30.1 (d), 31.7 (d), 83.2 (d, OCHS), 126.1 (d), 127.8 (d), 128.5 (d), 128.8 (d), 128.9 (d), 129.0 (d), 129.8 (d), 133.3 (d), 134.4 (d), 129.8 (s), 131.0 (s), 136.3 (s), 136.6 (s), 172.5 (s, C=O); MS (70 eV) *m*/*z* (%) = 327 (2, $M^+ - PhS$), 314 (2, $M^+ - PhCO_2$), 251 (2), 225 (19), 193 (6), 115 (25), 105 (100), 77 (23).

Irradiation of α-Chloro Sulfide 4 in the Presence of Tributyltin Hydride. A solution of 2.50 g (8.59 mmol) of *n*-Bu_3SnH in 50 mL of petroleum ether (bp 30–50 °C) was cooled to −30 °C while passing a stream of dry nitrogen gas. After addition of 0.960 g (4.84 mmol) of α-chloro sulfide **4**, the solution was irradiated for 24 h at $\lambda \geq 300$ nm. The solvent was evaporated, and the residue was purified by double column chromatography on silica gel by eluting with a 1:4 CH_2Cl_2/petroleum ether (bp 30–50 °C) solvent mixture to yield 320 mg (79%) of (*E*,*Z*)-1-butenyl phenyl sulfide (**6**). The ^1H and ^{13}C NMR spectral data were consistent with those reported.[30]

Photoinitiated Addition of Bromotrichloromethane to Cyclopropylmethane Thiones 7a,b. Thione 7a. A solution of 204 mg (1.60 mmol) of dicyclopropylmethane thione[31] in 2 mL (20.3 mmol) of bromotrichloromethane was irradiated for 30 min at −10 °C with a 150-W sodium lamp, which resulted in complete decoloration of the thione **7a**. The ^1H NMR spectra of the crude product mixture showed complete consumption of the thione **7a** and consisted exclusively of 4-bromo-1-cyclopropyl-1-((trichloromethyl)thio)-but-1-ene (**8a**) as a 60:40 ratio of *E*,*Z* isomers. On purification by column chromatography on silylated silica gel by eluting with a 1:1 CH_2Cl_2/petroleum ether (bp 50–60 °C) solvent mixture 323 mg (83%) of the *E*,*Z* isomers as colorless oil was obtained. IR (neat, cm^{-1}) 3090, 3010, 2960, 1440, 1260, 1205, 960, 750, 710; ^1H NMR of (*Z*)-**8** (250 MHz, $CDCl_3$) δ 0.75 and 0.91 (m, 4 H, cyclopropyl-CH_2), 1.79 (m, 1 H, CH), 2.99 (td, $J = 6.8, 6.8$ Hz, 2 H, $=CH-CH_2$), 3.40 (t, $J = 6.8$ Hz, 2 H, CH_2Br), 6.48 (td, $J = 7.1, 1.5$ Hz, 1 H, $=CH-$); ^1H NMR of (*E*)-**8** (250 MHz, $CDCl_3$) δ 0.75 and 0.91 (m, 4 H, cyclopropyl-CH_2), 1.96 (m, 1 H, CH), 2.99 (td, $J = 6.8, 6.8$ Hz, 2 H, $=CH-CH_2$), 3.51 (t, $J = 6.8$ Hz, 2 H, CH_2Br). 6.15 (td, $J = 7.1, 1.2$ Hz, 1 H, $=CH-$); ^{13}C NMR (63 MHz, $CDCl_3$), δ 8.0 (t), 8.7 (t), 13.6 (d), 19.1 (d), 30.5 (t), 31.5 (t), 32.7 (t), 33.2 (t), 98.7 (s, CCl_3), 137.4 (s), 138.2 (s), 137.8 (d), 145.9 (d); MS (70 eV) *m*/*z* (%) = 324 (6) [M^+], 298 (3) [$M^+ - Cl$], 243 (2) [$M^+ - Br$], 205 (32) [$M^+ - CCl_3$], 125 (31), 93 (21), 85 (68), 77 (66), 65 (43), 39 (100). Anal. Calcd for $C_8H_{10}BrCl_3S$: C, 29.61; H, 3.11. Found: C, 29.62; H, 3.19.

Thione 7b. Following the above procedure, a solution of 19.9 mg (0.123 mmol) of thione **7b** in 0.5 mL (5.04 mmol) of bromotrichloromethane was irradiated at −10 °C for 40 min. The excess $BrCCl_3$ was removed by evaporation in 20 °C and 19 Torr, and the residue was taken up in $CDCl_3$ and analyzed by ^1H NMR spectroscopy. Thione **7b** was converted exclusively into the thioenol ether **8b**: ^1H NMR (250 MHz, $CDCl_3$) δ 3.22 (dt, $J = 7.0, 7.0$ Hz, 2 H, $=CH-CH_2$), 3.50 (t, $J = 7.0$ Hz, 2 H, CH_2Br), 6.63 (t, $J = 7.0$ Hz, 1 H, $=CH$), 7.39 (m, 5 H, aromatic H).

Control Experiments. Reaction of Benzoic Anhydride with Sulfoxide 2a. A mixture of 20.0 mg (0.111 mmol) of sulfide **2a** and 25.0 mg (0.111 mmol) of benzoic anhydride in 0.5 mL of $CDCl_3$ was allowed to stand at ca. 20 °C for 3 days. No reaction was detected by ^1H NMR spectroscopy.

Irradiation of Thione 7a in the Absence of Bromotrichloromethane. In a control experiment, a 0.5 M solution of thione **7a** was irradiated in CH_2Cl_2 at −10 °C for 1 h. Under these conditions thione **7a** was stable, as confirmed by ^1H NMR monitoring.

Attempts of Detecting α-Bromo Sulfide 9. In a control experiment a solution of thione **7a** (ca. 0.3 M) and $BrCCl_3$ (ca. 0.6 M) in $FCCl_3$ was irradiated at −75 °C for 15 h and examined by low-temperature (−70 °C) ^1H NMR spectroscopy. Only the ring-opened product, namely thioenol ether **8a** was observed.

Oxidation Potentials of Sulfides 1a,c. Cyclic voltammetry curves for sulfides **1a** and **1c** were obtained at a platinum electrode by employing a 500 mV/s sweep rate against a Ag/AgCl reference electrode at 20 °C. The sulfide concentrations were ca. 7.5 M in 0.10 M $LiClO_4$ solution of acetonitrile. Both sulfides showed irreversible oxidation reactions at 1.81 ± 0.02 V for **1a** and 1.69 ± 0.02 for **1b**.

Oxidation of Sulfide 1a by Tris(2,4-dibromophenyl)ammoniumyl Hexachloroantimonate (Magic Green). To a solution of 0.328 g (2.00 mmol) of sulfide **1a** in 10 mL of CH_3CN was added dropwise a solution of 2.11 g (2.00 mmol) of Magic Green[19] in 15 mL of CH_3CN. The green color of the radical cation disappeared at once. After addition of 20 mL of water, the solution was extracted with ether (3 × 20 mL), and the ethereal phase washed with 20 mL of 10% $NaHSO_3$ solution. Drying over Na_2SO_4 and evaporation of the solvent at 20 °C and 18 Torr yielded a dark oil. ^1H NMR and TLC revealed that, besides tris(2,4-dibromophenyl)amine, a complex, intractable mixture of sulfide-derived products were formed. No efforts were made to characterize these products.

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Substituent Effects on the Stabilities of Phenoxyl Radicals and the Acidities of Phenoxyl Radical Cations

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Abstract: Oxidation potentials for 35 phenoxide ions and 3 naphthoxide ions have been combined with their pK_{HA} values to estimate homolytic bond dissociation energies (BDEs) for the O–H bonds in phenols. Comparison with literature values shows that there is remarkably good agreement between ΔBDE values determined by different methods. A plot of oxidation potentials for *m*-phenoxides vs pK_{HA} values was found to be linear over a range of 18 kcal/mol, pointing to the presence of an inherent group electronegativity factor, related to basicity, that strengthens the O–H bond in phenols. Deviations of points for para substituents from this line have provided a measure of their radical-stabilizing ability that is devoid of such inherent bond-strengthening effects. A good correlation of $E_{ox}(A^-)$ values for *p*-$GC_6H_4O^-$ phenoxide ions with σ^+ constants was observed over a range of greater than 40 kcal/mol. The acidities of 35 phenoxyl radical cations have been estimated from pK_{HA}, $E_{ox}(A^-)$, and $E_{ox}(HA)$ values. A good correlation of $E_{ox}(HA)$ vs $pK_{HA}{}^{\bullet+}$ was observed for *m*-$GC_6H_4OH^{\bullet+}$ radical cations, but the points for para donors were found to deviate from the line.

Proximate substituent effects on radicals vary with the nature of the radical. The radical-stabilizing energies (RSEs) of methyl radicals, $GCH_2^{\bullet}$, where G is an α-donor substituent as judged by the homolytic bond dissociation energies (BDEs) of GCH_2–H relative to that of CH_3–H (105 kcal/mol), increase in the following order: F (5) < Me (7) MeO (12) < Ph (17) < Me_2N (21).[1a] (The numbers in parentheses are in kilocalories per mole, hereafter

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abbreviated as kcal.) The α-acceptor groups CN and MeCO are also radical stabilizing, each by 12 kcal, but the CF_3 group is destabilizing by 2 kcal.[1] In 9-substituted fluorenes, 9-G-Fl-H (where Fl is fluorene), the ΔBDEs of the α-C-H bonds, relative to the 9-C-H bond in fluorene for donor substituents, are estimated to be the following: Me (4.5) < MeS (5.4) < Ph (5.9) < MeO (7) < Me_2N (9).[2] Here, the RSEs are believed to be attenuated, relative to GCH_2-H compounds, by steric and saturation effects. The acceptor groups H_2NCO (2.3), MeOCO (3.0), and CN (5.7) are also stabilizing,[2] but $PhSO_2$ (−2.1)[2] and Me_3N^+ (−5)[3] are destabilizing. In α-substituted acetophenones, $PhCOCH_2G$, the ΔBDEs for donors, relative to that of $PhCOCH_2$-H, are estimated to be Me (5)[4] < MeO (13)[5] <Me_2N (21);[5] the acceptors CN (3) and MeCO (1) are mildly stabilizing,[4] but $PhSO_2$ (−2) and Me_3N^+ (−4) are destabilizing.[4]

Remote substituent effects on radical stabilities are much smaller and are difficult to evaluate. Since the high reactivity of radicals usually precludes studies of equilibria, relative rates of abstraction of benzylic hydrogen atoms in meta- and para-substituted toluenes, $GC_6H_4CH_3$, have been the principal source of information concerning the remote effects of G on the stability of $GC_6H_4CH_2^{\bullet}$ radicals. More than 20 different radicals have been used as reagents in these investigations. Many of these reactions give surprisingly good Hammett correlations,[6] which has been interpreted to mean that there are strong polar contributions to the transition states. The attempts to define Hammett-type $\sigma^{\bullet}$ constants from such kinetic data and by other methods, have been summarized and ably discussed by Arnold,[7a] who has established a $\sigma_\alpha^{\bullet}$ scale, believed to be devoid of polar effects, that is based on the effect of substituents on hyperfine ESR coupling constants for benzyl radicals.[7b] The order of radical-stabilizing effects for para donor substituents ($\sigma_\alpha^{\bullet}$ scale) is as follows: *t*-Bu (0.008) < Cl (0.011) < Me (0.015) < MeO (0.018) < PhS (0.058) < MeS (0.063).[7b] For para acceptors the order is as follows: $PhSO_2$ (0.018) < CN (0.040) < CO_2Me (0.043) < PhCO (0.055) < MeCO (0.060). In this $\sigma_\alpha^{\bullet}$ scale, meta groups (except *m*-Me) are destabilizing, as are *p*-F and *p*-CF_3 groups. The $\sigma_\alpha^{\bullet}$ scale is in reasonable accord with a $\sigma_C^{\bullet}$ scale devised by Creary,[8] which is based on the effects of *m*- and *p*-GC_6H_4 substituents on the relative rates of thermal rearrangements of methylenecyclopropanes. These reactions involve diradical intermediates and are believed to be minimally affected by polar transition-state effects. For para donors, the order ($\sigma_C^{\bullet}$ scale) is as follows: F (−0.083) < H (0.0) < Me (0.11) < Cl (0.12) < Br (0.14) < MeO (0.24) < MeS (0.43). (The numbers in parentheses are log (k/k_0) values.) The order for para acceptors is as follows: H (0.0) < CF_3 (0.08) < SO_2Me (0.18) < SOMe (0.18_5) < CO_2Me (0.35) < CN (0.59). Meta substituents are radical destabilizing.

In our laboratory, we have examined the effects of remote substituents on the ΔBDEs of the benzylic type C-H bonds in fluorenes as a measure of ΔRSEs. The ΔBDEs were estimated from eq 1, which is based on a thermodynamic cycle.[2]

$$\Delta\text{BDE} \simeq \Delta\text{RSE} = 1.37\Delta pK_{\text{HA}} + 23.06\Delta E_{\text{ox}}(\text{A}^-) \qquad (1)$$

A plot of oxidation potentials in DMSO for 2-substituted and 2,7-disubstituted fluorenide ions vs the pK_{HA} values in DMSO of their conjugate acids was found to be linear over a range of 14 kcal.[2] The slope was near unity when both axes were expressed in kcal, which showed that meta substituents in these fluorenide ions exhibited little or no ability to either weaken or strengthen bonds or stabilize or destabilize the incipient radicals derived therefrom. (The meta position in fluorene can exhibit some para character by interactions through the second benzene ring.[2]) On the other hand, the points of fluorenes bearing 3-Me, 3-MeO, or 3-MeS (para) substituents deviated from the line. The ΔBDE (or ΔRSE) values were 0.4, 1.0, and 1.1 kcal, respectively, which is the order predicted by the Arnold and Creary scales.

This method was then applied to estimate ΔBDEs for the benzylic type C-H bonds in arylacetonitriles[9] and benzyl phenyl sulfones.[10] In these papers, we used eq 2, an expanded version of eq 1, that allowed us to relate the BDEs obtained from measurements in DMSO for different kinds of H-A bonds to absolute gas-phase data.[11]

$$\text{BDE (kcal)} = 1.37pK_{\text{HA}} + 23.06E_{\text{ox}}(\text{A}^-) + C \qquad (2)$$

Although eq 2 is semiempirical in the sense that some of the entropy and solvation terms making up constant *C* are difficult to evaluate, the BDEs estimated in this way are usually found to agree to within ±3 kcal with the best gas-phase BDEs.[11] Relative ΔBDEs (or ΔRSEs) within a family of anions are, of course, governed by eq 1 and are independent of the value of *C*. These relative values are believed to be accurate to about ±1 kcal.

This method of estimating relative and absolute BDEs was originally described as the solution counterpart of the method of Brauman[12] for determining gas-phase BDEs from gas-phase acidities and electron affinities.[2] After we had applied eq 2 to estimate BDEs of several types of H-A bonds from measurements of acidities and oxidation potentials in DMSO solutions, it was brought to our attention that a nearly identical equation had been applied earlier by Friedrich to estimate the BDEs of the O-H bonds in hydroquinone and phenol from measurements in aqueous medium.[13] Recently, this method has been applied to additional phenols by combining reduction potentials of phenyl radicals generated by pulse radiolysis in water with aqueous pK_as by Merényi[14] and to metal-hydrogen bonds in metal carbonyl hydrides from measurements made in acetonitrile by Parker.[15]

Our study with benzyl phenyl sulfones revealed an insensitivity of the acidic C-H bonds to meta- or para-substituent effects. The SO_2Ph group has a tendency to strengthen α-C-H bonds and evidently levels the effects of remote substituents theron. The effects of the following substituents appear to be within ±1 kcal of that of the parent $PhCH_2SO_2Ph$, (BDE = 90 kcal): *p*-CF_3, *p*-F, *m*-F, *p*-Cl, *m*-Cl, *p*-Me, *m*-Me, *p*-*t*-Bu, *p*-MeO, *m*-MeO, *p*-PhS, *m*-PhS, and *m*-Me_2N. *m*-CF_3, *m*-CN, and *p*-CN appear to further strengthen the bond by 1–2 kcal, and *p*-Me_2N appears to weaken it by 5 kcal.[10] On the other hand, the CN group appears to weaken an α-C-H bond, judging from the BDE of that in $PhCH_2CN$ (82 kcal) compared to that in toluene (88 kcal). As a consequence, the BDEs of the acidic C-H bonds in arylacetonitriles are much more sensitive to remote substituent effects. Donors cause the BDE's to be slightly lower than that in the parent, whereas acceptors cause the BDEs to be slightly higher.[9] A plot of $E_{\text{ox}}(\text{A}^-)$ vs pK_{HA} (both in kcal) for *meta*-substituted arylacetonitriles was found to be linear, with a slope of 1.2. The deviations from this line indicated radical-stabilizing effects for para substituents in the following order: MeO (0.5) < PhS (0.7)

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Table I. Homolytic Bond Dissociation Energies for O–H Bonds in Phenols

phenol	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[f]	ΔBDE[g]
H	18.0	0.550 (55)	89.85	(0.0)
2-Me	18.05	0.475 (55)	88.2	1.7
3-Me	18.2	0.519 (70)	89.4	0.44
4-Me	18.9	0.447 (70)	88.7	1.1
3,5-Me_2	18.4	0.494 (60)	89.1	0.74
2,6-Me_2	18.5	0.383 (60)	85.5	4.3
4-*t*-Bu	19.05	0.440 (55)	88.7	1.1
2,6-*t*-Bu_2	17.3	0.256 (60)	82.1	7.7
2,4,6-*t*-Bu_3	17.8	0.230 (60)[c]	82.2	7.6
4-Ph	17.1	0.505 (70)	87.6	2.3
2-MeO	17.8	0.394 (55)	86.0	3.9
3-MeO	18.2	0.553 (70)	90.2	−0.4
4-MeO	19.1	0.257 (55)	84.6	5.3
4-O^-	26.5	−0.682 (60)	73.0	17.0[h]
4-HO	19.76	0.085 (55)	81.5	8.3
3-NH_2	19.5	0.382 (100)	88.0	1.8
3-Me_2N	19.05	0.402 (55)	87.9	2.0
4-NH_2	20.75	−0.156 (80)[c]	77.3	12.6
4-Me_2N	19.8	0.028 (70)[d]	80.3	9.6
2-Cl	15.0	0.734 (65)	90.0	−0.13
3-Cl	15.8	0.769 (60)	91.8	−2.0
4-Cl	16.75	0.643 (55)	90.3	−0.42
3,5-Cl_2	13.56	0.990 (60)	93.9	−4.1
3,4,5-Cl_3	12.74	1.000 (55)	93.1	−3.2
4-Br	16.36	0.685 (55)	90.7	−0.86
3-CF_3	15.6	0.864 (70)	93.8	−4.0
4-CF_3	15.2	0.954 (65)	95.3	−5.5
3-$MeSO_2$	14.96	0.839 (65)[e]	92.3	−2.5
4-$MeSO_2$	13.64	1.033 (65)	95.0	−5.2
3-MeCO	16.6	0.720 (65)	91.8	−2.0
4-MeCO	14.0	0.915 (60)	92.8	−2.9
4-PhCO	13.4	0.937 (55)	92.5	−2.6
3-CN	14.76	0.921 (65)	93.9	−4.1
4-CN	13.2	1.025 (70)	94.2	−4.4
3-NO_2	14.4	0.957 (70)	94.3	−4.5
4-NO_2	10.8	1.189 (70)	94.7	−4.8
2-NpOH	17.14	0.522	88.0	(0.0)
6-Br-2-NpOH	16.2	0.600	88.5	−0.50
1-NpOH	16.2	0.402	84.0	4.0

[a] Bordwell, F. G.; Olmstead, W. N.; Cripe, T. A.; Taft, R. W. Unpublished results. Corrected for homohydrogen bonding (see ref 18). [b] Anodic potentials (E_p) measured by cyclic voltammetry in DMSO with a 0.1 M $Et_4N^+BF_4^-$ supporting electrolyte and a Pt electrode. The concentration of neutral substrates was 3 mM and of anions 1 mM. The potentials are reported relative to Ag/AgI taken with the ferrocenium couple as an internal standard ($E_{1/2}$ = 875 mV). They are irreversible unless otherwise noted. [c] Reversible potential. [d] Partially reversible potential. [e] In CH_3CN. [f] Estimated, after adding −0.125 to relate to SHE, by eq 2, with C = 55.39.[11] [g] Relative to the BDE of phenol. [h] Measured by A. V. Satish.

< Cl (1.2) < CN (1.3) < PhCO (2.3) < Me_2N (2.5) < Ph (3.2).

In summary, it would appear that ΔRSEs for a given group G in radicals of the type $GC_6H_4X^\bullet$ may vary appreciably, depending on the nature of the atom X. In this paper, we examine the substituent effects on the stabilities of phenoxyl radicals, $GC_6H_4O^\bullet$, and the acidities of radical cations, $GC_6H_4OH^{\bullet+}$.

Results and Discussion

The results of the measurements in DMSO of the oxidation potentials of 35 phenoxide ions and 3 naphthoxide ions are given in Table I. Combination of these potentials with pK_{HA} values in DMSO of their conjugate acids according to eq 2 (C = 55.4)[11] gives the BDEs shown in Table I.

Table II. Comparison of ΔBDEs for Phenols, GC_6H_4OH, in DMSO with Literature Values

	ΔBDE					
G	*a*	*b*	*c*	*d*	*e*	*f*
H	0.0	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
4-Me	1.1	2.1	4.5	1.8		
4-*t*-Bu	1.1		1.7		1.9	
2,6-Me_2	4.3			4.5		
4-Ph	2.3			4.8		
4-MeO	5.3	5.6	5.3	5.9	5.9	
4-HO	8.3	8.0		6.3		5
4-O^-	16.8	15.8				23
4-NH_2	12.6	12.7				
4-Me_2N	9.6	14.1				
4-Cl	−0.42	0.60	−1.8		−0.40	
4-Br	−0.86	0.10				
4-CF_3	−5.5				−3.2	
4-MeCO	−2.9	−2.1	−2.7			
4-CN	−4.4	−4.7	−1.4			
4-NO_2	−4.5	−6.0	−2.2			

[a] Present work. [b] Merényi et al. from E_{rd} ($ArO^\bullet$ and pK_as of ArOH in aqueous medium).[14] [c] Arnett et al. from $E_{ox}(PhO^-)$ in sulfolane and pK_as in DMSO.[17b] [d] Mahoney, L. R.; DaRooge *J. Am. Chem. Soc.* **1975**, *97*, 4722–4731 (from rate constants for reactions of $ArO^\bullet$ radicals in C_6H_5Cl with hydroperoxides and differences in the heats of formation of the hydroperoxides). [e] Griller et al. from photoacoustic calorimetric measurements.[16] [f] Friedrich, L. E. from pK_as and $E_{ox}(A^-)$ values in aqueous solution.[13]

The BDE estimated for phenol, $89.8_5 \pm 3$ kcal, agrees reasonably well with that of Merényi (88.2 kcal),[14] which was obtained by a different electrochemical method and by using a solvent correction based on water instead of DMSO. But these values are higher by 3–5 kcal than the best gas-phase value (85 ± 1 kcal).[16] Comparison of our irreversible oxidation potentials for fluorenide and phenoxide ions with the reversible potentials obtained by Arnett[17] has shown a negative shift for the latter averaging 55 mV. This effect is counteracted, however, by homohydrogen bonding,[18] which causes positive shifts in $E_{ox}(A^-)$ of about the same size. In any event, ΔBDEs depend only on ΔpK_{HA} and $\Delta E_{ox}(A^-)$ and are independent of the size of C.

Strictly speaking, ΔBDEs cannot be directly related to ΔRSEs because substituents may introduce changes in the ground-state energy of the molecule and bond.[7a,19] It seems likely, however, that in a family of phenols the effects of remote substituents on the ground state of the parent molecules will be small compared to that on the radicals. Furthermore, in the method we are using, the major factor determining the size of ΔBDE is usually $\Delta E_{ox}(A^-)$, which varies over a range of 35 kcal for phenoxide ions. The relative energies needed to remove an electron from anions should be intimately related to the stability of the radicals being formed, when corrected for basicity. As will be brought out later, the ΔpK_{HA} values, which cover a range of 14 kcal for phenols, serve essentially to compare $E_{ox}(A^-)$ values at the same basicity.

Comparisons of ΔBDEs with Literature Values. In Table II, we compare our ΔBDEs with recent literature values.

Examination of Table II shows that there is remarkably good overall agreement between the various ΔBDEs despite the diversity in the media (DMSO, H_2O, sulfolane, chlorobenzene, and the gas phase) and the methods (thermodynamic cycles involving redox and pK_a measurements, kinetics and heats of formation, and photoacoustic calorimetry) used to obtain the data.

Note the excellent agreement for the independent measurements for 4-methoxyphenol. It follows that solvation must play only a minor role in determining relative radical stabilities. Solvation does apparently play a significant role in determining absolute BDEs, however, since the values for phenol estimated by the various redox-pK_{HA} methods are all 3–5 kcal higher than the best gas-phase value.

Correlation of Oxidation Potentials of Phenoxide Ions with pK_{HA}'s. We have mentioned earlier that $E_{ox}(A^-)$ values for meta-substituted fluorenide ions gave a good linear plot with pK_{HA}

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(17) (a) Arnett, E. M.; Amarnath, K.; Harvey, N. C.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344–355. (b) Arnett, E. M.; Amarnath, K.; Harvey, N. C.; Venimadhaven, S. *J. Am. Chem. Soc.* **1990**, *112*, 344–355.

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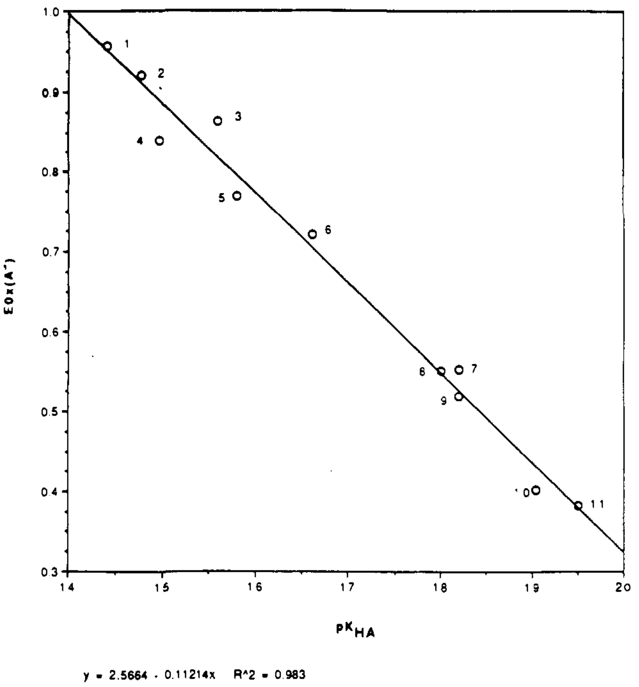


Figure 1. Oxidation potentials of *m*-phenoxide ions plotted against pK_{HA} values for *m*-phenols: 1 (NO_2), 2 (CN), 3 (CF_3), 4 ($MeSO_2$), 5 (Cl), 6 (MeCO), 7 (MeO), 8 (H), 9 (Me), 10 (Me_2N), 11 (NH_2).

Table III. Radical Stabilization Energies Estimated in the Absence of Intrinsic Anion Basicities

substituent	ΔRSE[a] (kcal)	substituent	ΔRSE[a] (kcal)
		Donors	
H	(0.0)	4-Ph	3.1
4-NH_2	8.8	3,4,5-Cl_3	2.3
26-*t*-Bu_2	8.3	2,6-Me_2	1.5
4-NMe_2	6.85	2-Me	1.15
4-OH	5.5	4-Br	0.92
2-MeO	3.6	4-Cl	0.74
4-MeO	3.4	4-*t*-Bu	0.0
2-Cl	3.25	4-Me	-0.20
		Acceptors	
4-NO_2	5.8	4-CN	0.81
4-PhCO	2.6	4-SO_2Ph	0.0
4-MeCO	1.5	4-CF_3	-1.9

[a] Calculated from eq 3.

values (slope ≃ 1) and that a similar plot was obtained for arylacetonitrilide ions (slope = 1.2). A plot of $E_{ox}(A^-)$ vs pK_{HA} for meta-substituted phenoxide ions is shown in Figure 1.

The slope of 1.9 in Figure 1 indicates that the ΔBDEs for *m*-GC_6H_4O–H phenols and the stabilities of *m*-$GC_6H_4O^•$ radicals are nearly twice as sensitive to the effects of the *m*-G substituents as are ΔBDEs for *m*-$GC_6H_4CH(CN)$–H (or ΔRSEs for *m*-$GC_6H_4\dot{C}H(CN)$). The negative ΔBDEs for most of the *m*-G substituent effects in Table I show that they are generally bond strengthening (radical destabilizing). Only the *m*-NH_2 and *m*-Me_2N groups are bond weakening relative to hydrogen. Nevertheless, these points fit the line in Figure 1. These results suggest that all meta substituents possess an inherent bond-strengthening factor related to basicity that is radical destabilizing. We will see shortly that this group electronegativity factor, which inhibits release of the electron from the anion, is opposed in phenoxides bearing para donors by a resonance factor related to the ability of the group to delocalize the odd electron.

In Figure 2 parts a and b, the meta line has been drawn and extended to serve as a rough guide for the influence of the group electronegativity factor on para and ortho substituents, respectively. In other words, this line allows one to eliminate the electronegativity, or other, factor(s) controlling the anion basicity in order to reveal the size of delocalizing, or other, effects on the ΔBDEs or ΔRSEs of ortho and para groups.

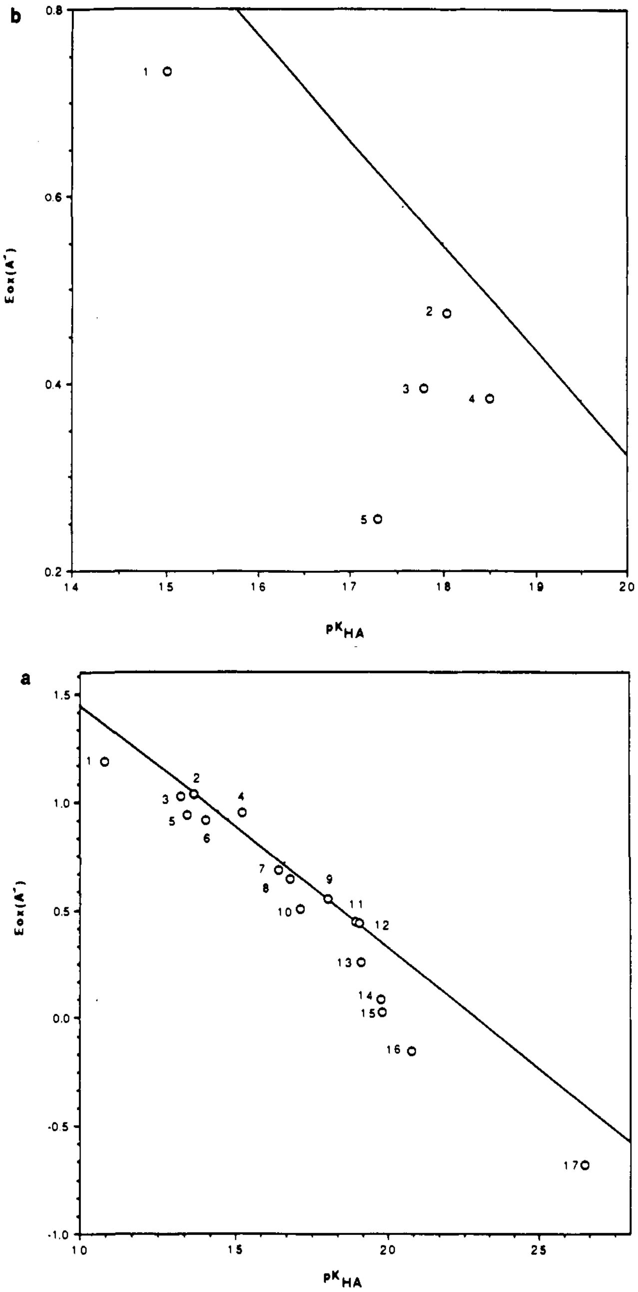


Figure 2. (a) Points for oxidation potentials of *p*-phenoxide ions plotted against pK_{HA} values for *p*-phenols shown relative to the line for meta substituents derived in Figure 1: 1 (NO_2), 2 ($MeSO_2$), 3 (CN), 4 (CF_3), 5 (PhCO), 6 (MeCO), 7 (Br), 8 (Cl), 9 (H), 10 (Ph), 11 (Me), 12 (*t*-Bu), 13 (MeO), 14 (HO), 15 (Me_2N), 16 (NH_2), 17 (O^-). (b) Points for oxidation potentials of *o*-phenoxides plotted against pK_{HA} values of *o*-phenols shown relative to the line for meta substituents derived in Figure 1: 1 (Cl), 2 (Me), 3 (MeO), 4 (2,6-Me_2), 5 (2,6-*t*-Bu_2).

ΔRSEs of Para-Donor Groups. Let us assume that the radical-stabilization energies, relative to the $C_6H_5O^•$ radical, can be estimated by the difference in oxidation potentials observed, $E_{ox}(A^-)_{obsd}$, and that calculated from the line, $E_{ox}(A^-)_{calcd}$, in Figure 2a by eq 3. In essence, we are assuming that field/inductive effects are the same from meta and para positions, an assumption that has often proved useful in the past.

$$\Delta RSE = (E_{ox}(A^-)_{calcd} - E_{ox}(A^-)_{obsd}) \tag{3}$$

From the results summarized in Table III, we see that the order of ΔRSEs for first-row para groups is Me (−0.2) < *t*-Bu (0,0) < MeO (3.4) < HO (5.5) < Me_2N (6.8) < NH_2 (8.8). This is roughly the same order as has been observed for these groups in $\sigma^•$ scales and for $GCH_2^•$, 9-G-Fl$^•$, $PhCO\dot{C}HG$, and *p*-

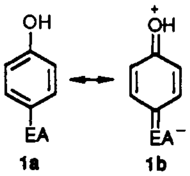
$GC_6H_4\dot{C}HCN$ radicals in earlier studies.[7-10] The effects for RO and R_2N groups are, however, much larger than those observed in p-$GC_6H_4\dot{C}HCN$ or in $\sigma^\bullet$ scales.

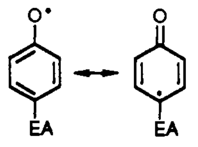
The negligible ΔRSEs for p-Me and p-t-Bu groups are unexpected from the earlier work. These groups have zero field/inductive effects, but examination of Table I shows that they increase anion basicity by about 1.3 kcal. The consequent increase in basicity accounts for a large part of the negative shift in $E_{ox}(A^-)$, and the apparent ΔRSE is small, as it is in p-$MeC_6H_4\dot{C}HCN$.

The RSE for $Me_2NCH_2^\bullet$ has been reported to be 10 kcal greater than that for $H_2NCH_2^\bullet$,[1,20] but the ΔRSEs for $H_2NFl^\bullet$, $H_2N\dot{C}HCOPh$, and $H_2N\dot{C}(CN)_2$ radicals have been found to be at least as large as those for the $Me_2NFl^\bullet$, $Me_2N\dot{C}HCOPh$, and $Me_2N\dot{C}(CO)_2$ radicals.[5] Our results in Table III indicate a 2 kcal greater ΔRSE for 4-$H_2NC_6H_4O^\bullet$ than 4-$Me_2NC_6H_4O^\bullet$, but Merényi's results indicate that the reverse is true by 1 kcal. We see in Table III, however, that 4-HO has a 2.1 kcal greater ΔRSE than 4-MeO, and examination of Table II shows that this order is supported by the data of Merényi and also that of Mahoney. The ΔRSE for 4-Ph is about the same as for 4-MeO, and the ΔRSEs for 4-Cl and 4-Br are smaller.

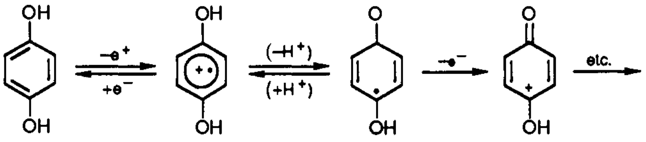
The apparent sizable radical-stabilizing effects for ortho substituents indicated by the deviations from the meta line in Figure 2b are perhaps the most notable feature in Table III. The interpretation is more difficult here because the field/inductive effects for ortho and meta substituents are not expected to cancel and steric effects may enter in. The 8.3 kcal ΔRSE for the 2,6-t-Bu_2 group is particularly striking. So much so that we must consider explanations other than radical stabilization. If an acid-weakening polarizability effect in 4-t-BuC_6H_4OH is responsible for its 1.3 kcal decrease in acidity, one would expect a much larger decrease in acidity for $2,6$-t-$Bu_2C_6H_3OH$ where this effect is augmented by steric inhibition of solvation in the anion. Evidently, these acid-weakening effects are overwhelmed by a more powerful acid-strengthening effect, resulting in a net 1 kcal *increase* in acidity! This increase is most likely caused by a large steric effect, which raises the ground-state energy of the phenol relative to its anion. Examination of Table I shows that 2-Me, 2-MeO, and 2-Cl phenols are also more acidic than their 4-isomers by 1.2, 1.8, and 2.4 kcal, respectively. It seems likely, therefore, that the apparent large ΔRSEs for the 2-isomers may be an artifact caused by higher ground-state energies of the parent phenols.

ΔRSEs of Para-Acceptor Substituents. All of the strong electron-acceptor substituents in Table I exert appreciable bond-strengthening effects. All para acceptors exert larger effects than their meta isomers, suggesting that delocalization of the electron pair in the undissociated phenol (**1a** ↔ **1b**) may be important. The delocalization effects, together with the field/inductive effects (σ_F = 0.59, 0.60, 0.65, and 0.26 for $MeSO_2$, CN, NO_2, and MeCO, respectively)[21,22] appear to overshadow delocalization of the odd electron in the radical (**2a** ↔ **2b**), which is bond weakening. These results are contrary to those derived from the Arnold and Creary $\sigma_\alpha^\bullet$ and $\sigma_C^\bullet$ scales, which indicate that most, if not all, electron-accepting groups are radical stabilizing.[7,8] The two sets of results can be reconciled, however, by the analysis given in Figure 2a and Table III, with use of eq 3. Here we find that when the group electronegativity is factored out, most, but not all, para acceptors are indeed radical stabilizing in the following order: CF_3 (−1.9) < $MeSO_2$ (0.0) < CN (0.81) < MeCO (1.5) < PhCO (2.6) < NO_2 (5.8). The strong delocalization of the odd electron by NO_2 is in agreement with the results from six different $\sigma^\bullet$ scales.[7a]


1a **1b**

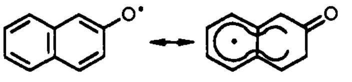

2a **2b**

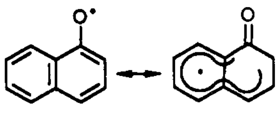
Scheme I



The failure of the $MeSO_2$ group to exhibit radical-stabilizing ability is not surprising since it appears to be relatively poor at delocalizing an odd electron and also appears to be radical destabilizing in several proximate situations.[3,4] The evidence that the CF_3 group is destabilizing, even when its group electronegativity is taken into account, agrees with Arnold's $\sigma_\alpha^\bullet$ analysis and the RSE of −2 kcal for F_3CCH_2–H.[1a]

Effects of Structural Changes in Naphthols in BDEs. The structural changes on BDEs for 1-naphthol (1-NpOH), 2-naphthol (2-NpOH), and 6-bromo-2-naphthol (6-Br-2-NpOH) follow a pattern consistent with that observed for phenols. The 2 kcal lower BDE found for 2-NpOH than for phenol is consistent with the more extensive delocalization that is possible for the odd electron in the 2-NpO$^\bullet$ radicals (**3b–3f**). In the 1-NpO$^\bullet$ radical, delocalization is comparable (**4b–4f**) but the ground-state energy may be slightly higher, leading to a further 2 kcal lowering in BDE. The −0.50 kcal ΔBDE for 6-bromo-2-NpOH, relative to 2-NpOH, is comparable to the −0.86 kcal ΔBDE observed for 4-bromophenol. (It should be kept in mind that the absolute BDEs for the H–O bonds in naphthols are probably about 5 kcal lower than those given in Table I, assuming a correction comparable to that for phenol.)


3a **3b–3f**


4a **4b–4f**

Correlation of $E_{ox}(A^-)$ with σ_p^+. Many dual-parameter Hammett-type correlations of relative rates of formation of benzylic radicals from para-substituted toluenes give better fits with σ^+ than σ constants.[6] This has been attributed to the electronegativity of most radicals, which tend to polarize the transition state in such a way as to place a positive charge on the benzylic carbon atom. But correlation with σ^+ is better also for rates of homolysis of para-substituted *tert*-butyl phenylperacetates[24] and even for rates of hydrogen atom abstraction from para-substituted phenols by peroxy radicals.[25] Furthermore, a recent correlation of the reduction potentials of phenoxyl radicals, p-$GC_6H_4O^\bullet$ (G = Me_2N, H_2N, HO, MeO, Me, F, H, Cl, Br, I, CO_2^-, MeCO, CN, NO_2), in aqueous solution against σ^+ values gave r = 0.895 and ρ^+ = 7.0.[14] A similar correlation has been reported for the BDEs of the O–H bond of para-substituted phenols (G = MeO, t-Bu, H, Cl, CF_3) in the gas phase (r = 0.98; ρ^+ = 7.3).[16] It is not surprising, then, to find that our $E_{ox}(A^-)$ values also correlate with σ^+. The correlation is remarkably good (Figure 3), but why should

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(21) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1–83 (Table 1, p 16).

(22) The traditional view that resonance in the phenoxide ion is the major factor in making phenol a stronger acid than cyclohexanol has been challenged by the calculations of Siggel and Thomas, which focus on electrostatic effects and the high energy of the phenol ground state.[23a,c] The traditional view has been supported by Exner,[23b] and more recently by Taft, Koppel, Topsom, and Anvia, who find (from an analysis of substituent effects on gas-phase acidities using a three-parameter equation, which takes into account polarizability, field/inductive, and resonance factors) that delocalization in the phenoxide ion is indeed the major factor contributing to the $10^{17.6}$ greater acidity of phenol than cyclohexanol.[23d]

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Table IV. Oxidation Potentials of Phenols, GC_6H_4OH, and Estimates of Acidities of Phenol Radical Cations

	$E_{ox}(HA)^a$				$E_{ox}(HA)^f$	
G	MeCN	Me_2SO	$pK_{HA}{}^{\bullet+e}$	G	MeCN	$pK_{HA}{}^{\bullet+e}$
H	2.10 (75)		−8.1	2-Cl	2.39	−13
2-Me	2.10 (1.39)		−9.3	3-Cl	2.34	−10.5
3-Me	2.07 (120)		−7.9	4-Cl	2.23	−9.9
4-Me	1.99 (110)		−7.1	$3,5-Cl_2$	2.61	−14
$3,5-Me_2$	2.00 (100)^b		−7.0	$3,4,5-Cl_3$	2.50	−12.5
$2,6-Me_2$	2.01 (90)		−9.7	4-Br	2.18	−8.8
4-*t*-Bu	2.00 (100)		−7.2	$3-CF_3$	2.60	−14
2,6-*t*-Bu_2	2.12 (110)		−14.0	$4-CF_3$	2.65	−13
2,4,6-*t*-Bu_3	1.85 (80)		−9.5	$3-MeSO_2$	2.67	−16
4-Ph	1.86 (70)		−5.7	$4-MeSO_2$	2.62	−13
2-MeO	1.83 (100)		−6.4	3-MeCO	2.42	−12
3-MeO	2.00 (110)		−6.2	4-MeCO	2.44	−12
4-MeO	1.67 (70)		−4.7	4-PhCO	2.45	−12
4-HO	1.57 (90)		−5.5	3-CN	2.61	−14
$3-NH_2$	1.36 (70)^c	1.38 (130)	3.0	4-CN	2.57	−13
$3-NMe_2$	1.19 (60)^d	1.23 (75)^d	5.9	$3-NO_2$	2.66	−14
$4-NH_2$	0.90 (100)	0.81 (90)	4.5	$4-NO_2$	2.74	−15
$4-Me_2N$	0.84 (70)	0.83 (70)	6.2	1-NpOH	1.76	−6.7
				6-Br-2-NpOH	1.91	−5.9
				2-NpOH	1.87	−5.5

^{a}Oxidation potential of the neutral measured by cyclic voltammetry against a Ag/AgI electrode referenced to a ferrocenium couple; irreversible unless otherwise noted. The wave width defined at ($E_p - E_p/2$) is given in parentheses. ^{b}Appeared as a shoulder. ^{c}Partially reversible potential; E_p reported. ^{d}Reversible potential; E_p reported. ^{e}Calculated by use of eq 4. ^{f}The peaks observed often were shoulders on broad peaks (90–120).

$E_{ox}(A^-)$ values, which provide a measure for radical stabilization energies, correlate with σ^+ values for rates of solvolysis of cumyl chlorides (for para donors) and σ constants (for para acceptors)? For para donors, the facilitation of the loss of one electron from the anion on oxidation can be related to the facilitation of the loss of one electron from carbon during heterolytic (solvolytic) cleavage of the C–Cl bond in cumyl chlorides. For acceptors, Hammett σ constants evidently provide a resonable measure of field/inductive effects that impede the loss of an electron in the two types of reactions.

Radical-Cation Acidities of Phenols. A likely pathway for the oxidation of hydroquinone in nonaqueous solution involves the formation of a radical cation in the initial step (Scheme I).[26] The acidities of radical cations, such as **6**, can be estimated by eq 4, which is based on a thermodynamic cycle.[27] The results of the application of eq 4 to phenols are given in Table IV.

$$pK_{HA}{}^{\bullet+} = pK_{HA} + (E_{ox}(A^-) - E_{ox}(HA))23.06/1.37 \quad (4)$$

A comparison of our oxidation potentials for phenols with literature values shows reasonable agreement, considering the differences in electrodes, solvents, and temperatures (Table V). The good correlations of $E_{ox}(A^-)$ for *m*-phenoxide ions with pK_{HA} (Figure 1), and of $E_{ox}(A^-)$ for *p*-phenoxides with $\sigma_p{}^+$ (Figure 3) provide the best testimony for the consistency of our data, however.

The radical cation derived from phenol is estimated to have $pK_{HA}{}^{\bullet+} = -8.1$. This is 6 units lower than the value reported by Dixon and Murphy from an ESR study in aqueous medium.[34] They observed only small substituent effects on the acidities, e.g., $pK_{HA}{}^{\bullet+}$ increases of only 1.2 units for *p*-HO and 0.4 unit for *p*-Me, compared to 2.6 and 1.0 units, respectively, in DMSO (Table IV). The acidities of phenoxyl radical cations in H_2O are limited, however, by the acidity of H_3O^+, so the smaller effects than those that we estimate in DMSO are probably the result of a leveling effect.

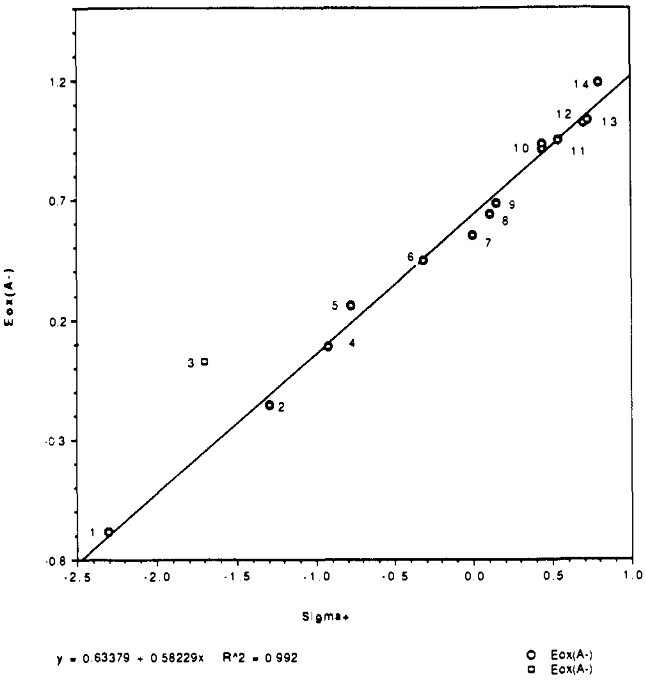

Figure 3. Oxidation potentials of *p*-phenoxides plotted against σ^+ values (for donors) and σ values (for acceptors): 1 (O^-), 2 (NH_2), 3 (Me_2N), 4 (HO), 5 (MeO), 6 (Me), 7 (H), 8 (Cl), 9 (Br), 10 (MeCO), 10 (PhCO), 11 (CF_3), 12 (CN), 13 ($MeSO_2$), 14 (NO_2).

Substituents can affect the acidities by stabilizing either the radical cation (acid weakening) or the radical (acid strengthening). For arylacetonitriles (eq 5) the effect of the substituent on the radical cation was observed to be the dominant factor, and a linear

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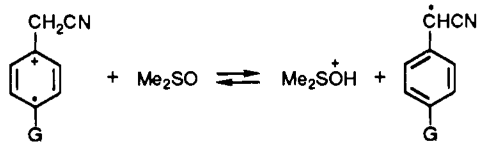
Table V. Comparison of Oxidation Potentials for Phenols and Phenoxide Ions with Literature Data

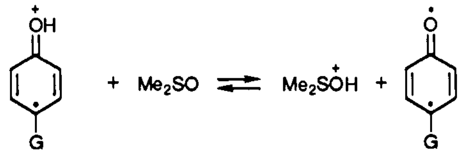
substrate	E_{ox}/V (solvent) (this work)[a]	E_{ox}/V (solvent) (lit.)[e]	ref
PhO^-	0.550 (DMSO)	0.605[f]	28
p-PhC_6H_4OH	1.86 (MeCN)	1.85 (CH_2Cl_2, −50 °C)	29
		1.96 (9:1 CH_2Cl_2–FSO_3H)	30
p-hydroquinone	1.59 (MeCN)	1.57 (CH_2Cl_2, −50 °C)	30
		1.60[c] (94:2:4 CH_2Cl_2)–TFA–$MeSO_3H$)	30
		1.72[c] (91:2:4:3 CH_2Cl_2–TFA–$MeSO_3H$–FSO_3H)	
p-$NH_2C_6H_4OH$	0.90[b] (MeCN)	0.91[b] (H_2O–H_2SO_4)	31
p-$Me_2NC_6H_4OH$	0.84[c] (MeCN)	0.87[c] (H_2O–H_2SO_4)	32
p-$MeOC_6H_4OH$	1.67 (MeCN)	1.57 (CH_2Cl_2, −50 °C)	29
		1.86 (9:1 CH_2Cl_2–FSO_3H)	29
2,4,6-*t*-$Bu_3C_6H_2OH$	1.83[d] (MeCN)	1.7[d] (MeCN)	33
	1.85 (MeCN)		
2,4,6-*t*-$Bu_3C_6H_2O^-$	0.193[c,d] (MeCN)	0.1[c,d] (MeCN)	33

[a] Irreversible oxidation potentials (except where noted) measured under the conditions described in Table I, footnote *b*. [b] Partially reversible. [c] Reversible. [d] Measured at a carbon electrode; $[A^-] = 1$ mM. [e] Irreversible oxidation potentials (except where noted) vs Ag/AgI (obtained by use of the relationship $E_{Ag/AgI} = E_{SCE} + 0.365$). [f] Obtained from a potential vs SHE by adding −0.125.

plot for E_{ox}(HA) vs $pK_{HA}{}^{•+}$ was observed, which included both para donor and acceptor substituents. A similar plot for phenoxyl radical cations (eq 6) is not linear because phenoxyl radicals are much more sensitive to remote substituent effects, and the radical-stabilizing term in eq 4, as well as the E_{ox}(HA) term, comes into play.



(5)



(6)

A plot of E_{ox}(HA) vs $pK_{HA}{}^{•+}$ is linear for meta-substituted phenols, however, because here E_{ox}(HA) remains dominant (Figure 4). The para-donor points are deviant to the degrees to which their greater radical-stabilizing ability shifts eq 6 to the right. The para-acceptor points fit close to the line.

The 4-Me_2N and 4-NH_2 groups are best at stabilizing both phenoxyl radical cations and radicals; 4-$Me_2NC_6H_4OH^{•+}$ is less acidic than $C_6H_5OH^{•+}$ by nearly 20 kcal (Table IV), and the 4-$Me_2NC_6H_4O^•$ radical is more stable than the $C_6H_5O^•$ radical by nearly 10 kcal (Table I). In the 4-$Me_2NC_6H_4CH_2CN^{•+}$ radical cation, the acid-weakening effect of 4-Me_2N is even larger (37 kcal) but its effect on the radical is much smaller (4 kcal).[9] The effects of the 4-NO_2 group on the phenol radical cation (9.4 kcal destabilization; Table IV) and phenoxyl radical (4.8 kcal destabilization; Table I) are typical of strong electron-withdrawing groups.

Summary and Conclusions

The observation of a linear plot of $E_{ox}(A^-)$ for meta-substituted phenoxide ions vs pK_{HA} has led to the conclusion that all meta substituents possess an inherent bond-strengthening factor related to group electronegativity that is radical destabilizing. The apparent larger radical-stabilizing effects for 2-alkyl than 4-alkyl groups are probably caused by increases in the phenol ground-state energies. After group electronegativity effects are factored our, para acceptors are stabilizing in the following order: CN < MeCO < PhCO < NO_2. CF_3 is destabilizing. para donors are stabilizing in the following order: Br, Cl < Ph, MeO < HO < Me_2N, NH_2. The effects for *p*-RO and *p*-R_2N donors are much larger than observed previously for carbon radicals.[9,10] A good correlation of $E_{ox}(A^-)$ for *p*-$GC_6H_4O^-$ vs σ^+ is attributed to a comparable effect of para donors in facilitating loss of an electron from phenoxide ions on the one hand and from carbon in heterolytic cleavage of the C–Cl bond in cumyl chlorides on the other; para acceptors evidently impede the loss of an electron in a comparable manner. The good correlation for E_{ox}(HA) vs $pK_{HA}{}^{•+}$ for *m*-$GC_6H_4OH^{•+}$ results from the dominant effect of the destabilizing effects of G on the oxidation potentials of the radical cations. Points for *p*-$GC_6H_4OH^{•+}$ deviate because of the stabilizing effect of G on the radicals formed on deprotonation.

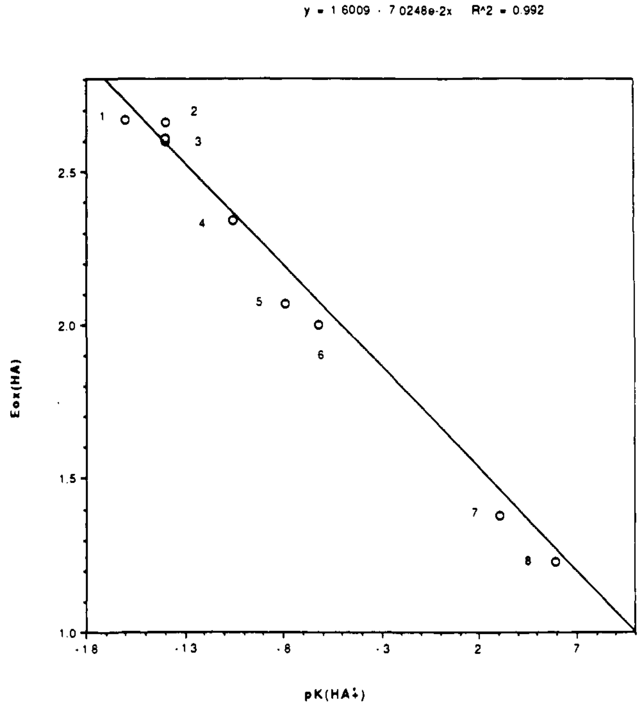


Figure 4. Plot of oxidation potentials for *m*-phenols against their radical-cation acidities: 1 ($MeSO_2$), 2 (NO_2), 3 (CF_3), 3 (CN), 3 (3,5-Cl_2), 4 (Cl), 5 (Me), 6 (MeO), 7 (NH_2), 8 (Me_2N).

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Registry No. PhOH, 108-95-2; *o*-MeC_6H_4OH, 95-48-7; *m*-MeC_6H_4OH, 108-39-4; *p*-MeC_6H_4OH, 106-44-5; *p*-*t*-BuC_6H_4OH, 98-54-4; *p*-PhC_6H_4OH, 92-69-3; *o*-MeO_6H_4OH, 90-05-1; *m*-$MeOC_6H_4OH$, 150-19-6; *p*-$MeOC_6H_4OH$, 150-76-5; *p*-$O^-C_6H_4OH$, 20217-26-9; *p*-HOC_6H_4OH, 123-31-9; *m*-$H_2NC_6H_4OH$, 591-27-5; *m*-$Me_2NC_6H_4OH$, 99-07-0; *p*-$H_2NC_6H_4OH$, 123-08-0; *p*-$Me_2NC_6H_4OH$, 619-60-3; *o*-ClC_6H_4OH, 95-57-8; *m*-ClC_6H_4OH, 108-43-0; *p*-ClC_6H_4OH, 106-48-9; *p*-BrC_6H_4OH, 106-41-2; *m*-$F_3CC_6H_4OH$, 98-17-9; *p*-$F_3CC_6H_4OH$, 402-45-9; *m*-$MeSO_2C_6H_4OH$, 14763-61-2; *p*-$MeSO_2C_6H_4OH$, 14763-60-1; *m*-AcC_6H_4OH, 121-71-1; *p*-AcC_6H_4OH, 99-93-4; *p*-$PhCOC_6H_4OH$, 1137-42-4; *m*-NCC_6H_4OH, 873-62-1; *p*-NCC_6H_4OH, 767-00-0; *m*-$O_2NC_6H_4OH$, 554-84-7; *p*-$O_2NC_6H_4OH$, 100-02-7; $PhO^•$, 2122-46-5; *p*-$H_2NC_6H_4O^•$, 6119-34-2; *p*-$Me_2NC_6H_4O^•$, 54737-34-7;

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p-$\mathrm{HOC_6H_4O^\bullet}$, 3225-30-7; o-$\mathrm{MeOC_6H_4O^\bullet}$, 41115-74-6; p-$\mathrm{MeOC_6H_4O^\bullet}$, 6119-32-0; o-$\mathrm{ClC_6H_4O^\bullet}$, 63125-12-2; p-$\mathrm{PhC_6H_4O^\bullet}$, 35645-18-2; o-$\mathrm{MeC_6H_4O^\bullet}$, 3174-49-0; p-$\mathrm{BrC_6H_4O^\bullet}$, 63125-13-3; p-$\mathrm{ClC_6H_4O^\bullet}$, 3148-13-8; p-t-$\mathrm{BuC_6H_4O^\bullet}$, 35645-16-0; p-$\mathrm{MeC_6H_4O^\bullet}$, 3174-48-9; p-$\mathrm{O_2NC_6H_4O^\bullet}$, 41071-23-2; p-$\mathrm{PhCOC_6H_4O^\bullet}$, 131761-88-1; p-$\mathrm{AcC_6H_4O^\bullet}$, 54560-34-8; p-$\mathrm{NCC_6H_4O^\bullet}$, 41071-24-3; p-$\mathrm{PhSO_2C_6H_4O^\bullet}$, 131588-31-3; p-$\mathrm{F_3CC_6H_4O^\bullet}$. 73073-68-4; PhOH (radical cation), 40932-22-7; o-$\mathrm{MeC_6H_4OH}$ (radical cation), 60715-73-3; m-$\mathrm{MeC_6H_4OH}$ (radical cation), 60715-74-4; p-$\mathrm{MeC_6H_4OH}$ (radical cation), 51921-65-4; p-t-$\mathrm{BuC_6H_4OH}$ (radical cation), 122060-12-2; p-$\mathrm{PhC_6H_4OH}$ (radical cation), 58587-96-5; o-$\mathrm{MeOC_6H_4OH}$ (radical cation), 60715-77-7; m-$\mathrm{MeOC_6H_4OH}$ (radical cation), 60715-78-8; p-$\mathrm{MeOC_6H_4OH}$ (radical cation), 34471-10-8; p-$\mathrm{HOC_6H_4OH}$ (radical cation), 34507-04-5; m-$\mathrm{NH_2C_6H_4OH}$ (radical cation), 34478-00-7; m-$\mathrm{Me_2NC_6H_4OH}$ (radical cation), 131588-33-5; p-$\mathrm{H_2NC_6H_4OH}$ (radical cation), 60715-76-6; p-$\mathrm{Me_2NC_6H_4OH}$ (radical cation), 131588-34-6; o-$\mathrm{ClC_6H_4OH}$ (radical cation), 73073-76-4; m-$\mathrm{ClC_6H_4OH}$ (radical cation), 73073-75-3; p-$\mathrm{ClC_6H_4OH}$ (radical cation), 73073-74-2: p-$\mathrm{BrC_6H_4OH}$ (radical cation), 80173-15-5; m-$\mathrm{F_3CC_6H_4OH}$ (radical cation), 73073-71-9; p-$\mathrm{F_3CC_6H_4OH}$ (radical cation), 73073-69-5; m-$\mathrm{MeSO_2C_6H_4OH}$ (radical cation), 131588-37-9; p-$\mathrm{MeSO_2C_6H_4OH}$ (radical cation), 131588-38-0; m-$\mathrm{AcC_6H_4OH}$ (radical cation), 73073-63-9; p-$\mathrm{AcC_6H_4OH}$ (radical cation), 73073-62-8; p-$\mathrm{PhCOC_6H_4OH}$ (radical cation), 131588-39-1; m-$\mathrm{NCC_6H_4OH}$ (radical cation), 131588-40-4; p-$\mathrm{NCC_6H_4OH}$ (radical cation), 131588-41-5; m-$\mathrm{O_2NC_6H_4OH}$ (radical cation), 73089-74-4; p-$\mathrm{O_2NC_6H_4OH}$ (radical cation), 73089-73-3; 3,5-dimethylphenol, 108-68-9; 2,6-diethylphenol, 576-26-1; 2,6-di-*tert*-butylphenol, 128-39-2; 2,4,6-tri-*tert*-butylphenol, 732-26-3; 3,5-dichlorophenol, 591-35-5; 3,4,5-trichlorophenol, 609-19-8; 2-naphthol, 135-19-3; 6-bromo-2-naphthol, 15231-91-1; 1-naphthol, 90-15-3; 2,6-di-*tert*-butylphenoxy radical, 15773-11-2; 3,4,5-trichlorophenoxy radical, 131761-87-0; 2,6-dimethoxyphenoxy radical, 3229-35-4; 3,5-dimethylphenol radical cation, 73073-77-5; 2,6-dimethylphenol radical cation, 131588-32-4; 2,6-di-*tert*-butylphenol radical cation, 42150-58-3; 2,4,6-tri-*tert*-butylphenol radical cation, 42150-54-9; 3,5-dichlorophenol radical cation, 131588-35-7; 3,4,5-trichlorophenol radical cation, 131588-36-8; 1-naphthol radical cation, 72773-99-0; 6-bromo-2-naphthol radical cation, 131588-42-6; 2-naphthol radical cation, 67977-56-4.

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[3]Rotane: Crystal Structure, X–X Difference Electron Density, and Phase Transition[†]

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Abstract: The newly redetermined X-ray crystal structure of [3]rotane (**1**) provides structural parameters in close agreement with theoretical calculations. In relation to cyclopropane, a shortening of the vicinal bonds at the spiro carbon atoms and a lengthening of the distal bonds is observed. The latter is apparently due to the increased angular strain at the spiro carbon atoms. In a series of spiro[2.n]alkanes the angle in the (n+1)-membered ring correlates inversely with the length of the distal bond in the cyclopropane group. The determined X–X difference electron density for **1** strongly corroborates the theoretically predicted surface delocalization of electrons in three-membered rings; this adds an essential argument in favor of the concept of "σ-aromaticity". Upon cooling, the crystal of **1** undergoes a reversible phase transition at 108.2 K. Crystal symmetry changes from space group $P6_3/m$ to $P2_1/n$. Structural and cell parameters were determined at different temperatures to understand this molecular reorganization. Most probably the increasing number of van der Waals contacts in the low-temperature form provides the driving force for the phase transition.

Introduction

As the most highly strained member in the [n]rotane series, [3]rotane (**1**)[2] has been the object of considerable research effort.

Calculations to evaluate the hybridization of the spiro carbon atoms were reported by Randič et al. and by Maksič et al.[3] [3]Rotane (**1**) was first synthesized by Fitjer and Conia[4] in 1973; a different synthesis was later developed by Erden et al.[5] Photoelectron spectroscopy revealed an unusually large resonance integral between the spirocyclopropane groups in **1**.[6] Semiempirical calculations (MINDO/3) were carried out by Zil'berg et al.[7] to evaluate the geometry and strain energy of **1**. Other theoretical methods were applied by Rasmussen and Tosi[8] (consistent force field calculation) and by Ioffe et al.[9] (molecular mechanics calculation). Except for the MINDO/3 method, all theoretical calculations for **1** predict a lengthening of the distal bond c relative to the proximal bond b and the central bond a (Figure 1). The distal bond lengthening apparently would result from a partial release of the additional angle strain at the spiro atoms. These reasonable theoretical results contradict the experimentally derived parameters from an X-ray crystal structure analysis at 228 K.[10]

Results

In order to resolve this discrepancy we redetermined the X-ray crystal structure of **1** at 120 K. Furthermore, the X–X difference electron density was evaluated to verify the predicted surface delocalization of σ-electrons in cyclopropane and its derivatives.[11] On cooling, the crystal undergoes a reversible phase transition with a change of crystal symmetry. In order to understand this

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[†] Dedicated to Prof. B. Schrader on the occasion of his 60th birthday.

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(2) The systematic name of [3]rotane is trispiro[2.0.2.0.2.0]nonane.

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