Flash Photolysis Study of Phenyl-substituted Phenols, Quinones, and Corresponding Free Radicals. Part 3.† Intermediates in the Photolysis of Phenyl-substituted Phenols

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Aryloxyl radicals are formed on photoexcitation of phenyl-substituted phenols in a biphotonic process involving the triplet excited state. These aryloxyl radicals are also formed on photolysis of the corresponding phenolate ions in the presence of oxygen involving the singlet excited state.

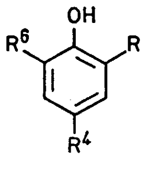
THE photolysis of certain simple phenols in the liquid phase affords phenoxyl radicals, solvated electrons, and hydrogen.[1] These processes have been shown to occur by a biphotonic mechanism (1) involving the triplet excited states of the given phenols.[2-4] Photoexcitation

$$\mathrm{ArOH} \xrightarrow{h\nu_1} [\mathrm{ArOH}]_T^*$$

$$[\mathrm{ArOH}]_T^* \xrightarrow{h\nu_2} \begin{cases} \mathrm{ArO\cdot} + e_{\mathrm{solv.}} + \mathrm{H}^+ \\ \mathrm{ArO\cdot} + \mathrm{H\cdot} \end{cases} \qquad (1)$$

of sterically hindered phenols bearing *o*-t-butyl groups failed to produce the corresponding phenoxyl radicals.[5]

This paper deals with the photoionisation (photodissociation) of some phenyl-substituted phenols (I)—(V) as studied by flash photolysis. The spectral characteristics of the phenols are listed in Table 1. The phenoxyl radicals corresponding to phenols (I)—(V) are denoted as (Ia)—(Va).



(I) $R^2 = R^6 = Ph, R^4 = OCH_3$
(II) $R^2 = R^4 = R^6 = Ph$
(III) $R^2 = R^6 = Ph, R^4 = H$
(IV) $R^2 = R^4 = Ph, R^6 = H$
(V) $R^2 = R^6 = Ph, R^4 = 2,6\ (Ph)_2C_6H_3O$

RESULTS AND DISCUSSION

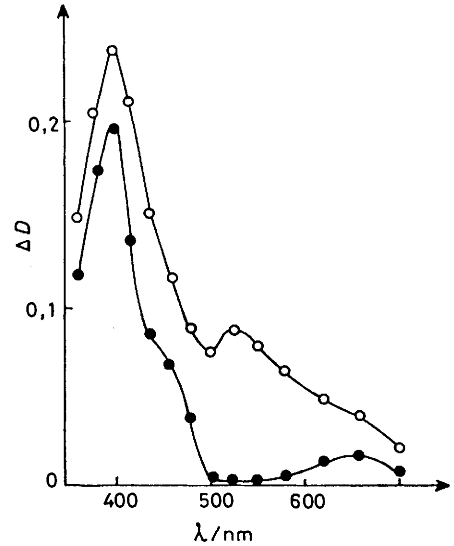
Phenols.—Pulsed photoexcitation of deoxygenated solutions of phenols (I)—(V) (5×10^{-4}M) in propanol results in the appearance of short-lived (τ *ca.* 10^{-4} s) species (Figure). The absorption spectra of these species show maxima in the region of λ 480—540 nm and are ascribed to triplet–triplet absorption of the phenols. The triplet lifetimes of phenols (I)—(V) in solution are two orders of magnitude longer than those of phenol, *p*-cresol, and tyrosine (τ *ca.* 3×10^{-6} s).[2] This must be ascribed to the increased conjugation upon the introduction of phenyl substituents into the molecule. The same effect is observed on going from benzene (τ *ca.* 2×10^{-6} s) to biphenyl (τ *ca.* 10^{-4} s).[6]

TABLE 1

Spectral characteristic of phenyl-substituted phenols

Phenol	$\lambda_{\max.}$/nm	$10^{-3}\varepsilon$/l mol^{-1} cm^{-1}
(I)	315	9.0
(II)	308 [a]	4.5
(III)	298	6.0
(IV)	308 [a]	4.5
(V)	318	7.0

[a] Shoulder. Error in $\lambda_{\max.}$ ± 2 nm, in ε $\pm 0.5 \times 10^3$ l mol^{-1} cm^{-1}.



Absorption spectra of the transient species produced on photoexcitation at λ 320—390 nm of 4-methoxy-2,6-diphenylphenol (5×10^{-4}M) in propanol. Optical density read at 2.5 μs (○) and 500 μs (●) after the 2.0 μs flush

The triplet energy level of (I), estimated from the fluorescence spectrum to be 60 kcal mol^{-1}, is markedly diminished compared with phenol (70—85 kcal mol^{-1}).[7]

The relatively long-lived species obtained by flash photolysis of solutions of phenols (I)—(V) are the phenoxyl radicals (Ia)—(Va).[8] The absorption maxima of (Ia)—(Va) are shown in Table 2. The lifetime of the triplet excited state of phenol (I) decreases with increasing light intensity. This is caused by an increased yield of (Ia) and subsequent quenching of the triplet by the radical ($k_2 = k_{\mathrm{diff.}}$). Quenching occurs by energy

$$[\mathrm{ArOH}]_T^* + \mathrm{ArO\cdot} \longrightarrow \mathrm{ArOH} + [\mathrm{ArO\cdot}]^* \qquad (2)$$

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† Part 2, I. V. Khudyakov, P. P. Levin, jun., V. A. Kuz'min, H. J. Hageman, and C. R. H. I. de Jonge, preceding paper.

TABLE 2

Spectral characteristics of phenyl-substituted phenoxyl radicals

Radical	$\lambda_{max.}$/nm	Relative intensities
(Ia)	405	12
	650	1
(IIa)	380	4.5
	550	3
	750	1
(IIIa)	360	10
	760	1
(IVa)	350	11
	520	2.5
	660	1
(Va)	395	14
	650	1

Error in $\lambda_{max.}$ is 1%.

transfer to form the excited state (Ia).[9] Addition of azulene (A) to deoxygenated solutions of phenol (I) resulted in quenching of the triplet excited state. The high rate constant of quenching ($k_3 = k_{diff.}$) indicates that quenching occurs by triplet–triplet energy transfer.

$$[ArOH]_T^* + A_{S_0} \longrightarrow ArOH_{S_0} + A_T^* \qquad (3)$$

Quenching with $Ni(NO_3)_2{\cdot}6H_2O$ has a rate constant k of 10^6 l mol^{-1} s^{-1} which is close to the rate constant of

$$[ArOH]_T^* + Ni^{2+} \longrightarrow ArOH_{S_0} + Ni^{2+*} \qquad (4)$$

triplet-state quenching of aromatic hydrocarbons by transition metal ions.[10] The yield of radical (Ia) decreases upon addition of sufficiently high amounts of azulene or $Ni(NO_3)_2{\cdot}6H_2O$ at which the lifetime of the triplet excited state of phenol becomes shorter than the light pulse duration.

The radical yield of an aerated solution of phenol (I) is lower (by one-third) than that of a deoxygenated solution.

These facts indicate a contribution by the triplet excited state of phenol (I) to photodissociation.

The phenoxyl radical concentration upon pulsed photoexcitation of both deoxygenated and aerated solutions of phenol (I) at 320—290 nm is directly proportional to the square of the light intensity. Thus, when phenol (I) is photoexcited in the long wavelength region, photodissociation seems to occur by a biphotonic mechanism involving the triplet excited state. The radical yield of photoexcitation in the long- and short-wave absorption bands of phenol (I) (in the range $\lambda > 200$ nm) increases with I^n where $n \approx 1.5$. The various dependences of the yield of (Ia) can probably be explained as follows: (i) dissociation of phenol (I) may also occur from the high singlet excited state; (ii) the radical yield can be directly proportional to the light intensity in a biphotonic process, if photoionisation by the second light quantum becomes the main channel of triplet state decay.

Phenolate Anions.—Pulsed photoexcitation of a deoxygenated solution of the anion of phenol (I) fails to give radical (Ia). However, flash photolysis of an aerated solution of the anion of (I) in propanol containing 2M-KOH [$\lambda_{max.}$ 360 nm (ε 1.1 × 10^4 l mol^{-1} cm^{-1})] in the 320—290 nm region results in the formation of an intermediate with an absorption spectrum coinciding with that of radical (Ia). Thus the phenoxyl radical is presumably formed by reaction (5). With pulsed

$$[ArO^-]^* + O_2 \longrightarrow ArO{\cdot} + O_2^{-{\cdot}} \qquad (5)$$

photoexcitation of an aerated solution of the anion of phenol (I) in the 320—390 nm region, the yield of (Ia) builds up in proportion to the light intensity, which indicates the contribution of one light quantum to ionisation.

When the temperature of the solution is raised from 20 to 80 °C the radical yield shows a 1—5-fold increase, which is ascribed to the activation energy of reaction (5).

The excited state of the anion of phenol (I) involved in reaction (5) must be the excited singlet state as concluded from the following observations. The fluorescence quantum yield Φ_f of the anion of phenol (I) is found to be 0.96 [*cf.* Φ_f of phenol (I) in propanol is 0.17 using anthracene as a reference, which is close to the value of 0.16 reported[11] for phenol]. The introduction of phenyl substituents into the ring apparently raises Φ_f from *ca.* 0[12] to *ca.* 1. Moreover, the fluorescence lifetime of the anion of phenol (I) is 6.2 ns. [*cf.* 1.4 ns for phenol (I)], which is sufficiently long for reaction. A contribution from the triplet excited state of anion (I) is considered unlikely on account of the high Q_f of anion (I). Final support for the involvement of the excited singlet state of anion (I) comes from laser photolysis, using exciting light of λ 353 nm. Radical (Ia) was formed in <20 ns.

EXPERIMENTAL

The spectra and decay kinetics of intermediates were studied by means of flash photolysis with 2-μs flash duration and 500 J energy. U.v. light filters UVS-6 (320—390 nm), UVS-5 (260—380 nm), and a water filter (>200 nm) were used A neodymium laser ($\lambda_{exc.}$ 353 nm) with a 20-ns resolution time was used in the experiments with phenolate ions.

Phenol (I) was synthesised as previously described.[13] Phenol (II) was a commercial sample. Phenol (III) was synthesised as described.[14]

Phenol (IV).—To 4-phenylphenol (170 g, 1 mol) was added aluminium foil (1 g) and the mixture was heated to 250 °C. After cooling to 60 °C cyclohexene was introduced over 2 h.[15] Crude 2-cyclohexyl-4-phenylphenol was dehydrogenated with a Pt–C catalyst to yield 2,4-diphenylphenol (167 g, 68%), m.p. 97.5—98.0 °C.

Phenol (V).—This phenol was synthesised in a four-step procedure starting from 2,6-diphenylphenol. (i) Methylation, using dimethyl sulphate afforded 2,6-diphenylanisole in 93% yield, m.p. 40.5—41.5 °C. (ii) The anisole was brominated in glacial acetic acid to 4-bromo-2,6-diphenylanisole in 51% yield, m.p. 93.1—93.8 °C. (iii) Using the Ullmann coupling procedure 4-bromo-2,6-diphenylanisole was converted to 2,6-diphenyl-4-(2,6-diphenylphenoxy)anisole with sodium 2,6-diphenylphenolate and CuCl–pyridine catalyst in 50% yield, m.p. 148.5—149.4 °C. (iv) Demethylation, using HI in acetic acid finally gave 2,6-diphenyl-4-(2,6-diphenylphenoxy)phenol in 38% yield, m.p. 164.3—165.0 °C (from benzene–acetone 1 : 1).

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REFERENCES

[1] I. V. Khudyakov and V. A. Kuz'min, *Usp. Khim.*, 1975, **44**, 1748.

[2] D. V. Bent and E. Hayon, *J. Am. Chem. Soc.*, 1975, **97**, 2599.

[3] J. Feitelson, E. Hayon, and A. Treinin, *J. Am. Chem. Soc.*, 1973, **95**, 1025.

[4] M. P. Pileni, D. Lavalette, and B. Muel, *J. Am. Chem. Soc.*, 1975, **97**, 2283.

[5] V. A. Kuz'min, I. V. Khudyakov, A. S. Tatikolov, A. L. Prookof'ev, and N. M. Emanuel, *Dokl. Akad. Nauk. SSSR*, 1976, **227**, 122.

[6] K. Sandros, *Acta Chem. Scand.*, 1969, **23**, 2815.

[7] R. S. Becker, 'Theory and Interpretation of Fluorescence and Phosphorescence', Wiley-Interscience, New York, 1969.

[8] V. A. Kuz'min, I. V. Khudyakov, P. P. Levin, N. M. Emanuel, C. R. H. I. de Jonge, H. J. Hageman, M. E. F. Biemond, F. P. B. v. d. Maeden, and W. J. Mijs, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1540.

[9] A. S. Tatikolov and V. A. Kuz'min, *Dokl. Akad Nauk SSSR*, 1975, **223**, 403.

[10] V. L. Ermolaev, E. B. Sveshnikov, and T. A. Shakhverdov, *Usp. Khim.*, 1974, **44**, 48.

[11] H. C. Borresen and C. A. Parker, *Anal. Chem.*, 1966, **38**, 1073.

[12] R. T. Williams and J. W. Bridges, *J. Clin. Pathol.*, 1964, **17**, 371.

[13] C. R. H. I. de Jonge, H. J. Hageman, W. G. B. Huysmans, and W. J. Mijs *J. Chem. Soc., Perkin Trans. 2*, 1973, 1276.

[14] J. Plesek, *Collect. Czech. Chem. Commun.*, 1956, **21**, 375.

[15] A. S. Hay, *J. Org. Chem.*, 1969, **34**, 1160.