

Electron Ejection and Electron Capture by Phenolic Compounds

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The flash photolysis of air-free aqueous solutions of *p*-cresol, *p*-hydroxyphenylpropionic acid, tyramine, and tyrosine was studied on illumination of their long-wavelength absorption bands. The photodissociation into phenoxy radicals, solvated electrons, and hydrogen atoms was examined. Experiments in the presence of 2,4-hexadiene, a typical triplet quencher, showed that the photoelectron ejection of these phenolic compounds in aqueous solution at 25° takes place from a long-lived excited state, probably the triplet excited states of these molecules. The transient absorption spectra, extinction coefficients, and decay kinetics of the phenoxy radicals were determined. The reactivity of all four substances toward hydrated electrons was studied by pulse radiolysis. The reaction rate constants were found to be dependent on the state of protonation of the hydroxyl and the amino groups. The transient absorption spectra due to the reaction of e_{aq}^- and H atoms (produced by photolysis or radiolysis) with these phenolic compounds were observed, with $\lambda_{max} \sim 350$ nm. It is shown that e_{aq}^- and H atoms add predominantly to the phenol ring of the compounds examined.

When phenolic substances are excited by high-intensity light flashes to their first singlet excited state, phenoxy radicals and solvated electrons (possibly also hydrogen atoms) are produced. Such photodissociations of phenolic substances have been studied in the steady state¹ and by flash photolysis.^{2,3} Land and Porter² have described the phenoxy radical with its very characteristic sharp absorption band in the vicinity of 400 nm, and Grossweiner, *et al.*,³ have found that hydrated electrons ($\lambda_{max} \sim 710$ nm) are formed simultaneously with the phenoxy radical. The nature of the excited state (singlet or triplet) precursor of the photoionization of phenolic compounds has not been defined as yet. Furthermore, while excited phenol molecules release electrons into aqueous solutions, phenolic substances in their ground state act as electron scavengers (see below). This reactivity with solvated electrons seems to depend to a great extent on the nature of the side chain on the phenol ring.

Because of the importance of tyrosine in the photochemistry and electron transfer processes in some proteins,^{4,5} this work was initiated with the object of determining the nature of the precursor leading to the ejection of an electron, as well as electron capture processes by phenol derivatives. This latter process is of particular interest since it has been suggested⁵ that in proteins exposed to ionizing radiation part of the reducing equivalent (electrons) primarily absorbed by any group in the protein ultimately finds its way to an aromatic amino acid residue.

Flash photolysis and pulse radiolysis techniques were used and all the compounds examined had a side chain in the para position of the phenol ring (tyrosine, tyramine, *p*-hydroxyphenylpropionic acid, and *p*-cresol, the latter as a model for the chromophore).

Experimental Section

Flash photolysis was carried out with a 2000-J apparatus, which has been described previously.⁶ The photoelectric detection system consisted of a Bausch and Lomb monochromator and an EMI 9558Q photomultiplier. The signal was fed into a double beam oscilloscope (Tektronix

565) where the transient trace was simultaneously recorded with a slow and with a fast sweep. Monochromator slit widths were kept narrow (<0.2 mm) in order to improve the spectral resolution, particularly when the absorbance of the narrow 410-nm peak of the phenoxy radicals was measured. γ -Irradiated and photolyzed triply distilled water was used throughout.

Tyrosine and tyramine were Mann Research Laboratories products. *p*-Cresol was obtained from Baker and Adamson and from Mallinckrodt, and *p*-hydroxyphenylpropionic acid from K & K Laboratories. N₂O was supplied by Matheson & Co., and *tert*-butyl alcohol by Mallinckrodt.

The solutions were illuminated at selected wavelength regions by placing appropriate solution filters in the outer jacket of the optical cell. The following filter solutions were used: acetic acid 90%, cut off at 250 nm; dimethylformamide-water 7:3 by volume, cut off at 265 nm; sodium benzoate 0.01 *N* (pH 10.1), cut off at 280 nm. The last two solutions undergo photochemical changes and therefore could be used for a maximum of six light flashes before being replaced by a fresh solution. Generally, solutions were illuminated in their long-wavelength absorption band only, *i.e.*, above 250 nm at neutral pH and above 265 nm at high pH. In some experiments carried out at very low solute concentrations ($\sim 2 \times 10^{-5}$ *M*) water instead of a cut-off filter solution was placed in the cell jacket.

The pulse radiolysis technique and set-up used has been described elsewhere.⁷ The reaction rate constants of e_{aq}^- with phenolic compounds were determined in presence of

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- (2) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963).
- (3) L. I. Grossweiner, G. W. Swenson, and E. F. Zwicker, *Science*, **141**, 805, 1042 (1963).
- (4) G. Stein, "Energetics and Mechanisms in Radiation Biology," G. O. Phillips, Ed., Academic Press, New York, N.Y., 1968, p 467.
- (5) R. Shapira and G. Stein, *Science*, **162**, 1489 (1968).
- (6) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, **71**, 2511 (1967); M. Langmiur and E. Hayon, *ibid.*, **71**, 3808 (1967).
- (7) (a) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73**, 3794 (1969); (b) J. P. Keene, E. D. Black, and E. Hayon, *Rev. Sci. Instrum.*, **40**, 1199 (1969).

$\sim 0.1 M$ *tert*-butyl alcohol (to scavenge the OH radicals produced in the radiolysis of water) by following the pseudo-first-order decay of e_{aq}^- at 690 nm. The extinction coefficients derived in pulse radiolysis work were determined based on $G(e_{aq}^-) = G(OH) = 2.75$, using KCNS as a dosimeter.

Results

In neutral aqueous solution the absorption spectra and the extinction coefficients, ϵ , of *p*-cresol, *p*-hydroxyphenylpropionic acid, tyramine, and tyrosine are almost identical. The spectra have maxima at 276 nm and a shoulder at 282 nm, with $\epsilon_{max} \sim 1450 M^{-1} cm^{-1}$, and more intense absorptions in the far-ultraviolet. Using appropriate cut-off filters, the long-wavelength absorption bands only were photolyzed. The transient absorption spectra produced on flash photolysis of $\sim 3 \times 10^{-4} M$ air-free aqueous solutions of these phenolic compounds at neutral pH (pH 6.5–7.8) are shown in Figure 1. It is seen that all these compounds show the characteristic optical absorption due to phenoxyl radicals with a maximum at ~ 410 nm, and a second broader band with a maximum at ~ 390 nm. For all four substances, these transient absorption bands decay by second-order kinetics.

Another broad absorption band is centered at 350 nm. However, the intensity of this band differs from substance to substance. Moreover, as shown in Figure 1b for tyrosine, its absorbance relative to the 410-nm peak increases with increase in the concentration of tyrosine in solution. The decay of this band follows neither first- nor second-order kinetics. Furthermore, it is not observed in solutions saturated with N_2O .

In alkaline solutions the ground-state absorption spectra of all four phenolic compounds are shifted to longer wavelength. The absorption band at high wavelength lies at 295 nm and has an extinction coefficient of $\epsilon 2300 M^{-1} cm^{-1}$. The transient spectra obtained on flash photolysis at pH ~ 11.5 are similar to those at neutral pH except that the 410-nm peak is somewhat broadened and the 350-nm band is very weak. However, the decay rate constants for all substances are very similar to those in neutral solutions. We therefore attribute the small spectral changes observed to environmental effects and conclude that the same radical is formed both in neutral and in alkaline solutions. As will be presently explained, the 350-nm band is attributed to an intermediate produced from the reaction of e_{aq}^- with the solutes.

At low solute concentration ($\sim 2.5 \times 10^{-5} M$) another transient with a broad absorption band and a maximum at about 700 nm is observed. This has been attributed to the solvated electron, in agreement with the results of Grossweiner, *et al.*³ Both in neutral and in alkaline solution it decays with pseudo-first-order kinetics, probably by reaction with the ground-state solute molecules (see more below).

In order to characterize the 350-nm band produced from the reaction of photoejected electrons with phenolic compounds, Figure 1, these compounds were made to react with e_{aq}^- produced from the radiolysis of aqueous solutions. The reaction rate constants of e_{aq}^- with these compounds were determined by pulse radiolysis, and the results are given in Table I and Figure 2. It can be seen that (a) the reactivity of e_{aq}^- is dependent upon the state of protonation of both the $-NH_3^+$ and the $-OH$ groups in tyrosine, with the rate decreasing on deprotonation of these functional groups; (b) the rate of e_{aq}^- with *p*-hydroxy-

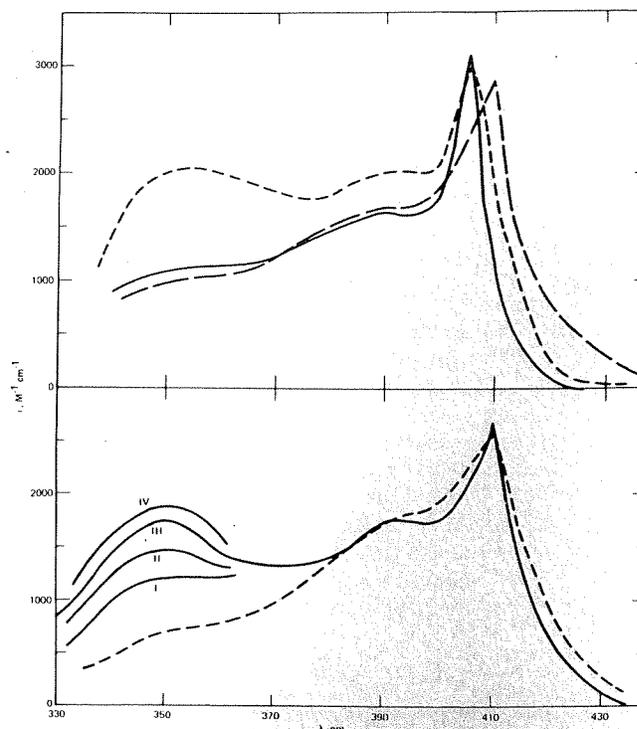


Figure 1. Transient absorption spectra produced in the flash photolysis of oxygen-free aqueous solutions of the following: top, *p*-cresol (—), *p*-hydroxyphenylpropionic acid (---), and tyramine (· · ·) all at pH $\sim 6-7$ and $\sim 3 \times 10^{-4} M$; bottom, tyrosine at pH 7.7 at the following concentrations: $3 \times 10^{-5} M$ (I), $1.5 \times 10^{-4} M$ (II), $3.0 \times 10^{-4} M$ (III), and $7.5 \times 10^{-4} M$ (IV). Dotted spectrum obtained in $7.5 \times 10^{-4} M$ tyrosine at pH 11.5.

phenylpropionate and *p*-cresol is about a factor of 6 lower than with tyrosine or tyramine, indicating that the presence of an amino group increases significantly the reactivity of these compounds toward attack by e_{aq}^- .

Figure 3 shows the transient absorption spectrum produced from the reaction of e_{aq}^- with tyrosine at pH 7.1 (after correction for the absorption due to the H atom adduct to tyrosine, $G(H) = 0.6$ in neutral solution) and the H atom adduct to tyrosine at pH 0.8. Figure 4 shows the e_{aq}^- adduct to tyramine and *p*-hydroxyphenylpropionic acid, and the H atom adduct to tyramine. Figure 5 shows the H atom adducts to *p*-hydroxypropionic acid and *p*-cresol. These H atoms are produced in acid solution by the reaction $e_{aq}^- + H^+ \rightarrow H$, with $k = 2.3 \times 10^{10} M^{-1} sec^{-1}$ (ref 8). The absorption maxima, extinction coefficients, and decay kinetics of the intermediates produced on reaction with e_{aq}^- and H atoms are given in Table II.

The reaction rate constants of H atoms with tyrosine and *p*-hydroxyphenylpropionic acid were determined by pulse radiolysis at pH 9.0 in presence of 1.0 *M* *t*-BuOH (to scavenge OH radicals) by following the formation of the H atom adduct. Values of $2.0 \pm 0.5 \times 10^9$ and $4.0 \pm 1.0 \times 10^9 M^{-1} sec^{-1}$, respectively, were obtained.

Hydrated electrons have been shown⁹ to lead to deamination on reaction with aliphatic amino acids and peptides. The resulting radicals $R\dot{C}HCOO^-$ absorb^{9,10} in the near-uv, and have relatively low extinction coefficients. However, from the similarity in the transient absorption and extinction coefficients of the intermediates produced

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TABLE I: Reaction Rate Constants of e_{aq}^- and OH Radicals with Phenolic Compounds in Aqueous Solution

Compound	pK_a	$k(e_{aq}^- + S), M^{-1} sec^{-1}{}^a$	$k(OH + S), M^{-1} sec^{-1}{}^{a,b}$
Tyrosine	2.2, 9.1, 10.1	$2.8 \pm 0.5 \times 10^8$ (6.6)	$1.4 \pm 0.3 \times 10^{10}$ (5.2)
Tyramine	9.5, 10.8	$9.6 \pm 1.0 \times 10^7$ (12.5)	$1.3 \times 0.3 \times 10^{10}$ (11.2)
<i>p</i> -Hydroxyphenylpropionic acid	4.6, 10.1	$5.8 \pm 0.5 \times 10^7$ (11.2)	$1.5 \pm 0.2 \times 10^{10}$ (11.2)
<i>p</i> -Cresol	10.2	$4.6 \pm 0.5 \times 10^7$ (7.0)	$1.2 \pm 0.2 \times 10^{10}$ (6.3)
		$2.1 \pm 0.2 \times 10^7$ (12.5)	$1.6 \pm 0.2 \times 10^{10}$ (11.0)
		$4.2 \pm 0.5 \times 10^7$ (7.9)	$1.2 \pm 0.2 \times 10^{10}$ (5.5)

^a Values in parentheses are the pH at which rates were determined. ^b Rates determined using KCNS method, and taking $k(OH + CNS^-) = 1.1 \times 10^{10} M^{-1} sec^{-1}$.

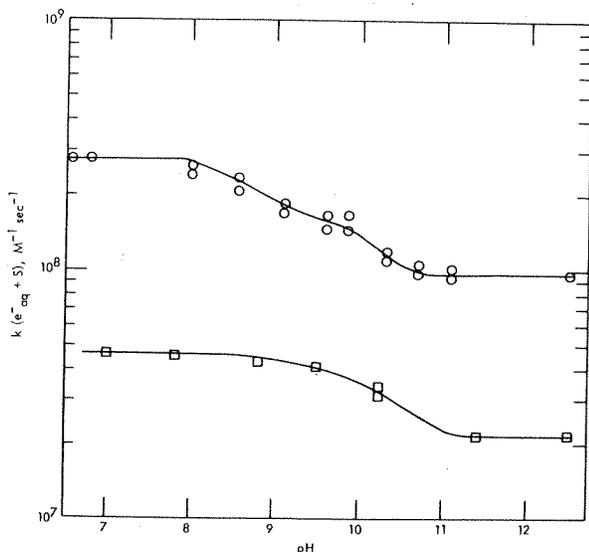


Figure 2. Dependence upon pH of the reaction rate constants of e_{aq}^- with tyrosine (O) and *p*-hydroxyphenylpropionic acid (□).

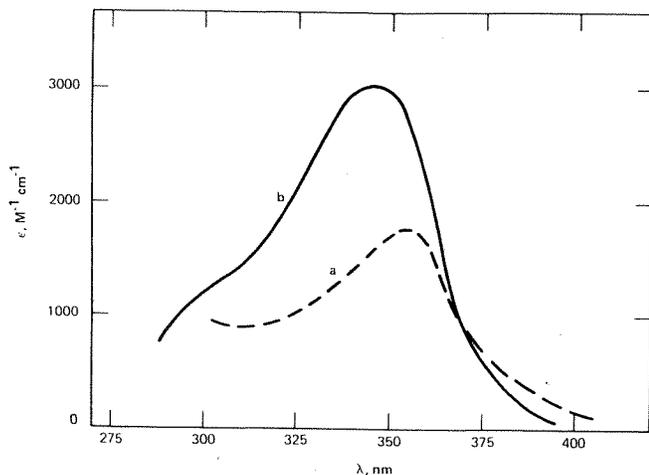


Figure 3. Transient absorption spectra produced in the pulse radiolysis of $10^{-3} M$ tyrosine, $1.0 M$ *tert*-butyl alcohol, and Ar (1 atm) due to the interaction with e_{aq}^- (curve a, pH 7.1) and with H atoms (curve b, pH 0.8).

from the reaction of e_{aq}^- with tyrosine, tyramine, and *p*-hydroxyphenylpropionate (Figures 2-4 and Table II), it is concluded that most of the electrons add to the phenol aromatic ring.

From a comparison of Figures 1b and 3a, it is seen that the 350-nm absorption band produced in the flash photolysis of tyrosine and tyramine resembles the spectrum ob-

tained by pulse radiolysis, both in its wavelength dependence and in its extinction coefficient (see Discussion below). Hidden under the spectrum of this radical in Figure 1 is still some absorbance ($\epsilon \sim 3-4 \times 10^2 M^{-1} cm^{-1}$) of the phenoxyl radical, as found in N_2O -saturated solutions. The low absorbance at 350 nm in alkaline tyrosine and in neutral *p*-cresol and *p*-hydroxyphenylpropionate can be attributed to the lower reactivity (Table I) of these solutes with e_{aq}^- under the experimental conditions used.

The decay rates of the solvated electrons in our flash illuminated solutions yielded, in all cases, larger rate constants than those found by pulse radiolysis (Table I). The discrepancy is probably due to reactions of the solvated electron with impurities, mainly residual oxygen, present in the flashed solutions. If no other electron scavengers were present all solvated electrons would ultimately react with tyrosine even when the latter is present at very low concentration. The fact that the absorbance by the electron adduct is concentration dependent (see Figure 1b) means that a smaller proportion of e_{aq}^- decays *via* reaction with tyrosine, the rest reacting with another scavenger in the solution. Similarly, the absence of the 350-nm absorption band in the transient spectrum produced from *p*-cresol or *p*-hydroxyphenylpropionate reflects only the lower reactivity of these species for solvated electrons relative to other electron scavengers. Withstanding the uncertainty in the actual rate, an extrapolation of the pseudo-first-order decay plots of the solvated electrons formed in flash photolysis to zero time yields nevertheless the initial absorbance of electrons produced in solution. This data, together with the corresponding absorbances of radicals at time zero, allow us to estimate the relative initial quantum yields of the photodissociation products.

Discussion

Various values have been assigned to the molar extinction coefficients of phenoxyl radicals. Values as low as $1800 M^{-1} cm^{-1}$ for *tert*-butylphenoxyl,¹¹ or as high as 11,000 for phenol and 15,000 for *p*-cresol¹² have been obtained by flash photolysis. Data obtained indirectly from pulse radiolysis¹³ yielded a value for phenoxyl of ϵ 2200 $M^{-1} cm^{-1}$ from phenol and 2400 for the corresponding radical from *p*-cresol. From measurements of the absorption spectra and the decay rates, it is concluded from this work that the same radical is formed on flash photolysis of both neutral solutions of phenols and alkaline solutions, when the phenolic chromophore in the ground state is in

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TABLE II: Absorption Maxima, Extinction Coefficients, and Decay Kinetics of Intermediates Produced from the Reaction of e_{aq}^- and H Atoms with Phenolic Compounds

Compound	e_{aq}^- adducts ^a			H atom adducts ^b		
	λ_{max} , nm	ϵ , $M^{-1} cm^{-1}$	$2k$, $M^{-1} sec^{-1}$	λ_{max} , nm	ϵ , $M^{-1} cm^{-1}$	$2k$, $M^{-1} sec^{-1}$
Tyrosine	355	$1.7 \pm 0.3 \times 10^3$	$6.8 \pm 1.6 \times 10^8$	345	$3.1 \pm 0.3 \times 10^3$	$6.2 \pm 1.5 \times 10^8$
Tyramine	350	$1.8 \pm 0.3 \times 10^3$	$7.0 \pm 2.0 \times 10^9$	350	$5.6 \pm 1.0 \times 10^3$	
<i>p</i> -Hydroxyphenylpropionic acid	355	$1.5 \pm 0.3 \times 10^3$	$6.5 \pm 1.5 \times 10^8$	352 ^a	$3.3 \pm 0.5 \times 10^3$	
<i>p</i> -Cresol				355	$3.6 \pm 0.5 \times 10^3$	$2.0 \pm 0.4 \times 10^9$

^a Determined at pH $\sim 6-7$. ^b Determined at pH ~ 1.0 .

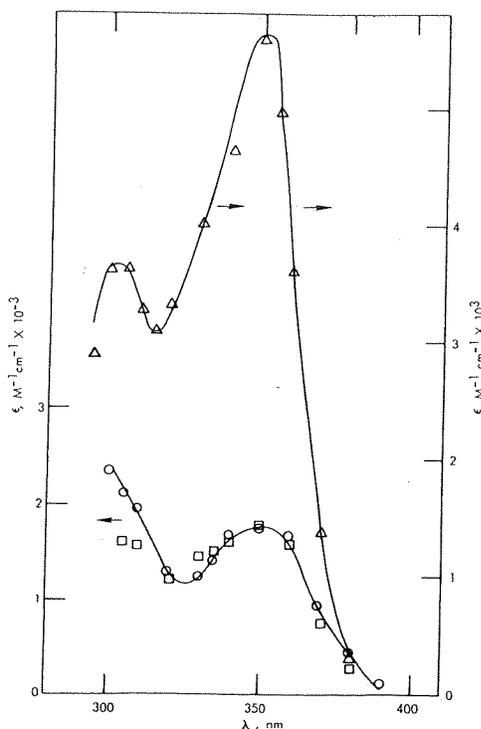
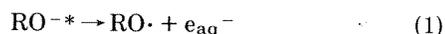


Figure 4. Transient absorption spectra produced from the reaction of e_{aq}^- with tyramine (O, $5 \times 10^{-3} M$, pH 7.7) and *p*-hydroxyphenylpropionic acid (□, $10^{-2} M$, pH 5.2) in 1.5 M *tert*-butyl alcohol, after correction for contribution from H atom adduct. Spectrum of H atom adduct to tyramine (Δ , $5 \times 10^{-3} M$, pH 0.9, 1.5 M *tert*-butyl alcohol).

its anionic form. We can assume that in the latter case the solvated electron is formed by direct electron ejection from the excited negative ion



In neutral solution either process 2



followed by release of a proton takes place, or a hydrogen atom is directly ejected from the excited molecule



We assume, therefore, that at high pH equivalent amounts of phenoxyl radicals and solvated electrons are formed, *i.e.*, $[RO\cdot]_0 = [e_{aq}^-]_0$, where the subscript zero indicates the initial concentrations. From an extrapolation of the pseudo-first-order electron decay plot the initial absorbance of solvated electrons was found. Somewhat arbitrarily we assigned 10 μ sec after triggering the flash, *i.e.*, a

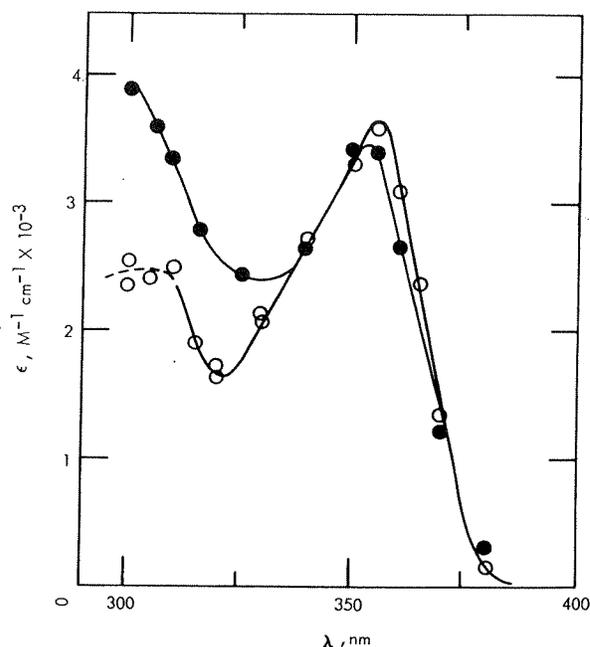


Figure 5. Absorption spectra of the H atom adduct to 2 mM *p*-cresol (pH 1.3, Ar, O) and *p*-hydroxyphenylpropionic acid (pH 6.4, N_2O (1 atm), ●) produced from the pulse radiolysis of 1.5 M aqueous *tert*-butyl alcohol solutions.

time close to the midpoint of the flash, as time zero. The extinction coefficient of the solvated electron at 690 nm equals $\epsilon(e_{aq}^-)$ 17,000 $M^{-1} cm^{-1}$ (ref 14). This wavelength was chosen for our measurements as a compromise between the increase in absorbance of the solvated electron and the decrease in sensitivity of the photomultiplier tube. Hence from the absorbancies at 410 (phenoxyl radical) and 690 nm (electron), and from the known value of $\epsilon(e_{aq}^-)$, the extinction coefficient of the phenoxyl radical can be found. The extinction coefficients of the phenoxyl radicals for the various phenolic compounds studied are presented in Table III. These values are fairly consistent but are higher than the $\epsilon(RO\cdot)$ 2200 $M^{-1} cm^{-1}$ obtained¹³ from the reaction of OH radicals with phenol by pulse radiolysis.

Similar pulse radiolysis experiments were carried out for the reaction of OH radicals with tyrosine in presence of N_2O (to convert $>98\%$ of e_{aq}^- to OH radicals, $e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^-$). At pH 5.3 a transient spectrum due to various isomers of the OH adducts to the phenol ring is observed, Figure 6. At pH 9.0, the OH adducts undergo¹³ a base-catalyzed unimolecular elimina-

(14) E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York, N.Y., 1970.

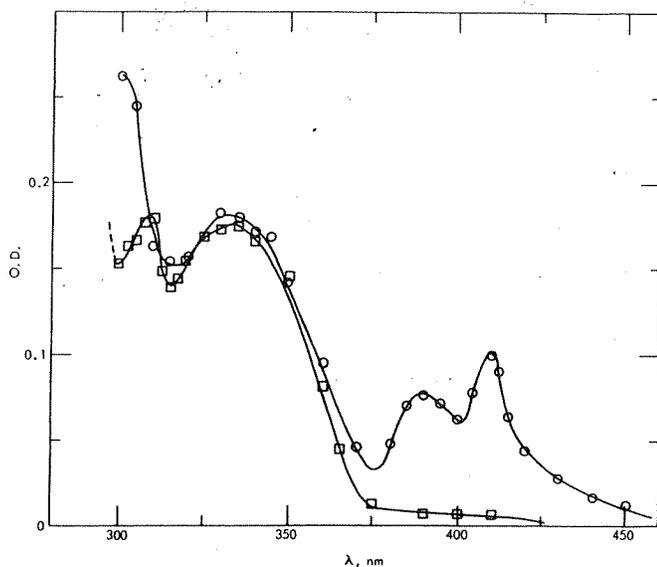


Figure 6. Transient spectra produced from the reaction of OH radicals with ~ 1.4 mM tyrosine, N_2O (1 atm), at pH 5.3 (\square) and 9.0 (O). Absorbances extrapolated to ~ 0.1 μ sec after the pulse. Total dose ~ 4.1 krad/pulse.

TABLE III: Extinction Coefficients of Phenoxy Radicals and Relative Amounts of e_{aq}^- and H Atoms Produced in the Flash Photolysis of Phenolic Compounds at pH ~ 7.0

Compound	$\epsilon(\text{RO}\cdot)$, $M^{-1} \text{cm}^{-1}$	$[e_{aq}^-]/$ $[\text{RO}\cdot]$	$[\text{H}]/$ $[\text{RO}\cdot]$
Tyrosine	2750 ± 200	0.77	0.23
Tyramine	3150 ± 300	0.72	0.28
<i>p</i> -Cresol	3200 ± 300	0.78	0.22
<i>p</i> -Hydroxyphenylpropionic acid	2800 ± 300	1.00	0

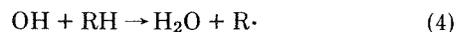
tion of water to form the phenoxy radical $\text{RO}\cdot$, see Figure 6. At pH 9.0 the rate of formation of $\text{RO}\cdot$ at 400 nm was found to be $4.2 \times 10^5 \text{ sec}^{-1}$ and the rate of decay of the OH adducts at 320–345 nm to be $3.4 \times 10^5 \text{ sec}^{-1}$. Since all the OH adducts do not give rise to phenoxy radicals (various isomers of the OH adduct are probably formed), an $\epsilon_{410} > 2.3 \times 10^3 M^{-1} \text{ cm}^{-1}$ was calculated. This supports the higher ϵ values derived in Table III from flash photolysis experiments.

By using the above extinction coefficients one can now estimate the relative amounts of e_{aq}^- and H atoms produced at neutral pH, since

$$[e_{aq}^-]/[\text{RO}\cdot] = (\text{OD})_{e_{aq}^-} / (\text{OD})_{\text{RO}\cdot} (\epsilon_{\text{RO}\cdot}) / (\epsilon_{e_{aq}^-})$$

in any given optical cell. The relative amounts of H atoms produced are given in Table III.

The amount of electrons produced in neutral solution can also be derived independently from the amount of the electron adduct formed. We have seen that at comparatively high tyrosine concentrations, $[\text{Tyr}] > 10^{-3} M$, in a deaerated solution all electrons are scavenged by ground-state tyrosine forming an electron adduct with an absorption peak at 350 nm. On the other hand, in N_2O -saturated solutions containing *t*-BuOH no electron adduct will be formed since all electrons (but not H atoms) will react under these conditions with N_2O yielding OH radicals, as pointed out before. The latter react with *t*-BuOH according to



The *tert*-butyl alcohol radical^{7a} formed its relatively unreactive and does not absorb above 280 nm. Therefore the difference in absorbance at 350 nm between solutions saturated with nitrogen and with N_2O will be proportional to the concentration of electrons formed and

$$[\text{OD}(N_2) - \text{OD}(N_2O)] / \epsilon(\text{electron adduct}) = \text{concentration of adduct} = [e_{aq}^-]_0$$

where $[e_{aq}^-]_0$ is the concentration of solvated electrons formed by flash. The extinction coefficient of the electron adduct of tyrosine was found by pulse radiolysis, as mentioned above. The estimate of the concentration of electrons and hence of the H atoms formed in neutral solutions agrees with that based on the extinction coefficient of the phenoxy radical and the directly measured absorbance of e_{aq}^- . For tyrosine we find that electrons account for 82% of the phenoxy radicals as calculated from the electron adduct, while the value in Table III is 77%.

One can see from Table III that, except for *p*-hydroxyphenylpropionate, in all cases the ratio of H atoms to e_{aq}^- formed from the excited phenol ring in neutral solutions is about 1:4.

Nature of Excited State Precursor. The phenoxy radicals and the electrons formed from the excited phenol derivatives can be produced either from the singlet or from the triplet excited states of the molecule. The lifetime of the singlet ^1Tyr is ~ 5.1 nsec,¹⁵ and the dissociation constants of the singlet and triplet excited states of tyrosine have been estimated,¹⁶ $pK_{S1} \sim 4.5$ and $pK_{T1} \sim 8.5$. In order to determine the origin of the excited state leading to the photoionization of these phenolic compounds, the influence of the typical triplet quencher 2,4-hexadiene¹⁷ on the yield of radicals was tested. Relatively low concentrations of hexadiene were found to reduce the yield of phenoxy radicals at 410 nm. A Stern-Volmer plot

$$\phi^0/\phi = 1 + k_q[\text{hexadiene}] \quad (5)$$

is shown in Figure 7. The quenching constant of tyrosine by hexadiene is $k_q = 400 M^{-1}$. At the concentrations of hexadiene used it is not possible for it to interact with the short-lived singlet excited state of tyrosine, $\tau \sim 5.1$ nsec, even assuming a quenching rate of $5 \times 10^{10} M^{-1} \text{ sec}^{-1}$.

If one assumes a diffusion-controlled rate constant for the interaction of hexadiene with the excited state precursor of these phenolic compounds one can arrive at a lower limit for the excited state lifetime. From steady-state kinetics $k_q = k\tau$, where k is the bimolecular rate constant for the reaction between hexadiene and the excited tyrosine and τ is the lifetime of the latter. We see that for $k = 10^{10} M^{-1} \text{ sec}^{-1}$, τ is at least $2.5 \times 10^{-7} \text{ sec}$, and is in fact probably much longer. We therefore think that the precursor of the electrons and the phenoxy radicals is the longer lived triplet rather than the singlet excited state of the phenolic chromophore.

This conclusion is also borne out by quenching experiments with compounds containing a disulfide bridge.¹⁸ The most striking finding for us in these experiments is the fact that in *alkaline* solution where the lifetime of the singlet excited phenol derivative is extremely short ($\tau \ll$

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(17) A. A. Lamola, *Tech. Org. Chem.*, **12**, (1969).

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TABLE IV: Second-Order Decay Kinetics of Phenoxy Radicals in Aqueous Solution

Compound	$2k/\epsilon$ (pH 7.5)	$2k/\epsilon$ (pH 11.5)	$2k, M^{-1} \text{sec}^{-1} a$
Tyrosine	4.7×10^5	4.3×10^5	$1.2 \pm 0.2 \times 10^9$ $1.0 \pm 0.2 \times 10^9 b$
Tyramine	6.3×10^5	5.8×10^5	$1.9 \pm 0.3 \times 10^9$
<i>p</i> -Hydroxyphenylpropionic acid	2.9×10^5	2.5×10^5	$6.2 \pm 0.2 \times 10^8$
<i>p</i> -Cresol	6.2×10^5	5.6×10^5	$1.9 \pm 0.3 \times 10^9$

^a Based on extinction coefficients given in Table III. ^b From pulse radiolysis of ~ 1.4 mM tyrosine with N_2O (1 atm) at pH 9.0.

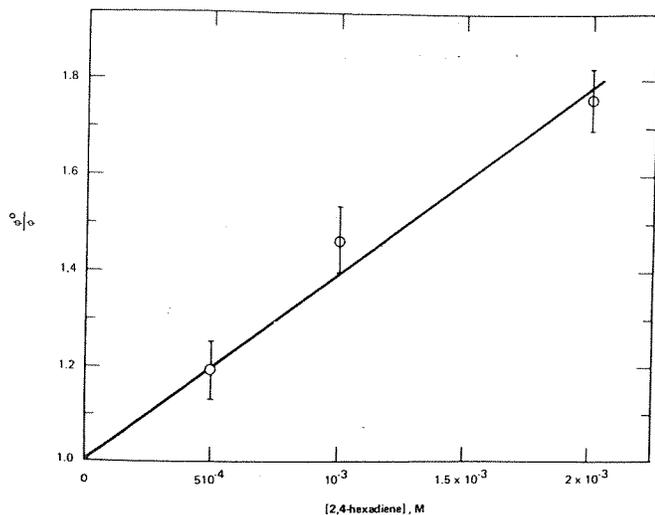


Figure 7. Reciprocal yield plot (Stern-Volmer plot) of the phenoxy radical produced in the flash photolysis of $\sim 7 \times 10^{-4}$ M tyrosine, pH 7.7, as a function of the concentration of 2,4-hexadiene present in solution. Radical monitored at 410 nm using a 280-nm cut-off filter.

10^{10} sec), a reaction between the excited phenolic molecule and a low concentration ($\sim 10^{-3}$ M) of disulfide bridges produces the disulfide negative radical ion

RSSR^- , a reaction which clearly requires a lifetime of more than 1 μsec for the triplet excited species to interact to a measurable extent with the disulfide linkages.

In conclusion, it was found that all four phenol derivatives studied form phenoxy radicals with very similar spectra and similar decay rates both in neutral and in alkaline solutions, see Table IV. The second-order decay of the resonance-stabilized¹⁹ phenoxy radicals probably produces *o,o'*-biphenol derivatives. Astonishingly large differences are found when one compares the rates of reaction between the phenol derivatives in their ground state with solvated electrons or with H atoms. Both *p*-cresol and alanine have rate constants for their reaction with solvated electrons of $\sim 4.2 \times 10^7$ (Table I) and $\sim 5 \times 10^6 M^{-1} \text{sec}^{-1}$ (ref 9), respectively. However, tyrosine (a β -hydroxyphenylalanine) reacts with a rate constant of $2.8 \times 10^8 M^{-1} \text{sec}^{-1}$ (Table I). With all the phenolic compounds studied, the main reaction with e_{aq}^- appears to be addition to the aromatic ring. For both phenol and phenolate derivatives, the photoejection processes occur from the triplet excited states of these molecules.

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(19) H. Musso, "Oxidative Coupling of Phenols," W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, New York, N.Y., 1967.