PRIMARY PHOTOCHEMICAL PROCESSES IN AROMATIC MOLECULES

PART 6.—THE ABSORPTION SPECTRA AND ACIDITY CONSTANTS OF PHENOXYL RADICALS

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Phenoxyl radicals and their derivatives have been prepared by flash photolysis in gaseous and liquid systems, by chemical oxidation and by photolysis of rigid solutions. Their spectra have been recorded and the longer wavelength system, expected on theoretical grounds, has been observed. Investigations of the spectrum as a function of pH show that these radicals are very weak bases and that, contrary to the interpretations of some other workers, the spectra observed under all conditions except those of very high acidity are to be attributed to neutral unprotonated radicals.

The photolysis of aromatic hydrocarbons having alkyl, amino or hydroxyl groups, gives rise to transient products which have been attributed to the benzyl, anilino and phenoxyl radicals respectively and to their derivatives. These absorption spectra were first observed by Porter and Wright [1] in flash photolysis studies of aromatic vapours and were detected shortly afterwards by Norman and Porter [2] as trapped products of photolysis in glassy solutions at low temperatures. Whilst the benzyl and anilino radicals gave rise to strong and rather sharp characteristic band spectra which for benzyl have now been well established,[3] the spectrum of the phenoxyl radical was weak and diffuse and not readily identified since it appeared only at short wavelengths close to that of the parent molecule.

Subsequent work on the semiquinone radicals showed that these species have their most characteristic spectra, though not necessarily the strongest, at longer wavelengths in the region of 4000 Å, and this fact, as well as theoretical considerations and analogy with benzyl, led us to believe that phenoxyl radicals should also have a longer wavelength absorption. This paper describes the detection of such spectra in solutions of phenol and related compounds, as the stabilized products of photolysis at low temperatures, in flash photolysis of fluid solutions, and by chemical oxidation of sterically hindered phenols. During the course of this work, Grossweiner and Mulac [4] have reported some of these spectra but have given a different interpretation to that proposed in this communication.

LOW TEMPERATURE STABILIZATION STUDIES

Experiments carried out in a cell of 1 cm path length and in an apparatus similar to that described earlier [2] showed that photolysis of phenol and anisole in non-polar hydrocarbon glasses (M.P.) and also in polar glasses (E.P.A.) gave only the diffuse low wavelength spectrum previously found and attributed to phenoxyl. When the path length was extended to 20 cm by means of the apparatus used for the detection of the longer wavelength system of benzyl and previously described,[3] additional bands appeared after photolysis of phenol, the longest wavelength absorption being a sharp band at 4031 Å. This band was also observed after photolysis of anisole under the same conditions. Other bands were observed at lower wavelengths but these occurred at different positions in phenol and anisole.

The wavelengths of all assigned absorption maxima are recorded in the table. The spectra were readily visible after 4 min irradiation with a low-pressure mercury arc, were stable indefinitely in the glass at 77°K and disappeared irreversibly on raising the temperature of the glass.

These spectra are very similar in position to those of the semiquinone radicals observed from photolysis of benzoquinone and hydrobenzoquinone under similar conditions. Photolysis of β naphthol in rigid M.P. solution results in a strong band at 4638 Å which we attribute to the neutral β naphthoxyl radical. This assignment is supported by independent flash-photolysis studies on β naphthol[5] where the same band appeared but shifted 12 Å to longer wavelengths.

TABLE 1.—PHENOXYL RADICAL SPECTRA

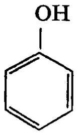
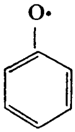
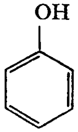
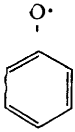
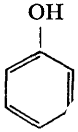
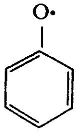
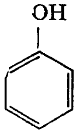
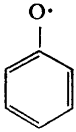
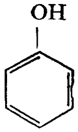
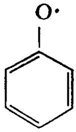
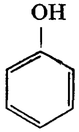
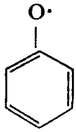
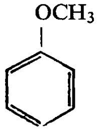
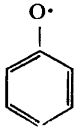
parent molecule	radical	method of production*	solvent	radical absorption maxima	approximate relative intensities
		*a*	MP glass	4031 3833	1 1
		*b*	liquid paraffin	4030 3840 3000	7 5 8
		*b*	CCl_4	4010 3830 3000	6 4 10
		*b*	hexane	4020 3840 2990	5 4 10
		*b*	H_2O	4000 3820 2960	10 7 5
		*b*	vapour phase	3950 3800 2920	2 1 20
		*a*	MP glass	4031 3833	1 1

TABLE 1—*contd.*

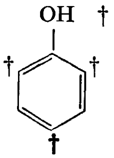
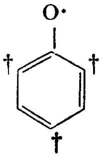
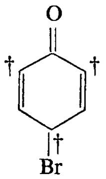
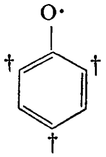
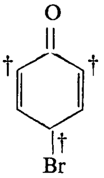
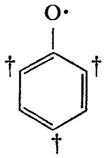
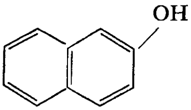
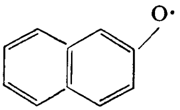
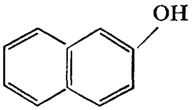
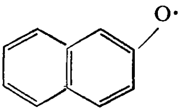
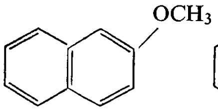
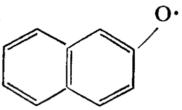
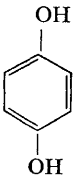
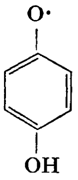
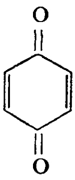
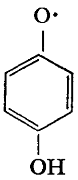
parent molecule	radical	method of production*	solvent	radical absorption maxima	approximate relative intensities
		*b*	hexane	4020 3840 3130	5 4 10
		*c*	hexane	6250 4000 3820 3125 3025 2700	2 9 7 28 28 42
		*c*	CCl_4	6150 4010 3830 3130	1 4 3 10
		*a*	MP glass	4638	—
		*b*	liquid paraffin	4650	—
		*b*	liquid paraffin	4650	
	 17	*a*	EPA glass	4140 3550	10 6
 (+RH)	 17	*a*	EPA glass	4140 3550	10 6

TABLE 1—*contd.*

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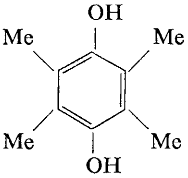
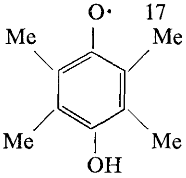
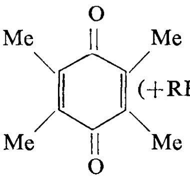
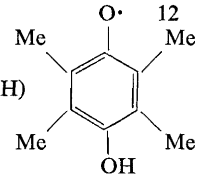
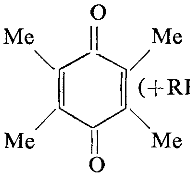
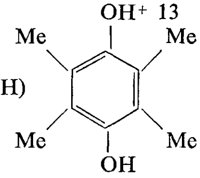
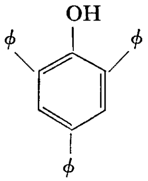
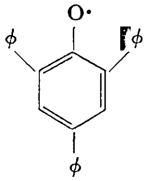
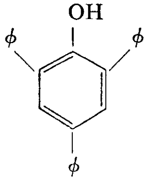
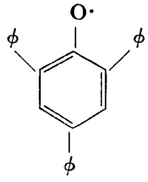
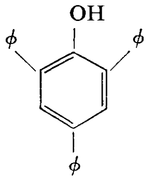
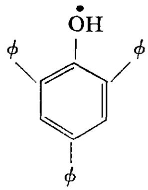
	 17	*a*	EPA glass	4220 4041 3300	10 4 8
 (+RH)	 12	*b*	50 % EtOH+ H_2O+0·1 N H_2SO_4	4150 ~3950	3 2
 (+RH)	 13	*b*	50 % EtOH+ H_2O+12 N H_2SO_4	4450 ~4200	3 2
	 †	*b*	50 % EtOH+ H_2O	3800 ~5600	3 2
	 +	*b, d*	CCl_4	3825 ~5250	3 2
		*b*	25 % EtOH+ H_2O+50 % $HClO_4$, 50 % EtOH+ 50 % H_2SO_4	3925	—

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* Methods of production of radicals: (*a*) photolysis in a rigid medium at liquid nitrogen temperature; (*b*) flash photolysis; (*c*) reaction with mercury; (*d*) chemical oxidation.

† ≡ tri-tertiary butyl group $(CH_3)_3C$—

FLASH PHOTOLYSIS INVESTIGATIONS

These were carried out using a flash of 1460 J and photographic spectral recording. The first experiments in air-free and air-saturated viscous paraffin solutions of phenol of concentration approximately 10^{-3} M showed a transient absorption having a sharp maximum at 4030 Å and a broader absorption around 3000 Å, lifetimes being over 100 μsec. Later, aqueous solutions of phenol were studied over the acidity range bounded by 2 M NaOH and 12 M H_2SO_4; in all cases the same species absorbing at $\sim$4000 Å was observed as the primary product, but the lifetime was shorter than that in liquid paraffin. On flashing the solution of phenol in 1 M NaOH several times, a broader transient spectrum, with ill-defined maxima at 4200, 4300 and 4500 Å, appeared whose intensity increased with the number of flashes (fig. 1). This secondary product has a spectrum similar to that reported by Grossweiner and Zwicker[6] and assigned by them to the phenoxyl radical. Blank runs using the degassed NaOH solution alone showed the weak broad transient absorption reported by these latter workers. Vapour-phase photolysis of phenol was carried out in an all-quartz reaction vessel 22 cm in length surrounded by a jacket containing distilled water at about 90°C. Photolysis of 20 mm Hg pressure of phenol, with 300 mm Hg pressure of krypton resulted in the observation of the 2920 Å peak previously reported by Porter and Wright[1] and also, relatively weakly, the longer wavelength band at 3950 Å (fig. 2).

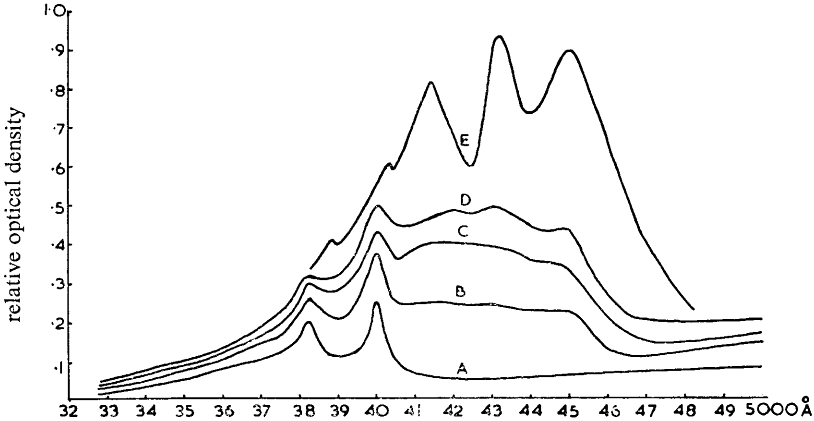


FIG. 1.—Graph showing build-up of a transient of a product after photolyzing phenol in degassed 1 N NaOH.

A, 1st flash; B, 2nd flash; C, 3rd flash; D, 4th flash.

E, spectrum of ϕO· reported by Grossweiner and Zwicker.

Cook and co-workers,[7] and Muller and co-workers,[8] have studied several fairly stable radicals formed by oxidation of sterically hindered phenols. The first, and one of the most stable, was tri-tertiary butyl phenoxyl, which can be prepared readily by oxidizing tri-tertiary butyl phenol with PbO_2 or alkaline ferricyanide. The resulting blue solution maintains its colour for weeks if air is excluded, oxygen reacting rapidly with the radical to form bis (1, 3, 5-tri-tertiary butyl 2, 5-cyclohexadiene-4-one) peroxide. The radical may be prepared essentially quantitatively[7] by reaction of 2, 4, 6-tri-tertiary butyl-4-bromo 2, 5-cyclohexadienone with mercury and its spectrum studied at leisure on account of its stability. The spectrum obtained by preparing the radical in this way in hexane solution is shown in fig. 2. Cook *et al.*[9] give the molar extinction coefficient of the weak broad visible band at 6250 Å as 400 ± 3 in benzene and if we assume that the extinction coefficient in hexane is approximately the same, then the extinctions of the 4000 and 3125 Å peaks are 1800 and 5500 respectively. The radical produced either chemically or by flash photolysis from tri-tertiary butyl phenol has a spectrum almost identical with that of the radical produced by flash photolysis of unsubstituted phenol in hexane, liquid paraffin, carbon tetrachloride or water, and

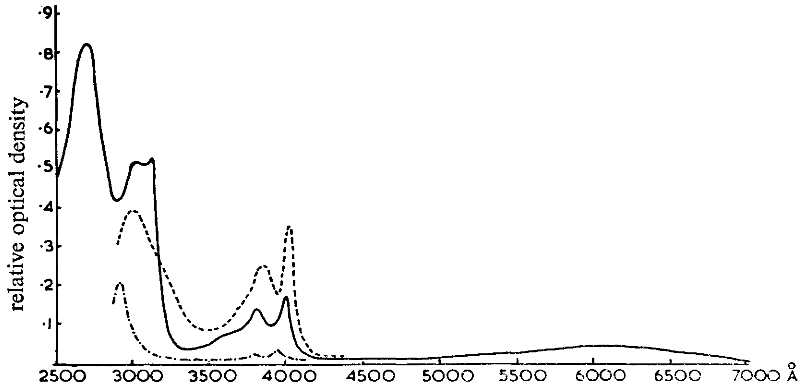


FIG. 2.—Phenoxyl radical spectra: —— $\phi O\cdot$ in liquid paraffin produced by flash photolysis; —— tri-tertiary butyl $\phi\dot{O}$ in hexane produced chemically; —.—.—. $\phi\dot{O}$ (gas phase) produced by flash photolysis.

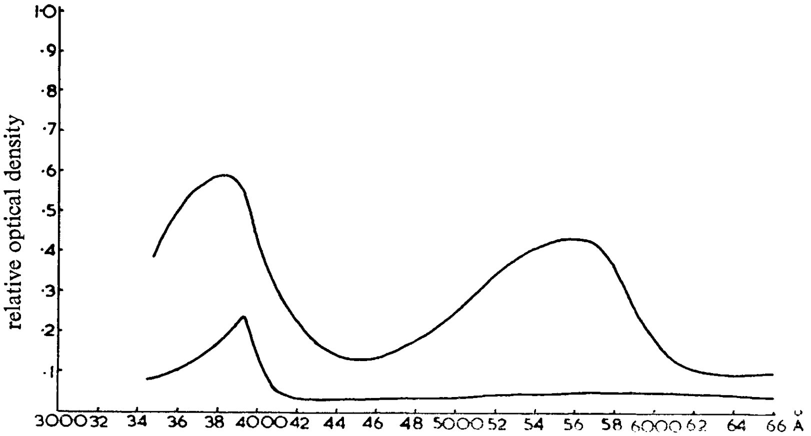


FIG. 3.—Spectrum of 2, 4, 6-triphenyl phenoxyl and its corresponding protonated radical cation. Upper curve: $\phi_3\phi O\cdot$ in 50 % EtOH+50 % H_2O; lower curve: $\phi_3\phi OH^+$ in 50 % H_2SO_4+50 % EtOH.

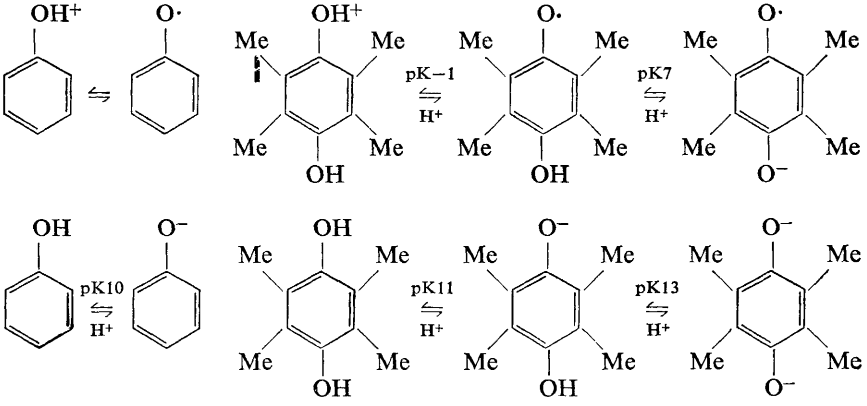
the extinction coefficients of both radicals are probably of the same order of magnitude although the relative strengths of the 6000, 4000 and 3000 Å bands may be different. Approximately 1 or 2 % conversion of simple or hindered phenol to the corresponding phenoxyl radical was observed after each flash assuming an extinction coefficient for the radical of 1800 at 4000 Å.

Another stable phenoxyl radical that can be prepared chemically or photochemically is that derived from 2, 4, 6-triphenyl phenol. This red-coloured radical, discovered by Dimroth and Neubauer,[10] does not react with oxygen and exists in solution in equilibrium with its dimer. On adding strong acid (70 % $HClO_4$ or conc. H_2SO_4) to a solution of this radical in CCl_4, a blue substance is produced at the junction between the two layers, which on shaking is extracted into the acid, the red colouration at the same time being removed from the organic layer. Dimroth *et al*[11] suggested that this blue substance, which is only stable for a short time, might be the corresponding protonated radical cation $\phi_3\phi OH^+$. Flash photolysis of solutions of 2, 4, 6-triphenyl phenol in ethanol+water mixtures containing 50 % $HClO_4$ or 50 % H_2SO_4 produces a quite different transient radical species to that observed when no mineral acid is present in the solvent (fig. 3). The spectrum we observe in neutral 50 % ethanol+water is very similar to that seen by Dimroth in other solvents and assigned by him to 2, 4, 6-triphenylphenoxyl. We therefore attribute the different transient spectrum obtained in strongly acidic solution to the protonated radical cation. Our radical concentrations decay rapidly to a low value owing to dimer formation.

Spectra of stable radical solutions were measured using a Unicam S.P. 500 spectrophotometer and transients were recorded on Ilford HP 3 photographic plates followed by photometry with the aid of a Joyce-Loebl double beam microdensitometer. We are grateful to Prof. K. Dimroth for the gift of a sample of 2, 4, 6-triphenyl phenol; other phenols and the spectroscopic grade solvents used were obtained commercially. Impurities absorbing above 250 $m\mu$ were removed from BP 890 liquid paraffin by passing it repeatedly over activated silica gel.

DISCUSSION

By analogy with the durohydroquinone system studied by Bridge, Porter and Land[12, 13] the acidity constant of the phenoxyl radical+phenol radical cation system would be expected to lie well on the acid side of pH 7, rather than at pH 13 as proposed by Grossweiner and Zwicker.



Phenol system

Durohydroquinone system

We studied phenol solutions of varying acidity up to concentrated sulphuric acid hoping to observe a shift in the 4000 Å peak system corresponding to protonation of the phenoxyl radical. However, we found the same band system at all concentrations up to 12 M H_2SO_4 and no transients in solutions above this molarity in H_2SO_4. The 2700 Å peak of phenol when dissolved in more concentrated solutions of H_2SO_4 than 12 M is irreversibly shifted by about 150 Å to longer wavelengths. Work on the cryoscopic constants of phenol solutions in pure sulphuric acid[14] suggests that phenol rapidly sulphonates and esterifies in such a medium. It seems likely, therefore, that phenol is unstable in acid solutions greater than 12 M in H_2SO_4 which explains why the 4000 Å band is no longer observed when such solutions are photolyzed. The expected shift may be observable in a solvent of higher protonating power which does not react substitutively with phenol. Photolysis of phenol solutions containing more than 25 % perchloric acid produces an unidentified transient absorption at 5000 Å as well as the phenoxyl absorption at 4000 Å.

However, photolysis of increasingly acidic solutions of 2, 4, 6-triphenyl phenol results in a falling off of the neutral radical intensity accompanied by the appearance of a different transient spectrum (fig. 3 and 4) which we assign to the corresponding protonated radical cation. A plot of concentration of neutral radical against concentration of acid in the solvent shows the pK of the $\phi_3\phi O\cdot + \phi_3\phi OH^+$ system to be approximately at the acidity of 15 N H_2SO_4 in 50 % ethanol+water, the assumption being made that equilibrium has been attained between protonated and unprotonated forms when we observe them and that equal concentrations of the parent phenol give rise to equal amounts of radical under all the different acidity conditions. Solutions of 15 N H_2SO_4 in water alone and in 20 % EtOH have acidity functions of −3·6 and −5·0 respectively.[15]

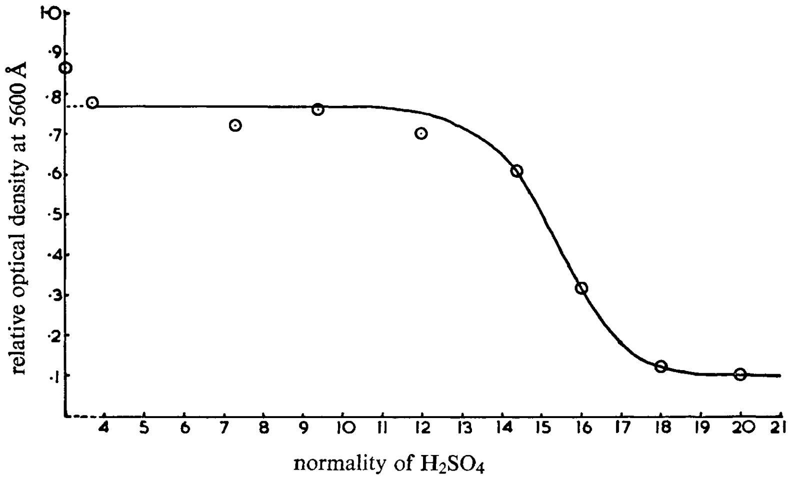


FIG. 4.—Graph to show the reduction of $\phi_3\phi O\cdot$ absorption, due to the equilibrium: $\phi_3\phi O\cdot + H^+ \rightleftharpoons \phi_3\phi OH^+$, on increasing the solvent acid concentration.

2, 4, 6-tri-tertiary butyl phenoxyl has a very similar spectrum to that of phenoxyl itself whereas introduction of aromatic substituents changes the spectrum of the corresponding phenoxyl radical considerably (fig. 2 and 3). Triphenyl phenoxyl has many more possible resonance structures than phenoxyl itself and its longest wavelength absorption band has a much higher extinction coefficient.[11] We attribute the ~4000 Å band produced by photolysis of phenol to the neutral phenoxyl radical for the following reasons.

(*a*) It is a product of photolysis of both phenol and anisole.

(*b*) It appears in non-polar solvents in which the stabilization of ionic species seems improbable.

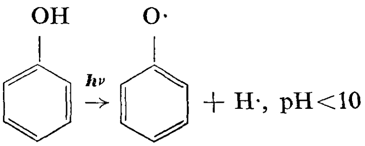
(*c*) It is observed in the gas phase where ionic species are energetically excluded.

(*d*) The spectrum is very similar to that of the semiquinone radical produced by photolysis of benzoquinone or benzohydroquinone, and that of β naphthoxyl from rigid M.P. solutions of β naphthol.

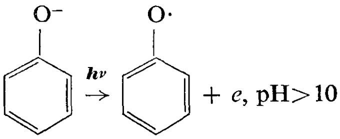
(*e*) An almost identical band is present in the spectrum of tri-tertiary butyl phenoxyl, a radical whose assignment is supported by e.s.r. evidence of several groups of workers.[16]

Thus the observed primary product in the photolysis of both phenol and phenolate ion is the phenoxyl radical, the corresponding primary acts being hydrogen atom ejection and electron ejection (i) and (ii):

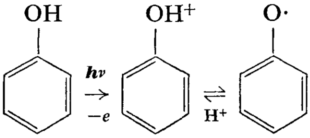
(i)



(ii)



(iii)



Another possible primary act is electron ejection from phenol to give the phenoxyl radical cation followed by equilibration between this and neutral phenoxyl in protonic solvents (iii). This seems unlikely as the neutral phenoxyl radical is readily observed in rigid paraffinic solvents where loss of a proton from the radical cation would be very slow if it occurred at all.

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