Triplet-State Characteristics and Photoionization Behavior of 2,2′- and 4,4′-Biphenyldiol Studied by 248 nm Laser Flash Photolysis in Aqueous Solutions[†]

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Received: June 26, 2001; In Final Form: September 28, 2001

Triplet-state characteristics and the photoionization behavior of 2,2′- and 4,4′-biphenyldiol have been investigated in aqueous solutions using the 248 nm nanosecond laser flash photolysis (LFP) technique. For 2,2′-biphenyldiol, the neutral form of the triplet state is mainly produced following the laser excitation in aqueous solutions for the pH conditions in which the ground state of the diol exists in its neutral form ($\mathrm{p}K_a^G = 7.5$). In aqueous alkaline solutions, in which the diol exists in its monoanionic form, photoexcitation leads to the formation of the anionic form of the triplet state along with phenoxyl radical and hydrated electron (e_{aq}^-). Under similar conditions, the 4,4′-biphenyldiol behaves somewhat differently. Unlike 2,2′-biphenyldiol, the LFP of its 4,4′-analogue not only produces the neutral form of the triplet state but also gives phenoxyl radical, even when the ground state of the diol exists in its neutral form in solution ($\mathrm{p}K_a^G = 9.4$). In alkaline solutions (pH $\gtrsim 11$), though, like its 2,2′-analogue, the 4,4′-biphenyldiol also produces the anionic form of its triplet state along with the phenoxyl radical and e_{aq}^-, the photoionization (PI) yield is higher for 4,4′-biphenyldiol. Further, it is interesting to observe that the mechanism of PI in the two diols is different, monophotonic for the 4,4′-analogue and biphotonic for the 2,2′-analogue. The differences in the above results on the two diols have been explained on the basis of the presence and absence of intramolecular hydrogen bonding in the diol molecules.

1. Introduction

Phenols and their derivatives are important probe molecules for investigating some of the fundamental processes occurring in many chemical and biological systems, namely, proton-transfer and hydrogen-bonding interactions.[1−5] Behavior of phenols in their excited states is also of great significance because they closely resemble the chromophoric structures of the aromatic amino acids. It is well-known that the photoionization (PI) of aromatic amino acids plays a crucial role in the photodegradation of proteins.[6−15] Though considerable efforts have been made to understand the excited-state behavior of phenols, indoles, and aromatic amino acids, the mechanistic details of the PI processes in these molecules are not yet very clear.[6−15] In many phenolic molecules, it has been observed that the fluorescence quantum yield (Φ_f) is largely dependent on the excitation energy.[14−16] Thus, Φ_f is seen to drop drastically when the molecules are excited to electronic states (S_n) higher than the S_1 state.[14−16] It has been observed that in many phenolic molecules the PI follows both mono- and biphotonic pathways, depending on the experimental conditions.[6−15] Though the involvement of the triplet states has been proposed for the biphotonic ionization of these molecules,[10,11] the mechanism is not very clear in many cases. In some phenolic molecules, the PI from their singlet manifold has also been suggested.[9] For many phenol derivatives, the detailed triplet-state characteristics are not available in the literature.

Biphenyldiols are considered to be simple model compounds for complex biomolecules, such as dityrosines and calmodulin.[17] These dihydroxy compounds are present in oils and oil derivatives and are reported to be good antioxidants.[18] Biphenyldiols are formed during the metabolism of biphenyl derivatives and are also reported to be photochemically active.[19] Because of the possibilities of both intra- and intermolecular hydrogen bonding, these molecules often show interesting chemical and photochemical properties.[20−23] We have recently reported the fluorescence characteristics and the proton-transfer behavior of 2,2′- and 4,4′-biphenyldiol in different solvents.[24,25] These studies indicate that because of the presence of intramolecular hydrogen bonding the 2,2′-biphenyldiol behaves drastically differently than its 4,4′-analogue. Except for some preliminary reports on the triplet state of 4,4′-biphenyldiol in solid matrixes[26] and in solution under pulse radiolytic condition,[27] the detailed triplet-state characteristics of the two diols are not reported in the literature. Recently, we have investigated the triplet-state characteristics of the two diols in different organic solvents[28] using a nanosecond laser flash photolysis (LFP) technique and observed substantial differences in their behavior. Because the photochemical behavior of phenols and related molecules in aqueous solutions is more important,[1−19] in the present work, we have investigated the triplet-state and PI/photodissociation (PD) characteristics of the two diols in aqueous solutions under different pH conditions. The aim of this work is to understand in detail how the presence and absence of the intramolecular hydrogen bonding in the two biphenyldiols affect their photochemical behavior in aqueous solutions under 248 nm laser excitation. The chemical structures of the two diols investigated are shown in Chart 1 along with their prototropic equilibrium constants (pK_a) in the ground and excited S_1 states (pK_a^G and pK_a^{S1}, respectively).[24]

2. Materials and Methods

The 2,2′- and 4,4′-biphenyldiol obtained from Aldrich were purified by repeated crystallization from cyclohexane (CHX)

[†] Part of the special issue "Noboru Mataga Festschrift".

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10.1021/jp012445v CCC: $22.00

CHART 1

2,2′-biphenyldiol [$2,2'\text{-Bp(OH)}_2$]

$pK_a^G(1) = 7.5$; $pK_a^G(2) = 14.7$

$pK_a^{S1}(1) = 0.37$; $pK_a^{S1}(2) = 15.8$

4,4′-biphenyldiol [$4,4'\text{-Bp(OH)}_2$]

$pK_a^G(1) = 9.4$; $pK_a^G(2) = 14.1$

$pK_a^{S1}(1) = 3.24$; $pK_a^{S1}(2) = 12.8$

and methanol (MeOH), respectively. Purest grade acetophenone (ACP), benzophenone (BZP), and biphenyl (BP) obtained from J. T. Baker Chemical Co. were used without further purification. Nanopure water (Barnsted system, resistivity of 18.3 MΩ cm) was used to make all of the aqueous solutions. Reagent grade perchloric acid (60%; E. Merck India Ltd.) and NaOH (S. D. Fine Chemicals, India) were used to adjust the pH of the solutions. Unless otherwise stated, all of the LFP experiments were carried out with deaerated solutions, purging high purity N_2 gas (Indian Oxygen Ltd.) through the solutions for about 10 min before the experiment.

A Shimadzu model 160-A UV−vis spectrophotometer was used for the ground-state absorption measurements. The nanosecond LFP setup used in the present work has been described elsewhere.[29,30] Briefly, 248 nm, 12 ns laser pulses from a KrF excimer laser (Oxford, U.K.) were used to excite the sample in a 1 cm × 1 cm quartz cuvette, and a 250 W pulsed xenon arc lamp was used as the monitoring light source for kinetic spectrometric detection of the transients.

3. Results and Discussion

3.1. Characterization of the Transients Formed by 248 nm LFP of 2,2′-Biphenyldiol. The time-resolved transient absorption spectra for 2,2′-biphenyldiol in aqueous solutions have been measured at different pH conditions following 248 nm laser excitation. Figure 1A shows the transient spectra obtained at pH ≈ 1, having the main transient absorption band in the 300−500 nm region with peak at ∼370 nm. The transient decay kinetics are found to be effectively first order. Further, there is almost no residual absorption in the transient decay traces at fairly long delays (>50 μs). A representative decay trace obtained at 370 nm is shown in the inset of Figure 1A. It is seen that the transient absorption at pH ≈ 1 is drastically reduced in the presence of oxygen, a typical triplet quencher.[31,32] Further, it is seen that the transient spectra obtained at pH ≈ 1 are qualitatively very similar to the triplet−triplet (T−T) absorption spectra of 2,2′-biphenyldiol observed by us in acetonitrile (ACN) and MeOH solutions.[28] We thus infer that the neutral form of the triplet state of the diol, $^3[2,2'\text{-Bp(OH)}_2]^*$, is formed in aqueous solution at pH ≈ 1 following 248 nm laser excitation. The absorption peak (λ_T^{max}) and the decay constant (k_T) for $^3[2,2'\text{-Bp(OH)}_2]^*$ at pH ≈ 1 are listed in Table 1 along with those in MeOH and ACN solutions. It is seen from Table 1 that the k_T values are somewhat lower in aqueous (pH ≈ 1) and MeOH solutions than in ACN. It is inferred that the protic nature of water and MeOH perturbs the deexcitation mechanism of the triplet state of the diol, probably via the formation of intermolecular hydrogen bonding between the solvent and the diol molecules.

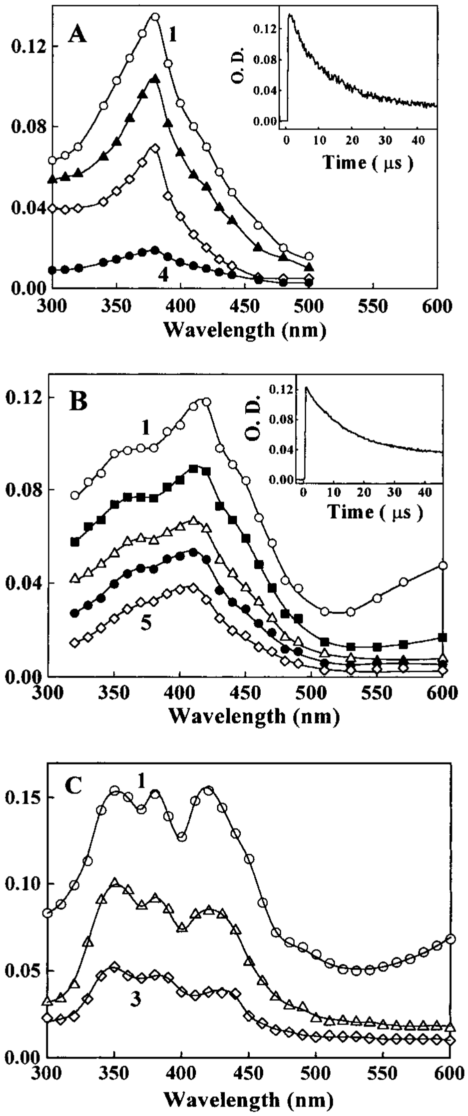


Figure 1. Time-resolved transient absorption spectra of 2,2′-biphenyldiol in deaerated aqueous solution at (A) pH ≈ 1, (B) pH ≈ 11, and (C) pH ≈ 7. The time delays are (A) 2, 6, 15, and 40 μs, respectively, for spectra 1−4, (B) 2, 6, 15, 25, and 45 μs, respectively, for spectra 1−5, and (C) 2, 10, and 40 μs, respectively, for spectra 1−3. Insets show the transient decay traces measured at (A) 370 nm and (B) 420 nm.

The time-resolved transient absorption spectra obtained for 2,2′-biphenyldiol in alkaline solution (pH ≈ 11) following laser excitation have two distinct absorption bands as shown in Figure 1B. The lower wavelength band appears in the 320−500 nm region with peak at ∼420 nm along with a shoulder at ∼360 nm. The longer wavelength band appears above 500 nm and extends beyond 600 nm. In the 320−500 nm region, it is seen that the transient decay traces always have a substantial residual absorption at long delays. A typical decay trace at 420 nm is shown in the inset of Figure 1B. It is indicated from the present results that for the 320−500 nm absorption band at least one short-lived and one long-lived transient species are involved.

The transient absorption for the longer wavelength band above 500 nm at pH ≈ 11 is seen to decay faster than that at the shorter wavelength band. Further, it is seen that the longer wavelength band completely disappears on saturating the solution with N_2O, an excellent scavenger of hydrated electron (e_{aq}^-).[33] It is thus inferred that the broad absorption band above 500 nm is due to the e_{aq}^- absorption. Because in alkaline solutions the ground state of the diol exists in its monoanionic form ($pK_a^G = 7.5$), formation of e_{aq}^- in these solutions indicates the PI of 2,2′-Bp(OH)O$^-$ by 248 nm light.

$$2,2'\text{-Bp(OH)O}^- \xrightarrow{h\nu} 2,2'\text{-Bp(OH)O}^\bullet + e_{aq}^- \qquad (1)$$

TABLE 1: Characteristics of the Neutral and the Monoanionic Forms of the Triplet State of 2,2′- and 4,4′-Biphenyldiol in Different Solvents

chemical species	solvent	λ_T^{max} (nm)	ϵ_T^{max} ($10^4 \times dm^3 mol^{-1} cm^{-1}$)	Φ_T	k_T ($10^4 s^{-1}$)
$^3[2,2'\text{-Bp(OH)}_2]^*$	water, pH ≈ 1	370	3.72	0.20	8.9
	water, pH ≈ 4	370	3.72	0.24	9.0
	MeOH	360	3.72	0.24	9.1
	ACN	360	3.72	0.29	12.0
$^3[2,2'\text{-Bp(OH)O}^-]^*$	water, pH ≈ 11	420	4.47	0.26	7.6
$^3[4,4'\text{-Bp(OH)}_2]^*$	water, pH ≈ 1	380	4.50	0.44	8.8
	water, pH ≈ 7	380	4.50	0.45	9.0
	MeOH	380	4.50	0.67	8.5
	ACN	380	4.50	0.46	13.3
$^3[4,4'\text{-Bp(OH)O}^-]^*$	water, pH ≈ 11	440	5.40	0.42	7.5

As already mentioned, one short-lived and one long-lived transient absorb in the 320−500 nm region at pH ≈ 11. Because 2,2′-Bp(OH)O$^-$ is seen to undergo PI at this pH, one of the transients absorbing in the 320−500 nm region is expected to be the phenoxyl radical (see eq 1). Because the phenoxyl radicals are usually very long-lived,[33] the long-lived transient in the 320−500 nm region is attributed to the phenoxyl radical of 2,2′-biphenyldiol. In eq 1, although the diol radical is presented in its neutral form, 2,2′-Bp(OH)O$^\bullet$, the species can also exist in its monoanionic form, 2,2′-Bp(O$^-$)O$^\bullet$, depending on the pH of the solution and the acid dissociation constant, pK_a^R, of the radical.

$$2,2'\text{-Bp(OH)O}^{\bullet} \overset{pK_a^R}{\rightleftharpoons} 2,2'\text{-Bp(O}^-\text{)O}^{\bullet} + \text{H}^+ \qquad (2)$$

From the above results at pH ≈ 11 alone, however, it is not possible to characterize the prototropic form of the radical formed at pH 11. We will discuss this issue in section 3.2.

In the 320−500 nm band at pH ≈ 11, the transient absorption is significantly reduced in the presence of a triplet quencher like oxygen,[31,32] indicating the short-lived transient to be a triplet state. Because the absorption characteristics of the short-lived species do not match with those of $^3[2,2'\text{-Bp(OH)}_2]^*$ obtained at pH ≈ 1, we infer that the former might be the monoanionic form of the triplet state, $^3[2,2'\text{-Bp(OH)O}^-]^*$. The decay constant k_T of $^3[2,2'\text{-Bp(OH)O}^-]^*$ was estimated by first-order kinetic analysis of the decay traces at 420 nm considering an appropriate residual absorption for the long-lived phenoxyl radical. The k_T value thus obtained is listed in Table 1 along with the λ_T^{max} for the species.

Figure 1C shows the time-resolved transient absorption spectra obtained in neutral aqueous solution (pH ≈ 7) of the diol. A critical comparison of the spectra in Figure 1C with those in Figure 1A,B indicates that the spectra at pH ≈ 7 are a combination of those in acidic (pH ≈ 1) and alkaline (pH ≈ 11) conditions. The longer wavelength absorption band above 500 nm at pH ≈ 7 is attributed to the e_{aq}^-, following the N_2O quenching experiment.[33] From oxygen quenching experiments, it has been inferred that at pH ≈ 7 the short-lived transients for the 300−500 nm absorption band are the triplet species. Comparing Figure 1A,B with Figure 1C, we thus infer that at pH ≈ 7 both the neutral and the monoanionic form of the triplet states ($^3[2,2'\text{-Bp(OH)}_2]^*$ and $^3[2,2'\text{-Bp(OH)O}^-]^*$) coexist in the solution.

The acid dissociation constant (p$K_a^T(1)$) for the triplet state of 2,2′-biphenyldiol was estimated to be ∼7.8 from the pH-dependent changes in the $^3[2,2'\text{-Bp(OH)}_2]^*$ absorption at 370 nm (see Figure 2A) and assuming that the triplet quantum yield (Φ_T) remains similar for the pH range studied. In section 3.3, in which we discuss the Φ_T values of the diol, it will be seen that the above assumption is quite reasonable. It is interesting to see that the estimated p$K_a^T(1)$ of the diol is close to its ground-state p$K_a^G(1)$ of 7.5.[24] Thus, the acidity of the diol does not change significantly in its triplet excited state in comparison to its ground-state acidity. Interestingly, it may be noted, however, that in the S_1 state the 2,2′-biphenyldiol behaves as a much stronger acid (p$K_a^{S1}(1) = 0.37$)[24] than its ground state. The present results thus indicate that the strength of the intramolecular hydrogen bonding in 2,2′-biphenyldiol in the triplet state is comparable to that in the ground state though it becomes much stronger in the S_1 state of the diol.[24]

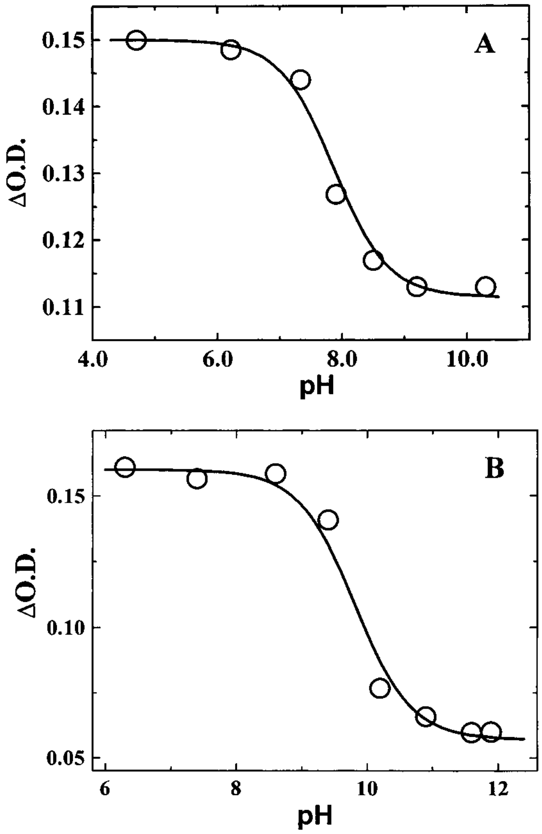


Figure 2. Changes in the transient OD with pH for (A) 2,2′-biphenyldiol observed at 370 nm and (B) 4,4′-biphenyldiol observed at 380 nm. The open circles are the experimental points and the continuous curves are the fitted results based on the acid−base equilibria.

Because there are two hydroxyl groups in the diol (see Chart 1), a second acidity constant (p$K_a^T(2)$) is also expected for the triplet state for the molecule. Considering the fact that the acidity of the diol in the triplet and ground states is comparable, it is likely that the p$K_a^T(2)$ of the diol is also comparable to its ground-state p$K_a^G(2)$ of 14.7.[24] The p$K_a^T(2)$ value of the diol, however, could not be estimated in the present work because of large PI yield at highly alkaline conditions.

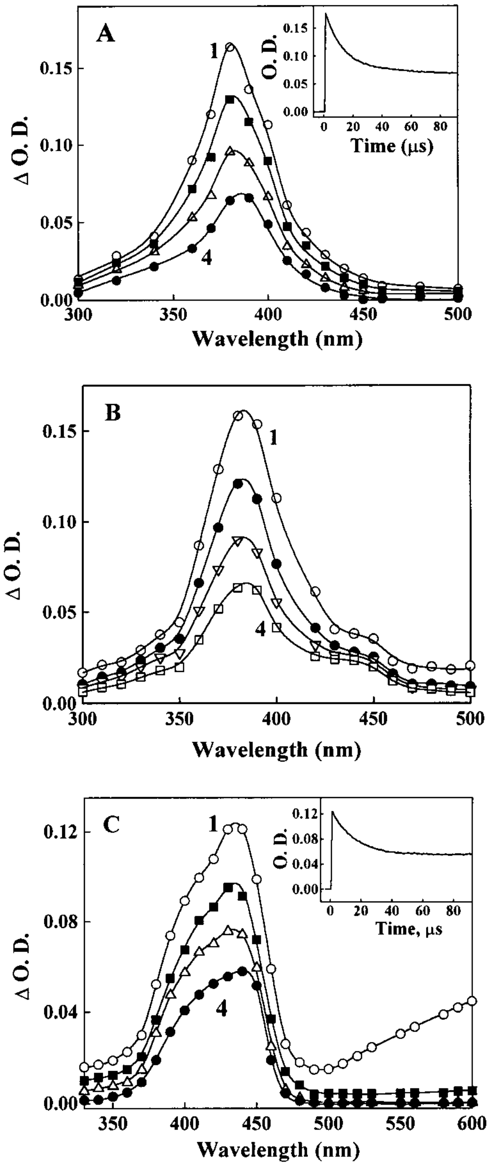


Figure 3. Time-resolved transient absorption spectra of 4,4′-biphenyldiol in deaerated aqueous solution at (A) pH ≈ 1, (B) pH ≈ 7, and (C) pH ≈ 11. The time delays are (A) 2, 8, 20, and 90 μs, respectively, for spectra 1−4, (B) 1, 10, 20, and 90 μs, respectively, for spectra 1−4, and (C) 2, 20, 50, and 90 μs, respectively, for spectra 1−4. Insets show the transient decay traces measured at (A) 380 nm and (C) at 420 nm.

3.2. Characterization of the Transients Formed by 248 nm LFP of 4,4′-Biphenyldiol. The time-resolved transient absorption spectra for 4,4′-biphenyldiol have also been obtained in aqueous solutions at different pH conditions. Figure 3A,B,C shows such spectra obtained at pH ≈ 1, 7, and 11, respectively. It is indicated from the spectra in Figure 3A and the decay trace in the inset of this figure that at least one short-lived and one long-lived transient are formed by LFP of the diol at pH ≈ 1. The transient spectra in Figure 3A at the shorter time windows (1−10 μs) are similar to the reported T−T absorption spectra of the diol in ACN and MeOH solutions.[28] The short-lived transient formed at pH ≈ 1 is thus attributed to the neutral form of the diol triplet state, $^3[4,4'\text{-Bp(OH)}_2]^*$. The $\lambda_T^{\max}$ and k_T values for $^3[4,4'\text{-Bp(OH)}_2]^*$ at pH ≈ 1 are listed in Table 1.

The lifetime of the other transient formed at pH ≈ 1 is seen to be very long, >100 μs, and could not be estimated accurately in the present work. The transient absorption spectrum taken at ~90 μs (see Figure 3A) shows that this species also absorbs in the 300−450 nm region, with a peak at ~390 nm. In the photolysis of phenolic molecules, phenoxyl radicals are often formed, which absorb in the 350−450 nm region depending on the nature of the substituents and have a very long lifetime.[6,15,34,35] We thus infer that the long-lived transient formed at pH ≈ 1 is the neutral form of the phenoxyl radical, $4,4'\text{-Bp(OH)O}^\bullet$. The transient absorption spectrum obtained at ~90 μs at pH ≈ 1 is also seen to match with the absorption spectrum of $4,4'\text{-Bp(OH)O}^\bullet$ reported by Das[36] using a pulse radiolytic technique. We thus infer that the photolysis of 4,4′-biphenyldiol by 248 nm light produces both the triplet species $^3[4,4'\text{-Bp(OH)}_2]^*$ and the radical species $4,4'\text{-Bp(OH)O}^\bullet$ at pH ≈ 1.

$$4,4'\text{-Bp(OH)}_2 \xrightarrow{h\nu} {}^3[4,4'\text{-Bp(OH)}_2]^*$$

$$4,4'\text{-Bp(OH)}_2 \xrightarrow{h\nu} 4,4'\text{-Bp(OH)O}^\bullet + \text{H}^\bullet \qquad (3)$$

The time-resolved transient absorption spectra obtained for 4,4′-biphenyldiol at pH ≈ 7 (see Figure 3B) are seen to be quite similar to those obtained at pH ≈ 1 (see Figure 3A), especially at the shorter time windows (1−10 μs). The time-resolved spectra and the kinetic traces at pH ≈ 7 also indicate the presence of a short-lived and a long-lived transient species. It is seen that for the shorter time windows the decay could be fitted with first-order kinetics considering a suitable residual absorption for the long-lived species. From these observations, we infer that the short-lived species formed at pH ≈ 7 is $^3[4,4'\text{-Bp(OH)O}^-]^*$, similar to the one formed in solution at pH ≈ 1. The transient spectra at long delays (~90 μs) are, however, seen to be different at pH ≈ 7 than those at pH ≈ 1, having a hump at ~450 nm and a peak at ~390 nm. Because the $4,4'\text{-Bp(OH)O}^\bullet$ radical is reported to have a $\text{p}K_a^R$ value of 7.5,[36] the 450 nm hump in the transient spectra at pH ≈ 7 could be due to the presence of a small amount of the anionic form of the radical species.

LFP of 4,4′-biphenyldiol in alkaline aqueous solution at pH ≈ 11 (see Figure 3C) results in transient absorption spectra quite different than those obtained at pH ≈ 1 and 7. At pH ≈ 11, the main transient absorption band appears in the 330−470 nm region with peak at ~440 nm. There is also a broad long-wavelength absorption band beyond 500 nm, as was also observed in the case of 2,2′-biphenyldiol under similar conditions, which has been characterized as being due to the e_{aq}^- following the N_2O quenching experiment.[33]

The time-resolved transient absorption spectra and the kinetic traces at pH ≈ 11 (see Figure 3C and its inset) clearly indicate that one short-lived and one long-lived transient absorb in the 330−470 nm region. Because e_{aq}^- is seen to be formed at pH ≈ 11, we infer that the long-lived transient for the 330−470 nm absorption band is the phenoxyl radical of the diol, as these radicals are usually very long-lived.[6,15,34,35] Because the spectral shape of the long-lived species at pH ≈ 11 does not match with that of the $4,4'\text{-Bp(OH)O}^\bullet$ formed at pH ≈ 1 and because the $\text{p}K_a^R$ value of the diol is about 7.5,[36] the prototropic form of the radical at pH ≈ 11 has been inferred to be its anionic form, $4,4'\text{-Bp(O}^-)\text{O}^\bullet$. This assignment has been confirmed by comparing the absorption spectrum of the transient at ~90 μs with that of the $4,4'\text{-Bp(O}^-)\text{O}^\bullet$ radical anion reported by Das.[36]

The absorption characteristics of the short-lived transient produced at pH ≈ 11 for 4,4′-biphenyldiol are different from those of $^3[4,4'\text{-Bp(OH)}_2]^*$, formed at pH ≈ 1 and 7. Drawing an analogy with the LFP results of 2,2′-biphenyldiol, we infer that the short-lived transient formed for 4,4′-biphenyldiol at pH

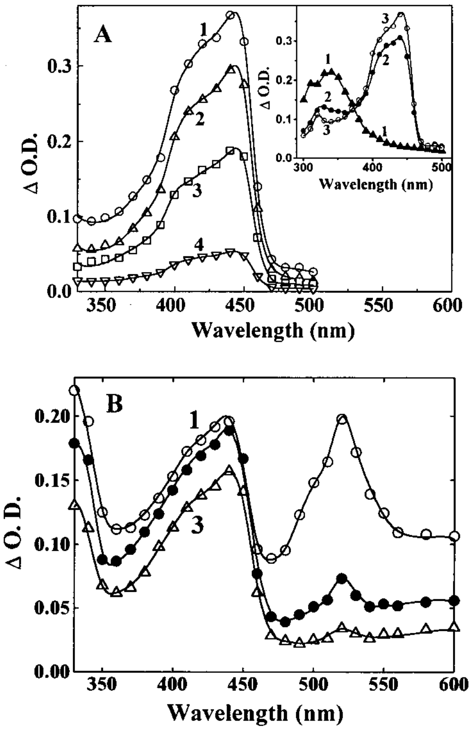


Figure 4. Time-resolved sensitized transient absorption spectra obtained for 4,4′-biphenyldiol at pH ≈ 11 using (A) acetophenone and (B) benzophenone as the sensitizers for TTET. Time delays are (A) 6, 18, 45, and 90 μs, respectively, for spectra 1−4 and (B) 6, 18, and 45 μs, respectively, for spectra 1−3. Inset in panel A shows the time-resolved transient absorption spectra obtained at (2) 2 μs and (3) 6 μs after the laser pulse for the acetophenone−4,4′-biphenyldiol system, indicating the spectral changes in the initial time windows due to TTET process. Spectrum 1 in panel A inset shows the absorption spectrum of acetophenone triplet only (at 2 μs) in absence of the diol.

≈ 11 is the monoanionic form of its triplet state, $^3[4,4'\text{-Bp(OH)O}^-]^*$. Thus the LFP results of 4,4′-biphenyldiol at pH ≈ 11 can be presented by eq 4.

$$\begin{aligned} &4,4'\text{-Bp(OH)O}^- \xrightarrow{h\nu} {}^3[4,4'\text{-Bp(OH)O}^-]^* \\ &4,4'\text{-Bp(OH)O}^- \xrightarrow{h\nu} 4,4'\text{-Bp(O}^-\text{)O}^\bullet + \text{H}^+ + \text{e}_{\text{aq}}^- \qquad (4) \end{aligned}$$

One interesting point to be mentioned here is that unlike the case of 2,2′-biphenyldiol the transient absorption in the 330−470 nm region does not get quenched efficiently by a triplet quencher like oxygen. Thus, for an unambiguous characterization, we attempted the triplet−triplet energy transfer (TTET) method[37,38] to obtain the T−T absorption spectrum for 4,4′-Bp(OH)O$^-$ using a suitable triplet reference (R).

$$^3\text{R}^* + 4,4'\text{-Bp(OH)O}^- \xrightarrow{\text{TTET}} \text{R} + {}^3[4,4'\text{-Bp(OH)O}^-]^* \qquad (5)$$

From low-temperature (77 K) phosphorescence studies, the triplet state energy (E_T) of 4,4′-Bp(OH)O$^-$ was estimated to be about 65 kcal mol^{-1}.[39] Experiments were carried out using acetophenone (ACP) as the reference triplet sensitizer (E_T = 74 kcal mol^{-1})[40] at pH ≈ 11 at which the ground state of the diol exists in the 4,4′-Bp(OH)O$^-$ form.[24] The experimental conditions were kept such that the 248 nm excitation light is mainly absorbed by ACP and the direct excitation of 4,4′-Bp(OH)O$^-$ is negligible. The sensitized time-resolved transient absorption spectra thus obtained are shown in Figure 4A. The inset of Figure 4A shows the time-resolved transient absorption spectra at very short time windows indicating the conversion of the ACP triplet to the sensitized transient of interest for 4,4′-biphenyldiol. It is seen from Figure 4A that the sensitized absorption spectra in the 330−470 nm range are very similar to those observed for the short-lived transient in the direct LFP of the diol at the same pH (cf. Figure 3C). The TTET results thus indicate that the concerned short-lived transient formed for 4,4′-biphenyldiol at pH ≈ 11 should be the monoanionic form of its triplet state, $^3[4,4'\text{-Bp(OH)O}^-]^*$. To substantiate this further, the TTET experiments were also carried out using benzophenone (BZP; E_T = 68 kcal mol^{-1})[40] as the triplet sensitizer. The results of these experiments shown in Figure 4B clearly indicate that the sensitized absorption spectra obtained for 4,4′-biphenyldiol by the compensation of the BZP triplet (absorption peak for ^{3}BZP* at ∼520 nm)[31,32] are very similar to those observed by using ACP as the triplet sensitizer. Thus it is evident that the short-lived transients for 4,4′-biphenyldiol formed either in direct photolysis or in TTET experiments are all the same and are attributed to the monoanionic form of the triplet state, $^3[4,4'\text{-Bp(OH)O}^-]^*$.

At this point, however, an interesting aspect to be considered is the use of ACP and BZP as the triplet sensitizers, because these molecules are also good electron acceptors and thus can participate in electron transfer (ET) from 4,4′-Bp(OH)O$^-$ to the triplets of ACP/BZP.

$$^3\text{R}^* + 4,4'\text{-Bp(OH)O}^- \xrightarrow{\text{ET}} \text{R}^{\bullet -} + [4,4'\text{-Bp(OH)O}^\bullet]^* \qquad (6)$$

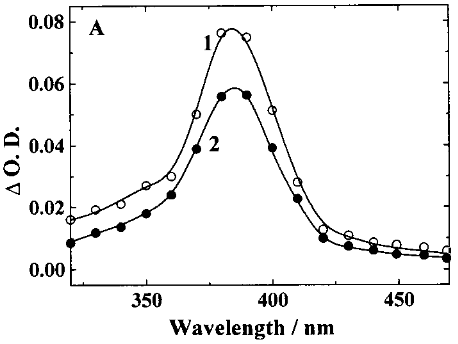
This aspect is pertinent because Shizuka et al.[41,42] have observed that when BZP is used as triplet sensitizer for naphtholate ions in aqueous alkaline solutions, the ET reaction predominates over the TTET mechanism. Because both ACP/4,4′-Bp(OH)O$^-$ and BZP/4,4′-Bp(OH)O$^-$ systems chemically resemble the BZP/naphtholate system, the sensitized transient spectra in Figure 4 parts A and B may also have some contribution from the transients formed by ET interaction. This is particularly so because both of the transients, $^3[4,4'\text{-Bp(OH)O}^-]^*$ and 4,4′-Bp(O$^-$)O$^\bullet$, formed by the TTET and ET mechanisms, respectively, will have strongly overlapping absorption in the 330−470 nm region (cf. Figure 3C). Further, the anion radical of ACP formed by the ET mechanism will have significant absorption at ∼450 nm.[43,44] Thus, for the ACP/4,4′-Bp(OH)O$^-$ system, it is not possible to assess the contribution of the ET process unequivocally. For the BZP/4,4′-Bp(OH)O$^-$ system at pH ≈ 11, however, Figure 4B clearly indicates that the ET mechanism is not operative, as the growth of the BZP anion radical at ∼630 nm[43,44] following reaction 6 is not observed in these experiments. Thus, we infer that for both ACP/4,4′-Bp(OH)O$^-$and BZP/4,4′-Bp(OH)O$^-$ systems at pH ≈ 11, the ET mechanism is not operative, and the sensitized transient spectra in the 330−470 nm region are attributed to the $^3[4,4'\text{-Bp(OH)O}^-]^*$ species (see Figure 4A,B). This is further supported by the fact that there is no sensitization reaction for 2,2′-Bp(OH)O$^-$ by the triplet state of BZP, because the E_T for the former (∼70 kcal mol^{-1})[39] is more than that of BZP (68 kcal mol^{-1}).[40] With the triplet ACP, however, we could observe the sensitization of $^3[2,2'\text{-Bp(OH)O}^-]^*$ in the present work, because the E_T of ACP (74 kcal mol^{-1})[40] is higher than that of 2,2′-Bp(OH)O$^-$. If the ET mechanism was operative in these systems, interaction of 2,2′-Bp(OH)O$^-$ with the BZP was expected to be more efficient than with ACP because the former is a stronger electron acceptor than the latter (E_red = −1.42 and −1.64 V vs NCE for BZP and ACP, respectively, in 48% EtOH solution at pH = 11.3).[45] That the TTET mechanism is operative in the systems studied is also supported by the fact that the sensitized transient species formed for both the diols at pH ≈ 11 using ACP/BZP as the sensitizers decay by first-order kinetics, suggesting the transients to be the triplet states. It should be noted that radical species usually decay following second-order kinetics.[6−15,34,35]

From the T−T absorption spectra of 4,4′-biphenyldiol at pH ≈ 1, 7, and 11 (see Figure 3 parts A, B, and C), it is inferred that $pK_a^T(1)$ of the diol exists between 7 and 11. Following pH-dependent changes in the transient OD at 380 nm immediately after the laser excitation (see Figure 2B) and assuming that Φ_T does not appreciably change in the pH range of ∼7−11, the $pK_a^T(1)$ value has been estimated to be 9.8. It is seen that similar to 2,2′-biphenyldiol, $pK_a^T(1)$ of its 4,4′-analogue is also close to its ground-state $pK_a^G(1)$ of 9.4.[24] Thus, it is indicated that the differences in the acidity of both diols in their ground and triplet states are very minor. For both diols, however, the S_1 states have been found to be far more acidic than their respective ground states.[24]

An interesting point to be noted here is that at all of the pH conditions studied, the 4,4′-biphenyldiol produces phenoxyl radicals following 248 nm LFP. Unlike 4,4′-biphenyldiol, its 2,2′-analogue does not produce any phenoxyl radical by 248 nm LFP in aqueous solutions as long as the diol exists in its neutral form in the solution (pH < ∼6; $pK_a^G(1) = 7.5$). Our results thus indicate that the neutral form of 4,4′-biphenyldiol also undergoes photodissociation (PD) by 248 nm light in aqueous solutions (see eq 3), whereas that of its 2,2′-analogue does not. Similar observations were also made in our earlier work on the LFP of the two diols in organic solvents.[28] It is thus evident that the behavior of the two diols under 248 nm LFP is quite different. Because in 2,2′-biphenyldiol there exists a strong intramolecular hydrogen bonding, which is absent in 4,4′-biphenyldiol,[24,25] we infer that the differences in the PD behavior of the two diols arise because of the presence and absence of the intramolecular hydrogen bonding.[28] It appears that because of intramolecular hydrogen bonding both the S_0 and S_1 state of 2,2-biphenyldiol gain some extra stabilization; hence, the energy of the 248 nm photon (∼5 eV) is not sufficient to dissociate the molecule. For 4,4′-biphenyldiol, as the stabilization due to hydrogen bonding is absent, the energy of the 248 nm photon is sufficient to excite the molecule to a vibrational level of the S_1 state higher in energy than the dissociative state and thus to make dissociation possible.

As mentioned earlier, unlike the case of 2,2′-biphenyldiol, the transient absorption for 4,4′-biphenyldiol is not significantly reduced in the presence of triplet quencher, like oxygen. It is thus important to know the nature of the transients formed in the LFP of 4,4′-biphenyldiol in the presence of oxygen. We thus carried out the LFP experiments of 4,4′-biphenyldiol in aerated aqueous solutions. Typical time-resolved transient absorption spectra obtained in aerated solutions at pH ≈ 4 and 11 are shown in Figure 5, parts A and B, respectively. It is seen that the shape of the transient absorption spectra under aerated conditions at pH ≈ 4 and 11 is quite similar to that of the respective spectra of the long-lived 4,4′-Bp(OH)O$^\bullet$ and 4,4′-Bp(O$^-$)O$^\bullet$ radicals obtained under deaerated conditions (cf. spectra at longer delays (∼90 μs) in Figure 3, parts A and C). We thus infer that the radical species 4,4′-Bp(OH)O$^\bullet$ and 4,4′-Bp(O$^-$)O$^\bullet$ are formed in the LFP of 4,4′-biphenyldiol under aerated conditions at pH ≈ 4 and 11, respectively.

Formation of the phenoxyl radicals of 4,4′-biphenyldiol in the LFP under aerated conditions is a very interesting observation, especially because no such species are seen to be formed for 2,2′-biphenyldiol under similar conditions. Because oxygen is a good triplet quencher, the results under aerated conditions indicate that the PD/PI mechanism for 4,4′-biphenyldiol does not involve the triplet state of the molecule. Thus, the excitation of 4,4′-biphenyldiol by 248 nm light to its S_1 state seems to directly lead to PD/PI of the molecule. Because phenoxyl radicals are not formed for 2,2′-biphenyldiol under aerated conditions, it is indicated that the triplet state of the diol might be involved in its PD/PI process. Thus, the LFP results of 4,4′-biphenyldiol in aerated aqueous solutions can be represented by the following reaction sequences.



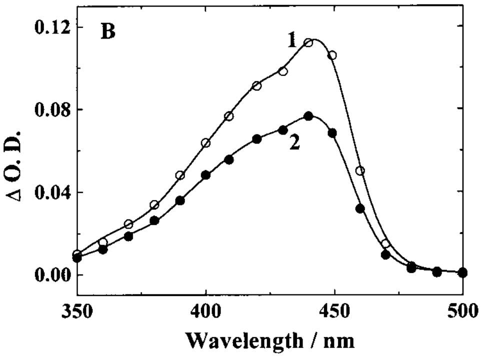


Figure 5. Time-resolved transient absorption spectra of 4,4′-biphenyldiol in aerated aqueous solutions at (A) pH ≈ 4 and (B) pH ≈ 11. The time delays are 1.5 and 45.0 μs, respectively, for spectra 1 and 2.

$$4,4'\text{-Bp(OH)}_2 \xrightarrow{h\nu} 4,4'\text{-Bp(OH)O}^\bullet + \text{H}^\bullet \quad (7)$$

$$\text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}_2^\bullet \quad (8)$$

$$4,4'\text{-Bp(OH)O}^- \xrightarrow{h\nu} 4,4'\text{-Bp(O}^-\text{)O}^\bullet + \text{H}^+ + e_{aq}^- \quad (9)$$

$$e_{aq}^- + \text{O}_2 \rightarrow \text{O}_2^{\bullet -} \quad (10)$$

Because reactions 8 and 10 occur with almost diffusion-controlled rates,[33] the presence of oxygen effectively scavenges H$^\bullet$ and e_{aq}^- and thus enhances the yield of the phenoxyl radicals. It is evident from the above results that the differences in the behavior of 2,2′- and 4,4′-biphenyldiol in 248 nm LFP under aerated conditions reflect the mechanistic differences in the PD/PI processes for the two diol analogues. This aspect will be discussed in detail in section 3.4.

From the LFP results of 4,4′-biphenyldiol, it is seen that the phenoxyl radical of the diol is formed both under aerated and under deaerated conditions and the radical species exists in neutral form, 4,4′-Bp(OH)O$^\bullet$, at pH ≈ 4 and in anionic form, 4,4′-Bp(O$^-$)O$^\bullet$, at pH ≈ 11. These results are consistent with the reported pK_a^R value of 7.5 for the phenoxyl radical of 4,4′-biphenyldiol.[36] For 2,2′-biphenyldiol, it is seen in section 3.1 that the phenoxyl radical of the diol is also formed following LFP under deaerated conditions at pH ≈ 7 and 11 and at both pH's the absorption spectra of the radical species are very similar with absorption peaks at around 420 nm (see ~90 μs spectra; Figure 1, parts B and C). It is thus indicated that at both pH conditions the radical species for 2,2′-biphenyldiol exist in the same prototropic form. Because in 2,2′-biphenyldiol there is a strong intramolecular hydrogen bonding, the absorption peaks for both neutral and anionic forms of its phenoxyl radical are expected to appear at slightly longer wavelengths than the corresponding peaks of the phenoxyl radical of 4,4′-biphenyldiol. Because the absorption peaks for 4,4′-Bp(OH)O$^\bullet$ and 4,4′-Bp(O$^-$)O$^\bullet$ appear at around 390 and 440 nm, respectively, the prototropic form of the phenoxyl radical of 2,2′-biphenyldiol with an absorption peak at ~420 nm is expected to be the neutral form, 2,2′-Bp(OH)O$^\bullet$. Thus, it is indicated that for 2,2′-biphenyldiol its phenoxyl radical exists in the neutral form at least up to pH $\approx$ 11. We infer from the present results that the pK_a^R of 2,2′-Bp(OH)O$^\bullet$ is much higher than 11 and that such a high pK_a^R value arises because of the presence of strong intramolecular hydrogen bonding in the radical, which makes the deprotonation of the OH group very difficult. The exact pK_a^R value for 2,2′-Bp(OH)O$^\bullet$, however, could not be estimated in the present work.

3.3.Triplet Quantum Yields (Φ_T) of 2,2′- and 4,4′-Biphenyldiol. The Φ_T values of the two biphenyldiols in aqueous solutions at different pH conditions were estimated by a comparative method using the following expression.[29,46,47]

$$\Phi_T^S = \Phi_T^R\left(\frac{OD_T^S}{OD_T^R}\right)\left(\frac{\epsilon_T^R}{\epsilon_T^S}\right) \tag{11}$$

where Φ_T^S and Φ_T^R are triplet quantum yields, OD_T^S an OD_T^R are the maximum triplet OD values observed, and ϵ_T^S and ϵ_T^R are the molar extinction coefficients at the wavelengths of observation for the T−T absorption for the sample and the reference, respectively. In these estimations, the biphenyl triplet in cyclohexane (CHX) was used as the reference ($\Phi_T^R = 0.84$[40] and $\epsilon_T^R = 4.28 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 361 nm).[47] For the neutral form of the triplet states of 2,2′- and 4,4′-biphenyldiol, the ϵ_T^S values were considered to be 3.72×10^4 dm^3 mol^{-1} cm^{-1} at 370 nm and 4.5×10^4 dm^3 mol^{-1} cm^{-1} at 380 nm, respectively.[27,28] The Φ_T values thus estimated for the neutral form of the triplet states of the two diols at selected pH conditions are listed in Table 1.

For the monoanionic form of the triplet states of the two diols, the ϵ_T^S values were estimated at pH $\approx$ 11 using the TTET method.[37,38,46,47] The reference triplet donors used in these measurements were ACP ($\epsilon_T^R = 1.31 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 337 nm)[47] for 2,2′-biphenyldiol and BZP (5.8×10^3 dm^3 mol^{-1} cm^{-1} at 520 nm)[47] for 4,4′-biphenyldiol. Necessary corrections were used for (i) the decay of the ACP/BZP triplet states by means other than the TTET mechanism, (ii) the small amount of the direct excitation of the diols by the laser light, and (iii) the decay of the diol triplets after their formation by TTET. The ϵ_T values for the monoanionic form of the triplet states of 2,2′- and 4,4′-biphenyldiol thus estimated are 4.47×10^4 dm^3 mol^{-1} cm^{-1} at 420 nm and 5.4×10^4 dm^3 mol^{-1} cm^{-1} at 440 nm, respectively. The Φ_T values for the monoanionic form of the triplet states of the two diols thus estimated using the above ϵ_T values are also listed in Table 1.

It is seen from Table 1 that the Φ_T values for 2,2′-biphenyldiol are generally lower than those of its 4,4′-analogue. In our earlier studies, it has been observed that the fluorescence lifetime (τ_f) of 2,2′-biphenyldiol in different solvents is much shorter than that of its 4,4′-analogue.[24] The shorter τ_f for 2,2′-biphenyldiol arises as a result of a faster radiative decay constant (k_f) of the S$_1$ state of 2,2′-biphenyldiol due to the presence of intramolecular hydrogen bonding (see Chart 1), though the effective nonradiative decay constant (k_{nr}) is estimated to be quite similar for both the diols.[24] Thus, it is expected that in the S$_1$ state the nonradiative intersystem crossing (ISC) process for 2,2′-biphenyldiol must contribute less as compared to that for 4,4′-biphenyldiol, resulting in a lower Φ_T for the former. It is thus evident that the estimated Φ_T values of the two diols correlate well with their fluorescence characteristics and the lower Φ_T for 2,2′-biphenyldiol is related to the presence of intramolecular hydrogen bonding in this molecule.

3.4. Photoionization of 2,2′- and 4,4′-Biphenyldiol in Aqueous Alkaline Solutions. It is evident from earlier discussions in sections 3.1 and 3.2 that monoanionic forms of both 2,2′- and 4,4′-biphenyldiol undergo efficient PI in aqueous alkaline solutions. To get insight into the PI mechanism of the two diols, their PI behavior has been further investigated in a systematic way at pH $\approx$ 11. Intensity-dependent PI yields for both 2,2′- and 4,4′-biphenyldiol have been estimated by measuring the OD values for e$_{aq}^-$ at 550 nm at different laser intensities. The laser intensities were varied by using biphenyl solutions in CHX (having different OD at 248 nm) in the path of the laser beam before the sample cell. The laser intensities were estimated relative to the transient OD values at 361 nm for the reference solutions of biphenyl in CHX.[38,45]

At moderate laser intensities, the yield of the e$_{aq}^-$ is expected to follow eq 12.[11]

$$OD_0 = kI^n \tag{12}$$

where OD$_0$ is the optical density of e$_{aq}^-$ at 550 nm, I is the laser intensity, n is an integer representing the number of photons required for the PI process, and k is the proportionality constant. Lachish et al.[11] have suggested that eq 12 holds good provided that there is no saturation in the excitation of the sample and that the condition $\sigma(I_t) < 1$ is satisfied, where σ is the absorption cross section and I_t is the laser fluence. Under the experimental conditions used, it was estimated that $\sigma(I_t) \leq 0.1$ even at the highest laser energy used (~50 mJ), and thus the saturation effects were avoided.

To estimate n, the experimental data were analyzed using the logarithmic form of eq 12.

$$\log[OD_0] = \log(k) + n\log(I) \tag{13}$$

Figure 6, parts A and B, represents the plot of log(OD$_0$) vs log(I) for 2,2′- and 4,4′-biphenyldiol, respectively, in aqueous solutions at pH $\approx$ 11. The slope is determined to be 2.05 for 2,2′-biphenyldiol (Figure 6A) and 1.1 for 4,4′-biphenyldiol (Figure 6B). These results indicate that the PI of 2,2′-biphenyldiol is a biphotonic process, whereas that of the 4,4′-analogue proceeds by a monophotonic mechanism. That 2,2′-Bp(OH)O$^-$ undergoes biphotonic ionization and 4,4′-Bp(OH)O$^-$ undergoes monophotonic ionization explains why PI efficiency is much lower in the former than in the latter case under similar conditions.

Earlier literature reports suggested that the PD/PI mechanism of phenols and phenolate ions can follow either a monophotonic or a biphotonic mechanism depending on the experimental conditions.[6−15] In the monophotonic mechanism, the PI has been proposed to occur directly from the singlet manifold of the molecules.[9] In the biphotonic mechanism, the triplet state (T$_1$) of the phenols is proposed to be the precursor.[6−15] For the two

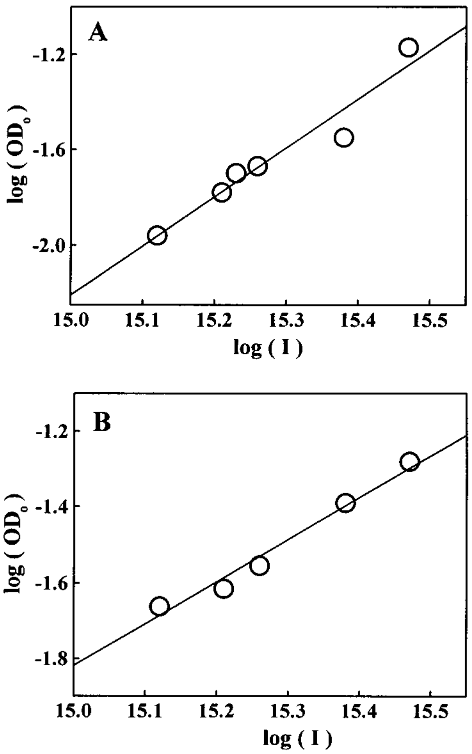
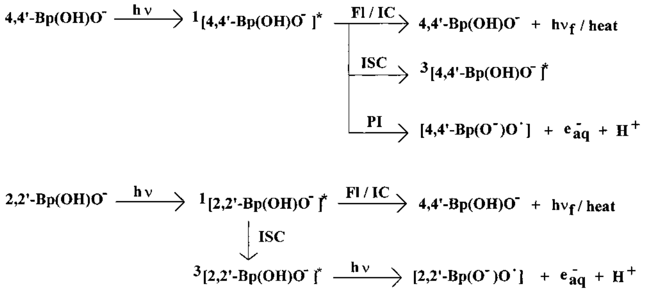


Figure 6. Plot of log(OD$_0$) vs. log(I) in relation to the photoionization of (A) 2,2′-biphenyldiol and (B) 4,4′-biphenyldiol in aqueous alkaline solutions at pH ≈ 11 (see eq 13). The photoionization process is biphotonic for 2,2′-biphenyldiol and monophotonic for 4,4′-biphenyldiol, as indicated by the slopes of these plots (2.05 and 1.1, respectively, for plots A and B).

SCHEME 1



biphenyldiols investigated, the experimental results indicate that similar mechanisms are also valid for their PD/PI behavior (see sections 3.1 and 3.2) and can be represented by the Scheme 1.

Let us now consider the energetics of the PI processes. For 4,4′-biphenyldiol, monophotonic ionization occurs with a 248 nm photon, which corresponds to an absorbed energy of about 5.04 eV. Gas-phase ionization potentials (IP$_g$) for typical phenols are known to be ~8 eV.[48] It is known that the IP in liquid phase (IP$_l$) is usually lower than IP$_g$ and that these two are related to each other by the following relation,[49,50]

$$\mathrm{IP_g} = \mathrm{IP_l} + P + V \qquad (14)$$

where P and V are the polarization energy of the hole (positive ion) and the ground-state conduction band potential (electron affinity) of the liquid, respectively. Because P and V are negative quantities, IP$_l$ is always lower than IP$_g$. It is reported that the lowering in IP in a highly polar solvent like water is approximately 3.4 eV.[49] The IP$_l$ for the typical phenols in aqueous solutions is thus expected to be ~4.6 eV. Hence, for the monoanionic form of 4,4′-biphenyldiol, in which intramolecular hydrogen bonding is absent, the ejection of an electron by absorption of a 248 nm photon of energy, ~5.04 eV, appears to be possible. For the monoanionic form of 2,2′-biphenyldiol, because of the presence of the intramolecular hydrogen bonding (see Chart 1), the IP$_l$ is expected to be higher than that of its 4,4′-analogue. Because 2,2′-Bp(OH)O$^-$ does not undergo monophotonic ionization by 248 nm light, which is about 0.4 eV more than the typical IP$_l$ values (4.6 eV), and because hydrogen-bond energy is typically of about 0.2 eV, it is expected that the seven-membered ring formed through intramolecular hydrogen bonding (see Chart 1) offers extra stability due to resonance effect with the aromatic rings.[24] For the monoanionic form of 4,4′-biphenyldiol, in the absence of the intramolecular hydrogen bonding, there is no such stabilization and the PI is monophotonic at 248 nm.

In terms of the potential energy diagrams, the differences in the PI behavior of 2,2′- and 4,4′-biphenyldiol can qualitatively be understood by Figure 7A,B. Similar potential energy diagrams have also been used to explain the PD/PI behavior of other phenols[34] and aromatic hydrocarbons.[51] In biphenyldiols and other phenols, the photoexcitation by UV photons (e.g., 248 nm) leads to the excitation of a π electron to the π^* orbital.[24,34] Because the photoexcited 4,4′-Bp(OH)O$^-$ (and other phenolate ions) undergoes PI giving the phenoxyl radical and e$_{aq}^-$, it is evident that the initial excitation energy in the π−π^* state migrates to the MO of HOΦΦ-O$^-$, which has a σ character. Though on a single potential energy diagram it is not possible to represent the motions of all of the nuclei of the molecule simultaneously, the migration of π−π^* excitation energy to the σ MO of HOΦΦ-O$^-$ from which the electron is ejected can qualitatively be represented as in Figure 7. In this presentation, only the distance, r_{rxn}, between HOΦΦ-O$^•$ and e$_{aq}^-$ is considered as the reaction coordinate. Though the exact shape of the PE surfaces for different electronic states of biphenyldiols is not known, it is obvious in relation to Figure 7 that as the species HOΦΦ-O$^•$ and e$_{aq}^-$ approach each other, it will result in the formation of a bonding and an antibonding (repulsive) σ orbital. Similarly one bonding and one antibonding σ state are also formed as the excited (HOΦΦ-O$^•$)* and e$_{aq}^-$ approach each other. Because only the repulsive states are involved in PI, only the repulsive σ states are shown in Figure 7 with the notations of $^3\sigma_0$ and $^3\sigma_1$, adopted from Land and Porter,[34] along with the ground and excited π states ($^1\pi_0$ and $^1\pi_1$, respectively) involved in the initial excitation. As shown in Figure 7A, the $^1\pi_0$ and $^1\pi_1$ states for 2,2′-Bp(OH)O$^-$ gain extra stabilization due to intramolecular hydrogen bonding. Thus, the π−π^* excited state produced by the absorption of a 248 nm photon is much lower in energy than the repulsive $^3\sigma_0$ state and cannot undergo monophotonic ionization. For the biphotonic ionization of 2,2′-Bp(OH)O$^-$, a second photon has to be absorbed by an excited molecule either in its S$_1$ or T$_1$ state. The fact that there is no PI for 2,2′-Bp(OH)O$^-$ under aerated conditions indicates the involvement of the triplet state of the molecule in the PI process. Thus, the biphotonic ionization of 2,2′-Bp(OH)O$^-$ seems to occur via the T$_1$ state as shown in Figure 7A. In the case of 4,4′-biphenyldiol (see Figure 7B), because of the absence of intramolecular hydrogen bonding, the π−π^* state is higher in energy than the dissociative $^3\sigma_0$ state. Thus, a fraction of the excited molecules in the π−π^* state produced by 248 nm photon absorption can crossover to the $^3\sigma_0$ state resulting in PI. An important point to be noted here is that the π and σ states involved in the PE crossover are of different symmetry. It is thus expected that the crossing of the PE surfaces in the present cases should be symmetry

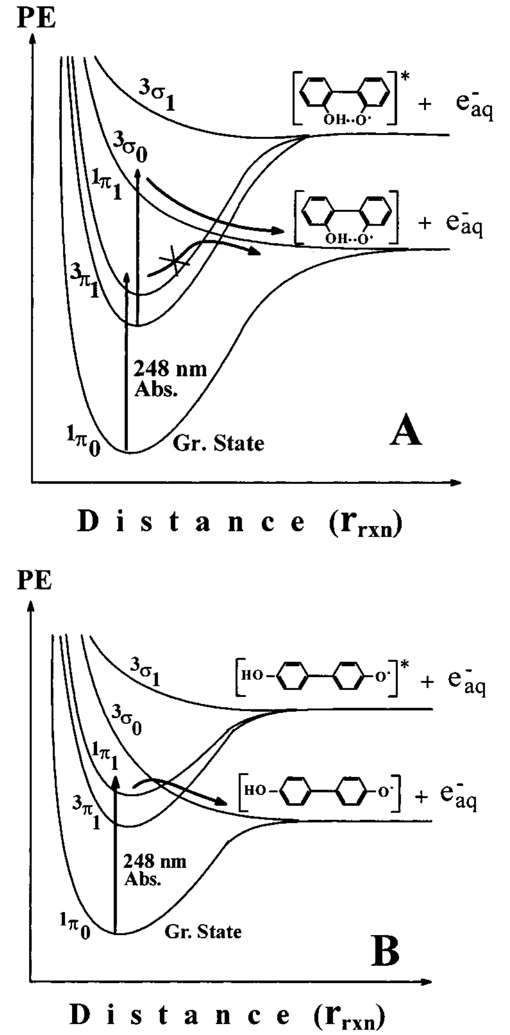


Figure 7. Potential energy diagrams of (A) 2,2′-biphenyldiol and (B) 4,4′-biphenyldiol, qualitatively showing the differences in their photoionization behavior. For 2,2′-biphenyldiol, phtoionization is a biphotonic process involving the T_1 state of the molecule ($^3\pi_1$) as the intermediate. For 4,4′-biphenyldiol, photoionization occurs by a monophotonic mechanism directly from the S_1 state ($^1\pi_1$).

forbidden. However, as the PI of the phenolate ions following UV excitation is quite common,[1−15,34] there seems to be a reasonable mixing between the π and σ states at the crossing point, probably due to an appreciable change in the molecular geometry, which causes a switch from the $^1\pi_1$ state to the $^3\sigma_0$ state to be possible.

4. Conclusions

Nanosecond laser flash photolysis of 2,2′- and 4,4′-biphenyldiol has been investigated in aqueous solutions at different pH conditions. For 2,2′-biphenyldiol, the triplet state is the main transient produced in solutions where the diol exists in its neutral form in the ground state (e.g., pH ≈ 1−6; $pK_a^G(1) = 7.5$) following 248 nm laser excitation. For 4,4′-biphenyldiol, besides the triplet state, phenoxyl radicals are also formed following the laser excitation under similar pH conditions ($pK_a^G(1) = 9.4$). The $pK_a^T(1)$ values for the triplet states of the 2,2′- and 4,4′-biphenyldiol have been estimated to be 7.8 and 9.8, respectively. It is indicated from the $pK_a^T(1)$ values that both diols have similar acidities in their ground and T_1 states. The triplet quantum yields (Φ_T) for the two diols have been estimated and are found to be substantially lower for 2,2′-biphenyldiol than for its 4,4′-analogue. The Φ_T values of the two biphenyldiols are seen to correlate well with the fluorescence quantum yields and lifetimes of the two diols. The difference in the Φ_T values of the two diols is explained in terms of the presence and absence of intramolecular hydrogen bonding in 2,2′- and 4,4′-biphenyldiol, respectively. It is seen that in alkaline aqueous solutions both diols undergo efficient photoionization (PI). The PI yield appears to be relatively higher for 4,4′-biphenyldiol than for its 2,2′-analogue. It is seen that, whereas the PI process for 4,4′-biphenyldiol following 248 nm laser excitation is monophotonic, that for the 2,2′-analogue is a biphotonic process. The differences in the PI mechanism have been discussed in terms of the stabilization of the ground and the excited states of the diols due to the presence and absence of the intramolecular hydrogen bonding in the two molecules.

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