solvent molecules. Each of these considerations regarding transition-state formation would contribute to the solvent dependence exhibited by the kinetic activation parameters listed in Table II. Both mass effects and relative hydrogen-bonding versus deuterium-bonding energies (and structure)[28] are likely contributors to the different rates of racemization observed for $Eu(dpa)_3^{3-}$ in H_2O versus D_2O solutions.

Conclusion

This is the first report of time-resolved circularly polarized luminescence (TR-CPL) from a racemic mixture of enantiomeric species excited with circularly polarized light. It is also the first report of kinetic parameters for optical isomerization of a chiral lanthanide complex. Enantioselective TR-CPL measurements provide an excellent diagnostic probe of excited-state chiroptical properties in systems that exhibit stereochemical lability on a time scale comparable to luminescence decay. In the present study, TR-CPL measurements were used to investigate the kinetics of enantiomer interconversion processes in enantioselected excited-state populations of $Eu(dpa)_3^{3-}$ in H_2O and D_2O. The results reported here are specific to $Eu(dpa)_3^{3-}$, but they also have relevance to stereochemical lability in other metal complexes.

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The One-Electron Reduction Potential of 4-Substituted Phenoxyl Radicals in Water

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Abstract: By means of pulse radiolysis the one-electron reduction potentials of twelve 4-substituted phenoxy radicals have been determined. The main reference used was the $ClO_2^•/ClO_2^-$ couple. By combining the redox potentials of phenoxyl radicals with the aqueous acidities of phenols the bond strength of the phenolic O–H bond was calculated. These values were found to be in good agreement with O–H bond dissociation enthalpies measured in the gas phase.

Phenols are of special interest in organic chemistry in that their acid–base equilibria are often used as reference values in establishing linear free energy relationships. Consequently, much effort has been expended in the past to understand the factors governing phenol acidities both in solution[1,2] and in the gas phase.[3,4] Much less is known about the redox properties of phenolates. In earlier studies the redox potentials of certain phenoxyl radicals harboring electron-donating substituents have been established in water.[5] For phenoxyl radicals with high redox potentials only relative estimates based on kinetics exist.[6,7]

The structural modification of the phenoxyl radicals by the substituent has also been investigated[8,9] in water solvent. In the gas phase, only the electron affinity of the unsubstituted phenoxyl radical has been measured up to date.[10]

The present work will explore the effect of para substituents on the redox properties of phenoxyl/phenolate couples in water over a large span. When combined with the acid dissociation constants of the corresponding phenols these values give a quantitative measure of the relative strengths of the phenolic O–H bond in water and at least semiquantitative ones for the corresponding bond strengths in the gas phase. Whenever gas-phase proton affinities are available the latter values allow the electron affinities of the corresponding phenoxyl radicals to be predicted. The use of thermochemical cycles to predict gas-phase properties from liquid-state measurements or vice versa was pioneered by Eberson.[11] Extensive use of this method has been made in a series of papers by Bordwell et al.[12-14] where the cycles are described in detail.

Experimental Section

The pulse radiolysis equipment consists of a microtron accelerator[15] delivering 7 MeV electrons and a computerized optical detection system.[16] For dosimetry air-saturated 10^{-2} M KSCN solutions were employed. The $G\epsilon$ value of the $(SCN)_2^{•-}$ radical was taken to be 2.2×10^{-4} m^2/J at 500 nm.[17] All experiments were performed in N_2O-saturated aqueous solutions where the primary radiation chemical yield of $OH^•$ radicals, G_{OH}, was set to 5.6×10^{-7} mol/J. The pH was sufficiently high for more than 95% of the phenols to be in the deprotonated form, i.e., in most cases between 11 and 12. The primary oxidation of the phenolates was achieved by $N_3^•$ produced in the reaction of $OH^•$ radicals with N_3^- which was added in sufficient excess to scavenge at least 90% of the $OH^•$ radicals. The pulses employed were $1-2 \times 10^{-7}$ s long generating total radical concentrations on the order of 10^{-6} M.

$NaClO_2$ was purified according to ref. 18. The various phenols, 1-Me-Indole (Aldrich, purest grade available), NaN_3, KSCN, KI and the various buffers (Merck, p a quality) were employed without purifi-

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cation. Water was triple distilled in quartz.

Methods. One-electron redox potentials can in principle be obtained by electrochemical methods, such as cyclic voltametry. Reliable data presuppose, however, reversible or quasireversible processes and a reasonable lifetime of the radical. None of these conditions are met by the phenolates. The phenoxy radical is more easily oxidized than the phenolate. The second oxidation will be followed by irreversible hydrolysis to yield hydroquinones. In addition, at high current densities, the phenoxyl radicals will rapidly undergo coupling reactions yielding biphenylic compounds. Pulse radiolysis makes use of the rapid establishment of equilibrium between the phenoxyl/phenolate couple and a reliable reference pair. The technique is discussed in ref 19. It will be noted that the present method is the liquid-phase analogue of the pulsed electron beam high pressure mass spectrometer technique utilized in ref 3. Admittedly, the latter technique yields very reliable values for electron and proton affinities of gaseous compounds.

We consider the general electron-transfer reactions

$$A^{\bullet} + D^{-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^{-} + D^{\bullet} \qquad K = k_f/k_r$$

or

$$(A)_2^{\bullet -} + D^{-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2A^{-} + D^{\bullet}$$

where $A^{\bullet}$, $(A_2)^{\bullet -}$, $D^{\bullet}$, A^{-}, and D^{-} signify the acceptor and donor radicals and their parent anions. In a few cases the radicals will be anions or cations and the parents neutral. We assume further that the optical measurements are performed at wavelengths were $D^{\bullet}$ absorbs much stronger than $A^{\bullet}$, $(A_2)^{\bullet -}$, or vice versa, whereas A^{-} and D^{-} are transparent. If the measurements are normalized to the same dose and the concentrations of A^{-} and D^{-} are in excess of those of the radicals the following relationships are obtained:

$$(OD_e - OD^0(A^{\bullet}))^{-1} = (OD^0(D^{\bullet}) - OD^0(A^{\bullet}))^{-1}(1 + K^{-1}[A^-]/[D^-]) \tag{Ia}$$

or

$$(OD_e - OD^0((A_2)^{\bullet -}))^{-1} = (OD^0(D^{\bullet}) - OD^0((A_2)^{\bullet -}))^{-1}(1 + K^{-1}[A^-]^2/[D^-]) \tag{Ib}$$

$$\ln (OD_e - OD(t)) = \ln (OD_e - OD(0)) - k_{exp}t \tag{II}$$

$$k_{exp} = k_f[D^-] + k_r[A^-] \tag{IIIa}$$

or

$$k_{exp} = k_f[D^-] + k_r[A^-]^2 \tag{IIIb}$$

Here, OD_e, $OD(t)$, and $OD(0)$ denote the optical densities at equilibrium, at time t, and at zero time (i.e. immediately after the electron pulse). $OD^0(A^{\bullet})$ or $OD^0((A)_2^{\bullet -})$ and $OD^0(D^{\bullet})$ are the initial optical densities measured if only A^- or D^- is present in the solution. Equations Ia and Ib simplify further if one of the radicals is completely transparent at the working wavelength. By varying the concentration of A^- and D^- the equilibrium constant K was obtained either directly from appropriate plots derived from eq I or as the ratio of k_f to k_r with the latter extracted from plots according to eq II and III. Typical plots utilizing eq I and III are presented in Figure 1. The above measurements are the more reliable the faster equilibrium is attained. This is because radical recombination reactions are always in competition with the equilibration. If the latter becomes too slow, the "final" level starts sloping and thus the true equilibrium absorbance becomes somewhat uncertain. Alternatively, the dose has to be diminished whence the signals become too weak to be reliable.

Most measurements were done by having the $ClO_2^{\bullet}/ClO_2^-$ couple equilibrate with the different phenoxy/phenolate couples. The kinetics of equilibration was monitored optically at wavelengths where the phenoxy radical absorbed much more than $ClO_2^{\bullet}$ (for $ClO_2^{\bullet}$ λ_{max} = 360 nm and ϵ_{max} = 1250 M^{-1} cm^{-1}).[18] In cases where different phenolates were run against each other the monitoring wavelength corresponded to the maximum difference in extinction coefficient of the phenoxy radicals. In experiments where a phenolate was run against I^-, SCN^-, or 1-methyl-indole the measurements were made at the λ_{max} for the oxidized radicals of the latter compounds. Spectral information about them is found in ref 20 and 21. For the sake of clarity we present in Figure 2 the spectra of some representative phenoxyl radicals. The spectra of $PhO^{\bullet}$, 4-Me-$PhO^{\bullet}$, and $Tyr^{\bullet}$ are very similar to that of 4-F-$PhO^{\bullet}$ and are not presented here. Also omitted are the spectra of 4-$COCH_3$-$PhO^{\bullet}$ and 4-CN-$PhO^{\bullet}$ which closely resemble that of 4-CO_2^--$PhO^{\bullet}$. Spectral information about other phenoxyl radicals that are studied in this work but do not occur in Figure 2 are available from ref 5, 8, and 9.

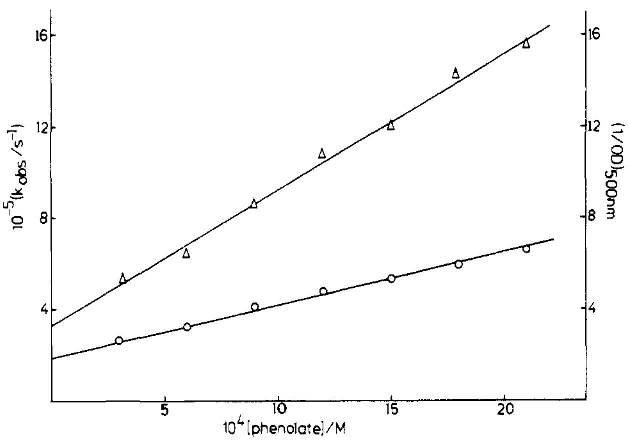

Figure 1. Measured rate constant of and stationary optical density at 500 nm after equilibration in the reaction $PhO^{\bullet}$ + 4-I-PhO^- ⇌ PhO^- + 4-I-$PhO^{\bullet}$ as a function of the phenol concentration: (Δ) rate constants; (○) inverse optical densities. Conditions: pH 11.5, 2 × 10^{-3} M 4-I-PhO^-, 0.1 M N_3^-, N_2O saturated.

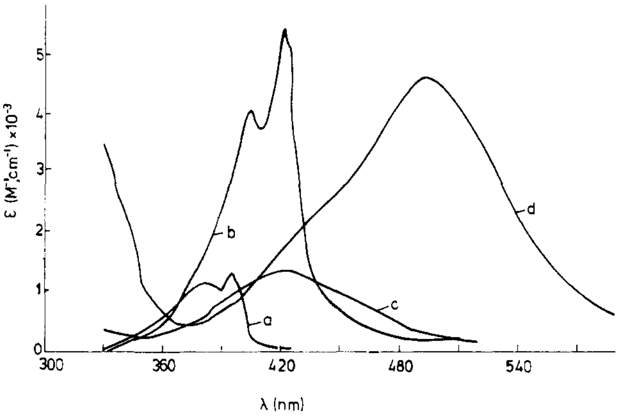

Figure 2. Spectra of phenoxy radicals: (a) 4-F-$PhO^{\bullet}$; (b) 4-Cl-$PhO^{\bullet}$; (c) 4-CO_2^--$PhO^{\bullet}$; and (d) 4-I-$PhO^{\bullet}$.

It is noted that traversing the series F, Cl, Br, I the spectra of the phenoxyl radicals become more and more red shifted and the oscillator strength increases. Interestingly, the spectrum of the 4-I-$PhO^{\bullet}$ radical is reminiscent of a charge-transfer band of an arene/I_2 complex.

Results and Discussion

Table I compiles rate and equilibrium constants determined in this work. It is seen that the equilibrium constants determined kinetically or thermodynamically are in good agreement. Also, the measurements are internally consistent. When running 4-iodophenolate against 4-chlorophenolate the kinetics of equilibration could not be observed as the $N_3^{\bullet}$ radical produced the corresponding phenoxyl radicals close to their equilibrium concentrations. When the redox potential of 4-nitrophenolate was studied the spectrum of the phenoxyl radical cound not be obtained being masked by the strong absorbance of 4-nitrophenolate itself.

The One-Electron Reduction Potentials. In order to determine E° vs NHE the experimentally determined equilibrium constants have to be anchored to established reference potentials. E° values

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Table I. Equilibrium Constants and Rate Constants for Equilibration

A	D	nm	k (M^{-1} s^{-1})		K		I^b
			k_f	k_r	k_f/k_r	OD^a	
			$A^\bullet + D^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^- + D^\bullet$				
$ClO_2^\bullet$	Ph	402	3.5×10^7	1.3×10^5	270	300	1
$ClO_2^\bullet$	4-Me-Ph	412	2.4×10^8	2×10^4	12000	10000	1
$ClO_2^\bullet$	4-F-Ph	396	5.1×10^7	7×10^4	730	700	1
$ClO_2^\bullet$	4-Cl-Ph	420	2.5×10^7	9×10^4	280	200	0.2
$ClO_2^\bullet$	4-Br-Ph	430	1.7×10^7	1.8×10^5	94	120	0.2
$ClO_2^\bullet$	4-I-Ph	500	3.5×10^7	2.8×10^5	125	110	0.2
$ClO_2^\bullet$	4-I-Ph	500	2.8×10^7	1.9×10^5	150	160	1
$ClO_2^\bullet$	4-Ac-Ph	445	1.4×10^6	1.2×10^7	0.11	0.08	1
Ph	4-Me-Ph	412	1.3×10^9	2×10^7	65	84	0.1
Ph	tyr	416	4.9×10^8	2.8×10^7	18	21	0.5
Ph	4-I-Ph	500	1.6×10^8	6×10^8	0.27	0.4	0.1
4-I-Ph	4-F-Ph	500	1.4×10^9	9×10^7	16	12	0.1
4-I-Ph	4-Cl-Ph	500				2	0.1
4-I-Ph	4-Br-Ph	500	$\sim 7 \times 10^8$	$\sim 7 \times 10^8$	1	1.1	0.1
4-I-Ph	4-CO_2^--Ph	500	7×10^7	2.2×10^9	0.032	0.042	0.1
4-Me-Ph	4-MeO-Ph	425	1.4×10^9	5.5×10^6	255	250	0.2
1-Me-Ind	4-NO_2-Ph	580	$\sim 1.1 \times 10^9$	$\sim 3 \times 10^8$	3.7	1.7	0.1
$N_3^\bullet$	1-Me-Ind	580	$\sim 10^{10}$	$\sim 5 \times 10^7$	200	150	0.1
					K		
A	D	nm	k_f, M^{-1} s^{-1}	k_r, M^{-2} s^{-1}	k_f/k_r	OD^a	I^b
			$(A_2)^{\bullet-} + D^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2A^- + D^\bullet$				
$(SCN)_2^{\bullet-}$	4-NO_2-Ph	500	1.4×10^7	5.2×10^5	27	20	0.5
$(SCN)_2^{\bullet-}$	1-Me-Ind	475	4.9×10^8	2×10^6	245	105	0.5
$(I_2)^{\bullet-}$	4-CN-Ph	385	7×10^4	1×10^6	0.07	0.1	1

[a] The equilibrium constant K as determined from optical density measurements utilizing eq 1a or 1b. [b] Ionic strength (M).

Table II. One-Electron Reduction Potentials in Volt vs NHE

species	$E°$	ref	$E°$ (this work)	$E°$ (pH 7)
$ClO_2^\bullet$	0.936 ± 0.003	22		
$(SCN)_2^{\bullet-}$	1.331 ± 0.008	23		
$I_2^{\bullet-}$	1.06 ± 0.01	23		
$N_3^\bullet$	1.33 ± 0.02	24, 25		
1-Me-Ind$^{\bullet+}$	1.23	26	1.20 ± 0.02	
4-O^--PhO$^\bullet$	0.023	5, 27		0.46
4-OH-PhO$^\bullet$	0.454	5, 27		0.46
4-$(CH_3)_2N$-PhO$^\bullet$	0.174	5		0.36
4-NH_2-PhO$^\bullet$	0.217	5		0.42
4-OCH_3-PhO$^\bullet$			0.54 ± 0.02	0.72
PhO$^\bullet$	0.80	26	0.79 ± 0.01	0.97
4-CH_3-PhO$^\bullet$			0.68 ± 0.02	0.87
tyrosyl$^\bullet$			0.71 ± 0.02	0.89^a
4-F-PhO$^\bullet$			0.76 ± 0.02	0.93
4-Cl-PhO$^\bullet$			0.80 ± 0.02	0.94
4-Br-PhO$^\bullet$			0.82 ± 0.02	0.96
4-I-PhO$^\bullet$			0.82 ± 0.01	0.96
4-CO_2^--PhO$^\bullet$			0.90 ± 0.02	1.04
4-$COCH_3$-PhO$^\bullet$			1.00 ± 0.02	1.06
4-CN-PhO$^\bullet$			1.12 ± 0.03	1.17
4-NO_2-PhO$^\bullet$			1.22 ± 0.06	1.23

[a] Assuming that the protonation state of the side chain is independent on whether it is attached to a phenol or a phenoxy radical.

for couples used as references in this work are presented in Table II alongside $E°$ values of the phenoxyl/phenolate couples studied. Whenever a phenolate is run against both ClO_2 and another phenolate we judge the inter-phenolate measurements more reliable (even though the discrepancy does not amount to more than ca. 20 mV). This is because the rate of equilibration between phenolates is more rapid than that with ClO_2, the reason being the much higher self-exchange rate constants of the PhO$^\bullet$/PhO$^-$ couples ($k_{ex} \sim 2 \times 10^8$ M^{-1} s^{-1})[8] as compared to[26] $k_{ex} \sim 3 \times 10^4$ M^{-1} s^{-1} for $ClO_2^\bullet/ClO_2^-$. The largest error occurred in the determination of $E°$ for 4-nitrophenolate. The values obtained against $(SCN)_2^{\bullet-}$ or the 1-methylindolyl cation differ by ca 70 mV. While we believe the lower value to be more accurate (SCN^- may complex the phenoxyl radical) we cannot be sure and therefore present $E°$ as the average of the two measurements.

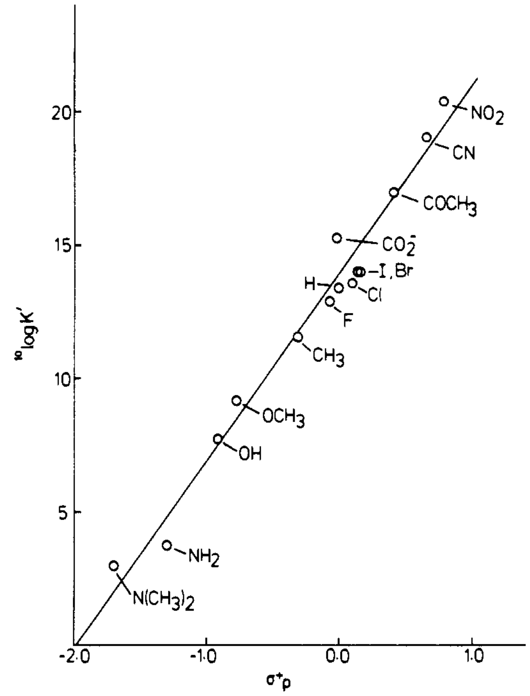

Figure 3. Hammett plot of log $K' = E°/0.059$ versus σ^+_p values where $E°$(V) is the one-electron reduction potential of 4-substituted phenoxy radicals vs NHE.

In Figure 3 the normalized reduction potentials of several phenoxyl radicals are plotted against σ^+_p values with the latter taken from ref 28. Considering that more than 1 V is covered

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Table III. Calculated Upper Limits to Bond Dissociation Energies D(O–H) and Electron Affinities (EA) of Phenols[a]

subst	pK_a[b]	D(O–H) calc[c]	D(O–H) lit.[d]	(PA–IP(H))[e] lit.	EA calc
4-H	10.0	88.2 ± 0.3	86.5 ± 1.9	33.3[f]	54.9[g]
4-CH_3	10.3	86.1 ± 0.5	86.5 ± 3.1	34.6,[f] 34.4[h]	51.6
4-OCH_3	10.1	82.6 ± 0.5	86.5 ± 3.1	34.1,[f] 34.5[h]	48.3
tyrosine	10.1	86.5 ± 0.5			
4-F	9.9	87.4 ± 0.5	86.5 ± 3.1	30.7,[f] 31.0[h]	56.6
4-Cl	9.4	87.6 ± 0.5	86.5 ± 3.1	26.7,[f] 27.4[h]	60.6
4-Br	9.4	88.1 ± 0.5			
4-I	9.3	87.9 ± 0.3			
4-CO_2^-	9.4	89.9 ± 0.5			
4-$COCH_3$	8.0	90.3 ± 0.5			
4-CN	7.9	92.9 ± 0.7		15.6,[f] 16.7[h]	76.8
4-NO_2	7.1	94.2 ± 1.4		12.4[h]	81.8
4-O^-	11.4	72.4			
4-OH	9.9	80.2		34.5[h]	45.7
4-$(CH_3)_2N$	10.1	74.1		35.4[h]	38.7
4-NH_2	10.4	75.5	88.0 ± 3.1	37.5,[f] 36.6[h]	38.5

[a] All quantities are given in kcal/mol. [b] Reference 29. [c] The error limit given accounts for the accuracy of the present experiments including the errors in the redox references and pK_a values used. [d] The tabulated values are taken from ref 33. In ref 34 the following D(O–H) values in kcal/mol were measured for some 4-substituted phenols: H, 84.0; Cl, 84.4; *t*-Bu, 82.1; MeO, 78.1. [e] The electron affinities are calculated from the formula $D(O–H) = EA(PhO^•) + PA(PhO^-) - IP(H)$ where PA and IP(H) denote respectively the proton affinity of the phenolate and the ionization potential of the hydrogen atom. [f] Reference 3. [g] In ref 10 the electron affinity of the phenoxy radical is measured to be 54.4 kcal/mol. [h] Reference 4.

the plot has a good linearity with a correlation coefficient of 0.985. The slope corresponds to a ρ^+ value of 7.0. The correlation between $E°$ and σ^+_p suggests that the dipolar phenoxyl radical is stabilized by partial transfer of negative charge from the substituent to the radical site.

O–H Bond Strengths and Electron Affinities of Phenoxyl Radicals

In the following thermodynamic analysis the standard states used refer throughout to 1 M in the aqueous phase (aq) and 1 atm of pressure (fugacity 1) in the gaseous phase (g).

Combining the aqueous redox potentials with pK_a values[29] one can calculate $\Delta G°$ for reaction 1.

$$PhOH(aq) \rightarrow PhO(aq) + \tfrac{1}{2}H_2(g) \qquad (1)$$

$$\Delta G°_1 = 23.06E° + 1.363\ pK_a$$

The calculation of the gaseous bond dissociation energy, D(O–H), i.e. $\Delta H°_2$ for reaction 2

$$PhOH(g) \rightarrow PhO^•(g) + H^•(g) \qquad (2)$$

requires the following additional reactions.

$$\tfrac{1}{2}H_2(g) \rightarrow H^•(g) \qquad (3)$$

$$PhOH(aq) \rightarrow PhOH(g) \qquad (4)$$

$$PhO^•(aq) \rightarrow PhO^•(g) \qquad (5)$$

We obtain $\Delta H_2° = \Delta G°_1 + \Delta G°_3 - \Delta G°_4 + \Delta G°_5 + T\Delta S°_2$.

The value for $\Delta G°_3$ is equal to 48.55 kcal/mol,[30] and $\Delta S°_2$ can be written as $S°(H^•) + \Delta S°(PhO^•–PhOH)$. The well-established value of $S°(H^•)$ is 27.5 cal/mol/K.[30] From the literature we calculate $\Delta S°(PhO^•–PhOH)$ for phenol to be −1.43 cal/mol/K.[31,32] This value, which at 298 K contributes only −0.43 kcal/mol to $\Delta H_2°$, will be assumed to hold for all the 4-substituted phenols as well. As the generation of $PhO^•$ from PhOH in water implies the loss of a hydrogen bond we expect PhOH to be more strongly solvated than $PhO^•$. Therefore, $\Delta G°_{solv} = \Delta G°_5 - \Delta G°_4$ is surely negative. Regardless of the exact value of $\Delta G°_{solv}$ it is expected to be a local property of the OH group and thus insensitive to the substituent in the 4 position. The D(O–H) values in Table III are calculated by setting $\Delta G°_{solv}$ to zero. Consequently, the values presented in Table III can be viewed as safe upper limits to D(O–H) (within the small experimental uncertainties indicated). By approximating the effect of the unpaired electron to that of a CH_3 group[35] we are sure to underestimate the solvation energy of the phenoxy radical. Therefore $\Delta G°_{(solv)}(\text{anisole}) - \Delta G°_4 = -5.4$ kcal/mol. Schwarz and Dodson[36] have concluded that for H_2O and alcohols the loss of a hydrogen atom diminishes the solvation by 2–3 kcal/mol, the average strength of a hydrogen bond. This line of reasoning has been adopted in ref 37 for phenol. Perusal of the literature, in particular ref 34, suggests that the safest value of the D(O–H) of unsubstituted phenol is 85 ± 1 kcal/mol. If so, $\Delta G°_{solv}$ turns out as −3 ± 1 kcal/mol, which seems to support the suggested value in ref 36 and 37. Thus, the true absolute D(O–H) values of the substituted phenols are probably ca. 3 kcal/mol lower than the upper limits compiled in Table III. Inspecting the table it is seen that the trend in the few bond strengths reported by Griller et al.[34] is in good agreement with our own. This is evidence for the correctness of the assumption that $D(O–H) = \text{constant} + \Delta G°_1$. In the above work of the OH bond strengths were found to correlate with σ^+_p. In our case, the derived D(O–H) values correlate also very nicely with σ^+_p, yielding the equation

$$D(O–H)_{max} = 87.7 + 8.07\sigma^+_p \ (r = 0.984)$$

The finding that both the reduction potentials of the phenoxyl radicals and the bond strengths of the phenolic O–H bonds relate equally well with σ^+_p is readily understood if one considers that ca. 85% of the variation of D(O–H) with the substituent is made up of the variation of the $E°$ values while only 15% is accounted for by the change in the acidities. It is seen in Table III that our calculated D(O–H) values are well within the spread given in ref 33. The only apparent exception is 4-aminophenol, where we suspect the literature value to be incorrect.

In conclusion we believe that the substituent-dependent trend in the tabulated D(O–H) values is significant within 1 kcal/mol. A similar reasoning applied to the calculated gaseous electron affinities that are presented in the last entry of Table III.

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Registry No. 4-OCH_3-$PhO^•$, 6119-32-0; $PhO^•$, 2122-46-5; 4-CH_3-$PhO^•$, 3174-48-9; 4-F-$PhO^•$, 2145-21-3; 4-Cl-$PhO^•$, 3148-13-8; 4-Br-$PhO^•$, 63125-13-3; 4-I-$PhO^•$, 63125-16-6; 4-CO_2^--$PhO^•$, 52467-44-4; 4-$COCH_3$-$PhO^•$, 54560-34-8; 4-CN-$PhO^•$, 41071-24-3; 4-NO_2-$PhO^•$, 41071-23-2; PhOH, 108-95-2; 4-CH_3-PhOH, 106-44-5; 4-OCH_3-PhOH, 150-76-5; 4-F-PhOH, 371-41-5; 4-Cl-PhOH, 106-48-9; 4-Br-PhOH, 106-41-2; 4-I-PhOH, 540-38-5; 4-CO_2^--PhOH, 456-23-5; 4-$COCH_3$-PhOH, 99-93-4; 4-CN-PhOH, 767-00-0; 4-NO_2-PhOH, 100-02-7; 4-O^--PhOH, 20217-26-9; 4-OH-PhOH, 123-31-9; 4-$(CH_3)_2N$-PhOH, 619-60-3; 4-NH_2-PhOH, 123-30-8; tyrosyl, 124177-81-7.

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