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Redox and Acidity Properties of 2,2′- and 4,4′-Biphenol and the Corresponding Phenoxyl Radicals

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The redox and acidity properties of 2,2′- and 4,4′-biphenol and the corresponding phenoxyl radicals have been determined using UV−vis spectrophotometry, pulse radiolysis, and cyclic voltammetry. The pK_a’s for 4,4′-HO-Ph-Ph-OH, 4,4′-$^-$O−Ph-Ph-OH, 4,4′-$^\bullet$O-Ph-Ph-OH, 2,2′-HO-Ph-Ph-OH, 2,2′-$^-$O-Ph-Ph-OH, and 2,2′-$^\bullet$O-Ph-Ph-OH were determined to be ca. 9.7, ca. 9.7, 6.3, 7.6, 13.7, and 10, respectively. At the same time, the one-electron reduction potentials for 4,4′-$^-$O-Ph-Ph-O$^\bullet$ and 2,2′-HO-Ph-Ph-O$^\bullet$ were determined to be 0.44 and 1.00 V vs NHE, respectively. By using a thermochemical cycle, the experimentally inaccessible one-electron reduction potentials for 4,4′-HO-Ph-Ph-O$^\bullet$ and 2,2′-$^-$O-Ph-Ph-O$^\bullet$ were calculated to be 0.64 and 0.78 V vs NHE, respectively. From the redox and acidity data we also estimated the O−H bond dissociation enthalpies for 4,4′-HO-Ph-Ph-OH, 4,4′-$^-$O-Ph-Ph-OH, 2,2′-HO-Ph-Ph-OH, and 2,2′-$^-$O-Ph-Ph-OH to be 349, 330, 372, and 385 kJ mol^{-1}, respectively. The results are discussed in light of previously established substituent effects on the thermochemistry of phenols and phenoxyl radicals.

Introduction

Phenols are of great importance, e.g., in biological systems and as food additives. In both cases they can act as antioxidants protecting against destructive oxidation. Phenols are also constituents of lignin in wood and are commonly used as antioxidants in synthetic polymers. The antioxidant activity and degradation of many natural materials inevitably results in the formation of phenoxyl radicals.[1] Consequently, the properties and reactivity of phenoxyl radicals are of great importance for the understanding of many natural and industrial processes.

During the past decade, redox and thermochemical properties and reaction kinetics of phenols and phenoxyl radicals have been studied quite extensively. Pulse radiolysis has been successfully utilized to determine one-electron reduction potentials of numerous substituted phenoxyl radicals and also, in addition to laser flash photolysis, to study the kinetics of several reactions involving phenoxyl radicals.[2−5] Recently, electrochemical methods have been used to determine one-electron reduction potentials of some phenoxyl radicals. In comparable cases the two methods give virtually identical potentials, although the lifetime of the phenoxyl radicals is too short to allow for direct measurement of half-wave potentials by cyclic voltammetry.[6] By using the one-electron reduction potentials of phenoxyl radicals and pK_a’s of the corresponding phenols in a thermodynamical cycle, it is possible to estimate the homolytic O−H bond dissociation enthalpies of phenols (Figure 1, eqn. 1).[2,7] However, it is also possible to measure the bond dissociation enthalpy by using photoacoustic calorimetry.[8]

$$\mathrm{BDE(O{-}H)} = 96.48E^\circ + 5.70\mathrm{p}K_\mathrm{a} + 232\ (\mathrm{kJ\ mol^{-1}}) \quad (1)$$

$$\begin{tikzcd}
\mathrm{PhOH} \arrow[r, "-\mathrm{H}^+"] \arrow[dr, "-\mathrm{H}^\bullet"'] & \mathrm{PhO}^- \arrow[d, "-e^-"] \\
 & \mathrm{PhO}^\bullet
\end{tikzcd}$$

Figure 1. Thermochemical cycle for monoprotic phenols.

All these studies have resulted in increased understanding of the substituent effects on redox properties, O−H bond dissociation enthalpies, and reactivity. Using the resulting simple structure−activity relationships, it is possible to predict the one-electron reduction potentials of substituted phenoxyl radicals and the O−H bond dissociation enthalpies of substituted phenols (eqs 2 and 3, respectively).[9] σ_i^+ in eqs 2 and 3 are σ_o^+ for

$$E^\circ = 0.79 + 0.34\sum_{i=2}^{6}\sigma_i^+\ (\mathrm{V\ vs\ NHE}) \quad (2)$$

$$\mathrm{BDE(O{-}H)} = 365 + 30\sum_{i=2}^{6}\sigma_i^+\ (\mathrm{kJ\ mol^{-1}}) \quad (3)$$

substituents in position 2 and 6, σ_m^+ for substituents in position 3 and 5, and σ_p^+ for substituents at position 4. σ_o^+ has been found to be proportional to σ_p^+ ($\sigma_o^+ = 0.7\sigma_p^+$) for one-electron reduction potentials of phenoxyl radicals and substituted benzene radical cations and for X−Y bond dissociation enthalpies of molecules with the general structure $C_6H_5{-}X{-}Y$.[10]

2,2′- and 4,4′-biphenol are two possible products of phenoxyl radical recombination (Figure 2).[11] Thus, to fully understand the chemistry of phenoxyl radical-containing systems, one also needs to know the redox behavior of the recombination products. Biphenols are also used as lubricants and fuel additives, antioxidants, polymerization intermediates, and fungicides.[12,13] In this work we have studied the redox and acidity properties of 2,2′- and 4,4′-biphenol and of their corresponding phenoxyl radicals. During the preparation of this manuscript a paper on the redox and acidity properties of 4,4′-biphenol and the

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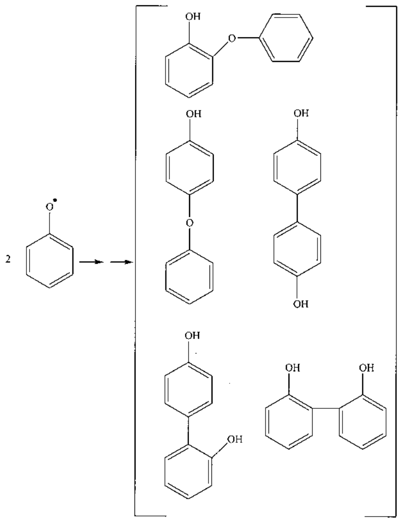

Figure 2. Products formed upon radical−radical combination of phenoxyl radicals.

corresponding phenoxyl radical appeared in *The Journal of Physical Chemistry A*.[14] The results of this paper will also be discussed.

Experimental Section

All chemicals of the purest grade available (Lancaster and Aldrich) were used as supplied.

Pulse Radiolysis. Radiolysis of water results in the formation of $OH^\bullet$, e_{aq}^-, $H^\bullet$, H_2O_2, H_2, and H_3O^+, with $OH^\bullet$ and e_{aq}^- being the major radical species with primary radiation chemical yields of 0.28 μmol/J each above pH 3.[15] N_2O-saturated solutions were used throughout in order to convert the reducing solvated electron into the oxidizing hydroxyl radical ($G_{OH} = 5.6 \times 10^{-7}$ mol/J).[15] Millipore Milli-Q filtered water was used throughout.

The pulse radiolysis equipment consists of a linear accelerator delivering 3 MeV electrons and a computerized optical detection system.[16] The pulses were of 5−10 ns duration delivering doses of 3−6 Gy. For dosimetry, a N_2O-saturated 10^{-2} KSCN solution was used.[17] The $G\epsilon$ value of $(SCN)_2^{\bullet -}$ was taken to be 4.78×10^{-4} m^2/J at 500 nm.

Primary oxidation of the phenolates (pH adjusted by NaOH or borate) was achieved by $N_3^\bullet$, produced in the reaction of $OH^\bullet$ with N_3^- (10^{-2} to 1 M NaN_3). To determine one-electron reduction potentials of the phenoxyl radicals, the redox equilibrium between the radical of interest and a redox couple with a known one-electron reduction potential was studied (reaction 4). The equilibrium constant can be derived from the rate constants of the electron-transfer reaction and the back-reaction and/or the equilibrium concentrations of the two redox couples.[18]

$$PhO^\bullet + ref \rightleftharpoons {}^\bullet PhO^- + ref^{\bullet +} \qquad (4)$$

The one-electron reduction potential of interest is then calculated from the equilibrium constant and the one-electron reduction potential of the redox reference couple using Nernst's equation ($\Delta E° = 0.0591 \log K$).

pK_a. The pK_a's of the phenols were determined by recording the UV−vis spectra at a number of different pH values. The spectral differences between the phenols and the corresponding phenolates were plotted against the pH, and from such plots the pK_a of the phenol could be determined. The pK_a's of the phenoxyl radicals were determined in the same way using pulse radiolysis.

Cyclic Voltammetry. Cyclic voltammetry was performed on a PAR 263A potentiostat/galvanostat interfaced to a base PC using the EG&G Model 270 software package. The cell was a standard three-electrode setup equipped with a 5 mm diameter platinum button working electrode, a platinum coil counter electrode, and a calomel reference electrode. Millipore Milli-Q filtered water was used with 1 M KCl as supporting electrolyte. The scan rate was 500 mV/s and full IR compensation was employed in all measurements.

Results and Discussion

Table 1 comprises the experimental results and conditions and previously published data on some relevant phenols and phenoxyl radicals.

For biphenols and other diprotic acids the thermochemical cycle given in Figure 1 can be extended to the cycle shown in Figure 3.

Biphenols have two pK_a's (denoted pK_{a1} and pK_{a2}), and we can thus define two different one-electron reduction potentials, one for HO-Ph-Ph-$O^\bullet$ ($E°(1)$) and one for $^-$O-Ph-Ph-$O^\bullet$ ($E°(2)$) The neutral radical has also a pK_a (pK_{ar}) and it is thus possible to calculate any one of $E°(1)$, $E°(2)$, pK_{a2}, or pK_{ar}, if three of these entities are known (eq 5). Furthermore, the bond dissociation enthalpies for both HO-Ph-Ph-OH (BDE_1) and $^-$O-Ph-Ph-OH (BDE_2) can be calculated from eq 1.

$$E°(1) + 0.059pK_{ar} = E°(2) + 0.059pK_{a2} \qquad (5)$$

pK_a Values of Phenols. The pK_a value of phenol itself is 10.0 and normally it is slightly higher for phenols with electron-donating substituents and significantly lower for phenols with electron-withdrawing substituents. One of the strongest electron-donating substituents is $-O^-$, and the pK_a of 4-$^-$O-PhOH is 11.5,[20] which is only 1.5 units higher than for unsubstituted phenol. The main effect of electron-donating substituents on the pK_a is inductive stabilization of the phenol. For symmetrical 2,2′-biphenols the first pK_a is usually significantly lower than for the corresponding monomeric phenol, while the second pK_a is significantly higher.[23] In the case of unsubstituted 2,2′-biphenol, the first pK_a is lower by 2.4 units while the second pK_a is higher by 3.7 units than the pK_a of phenol. This pK_a splitting can be attributed to a stabilizing intramolecular hydrogen bond between $-O^-$ and $-OH$ in the monoprotonated 2,2′-biphenol. The stabilizing effect of the intramolecular hydrogen bond is also reflected in the one-electron reduction potential of the corresponding phenoxyl radical (see below). The symmetrical splitting of the first and second pK_a has also been observed for some 4,4′-biphenols where the phenyl rings are not directly connected, e.g., 4-[(1*E*)-2-(4′-hydroxy-3′-methoxyphenyl)vinyl]-2-methoxyphenol.[23] The pK_a = 9.7 for 4,4′-biphenol determined in this work is virtually identical to the pK_a of phenol (10.0) and we do not find any spectral evidence for a large pK_a splitting, i.e., we conclude that the first and second pK_a are nearly identical. Clearly, this shows that the inductive effect of the 4-$^-$O-$C_6H_4^-$ substituent is negligible. The effect of $-O^-$ is considerably reduced by the introduction of the $-C_6H_4$ group. Das,[14] on the other hand, has reported the first and second pK_a to be 9.4 and 14.1, respectively. The second pK_a is extremely high for a para-substituted phenol and it would imply that the 4-$^-$O$-C_6H_4^-$ substituent has a very strong inductive effect. However, we do not observe any spectral difference between pH 12 and 13, which we would expect were the second pK_a as high as 14.1. Since our results on the pK_a's of 4,4′-biphenol are in disagreement with those in ref 14, we

TABLE 1: Redox and Acidity Properties of Some Phenols and Phenoxyl Radicals

phenol	redox ref	λ, nm	K	$E°(1)$, V vs NHE	$E°(2)$, V vs NHE	pK_{a1}	pK_{a2}	pK_{ar}	BDE$_1$,[c] kJ mol^{-1}	BDE$_2$,[c] kJ mol^{-1}
2,2′-biphenol	promethazine ($E° = 0.91$ V vs NHE)[19]	525	$K_{abs} = 29$ $K_{kin} = 2.8$	1.00[a] (pH 9.2)	0.78[b]	7.6	13.7	10	372	385
4,4′-biphenol	4-MeO−PhOH ($E° = 0.54$ V vs NHE)[2]	740	$K_{abs} = 57.3$ $K_{kin} = 57.8$	0.64[b]	0.44 (pH 12)	9.7	9.7	6.3	349	330
phenol				0.79[2]		10.0[20]			365.3[8]	
1,4-hydroquinone				0.46[b]	0.023[21]	10.0[20]	11.5[20]	4.0[22]	333	300

[a] We believe K_{abs} to be more reliable than K_{kin}, the former being based on a larger set of data. Hence, we have used K_{abs} to calculate the thermochemical data. [b] Calculated from eq 5. [c] Calculated from eq 1.

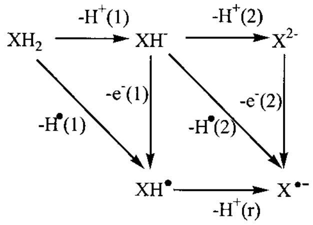

Figure 3. Thermochemical cycle for diprotic acids.

performed some additional control experiments to check our results and to verify the identity of the purchased 4,4′-biphenol (Lancaster). Proton NMR showed that we do indeed have 4,4′-phenol and that the level of impurities is below the detection limit.

To check whether the second pK_a for 4,4′-biphenol is 14.1, as was reported by Das,[14] we performed a very simple experiment. We mixed 4,4′-phenol (10^{-2} M) with NaOH (2×10^{-2} M) in water and measured the pH. If the second pK_a is 14.1, then we would expect the pH of the mixture to be around 12, while if both pK_a values are around 10, the pH should be around 11. As a reference experiment we used a 1:2 mixture of 4-CH_3O-C_6H_4OH and NaOH for which the expected pH would be around 12. The pH of the 4,4′-biphenol solution was found to be one unit lower than that of the reference solution (11.2 and 12.1, respectively), which confirms our assumption that both the first and the second pK_a for 4,4′-biphenol are around 10. As will be seen below, the one-electron reduction potential of the phenoxyl radical was independent of pH between pH 12 and 13, which would not have been the case were the second pK_a to be 14.1.

pK_a Values of Phenoxyl Radicals. The pK_a values of the phenoxyl radicals were determined to be 6.3 and 10.0 for 4,4′- and 2,2′-biphenol, respectively. If we compare these values to the pK_a of phenol, we can see that the 4-phenoxyl radical in the para position is electron-withdrawing, as evidenced by the decrease in pK_a by more than 3 units as compared to unsubstituted phenol. This effect is comparable to the effect of a 4-NO_2 substituent.[20] This also reflects the stability of the radical anion. The effect of the 2-phenoxyl radical in the ortho position is negligible, since the pK_a is identical to that of the unsubstituted phenol.

One-Electron Reduction Potentials. The one-electron reduction potentials of the phenoxyl radicals of 4,4′-$^{-}$O-Ph-Ph-O$^{\bullet}$ and 2,2′-HO-Ph-Ph-O$^{\bullet}$ were determined to be 0.44 and 1.00 V vs NHE, respectively. The experimental conditions for the two determinations were as follows: 4,4′-$^{-}$O-Ph-Ph-O$^{\bullet}$ (1 M NaN_3, pH 12 (NaOH), 7×10^{-5} to 2.8×10^{-4} M 4,4′-biphenol, 3×10^{-3} to 1.0×10^{-2} M 4-methoxyphenol, N_2O-sat.) and 2,2′-HO-Ph-Ph-O$^{\bullet}$ (10^{-2} M NaN_3, pH 9.2 (10^{-2} M disodium tetraborate), 1×10^{-3} to 5×10^{-3} M 2,2′-biphenol, 5×10^{-5} to 1×10^{-3} M promethazine, N_2O-sat.). It should be noted that the ionic strengths in these two determinations are approximately 1 and 0.02 M, respectively. If extrapolated to zero ionic strength, both potentials should be somewhat lower. From eq 5 we calculate the experimentally inaccessible one-electron reduction potentials for 4,4′-HO-Ph-Ph-O$^{\bullet}$ and 2,2′-$^{-}$O-Ph-Ph-O$^{\bullet}$ to be 0.64 and 0.78 V vs NHE, respectively. By way of comparison, the one-electron reduction potential of the unsubstituted phenoxyl radical is 0.79 V vs NHE. As can be seen, the potential for 4,4′-$^{-}$O-Ph-Ph-O$^{\bullet}$ is considerably lower than that of the unsubstituted phenoxyl radical while the potential for 2,2′-HO-Ph-Ph-O$^{\bullet}$ is considerably higher. Judging by the potential, the 4-phenolate substituent in the para position appears to be strongly electron-donating. We attribute this effect mainly to resonance stabilization of the radical rather than to a purely inductive effect. Assuming that the one-electron reduction potential follows eq 2, we estimate σ_p^+ for the 4-phenolate substituent to be −1.03. Again, if we compare the effect of the 4-$^{-}$O-C_6H_4− substituent ($E°$($^{-}$O-Ph-Ph-O$^{\bullet}$/$^{-}$O-Ph-Ph-O^{-}) = 0.44 V) to that of the 4-$^{-}$O− substituent ($E°$($^{-}$O-Ph-O$^{\bullet}$/$^{-}$O-Ph-O^{-} = 0.023 V), we see that, while the effect of −O^{-} is considerably reduced by the introduction of the −C_6H_4 group, it is still relatively strong. The effect of a 4-phenol substituent in the para position is considerably smaller than the effect of a 4-phenolate substituent. The estimated σ_p^+ value for 4-HO-Ph− is −0.69, which should be compared to the σ_p^+ value for 4-HO− (−0.92).[24] The relatively strong substituent effects expressed by 4-$^{-}$O-Ph− would seem to imply some degree of planarity for the radical anion, planarity being a prerequisite for resonance stabilization. The increase in one-electron reduction potential caused by the 2-phenol substituent in the ortho position can be attributed to the stabilizing effect of the intramolecular hydrogen bond present in monoprotonated 2,2′-biphenol. This kind of effect would not be possible to predict using eq 2. In addition, the potential for 2,2′-$^{-}$O-Ph-Ph-O$^{\bullet}$ is virtually identical to that of PhO$^{\bullet}$, which demonstrates that the high potential for 2,2′-HO-Ph-Ph-O$^{\bullet}$ can be solely attributed to the intramolecular hydrogen bond. It should be noted that, due to steric hindrance, the 2,2′-biphenol phenoxyl radical is prevented from forming a stabilizing planar structure.

The one-electron reduction potential for the 4,4′-biphenol phenoxyl radical, as reported by Das, is 0.448 V vs NHE at pH 12, based on a pulse radiolytic measurement using $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ as the reference couple.[14] However, we believe the formal agreement between our value and that of Das at pH 12 to be coincidental. In fact, the following observations suggest that what Das was observing in the above system may not have been the approach to equilibrium. (1) Our measured reduction potential remains constant between pH 12.3 and 13.3. By contrast, in ref 14 the reduction potential is reported to decrease from 0.463 to 0.422 when the pH is increased from 11.7 to 12.4. (2) Using the known self-exchange values for phenolate/phenoxyl radicals[25] and $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ [26] we estimate, using the Marcus equation, the rate constant for the exothermic reaction between the phenoxyl radical ($C_6H_5O^{\bullet}$) and $Fe(CN)_6^{4-}$

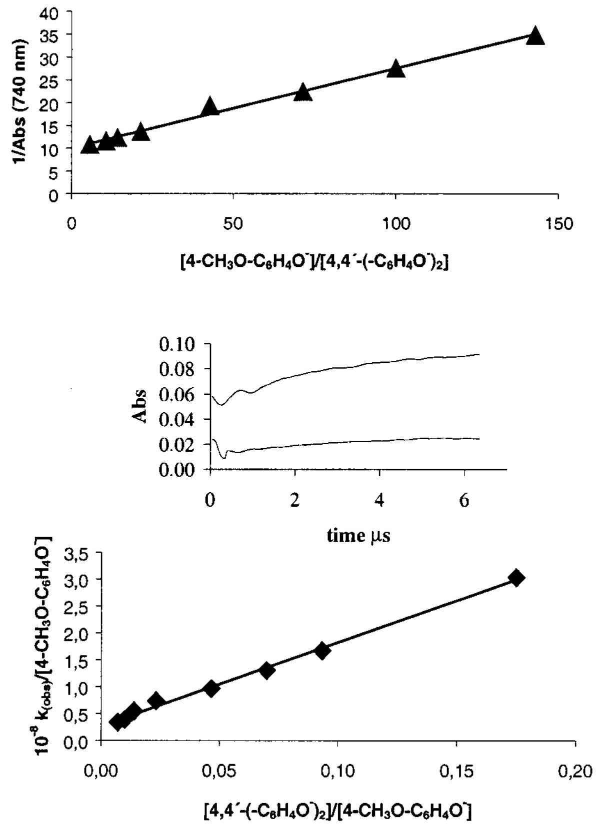

Figure 4. Data from equilibrium measurements on the 4,4′-biphenolate/4-methoxyphenolate system. (Top) inverse optical densities plotted against the concentration ratio between 4-methoxyphenolate and 4,4′-biphenolate. (Bottom) measured rate constants of equilibration normalized with respect to the concentration of 4-methoxyphenolate plotted against the concentration ratio between 4,4′-biphenol and 4-methoxyphenol. (Inset) approach to equilibrium at 2.8×10^{-4} M 4,4′-biphenolate and 1.6×10^{-3} M 4-methoxyphenolate (top) and at 5.0×10^{-5} M 4,4′-biphenolate and 1.0×10^{-2} M 4-methoxyphenolate (bottom).

to be ca. 10^8 M^{-1} s^{-1}. In a pulse radiolysis experiment we measured $k(C_6H_5O^\bullet + Fe(CN)_6^{4-})$ to be 10^8 M^{-1} s^{-1}, in excellent agreement with this estimation. The rate constant for the reaction between the 4,4′-biphenol phenoxyl radical and $Fe(CN)_6^{4-}$ is then predicted to be ca. 10^5 M^{-1} s^{-1}. In view of the above agreement this estimate should be reliable. Therefore, the rate of equilibration in the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system would appear to be far too slow for the pulse radiolysis method. In contrast to the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system, the rate of equilibration with the $4\text{-}CH_3O\text{-}C_6H_4O^\bullet/4\text{-}CH_3O\text{-}C_6H_4O^-$ couple as reference is very rapid ($k_f = 2.7 \times 10^7$ M^{-1} s^{-1} and $k_r = 1.6 \times 10^9$ M^{-1} s^{-1}) and the agreement between the equilibrium constants determined from the kinetics and from the equilibrium absorbance is excellent (Figure 4). The rate constants for the reaction between the 2,2′-biphenol phenoxyl radical and promethazine were determined to be 1.9×10^8 M^{-1} s^{-1} and the rate constant for the reverse reaction is 6.7×10^7 M^{-1} s^{-1}.

Cyclic Voltammetry. By using cyclic voltammetry we managed to measure the potential for the 4,4′-biphenol phenoxyl radical at pH 12 and 13 using both $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and $ClO_2^-/ClO_2^\bullet$ as references. The oxidation of the 4,4′-biphenolate is quasi reversible and it is thus possible to obtain a fairly accurate $E_{1/2}$ value in water. The difference in potential between the 4,4′-biphenol phenoxyl radical and the two reference redox couples did not vary between pH 12 and 13 and the resulting pH independent $E_{1/2}$ value is 0.35 V vs NHE (without correction for ionic strength). Previously, Fraser had determined the potential to be ca. 0.30 V vs NHE at pH 11 using cyclic voltammetry with a glassy carbon working electrode.[27] The potentials determined by cyclic voltammetry are 100−150 mV lower than the potential determined by pulse radiolysis. This is puzzling given the almost reversible nature of the voltammograms. The fact that we obtain almost reversible voltammograms is even more puzzling when we consider that the rate constant for the radical−radical reaction is 8×10^8 M^{-1} s^{-1} $(2k)$.[14] Thus, we should not be able to observe the reduction peak at the scan rates used in this work or in the work by Fraser. The difference of 50 mV between the potential determined in this work and in the work by Fraser could indicate that this phenomenon is related to the electrode since different working electrodes were used in these two studies (glassy carbon and platinum).

O−H Bond Dissociation Enthalpies. Using a thermochemical cycle (eq 1, Hess' law), we calculate the O−H bond dissociation enthalpies of 2,2′-HO-Ph-Ph-OH, 2,2′-⁻O-Ph-Ph-OH, 4,4′-HO-Ph-Ph-OH, and 4,4′-⁻O-Ph-Ph-OH to be 372, 385, 349, and 330 kJ mol^{-1}, respectively. For comparison, the O−H bond dissociation enthalpy of phenol is 365.3 kJ mol^{-1} and for 4-HO-Ph-OH and 4-⁻O-Ph-OH the corresponding values are 333 and 300 kJ mol^{-1}, respectively. The O−H bond dissociation enthalpy for 2,2′-HO-Ph-Ph-OH and 2,2′-⁻O-Ph-Ph-OH are slightly higher than for phenol. The difference in BDE between the neutral and monodeprotonated 2,2′-biphenol can be attributed to the intramolecular hydrogen bond present in the monodeprotonated form. The weak O−H bond present in 4,4′-biphenol clearly demonstrates the suitability of this compound as an antioxidant.

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References and Notes

(1) Denisov, E. T.; Khudyakov, I. V. *Chem. Rev.* **1987**, *87*, 1313.

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

(3) Jovanovic, S. V.; Tosic, M.; Simic, M. G. *J. Phys. Chem.* **1991**, *95*, 10824.

(4) Jonsson, M.; Lind, J.; Reitberger, T.; Eriksen, T. E.; Merényi, G. *J. Phys. Chem.* **1993**, *97*, 8229.

(5) Jin, F.; Leitich, J.; von Sonntag, C. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1583.

(6) Li, C.; Hoffman, M. Z. *J. Phys. Chem. B*, **1999**, *103*, 6653.

(7) Malmström, J.; Jonsson, M.; Cotgreave, I. A.; Hammarström, L.; Sjödin, M.; Engman, L. *J. Am. Chem. Soc.* **2001**, *123*, 3434 and references therein.

(8) Laarhoven, L. J. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342 and references therein.

(9) Jonsson, M.; Lind, J.; Eriksen, T. E.; Merényi, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1567.

(10) Jonsson, M.; Lind, J.; Merényi, G.; Eriksen, T. E. *J. Chem. Soc., Perkin Trans. 2* **1995**, 61.

(11) Ye, M.; Schuler, R. H. *J. Phys. Chem.* **1989**, *93*, 1898.

(12) Gibban, G. A.; White, C. M.; Douglas, L. J. *Am. Chem. Soc., Div. Fuel Chem.* **1985**, *30*, 179.

(13) Schwartz, R. D.; Willians, A. L.; Hutchinson, D. B. *Appl. Environ. Microbiol.* **1980**, *39*, 702.

(14) Das, T. N. *J. Phys. Chem. A* **2001**, *105*, 5954.

(15) Spinks, J. W. T.; Woods, R. J. *Introduction to Radiation Chemistry*; Wiley: New York, 1990.

(16) Eriksen, T. E.; Lind, J.; Reitberger, T. *Chem. Scr.* **1976**, *10*, 5.

(17) Fielden, E. M. In *The Study of Fast Processes and Transient Species by Pulse Radiolysis*; Baxendale, J. H., Busi, F., Eds.; NATO Advanced Study Institutes Series; Reidel: Dordrecht, The Netherlands, 1982; pp 49−62.

(18) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(19) Jonsson, M.; Lind, J.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1994**, *116*, 1423.

(20) Serjeant, E. P.; Dempsey, B. In *Ionisation Constants of Organic Acids in Aqueous Solution*; Pergamon Press: Oxford, U.K., 1979.

(21) Steenken, S.; Neta, P. *J. Phys. Chem.* **1979**, *83*, 1134.

(22) Adams, G. E.; Michel, B. D. *Trans. Faraday Soc.* **1967**, *63*, 1171.

(23) Ragnar, M.; Lindgren, C. T.; Nilvebrant, N. O. *J. Wood Chem. Technol*. **2000**, *20*, 277.

(24) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 5.

(25) Schuler, R. H.; Neta, P.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 3825.

(26) Weston, R. E., Jr.; Schwarz, H. A. *Chemical Kinetics*; Prentice-Hall: Englewood Cliffs, NJ, 1972.

(27) Fraser, D. M. *Anal. Lett.* **1994**, *27*, 2039.