Photoionization of Phenols in Water. Effects of Light Intensity, Oxygen, pH, and Temperature

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Abstract: The effect of flash intensity, oxygen, pH, and temperature on the photoionization of *p*-cresol and tyrosine were investigated by measuring the yields of the phenoxyl radicals generated in aqueous solutions. Photoionization of the phenols and their anions in alkaline solution are shown to occur *via* biphotonic and monophotonic processes, respectively. The [phenoxyl] is proportional to I^n, where n changes from 2 to 1 over a relatively narrow pH range. In air-saturated solutions of the phenols, the transient absorption spectra of the phenoxyl radicals are observed but their initial yields are somewhat lower and are proportional to $\sim I^{1.5}$. There is no distinct difference between the effects of 1 atm of air and 1 atm of O_2. In alkaline solutions (pH ~12) the effect of oxygen is relatively small. On the other hand, the anions display much higher sensitivity toward temperature; in alkaline solutions the radical yields are nearly doubled on raising the temperature from 20 to 70°, whereas in neutral solutions the yield of photoionization is hardly affected over the same temperature range. These results are interpreted on the basis of a mechanism involving ionization of triplet excited-state molecules. In neutral solutions the triplets exist in their acidic form and their ionization is induced by light, whereas in alkaline solutions the basic forms of the triplets, which are shorter lived, undergo thermal ionization with higher activation energy. A possible explanation of the oxygen effect is the formation of longer lived triplet–oxygen complexes which are then photoionized. Under all conditions employed the lifetimes of the precursors of phenoxyl radicals and e_{aq}^- appear to be short compared to the duration of the flash employed ($\tau \sim 10$ μsec).

There is considerable evidence that the photoionization of phenols and their anions in low-temperature rigid media proceeds through a biphotonic mechanism with triplet excited-state intermediacy (see ref 2 and 3 for review). The nature of this process in fluid media, in particular polar liquids, is less clear. Early attempts to detect a nonlinear dependence of the initial yield of solvated electrons, from the photolysis of *p*-cresol, on the flash intensity led to negative results.[2] It was proposed[4] that in some cases a monophotonic process can proceed *via* intermediate semiionized states which directly originate from the nonrelaxed excited singlet. Thus, owing to a relatively fast gain of solvation energy, photoionization can be induced by light with $h\nu$ which is 3 to 4 eV smaller than the gas-phase ionization potential.

This picture concerning fluid solutions has become rather doubtful in view of some recent results. On studying the flash photolysis of several phenolic compounds it was observed[5] that the yields of phenoxyl radicals produced from the phenols and their anions are comparable (more than 70% of the radicals generated from phenols are produced by ionization and the rest by rupture of the OH bond[5]). On the other hand, previous results obtained from steady-state photochemistry at 2288 Å indicate that the photoionization of phenol is much less efficient than that of its anion.[6] The two apparently conflicting observations suggest a biphotonic and a monophotonic mechanism for phenols and their anions, respectively. Furthermore, by studying the effect of sodium lipoate on the flash photolysis of tyrosine and tyrosinate, indirect evidence was presented[7] that their photoionization involves a long-lived excited state, which is probably the triplet state.[7]

Here we present results of a detailed investigation of the effect of light intensity on the photoionization of *p*-cresol and tyrosine (with some data on phenol) in neutral and alkaline solutions, both in the presence and the absence of oxygen. The proposed mechanisms are also supported by results on the effect of temperature.

Experimental Section

The flash photolysis experiments were carried out as described elsewhere.[8] The flash intensity was varied by changing the charging voltage of the capacitors in the range 17–23 kV (range of energies ~1.4–2.7 × 10^3 J). Flash duration (1/e) was ~10 μsec.

From the decay traces at the absorption maxima (410 nm for tyrosine and 405 nm for *p*-cresol), the decay kinetics and the initial absorbance of the phenoxyl radicals[5] were determined. Since the flash was practically over within 50 μsec and τ of the transients was more than 10 times longer, the maximum absorbance displayed by the trace was taken as the initial absorbance and it was considered to represent the efficiency of photoionization (each value of OD documented in this work is the average of three measurements with an experimental scatter of ±10%). This method was preferred to that previously employed,[2] because the yield of e_{aq}^- is sensitive to impurities and its lifetime is much shorter. By conducting parallel experiments with neutral and alkaline solutions, a convenient method of relative actinometry was established, because the conversion of phenols to their anions leads to a relatively small red shift (~20 nm) in its ground-state absorption spectrum.

For the purpose of recording the absorption spectra of the phenoxyl radicals, the monochromator slits were kept narrow (widths <0.2 mm) in order to improve the spectral resolution.

The flash photolysis cells were fitted with an outer jacket which contained an appropriate filter solution. Glacial acetic acid was used to cut off light below 250 nm and thus the irradiation could be almost confined to the long wavelength band (band A) of the phenols or their anions. Some experiments were also conducted with a filter solution of 0.1 *M* sodium benzoate (cut-off at 280 nm) so that any interference from the second band (band B) could be completely avoided. Irradiation just within band B was attained by using an aqueous solution of 0.1 *M* acetone as a filter.

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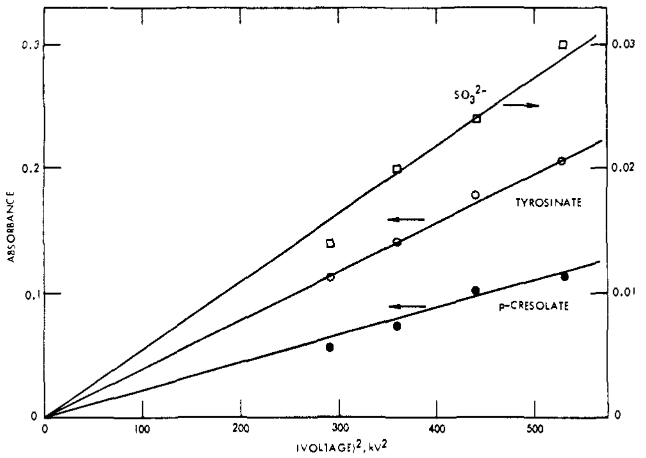

Figure 1. Dependence upon the square of the discharge voltage of the initial absorbance of free radicals produced in the flash photolysis of oxygen-free N_2O-saturated aqueous solutions of *p*-cresolate (1.2×10^{-4} *M*, pH 11.2, monitored at 405 nm), tyrosinate (1.3×10^{-4} *M*, pH 11.7, monitored at 410 nm), and sulfite ions (4×10^{-3} *M*, pH 9.6, monitored at 270 nm).

For studying temperature effects, the benzoate filter solution from a thermostated bath was circulated through the outer jacket of the optical cell. In these experiments the absorbance was measured at 385 nm, where the extinction coefficient is not as sensitive to temperature. In this way effects due merely to small spectral shifts were reduced.

Tyrosine (Swarz-Mann Research Lab.) and *p*-cresol (Mallinckrodt and Baker) were used without further purification. Some experiments were conducted with phenol (Mallinckrodt and Baker) in neutral solutions, but in alkaline solutions the transient phenoxyl absorption was replaced by some longer lived absorption; this is probably due to thermal instability of the alkaline solutions.

Water was triply distilled, radiolyzed, and photolyzed. Unless otherwise stated, the solutions were saturated with N_2O (Matheson) to scavenge solvated electrons $e_{aq}^- + N_2O \rightarrow N_2 + OH + OH^-$, together with ~1 *M tert*-butyl alcohol (Mallinckrodt) to replace the OH radicals by the relatively inert radicals of this alcohol.[9] This procedure was adopted since e_{aq}^- add to phenolic compounds to produce[5] an intermediate with λ_{max} ~350 nm.

Results and Discussion

With a certain set of flash lamps and using the cut-off filters, the yield of phenoxyl radicals produced from the flash photolysis of the anions was found to be nearly proportional to the square of the charging voltage *V*. This is shown in Figure 1. For comparison some results are also included on the SO_3^- radical which was produced[10] from the photoionization of SO_3^{2-}. On photolysis of neutral or slightly acidic solutions (pH 5.5–6.0) of phenol, *p*-cresol, and tyrosine, an almost linear relation was, however, found between the radical yield and V^4 (Figure 2). These results clearly suggest that the photoionization of phenols and their anions in water is biphotonic and monophotonic, respectively.

Direct proportionality between light intensity *I* and V^2, as exhibited in Figures 1 and 2, was not always obeyed with new sets of flash lamps. Moreover, on excitation with light below ~250 nm the effect of *V* on *I* appeared to decrease with λ. Therefore for a more detailed investigation, a method of relative actinometry was employed (see Experimental Section). Figures 3 and 4 (top curves) show logarithmic plots of the yields of phenoxyl radicals from the phenols against that generated from their anions under the same conditions. The slopes of the lines are 1.9 ± 0.1 and 1.7 ± 0.2 for tyrosine and *p*-cresol, respectively. Similar results were obtained with tyrosine on replacing the acetic acid filter by the benzoate filter, and with *p*-cresol by using the acetone filter to confine the irradiation to band B (see Experimental Section).

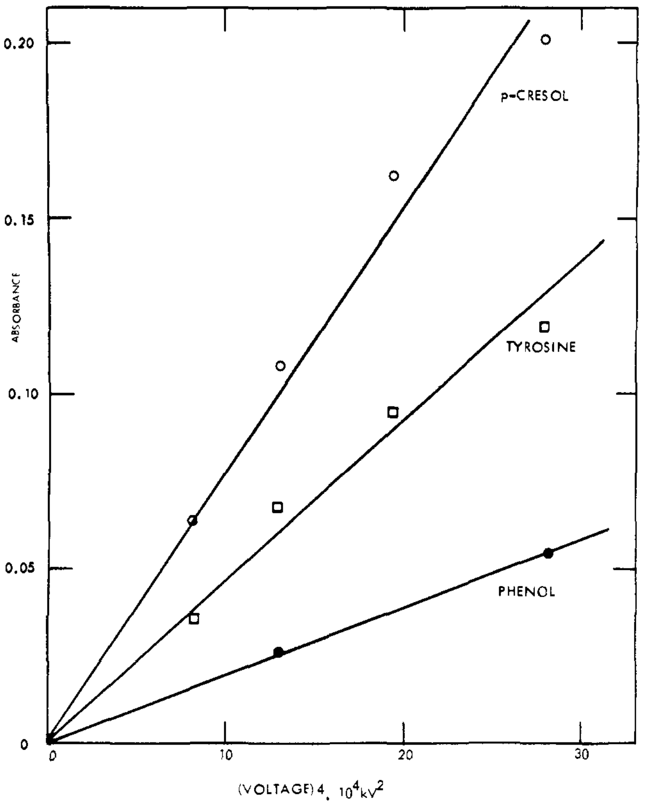

Figure 2. Dependence upon the fourth power of the discharge voltage of the initial absorbance of phenoxyl radicals produced in the photolysis at pH ~6 of 1.4×10^{-4} *M p*-cresol, 1.3×10^{-4} *M* tyrosine, and 9×10^{-4} *M* phenol.

Neutral Solutions. A kinetic analysis of consecutive biphotonic ionization under flash conditions[11] must differentiate between two cases, depending on whether the lifetime of the intermediate is long (case I) or short (case II) compared to flash duration. In case I the radical yield should be proportional to the square of the integrated light intensity. In case II the situation is more complicated: when the deactivation rate of the intermediate is higher than the sum of rates of the two consecutive excitations, this case is usually indistinguishable from case I; but when the opposite occurs, lower orders than 2 might be obtained.

In the case of tyrosine, the precursor of the phenoxyl radical lives a few microseconds[7] and so one is probably dealing with case II. But since the radical yields were quite high (about 2 μ*M* of phenoxyl radicals per flash[12]), the rate of deactivation cannot be much higher than that of excitation. Therefore, the order of reaction with respect to light intensity might be somewhat lower than 2, as was really observed, especially with *p*-cresol (Figure 4). However, the occurrence of monophotonic reactions may also be responsible for these deviations since it is difficult to purify *p*-cresol,

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(12) This value is based on ϵ_{max} = 3000 M^{-1} cm^{-1} for the phenoxyl radicals.[5]

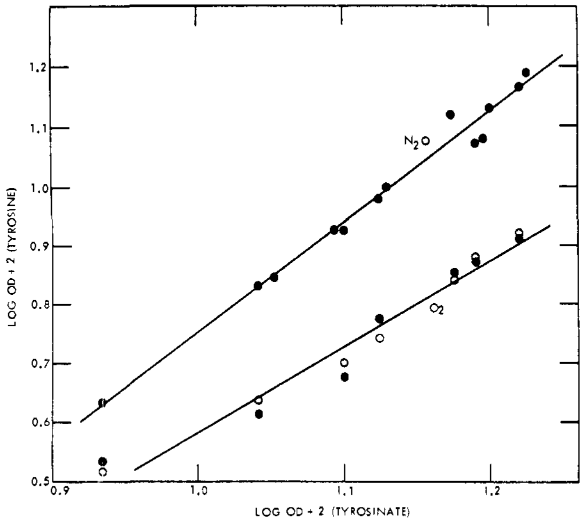

Figure 3. Logarithmic plots for the initial absorbance of phenoxyl radicals produced from 1.2 × 10^{-4} M tyrosine at pH ~6 against that produced from its anion at pH 12.1, in solutions saturated with N_2O (top curve), and with air (●) and with oxygen (○).

and therefore some oxidation of the intermediate by impurities might contribute to the overall production of phenoxyl radicals.

In oxygen-containing solutions no significant change in the absorption spectra of the phenoxyl radicals could be detected but their yields were reduced (Figure 5). This effect increases with light intensity and thus the reaction appears to be less sensitive to light intensity (Figures 3 and 4). In aerated or O_2-saturated solutions the radical yields from *p*-cresol and tyrosine are proportional to $\sim I^{1.5}$.

If triplet excited states are the precursor of the phenoxyl radicals, as was previously proposed,[5,7] then some effect of O_2 is expected. However, simple quenching of the triplets cannot account for the observed effects. A possible explanation is the occurrence of thermal oxidation of the triplets (T_1)

$$T_1 + O_2 \longrightarrow R\cdot + O_2^- \qquad (1)$$

where R· is the phenoxyl radical. If all the radicals are produced by reaction 1, the photolysis should be monophotonic. A combination of reactions 1 and 2

$$T_1 \xrightarrow{h\nu} R\cdot + e_{aq}^- \qquad (2)$$

followed by $e_{aq}^- + O_2 \rightarrow O_2^-$ ($k = 2.5 \times 10^{10}\ M^{-1}\ sec^{-1}$) and e_{aq}^- + Tyr → adduct ($k = 2.8 \times 10^{8}\ M^{-1}\ sec^{-1}$), could account for the apparent dependence on $\sim I^{1.5}$. However this cannot be the case, since no distinct difference was found between the effects of 1 atm of air and 1 atm of O_2 (Figures 3 and 4). Thus the observed dependence on $I^{1.5}$ represents the limiting effect of O_2.

The reason for this behavior is still obscure. A possible explanation is that reaction 1 is also induced by light and that it actually proceeds through a triplet–oxygen complex, which is the photoreactive species. Therefore, even in the presence of O_2 the photoreaction is biphotonic and the drop in sensitivity to light intensity, relative to air-free solutions, merely reflects an increase in ratio between the rate of excitation and the rate of deactivation of the triplet on its complexation with O_2.

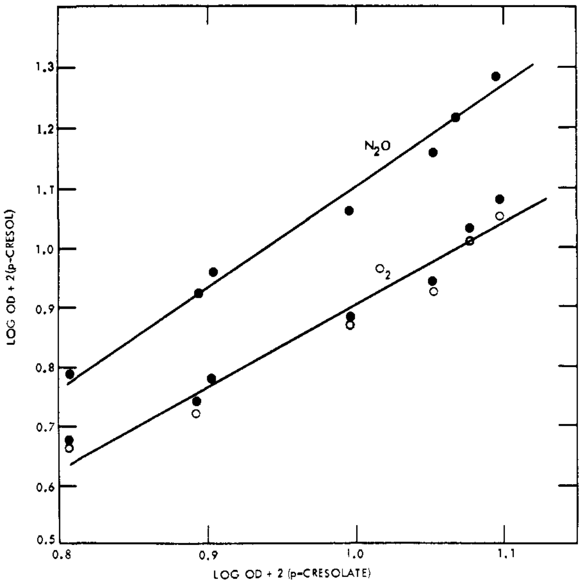

Figure 4. Logarithmic plots for the initial absorbance of phenoxyl radicals produced from 9 × 10^{-5} M *p*-cresol at pH ~6 against that produced from its anion at pH 12.0, in solutions saturated with N_2O (top curve) and with air (●) and with oxygen (○).

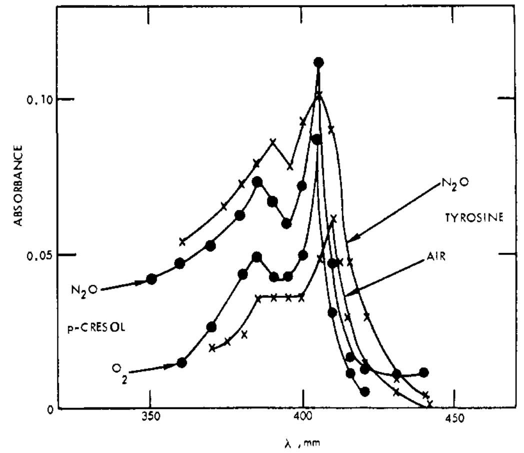

Figure 5. Absorption spectra of phenoxyl radicals produced in the flash photolysis of aqueous 1.2 × 10^{-4} M tyrosine (×) and 1.2 × 10^{-4} M *p*-cresol (○) solutions saturated with N_2O and air or oxygen.

Oxygen was also found to affect the decay of the phenoxyl radicals. In air-free solutions the decay is second order with $2k/\epsilon = 4.8 \times 10^5$ and 6.2×10^5 cm sec^{-1}, for the radicals from tyrosine and *p*-cresol, respectively, and it probably leads to formation of dimers such as dityrosine.[3] Taking $\epsilon = 3000\ M^{-1}\ cm^{-1}$ for phenoxyl radicals,[5] one derives a $2k = 1.4 \pm 0.2 \times 10^9\ M^{-1}\ sec^{-1}$ and $1.7 \pm 0.2 \times 10^9\ M^{-1}\ sec^{-1}$ for tyrosine and *p*-cresol, respectively. In the presence of $1.3 \times 10^{-3}\ M\ O_2$ the decay of the phenoxyl radicals was somewhat faster, close to first order with $k \sim 1.6 \times 10^3$ sec^{-1}. In air-saturated solutions ($2.5 \times 10^{-4}\ M\ O_2$) the decay appeared to follow a mixed kinetics of first- and second-order reactions. These results provide direct evidence for the formation of peroxide radicals, which were considered to be intermediates in the photoxidation of, *e.g.*, tyrosine to yield dihydroxyphenylalanine (DOPA).

We conclude that the nature of the photoinduced electron ejection processes from phenols are not altered on changing the medium from low-temperature rigid media to room-temperature water. In both phases

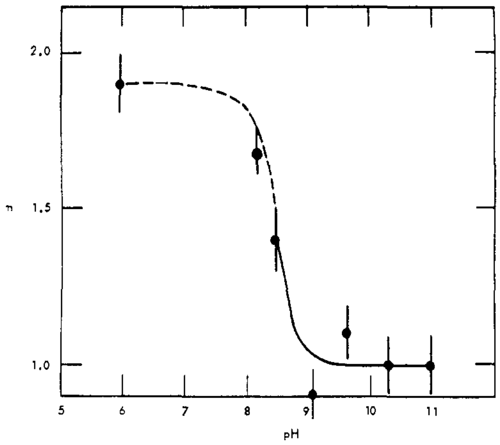

Figure 6. Dependence of n (from the relation, yield of radical $\propto I^n$; see text) upon pH in the photolysis of aqueous tyrosine solutions (saturated with N_2O and containing ~0.5 *M* *t*-BuOH).

ionization appears to proceed by a consecutive biphotonic process with the lowest triplets as the photoactive intermediate. An alternative mechanism involving triplet–triplet reaction can be discarded, since under our experimental conditions (~2 μM of intermediate) this reaction cannot be completed within the flash duration, and no build-up of radicals could be detected after the flash.

Here it is essential to point out that, contrary to some views,[13] the triplets produced in neutral solutions are most likely in their acidic forms since their p*K* is close to that of the ground-state molecules [for *p*-cresol $pK(S_0)$ and $pK(T_1)$ are 10.26 and 8.6, respectively[14]]. The excited singlet is a stronger acid [$pK(S_1)$ of *p*-cresol is 4.3[14]], but no appreciable dissociation of the acid can occur during its short lifetime. This was clearly shown in the case of tyrosine by measuring the dependence of fluorescence upon pH.[15] Therefore, even in neutral solution the triplets should also be produced in their acidic form.

From the foregoing discussion it is clear that at pH $> pK(S_0) > pK(T_1)$ the triplets are most likely to exist in their basic (anion) forms. These conclusions should help us to understand the change in the mechanism of photolysis on passing from neutral to alkaline solutions.

Alkaline Solutions. Triplet excited states of phenolate anions were proposed to be the precursors of solvated electrons, in both rigid[3] and fluid[7] solutions. However, contrary to the observations in neutral solutions one encounters a pronounced difference between low-temperature ice, where photoionization was reported to be biphotonic,[3] and water, where our results clearly reveal its monophotonic nature. This behavior may be explained as follows. (a) The ionization potential of the anion is considerably lower than that of the acid, and the extra energy required to induce electron ejection from triplet anions should be correspondingly lower. This energy may not be gained rapidly enough in ice but can be efficiently acquired in water in competition with deactivation. (b) The lifetime of the triplet anions in water is shorter than that of the neutral triplets and much shorter than in low-temperature ice; hence their chance to absorb another photon is reduced. This conclusion is based on our observation that oxygen has little effect on the yield of radicals in alkaline solutions. For example, the yield of radicals from tyrosine (pH 5.7, discharge voltage 23 kV) is almost doubled by replacing O_2 by N_2O in the presence of *tert*-butyl alcohol, whereas at pH 12.0 almost identical yields were obtained. This result suggests that the triplet anion has $\tau \lesssim 0.1$ μsec. Stronger interaction of the anion (which is a relatively small chromophore) with its environment may be responsible for this shortening of lifetime.

It is of special interest to study the change from a monophotonic to a biphotonic mechanism as a function of pH. Some data are shown in Figure 6 for tyrosine, where n is the order of the reaction with respect to light intensity (derived from plots as in Figures 3 and 4). From our limited data we may still infer that the plot of n against pH resembles a titration curve with an inflection around pH ~8.5. This is very close to $pK(T_1)$ of *p*-cresol.[14] Therefore we believe that these results strongly support the view that triplets are the precursors of e_{aq}^- and that their acidic and basic forms undergo photo- and thermal ionization, respectively.

Temperature Effects. The phenolate anions display much higher sensitivity toward temperature effects than the phenols. In alkaline solutions the radical yields are nearly doubled on raising the temperature from 20 to 70°, whereas in neutral solutions photoionization is hardly affected. Even higher temperature coefficients have recently been reported[16] in the case of PhO^-. Now, if both reactions were monophotonic the reverse order should occur, *i.e.*, the higher the ionization potential the larger the temperature coefficient. Thus we have further evidence to the difference in the number of photons involved in the ionization of phenols and their anions, respectively.

Cook and Logan[16] tried to determine the activation energy of the autoionization of some excited phenolates. Assuming that this state is produced with a quantum yield $\Phi = 1$, they derived a simple equation. It appears to fit PhO^-, but some substituted phenolates showed marked deviations. Modifying their equation by considering the triplets as precursors of e_{aq}^-, eq 3 can be readily derived, where Φ_{isc} and Φ_{e^-} are

$$\ln\left(\frac{\Phi_{isc}}{\Phi_{e^-}} - 1\right) = C - \frac{E_2 - E_1}{RT} \qquad (3)$$

the quantum yields of intersystem crossing and electron ejection, respectively; E_2 and E_1 are the activation energies of autoionization and deactivation of triplets, respectively. However, we believe that Φ_{isc} is also temperature dependent. The fluorescence yield Φ_f of tyrosine decreases with increase in temperature and this was ascribed to a temperature effect on the competing reaction–deactivation of the excited singlet.[17] If this view is correct then the temperature dependence of Φ_{isc} should be identical with that of Φ_f. Therefore in order to evaluate E_2, eq 3 should be modified to include the dependence of Φ_{isc} on temperature.

From the foregoing discussion it is clear that the temperature effect on the radical yield is less than that

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exerted on the triplet autoionization. The former reflects a balance of the effects on autoionization and deactivation of the excited-singlet and triplet states. If this picture is correct, then reaction 2 is not a one-stage process but proceeds through a higher excited triplet T_2 which then undergoes autoionization with some activation energy. Apparently by coincidence this activation energy is almost balanced by the activation energies of the deactivating processes, and therefore the overall photoionization of phenols in neutral solutions appears to be little affected by temperature.

For tyrosine $E(T_1) = 3.5$ eV[18] and the triplet–triplet transition displays a broad ill-defined band in the region 300–700 nm,[19] where tyrosine (S_0) hardly absorbs. Therefore most molecules in the T_2 state are produced with $E < 7.5$ eV above ground state. The ionization potential of phenol in the gas phase is 8.5 eV.[20] The effective IP in water is not known; a reduction of ~1 eV due to relatively fast polarization effects is in accordance with the foregoing discussion.

In the case of the phenolate anions, fast intersystem crossing (no fluorescence was observed[15]), low ionization potentials (the electron affinity of PhO^- is ~1.2 eV[21]), and relatively high triplet energies—these three factors account for the reaction proceeding by thermal ionization of their triplets. This combination of factors is not common, *e.g.*, at 337 nm β-naphtholate undergoes direct ionization from its S_1 state,[22] which is longer lived than the S_1 state of phenolate.

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Addition of Hydroxyl Radicals to Pyrimidine Bases and Electron Transfer Reactions of Intermediates to Quinones

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Abstract: The transient optical absorption spectra of the radicals produced from the reaction of hydroxyl radicals with pyrimidine bases in aqueous solution have been determined using the technique of pulse radiolysis. Uracil, thymine, cytosine, 1- and 3-methyluracil, 1,3-dimethyluracil, and dihydrouracil have been studied as a function of pH in order to examine the role of the tautomeric forms of the pyrimidine bases with regard to the site(s) of OH radical addition. The transient spectra obtained at pH ~11.0 in solutions of uracil, thymine, and 1- and 3-methyluracil were different from those observed in neutral solution. Examination of the change in initial absorbance at a fixed wavelength with pH revealed a "titration-type" curve from which a pK was derived. In all cases, the pK value obtained was identical with the p$K_a{}^1$ of the pyrimidine base used, indicating that the changes in the spectra are due to the tautomerization of the molecule and not to the acid–base properties of the OH-radical adducts to the pyrimidines. The transient spectrum of the radical produced from OH addition to 1,3-dimethyluracil was identical in neutral and alkaline solutions, supporting the above conclusion. With cytosine, the pK ~ 4.5 ± 0.1 obtained corresponded to the p$K_a{}^1$ ~ 4.6 for the proton dissociation of N_3. The observed red shift of the transient spectra in alkaline solution, compared to neutral solution, is probably due to the increased resonance energies of the lactim form *vis-à-vis* the lactam form of the pyrimidines radicals. From the decay kinetics of the intermediates, it is suggested that substitution at the N_1 position reduces the extent of ring opening which results from radical addition across the 5,6 double bond. The intermediates produced were found to react with menaquinone (vitamin K_3, $E° = 0.42$ V) leading to the formation of the semiquinone radical anion MQ^-. The reaction rate constants for electron transfer to MQ were found to be relatively high, ~1–5 × 10^9 M^{-1} sec^{-1}, for the large number of bases examined. The efficiency of electron transfer, (*i.e.*, percentage) was found to be markedly dependent upon the nature of the pyrimidine and nucleotide examined, as well as on the tautomeric form. Increased efficiency of electron transfer occurs when the odd electron is resonating with ionic tautomeric forms of the pyrimidine radicals. Various explanations are offered for these results. The dissociation constant of the semiquinone radical of menaquinone was found to be 4.5 ± 0.1.

The study of the effect of high energy radiations on biochemicals has become a subject of increasing interest in recent years. The reactions of hydroxyl radicals, the main oxidizing species produced from the radiation chemistry of water, with various pyrimidine bases have been investigated using different fast-reaction techniques in order to establish the site(s) of attack on the pyrimidines and the effect of molecular

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