of the evidence, based on flash photolysis, products, and thermochemistry, favors process 5.

Although spectral properties[5,6] of some of the transient species produced in the photolysis of the phenoxyphenols were measured for this study, they have been listed elsewhere.[4b] The electron, as in eq 3, or the phenoxyl radical, as in eq 4, were not observed.[4b] Both have characteristic spectra which are known: the band maximum of the hydrated electron is at *ca.* 720 mμ; the maxima of the phenoxyl radical are at 362, 383, and 399 mμ.[4b,5a,6a] Each hydroxyphenoxyl radical was produced from at least two sources, that is, the dihydroxybenzene and the phenoxyphenol. In each case, the photolysis of phenoxyphenols or dihydroxybenzenes gave identical hydroxyphenoxyl radicals, but only the dihydroxybenzenes also gave the hydrated electron.



(6)

The over-all reactions of the phenoxyphenols are best given as follows. Similar products were obtained



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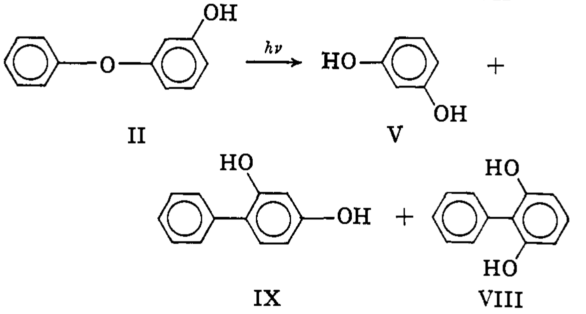

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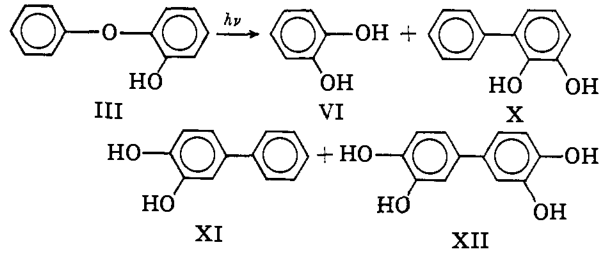
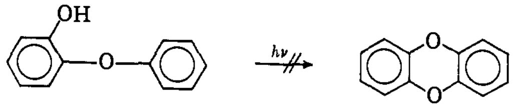


(9)

from each phenoxyphenol in the presence or absence of oxygen in aqueous solution (see Table II). Product separation in cyclohexane solvent was complicated by tar formation, but in one case at least, eq 9 seemed to apply.

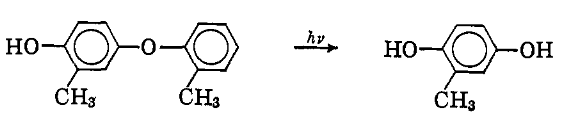
The possibility of one other reaction was checked.



(10)

Although several chemical oxidations of this type have been described,[13] no diphenylene oxide could be found in the products.

A few experiments were carried out with tolyloxycresols in water. The irradiations of 2-hydroxy-4',5-dimethyldiphenyl ether and 4-hydroxy-2',3-dimethyldiphenyl ether produce 3,4- and 2,5-dihydroxytoluene, respectively. These products are consistent with the cleavages in eq 7–9, *e.g.*



(11)

Clearly, it is improbable that process 3 would lead to the observed products (eq 7–9, Table II) so that (3) must be discarded on this count. As for eq 4, the characteristic products expected from the intermediate radicals were not obtained. The reactions of phenoxyl have been discussed elsewhere.[7] The hydroxyphenyl radicals ($HOC_6H_4\cdot$) have not yet been identified spectrally but their reactions are known in part from the

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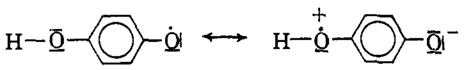
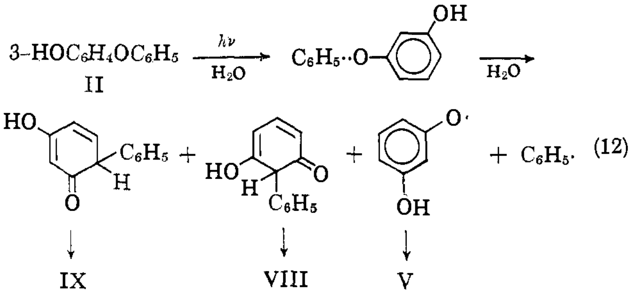
[13] H. Musso, *Angew. Chem. Intern. Ed. Engl.*, **2**, 723 (1963).

photolyses of the bromophenols (eq 1): these radicals lead to *sym*-dihydroxybiphenyls which were not detected. We are left with eq 5 which can plausibly lead to the observed products. A mechanism will be given presently.

Finally, it was possible to piece together thermochemical data which indicated that eq 5 should be favored over eq 4 by a small margin and over eq 3 by *ca.* 15 kcal/mole in the enthalpy of reaction.[12] One additional factor, not otherwise mentioned, should also favor (5) over (4). This arises from the conjugation in the product of (5). As for the hydroxyphenyl radical ($HOC_6H_4\cdot$) in eq 4, we do not consider that its unpaired electron can interact appreciably with the ring π electrons.



Concerning the mechanism of the photolysis, we believe that following the absorption of energy (113 kcal), a radical pair is formed, *e.g.*



(12)

In this example, the partners in the first radical pair could become reoriented within the solvent cage to give secondary radical pairs, then the dienones. In this process, the phenyl radical ends up three or four atoms away from its original position. At the same time, excess energy in the radical pair(s) is presumably dissipated rapidly by collisions with the solvent molecules.

A second alternative for the radicals in the solvent cage is for one of them to react with the solvent or to diffuse into the solvent and then react. This would account for the dihydroxybenzenes produced (see eq 7–9 and 11). Since photolysis of the dihydroxybenzenes yields *sym*-tetrahydroxybiphenyls, the formation of 3,3′,4,4′-tetrahydroxybiphenyl in eq 9, presumably by coupling of two 2-hydroxybiphenyl radicals, has strong precedent.[7] The fate of the aryl radical in processes 7–9 and 11 was not determined: it may react with water to form benzene or phenol, it may couple to form biphenyl,[8] it may be scavenged by starting material and form products of high molecular weight. We do know, however, that no large quantities of phenol were formed (Table II).

In all of these reactions, radical recombination appears to be highly selective and nonrandom. Indeed, the products are *always* those expected from coupling in positions *ortho* or *para* to the oxygen involved in cleavage. Compound II provides the critical test of this selectivity for no major product ($>1\%$) is detected that cannot be accounted for in the tlc analysis; 3,5-dihydroxybiphenyl is probably absent in eq 8 and 12.

The composition of the products of photolysis changes with the solvent. Apart from preferential solvation, major changes can be expected when the solvent is also a reactant. For example, proton abstraction from cyclohexane is some 20 kcal mole^{-1} easier than from water; this could accommodate the differences we observed (Table II). It has been reported that irradiation of 2- or 4-iodophenol in methanol gives phenol (80–90%)[14] whereas we obtained dihydroxybenzenes and dihydroxybiphenyls from the bromophenols in water (Table III). This is one of many examples in which proton (rather than hydroxyl) abstraction from methanol has been observed.[15]

Appendix

We wish to estimate the enthalpies of reaction of eq 3–5. For these calculations and others in the text, we need the following bond dissociation energies in kcal mole^{-1}: HO–H (116), C_6H_5O–H (90), C_6H_5–OH (104), CH_3O–H (100), CH_3–OH ($\sim$90), $HOCH_2$–H ($\sim$90), C_6H_5–H (102), C_6H_{11}–H ($\sim$94), HOC_6H_4–Br (67). Some of these were calculated from heats of formation.[16,17]

A recent estimate of the bond dissociation energy in phenol (RO–H) is 83–93.[18] In this paper, we shall use the value $D + \Delta$ for phenol and D for the phenoxyphenols (RO–H). Following Hush, one might estimate Δ from electrode potentials as 7, 2, and 12 for the 2-, 3-, and 4-dihydroxybenzenes, respectively.[19]

Now, we also need the gas-phase heats of formation (kcal/mole): H (52), C_6H_6 (20), C_6H_5 (70), C_6H_5OH (-23), HOC_6H_4OH (-66), and $HOC_6H_4OC_6H_5$ (-33) which are available or can be estimated from Cox's tables.[17] From these, we calculate the heats of formation for the radicals $HOC_6H_4\cdot$ (27), $C_6H_5O\cdot$ ($D + \Delta - 75$), $HOC_6H_5O\cdot$ ($D - 118$), and $C_6H_5OC_6H_4O\cdot$ ($D - 85$). Using these values, we find the enthalpy of process 4 is $D + \Delta - 15$ and of process 5, $D - 15$.

In the first paper, we found that $\Delta H(e_{aq}^-) \simeq 81$–$93$ for the formation of the hydrated electron from phenol.[7] This is roughly equal to the energy required for homolytic oxygen–hydrogen bond breaking in phenol. The fact that photolysis of phenol does produce the hydrated electron indicates that photolysis is slightly favored energetically. In the phenoxyphenols, the corresponding energies should have the same relation. Therefore we take a value $\sim D$ as the enthalpy of process 3.

Acknowledgment. We wish to thank Professor L. I. Grossweiner for some stimulating discussions. We are grateful to Mr. R. Niinemae and Mr. E. Stedronsky who synthesized three of our reference compounds.

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[14] N. Kharasch and P. Friedman, Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 27S. For photolysis in benzene, see W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

[15] J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 342–347.

[16] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths and Co. (Publishers) Ltd., London, 1958; A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths and Co. (Publishers) Ltd., London, 1955, Chapter 1; C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press Inc., New York, N. Y., 1962, Chapter 7.

[17] J. D. Cox, *Tetrahedron*, **18**, 1337 (1962); N. A. Lange, "Handbook of Chemistry," 9th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1956.

[18] I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Am. Chem. Soc.*, **86**, 2741 (1964).

[19] N. S. Hush, *J. Chem. Soc.*, 2375 (1953); T. Fueno, T. Ree, and H. Eyring, *J. Phys. Chem.*, **63**, 1940 (1959).