Photooxidation of Phenol, Cresols, and Dihydroxybenzenes[1,2]

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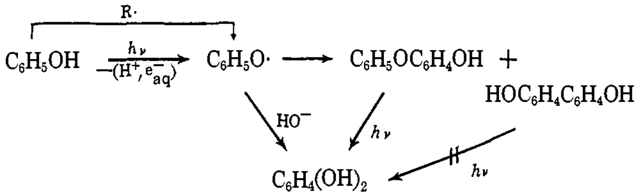
Abstract: The steady irradiation at 2537 A of aqueous solutions of phenol in the presence of oxygen, dinitrogen oxide, and cupric acetate or under nitrogen yields rather similar products. Five carbon–carbon or carbon–oxygen dimers and two dihydroxybenzenes, but no trihydroxybenzenes, were identified. The hydroxylation products arise in part from the carbon–oxygen dimers and in part by direct hydroxylation but not from the carbon–carbon dimers. These photooxidation results differ substantially from those reported for chemical or electrochemical oxidations of phenol; we find 2,2′-dihydroxybiphenyl as the only isolable product in the oxidation of phenol with permanganate or ferricyanide. The irradiation of the cresols is similar, that is, analogous dimerization and hydroxylation occurs. The dihydroxybenzenes give only dimerization products. *p*-Quinone yields *p*-hydroquinone as well as hydroxylated products. The following routes to products appears to hold for the simple phenols.



In this paper, we report on the products of the photooxidation of phenols in water under steady irradiation. This information is combined with literature data on the kinetics and thermochemistry of relevant species in water, *e.g.*, phenoxyl, hydroxyl, dioxide (O_2^-), hydrogen atom, the electron, etc., and a detailed mechanism of the reactions is proposed. It should be noted that the role of the hydrated electron[2–7] is still sufficiently novel in photolytic processes[5d,5e,5h,6,7] so that it has not yet appeared in some recent reviews.[8] Furthermore, the oxidation of phenols is of wide interest[9–15] in such areas as enzymatic hydroxylation, biogenesis of alkaloids, gallotannins,[13a] photobiology,[6,11a] lignin chemistry,[13b] inhibition,[13c,d] color reactions,[13e] and electrochemistry of phenols and quinones.[15] Two recent surveys provide an excellent over-all view.[9,10]

From the published results of flash photolysis of phenols,[6,7,11,16–18] it appears that the primary processes of interest to us are best given by the scheme

$$\begin{tikzcd}
C_6H_5OH \arrow[r, rightleftharpoons, "h\nu"] \arrow[dd, shift right, "-H^+"'] & (C_6H_5OH)^* \arrow[dr, "-H^+"] & \\
 & & \underset{\mathbf{1}}{C_6H_5O\cdot} + e_{aq}^- \\
C_6H_5O^- \arrow[r, rightleftharpoons, "h\nu"] \arrow[uu, shift right] & (C_6H_5O^-)^* \arrow[ur] &
\end{tikzcd} \qquad (1)$$

The solvated electron, e_{aq}^-, has been identified spectrophotometrically,[3–7] and considerable kinetic and product evidence from scavenging experiments in many systems require its existence.[3–5,16,18] Phenoxyl (**1**) is a more familiar intermediate in radical processes involving phenol.[9,10] It has been generated and detected by flash spectroscopy with and without dye (eosin) sensitization;[6,7,11,17] it has been produced from phenol chemically, *e.g.*, with cerium(IV) or titanium(III)–hydrogen peroxide, and identified as a transient in a flowing stream by electron spin resonance[19]—rather more information of this same general type is available for the highly alkylated phenols, *e.g.*, 2,6-di-*t*-butylphenol, simply because the radicals formed lived longer.[9,10] From the spin resonance work, it was

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[1] This work has been supported by the National Institutes of Health, U. S. Public Health Service. Inquiries about this paper should be addressed to S. I. Miller.

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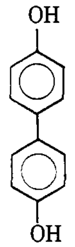
possible to deduce that 75-80% of the unpaired spin density resides on the *ortho* and *para* ring carbon atoms.[19] The disappearance of **1** in deaerated water is essentially encounter controlled;[7a] it is second order in **1** with $k \simeq 5.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at 25°, and the rate appears to be independent of the phenol concentration and the pH.[7a,11b,17b]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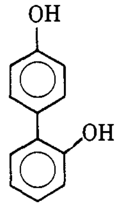
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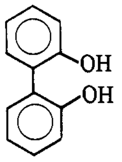
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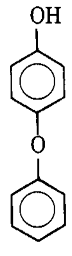
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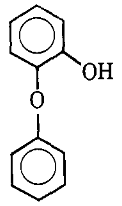
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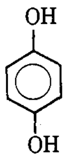
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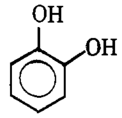
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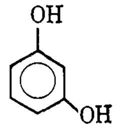
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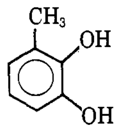
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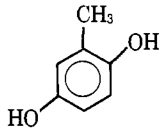
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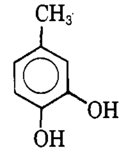
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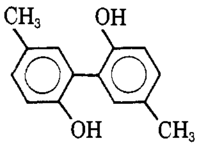
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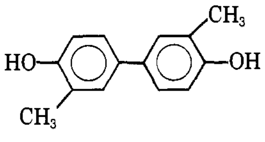
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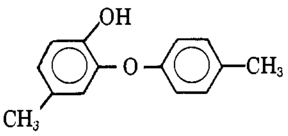
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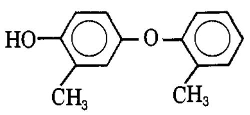
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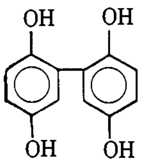
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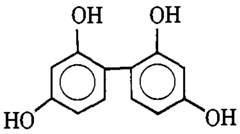
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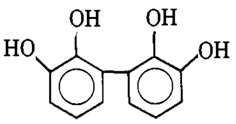
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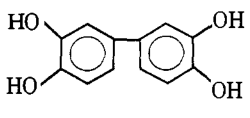
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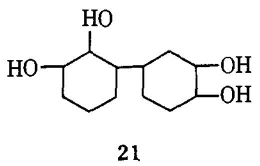
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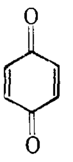
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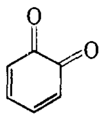
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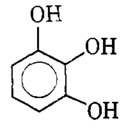
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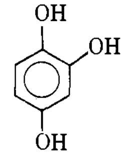
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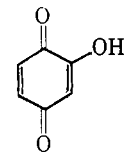
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The oxidation of simple phenols has been induced photolytically, electrolytically, chemically, enzymatically, and by high-energy particles of radiations.[9,10,14,20,21] Historically, the earliest observations of products begin with the reddish colors formed when phenol is exposed to air.[20] The products that have been found by one oxidation method or another might include one or more of **2**, **3**, **4**, **5**, **6**, **7**, **8**, **22**, **23**, **25**, ring cleavage products such as maleic acid, *cis,cis*-1,3-butadiene-1,4-dioic acid, glycolic acid, oxalic acid, and usually unidentified materials of higher molecular weight. In fact, "Amorphous polymers containing some ether linkages often constitute the main products of chemical oxidation of phenols."[14b]

Typical "dirty" reactions are by no means inevitable, as has been demonstrated in the electrolytic[15] or potassium nitrosodisulfonate[12] oxidations of phenols. It is worth emphasizing that even if one considers only those processes that appear to involve free-radical oxidation, one finds wide and variable distributions of products. In this work, our methods of analysis were unsuitable for nonhydroxylic, polymeric, or ring-cleavage products so that we do not consider them here. Nevertheless, we find that our photooxidations generally produce more of the relatively simple products from phenol, the cresols, and dihydroxybenzenes than are normally found by other methods.

Experimental Section

Phenol and the cresols were distilled under prepurified nitrogen (oxygen content specified as <8 ppm) before irradiation. The dihydroxybenzenes could be used as purchased. All other compounds, whether purchased or prepared, were recrystallized before irradiation. For a few runs, Fisher Spectrograde cyclohexane was used as a solvent.

Except as indicated in Tables III–V, the compounds to be irradiated were dissolved in distilled water without any buffering. Each irradiation was normally run on 300 ml of solution. To assure saturation with oxygen, oxygen was allowed to bubble through a solution for 10 min prior to and throughout the irradiation period. The concentration of oxygen in such solutions at 25° is *ca.* $2 \times 10^{-3}\ M$. To exclude oxygen, the distilled water or cyclohexane solvents were first boiled for several hours and then distilled under prepurified nitrogen. In the case of 1 *N* sulfuric acid or 1 *N* sodium hydroxide solutions, the solvent was boiled, then cooled under prepurified nitrogen. The solutions were made and the reaction vessel filled under streaming nitrogen. The oxygen concentration in these solutions should be of the order of $5 \times 10^{-7}\ M$.

In order to obtain solutions saturated with dinitrogen oxide, the same procedure as with nitrogen was followed, then dinitrogen oxide was allowed to bubble through the solutions for about 10 min prior to and then during the irradiation period. Under all of these reaction conditions, phenol does not undergo reaction without irradiation. Two runs were carried out in commercial liquid ammonia (oxygen content, if any, was unknown) at *ca.* −70°. In the first, ammonia was distilled into the irradiation flask containing the phenol to give 300 ml of solution. In the second run, sodium amide in ammonia was prepared and the weighed amount of phenol was then added. After irradiation, the ammonia was allowed to evaporate and the residues were worked up as described below.

A few flash photolysis spectra were taken on the apparatus of Professor L. I. Grossweiner of our Physics department.[11]

The steady irradiations were carried out in Delmar glassware fitted with greaseless rubber seals. The Delmar illuminator, DM

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[20] F. K. Beilstein, "Handbuch der Organischen Chemie," Verlag Von Julius Springer, Berlin, Vol. VI, Syst No. 512, H 115, EI 115, EII 124, 1923.

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580, is a low-pressure 2537-A mercury resonance lamp (at 2000 v and 265 mamp) which dips directly into the solution. The solutions were generally kept at 0–20° and were stirred magnetically. For phenol (ϵ_{2537} 520), we estimate that *ca.* 99% of the light was absorbed within 1.9 or 19 mm of the light source at 2×10^{-2} *M* and 2×10^{-3} *M*, respectively. The dilution effect for this tenfold concentration change would be 10^3 since the third power of the distance is involved. Molecular extinction coefficients of several of the important compounds are given in Table II.

After the irradiations were complete, the solutions were acidified with several milliliters of 2 *N* sulfuric acid and extracted four times with freshly distilled ether. The ether solutions were dried and the ether was removed by aspiration. The residue was distilled under reduced pressure (runs in cyclohexane were distilled directly). Both the pot residue and the distillate were analyzed by thin layer chromatography (tlc). This separation tends to leave behind water-soluble materials, *e.g.*, polyhydroxy polymers.

For the tlc analyses, the apparatus, accessories, and stationary phases (Table I) of Desaga–Brinkmann were used. The identification of each product by ascending tlc was carried out by at least two methods on carrier slides of 20 × 20 cm. The solvent was allowed to ascend 15 cm in each chromatogram. The thickness of the layers was 0.25 cm for each stationary phase. The spots were developed by diazotized benzidine or by diazotized sulfanilic acid. For the compounds of this study, the R_f values on stationary phases G and GF were essentially identical. Chromatograms on GF did not show more spots under a ultraviolet lamp than they showed after being developed with diazotized benzidine. Table I summarizes the elution technique and Table II gives a list of R_f values of compounds that were acquired or synthesized for this study. The sensitivity of the identification of 4,4′-dihydroxybiphenyl is in the range of 1 μg and the corresponding value for catechol is 0.1 μg. In preparative tlc, no layers of polyamide thicker than 0.3 cm could be used, as the layer would peel off the plate as it stood in the solvent chamber. The identity of some of the products was confirmed by comparison of infrared spectra taken on a Beckman IR-8 spectrophotometer.

Table I. Tlc Elution Technique

Method	Stationary phase[a]	Solvent[b]	No. of elutions[c]
1	G	B70, M8, A4	1
2	G	B70, M8, A4	2
3	G	B80, M1, A1	1
4	G	B80, M1, A1	2
5	G	B80, M1, A1	3
6	P	B70, M8, A4	1
7	P	B70, M8, A4	2
8	C	B9, Bul, H_2O 10[d]	1

[a] G is silica gel G7731; GF is silica gel GF_{254} 7730; P is polyamide MN; C is cellulose powder 300 GF_{254}. Aluminum oxide (Al_2O_3 G1090) was not very useful for phenolic compounds; however, the best results were obtained with the solvent B 100, M2, A2. [b] B, benzene; M, methanol; A, acetic acid; Bu, *n*-butyl alcohol. The figures represent the volume composition of the solvent. [c] When the solvent front reached the end of the chromatogram, the plate was dried and run in the same solvent again. [d] The lower phase of the mixture was used.

In connection with the steady irradiation products, a few brief observations on the phenol runs may be generally useful. After *ca.* 4 hr of exposure to the lamp, the solutions turn sensibly brown; after 8 hr, the over-all yield of ether-soluble products is 5–10%. The apparent conversion rate and amount of tarry products increase at the higher temperatures, higher acidity (pH 1), or higher basicity (pH 14).

Products of Phenol Oxidations. A solution of phenol (2 g) was irradiated in 1 l. of distilled water saturated with oxygen for 8 hr at 0–20° in 20 separate experiments. Each run was worked up as described above. Phenol was removed from the combined residue at 80° (20 mm) in a 20-cm Vigreux column. The residue was heated up to 120° (10^{-3} mm) and gave the greater part of the catechol and hydroquinone produced. These were separated by preparative tlc, method 7; **8** was recrystallized from benzene and **7** was purified by sublimation. The next fraction was taken at 120–150° (10^{-3} mm) giving the dihydroxybiphenyls. Preparative tlc, method **7**, gave three fractions: 2,2′-dihydroxybiphenyl (**4**), 2,4′-dihydroxybiphenyl (**3**) plus **8**, and 4,4′-dihydroxybiphenyl (**2**) plus **7**. Tlc (method 2) was used to separate **3** from **8** and pure **2** from **7**. The dimers **3** and **4** were repurified by sublimation. Infrared spectra were taken to confirm these assigned structures.

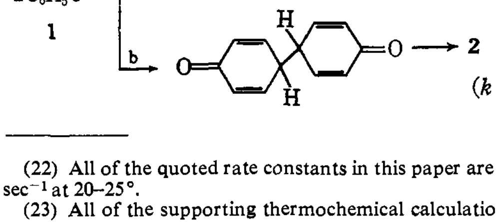
Chemical Oxidations. Phenol (0.508 g, 5.4 mmoles) was dissolved in a solution of 2 *N* sulfuric acid (8 ml) and 300 ml of distilled water. Potassium permanganate (0.55 mmole) in 8 ml of water was added at 5° over a 1-hr period to the stirred phenol solution. In a second experiment, phenol (0.47 g, 5 mmoles) was dissolved in a solution of sodium carbonate (0.715 g, 2.5 mmoles) in water (300 ml). Potassium ferricyanide (0.823 g, 2.5 mmoles) dissolved in water (20 ml) was added at 5° over a 1-hr period to the stirred phenol solution. The usual work-up and tlc analysis were applied; only **6**, besides tar, was found for both oxidants.

Results and Discussion[22,23]

Phenol. To provide a detailed account of the photolysis at the molecular level from the instant a photon is absorbed by phenol, we draw on assorted observations. Published flash photolysis studies gave us data about some of the intermediates in the first few microseconds of reaction. In this work, we identified many of the products of steady irradiation so that we know where the processes terminate. With these assumed boundary conditions, we then try to bridge the time gap. Here, alternative and competing reactions are considered in the light of what is known about the properties of reactive species. Because of the importance of phenol, we consider the complex problem of mechanism in detail; it turns out, however, that the final mechanistic picture is fairly simple.

The products of the steady irradiation of phenol under various conditions are listed in Table III. Three carbon–carbon dimerization products (**2**, **3**, and **4**), traces of two carbon–oxygen (**5** and **6**) dimers, as well as two hydroxylated compounds (**7** and **8**) have been identified; **2**, **3**, **4**, **7**, and **8** were isolated by preparative tlc and confirmed by their infrared spectra. Short irradiations (0.5–4 hr) show exclusive or predominant formation of the three carbon–carbon dimerization products. In the course of longer irradiations (12–54 hr), first **2** and then **3** disappears although phenol is still present. If the phenol concentration is decreased (0.002 *M*), the hydroxylation products (**7** and **8**) predominate. Trihydroxybenzenes **23** and **24** were sought but could not be found. In addition to those in Table III, there may be many other products, *e.g.*, trimers, but these were not identified. However, it is probable that all of the *first* isolable products have been found.

Recent reports give the scheme in eq 1 to describe the photolysis of phenol.[5e,7a] The kinetic results of flash photolysis, measured in deaerated solutions, further require that **1** disappears by dimerization[7a,17] and strongly suggest that **1** is not significantly involved



(2)

$(k = 5.6 \times 10^9)^{7a}$

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(22) All of the quoted rate constants in this paper are in the units M^{-1} sec^{-1} at 20–25°.

(23) All of the supporting thermochemical calculations are found in the Appendix.

Table II. Tlc R_f Values and Selected Molar Extinction Coefficients in Water at 2537 A[a]

Compound	Source	Tlc method (from Table I)[p]								ϵ_{2537}
		1[o]	2[o]	3[o]	4[o]	5[o]	6	7	8	$\times 10^{-2}$
Phenol	*a*	6.3	8.0	2.3	5.3	6.4	6.2	8.1		5.2
Hydroquinone (**7**)	*a*	3.2	5.0	0.2	0.6	0.8	2.3	3.6	7.9	1.4
Resorcinol (**9**)	*a*	3.8	5.8	0.2	0.8		2.2	3.3	7.7	3.3
Catechol (**8**)	*a*	4.8	7.0	0.6	1.8	2.2	3.5	5.2	8.2	4.6
1,2,3-Trihydroxybenzene	*a*	2.7	4.4	0.2	0.3	0.5	1.8	2.7	7.5	4.3
1,2,4-Trihydroxybenzene	*b*	2.0	3.0	0.0	0.1	0.0	1.4	2.2		
1,3,5-Trihydroxybenzene	*a*	1.7	2.7	0.0	0.0	0.0	1.0	1.7	6.3	2.3
2-Hydroxydiphenyl ether (**6**)	*c*	7.7	9.1	6.5	8.0	9.3	8.3	9.5	t	13
3-Hydroxydiphenyl ether	*a*	6.4	8.6	4.9	5.8	6.9	7.5	8.9	t	10.2
4-Hydroxydiphenyl ether (**5**)	*d*	5.9	8.3	4.0	5.5	6.5	7.8	9.2	t	12.4
o-Aminophenol	*a*	2.4	4.0				4.5	6.7		
m-Aminophenol	*a*	2.3	4.4				4.3	6.2		
p-Aminophenol	*a*	0.9	1.2				2.3t	3.8		
o-Cresol	*a*	6.2	9.0	3.8	5.5	7.6	6.3	8.7		
m-Cresol	*a*	5.9	8.8	3.0	5.0	6.5	5.7	8.5		
p-Cresol	*a*	6.0	8.6	2.6	4.6	6.1	5.8	8.5		
2,3-Dihydroxytoluene (**10**)	*a*	5.1	7.8	1.1	2.5		4.4	6.5	7.5	
2,5-Dihydroxytoluene (**11**)	*e*	3.5	6.7	0.4	1.2		2.7	4.2	7.6	
2,6-Dihydroxytoluene	*a*	4.4		0.7	1.8		2.6	4.2		
3,4-Dihydroxytoluene (**12**)	*a*	4.6	7.8	0.7	1.7		3.5	5.9	7.4	
3,5-Dihydroxytoluene	*a*	4.0	6.6	0.3	0.8		2.3	4.2	7.4	
2,2′-Dihydroxybiphenyl (**4**)	*a*	5.8	8.6	1.4	3.4	4.3	5.6	7.9	6.9	27.2
2,4′-Dihydroxybiphenyl (**3**)	*f*	5.0	7.8	0.9	2.4		3.2	5.0	5.4	77
2,5-Dihydroxybiphenyl	*a*	4.9	7.7	1.1	2.4	3.5	3.7	5.2	6.2	
3,3′-Dihydroxybiphenyl	*e*	4.7	7.3	0.5	1.3	1.7	1.9	3.5	3.3	120
4,4′-Dihydroxybiphenyl (**2**)	*a*	4.2	6.9	0.5t	1.3t	1.9	1.7	3.0	2.2t	97.5
2,3,2′,3′-Tetrahydroxybiphenyl (**19**)	*g*	3.0t	5.0t	0.1	0.3	0.4	1.9	3.3	6.1	
3,4,3′,4′-Tetrahydroxybiphenyl (**20**).	*h*	1.8	2.8	0.0	0.0		0.3	0.7	2.2	
2,5,2′,5′-Tetrahydroxybiphenyl (**17**)	*i*	1.9	2.8	0.0	0.0		0.4	0.9	6.7	
2,6,2′,6′-Tetrahydroxybiphenyl (**18**)	*j*	3.0	4.4	0.0	0.0		1.5	3.0	4.9	
2,4,2′,4′-Tetrahydroxybiphenyl	*a*	2.2	3.0	0.0	0.0		0.6	1.0	6.0	
4,4′-Dihydroxystilbene	*a*	4.5	6.5	0.0	0.0		1.9	3.4	0.0	
4,4′-Dihydroxydiphenylmethane	*a*	4.8	6.6		1.3	2.0	3.6	5.8	t	
2,2′-Dihydroxydiphenylmethane	*a*	6.4	7.8		3.0	5.1	5.3	7.5		
4-Hydroxybenzyl alcohol	*a*	3.5	4.8		0.5	0.7	3.7	5.7		
p-Benzoquinone (**22**)	*a*			5.6	7.7			9.9		190
Diphenoquinone	*k*		9.7					9.9		10
Tetrahydroxy-*p*-benzoquinone	*a*			0.0	0.0			1.7t		
2,5-Dihydroxy-*p*-benzoquinone	*a*			0.0	0.2t			4.0t		
2,2′-Dihydroxy-5,5′-dimethylbiphenyl (**13**)	*l*	6.0	8.3	2.2	3.8	5.5	6.7	8.5	t	
2-Hydroxy 4′,5-dimethyldiphenyl ether (**15**)	*l,m*	8.2	9.2	5.3	7.8	9.5	8.9	9.7	0.0	
4,4′-Dihydroxy-3,3′-dimethylbiphenyl (**14**)	*a*	5.6	7.0	1.3	3.0		2.8	4.5	t	
4-Hydroxy 2′,3-dimethyldiphenyl ether (**16**)	*n*				8.5		9.0	9.7		

[a] The compounds were purchased when available and purified if necessary. Other citations here generally indicate the method of synthesis. A supplementary list of R_f values is given in ref 7. [b] F. K. Beilstein,[20] H1087. [c] J. F. Norris, B. G. Macintire, and W. M. Corse, *Am. Chem. J.*, **29**, 120 (1903). [d] C. R. Harington, *Biochem. J.*, **20**, 300 (1926). [e] The dimethoxy compound was purchased and demethylated. [f] G. Schultz, H. Schmidt, and H. Strasser, *Ann.*, **207**, 348 (1881). [g] H. Gilman, J. Swiss, and L. C. Cheney, *J. Am. Chem. Soc.*, **62**, 1963 (1940); the tetramethoxy compound was demethylated. [h] E. Späth and K. Gibian, *Monatsh*, **55**, 239 (1930). [i] H. Kauffmann and I. Fritz, *Ber.*, **41**, 4413 (1908); F. Ullmann and O. Loewenthal, *Ann.*, **332**, 62 (1904). [j] H. Lettré and A. Jahn, *Ber.*, **85**, 346 (1952). [k] B. R. Brown and A. R. Todd, *J. Chem. Soc.*, 1280 (1954). [l] R. Pummerer, D. Melamed, and H. Puttfarcken, *Ber.*, **55**, 3116 (1922). [m] 3-Bromo-4-methoxytoluene was used for the 3-chloro-4-hydroxytoluene. [n] S. Goldschmidt, E. Schulz, and H. Bernard, *Ann.*, **478**, 11 (1930). Instead of 2-methoxy-5-bromotoluene, we used 2-methoxy-5-chlorotoluene. [o] Almost all of the tlc spots on support G developed with diazotized benzidine have a brown color; the exceptions follow: **2** (green), **6** (yellow), 3-hydroxydiphenyl ether (red-brown), **5** (yellow), phenol (yellow), **22** (yellow), **9** (red-brown), **11** (yellow), and 1,2,3-trihydroxybenzene (red-brown). [p] t indicates "tail."

in routes leading to products other than dimers. Five dimerization products (**2**–**6**) of radical coupling in *ortho* and *para* positions or at oxygen have been identified in this work—representative carbon–oxygen and carbon–carbon coupling products are given in eq 2. A sixth dimer, diphenyl peroxide,[17] would probably be unstable and need not be considered.[9,24]

Let us now go beyond the conventional reaction scheme 2 and consider the role of the hydrated electron which was formed in eq 1. We cite the relevant processes and rate constants (all in M^{-1} sec^{-1} at 20–25°).[3–5,22]

The ratio of hydrated electron to radical **1** reported for deaerated aqueous solutions appears to increase markedly from pH 7 to 12 in process 1.[7a] The hydrated electron disappears by an apparent first-order process ($k = 4.3 \times 10^4$ sec^{-1}), which appears to be independent of **1**, phenol concentration, and the pH above 7.[7a] Because the disappearance is too fast to be simply the reaction with water (eq 3a) considered as a pseudo-first-order process, trace quantities of oxygen may be implicated here.[3b] In the presence of dinitrogen oxide,

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[24] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 466.

Table III. Products of the Steady Irradiation of Phenol at 10–20°[a]

Irradiation time, hr	Phenol concn, M	Atmosphere	Medium	Products[b,c] 2	3	4	5, 6	7	8	9	20	
0.5, 1.0	2×10^{-2}	O_2	H_2O	+	+	+		−	−			
2.0				+	+	+		−	*			
4.0				+	+	+		*	−	−		
8.0				+	+	+	Tr	+	+	−		*d*
23.0				−	+	+	Tr	+	+	−	*	*d*
54.0				−	*	+	Tr	+	+	−	+	*d*
5.0	2×10^{-2}	N_2	H_2O	+	+	*		−	−			
8.5				+	+	+			+			
48.0, 72.0				+	+	+		+	+	−		
2.0	2×10^{-2}	N_2O	H_2O	+	+	+		*	+			
5.5				+	+	+		*	+	−		
24.0				+	+	+		+	+	−	+	
3.5	2×10^{-2}	O_2	H_2O, 2×10^{-5} M CuOAc	+	+	+		+	+			
11.5		O_2		+	+	+	Tr	+	+			
47.0		N_2		+	+	+	Tr	+	+			
4.5	2×10^{-2}	O_2	0.5 M H_2SO_4	+	+	+			+	−		
8.5		O_2	1 M HCl + 0.5 M NaCl	+	+	+		+	+	−		
8.0		N_2	0.5 M H_2SO_4	+	+	+			*			
2.5, 4.0	2×10^{-2}	O_2	1 M NaOH	Products could not be identified								
6.0		O_2		No products[e]								
5.0, 9.0		N_2		+	+	+		−	−			
0.5	2×10^{-3}	O_2	H_2O	*	*	*		−	+			
4.5				*	*	*		*	+			
7.0				−	*	*		+	+			
23.0				−	*	*		+	+		+	
7.0		N_2		+	+	+		+	+			
2.0	0.2	O_2	H_2O	+	+	+			+			
47.0				+	+	+		+	+			
5.0	2×10^{-2}	O_2	H_2O (50–70°)	*	+	+		+	+			
45.0	2.0			+	+	+		+	+			
3.9	2×10^{-2}	NH_3	NH_3 (*ca.* −70°)	Products could not be identified								
6.0			NH_3 + 2×10^{-2} M $NaNH_2$ (*ca.* −70°)	Products could not be identified								
2.0	2×10^{-2}	O_2	H_2O, 10^{-6} M eosin	+	+	−			*			
3.0	2×10^{-2}	O_2	Cyclohexane	−	+	+		−	+	−		
24.0		O_2		−	+	+		−	+			
3.0		N_2O		−	+	+		−	*	−		

[a] Runs with different temperatures or with no radiation are noted in the table. Except as noted, phenol at its natural pH, ≃ 6 in water, was used. [b] Of necessity, the tlc analyses were qualitative. The presence of a compound is noted by an asterisk (*); if substantial quantities 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. [c] 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. [d] Quinone (**22**) and 3,3′-dihydroxybiphenyl were sought but not found (−). [e] No irradiation.

which consumes the electron as in eq 3f, the quantum yield for nitrogen rises moderately (0.16–0.3) with tenfold increases in dinitrogen oxide (10^{-2}–10^{-3} M) or hydroxide ion (10^{-1}–10^{-2} M).[16] All of these observations suggest that reversal of eq 1 is important, and that it is or could be competitive with some of the rapid processes, 3b, 3c, 3d, 3e, and 3f. Under conditions of oxygen saturation, process 3b seems most probable.

$$e_{aq}^- + H_2O \xrightarrow{a} H + OH^- \qquad (k \simeq 16)^{5b}$$

$$e_{aq}^- + O_2 \xrightarrow{b} O_2^- \; (HO_2 \rightleftharpoons H^+ + O_2^-;\ \mathrm{p}K_a = 4.45)^{3b} \quad (k = 1.9 \times 10^{10})^{5g}$$

$$e_{aq}^- + H^+ \xrightarrow{c} H \qquad (k = 2.1 \times 10^{10})^{5b}$$

$$e_{aq}^- + C_6H_5OH \xrightarrow{d} (C_6H_5O^- + H) \qquad (k \simeq 4 \times 10^{6})^{3b} \qquad (3)$$

$$e_{aq}^- + H_2O_2 \xrightarrow{e} HO + OH^- \qquad (k = 1.2 \times 10^{10})^{5g}$$

$$e_{aq}^- + N_2O \xrightarrow{f} N_2 + O^- \; (OH + OH^- \longrightarrow H_2O + O^-;\ \mathrm{p}K_a = 11.9)^{5b} \quad (k = 5.6 \times 10^{9})^{5g}$$

$$e_{aq}^- + Cu^{2+} \xrightarrow{g} Cu^+ \qquad (k = 3.3 \times 10^{10})^{5c}$$

In an oxygen-free system (pH ~7), the concentration of phenol would have to be *ca.* 2×10^{-4} M or larger for the rates of 3d and 3a to be equal. In runs of low pH, 3c becomes important. Clearly, one cannot consider the mechanism of the photooxidation of phenol in water without involving the hydrated electron.

We take up the fate of several of the other transients. According to Thomas, step 4a is endothermic, so that

$$C_6H_5OH + HO_2 \underset{a'}{\overset{a}{\rightleftharpoons}} \mathbf{1} + H_2O_2 \; (K \leq 1.5 \times 10^{-2},\ k_{a'} = 10^{9})^{13d}$$

$$C_6H_5OH + HO \xrightarrow{b} \mathbf{1} + H_2O \qquad (4)$$

$$C_6H_5OH + R\cdot \xrightarrow{c} \mathbf{1} + RH$$

we cannot expect it to be important here. Both 4b and the generalized reaction 4c are propagating steps for radical **1**. Process 4b is strongly exothermic (*ca.* 25–30 kcal/mole);[23] if its rate constant is at least as high as that for the reaction of hydroxyl with hydrogen peroxide (4.5×10^{7} M^{-1} sec^{-1}),[3b] which is quite probable,[25] eq 4b could be a significant route taken by

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(25) R. W. Matthews and D. F. Sangster, *J. Phys. Chem.*, **69**, 1938 (1965).

hydroxyl radicals in phenol solutions. One other necessary path for hydroxyl is considered below with reaction scheme 8.

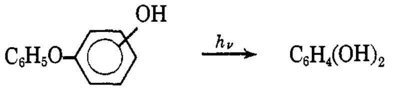
Since the hydrogen atoms formed in (3a) or (3c) must consumed, we consider the following steps.[3,4b,4e]

$$\begin{array}{lr} H + O_2 \xrightarrow{a} HO_2 & (k = 2 \times 10^{10})^{3a} \\ H + C_6H_5OH \xrightarrow{b} 1 + H_2 & \\ H + C_6H_5OH \xrightarrow{c} C_6H_6OH & \\ H + HO_2 \xrightarrow{d} H_2O_2 & \\ H + H_2O_2 \xrightarrow{e} H_2O + HO & (k = 9 \times 10^{7})^{5b} \\ H + H \xrightarrow{f} H_2 & (k = 2 \times 10^{10})^{5b} \end{array} \qquad (5)$$

Because of the low concentrations of the reactants, steps 5d-5f are probably unimportant. In the presence of oxygen, step 5a should be favored. In the absence of oxygen, steps 5b and 5c both merit consideration; both should be exothermic, the first more so than the second. Determinations of the yield of molecular hydrogen would be informative concerning 5b. As for 5c, this would presumably be on one of several paths to polymeric products; the analogous process in which benzene scavenges hydrogen atoms has $k = 10^8\ M^{-1}\ \text{sec}^{-1}$.[3b]

Although a major route leads to hydrogen peroxide through eq 1 and 3b, peroxide is not stored in our system for we detected none after irradiation. In the absence of other reagents, *e.g.*, strong base or metal salts, hydrogen peroxide and phenol react very slowly.[10,12,14] Therefore, hydrogen peroxide must be destroyed as in 3e, 4a′, or 5e, as well as by photolysis (quantum yield 0.45)[26] to give hydroxyl radicals.

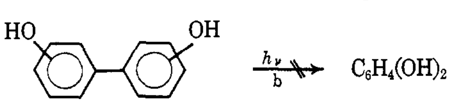
To account for the hydroxylation products, **7** and **8**, we note their formation by cleavage reactions of the product dimers (eq 6) and by direct hydroxylations (see below). Detailed evidence for the photolytic



(6)

cleavage of several hydroxydiphenyl ethers, as in eq 6, is presented elsehwere.[2] The fact that the hydroxydiphenyl ethers are normally minor products of the photolysis of phenol may be ascribed to the higher efficiency of process 6 as compared to process 1.

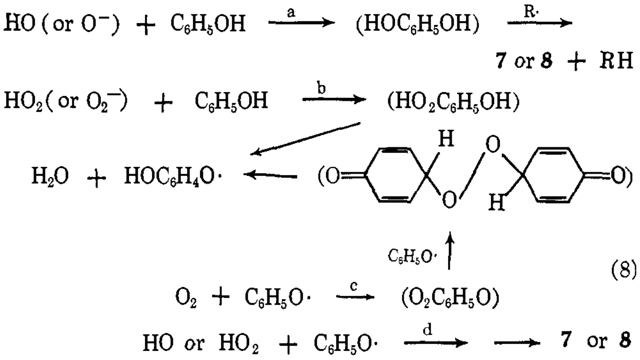
It is also clear that the carbon-carbon dimers (3 × 10^{-4} and 1 × 10^{-2} *M*, 2-15 hr of irradiation) *do not give* the corresponding hydroxylated products as in reaction 7. This was demonstrated for the compounds **2**, **3**, and



(7)

4, 3,3′-dihydroxybiphenyl, **13**, and **14**. In addition, cleavage of the middle bond of **2**, say, would lead to the 4-hydroxyphenyl radical, a species whose reactions are known[2] but not found here. Moreover, the photolytic production of the hydrated electron from these compounds has been established,[5h,7] and, in the case of **2**, the presence of 4-(4-hydroxyphenyl)phenoxyl radical was verified;[5h,7b] this suggests that the dimers (**2**, **3**, and **4**) are in turn converted to the tetramers or trihydroxybiphenyls.

Direct hydroxylation as well as *ortho-para* oriented attack on phenols has ample precedent.[9,10,12,15,27] In fact, where rate constants for additions of hydroxyl to simple aromatic molecules are known, rate constants are *ca.* 10^8-10^9 M^{-1} sec^{-1}.[3,25] Although the radical-radical reactions of (8d) may be less probable, all of the processes 8a-d seem possible, for the individual steps are exothermic.[23] Concerning the peroxide intermediates in (8c), stable analogs have been reprted only for some substituted phenols.[9,10] Finally, we have examined the possibility of a "hot" phenoxyl reaction with the solvent.[28] We judge that eq 9a is precluded on thermochemical grounds, whether **1** is hot or cold.[23]



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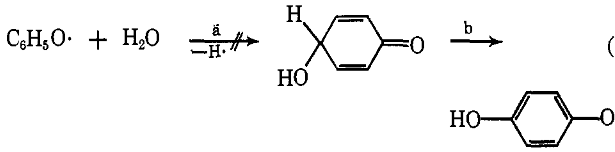

(9)

One of the striking features of the irradiations of phenol under different conditions is the similarity in the products. Because oxygen, dinitrogen oxide, hydrogen ion, and copper(II) presumably lead to species **1** as outlined in reactions 3-5, this similarity is qualitatively acceptable. What is perhaps most significant is that the same sort of products are formed under nitrogen, albeit more slowly and accompanied by far less tar. Clearly, the hydroxylations in reaction scheme 8 cannot occur under nitrogen—*oxygen is not essential for the photooxidation of phenol.* This suggests that hydroxylation of phenol derives from process 6 under nitrogen and from reaction 6 and at least some of 8 under oxygen.[29]

At the two limits of our pH (pH 1 and 14), the rates of phenol conversion as well as tar formation increased.

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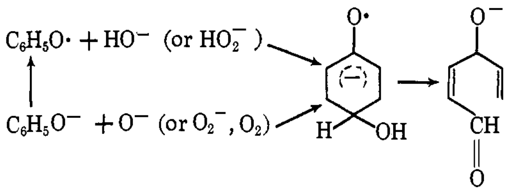
[26] M. C. R. Symons, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p 137 ff.

[27] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Ltd., London, 1960, Chapter 7.

[28] As the kinetic measurements can begin only after a delay of *ca.* 100 μsec following the flash, it is probable that by then all of the phenoxyl radicals have lost their excess energy by collisions with the solvent.

[29] There are variations in the relative amounts of products (Table III) that require explanation. For example, the dihydroxybenzenes (**7**, **8**) appear to be formed relatively more rapidly in the presence of oxygen than in the presence of nitrogen. Secondly, the ratio of carbon-carbon dimers to dihydroxybenzenes changes from a figure >1 to <1 when the phenol concentration decreases (Table III); a tentative interpretation is that the relative importance of processes 2 and 8a-c changes to favor 8a-c. Recall that 99% of the radiation is absorbed within 1.9 and 19 mm of the lamp at the higher (2 × 10^{-2} *M*) and lower (2 × 10^{-3} *M*) concentrations, respectively. Therefore, processes 8a-c could compete more effectively in the dilute phenol solutions. Until the kinetics of the decay of **1** are measured in oxygen-saturated solutions, this explanation of the concentration effect should be treated with reserve.

In basic solution, phenoxide predominates over phenol and process 1 becomes very efficient;[7a] in acid solution, electron capture (as in reaction 3c) presumably prevents the reversal of reaction 1. In strongly basic solutions, it is known that the rates of oxidation of phenols by hydrogen peroxide or oxygen increase enormously; undoubtedly, this is due to an increased importance of reaction of the intermediates, HOC_6H_5OH or C_6H_6OH with oxygen, and of processes such as



etc. (10)

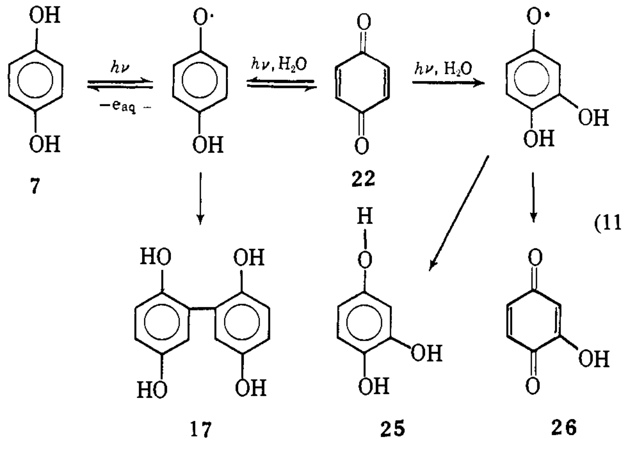
At the low and high pH limits, the dienone forms of phenol and its first products[9,10] are likely to be most susceptible to condensation and cleavage processes. In ammonia one can expect amination (for hydroxylation) which further facilitates condensations; in fact, we obtained only tars from irradiations in liquid ammonia.

Of course, there was evidence of higher molecular weight products even under oxygen-free conditions. Process 6 shows how it is possible to obtain dihydroxybenzenes from phenol *via* the phenoxyphenols.[2] Both kinds of products may form further dimers, tetramers, etc. The *o*- and *p*-dihydroxybenzenes can also give quinones which, as will be shown later, are themselves photolyzed with high efficiency.

The preceding results may be compared with our oxidations of phenol with potassium permanganate or potassium ferricyanide: both reagents produced substantial quantities of tar; the only product that could be identified was **4**. For phenol, at least, these are the typical results of chemical oxidation.

In contrast to chemical oxidations of phenol, which tend to be "dirty," electrochemical oxidations provide an excellent analogy with the present work; Fichter, *et al.*, found **2**, **3**, **6**, **7**, **8**, **22**, **25**, **26**, maleic acid, and resins.[15] These workers demonstrated that **7** and **8** as well as further oxidation products could be derived from both carbon-carbon and carbon-oxygen dimers, a result which has been largely overlooked. By comparison, our photolysis of phenol leads to all of the "first" products **2-8** and none of those related to quinone; moreover only the carbon-oxygen dimers but not the carbon-carbon dimers (**2**, **3**, and **4**) give dihydroxybenzenes on photolysis. Despite the obvious differences in "oxidant," mechanisms, scale of operation, phenol conversion, product work-up, and identification, the similarity in the photolytic and electrolytic products is remarkable. It would appear that most chemical oxidations of phenol are more destructive.

Hydroxyphenols. The irradiation of the dihydroxybenzenes produces carbon-carbon dimerization (see Table IV). Hydroquinone **7** yields the one possible carbon-carbon dimer **18**. Catechol **8** produces the two symmetric carbon-carbon dimers **19** and **20** and very probably the unsymmetric dimer **21**.[30] Resorcinol (**9**) gives the dimer **18** but no 2,2′,6,6′-tetrahydroxybiphenyl, possibly for steric reasons. As authentic carbon-oxygen dimers were not available as tlc reference compounds, we do not know whether they were or were not present in the products.



(11)

Table IV. Products of the Steady Irradiation of the Dihydroxybenzenes and Quinones in Water at 10–20°[a]

Irradiation time, hr	Concn, *M*	Atmosphere	Products 2	7	17	18	19	20	24	25
		Catechol								
8.0	2×10^{-2}	O_2					+	+	–	–
7.5							+	+	–	–
0.5	10^{-2}	O_2						+	–	–
26.0							+	+	–	–[b,d]
3.0	2×10^{-3}	O_2					–	+	–	–
9.5							–	+	–	–
8.0	2×10^{-3}	N_2						+	–	–
40.5								+	–	–
9.0	2×10^{-4}	O_2						*	–	–
		Resorcinol								
9.0	2×10^{-2}	O_2				+			–	–[c]
1.0						+			–	–[c]
3.0						+			–	–[c]
16.0						Tr			–	–[c]
		Hydroquinone								
8.5	10^{-2}	O_2			+				–	–
48.0					+				–	–
22.0	2×10^{-3}	O_2			*				–	–
48.0		N_2			Tr					
18.5	2×10^{-4}	N_2			*				–	–
		p-Quinone								
0.5	2×10^{-4}	N_2		+	Tr					+
4.0	2×10^{-3}			+	Tr					+
4.5		O_2		+	Tr					
		Diphenoquinone								
21.0	8×10^{-3}	O_2	+							

[a] See Table III, footnotes *b* and *c*. [b] pH 2–3. [c] 2,2′,6,6′-Tetrahydroxybiphenyl has not been found. [d] Compound **21** is probably present (+); see ref 30.

Irradiation of **7**, **8**, and **9** yields the corresponding hydroxyphenoxyl radicals in several solvents.[2,5h,7,17] The detection of the hydrated electron also emphasizes a common property of the photolysis of many phenols.[5h,7] By contrast with phenol, we find no hydroxylation products; this will be taken up in the next section.

It is interesting that chemical oxidations of di- (or polyhydric phenols almost always give carbon–carbon coupling products—resorcinol derivatives are occasionally exceptional.[9,10] The chemical oxidations of **7** and **8** also led to quinones which can be hydroxyl-

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(30) An authentic reference sample of **21** was not available. To prepare it, we treated 4-iodoveratrole with 3-lithioveratrole and then demethylated the product. Tlc analysis showed three main compounds of which two were shown to be **19** and **20**; the third was probably **21**.

ated[9,10,12] while the electrochemical oxidations lead to quinones and hydroxyquinone, as well as 1,2,4-trihydroxybenzene (**25**).[15]

Quinones. Irradiation of *p*-quinone (**11**) under nitrogen with a mercury lamp was reported, to give **7**, **25**, and **26**.[31] These products and possibly traces of **17** were also found by us (Table IV) under nitrogen or oxygen. The conversion rate of quinone is the highest among the group of compounds studied here, presumably because of its high extinction coefficient (Table II) and its high quantum efficiency.

Although they did not seek any products, Bridge and Porter give a detailed kinetic decay scheme for excited (triplet) quinone.[32] This species can abstract a proton from water to give the *p*-semiquinone radical (eq 10);[32,33] the coproduct, hydroxyl, can then attack this radical or quinone and lead to **25** after several steps. Flash photolysis work has in fact shown that both **7** and **22** give the *p*-semiquinone radical,[5h,7b,17,32] and this disproportionates rapidly ($k = 4.6 \times 10^6\ M^{-1}\ \text{sec}^{-1}$) to **7** and **22**.[32]

According to eq 11, one should obtain the same products whether one irradiates **7** or **22**. However, we detected no **22** or **25** in the irradiation of **7**. This suggests that the semiquinone goes to **7** at least 10–100 times faster than it dimerizes to **17**. Secondly, we believe that the product-forming reactions from **22** and **7** take place on wholly different time scales such that **22** is essentially decomposed before the usual products of **7** appear (see Tables III and IV). Likewise, the photolysis of **25** is probably more efficient than that of **7** so that it too is not found as a product of **7**.

Diphenoquinone yields 4,4′-dihydroxybenzene (**2**) under irradiation. Other products could not be identified because of the lack of reference compounds.

Methylphenols. The steady irradiation products of the cresols are given in Table V. *p*-Cresol yields three (expected) products, the carbon–carbon (**13**) and carbon-oxygen (**15**) dimers as well as the hydroxylated compound **12**; *o*-cresol gave two dimers (**14** and **16**) and two hydroxylated products (**10** and **11**); *m*-cresol gave the three expected hydroxylation products **10**, **11**, and **12**. Irradiation of the carbon-carbon dimers **13** and **14** does not yield the corresponding hydroxylation products. It is probable that at least some of the other plausible dimers were formed because tlc analysis revealed more "spots" in the dimer region; unfortunately, authentic samples of these compounds were unavailable for comparison.

Table V. Products of the Steady Irradiation of the Methylphenols ($2 \times 10^{-3}\ M$) in Water at 10–20°

Irradiation time, hr	Atmosphere	Products[a] 10	11	12	13	14	15	16	7, 8, 9
				p-Cresol					
0.5	O_2			−	+				
2.25				Tr	+				
8.0				+	+				−
18.5				+	+		Tr		−
48.0	N_2				+				
				o-Cresol					
0.5	O_2	−	−			+			
2.25		Tr	−			+			
9.0		+	+			+			−
22.0		+	+			+		Tr	−
				m-Cresol					
0.5	O_2	*							
2.0		+	*	*					
4.0, 9.0		+	+	+					−

[a] See Table III, footnotes *b* and *c*.

The cresol products suggest that the mechanisms proposed for phenol are also appropriate here. In addition, flash spectroscopy shows that the cresols yield the methylphenoxyl radicals in several solvents[7,17] as well as the hydrated electron in water,[7] and like **1**, the decay of *p*-methylphenoxyl in water is second order with $k = 6.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[7]

As with the other phenols, chemical, electrochemical, or enzymatic oxidation of the cresols yields similar but fewer simple products than by our photooxidation.[9,10,12,14] On the other hand, 2,2′-dihydroxy-4,4′-dimethyldiphenyl ether,[15] Pummerer's ketone, trimers, etc.,[9,10] which have been obtained in one oxidation or another, may have been present in our products but were not sought. It is worth pointing out that dimerization of the *o*- and *p*-methylphenoxyl radical may also occur at the ring carbon atom to which the methyl group is attached. The resulting quinoid structures presumably have high extinctions (Table II) and would probably be photooxidized preferentially.

Appendix

For the thermochemical calculations we require: (a) these bond energies in kcal mole^{-1},[34] H—H (103), HO—H (116), HO_2—H (90), HO—OH (48), C_6H_5O—H (90), C_6H_5—OH (104), C_6H_5—H (102), $CH_2{=}CHCH_2$—H (77), $CH_2{=}CHCH_2$—CH_3 (62), $CH_2{=}CHCH_2$—OH (71), $C_6H_5CH_2$—H (78); and (b) the resonance stabilization in a methylpentadienyl radical, *ca.* 15 kcal mole^{-1}.[35]

The thermochemistry of eq 1 can be estimated as follows. For the hydrated electron, $E° \simeq 2.7$ v while for phenol $E° \simeq -1.2$ v[36] so that $E° = -3.9$ v or $E = -3.5$ v at pH 7 for eq 1.[4e,5h] Since 2537 A corresponds to 4.9 ev, this leaves 1.4 ev (32 kcal) excess energy in the products, provided that the entropy changes are neglected. Alternatively, apart from two relatively small hydration energies which partially cancel, enthalpy terms in the following scheme yield an estimate of $\Delta H(1) \simeq 4.0$ ev for eq 1.

$$\begin{tikzcd}
C_6H_5OH(g) \arrow[r, "3.9\ \text{ev}"] \arrow[dd, "?"] & C_6H_5O(g) + H(g) \arrow[dd, "?"] \arrow[dr, "13.5\ \text{ev}"] & & \\
& & H^+(g) + \arrow[d, "11.7\ \text{ev}"] & e^-(g) \arrow[d, "1.75\ \text{ev}^{4e}"] & \\
C_6H_5OH(aq) \arrow[r, "\Delta H(1)"] & C_6H_5O(aq) + & H^+(aq) + & e_{aq}^- & (12)
\end{tikzcd}$$

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(31) F. Poupé, *Collection Czech. Chem. Commun.*, **12**, 225 (1947).

(32) N. K. Bridge and G. Porter, *Proc. Roy. Soc.* (London), **A244**, 259, 276 (1958).

(33) An alternate or parallel process, namely, hydroxyl abstraction from the water followed by hydrogen attack on an unexcited quinone, would lead to the same products.

(34) 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.

(35) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p 51.

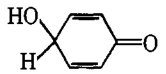
(36) T. Fueno, T. Ree, and H. Eyring, *J. Phys. Chem.*, **63**, 1940 (1959).

This estimate of the excess energy is *ca.* 0.9 ev (~21 kcal $mole^{-1}$).

To estimate whether reaction 9a is feasible, we write the sequence

$$C_6H_5O\cdot \longrightarrow HOC_6H_4\cdot \qquad \Delta H = 12 \text{ kcal mole}^{-1}$$

$$HOC_6H_4\cdot + H_2O \longrightarrow HOC_6H_4OH + H \qquad \Delta H = 12 \text{ kcal mole}^{-1}$$

$HOC_6H_4OH \longrightarrow$  ($\Delta H = 18$ kcal $mole^{-1}$)[37]

Summing the enthalpies, we find that process 9a is endothermic by 42 kcal $mole^{-1}$. Therefore, any excess vibrational energy in the range 21–32 kcal $mole^{-1}$ does not seem sufficient to allow phenoxyl to react with water.

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The Electronic Structure of Phosphate Esters

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Abstract: A simple self-consistent molecular orbital method is used to calculate the charge distributions and energies arising from 2p–3d orbital interactions in phosphates. Application of the method to different conformations of phosphate aliphatic esters gives energy values which can be correlated with the known structural features of these esters and the thermochemical data available for the heats of saponification of the acyclic and cyclic forms. The resulting charge distributions are in accord with the reaction rate data for these compounds and they offer a possible explanation for the exceptionally high reactivity of the cyclic esters. The theory implies that the rate of nucleophilic attack on the phosphorus atom is sensitive to the conformation of the ester groups about this atom and suggests that these conformational changes may be important factors in determining the reactivity of phosphates and polyphosphates.

Although phosphorus is an important constituent of biological systems and appears to play a fundamental role in metabolic processes, an understanding of its chemical behavior in living systems has been retarded by the lack of a sound conceptual scheme to describe the bonding within phosphate and polyphosphate esters. In this paper an attempt is made to develop a scheme that will be applicable to a study of both the chemistry and conformation of phosphate esters and the esters of pyro- and triphosphates as well as analogous compounds based on silicon, sulfur, and chlorine. The first application will be to diester and triester phosphates—particularly to an interpretation of their neutral and basic hydrolysis rates and their conformation in the solid state.

Molecular oribital calculations of the Hückel type have been carried out on phosphates by a number of workers,[2-4] but the calculations all suffer from the lack of explicit consideration of the geometry of the phosphate group.

Pauling[5] was probably the first to suggest that the 3d orbitals on the central atom could be involved in π-type bonds with the oxygen atoms in the tetrahedral MO_4^{-n} ions. These ideas have been extended by Van Wazer[6] to account for the properties of a large variety of phosphorus compounds. A more explicit proposal for 2p–3d bonding in tetrahedral ions has been put forward by Cruickshank[7] in which the geometrical properties of two of the five 3d orbitals were introduced in a qualitative manner and used to account for the bond distances and geometries of a large number of compounds in which Si, P, S, and Cl were involved in tetrahedral bonding.

The work to be reported here goes one step beyond the qualitative picture of Cruickshank. The basic idea of the importance of 2p–3d π-type bonding, superimposed on a σ-bond skeleton made up of sp^3-hybrid orbitals on the central atom, has been used. The formulation has been generalized by the removal of symmetry restrictions and by the introduction of all five 3d orbitals into the calculation, not just the two strong-bonding ones. A simple Hückel molecular orbital treatment has been used with self-consistent features to refine the Hückel parameters and both net charges and π-electron energies have been derived. The former quantity is used to interpret chemical reactivity; the latter to interpret thermodynamic quantities and conformation. Such an unsophisticated treatment of complex phenomena cannot be expected to give a complete quantitative understanding of phosphate chemistry, but, as will appear later, certain rather gross chemical and structural features can be correlated by such a treatment and implications arise which may be

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