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Reduction Potentials of Naphthoxyl and Pyridoxyl Radicals in Aqueous Solutions

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Reduction potentials of 1- and 2-naphthoxyl, 2-, 3-, and 4-pyridoxyl, and 4-phenylphenoxyl radicals in alkaline aqueous solutions are determined by pulse radiolysis. The potential of 1-naphthoxyl is determined to be 0.59 V versus NHE from the redox equilibrium involving 1-naphthol, 3-methylphenol, and their radicals. The reduction potential of the 3-methylphenoxyl radical (0.73 V) is obtained from its equilibrium with the phenoxyl radical. The potential for 2-naphthoxyl (0.69 V) is obtained from equilibrium with the phenoxyl radical. The reduction potentials of the three pyridoxyl radicals are measured from equilibria with the 4-cyanophenoxyl radical. The values are found to be 1.18 V for 2-pyridoxyl, 1.06 V for 3-pyridoxyl, and 1.24 V for 4-pyridoxyl. The reduction potential of 4-phenylphenoxyl radical (0.93 V) is obtained from equilibrium with the $I_2^{\bullet-}$ radical. From these reduction potentials and the known pK_a values of the phenolic compounds, we estimate the O−H bond dissociation energies.

Introduction

Reduction potentials of a number of phenoxyl radicals and related species in aqueous solutions have been determined by pulse radiolysis[1,2] because of the interest in phenolic compounds as biological and industrial antioxidants.[3] The antioxidant action[4,5] of these compounds is through their reactions with peroxyl radicals, which break the autoxidation chain reaction. The reactions of phenolic compounds with peroxyl radicals may take place via electron transfer (mainly in aqueous solutions) or via hydrogen abstraction (mainly in nonpolar organic solvents).[6] Therefore, the antioxidant activity is determined to a large extent by the reduction potential or the O−H bond dissociation energy of the phenolic compound, two properties that are related. For a series of substituted phenoxyl radicals, good correlations have been found between the reduction potentials in aqueous[2] or acetonitrile[7] solutions and the σ^+ substituent constants, which permit estimation of the values for other phenols. No measurements, however, have been reported on the reduction potentials of naphthoxyl or pyridoxyl radicals in aqueous solutions. Only measurements in organic solvents have been reported for the two naphthols: cyclic voltammetry in acetonitrile solutions[7] and estimated values in dimethylformamide solutions,[8] derived from excited-state electron-transfer kinetics and the Marcus relationship. Since a number of commercial antioxidants are derived from larger aromatic and heterocyclic systems,[3] and to broaden the scope of available measurements and predictive information, the values for the naphthoxyl and pyridoxyl radicals in aqueous solutions are determined in the present study by using the pulse radiolysis method described previously.[1,2] From the measured reduction potentials of the radicals and the known pK_a values of the phenolic compounds, we estimate the O−H bond dissociation energies.

Experimental Section

The organic compounds used were obtained from Aldrich[9] in the highest available purity (varying from 95% to >99%). Preliminary pulse radiolysis experiments with the naphthols and hydroxypyridines showed spectral changes that could be attributed to reactions of the principal radical with impurities. Therefore, we purified the compounds as described below, and indeed, the effects of impurities were eliminated. The naphthols and 3-hydroxypyridine were purified to white solids by vacuum sublimation, 2-hydroxypyridine was purified by recrystallizations from ethanol to give white crystals, 4-hydroxypyridine was recrystallized twice from mixtures of ethanol/ethyl acetate to give nearly white crystals, and 4-phenylphenol (sublimed, 99%) was used as received. The inorganic compounds were analytical reagents from Mallinckrodt. Water was purified by a Millipore Super-Q system. To minimize thermal oxidation of these compounds by dissolved O_2 at high pH, all solutions were first saturated with N_2O and then KOH was added to raise the pH to the desired level.

The equilibrium constants were measured by pulse radiolysis. Two independent facilities were used, one based on a Febetron 705 pulser providing single 50-ns pulses of 2-MeV electrons and the other on a Varian linear accelerator providing multiple pulses of ∼5-MeV electrons with pulse duration of 50 ns to 1.5 μs. The detection in both systems is based on optical absorption in the UV and visible range. All measurements were carried out at room temperature (20 ± 2 °C). Other experimental details for this type of equilibrium measurement were as described previously.[1]

Results and Discussion

The reduction potentials of the naphthoxyl and pyridoxyl radicals were determined by measurements of electron-transfer equilibria in alkaline solutions, where the naphthols and pyridols are dissociated into their anions. Since electron transfer from phenoxide anions takes place much more rapidly than that from

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TABLE 1: Reduction Potentials of Naphthoxyl, Pyridoxyl, and 4-Phenylphenoxyl Radicals in Aqueous Solutions

radical ($P^•$)	reference ($R^•$)	E_{ref}[a] (V)	pH	solutes[b]	pK_a	concn (mmol L^{-1})	λ (nm)	K[c]	E[d] (V)	O−H BDE[e] (kJ mol^{-1})
1-NpO$^•$	3-$MeC_6H_4O^•$	0.73	13	3-MeC_6H_4OH	10.0	7−300	400	$(2.0 \pm 0.3) \times 10^2$	0.59	346
				1-NpOH	9.3	0.4−1				
3-$MeC_6H_4O^•$	$C_6H_5O^•$	0.79	13	C_6H_5OH	9.99	66	410	$(1.24 \pm 0.08) \times 10^1$	0.73	364
				3-MeC_6H_4OH	10.0	3.3−10				
2-NpO$^•$	$C_6H_5O^•$	0.79	13.3	C_6H_5OH	9.99	4−50	490	$(4.46 \pm 0.25) \times 10^1$	0.69	358
				2-NpOH	9.6	1.2−1.6				
2-PyrO$^•$	4-$CNC_6H_4O^•$	1.12	13	N_3^-		200	420	$(1.09 \pm 0.06) \times 10^{-1}$	1.18	416
				4-CNC_6H_4OH	7.95	0.14−1.5				
				2-HOPyr	11.6	1.1−10				
3-PyrO$^•$	4-$CNC_6H_4O^•$	1.12	11	N_3^-		200	530	$(1.05 \pm 0.06) \times 10^1$	1.06	388
				4-CNC_6H_4OH	7.95	10−19				
				3-HOPyr	8.7	0.3−2.5				
4-PyrO$^•$	4-$CNC_6H_4O^•$	1.12	13	N_3^-		200	420	$(8.3 \pm 0.5) \times 10^{-3}$	1.24	419
				4-CNC_6H_4OH	7.95	0.1−0.44				
				4-HOPyr	11.1	10−14				
4-PyrO$^•$	$N_3^•$	1.33	12.5	N_3^-		10−50	350	(13.0 ± 2.0)	1.26	421
				4-HOPyr	11.1	1.0				
4-$PhC_6H_4O^•$	$I_2^{•-}$	1.03	10.8[f]	I^-		100	560	$(6.1 \pm 1.6) \times 10^1$	0.93	380
				4-PhC_6H_4OH	9.55	0.2−0.8	390			

[a] Reduction potential of the reference radical, versus NHE, taken from refs 2 and 13, except for the first value, which was determined in this work. [b] All solutions were saturated with N_2O. [c] Equilibrium constant for the reaction $R^• + P^- \rightleftarrows R^- + P•$ given as $K = ([R^-][P^•])/([R^•][P^-])$ with the estimated standard uncertainty. [d] Reduction potential of the $P^•/P^-$ pair, versus NHE, at the pH of the measurement. Overall estimated standard uncertainty ±0.01 V. [e] Bond dissociation energies, estimated as outlined in ref 2. [f] The solution also contained 0.06 mol L^{-1} HPO_4^{2-} as buffer.

the neutral compounds,[1] the equilibrium can be reached more rapidly in alkaline solutions and thus may be achieved before any significant decay of the radicals via other processes. To measure the reduction potentials, we selected a suitable redox pair to serve as reference for each compound. The selection was made after comparing the reaction kinetics of the oxidation of the respective anions with different oxidants. The necessity of using high pH limits the choice of the reference pair. In addition, we sought redox pairs that have relatively high self-exchange rates, so that the equilibrium can be reached before significant decay of the radicals. Since the self-exchange rates for phenoxyl-type radicals are known to be high,[10] this class of redox pairs was the best choice for most of the compounds studied.

The reduction potentials of the naphthoxyl and pyridoxyl radicals ($P^•/P^-$) have been determined by establishing an equilibrium (1) with a suitable reference redox pair ($R^•/R^-$).

$$R^• + P^- \rightleftarrows R^- + P^• \tag{1}$$

In a mixture of P^- and R^-, both of these anions are oxidized, either by the $^•OH$ or $^•O^-$ radicals, produced in the radiolysis of N_2O-saturated aqueous solutions, or by a secondary, more specific one-electron oxidant. We chose the azidyl radical for most of these studies.

$$H_2O \rightsquigarrow e_{aq}^- + H^• + {}^•OH + H_2 + H_2O_2 \tag{2}$$

$$e_{aq}^- + N_2O \rightarrow N_2 + O^- \tag{3}$$

$$O^- + H_2O \rightleftarrows OH^- + {}^•OH \tag{4}$$

$${}^•OH + N_3^- \rightarrow OH^- + N_3^• \tag{5}$$

$$N_3^• + P^- \rightarrow N_3^- + P^• \tag{6}$$

$$N_3^• + R^- \rightarrow N_3^- + R^• \tag{7}$$

After P^- and R^- are partly oxidized in reactions 6 and 7 or in analogous reactions with other oxidants, all four components of the equilibrium reaction 1 are present in the solution. It is first necessary to demonstrate that these species engage in reaction 1 and reach equilibrium before any significant decay of the radicals via other processes. This was demonstrated in all cases by sub-microsecond experiments, which clearly show that the initial distribution of radicals is different from the final one at equilibrium and that second-order decay of the radicals became apparent only at much longer times. In principle, these measurements should provide both the concentrations at equilibrium and the kinetics of approach to equilibrium. In the current experiments, however, the approach to equilibrium was observed but the kinetics could not be derived with sufficient accuracy. This is due to the use of relatively high concentrations of reactants to reach equilibrium before decay, and at these high concentrations, the kinetics were near the limit of the time resolution of our detection system. Therefore, although we observe the absorbance change due to reaction 1, we do not calculate the rates from these traces since they are slightly affected by the instrument time constant.

The equilibrium constant K_1 was obtained from the concentrations of the four components involved in the equilibrium reaction 1. In most cases, both radicals $P^•$ and $R^•$ absorb significantly at the selected wavelengths. Therefore, to estimate their equilibrium concentrations, the contribution of each radical was also measured in the absence of the other. These experiments were carried out at a pH at least 1 unit higher than the pK_a of the less acidic compound. The results for each compound are discussed below. The experimental conditions and results for all the compounds are summarized in Table 1. From the estimated standard uncertainties for the measured equilibrium constants, given in the table, and the uncertainties in the reduction potentials of the reference compounds, we estimate the standard uncertainties in the measured reduction potentials to be about ±0.010 V.

1-Naphthoxyl Radical. The spectrum of this radical was measured in a N_2O-saturated solution containing 1.5×10^{-3} mol L^{-1} 1-naphthol and 0.14 mol L^{-1} N_3^- at pH 12.6. Two peaks were observed at 400 and 530 nm (Figure 1a). Other one-electron oxidants, such as $ClO_2^•$ (0.936 V), phenoxyl (0.79 V), 4-methylphenoxyl (0.68 V), 4-cyanophenoxyl (1.12 V), and

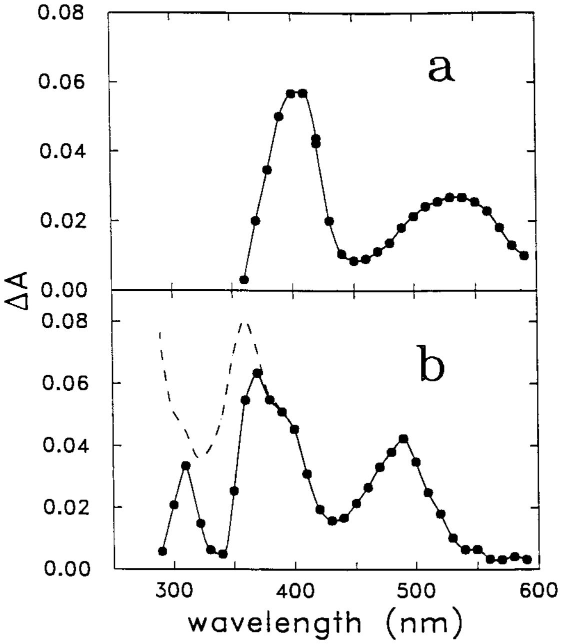

Figure 1. Differential absorption spectra of the naphthoxyl radicals, determined by pulse radiolysis of N_2O-saturated aqueous solutions at pH 12.6. (a) 1-Naphthoxyl, monitored with the solutions containing 0.14 mol L^{-1} N_3^- and 1.5×10^{-3} mol L^{-1} 1-naphthol, 20 μs after the pulse, dose/pulse 15 Gy and (b) 2-naphthoxyl, with the solutions containing 0.1 mol L^{-1} N_3^- and either 1.5×10^{-3} mol L^{-1} 2-naphthol (for $\lambda > 370$ nm) or 2.5×10^{-4} mol L^{-1} 2-naphthol (for $\lambda < 370$ nm), 20 μs after the pulse, dose 8.3 Gy; dashed line, corrected for the bleaching of 2-naphthol.

4-acetylphenoxyl radicals (1.00 V), also oxidized the 1-naphthoxide anion completely. From the reduction potentials for these radicals, given in the parentheses,[2] we conclude that the reduction potential of 1-naphthoxyl is lower than 0.7 V. In continuing our search for a suitable phenoxyl-type redox pair, we observed that the phenoxyl radical derived from 3-methylphenol has the desired characteristics. By using N_2O-saturated solutions at pH 13 with a 3-methylphenol concentration varying from 7×10^{-3} to 0.3 mol L^{-1} and a 1-naphthol concentration varying from 4×10^{-4} to 1×10^{-3} mol L^{-1} and measuring the absorbance at 400 nm, an equilibrium constant of 200 ± 25 was obtained. The reduction potential of the 3-methylphenoxyl radical has not been reported. Therefore, this value was determined from another equilibrium study between the phenoxyl and 3-methylphenoxyl radicals at pH 13 in N_2O-saturated solutions with 6.6×10^{-2} mol L^{-1} phenol and a varying concentration of 3-methylphenol between 3.3×10^{-3} and 1×10^{-2} mol L^{-1}. The equilibrium constant obtained from measurements at 410 nm was 12.4 ± 0.8, and by using the reduction potential of phenoxyl as 0.79 V versus NHE,[2] the reduction potential of the 3-methylphenoxyl radical is calculated to be 0.73 V. From this value, the reduction potential of 1-naphthoxyl is calculated to be 0.59 V (Table 1).

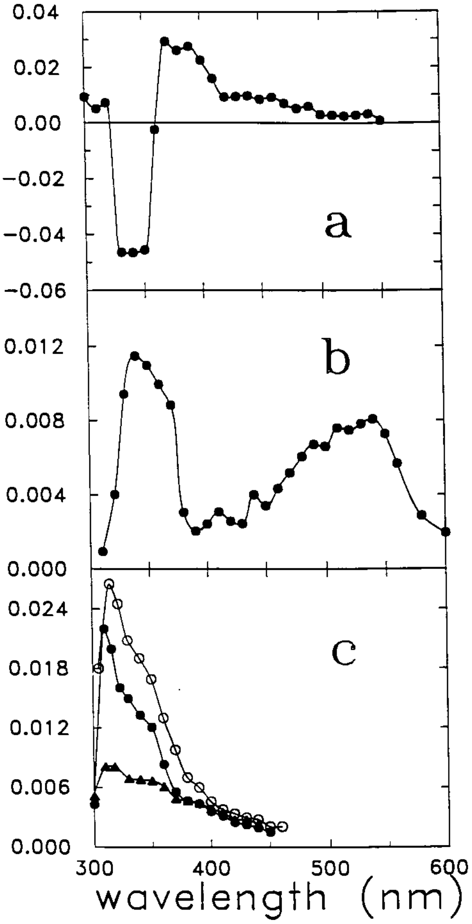

Figure 2. Differential absorption spectra of the pyridoxyl radicals. Determined by pulse radiolysis of N_2O-saturated aqueous solutions. (a) 2-pyridoxyl, monitored with solutions containing 1.24×10^{-3} mol L^{-1} 2-hydroxypyridine and 0.1 mol L^{-1} N_3^- at pH 12.6, 20 μs after the pulse, dose/pulse 15 Gy; (b) 3-pyridoxyl, with solutions containing 1.0×10^{-3} mol L^{-1} 3-hydroxypyridine and 0.1 mol L^{-1} N_3^- at pH 12.3, 20 μs after the pulse, dose 8.3 Gy; (c) 4-pyridoxyl, with solutions at pH 11.1 containing (●) 1.0×10^{-4} mol L^{-1} 4-hydroxypyridine saturated with N_2O, 480 μs after the pulse, dose 6 Gy; (○) 5.0×10^{-4} mol L^{-1} 4-hydroxypyridine and 0.01 mol L^{-1} $S_2O_8^{2-}$ saturated with N_2, 300 μs after the pulse, dose 14 Gy; (▲) 8.0×10^{-4} mol L^{-1} 4-hydroxypyridine and 0.01 mol L^{-1} N_3^- saturated with N_2O, 25 μs after pulse, dose 14 Gy.

2-Naphthoxyl Radical. The spectrum of the 2-naphthoxyl radical in a 1:2 mixture of benzene and di-*tert*-butyl peroxide exhibits two peaks at 355 and 480 nm.[11] The peaks at 360 and 490 nm obtained in the present study in N_2O-saturated aqueous solutions at pH 12.5 in the presence of 0.1 mol L^{-1} N_3^- (Figure 1b) are in good agreement with the reported spectrum. While searching for a suitable redox pair, we observed that whereas $ClO_2^{\bullet}$ and 4-cyanophenoxyl radicals caused complete oxidation of the 2-naphthoxide anion, an equilibrium was achieved with the phenoxyl radical. By using N_2O-saturated solutions at pH 13 and measuring the absorbance at 490 nm with mixtures of various concentrations of phenol and 2-naphthol, an equilibrium constant of 44.6 ± 2.5 was determined. Thus, the reduction potential of the 2-naphthoxyl radical is calculated to be 0.69 V (Table 1). This value is 0.10 V higher than the potential for 1-naphthoxyl. This comparison is in line with the +0.13 V difference found between the "formal potentials" of 2-naphtholate and 1-naphtholate measured by cyclic voltammetry in acetonitrile solutions,[7] although the absolute values in the two solvents are not comparable.

2-Pyridoxyl Radical. The spectrum of the 2-pyridoxyl radical was obtained in N_2O-saturated solutions containing 1.24×10^{-3} mol L^{-1} 2-hydroxypyridine and 0.1 mol L^{-1} N_3^- at pH 12.6 (Figure 2a). The same spectrum was obtained by using 0.1 mol L^{-1} CO_3^{2-} instead of azide. The spectrum exhibits a peak at 380 nm. At longer times, however, as this peak decayed, a new peak at 430 nm was obtained, in agreement with an earlier report.[12] The first-order rate of formation of the 430-nm absorption was measured to be $(4 \pm 1) \times 10^4$ s^{-1}. To understand the nature of this spectral transformation, we studied the effects of concentration and pH on this process. When the concentration of 2-hydroxypyridine was increased from 1 × 10^{-3} to 1.1 × 10^{-2} mol L^{-1}, no noticeable increase in the formation rate at 430 nm was observed, thus ruling out any reaction with the parent compound or with any impurity in this compound. On the other hand, the yield of the second species increased linearly with pH from pH 8 to pH 13.5, but its formation rate remained the same over this pH range. From these results it is suggested that the second transient is the OH-adduct of 2-hydroxypyridine, which is formed by reaction of the 2-pyridoxyl radical with a water molecule, followed by deprotonation. This is further confirmed by the finding that reaction of 2-hydroxypyridine with $^{\bullet}$OH radicals leads to formation of a similar peak at 430 nm along with a peak at 390 nm.

Therefore, to estimate the reduction potential under an equilibrium condition, it is necessary to use a reference couple that allows electron transfer at a faster rate than the formation of the secondary transient. While $(SCN)_2^{\bullet-}$ oxidized the 2-hydroxypyridine anion completely, $I_2^{\bullet-}$ did not react to any noticeable extent. From the known reduction potentials for these radicals,[13] we conclude that the potential of the 2-pyridoxyl radical is close to 1.1 V. The reduction potential of the 4-cyanophenoxyl radical has been reported[2] to be 1.12 V, and therefore we used this species as a reference for 2-pyridoxyl. By measuring the absorbance at 420 nm with N_2O-saturated solutions containing 0.2 mol L^{-1} N_3^- and various concentrations of 4-cyanophenol and 2-hydroxypyridine, an equilibrium constant of 0.109 ± 0.006 was determined. Thus, the reduction potential of the 2-pyridoxyl radical is 1.18 V (Table 1).

3-Pyridoxyl Radical. The spectrum of the 3-pyridoxyl radical, measured in N_2O-saturated solutions containing 1.0 × 10^{-3} mol L^{-1} 3-hydroxypyridine and 0.1 mol L^{-1} N_3^- at pH 12.3, showed two peaks, at 340 and 540 nm (Figure 2b). These peaks match closely with those reported earlier.[14] However, as in the case of the 2-pyridoxyl radical discussed above, a different spectrum was observed at longer times, probably due to similar processes. Redox equilibrium was established between 3-pyridoxyl and 4-cyanophenoxyl radicals. The results (Table 1) show an equilibrium constant of 10.5 ± 0.6 and a reduction potential of 3-pyridoxyl of 1.06 V.

4-Pyridoxyl Radical. The absorption spectrum of the 4-pyridoxyl radical in acidic solutions was reported to have a maximum at 370 nm.[15] In strongly alkaline solutions, the pyridoxyl radical was reported to exist in equilibrium with its OH-adduct radical, which has a peak absorption at 390 nm. In our measurements at pH 11.1 using the primary ($^{\bullet}$OH) and secondary $N_3^{\bullet}$ and $SO_4^{\bullet-}$ oxidizing radicals (experimental details in Figure 2), no peak was observed near 370 nm but a monotonic increase in the absorbance below 450 nm was obtained in each case. At this selected pH, the absence of any peak at 390 nm in each case confirms that the contribution of the OH-adduct is negligible. A comparison of the yields of the 4-pyridoxyl radical (Figure 2c) under the different conditions shows incomplete oxidation by $N_3^{\bullet}$. We ascribe this finding to an equilibrium between azide and 4-pyridoxyl radicals. The calculated molar absorptivity values at 370 nm (1.36 × 10^3 L mol^{-1} cm^{-1} for the $^{\bullet}$OH reaction, 1.58 × 10^3 L mol^{-1} cm^{-1} for $N_3^{\bullet}$ (see below), and 1.28 × 10^3 L mol^{-1} cm^{-1} for $SO_4^{\bullet-}$) are in agreement with the reported value of 1.5 × 10^3 L mol^{-1} cm^{-1}.[15]

To study the equilibrium between 4-hydroxypyridine and 4-cyanophenol (as the reference), we utilized N_2O-saturated solutions containing 0.2 mol L^{-1} N_3^- and various concentrations of 4-cyanophenol and 4-hydroxypyridine and measured the absorbance at 420 nm. From the results, we determined an equilibrium constant of (8.3 ± 0.5) × 10^{-3} and thus a reduction potential of 1.24 V for the 4-pyridoxyl radical (Table 1). Since this value is only 89 mV lower than the reduction potential of the azidyl radical, these measurements are expected to be affected by the additional equilibrium between 4-hydroxypyridine and azide. Therefore, we also studied the equilibrium between 4-hydroxypyridine and azide in the absence of 4-cyanophenol. From the absorbances measured with N_2O-saturated solutions at pH 12.5 containing 1.0 × 10^{-3} mol L^{-1} 4-hydroxypyridine and from 0.01 to 0.05 mol L^{-1} N_3^-, an equilibrium constant of 13 ± 2 and a reduction potential of 1.26 V were obtained. The concentration of N_3^- was not increased beyond 0.05 mol L^{-1} to avoid interference by the additional equilibrium between $N_3^{\bullet}$ and excess N_3^- (to form $N_6^{\bullet-}$). These estimations, therefore, explain the low yield of the 4-pyridoxyl radical in the spectral measurements with $N_3^{\bullet}$ shown in Figure 2; the molar absorptivity value in this case was estimated from the radical yields by taking into account the equilibrium constant, $K = 13$. The high reduction potential of 1.26 V for the 4-pyridoxyl radical allowed only 40% oxidation of the 4-hydroxypyridine at equilibrium for the solute concentrations used for Figure 2.

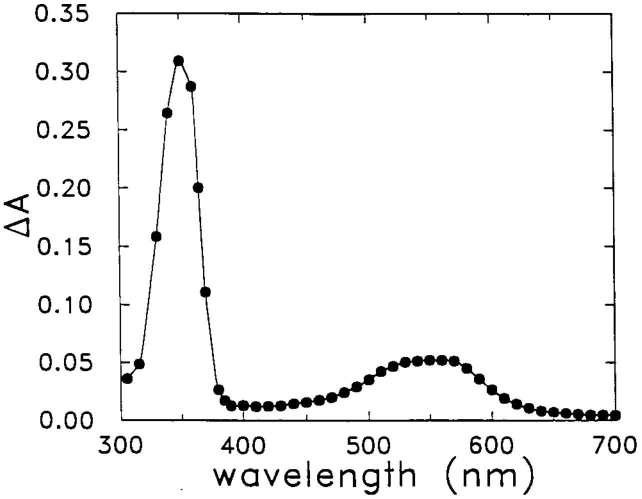

Figure 3. Absorption spectrum of the 4-phenylphenoxyl radical. Determined by pulse radiolysis of N_2O-saturated aqueous solutions containing 5.0 × 10^{-4} mol L^{-1} 4-phenylphenol and 0.1 mol L^{-1} N_3^- at pH 10.8, measured 20 μs after the pulse, dose 8.2 Gy.

4-Phenylphenoxyl Radical. The spectrum of this radical in a mixture of benzene and di-*tert*-butyl peroxide (1:2) exhibits a visible band with maxima at 480 and 530 nm and a sharp peak at $\lambda \leq 350$ nm.[11] Oxidation of 4-phenylphenol in N_2O-saturated aqueous solutions containing 5.0 × 10^{-4} mol L^{-1} 4-phenylphenol and 0.1 mol L^{-1} N_3^- at pH 12 formed a species that exhibits a peak at 350 nm and a visible band centered at 560 nm (Figure 3). For redox equilibrium studies, we found that the 4-cyanophenoxyl radical oxidizes the 4-phenylphenoxide ion completely, but reaction with $I_2^{\bullet-}$ at 0.1 mol L^{-1} I^- indicated the existence of an equilibrium. From kinetic measurements at 390 nm for the decay of $I_2^{\bullet-}$ and at 560 nm for the formation of the 4-phenylphenoxyl radical in the presence of varying concentrations of 4-phenylphenol at pH 10.8, an equilibrium constant $K = 78$ was obtained. By comparison, from measurements of the absorbance values at equilibrium at the same two wavelengths, we calculated $K = 45$. By taking the average $K = 61 \pm 16$, the reduction potential of the 4-phenylphenoxyl radical is determined to be 0.93 ± 0.02 V versus NHE (Table 1).

O−H Bond Dissociation Energies. The gas-phase O−H bond dissociation energies (BDE) for a series of substituted phenols and several other antioxidants have been estimated experimentally[2,5,16] and by theoretical calculations.[17] To estimate the BDEs for the naphthols and pyridols from the experimental results of this study, we use the method described before.[2] From the reduction potentials and the pK_a values, given in Table 1, we calculate the potentials at pH 0, and from these values, by using the same approximations as before,[2] we calculate the O−H BDEs (Table 1). The values calculated for 1-naphthol (346 kJ mol^{-1}) and 2-naphthol (358 kJ mol^{-1}) are 5−10 kJ mol^{-1} lower than those estimated from irreversible anodic potentials and pK_a values in DMSO solutions.[18] The naphthols have weaker O−H bonds than phenol;[2] the difference is ∼23 kJ mol^{-1} for 1-naphthol and ∼12 kJ mol^{-1} for 2-naphthol. These differences are very similar to those found[19] when comparing the $O-CH_3$ BDEs in 1- and 2-methoxynaphthalenes with that of anisole, although the absolute BDE values for the hydroxy derivatives are considerably higher than those for the methoxy derivatives. The O−H BDEs for the pyridols are larger than those for phenol, reflecting the electron-withdrawing effect of the ring nitrogen. By comparing the BDE for 4-pyridol with those for 4-substituted phenols[2] and using the correlation with the σ^+ substituent constants,[2] one can conclude that σ^+ for the ring nitrogen is much greater than those for CN or NO_2 substituents.

The above results show that, in general, naphthols may be expected to act as more effective antioxidants than similarly substituted phenols, whereas pyridols will be less effective, particularly when the nitrogen is *ortho* or *para* to the OH group. It is interesting to compare the trends in the reduction potentials of these phenoxyl-type radicals with those observed for arylperoxyl-type radicals.[20] In the case of pyridyl versus phenyl, both pyridoxyl and pyridylperoxyl are stronger or more reactive oxidants than phenoxyl and phenylperoxyl, respectively. On the other hand, in the case of naphthyl versus phenyl, the situation is reversed; while naphthoxyl is a weaker oxidant than phenoxyl, naphthylperoxyl is a more reactive oxidant than phenylperoxyl. This is clearly due to the fact that in the peroxyl radicals the unpaired electron does not delocalize onto the ring and thus the effect of the ring is mostly an inductive effect, which is stronger for naphthyl than for phenyl, whereas in the phenoxyl-type radicals the unpaired electron is delocalized over the rings and thus the mesomeric effect predominates.

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