Bond Dissociation Energies of O−H Bonds in Substituted Phenols from Equilibration Studies

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Bond dissociation energies (BDE) of several phenolic compounds have been determined by studying the equilibration of couples of phenols and of the corresponding phenoxyl radicals by means of EPR spectroscopy. Measurements were carried out in highly concentrated solutions submitted to continuous photolysis in the presence of di-*tert*-butyl peroxide. Since under this experimental condition the decay of the phenoxyl radicals was slower than the hydrogen transfer reaction from phenols to phenoxyls, equilibrium concentrations of the two radicals were actually measured. Due to the fact that the radical species are continuously generated in solution, phenols giving short-lived phenoxyl radicals could also be investigated by this method. All of the examined phenols are characterized by O−H bonds weaker than that of the parent compound, PhOH, and their BDE values can be calculated to a good approximation by an additive rule using fixed contributions for the various substituents. Only in the case of the sterically crowded 4-methoxytetramethylphenol (**5b**), where the *p*-methoxy substituent is compelled to stay out of the plane of the aromatic ring, is the experimental BDE remarkably different from the calculated value.

In a previous paper, we reported the determination of the O−H homolytic bond dissociation energies (BDE) in four substituted phenols of particular interest as antioxidants including α-tocopherol.[1] The values of these important thermochemical parameters were obtained by measuring, by means of EPR spectroscopy, the equilibrium constant, K_1, for the reaction between galvinoxyl (G$^\bullet$) and each of these phenols (eq 1) using as reference compound 2,4,6-tri-*tert*-butyl phenol whose BDE value is known from calorimetric studies.[2,3]

$$G^\bullet + ArOH \rightleftharpoons GH + ArO^\bullet \qquad (1)$$

The determination of K_1 was straightforward when the oxidation of the phenols, ArOH, reacting with galvinoxyl gave highly persistent phenoxyl radicals that did not decay appreciably during the recording of the EPR spectrum of the reaction mixture. With other phenoxyls, where the occurrence of other reactions such as reversible formation of dimers or disproportionation caused slow decay of the EPR signals, the equilibrium constants were obtained by performing careful kinetic analyses of the time evolution of the equilibrating species.

With respect to other techniques employed for the determination of bond dissociation energies, the EPR-based method presents the advantage of greater accuracy since even relatively large errors in the measurement of radical concentrations, and therefore, of K_1, give rise to small errors in the BDEs because of the logarithmic relation connecting these two quantities. It should, however, be emphasized that since the bond dissociation energies obtained by this method are all referred to the 81.24 kcal mol^{-1} value reported for 2,4,6-tri-*tert*-butylphenol,[2] their absolute values depend on the accuracy of the above measure and may be subject to changes.

A disadvantage of the above technique is that it can hardly be applied to the determination of BDE values of phenols affording by oxidation short-lived phenoxyl radicals. In these cases mixing of the reactants leads to the formation of radicals not surviving for the length of time needed to record an EPR spectrum of the mixture. This problem can be overcome by making use of the "radical buffer" method originally proposed by Hiatt and Benson[4] for the determination of the heats of formation of alkyl radicals. The approach used in the present work is similar to that described by Griller and co-workers[5] and consists of generating the equilibrating phenoxyl radicals by continuous photolysis. It has the advantage with respect to the procedure followed by Colussi *et al.*[6] and by Jackson *et al.*,[7] who generated the phenoxyls by reaction with galvinoxyl or diphenylpicrylhydrazyl, that phenols giving very short-lived radicals can be investigated as well.

We report here the determination of the O−H bond dissociation energies of phenols **1**−**6b**.

Results and Discussion

Radical Buffer. Bond dissociation energies are determined by measuring the equilibrium constants for the hydrogen transfer reaction (eq 5) taking place between couples of phenols and of the corresponding phenoxyl

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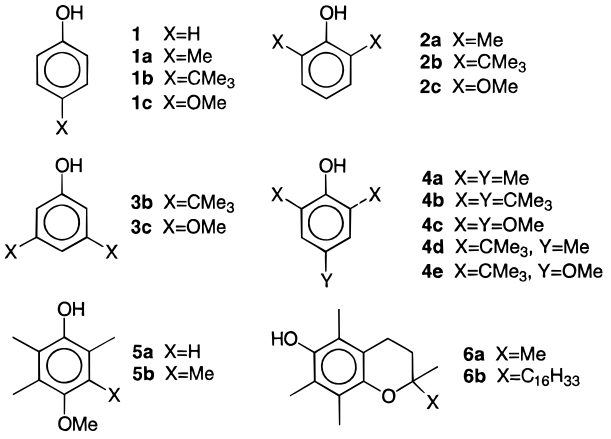

radicals. These are generated, within the cavity of an EPR spectrometer, by continuous photolysis of deoxygenated benzene solutions containing two phenols (see Figure 1), characterized by BDE values differing at most by 2.5 kcal mol^{-1}, and by the radical photoinitiator di-*tert*-butyl peroxide. The overall reaction scheme is described in eqs 2−8.

$$\mathrm{BuOOBu} \xrightarrow{h\nu} 2\mathrm{BuO}^{\bullet} \tag{2}$$

$$\mathrm{BuO}^{\bullet} + \mathrm{Ar_1OH} \rightarrow \mathrm{BuOH} + \mathrm{Ar_1O}^{\bullet} \tag{3}$$

$$\mathrm{BuO}^{\bullet} + \mathrm{Ar_2OH} \rightarrow \mathrm{BuOH} + \mathrm{Ar_2O}^{\bullet} \tag{4}$$

$$\mathrm{Ar_1O}^{\bullet} + \mathrm{Ar_2OH} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{Ar_1OH} + \mathrm{Ar_2O}^{\bullet} \tag{5}$$

$$2\mathrm{ArO}^{\bullet} \rightleftharpoons \text{dimers} \tag{6}$$

$$2\mathrm{ArO}^{\bullet} \xrightarrow{k_t} \text{products} \tag{7}$$

$$\text{dimers} \rightarrow \text{products} \tag{8}$$

The molar ratio of the two phenoxy radicals $[Ar_2O^{\bullet}]/[Ar_1O^{\bullet}]$ is obtained from the EPR spectra either by double integration of appropriate lines or by comparison with computer-simulated spectra when the lines from the two species strongly overlap. The equilibrium constant, K_5, is determined by introducing in eq 9 the initial concentrations of the phenols $[Ar_1OH]_0$ and $[Ar_2OH]_0$. In order to ensure that at the time of measurement, i.e., a few minutes after the start of irradiate the solution, no significant phenol depletion has occurred, high concentrations of the reactants (0.1−1 M) were used.

$$K_5 = \frac{[\mathrm{Ar_1OH}][\mathrm{Ar_2O}^{\bullet}]}{[\mathrm{Ar_1O}^{\bullet}][\mathrm{Ar_2OH}]} \tag{9}$$

Of course, this approach can only be applied if the hydrogen transfer reaction (eq 5) takes place rapidly relative to the decay of the phenoxyl (eqs 6−8), so that the equilibrium concentrations of the two radicals are actually measured. To check if this was the case, different experimental conditions were employed by changing either the initial absolute concentrations of the phenols and their ratios or the rate of initiation by partially cutting off the light with metal sectors of different diameters or by changing the amount of added peroxide. Actually, in each of these measurements we obtained, within experimental error, the same value of the equilibrium constant for a given couple of compounds.

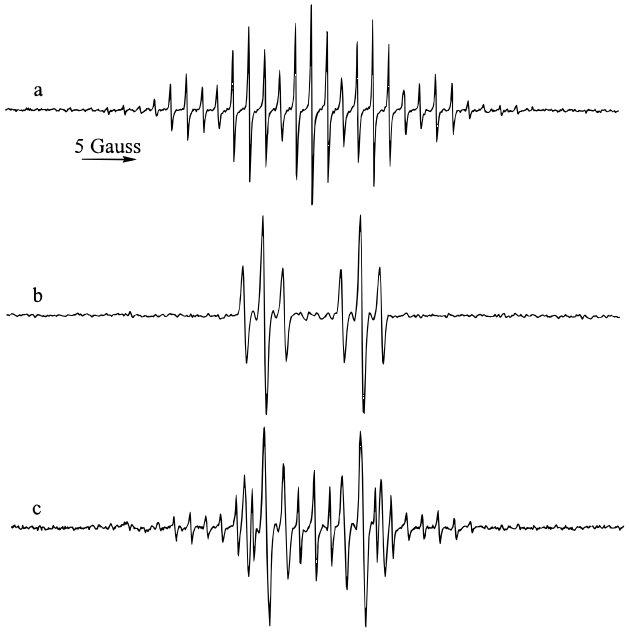

Figure 1. Room-temperature EPR spectra observed under continuous irradiation of deoxygenated benzene solutions of di-*tert*-butyl peroxide and (a) 4-methoxytetramethylphenol (**5b**), (b) 2,6-di-*tert*-butylphenol (**2b**), and (c) a mixture of **5b** (0.12 M) and **2b** (0.72 M).

Further support for the assumption that reaction 5 is faster than the decay of the equilibrating radicals is provided by the values recently measured by Ingold and co-workers[8] of the rate constants for the hydrogen transfer from some phenolic antioxidants to the phenoxyl radical, $C_6H_5O^{\bullet}$. This reaction has been found to be unexpectedly fast with values of k_5^{293K} as large as 1.1×10^9 M^{-1} s^{-1} for α-tocopherol and 8.4×10^7 M^{-1} s^{-1} for ubiquinol-10 in benzene solution. Also, the reactivity of phenoxyl radicals toward hindered phenols is surprisingly high; for instance, 4-methoxyphenoxyl in PhCl abstracts the hydroxylic hydrogen of 2,4,6-tri-*tert*-butylphenol with a rate constant of 4.75×10^5 M^{-1} s^{-1} at 333 K.[9] Given the radical concentration of ca. 10^{-5}−10^{-6} M, and given the rate constant for the self-reaction of 4-methoxyphenoxyl of 3.4×10^7 M^{-1} s^{-1} in benzene,[10] the decay of the equilibrating species is computed to be more than 2 orders of magnitude slower than the hydrogen transfer reaction provided the initial concentrations of the phenols are ca. 0.1 M or more.

When couples of phenols substituted at all *para* and *ortho* positions were studied, the EPR measurements were straightforward since clean and intense spectra of the two phenoxyl radicals were usually obtained under irradiation. On the other hand, with phenolic derivatives lacking at least one *ortho* or *para* substituent, EPR spectra of secondary radical species growing up with time were almost invariably observed. These were dimeric and polymeric aroxyls resulting from oxidation of the head to tail combination product of the primarily formed phenoxyls as exemplified in eq 10 for an *ortho*-substituted

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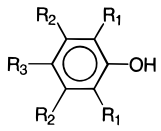
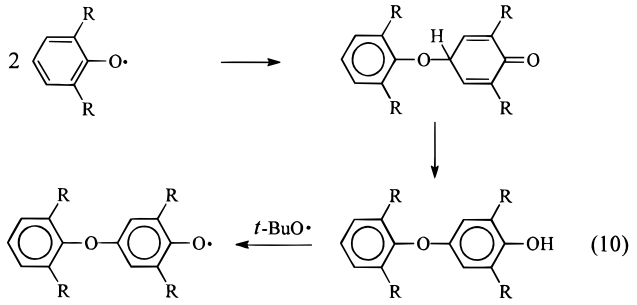
Table 1. Bond Dissociation Energies of Substituted Phenols



ArOH	R_1	R_2	R_3	n^a	BDE_{exp}/ (kcal mol^{-1})	BDE_{calc} (kcal mol^{-1})
1	H	H	H	3	88.3 ± 0.8	87.6
1a	H	H	Me	2	86.2 ± 0.6	85.9
1b	H	H	CMe_3	2	85.3 ± 0.5	85.7
1c	H	H	OMe	0	82.81 ± 0.21	83.2
2a	Me	H	H	1	84.50 ± 0.38	84.1
2b	CMe_3	H	H	0	82.80 ± 0.21	82.8
2c	OMe	H	H	0	83.16 ± 0.15	83.7
3b	H	CMe_3	H	1	86.62 ± 0.26	86.6
3c	H	OMe	H	2	86.7 ± 0.3	86.7
4a	Me	H	Me	1	82.73 ± 0.18	82.4
4b	CMe_3	H	CMe_3		81.24[b]	80.9
4c	OMe	H	OMe	0	80.00 ± 0.12	79.3
4d	CMe_3	H	Me	0	81.02 ± 0.13	81.1
4e	CMe_3	H	OMe	0	78.31 ± 0.13	78.4
5a	Me	H, Me	OMe	1	79.20 ± .15	79.2
5b	Me	Me	OMe	1	81.88 ± 0.20	78.7
6a	HPMC			1	78.25 ± 0.18	78.7
6b	α-tocopherol			1	78.23 ± 0.25	78.7

[a] The index *n* indicates if the BDE difference with respect to tri-*tert*-butylphenol (**4b**) has been determined directly (0) or through the intermediation of one (1), two (2), or three (3) other phenols. [b] Reference compound; see ref 2.



(10)

phenol. A study on the nature of these species has been reported elsewhere.[11]

Since these secondary aroxyls are quite persistent, they accumulate in solution and their spectra gradually replace those of the transient primary radicals. Thus, when performing equilibration studies, care had to be taken to avoid misassignments of the EPR signals, and the irradiated solutions were changed as often as possible.

The measured bond dissociation energies for the examined phenolic compounds are reported in Table 1. These values are indeed free energies rather than free enthalpies for the dissociation reaction of the O−H bond. Since, however, the entropic contribution to the free energy change for the equilibration reaction 5 has been found to be very small for several couples of phenols,[1] the ΔS has been neglected in all cases.

The reported data cover the range 78−88 kcal mol^{-1}, the higher values being found for phenol, PhOH (88.3 kcal mol^{-1}), and the lower one for α-tocopherol (78.23 kcal mol^{-1}). The agreement with the values previously reported by us and determined by equilibration with galvinoxyl[1] is good (differences are 0.32, 0.21, and −0.70 kcal mol^{-1} for **4d**, **4e**, and **6b**, respectively). With α-tocopherol (**6b**) the difference, larger than in the other two cases, could be due to the fact that in our previous paper this compound was a commercial product used as received. In fact, it has been recently shown by Bowry and Ingold[12] that commercial α-tocopherol contains a very minor impurity that can accelerate the decay of the α-tocopheroxyl radical; this might have resulted in a miscalculation of the equilibrium constant for the reaction of **6b** with galvinoxyl. In the present case this impurity was instead carefully removed before performing any measurement.[13]

A point worthy of comment is the magnitude of the experimental error that becomes larger as the BDE difference from the value of the chosen standard (81.24 kcal mol^{-1} for **4b**) becomes greater. This is due to the fact that direct equilibration with **4b** could only be performed with those phenols whose BDE values differ by 2.5 kcal mol^{-1} at most from that of the standard (**4b**); these, in turn, were used as reference substrates for measuring the BDE's of other phenols. Thus, a greater number of steps required for a given determination results in a larger experimental error.

Effect of Substituents on the ArO−H Bond Strengths. Table 1 and its pictorial equivalent (Figure 2) show how important the number and the nature of the substituents are in determining the strength of the ArO−H bond in phenols; actually, the measured BDE values span a range of 10 kcal mol^{-1} on passing from phenol to α-tocopherol. All the substituents taken into account in the present investigation produce a weakening of the O−H bond by preferentially stabilizing the phenoxyl and/or destabilizing the phenol as the result of electronic and steric factors.[14−18] Thus, *ortho*-substituted phenols are destabilized by the steric repulsion between the hydroxyl group and the substituent, especially when the latter is as bulky as a *tert*-butyl group.[19] Electronic factors are instead important in determining the O−H bond strength in phenols containing substituents that may conjugate with the aromatic system. Thus, electron-donating substituents are expected to weaken the O−H bond by a combination of effects, i.e., the destabilization of the phenol (see structures B) and the stabilization of the phenoxy radical due to the delocalization of the unpaired electron in the substituent (D), while electron acceptors are expected to stabilize both species (see B and D).

It is also apparent from Table 1 that, similar to what has been reported by other authors,[15−17] the decrease of the bond strength due to a given substituent is roughly constant in the variously substituted phenols. By using a multivariable minimization procedure we derived the contribution, ΔBDE(X), for each group in the *ortho*, *meta*,

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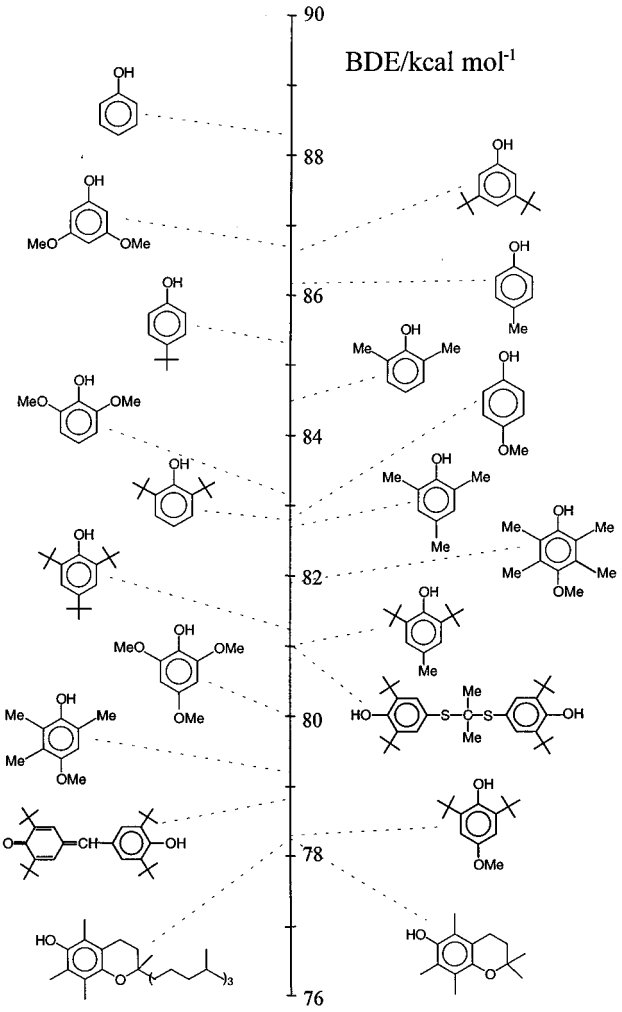
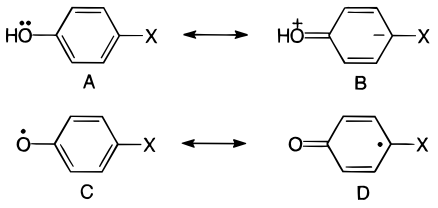


Figure 2. Experimental bond dissociation energy values for substituted phenols.



and *para* positions. These values are reported in Table 2, while the bond strengths calculated from them by means of eq 11 are shown in the last column of Table 1.

$$\mathrm{BDE}(C_6H_{5-n}X_nOH) = \mathrm{BDE}(C_6H_5OH) + \sum_i^n \Delta\mathrm{BDE}(X) \quad (11)$$

The agreement between experimental and calculated BDE's is reasonably good except for 4-methoxytetramethylphenol (**5b**), where the bond strength is 3.2 kcal mol^{-1} larger than the calculated value. This discrepancy is certainly due to an anomalous behavior of the 4-methoxy substituent that for steric reasons adopts the conformation where the 2p-type lone pair on oxygen is nearly perpendicular[14] to the symmetry axis of the $2p_z$ orbital on the *para* carbon atom. In this geometry conjugation between oxygen and the aromatic ring cannot take place, and both the stabilization of the phenoxyl and the destabilization of the phenol by the *para* methoxy substituent are substantially reduced. The contribution of the OMe group to the bond strength of **5b** results to be −1.2 instead of the −4.4 kcal mol^{-1} value reported in Table 2. On the other hand, in 2,3,6-trimethyl-4-methoxyphenol (**5a**), differing from **5b** only for the absence of one of the two *meta* substituents, the calculated and the experimental BDE values are coincident (79.20 kcal mol^{-1}) and much lower than in **5b** (81.88 kcal mol^{-1}). This, of course, is due to the fact that, in **5a**, the methoxy group lies coplanar with the aryl ring and can therefore conjugate with the aromatic π system.

Table 2. Additive Contributions (ΔBDE/ kcal mol^{-1}) for Calculating the BDE Values in Substituted Phenols[a]

substituent	*ortho* (two groups)	*meta* (two groups)	*para*
Me	−3.5	−1.0	−1.7
CMe_3	−4.8	−1.0	−1.9
OMe	−3.9	−0.9	−4.4

[a] The BDE value for phenol (87.6 kcal mol^{-1}) to be used in eq 11 was also obtained by the minimization procedure employed to derive the group contributions.

An other point worthy of mention is that both HPMC (**6a**) and α-tocopherol (**6b**) show experimental BDE values in good agreement with those calculated with the additive rule of eq 11. This means that these two compounds behave as a hypothetical 4-methoxytetramethylphenol where the methoxy substituent lies on the plane of the aromatic ring; they adopt this geometry particularly favorable to the conjugation between the phenolic ring and the oxygen lone pair, because of the presence of the condensed six-membered ring, as has been widely discussed in the literature.[6,7,14] These data suggest that, from a thermodynamic point of view, α-tocopherol has nothing special except the right structure to maximize the interactions responsible for weakening the O−H bond.

For phenolic compounds, containing *ortho* methyl substituents, for which no direct determination was known, Ingold and co-workers estimated the bond dissociation energy values from the measured rate constants for the reaction of the phenols with peroxy radicals (eq 12) by means of eq 13.

$$\mathrm{ROO}^\bullet + \mathrm{ArOH} \rightarrow \mathrm{ROOH} + \mathrm{ArO}^\bullet \quad (12)$$

$$D[\mathrm{ArOH}]\ (\mathrm{kcal/mol}) = 100.4 - 3.07 \log(k_{12}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) \quad (13)$$

Equation 13 implies that the BDE's should vary linearly with the logarithm of the rate constant k_{12}. To check this assumption, we plotted the bond strength obtained in the present work against the log k_{12} values reported for several *ortho*-disubstituted phenols.[14] Figure 3 shows that the data lie on two straight lines: one for the phenols containing methyl substituents and the other for phenols containing *tert*-butyl substituents. The correlation obtained in the former case and expressed by eq 14 is rather good (r = 0.987), and the derived coefficients are reasonably close to those of eq 13, while for the phenols *ortho* disubstituted with *tert*-butyl groups the correlation is given by eq 15.

$$D[\mathrm{ArOH}]\ (\mathrm{kcal/mol}) = 97.44 - 2.93 \log(k_{12}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) \quad (14)$$

$$D[\mathrm{ArOH}]\ (\mathrm{kcal/mol}) = 92.97 - 2.90 \log(k_{12}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) \quad (15)$$

It is remarkable that the two lines show the same slope

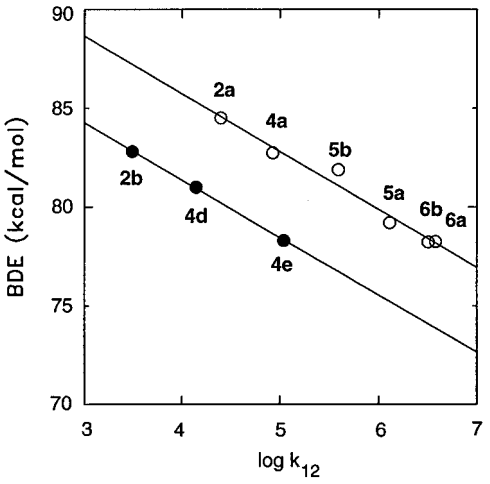


Figure 3. Bond dissociation energies, BDE's, of phenolic compounds against the logarithm of the rate constant for their reaction with peroxy radicals (eq 12) taken from ref 14. Empty and filled circles indicate phenols containing methyl (○) or *tert*-butyl (●) *ortho* substituents, respectively.

and that, for the same BDE values, the rate constants of inhibition k_{12} of the *o,o*-di-*tert*-butylphenols are 30 times lower than those of the *o,o*-dimethyl phenols. This difference emphasizes the importance of steric crowding about the hydroxylic group in decreasing the reactivity of phenols toward peroxy radicals and therefore in reducing their effectiveness as antioxidants.

Experimental Section

Materials. Phenol (**1**), 4-methylphenol (**1a**), 4-*tert*-butylphenol (**1b**), 4-methoxyphenol (**1c**), 2,6-dimethylphenol (**2a**), 2,6-di-*tert*-butylphenol (**2b**), 2,6-dimethoxyphenol (**2c**), 3,5-di-*tert*-butylphenol (**3b**), 3,5-dimethoxyphenol (**3c**), 2,4,6-trimethylphenol (**4a**), 2,4,6-tri-*tert*-butylphenol (**4b**), 2,6-di-*tert*-butyl-4-methylphenol (**4d**), 2,6-di-*tert*-butyl-4-methoxyphenol (**4e**), and α-tocopherol (**6b**) were commercial products used as such unless otherwise specified. 2,3,6-Trimethyl-4-methoxyphenol[20] (**5a**) and 6-hydroxy-2,2,5,7,8-pentamethylchroman[21] (HPMC) (**6a**) were prepared as described in the literature. α-Tocopherol was purified before use by column chromatography on silica gel.[13]

2,3,5,6-Tetramethyl-4-methoxyphenol (**5b**) was obtained from duroquinone and trimethyl phosphite by using a procedure similar to that described to prepare the analogous 2,3,5,6-tetramethyl-4-ethoxyphenol:[22] yield 56%, crystallized from aqueous ethanol: mp 112−113 °C; ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 6H, ArCH_3), 2.25 (s, ArCH_3), 3.67 (s, 3H, OCH_3), 4.52 (s, 1H, OH, D_2O exchanged); *m/z* 180 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$ (180.25): C, 73.30; H, 8.95. Found C, 73.23; H, 8.89.

2,4,6-Trimethoxyphenol (**4c**) was prepared by initial lithiation of trimethoxybenzene. To a vigorously stirred solution of 1,3,5-trimethoxybenzene (30 mmol), anhydrous TMEDA (30 mmol), and anhydrous ethyl ether (20 mL) cooled to 0 °C was gradually added a 1.2 M solution of buthyllithium in hexane (33 mmol) under argon; stirring was continued at the same temperature for 1 h. The resulting mixture was then poured dropwise at −10 °C into a solution of trimethyl borate (30 mmol) in anhydrous ethyl ether (10 mL). When the addition was complete the mixture was stirred for ca. 5 h at the same temperature and then treated with a solution of 30% hydrogen peroxide (5.8 mL) and glacial acetic acid (2.3 mL). The mixture was kept under stirring for 24 h at the same temperature and treated with a mixture of KOH (50 mmol), water (5 mL), and methanol (20 mL). The product was filtered and poured into water. This solution was washed with ethyl ether, acidified with aqueous 10% hydrochloric acid, extracted with ethyl ether, and dried (Na_2SO_4). The ethyl ether was evaporated, and the crude product was crystallized from ethanol: yield 61%; mp 63 °C; ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3H, OCH_3), 3.87 (s, 6H, OCH_3), 5.12 (s, 1H, OH, D_2O exchanged), 6.19 (s, 2H, Ar*H*); *m/z* 184 (M^+). Anal. Calcd for $C_9H_{12}O_4$ (184.19): C, 58.69; H, 6.57. Found: C, 58.58; H, 6.50.

EPR Spectra. EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with a Hewlett-Packard 5350B microwave frequency counter for the determination of the *g*-factors, which were corrected with respect to that of perylene radical cation in concentrated H_2SO_4 (g = 2.002 58). Photolysis was carried out by focusing the unfiltered light from a 500-W high-pressure mercury lamp on the EPR cavity. The temperature was controlled with a standard variable-temperature accessory and was monitored before and after each run with a copper−constantan thermocouple. Relative radical concentrations were determined by comparing the double integrals of at least two lines of the equilibrating phenoxyls or, when strong line overlap was present, by comparison of the digitized experimental spectra with computer simulated ones. In these cases an iterative least-squares fitting procedure based on the systematic application of the Monte Carlo method was performed in order to obtain the experimental spectral parameters of the two species including their relative intensities.

The couples of phenols investigated to derive the series of BDE values are the following ones: **1−1a**; **1a−2a**; **1a−3b**; **1a−3c**; **1b−3b**; **1c−2a**; **1c−2b**; **1c−2c**; **1c−4a**; **1c−4b**; **1c−4d**; **2a−2b**; **2a−2c**; **2a−3c**; **2a−4a**; **2b−2c**; **2b−3b**; **2b−4a**; **2b−4b**; **2b−5b**; **2c−4a**; **2c−4b**; **2c−4d**; **3b−3c**; **4a−4b**; **4a−4d**; **4b−4d**; **4b−4e**; **4c−4e**; **4d−6a**; **4d−6b**; **4e−5a**; **4e−6b**.

EPR Spectral Parameters of Phenoxy Radicals. Phenoxyl from **1**: a_o(2H) 6.57 G, a_m(2H) 1.84 G, a_p(1H) 10.07 G, g = 2.0047; **1a**: a_o(2H) 6.32 G, a_m(2H) 1.56 G, a(Me) 11.99 G, g = 2.0047; **1b**: a_o(2H) 6.24 G, a_m(2H) 1.96 G, a(CMe_3) 0.44 G, g = 2.0046; **1c**: a_o(2H) 5.57G, a_m(2H) 0.70 G, a(OMe) 1.81 G, g = 2.0049; **2a**: a(2Me) 6.75 G, a_m(2H) 1.94 G, a_p(1H) 9.48 G, g = 2.0047; **2b**: a(2CMe_3) 0.07 G, a_m(2H) 1.95 G, a_p(1H) 9.72 G, g = 2.0047; **2c**: a(2OMe) 1.31G, a_m(2H) 1.72 G, a_p(1H) 8.33 G, g = 2.0048; **3b**: a_o(2H) 6.51 G, a(2CMe_3) ∼0 G, a_p(1H) 10.34 G, g = 2.0048; **3c**: a_o(2H) 5.77 G, a(2OMe) 0.40 G, a_p(1H) 12.20 G, g = 2.0046; **4a**: a(2Me) 6.30 G, a_m(2H) 1.63 G, a(1Me) 10.96 G, g = 2.0046; **4b**: a(2CMe_3) ∼0 G, a_m(2H) 1.71 G, a(1CMe_3) 0.38 G, g = 2.0046; **4c**: a(2OMe) 1.09 G, a_m(2H) 0.95 G, a(1OMe) 1.19 G, g = 2.0050; **4d**: a(2CMe_3) ∼0 G, a_m(2H) 1.67 G, a(1Me) 11.20 G, g = 2.0046; **4e**: a(2CMe_3) ∼0 G, a_m(2H) 0.93 G, a(OMe) 1.53 G, g = 2.0047; **5a**: a(1Me) 6.36 G, a(1Me) 4.29 G, a(1Me) 1.53 G, a(1H) 0.90 G, a(1OMe) 0.90 G, g = 2.0048; **5b**: a(2Me) 6.18 G, a(2Me) 1.59 G, a(OMe) ∼0 G g = 2.0047; **6a**: a(1Me) 6.03 G, a(1Me) 4.54 G, a(1Me) 0.90 G, a(2H) 1.49 G, g = 2.0048; **6b**: a(1Me) 6.10 G, a(1Me) 4.65 G, a(1Me) 1.02 G, a(2H) 1.60 G, g = 2.0048.

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