Generation, Characterization, and Deprotonation of Phenol Radical Cations[1]

T. A. Gadosy,*,[2a,b] D. Shukla,[2a] and L. J. Johnston*,[2a]

Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa ON K1A 0R6, Canada, and Department of Chemistry and Biochemistry, Concordia University, 1455 DeMaisonneuve Boulevard West, Montreal QC H3G 1M8, Canada

Received: June 29, 1999; In Final Form: September 8, 1999

A variety of methoxy- and methyl-substituted phenol radical cations have been generated and characterized by laser flash photolysis in solution under ambient conditions. The radical cations were generated by either photosensitized electron transfer using 1,4-dicyanonaphthalene with biphenyl as a cosensitizer in acetonitrile or by direct excitation of the phenol at 266 nm. The phenol radical cations have absorption maxima between 410 and 460 nm, with the exception of the 3,5-dimethoxyphenol which absorbs at 580 nm. The assignment of the observed transients to phenol radical cations is based on their spectral similarity to matrix spectra for the same species and to the corresponding methoxybenzene radical cations, as well as their characteristic reactivity. In the presence of small amounts of water the radical cations are not detected and the phenoxyl radical is the only observed transient in the photosensitized electron transfer. For those phenols for which authentic phenoxyl spectra are not available, the identity of the radical was confirmed by its generation by hydrogen abstraction by the *tert*-butoxyl radical. Although several of the phenols can be photoionized in either 1:1 aqueous ethanol or in acetonitrile, this is a less general route for the formation and characterization of the phenol radical cations. The rate constants for deprotonation of the phenol radical cations by water were measured and fall within the range (0.6−6) × 10^8 M^{-1} s^{-1}; the 2-methoxyphenol radical cation is more reactive than the 4-methoxy, consistent with a recent estimate of the pK_a for these species.

Introduction

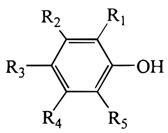
Lignin is a complex biopolymer that accounts for 20−30% of the dry weight of wood. It is formed by a free radical polymerization of substituted phenylpropane units to give an amorphous polymer with a number of different functional groups, including aryl ether linkages, free phenols, and benzyl alcohols. Most pulp processing methods involve oxidative degradation of lignin since its presence is a limitation to the use of wood pulps for high end uses such as print and magazine grade papers. This limitation is due to the photoinduced yellowing of lignin-rich, high-yield mechanical pulps and as a result the photooxidative yellowing has been extensively studied in hopes of understanding its mechanism and ultimately preventing its occurrence.[3,4] It is well established that phenoxyl radicals are produced during the photooxidation of lignin and that their subsequent oxidation ultimately leads to quinones that are responsible for the yellow color. A number of routes to the formation of phenoxyl radicals have been identified, including β-cleavage reactions of α-aryloxyacetophenones, hydrogen abstraction reactions of phenols, and cleavage of ketyl radicals derived from the photoreduction of aromatic ketones.[3,5] In the course of developing suitable methods for the generation of phenoxyl radicals for kinetic studies on paper, we have examined the photoinduced electron transfer and photoionization chemistry of 4-methoxyphenol in solution.[6] These results demonstrate that phenoxyl radicals are generated by both direct excitation and photoinduced electron transfer, with both routes involving formation of an initial phenol radical cation that subsequently deprotonates to yield the phenoxyl radical.

Literature reports indicate that photolysis of phenols leads to a variety of transients, including triplet phenol, phenol radical cation, phenoxyl radical, and solvated electrons.[7−13] For example, it has been suggested that in alcohols and *n*-butyl chloride excitation of phenols results in ionization via a biphotonic process to yield the phenol radical cation.[6,13] The radical cation is then deprotonated, a process with a very low barrier,[14−16] yielding the phenoxyl radical. It is also possible that there is a contribution from direct O−H bond homolysis in nonpolar solvents.[7,8,11−13] Phenol radical cations are potential intermediates in a number of photooxidative processes and have been observed directly in matrixes at low temperature,[21] in strong acid solution,[15] and in gas-phase clusters.[18] Evidence for their existence has also been provided by CIDNP[19] but in many cases only the phenoxyl radical has been observed, presumably due to rapid deprotonation of the initial radical cation.[20] The relatively stable 4-aminophenol radical cation has been detected spectroscopically in acidic aqueous solution,[17] and the 4-methoxyphenol radical cation has also been characterized as a complex with chloride or bromide counterions.[22] More recently, results from our laboratory[6] and from Brede and co-workers[13] have demonstrated that both pulse radiolysis and photoionization can be used to generate and characterize several phenol radical cations in solvents such as acetonitrile and *n*-butyl chloride at room temperature.

The above results suggest that it should be possible to characterize a variety of phenol radical cations and to study their reactivity. This has prompted us to generate and characterize the radical cations of a series of methyl and methoxy-substituted phenols (Scheme 1) and to examine their deprotonation kinetics. Both photoionization and photoinduced electron transfer have been used to produce the radical cations. The results demonstrate that although these radical cations deprotonate rapidly they are sufficiently stable for characterization in dry solvents at room temperature. This work also indicates

10.1021/jp992216x CCC: $18.00

SCHEME 1



	R1	R2	R3	R4	R5
1a	OMe	H	H	H	H
1b	H	OMe	H	H	H
1c	H	H	OMe	H	H
1d	OMe	H	H	H	OMe
1e	H	OMe	OMe	H	H
1f	H	OMe	H	OMe	H
1g	OMe	H	Me	H	H
1h	Me	H	Me	H	Me
1i	H	OMe	OMe	OMe	H

that electron transfer chemistry is an efficient method of generating phenoxyl radicals, particularly in hydroxylic solvents where the use of hydrogen abstraction is not always straightforward. In addition to the potential utility of this method for generating phenoxyl radicals for kinetic or mechanistic studies, the results are of potential significance with respect to the intermediacy of phenol radical cations in photoinduced oxidation processes and in enzymatic degradation of lignin.[23]

Experimental Section

Materials. Phenols were commercially available and were purified by sublimation, recrystallization, or distillation before use. 1,4-Dicyanonaphthalene was synthesized by a literature method and purified by chromatography followed by recrystallization from toluene.[24] Di-*tert*-butyl peroxide was purified by passage through an alumina column before use. Acetonitrile was dried by refluxing over calcium hydride followed by distillation. Lutidines, collidine, and biphenyl were purchased from Aldrich and used without further purification.

Laser Flash Photolysis. The flash photolysis setup has been described in detail.[25] For these experiments either a Lumonics HY750 Nd:YAG laser (266 or 355 nm; <50 mJ/pulse; 10 ns pulses), a Lumonics EX530 excimer laser (XeCl, 308 nm; <40 mJ/pulse; 8 ns pulses), or a Laser Photonics UV-24 nitrogen laser (337 nm; <10 mJ/pulse; 10 ns pulses) was used for sample excitation. Solutions were contained in 7 × 7 mm^2 quartz cells; flow samples were used for all spectra and individual static cells were used for quenching plots. Samples were purged with either oxygen or nitrogen prior to laser irradiation.

Results and Discussion

Generation of Phenol Radical Cations by Photosensitized Electron Transfer. Photosensitized electron transfer using 1,4-dicyanonaphthalene as sensitizer with biphenyl as a codonor has recently been shown to be an efficient means of generating the 4-methoxyphenol radical cation in polar nonaqueous solvents such as acetonitrile.[6] Herein we report the use of the same method for the generation of a variety of substituted phenol radical cations. Excitation (355 nm) of ~5 mM 1,4-dicyanonaphthalene in the presence of 0.3 M biphenyl in acetonitrile leads to rapid electron-transfer quenching of the excited singlet to give the biphenyl radical cation (eq 1) with λ_{max} at 670 and 380 nm. The sensitizer radical anion can be removed by purging

$$1,4\text{-DCN} \xrightarrow[\text{Bp}]{h\nu} 1,4\text{-DCN}^{\bullet-} + \text{BP}^{\bullet+} \xrightarrow{\text{ArOH}} \text{ArOH}^{\bullet+} \qquad (1)$$

the samples with oxygen. The biphenyl radical cation is relatively long-lived in the absence of phenol and can be quantitatively removed with a relatively low concentration of phenol (1−2 mM) that does not compete significantly with biphenyl for quenching of the initial excited singlet dicyanonaphthalene. For example, with 2 mM phenol, approximately 1% of the excited singlet sensitizer will react with phenol, based on the measured rate constant for fluorescence quenching of 1,4-dicyanonaphthalene by biphenyl and assuming a rate constant of 2 × 10^{10} M^{-1} s^{-1} for quenching by phenol.[26]

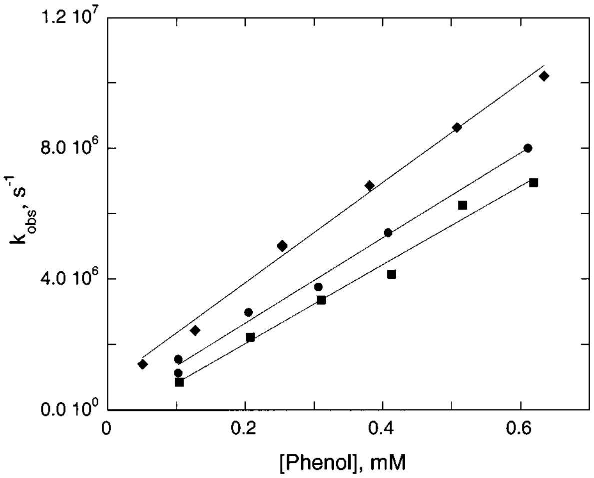


Figure 1. Plots of the observed rate constant for decay of the biphenyl radical cation as a function of phenol concentration in oxygen purged acetonitrile: 2,6-dimethoxyphenol (●); 3,5-dimethoxyphenol (■); 2-methoxy-4-methylphenol (◆). The biphenyl radical cation was generated by the 355 nm excitation of 1,4-dicyanonaphthalene.

The biphenyl radical cation reacts with a variety of phenols with rate constants in the range (1−2) × 10^{10} M^{-1} s^{-1}. Examples of plots of the observed rate constants for decay of the biphenyl radical cation as a function of phenol concentration are shown in Figure 1. The slopes of these plots gave rate constants of 1.2 × 10^{10}, 1.2 × 10^{10}, and 1.5 × 10^{10} M^{-1} s^{-1} for phenols **1d**, **1f**, and **1g**, respectively. Note that the essentially diffusion-controlled rate constants are in good agreement with the fact that the oxidation potentials for all of the phenols examined herein should be substantially lower than that of biphenyl (E_{ox} 1.96 V vs SCE in acetonitrile).[27] For example, phenol and a number of its methyl- and methoxy-substituted derivatives have oxidation potentials below 2.1 V (vs Ag/AgI; ~1.5 V after correction to SCE) in acetonitrile.[16]

Transient spectra recorded after complete quenching of the biphenyl radical cation with phenols **1b**, **1e**, and **1g** in acetonitrile are shown in Figure 2. In each case the spectra show an initial transient with a maximum between 400 and 500 nm; this species decays relatively rapidly (typically within ~1−2 μs), leaving a residual absorption that is shifted to shorter wavelength by 10−40 nm. For example, spectra measured at several different delays after excitation for **1b** show an initial transient with λ_{max} at 475 nm (Figure 2A) that decays to a longer lived species with maxima at 440 and 420 nm. The spectrum measured after 2.4 μs clearly shows a mixture of the two. In some cases the residual absorption that remains after the decay of the species at longer wavelength is relatively weak and only slightly shifted to shorter wavelength. However, the shorter wavelength species can be more easily characterized by addition of a small amount of water to the sample, as illustrated by the spectra shown in Figure 2B,C for **1e**. In dry acetonitrile the initial absorption maximum is at 450 nm, but the peak shifts to 440 nm as the signal decays. In the presence of 2% water a sharp 440 nm absorption is observed, in addition to a broad weak signal between 560 and 700 nm. Similar results are obtained for **1g** in the presence and absence of water (Figure 2D). The broad initial absorption in dry acetonitrile has λ_{max} at 420 nm and decays to give a weak signal at 400 nm. The latter is much more clearly visible when the same experiment is repeated in acetonitrile containing 2.5% water; in this case the

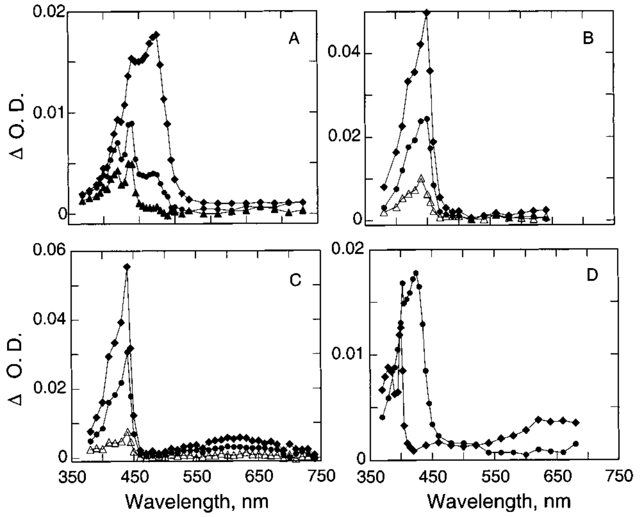


Figure 2. Transient absorption spectra obtained by 355 nm excitation of 1,4-dicyanonaphthalene in oxygen-saturated acetonitrile containing 0.25 M biphenyl plus phenols: (A) 3 mM 3-methoxyphenol, 0.1 (◆), 2.4 (●), and 6.6 μs (▲) after laser excitation; (B) 1 mM 3,4-dimethoxyphenol, 0.1 (◆), 1 (●), 5 (△) μs; (C) 1 mM 3,4-dimethoxyphenol plus 2% water, 0.1 (◆), 1 (●), 30 (△) μs; (D) 2.8 mM 2-methoxy-4-methylphenol, 0.1 μs after excitation in dry (●) and wet (2.5% water, ◆) acetonitrile.

transient has $\lambda_{\max}$ at 400 nm with a shoulder at 380 nm and a broad absorption beyond 600 nm.

For each of the three phenols discussed above the initial transient at longer wavelength decays relatively rapidly, disappears completely upon addition of small amounts of water and is insensitive to oxygen. These species are assigned to phenol radical cations based on their observed reactivity and the similarity of the spectra to that for the 4-methoxyphenol radical cation, which has $\lambda_{\max}$ at 440 nm.[6] The spectra are also similar to those reported for several di- and trimethoxybenzene radical cations generated by pulse radiolysis in aqueous solution, as would be expected.[28,29] In each case an additional longer-lived species remains after the decay of the transient assigned to the radical cation in the dry experiments. The same species is observed as the only transient in the presence of water. This transient can be assigned to the phenoxyl radical formed by deprotonation of the initial radical cation (eq 2). Spectra of many

$$\mathrm{ArOH}^{\bullet+} \xrightarrow{\text{base}} \mathrm{ArO}^{\bullet} + \mathrm{baseH}^{+} \tag{2}$$

phenoxyl radicals are available in the literature;[7,8,30−32] for example, the spectrum at later time shown in Figure 2A for 3-methoxyphenol is in good agreement with our earlier published spectrum for this phenoxyl radical.[33] For radicals for which literature spectra have not been reported, we have confirmed the identity of the phenoxyl radical by its generation by hydrogen abstraction from the substituted phenol using *tert*-butoxyl radical produced by photolysis of di-*tert*-butyl peroxide (eq 3).

$${}^{t}\mathrm{BuOO}{}^{t}\mathrm{Bu} \xrightarrow{h\nu} 2\,{}^{t}\mathrm{BuO}^{\bullet} \xrightarrow{\mathrm{ArOH}} \mathrm{ArO}^{\bullet} + {}^{t}\mathrm{BuOH} \tag{3}$$

These experiments were carried out using 308 or 337 nm excitation of samples containing 10% or 50% di-*tert*-butyl peroxide in acetonitrile. The use of 337 nm excitation and a high peroxide concentration were necessary in some cases to avoid direct excitation of the phenol. Spectra of several phenoxyl radicals generated by this route are shown for comparison in Figure 3. Both the 3,4-dimethoxyphenoxyl and the 2-methoxy-4-methylphenoxyl radicals have a characteristic band at approximately 400 nm, as observed for many other phenoxyl radicals. Both of these radicals also have an additional weak band at a longer wavelength, similar to those observed earlier for several 2-substituted phenoxyls[33] and in good agreement with the spectra obtained by photoinduced electron transfer in aqueous acetonitrile (Figure 2).

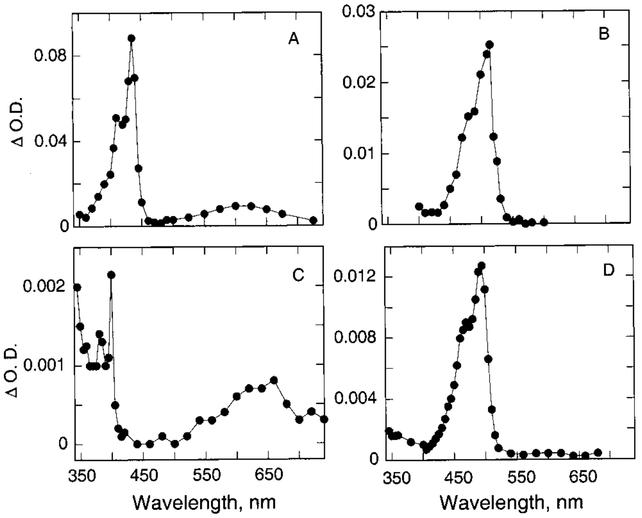


Figure 3. Transient absorption spectra of phenoxyl radicals generated by 308 or 337 nm laser excitation of di-*tert*-butyl peroxide in acetonitrile plus phenol: (A) 3,4-dimethoxyphenol; (B) 3,5-dimethoxyphenol; (C) 2-methoxy-4-methylphenol; (D) 3,4,5-trimethoxyphenol.

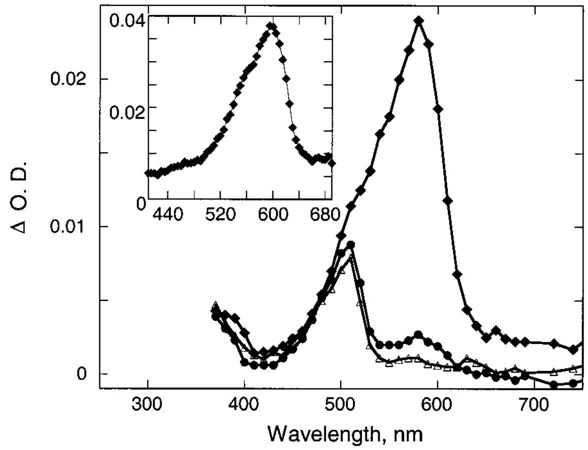


Figure 4. Transient absorption spectra measured 0.1 (◆), 2.4 (●), and 6.2 μs (△) after laser excitation of 1,4-dicyanonaphthalene in oxygen-saturated acetonitrile containing 0.25 M biphenyl and 1.1 mM 3,5-dimethoxyphenol. The inset shows a spectrum of the 1,3,5-trimethoxybenzene radical cation generated using the same sensitizer system in acetonitrile.

The spectra obtained with 3,5-dimethoxyphenol (**1f**) are somewhat anomalous in that the initial transient has $\lambda_{\max}$ at 580 nm and decays to give a signal at 510 nm (Figure 4). To confirm that the 580 nm transient is the phenol radical cation, the 1,3,5-trimethoxybenzene radical cation was generated using the 1,4-dicyanonaphthalene/biphenyl sensitizer system and has a spectrum ($\lambda_{\max}$ 595 nm, inset, Figure 4) that is almost identical to that generated from **1f**. This is in good agreement with the spectrum for the 1,3,5-trimethoxybenzene radical cation in a low-temperature matrix (613 and 645 nm in *sec*-butyl chloride)[34] and in aqueous solution (540, 580 nm).[28] The 3,5-dimethoxyphenoxyl radical was also generated independently from 2-(3,5-dimethoxyphenoxy)acetophenone; 308 nm excitation of this ketone in oxygen-saturated acetonitrile generated a transient with

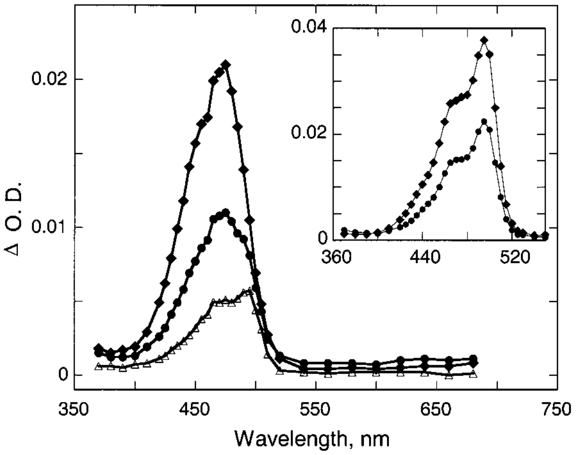


Figure 5. Transient absorption spectra measured 0.1 (◆), 2.2 (●), and 13 μs (△) after laser excitation of 1,4-dicyanonaphthalene in oxygen-saturated acetonitrile containing 0.25 M biphenyl and 2.3 mM 3,4,5-trimethoxyphenol. The inset shows spectra recorded 0.1 (◆) and 5 μs (●) after excitation of the same sample in acetonitrile plus 2.5% water.

TABLE 1: Absorption Maxima for Phenol Radical Cations and Phenoxyl Radicals in Acetonitrile

phenol	radical λ_{max}, nm	radical cation λ_{max}, nm
1a	395	410
1b	440	470
1c[a]	410	440
1d	370	430
1e	440	450
1f	510	580
1g	400	420
1h	390	380
1i	495	465

[a] Data from ref 6.

λ_{max} at 505 nm and a shoulder at 480 nm, similar to that obtained from phenol **1f** and *tert*-butoxyl radical in acetonitrile (Figure 3B). The better separation of the radical cation and radical peaks for this phenol allow one to clearly distinguish both the decay of the radical cation and the concomitant growth of the radical.

Spectra obtained using the same sensitizer for 3,4,5-trimethoxyphenol (**1i**) are shown in Figure 5. In this case the initial radical cation has λ_{max} at 465 nm and spectra measured at longer delays show a slight shift to longer wavelengths. Spectra in the presence of 2.5% water show a single transient with λ_{max} at 495 nm and a shoulder at ~460 nm that is identical to that obtained by generation of the phenoxyl radical by hydrogen abstraction (Figure 3D).

A comparison of spectra measured in dry and wet (1−3% water) acetonitrile for the various phenols indicates that the yield of phenoxyl radical is significantly higher in the presence of water. This suggests that deprotonation of the radical cation to give phenoxyl radical is not the only mechanism for decay of the radical cation in dry acetonitrile. It is likely that reaction with superoxide radical anion formed by trapping of the sensitizer radical anion with oxygen and reaction with traces of remaining water both contribute to the observed radical cation decay.

Experiments similar to those described above were carried out for the other phenols shown in Scheme 1 and the spectral data for the phenol radical cations and phenoxyl radicals are summarized in Table 1. The methoxy-substituted radical cations all have absorption maxima between 410 and 470 nm, with the exception of the 3,5-dimethoxyphenol radical cation, which is shifted to much longer wavelength. For the cases where literature data are available, the spectra agree closely with those for the equivalent methoxy-substituted benzene radical cation. The 2,4,6-trimethylphenol radical cation absorbs at somewhat shorter wavelengths; the weak and relatively short-lived absorptions of the alkyl-substituted radical cations make them somewhat more difficult to characterize.

Most of the phenoxyl radicals studied have a characteristic absorption in the 400 nm region. Exceptions are phenols **1f** and **1i** for which the phenoxyl radical spectra are significantly red-shifted with maxima at approximately 500 nm. Although this is unusual for methyl- and methoxy-substituted phenoxyls, it is worth noting that similar absorptions have been reported for the 4-iodophenoxyl (λ_{max} at 500 nm)[31] and for several di-*tert*-butyl phenoxyls.[7] Several of the radicals also show a weak long wavelength band (>600 nm), as reported for a number of 2-substituted phenoxyls. For example, the 3,4-dimethoxyphenoxyl has a weak band between 550 and 650 nm that is not detected in either the 3-methoxy or 4-methoxy radicals. The 2-methoxy-4-methylphenoxyl also has a long wavelength band, as might be anticipated from spectra for other *o*-methoxy substituted analogues.[33] In most cases the λ_{max} of the radical cation is at a shorter wavelength than that of the radical, with phenols **1h** and **1i** being the only exceptions to this trend. However, as noted above the phenoxyl radical from **1i** is significantly shifted with respect to other methoxy-substituted analogues, whereas the radical cation spectrum is in line with what has been observed in related phenol and methoxybenzene radical cations.[28,29] It is not clear whether the 500 nm band observed for the phenoxyl radical from **1f** and **1i** is the lowest energy transition; our results do not show any absorption at longer wavelength, but it is possible that the transition is either shifted to lower energy or is too weak to be detected.

The above results demonstrate that photosensitized electron transfer provides a useful approach for the generation of phenoxyl radicals, particularly in the presence of small amounts of water. We reasoned that in aqueous media the use of biphenyl as a cosensitizer would be unnecessary since rapid deprotonation of the radical cations would compete with back electron transfer, which usually limits the efficiency for free radical ion formation from singlet sensitizers such as 1,4-dicyanonaphthalene. In fact, the phenoxyl radical could be readily generated by excitation of the sensitizer alone (i.e., no biphenyl) in the presence of 0.22 M **1f** in acetonitrile containing 2.5% water; the yields are comparable to those obtained in the presence of biphenyl. The method is also suitable for the generation of phenoxyl radical in alcohol solvent. The use of hydrogen abstraction in alcohols is not always straightforward since the abstracting radical can react with both solvent and phenol.

Direct Excitation of Phenols. Direct excitation of phenols **1a**−**1h** in either aqueous ethanol or acetonitrile was also examined. Previous results have shown that phenol **1c** and several sterically hindered di-*tert*-butylphenols undergo biphotonic ionization to yield detectable phenol radical cations in solvents such as dry acetonitrile.[6,13] Results obtained by 266 nm excitation of 3-methoxyphenol are shown in Figure 6A. The spectrum obtained in nitrogen-saturated aqueous ethanol shows a moderately strong absorption at long wavelength, consistent with photoionization to give solvated electrons. Spectra recorded after the decay of the solvated electron or for oxygen saturated samples (Figure 6A) have λ_{max} at 440 nm with a shoulder at ~420 nm, in good agreement with the known spectrum for the 3-methoxyphenoxyl radical. Although there is no evidence for the initial phenol radical cation in aqueous ethanol, it is readily detected upon 266 nm excitation of **1b** in dry acetonitrile, as

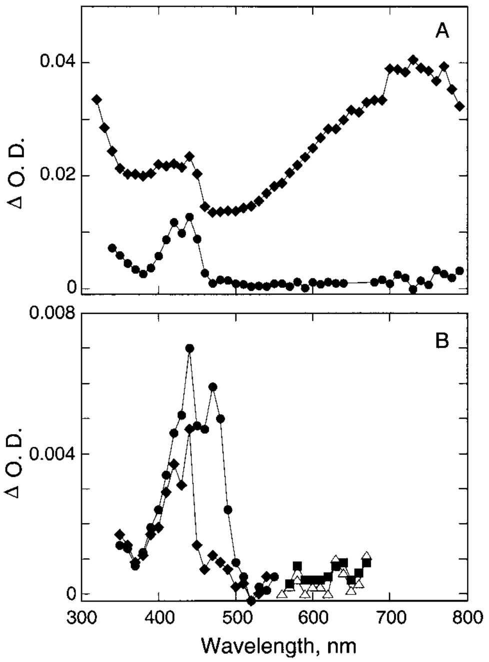


Figure 6. Transient absorption spectra measured after 266 nm laser excitation of 3-methoxyphenol: (A) 0.1 μs after excitation in nitrogen (◆) and oxygen (●) saturated 1:1 aqueous ethanol; (B) 0.1 (●) and 3 μs (◆) after excitation in acetonitrile.

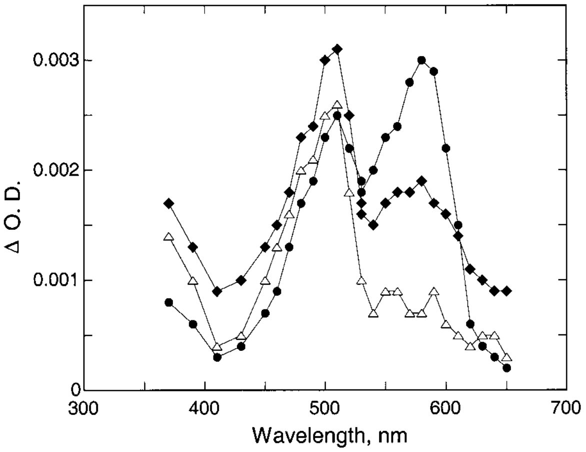


Figure 7. Transient absorption spectra measured 0.1 (●), 2.5 (◆), and 6.2 μs (△) after 266 nm laser excitation of 3,5-dimethoxyphenol in oxygen-saturated acetonitrile.

shown in Figure 6B. In this case the radical cation absorption at 470 nm disappears considerably more rapidly than that of the phenoxyl radical. It is possible that some of the phenoxyl radical is formed by direct photohomolysis rather than by photoionization/deprotonation since a significant amount of radical is visible immediately after the laser pulse.

Similar results were obtained by direct excitation of several other phenols. For example, spectra recorded for **1f** in oxygen-saturated acetonitrile show a mixture of radical cation and radical 100 ns after the laser pulse (Figure 7). At longer delay (2.5 μs) the radical cation has decayed substantially, generating additional radical at 510 nm. For this phenol, very similar results were obtained for either nitrogen- or oxygen-saturated samples. Qualitatively similar results were obtained for **1g** in that both radical cation and radical were observed in oxygen-saturated acetonitrile. However, in this case there was an additional broad absorption in the 350−420 nm region in the presence of nitrogen that was removed by the addition of 2,3-dimethylbuta-1,3-diene.

TABLE 2: Rate Constants for Deprotonation of Phenol Radical Cations by Water and Other Bases in Acetonitrile at Room Temperature

phenol	base	k_q, 10^8 M^{-1} s^{-1}
1a	H_2O	6.2
1b	H_2O	2.9
1c	H_2O	0.6
1f	H_2O	2.5
1g	H_2O	2.0
1f	CH_3OH	0.82
1f	2,6-lutidine	6.5
1f	3,5-lutidine	26.
1f	2,4,6-collidine	6.2

This is consistent with some triplet formation upon direct excitation, as has been observed previously for a number of other phenols.[6,9,11,12] Direct excitation of several of the other phenols (**1a**, **1d**, **1e**) provided some evidence for a small amount of photoionization and triplet formation but with considerably lower efficiency.

Deprotonation of Phenol Radical Cations. The results presented above clearly demonstrate that the phenol radical cations deprotonate rapidly in the presence of water. The second-order rate constants for the quenching of the radical cations by water are summarized in Table 2. For these experiments the radical cations were generated by photosensitized electron transfer in dry acetonitrile. It was only possible to obtain reliable kinetics from phenols for which there was a significant separation between the radical and radical cation spectra. The measured rate constants cover a range of approximately 1 order of magnitude ($(0.6-6) \times 10^8$ M^{-1} s^{-1}), with the 4-methoxyphenol being the least reactive and 2-methoxyphenol the most reactive. The other three phenol radical cations react with water with a rate constant of approximately 2×10^8 M^{-1} s^{-1}. These results are consistent with recent estimates of the acidity for a variety of phenol radical cations.[16] In this work the measured oxidation potentials for a series of phenols were used in a thermodynamic cycle to calculate pK_a values for the radical cations. Values of -6.4 and -4.7 were estimated for the 2-methoxy- and 4-methoxyphenol radical cations, consistent with the deprotonation rate constants for these species reported in Table 2.

Because of the separation between the absorption bands of the radical and radical cation of **1f**, the reactivity of this radical cation with other bases was also examined (Table 2). The data show the expected trends, with methanol being less reactive than water and the nitrogen-centered bases more reactive. The bimolecular rate constants for both 2,6-lutidine and 2,4,6-collidine are about 3 times faster than water. However, the rate constant for the less sterically hindered 3,5-lutidine is 1 order of magnitude faster than that for water. All of these results are consistent with the deprotonation of the radical cation by an external base to give the phenoxyl radical.

Conclusions

The results described above demonstrate that a variety of methyl- and methoxy-substituted phenol radical cations can be generated by either photoinduced electron transfer or photoionization in dry solvents such as acetonitrile. The radical cations are sufficiently long-lived for characterization under these conditions but are rapidly deprotonated in the presence of water and other bases. These and literature results indicate that the direct detection of phenol radical cations in solution at room temperature is straightforward for phenols with bulky ortho substitutents or electron-donating groups such as alkoxy or amino.[6,13,17] In aqueous solution the radical cations deprotonate rapidly to give phenoxyl radicals. The rate constants for deprotonation of phenol radical cations show the expected trends based on recent estimates of their acidity. The use of photoinduced electron transfer for the generation of phenoxyl radicals may be advantageous in cases where hydrogen abstraction is either slow or is limited by the concentrations of phenol that can be used or by competing hydrogen abstraction from the solvent. By contrast, photoionization is not expected to be a general route for generation of phenoxyl radicals. The present study also raises the interesting possibility that photoinduced electron-transfer reactions between aryl ketones and phenols may provide an alternate route for the formation of phenoxyl radicals during the photooxidation of lignin. Electron-transfer reactions may be more facile than direct hydrogen abstraction and the subsequent deprotonation of the phenol radical cation will be rapid, given the water content of wood and paper products.

Acknowledgment. Support from the Wood Pulps Network of Centres of Excellence is gratefully acknowledged.

Supporting Information Available: Two additional figures with representative decay traces for the radical cations derived from 3,5-dimethoxy and 3,4,5-trimethoxy-phenols. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Issued as NRCC 42191.

(2) (a) NRCC. (b) Concordia.

(3) *Photochemistry of Lignocellulosic Materials*; Heitner, C., Scaiano, J. C., Eds.; ACS Symposium Series, Vol 531; American Chemical Society, Washington, DC, 1993.

(4) Leary, G. J. *J. Pulp Paper Sci.* **1994**, *20*, J154.

(5) Schmidt, J. A.; Heitner, C. *J. Wood Chem. Technol*. **1993**, *13*, 309. Scaiano, J. C.; Whittlesey, J. K.; Berinstain, A. B.; Malenfant, P. R. L.; Bensimon, C. *Chem. Mater.* **1993**, *5*, 700. Huang, Y.; Page, D.; Wayner, D. D. M.; Mulder, P. *Can. J. Chem.* **1995**, *73*, 2079. Barclay, L. R. C.; Cromwell, G. R.; Hilborn, J. W. *Can. J. Chem.* **1994**, *72*, 35. Wan, J. K. S.; Depew, M. C. *Res. Chem. Intermed.* **1996**, *22*, 241. Argyropoulos, D. S.; Sun, Y. *Photochem. Photobiol*. **1996**, *64*, 510.

(6) Shukla, D.; Schepp, N. P.; Mathivanan, N.; Johnston, L. J. *Can. J. Chem.* **1997**, *75*, 1820.

(7) Land, E. J.; Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1961**, 1885. Land, E. J.; Porter, G. *Trans. Faraday Soc*. **1963**, 2016.

(8) Dobson, G.; Grossweiner, L. I. *Trans. Faraday Soc.* **1965**, *61*, 708.

(9) Yamada, H.; Nakashima, N.; Tsubomura, H. *J. Phys. Chem.* **1970**, *74*, 2897.

(10) Feitelson, J.; Hayon, E.; Treinin, A. *J. Am. Chem. Soc*. **1973**, *95*, 1025.

(11) Feitelson, J.; Hayon, E. *J. Phys. Chem.* **1975**, *77*, 10.

(12) Bent, D. V.; Hayon, E. *J. Am. Chem. Soc*. **1975**, *97*, 2599.

(13) Brede, O.; Orthner, H.; Zubarev, V.; Hermann, R. *J. Phys. Chem.* **1996**, *100*, 7097. Brede, O.; Hermann, R.; Orthner, H. *Radiat. Phys. Chem.* **1996**, *47*, 415.

(14) Yi, M.; Scheiner, S. *Chem. Phys. Lett.* **1996**, *262*, 567.

(15) Dixon, W. T.; Murphy, D. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1221.

(16) Bordwell, F. G.; Cheng, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1736.

(17) Kesper, K.; Diehl, F.; Simon, J. G. G.; Specht, H.; Schweig, A. *Chem. Phys.* **1991**, *153*, 511.

(18) Steadman, J.; Syage, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6786.

(19) Maruyama, K.; Furuta, H.; Osuka, A. *Tetrahedron* **1986**, *22*, 6149.

(20) Gradkowski, J.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 1205. Burrows, H. D.; Greatorex, D.; Kemp, T. J. *J. Phys. Chem.* **1972**, *76*, 20.

(21) Sun, Q.; Tripathi, G. N. R.; Schuler, R. H. *J. Phys. Chem.* **1990**, *94*, 6273.

(22) Shoute, L. C.; Neta, P. *J. Phys. Chem*. **1990**, *94*, 2447.

(23) Bietti, M.; Baciocchi, E.; Steenken, S. *J. Phys. Chem*. **1998**, *102*, 7337.

(24) Bayer, R. W.; O'Reilley, E. J. *J. Org. Chem*. **1958**, *23*, 311. Newman, M. S. *Organic Syntheses*; Wiley: New York, 1995; Collect. Vol. 3, p 631.

(25) Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem*. **1991**, *95*, 4430.

(26) Brancaleon, L.; Brousmiche, D.; Johnston, L. J. *Can. J. Chem*. **1999**, *71*, 787.

(27) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc*. **1990**, *112*, 4290.

(28) O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem*. **1975**, *79*, 2773.

(29) Jonsson, M.; Lind, J.; Reitberger, T.; Eriksen, T. E. *J. Phys. Chem*. **1993**, *97*, 11278.

(30) Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4162. Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154.

(31) Lind, J.; Shen, X.; Eriksen, T. E.; Merenyi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479.

(32) Steenken, S.; Neta, P. *J. Phys. Chem*. **1982**, *86*, 3661.

(33) Johnston, L. J.; Mathivanan; N.; Negri, F.; Siebrand, W. *Can. J. Chem*. **1993**, *71*, 1655.

(34) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1998.