

ACIDITIES AND HOMOLYTIC BOND DISSOCIATION ENTHALPIES OF 4-SUBSTITUTED-2,6-DI-*TERT*-BUTYLPHENOLS

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Equilibrium acidities and estimates of homolytic bond dissociation enthalpies (*BDEs*) in DMSO of the O–H bonds for α -tocopherol, 2,6-di-*tert*-butylphenol, six 4-substituted-2,6-di-*tert*-butylphenols, and ten related phenols are reported. The presence of a 2,6-di-*tert*-butyl group in a phenol increases its acidity and makes substituent effects on the acidity caused by a *para* electron-withdrawing group larger. The *BDEs* of the O–H bonds in 2,4,6-tri-*tert*-butylphenol, 4-methoxy-2,6-di-*tert*-butylphenol, 4-methyl-2,6-di-*tert*-butylphenol and α -tocopherol, estimated by combining their pK_{HA} values with the oxidation potentials of the conjugate anions, $E_{ox}(A^-)$, according to the equation $BDE = 1.37pK_{HA} + 23.1E_{ox}(A^-) + C$ have been found to agree to within 2 kcal mol⁻¹ with literature values (1 kcal = 4.184 kJ). Introduction of 2,6-di-*tert*-butyl groups into phenol and six 4-substituted phenols weakens the O–H bonds by amounts ranging from 3.6 to 10.3 kcal mol⁻¹. These effects are attributed to increases in ground-state energies which introduce strains that are relieved when homolytic cleavage of the O–H bond forms an oxygen-centered radical where the odd electron can be delocalized into the benzene ring.

INTRODUCTION

We have developed a simple method of estimating homolytic bond dissociation enthalpies (*BDEs*) of weak organic acids by combining the pK_{HA} values of their acidic H–A bonds with the oxidation potentials of their conjugate anions, $E_{ox}(A^-)$, both measured in DMSO solution:

$$BDE = 1.37pK_{HA} + 23.1E_{ox}(A^-) + C \quad (1)$$

The *BDEs* for the acidic C–H bonds in 14 hydrocarbons and for 12 hydrocarbons containing one or more heteroatoms using this method have been shown to give *BDEs* that agree with literature values to ± 3 kcal mol⁻¹ (1 kcal = 4.184 kJ) or better.¹ Although the method has been used to estimate *BDEs* for the O–H bonds in 38 phenols² and 37 oximes,³ the paucity of *BDE* literature values for O–H bonds has limited comparisons with the *BDEs* obtained by other methods. The *BDE* estimated for the O–H bond for phenol (90 kcal mol⁻¹) agrees well with a value of 88 kcal mol⁻¹ obtained by a similar method in aqueous solution,⁴ but is 3–5 kcal mol⁻¹ higher than the best gas-phase value (85 \pm 1 kcal mol⁻¹).⁵ (Henceforth kcal mol⁻¹ will be abbreviated as kcal). The relative effects of substituents on *BDEs* of phenols obtained by equation (1) agree

remarkably well, however, with those obtained in four other investigations.²

It was of interest to extend our acidity and *BDE* studies to 2,6-di-*tert*-butylphenols and related compounds, for several reasons. First, although 2,6-dimethyl and 4-*tert*-butyl groups cause a small decrease in the acidity of phenol, 2,6-di-*tert*-butylphenol and 2,4,6-tri-*tert*-butylphenol are slightly more acidic than phenol in DMSO. It was therefore of interest to carry out additional acidity studies. Second, there has been considerable interest in 2,6-dialkylphenols because of their antioxidant properties, and the *BDEs* of the O–H bonds in 2,4,6-tri-*tert*-butylphenol and α -tocopherol have been shown to be about 10 kcal lower than that of phenol. It was desirable to check these values by our method and to extend the studies to additional examples.

RESULTS AND DISCUSSION

The acidity and *BDE* data for 4-substituted 2,6-di-*tert*-butylphenols and related phenols are summarized in Table 1.

Equilibrium acidities

Examination of entries 1–4 in Table 1 shows that the presence of 4-Me, 2,6-diMe, or 4-*t*-Bu groups in phenols

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Table 1. Acidities and *BDEs* of the O–H bonds in 4-substituted 2,6-di-*tert*-butyl- and related phenols

Phenol	pK_{HA}^a	ΔpK_{HA}	$E_{ox}(A^-)^c$	<i>BDE</i> ^d	ΔBDE
C ₆ H ₅ OH	18.0 ^b	(0.0)	–0.325	89.9	(0.0)
4-MeC ₆ H ₄ OH	18.9 ^b	–0.9	–0.428	88.7	1.2
2,6-Me ₂ C ₆ H ₃ OH	18.5 ^b	–0.5	–0.492	87.3	2.6
4- <i>t</i> -BuC ₆ H ₄ OH	19.05 ^b	–1.0	–0.435	89.3	0.6
2,6- <i>t</i> -Bu ₂ C ₆ H ₃ OH	17.3 ^b	0.7	–0.619	82.7	7.2
4-Me-2,6- <i>t</i> -Bu ₂ C ₆ H ₂ OH	17.73	0.3	–0.755 ^R	80.1	9.8
2,4,6- <i>t</i> -Bu ₃ C ₆ H ₂ OH	17.8 ^b	0.2	–0.665 ^R	82.3	7.6
4-Et-2,6- <i>t</i> -Bu ₂ C ₆ H ₂ OH	17.71	0.3	–0.758 ^R	80.0	9.8
4-MeOC ₆ H ₄ OH	19.1 ^b	–1.1	–0.618	85.2	4.7
4-MeO-2,6- <i>t</i> -Bu ₂ C ₆ H ₂ OH	18.2	–0.2	–0.806 ^R	79.6	10.3
4-PhC ₆ H ₄ OH	17.1 ^b	0.9	–0.370	88.2	1.7
2,4,6-Ph ₃ C ₆ H ₂ OH	14.1	3.9	0.334 ^R	84.9	5.0
4-PhCOC ₆ H ₄ OH	13.4 ^b	4.6	0.062	93.1	–3.2
4-MeOCO-2,6- <i>t</i> -Bu ₂ C ₆ H ₂ OH	11.90	6.1	–0.229 ^R	84.3	5.6
4-NO ₂ C ₆ H ₄ OH	10.8 ^b	7.2	0.314	95.3	–5.4
4-NO ₂ -2,6-Me ₂ C ₆ H ₂ OH	9.95	8.0	0.147	96.3	–0.4
4-NO ₂ -2,6- <i>t</i> -Bu ₂ C ₆ H ₂ OH	7.3	10.7	0.127 ^R	86.2	3.6
α -Tocopherol	20.2	–2.2	–0.870	80.9	9.0

^a In pK_{HA} units, equilibrium acidities measured in DMSO solution.

^b Ref. 2.

^c Measured by cyclic voltammetry using the method previously described,¹ and referenced to the ferrocene/ferrocenium couple (0.875 V on our instrument). The cyclic voltammograms labeled with a superscript R are reversible at ordinary scan rates (100 mV s^{–1}).

^d In kcal mol^{–1}, estimated using equation (1). The values are 0.6 kcal mol^{–1}, higher than those in Ref. 2 because $C = 73.3^1$ instead of 72.7 kcal mol^{–1} has been used.

causes small decreases in acidity, but the introduction of 2,6-di-*t*-Bu leads to small increases in acidities. The introduction of the 2,6-di-*tert*-butyl groups into these phenols must lead to a large steric inhibition of solvation in the 2,6-di-*tert*-butylphenoxide ions. Ordinarily, one would expect inhibition of solvation of the anion to cause a sizable decrease in acidity. Evidently, introduction of the 2,6-di-*tert*-butyl groups into phenol must lead to a large acid-strengthening effect that overshadows the acid-weakening effect of desolvation. We believe that the acid-strengthening effect is due primarily to a sizable increase in the ground-state energies (*GSEs*) of these phenols relative to that of phenol.

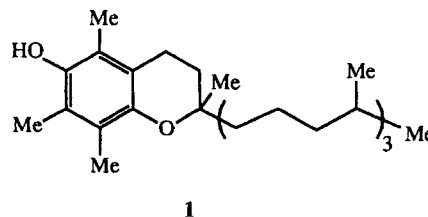
The introduction of 2,6-di-*tert*-butyl groups into 4-methoxyphenol also causes an increase in acidity for the same reason (entries 9 and 10).

The introduction of 2,6-diphenyl groups into 4-phenylphenol (entries 11 and 12) also causes an increase in acidity, which we believe to be due, at least in part, to increases in *GSEs*.

4-Phenylcarbonylphenol is 4.6 pK_{HA} units more acidic than phenol (entry 13). We do not have data for 4-phenylcarbonyl-2,6-di-*tert*-butylphenol, but the data for 4-methoxycarbonyl-2,6-di-*tert*-butylphenol (entry 14) can serve as an approximate model. Here we see that the acidity is increased by 1.5 units relative to that of 4-phenylcarbonylphenol (the effect would be expected to be larger relative to 4-methoxycarbonylphenol).

The acidity of phenol is increased by 7.2 pK_{HA} units by the introduction of a 4-nitro group (entry 15). Introduction of 2,6-dimethyl groups into 4-nitrophenol increases the acidity by only an additional 0.8 unit, but introduction of 2,6-di-*tert*-butyl groups causes a 3.5 pK_{HA} unit increase in acidity (entry 17). Here too we believe that the increases in acidities are due to increases in *GSEs*.

α -Tocopherol (1) is 2.2 pK_{HA} units less acidic than phenol (entry 18). This difference is expected from a summation of the acid-weakening effects of two *o*-Me (0.5), two *m*-R (0.4) and one RO (*ca* 1.1) = 2.0 pK_{HA} units.



A comparison of the slope of a Hammett-type plot of pK_{HA} values versus σ^- for 4-substituted-2,6-di-*tert*-butylphenols (Figure 1) with that of a similar plot for comparable 4-substituted phenols (Figure 2) serves to illustrate the enhancing effects that the 2,6-di-*tert*-butyl groups have on the acidifying effects of 4-substituents. The steeper slope in Figure 1 is understandable in terms of a large steric inhibition of solvation of the

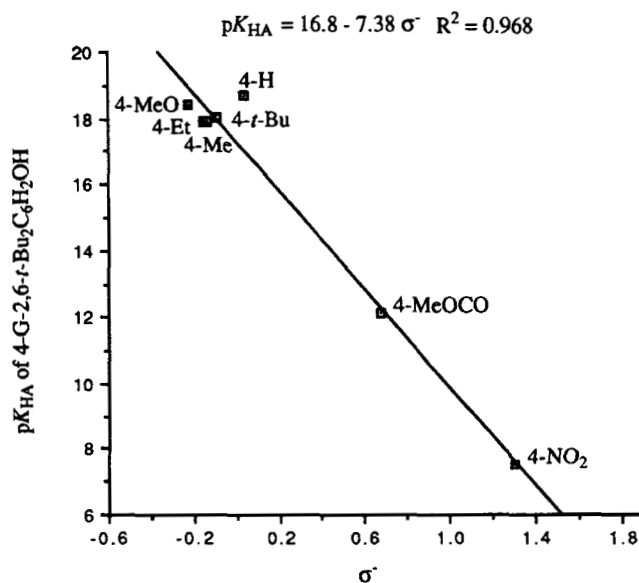


Figure 1. Hammett plot of the equilibrium acidities of 4-substituted-2,6-di-*tert*-butylphenols versus σ^- constants

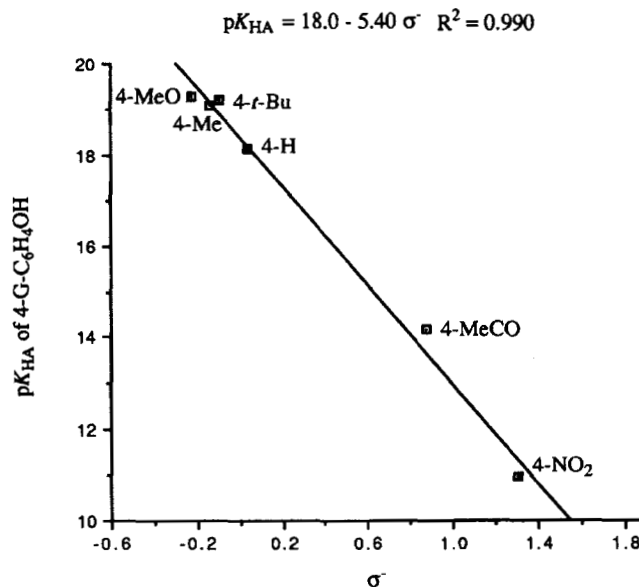


Figure 2. Hammett plot of the equilibrium acidities of 4-substituted phenols versus σ^- constants

phenoxide ion by the 2,6-di-*tert*-butyl groups, which causes an increased negative charge to be transferred from the phenoxide ion to the benzene ring. Note, for example, that the nitro group in 4-nitro-2,6-di-*tert*-butylphenol increases the acidity of 2,6-di-*tert*-butylphenol by 10 pK_{HA} units (13.7 kcal), whereas the nitro group in 4-nitrophenol increases the acidity of phenol by only 7.2 pK_{HA} units (9.86 kcal).

Comparisons of homolytic $BDEs$ of O–H bonds with literature values

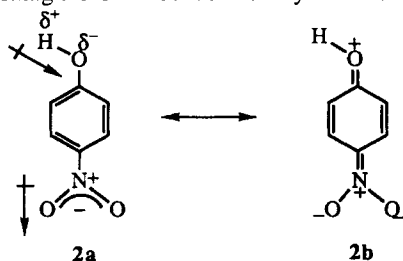
The BDE values for 4-substituted-2,6-di-*tert*-butyl- and related phenols are summarized in Table 1. The $BDEs$ relative to that of phenol itself, i.e. $\Delta BDEs$, given in the last column are believed to provide estimates of the relative radical stabilization energies ($RSEs$) of the

corresponding phenoxyl radicals, following the usual practice.⁶

A direct calorimetric method has been developed for measuring the *BDEs* of O–H bonds in weak acids forming oxygen-centered radicals on homolytic cleavage that are stable for many hours in concentrated solutions at room temperature and undergo clean, rapid, exothermic and reversible reactions with a suitable hydrogen atom donor.^{7a} The method has been applied successfully to measure the *BDEs* for several O–H bonds, including those in 2,4,6-tri-*tert*-butylphenol, di-*tert*-butyl ketoxime and *tert*-butyl-1-adamantyl ketoxime.^{7b} We have recently shown that the *BDEs* obtained using equation (1) for these two ketoximes in DMSO are in good agreement with those obtained using the direct calorimetric method in benzene.⁸ The *BDE* of the O–H bond for 2,4,6-tri-*tert*-butylphenol in DMSO using equation (1) is 82.3 kcal (Table 1), which is also in good agreement with that obtained in benzene by the direct calorimetric method (81.2 kcal).^{7b} The *BDE* of the O–H bond in α -tocopherol (**1**) has been estimated by kinetic measurements combined with a Polanyi-type correlation to be 80.4 kcal.⁹ The *BDE* of the O–H bond in α -tocopherol in DMSO estimated using equation (1) is 80.9 kcal, which is in excellent agreement with that obtained earlier.⁹

Effects of 4-substituents and 2,6-di-*tert*-butyl substituents on *BDEs* of phenols

Earlier work has shown that the *BDEs* of the O–H bonds in phenols are sensitive to the effects of substituents in the benzene ring.² 4-Donor substituents decrease the *BDE* of the O–H bond in phenol in the following order (kcal in parentheses): *t*-Bu (0.6) < Me (1.2) < Ph (1.7) < MeO (4.7) < HO (7.7) < Me₂N (9.0) < H₂N (12) < O[−] (16). 4-Acceptor substituents increase the *BDEs* in the order Br (0.3) < PhCO (2.0) < MeCO (2.3) < CN (3.8) < NO₂ (4.2) < MeSO₂ (4.6) < 4-CF₃ (4.9).² The bond-weakening effect of 4-donors has been associated with their ability to stabilize the corresponding radicals by delocalization.² A recent analysis suggests that the bond-strengthening effects of 4-acceptors is associated with their undergoing dipole–dipole stabilizing interactions with the OH group (e.g. **2a** ↔ **2b**) that decrease the ground-state energy of the undissociated phenol and thereby lead to strengthening of the O–H bond.¹⁰ This rationalization follows that of Clark and Wayner¹¹ for the effect of 4-acceptors in strengthening the C–Br bonds in benzyl bromides.



A plot of the *BDEs* of *m*- and *p*-acceptor substituents vs Hammett σ constants for 3-COMe, 4-COMe, 3-CN, 4-CN, 3-NO₂ and 4-NO₂ (Figure 3) is linear with a slope of 6.1. The points for hydrogen and the weak donor substituents 4-Me, 4-*t*-Bu and 4-Br also fit the plot (Figure 3). Stronger *p*-donors (4-O[−], 4-NH₂, 4-HO, 4-MeO and 4-Ph) have weak electron-withdrawing abilities, but strong radical-stabilizing abilities, and tend to form a separate line with a much steeper slope.¹⁰

It is noteworthy that, whereas the Hammett pK_{HA} plots (Figures 1 and 2) involving phenols require σ^- constants for strong electron-withdrawing groups, such as 4-NO₂, the Hammett *BDE* plot involving radicals (Figure 3) accommodates an ordinary σ_p for NO₂ because the 4-NO₂C₆H₄O[•] radical is poorly solvated.

Effects of 2,6-di-*tert*-butyl groups on the *BDEs* of phenols

The weakness of the O–H bond in 2,4,6-tri-*tert*-butylphenol relative to that in phenol itself ($\Delta BDE = 7.2$ kcal) has long been known.^{7a} It seems certain that steric congestion around the hydroxyl group is in some way responsible for this decrease, and a calculation of the heat of the isodesmic reaction of 2,4,6-tri-*tert*-butylphenol (**3**) with benzene to give 1,3,5-tri-*tert*-butylbenzene and phenol (Scheme 1) as being $\Delta H^\circ = -8.2$ kcal^{7a} shows that relief of this steric strain is indeed exothermic. Also, the rotation of the hydroxyl group in **3** has been shown to be severely hindered,¹² but the *tert*-butyl group in the corresponding phenoxyl radical is freely rotating.¹³ Nevertheless, the radical is clearly sterically hindered since it has a long enough lifetime on the electrode to allow reversal of the cyclic voltammetric sweep, and this is true also for the other 4-substituted 2,6-di-*tert*-butylphenoxyl radicals, including the radical derived from **3**.

Functional groups weaken bonds by increasing the electron density in the bond and strengthen the bond by decreasing the electron density. These effects are reflected in the effects of functions on the corresponding radicals. Thus, donor groups such as R₂N, RO or Ph stabilize radicals by delocalizing the odd electron and Me₃N⁺ groups destabilize radicals. Groups with both donor and acceptor properties such as pyridinium and nitro have dual effects on radicals. Donor functions increase the electron densities (basicities) of remote or proximate anions and thereby cause cathodic (negative) shifts in their $E_{ox}(A^-)$ values. A structural change that causes a cathodic shift in $E_{ox}(A^-)$ values is therefore indicative of an increase in the electron density of the anion and a weakening of the precursor H–A bond. Examination of Table 1 shows that introduction of a 2,6-di-*tert*-butyl group into phenol increases the $E_{ox}(A^-)$ of the corresponding anion by 0.294 V or 6.8 kcal (entry 5). We suggest that this effect arises because the phenoxide ion loses solvation when the 2,6-di-*tert*-butyl groups are introduced, and its effective electron density is thereby increased. (Note, for example,

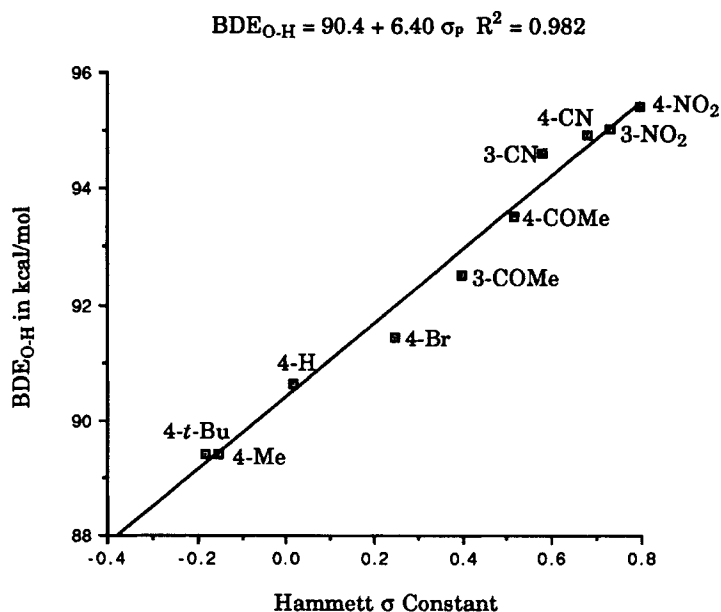
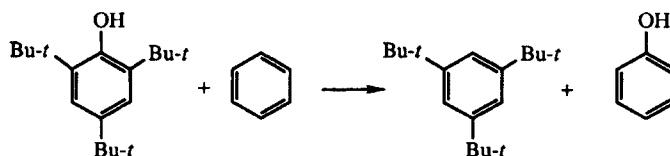


Figure 3. Hammett plot of the $BDEs$ of the $O-H$ bonds in phenols bearing 3- and 4-acceptor substituents vs σ



Scheme 1

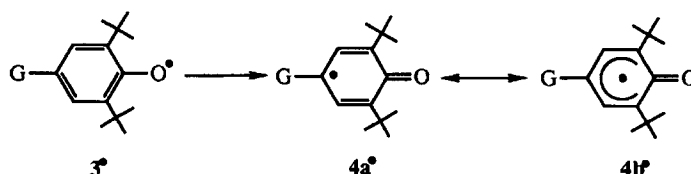
the increased electron density on the nitro group in 4-nitro-2,6-di-*tert*-butylphenol vs 4-nitrophenol.) The presence of the donor groups 4-Me, 4-*t*-Bu, 4-Et and 4-MeO increased the cathodic shifts by an additional 3.1, 1.1, 3.2 and 4.3 kcal, respectively. This leads to total bond-weakening (ΔBDE) effects for the $O-H$ bonds of 9.8, 7.6, 9.8 and 10.3 kcal, respectively, in these 4-substituted-2,6-di-*tert*-butylphenols (Table 1).

In addition, delocalization of the odd electron by conjugation into the benzene ring shortens the $C-O$ bond, and converts the oxygen-centered radical into a (more stable) hybrid oxygen-carbon-centered radical.

(Examination of the ESR spectrum of hybrid radicals of this type has shown that the spin density of the odd electron resides principally on carbon.¹⁴)

The $BDEs$ of the $O-H$ bonds in 4-methyl-2,6-di-*tert*-butylphenol, 4-methoxy-2,6-di-*tert*-butylphenol and α -tocopherol of 80.1, 79.6 and 80.9 kcal, respectively (Table 1), are in good agreement with the recently reported values of 80.7, 77.6 and 78.9 kcal, respectively, obtained by equilibrations with 2,4,6-tri-*tert*-butylphenol, $BDE = 81.2$ kcal, as a standard.¹⁵

Examination of Table 1 shows that α -tocopherol is less acidic than 4-methoxy-2,6-di-*tert*-butylphenol by



2 pK_{HA} units, and is evidently less subject to steric inhibition of solvation. Nevertheless, the cathodic shift of the oxidation potential of its anion is only 70 mV less and its O–H bond is only 1.3 kcal stronger. As Burton *et al.*⁹ have pointed out, the orientation of the *para* oxygen atom dictated by the ring structure in α -tocopherol (1) ensures favorable orbital overlap with the phenoxy radical formed.

The powerful electron-withdrawing (acceptor) effect of the *p*-nitro group in *p*-nitrophenol, together with a favorable dipole–dipole interaction between the OH and NO₂ groups, decreases the ground-state energy and causes a strengthening of the O–H bond (entry 15 in Table 1). The introduction of (donor) 2,6-di-*tert*-butyl groups raises the ground-state energy and reverses this trend. The net result is a 3.6 kcal weakening of the O–H bond (entry 17). The introduction of 2,6-di-*tert*-butyl groups into 4-methoxycarbonylphenol and of 2,6-diphenyl groups into 4-phenylphenol has similar effects.

The overall effects of these structural changes on *BDEs* conform to a general empirical rule that we have used as a working hypothesis which states that structural changes in weak organic acids that cause increases in ground-state energies will lead to decreases in the *BDEs* of the acidic H–A bonds and vice versa.¹⁶

In a recent related study, the *BDEs* of the O–H bonds in the ketoximes RR'C=NOH have been observed to decrease progressively over a 14 kcal range as the size of the R and R' groups increases from Me₂C=NOH to *t*-Bu(1-Ad)C=NOH. Here too the electron densities on the anions increase progressively,

as evidenced by a progressive cathodic shift in the $E_{ox}(A^-)$ values, and the O–H bonds are weakened by a combination of increases in ground-state energies of the weak acid and delocalization of the odd electrons in the corresponding radicals.⁸

CONCLUSION

The introduction of 2,6-di-*tert*-butyl groups into phenol, 4-*tert*-butylphenol, 4-methylphenol, 4-ethylphenol and 4-methoxyphenol has been observed to cause decreases in the *BDEs* (ΔBDE) of the O–H bonds of 7.2–10.3 kcal. The electron densities on the corresponding anions increase by a 4.3 kcal over this range, as shown by overall cathodic shifts of 0.187 V in the $E_{ox}(A^-)$ potentials. The weakening of these O–H bonds is attributed to increases in the ground-state energies together with stabilization of the corresponding radicals by delocalization of the odd electrons. A similar rationale is used to account for the 3.6 and 5.6 kcal $\Delta BDEs$ of 4-methoxycarbonyl- and 4-nitro-2,6-di-*tert*-butylphenols, respectively, the 5.0 kcal ΔBDE of 2,4,6-triphenylphenol and the 9 kcal ΔBDE of α -tocopherol. The agreement to within ± 2 kcal with literature values for three 4-substituted 2,6-di-*tert*-butylphenols and α -tocopherol adds credence to our simple method of estimating *BDEs* by using equation (1).

EXPERIMENTAL

All of the research samples were commercially available from Aldrich or Lancaster Synthesis. They were

Table 2. Equilibrium acidities of phenols determined by the overlapping indicator method^a

Compound	pK_{HA}	Indicator	pK_{in}^j	SD ^k	No. of runs	pK_{HA}
2,4,6-Triphenylphenol	14.45	HZF ^b	14.95	0.04	2	14.4
	14.5	HZFP2 ^c	14.15	0.05	2	
4-MeO-2,6- <i>t</i> -Bu ₂ -phenol	18.12	PFH ^d	17.9	0.01	2	18.2
	18.25	FMY30 ^e	18.1	0.01	1	
4-Me-2,6- <i>t</i> -Bu ₂ -phenol	17.73	PFH	17.9	0.02	2	17.7
	17.8	FMY30	18.1	0.02	1	
4-MeOCO-2,6- <i>t</i> -Bu ₂ -phenol	11.90	HZFO2 ^f	12.95	0.01	2	11.9
	11.89	HZFO2P ^g	11.98	0.01	1	
4-Et-2,6- <i>t</i> -Bu ₂ -phenol	17.71	PFH	17.9	0.005	1	17.7
	17.85	FMY30	18.1	0.012	1	
Vitamin E	20.16	CNAH ^h	18.9	0.03	1	20.1
	20.11	2NPANH ⁱ	20.6	0.02	1	

^a Ref. 17.

^b 9-Fluorenone, phenylhydrazine.

^c 9-Fluorenone, 4-chlorophenylhydrazine.

^d 9-Phenylfluorene.

^e 2-Phenylsulfonylfluorene.

^f 9-Fluorenone, 2-chlorophenylhydrazine.

^g 9-Fluorenone, 2,4-dichlorophenylhydrazine.

^h 4-Chloro-2-nitroaniline.

ⁱ 2-Naphthylacetonitrile.

^j pK_{HA} values of the indicators used.

checked for purity by ^1H NMR spectroscopy and by their physical properties. Equilibrium acidities in DMSO and oxidation potentials of the conjugate anions in DMSO were determined by the methods described previously.^{1a} Details of the acidity measurements are summarized in Table 2.

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REFERENCES

1. (a) F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, A. V. Satish and X.-M. Zhang, *J. Am. Chem. Soc.* **113**, 9790–9796 (1991); (b) F. G. Bordwell and X.-M. Zhang, *Acc. Chem. Res.* **26**, 510–517 (1993).
2. F. G. Bordwell and J.-P. Cheng, *J. Am. Chem. Soc.* **113**, 1736–1743 (1991).
3. F. G. Bordwell and G.-Z. Ji, *J. Org. Chem.* **57**, 3019–3025 (1992).
4. J. Lind, X. Shen, T. E. Eriksen and G. Merényi, *J. Am. Chem. Soc.* **112**, 479–482 (1990).
5. P. Mulder, O. W. Saastad and O. Griller, *J. Am. Chem. Soc.* **110**, 4090–4091 (1988).
6. (a) H. E. O'Neal and S. W. Benson, in *Free Radicals*, edited by J. I. Kochi, pp. 275–359. Wiley, New York (1973); (b) D. C. Nonhebel and J. C. Walton, *Free Radical Chemistry*, p. 102. Cambridge University Press, Cambridge (1974); (c) D. Griller and K. U. Ingold, *Acc. Chem. Res.* **13**, 493–532 (1980).
7. (a) L. R. Mahoney, F. C. Ferris and M. A. DaRouge, *J. Am. Chem. Soc.* **91**, 3883–3888 (1969); (b) L. R. Mahoney, G. D. Mendenhall and K. U. Ingold, *J. Am. Chem. Soc.* **95**, 8610–8614 (1973).
8. F. G. Bordwell and S. Zhang, *J. Am. Chem. Soc.* **117**, 4858–4861 (1995).
9. G. W. Burton, T. Duba, E. J. Gabe, L. Hughes, F. L. Lee and K. U. Ingold, *J. Am. Chem. Soc.* **107**, 7053–7065 (1985).
10. F. G. Bordwell, X.-M. Zhang, A. V. Satish and J.-P. Cheng, *J. Am. Chem. Soc.* **116**, 6605–6610 (1994).
11. K. B. Clark and D. D. M. Wayner, *J. Am. Chem. Soc.* **113**, 9363–9365 (1991).
12. M. Davis and L. Meakins, *J. Chem. Phys.* **26**, 1580 (1956).
13. K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi and H. Takaki, *Bull. Chem. Soc. Jpn.* **40**, 2731–2739 (1967).
14. G. A. Russell and J. Lokensgard, *J. Am. Chem. Soc.* **89**, 5059–5060 (1967); D. M. Camaioni, H. F. Walter and D. W. Pratt, *J. Am. Chem. Soc.* **95**, 4057–4059 (1973).
15. M. Lucarini, G. F. Pedulli and M. Cipollone, *J. Org. Chem.* **59**, 5063–5070 (1994).
16. (a) F. G. Bordwell, J. A. Harrelson, Jr., and T.-Y. Lynch, *J. Org. Chem.* **55**, 3337–3341 (1990); (b) F. G. Bordwell and A. V. Satish, *J. Am. Chem. Soc.* **114**, 10173–10176 (1992); (c) F. G. Bordwell, D. L. Singer and A. V. Satish, *J. Am. Chem. Soc.* **115**, 3543–3547 (1993); (d) F. G. Bordwell, X.-M. Zhang and R. Filler, *J. Org. Chem.* **58**, 6067–6071 (1993).
17. F. G. Bordwell, *Acc. Chem. Res.* **21**, 456–464 (1988), and references cited therein.