

Effects of sulfenyl, sulfinyl and sulfonyl groups on acidities and homolytic bond dissociation energies of adjacent C—H and N—H bonds

Frederick G. Bordwell* and Wei-Zhong Liu

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA

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ABSTRACT: Acidities and bond dissociation energies (BDEs) of the N—H bond in two phenylsulfenylamides, PhSNHBz and PhSNH-*t*-Bu, and four phenylsulfenylanilides, 4-GC₆H₄NHSPh, where G = MeO, H, Br and CN, were measured in order to compare the effects of substituents on acidities and BDEs of N—H bonds with those of C—H bonds. The effects of PhS groups on acidities and BDEs in a series of C—H acids were found to be comparable to those on acidities and BDEs of PhS in a similar series of N—H acids. Comparisons were also made of the effects of changing the oxidation state of sulfur in the series PhS, PhSO and PhSO₂ on the acidities and BDEs of adjacent N—H and C—H bonds in weak acids. Hammett-type plots of p*K*_{HA} values for phenyl benzyl sulfones (4-GC₆H₄CH₂SO₂Ph) and phenylsulfenylanilides (4-GC₆H₄NHSPh) were linear vs σ_p^- values. A linear plot was obtained and explained for a plot of BDE of the N—H bonds in remotely substituted phenylsulfonylanilides with σ^+ values. Plots of BDEs vs $E_{\text{ox}}(\text{A}^-)$ were also linear for 4-substituted phenylsulfenylanilides (4-GC₆H₄NHSPh), phenylsulfonylanilides (4-GC₆H₄NHSO₂Ph) and phenyl benzyl sulfones (4-GC₆H₄CH₂SO₂Ph). © 1998 John Wiley & Sons, Ltd.

KEYWORDS: bond dissociation energy; acidity; phenylsulfenylamides; phenylsulfenylanilides

INTRODUCTION

Sulfenyl (RS), sulfinyl (RSO) and sulfonyl (RSO₂) groups have found wide application in synthetic carbanion chemistry by virtue of their acidifying power on adjacent C—H bonds.¹ The corresponding N—H acids, i.e. sulfenamides (RSNH₂), sulfinamides (RSO₂NH₂) and sulfonamides (RSO₂NH₂) have also aroused considerable interest.² Equilibrium acidities for a number of sulfur-containing compounds have been measured in dimethyl sulfoxide (DMSO)^{3,4} and other solvents⁵ in order to obtain quantitative information concerning the relative basicities of the corresponding anions. In earlier papers we have also presented measurements in DMSO of the homolytic bond dissociation energies (BDEs) of the acidic C—H bonds in a number of sulfur-containing carbon acids by using the following equation (henceforth kcal mol⁻¹ will be abbreviated as kcal):⁴

$$\text{BDE}_{\text{HA}} = 1.37\text{p}K_{\text{HA}} + 23.1E_{\text{ox}}(\text{A}^-) + 73.3\text{kcal/mol}^{-1} \quad (1)$$

*Correspondence to: F. G. Bordwell, Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA

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Relatively little information is available concerning the acidities and BDEs of the corresponding nitrogen acids, however.

In this paper we present p*K*_{HA} and BDE estimates of the effect of increasing the oxidation state of sulfur in the series sulfenyl, sulfinyl and sulfonyl on adjacent C—H and N—H bonds for a number of carbon acids, and make comparisons with their nitrogen analogues.

RESULTS AND DISCUSSION

Effects of phenylsulfenyl groups on acidities and BDEs of α -C—H and α -N—H bonds

In Table 1, we compare the effects of α -PhS groups on the C—H and N—H bonds. Examination of Table 1 shows that α -PhS groups increase the acidities of methane and toluene by about 14 and 12 p*K*_{HA} units (19 and 16 kcal), respectively. The effects of an α -PhS group on the acidic C—H bonds in acetophenone and diphenylmethane are smaller (10.5 and 7.4 kcal) because of leveling and steric effects. The acidifying effects of an α -PhS group on N—H acidities are in a similar range (11–12 kcal).

The origin of acidifying effects caused by sulfenyl groups on carbon acids has been interpreted theoretically as being due to (a) polarization,¹⁰ (b) d-orbital participa-

Table 1. Effect of the PhS group on acidities and BDEs of α -C—H and α -N—H bonds

Entry	Acid	pK_{HA}^a	ΔpK_{HA}	$E_{\text{ox}}(\text{A}^-)^d$	BDE_{HA}^e	$\Delta \text{BDE}_{\text{HA}}$
1	CH ₄	~56	(0.0)		105 ^f	(0.0)
	CH ₃ SPh	~42	14		93 ^f	12
2	PhCH ₃	~43	(0.0)		87.5 ^f	(0.0)
	PhCH ₂ SPh	30.8	12	-1.446	82.2	5
3	Ph ₂ CH ₂	32.2	(0.0)	-1.557	81.5 ^g	(0.0)
	Ph ₂ CHSPh	26.8	5.4	-1.187	82.6 ⁱ	-1.1
4	PhCOCH ₃	24.7	(0.0)	-0.607	93.1 ^h	(0.0)
	PhCOCH ₂ SPh	17.1	7.6	-0.649	81.7 ^h	11.3
5	BzNH ₂	~40 ^b	(0.0)		~100 ^j	(0.0)
	BzNHSPH	30.6 ^c	~9	-1.228	86.9	~13
6	<i>t</i> -BuNH ₂	~40 ^b	(0.0)		~100 ^j	(0.0)
	<i>t</i> -BuNHSPH	30.8 ^c	~9	-1.223	87.1	~13
7	PhNH ₂	30.6	(0.0)	-0.994	92.3 ^g	(0.0)
	PhNHSPH	22.6 ^c	8.0	-0.943	82.6	9.7

^a Data from Ref. 3 unless indicated otherwise.

^b Estimated from the pK_{HA} of NH₃ (~41), and the substituent effect of a methyl group on PhNH₂ (30.6) vs PhNHMe (29.6).

^c See Table 7 for details.

^d Irreversible oxidation potentials measured in DMSO with 0.1 M Et₄N⁺BF₄⁻ at a sweep rate of 100 mV s⁻¹, and referred to the ferrocene/ferrocenium couple.

^e Estimated by Eqn (1), this work, unless indicated otherwise.

^f Ref. 6.

^g Ref. 7.

^h Ref. 8.

ⁱ Ref. 9.

^j Estimated relative to the BDE_{HA} of MeNH₂ (100 kcal).

tion¹¹ and (c) hyperconjugation.¹² The polarization mechanism suggests that the anion is stabilized by distributing its negative charge over the sulfenyl group. The results of *ab initio* calculations indicates that on going from CH₃SCH₃ to CH₃SCH₂⁻, the electron density on the SCH₃ group is increased by 0.334 electron unit.^{12a} The d-orbital participation model suggests that the anion might be stabilized by the presence of unoccupied 3d orbitals of the sulfur atom.¹¹ Recent higher level *ab initio* calculations indicate that the d-orbital participation is unimportant.^{12,13} The hyperconjugation mechanism involves the electrons from the carbanion center being donated into the C—S σ^* antibonding orbital. This view explains the increasing C—S bond order in the CH₃SCH₂-anion.^{12a}

Substituent effects can generally be separated into three major parts: steric, inductive and resonance effects.¹⁴ Based on the experimental results, the corresponding substituent constants have been evaluated.¹⁵ In terms of *R* and *F* values defined by Swain and Lupton^{15b} for separation of the resonance and field inductive effects, the sulfenyl groups have positive *F* values and negative *R* values. Their positive *F* values (+0.30 for PhS, +0.37 for MeS) indicate that they are electron-withdrawing groups, but they are considerably weaker than strong electron-withdrawing groups, such as CN (*F* = 0.51) and NO₂ (*F* = 0.65). The negative *R* value (-0.23 for both PhS and MeS groups) indicates that they can also be moderately strong electron donors [compare their *R* values with those of strong electron-donor groups, such as OMe (-0.56) and NMe₂ (-0.98)]. The acidifying effect of a sulfenyl

group can therefore be interpreted as a field/inductive effect, that stabilizes the anion and is only mildly opposed by a resonance effect that destabilizes the anion.

Examination of the BDEs in Table 1 shows that the introduction of a PhS group weakens the C—H bond of CH₄, PhCH₃, PhCOCH₃ by about 12, 5 and 11.3 kcal, respectively, and weakens the N—H bond of BzNH₂, *t*-BuNH₂ and PhNH₂ by about 13, 13 and 9.7 kcal, respectively. These bond weakening effects can be interpreted as being due to (a) the formation of three-electron, two-centered bonds as the result of interaction of the spin-orbital and the non-bonded electron pair of the sulfur atom and/or (b) delocalization of the spin to the sulfur atom by resonance (**1a** \longleftrightarrow **1b** or **2a** \longleftrightarrow **2b**). The bond weakening effect caused by a PhS group on the N—H bond in aniline is larger than that for the C—H bond in toluene (9.7 vs 5 kcal). This is understandable since the resonance contributor **2b** (a nitranion) is more stable than **1b** (a carbanion).



The bond-weakening effect of the α -PhS group on the acidic C—H bond in PhCOCH₂SPh is surprisingly large, i.e. about as large as that on methane, 11 kcal. On the other hand, the effect of the α -PhS group on the acidic C—H bond of Ph₂CHSPh is to *strengthen* the BDE of the acidic C—H bond by 1 kcal. The striking difference in the α -PhS effect on the BDEs in these two substrates can be attributed on the one hand to an unusually strong acceptor-donor resonance effect in the PhCOCH(SPh)[•]

Table 2. Effects of alkoxy and sulfenyl groups on acidities and BDEs of α -C—H and α -N—H bonds

Entry	Acid	pK_{HA}^a	ΔpK_{HA}	BDE_{HA}	ΔBDE_{HA}
1	CH ₃ —H	~56	(0.0)	105 ^e	(0.0)
	MeOCH ₂ —H	~49	7	93 ^e	12
	MeSCH ₂ —H	~45	11	92 ^e	13
2	FIH—H	22.6	(0.0)	79.6 ^f	(0.0)
	9—MeOFI—H	22.1 ^b	0.5	73.0 ^b	6.6
	9—MeSFI—H	18.0 ^b	4.6	74.6 ^b	5.0
3	FIH—H	22.6	(0.0)	79.6 ^f	(0.0)
	9—PhOFI—H	19.9 ^b	2.7	74.3 ^b	5.3
	9—PhSFI—H	15.4 ^b	7.2	74.8 ^b	4.8
4	PhCOCH ₃	24.7	(0.0)	93.1 ^g	(0.0)
	PhCOCH ₂ OPh	21.1 ^b	3.6	80.6 ^b	12.5
	PhCOCH ₂ SPh	17.1 ^b	7.6	81.3 ^b	11.8
5	PhNH ₂	30.6	(0.0)	92.0 ^g	(0.0)
	PhNHOBz	23.5 ^c	7.1	75.8 ^c	16.2
	PhNHSPH	22.6 ^d	8.0	82.6 ^d	9.4

^a Data from Ref. 3 unless indicated otherwise.

^b Ref. 4b.

^c Ref. 21.

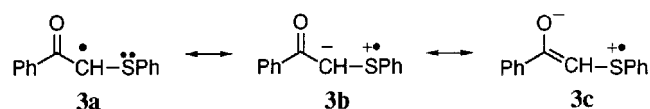
^d Table 1.

^e Ref. 6.

^f Ref. 7.

^g Ref. 8.

radical (**3a** \longleftrightarrow **3b** \longleftrightarrow **3c**, etc.) and on the other to strong steric constraints on the stability of the Ph₂C(SPh)[•] radical. Numerous other examples of the high sensitivity of radical stabilities to steric effects have been observed.¹⁶



The ΔBDE_{HA} values of about 10–13 kcal for the nitrogen-centered radicals formed in entries 5–7 in Table 1 point to an unusually strong stabilization of nitrogen-centered radicals by divalent sulfur. This is reminiscent of the 16 and 17 kcal weakening of the N—H bonds in benzamide and acetamide, respectively, on replacing the carbonyl group by a thiocarbonyl group.¹⁷

Comparison of the effects of alkoxy and alkylthio (alkylsulfenyl) groups on acidities and BDEs of α -C—H and α -N—H bonds

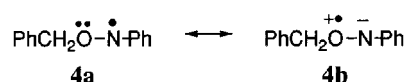
An alkylsulfenyl group (RS) has a superficial resemblance to an alkoxy group (RO). The two often exhibit different substituent effects, however, because sulfur has (a) longer bonds (1.8 Å for C—S vs 1.4 Å for C—O)^{18a} (b) a smaller electronegativity (2.58 for S vs 3.44 for O)¹⁹ and (c) a much higher polarizability (2.9 for S vs 0.8 for O).^{18b} Comparisons of the substituent effects of sulfenyl and alkoxy groups are presented in Table 2.

Examination of Table 2 shows that sulfenyl groups have larger acidifying effects than alkoxy groups on carbon acids. For example, an MeS group increases the

acidity of methane and fluorene by 11 and 4.6 pK_{HA} units, respectively, each about 4 pK_{HA} units larger than that for an MeO group (entries 1 and 2). The greater acidifying ability of a sulfenyl group than an alkoxy group can be explained by the larger polarizability of a sulfenyl group than an alkoxy group. Recent *ab initio* calculations suggest that the greater acidifying effect for a sulfenyl group is primarily due to the greater negative hyperconjugation in an RSCH₂[•] anion than that in an ROCH₂[•] anion.^{12a}

On the other hand, phenylsulfenyl and benzyloxy groups have similar acidifying effects on an N—H bond. Note that the acidity of PhNHSPH is only 0.9 pK_{HA} unit greater than that of PhNHOBz.²²

Examination of the BDEs in Table 2 shows that sulfenyl and alkoxy groups exert similar bond-weakening effects on carbon acids, e.g. 12 kcal (MeO) vs 13 kcal (MeS) for the H—CH₃ bond (entry 1), 6.6 kcal (MeO) vs 5 kcal (MeS) for the H—FIH bond (entry 2), 5.3 kcal (PhO) vs 4.8 kcal (PhS) for the H—FIH bond (entry 3) and 12.5 kcal (PhO) vs 11.8 kcal (PhS) for the H—CH₂COPh bond. Moreover, the BzO group has a much larger bond-weakening effect on the H—NHPh bond than does a PhS group (entry 5: 16.2 vs 9.4 kcal)²² owing to the unusually strong three-electron, two-center N—O bond in the corresponding radical (**4a** \longleftrightarrow **4b**):



(this is because the N and O atoms are of similar size and have 2p orbitals with similar energies). Similar strong bond-weakening effects have been observed for other N—H bonds where nitrogen is bonded to oxygen. For

Table 3. Effect of oxidation state of sulfur on BDEs of C—H and N—H bonds

Entry	Acid	pK_{HA}^a	ΔpK_{HA}	$E_{ox}(A^-)^d$	BDE_{HA}^e	ΔBDE_{HA}
1	CH ₃ SMe	45	(0.0)		92 ^f	(0.0)
	CH ₃ SOMe	35	10	-1.140	94	2.0
	CH ₃ SO ₂ Me	29	16	-0.733	99	7.0
2	PhCH ₂ SPh	30.8	(0.0)	-1.446	82.2	(0.0)
	PhCH ₂ SOPh	27.2	3.6	-0.943	88.8	6.6
	PhCH ₂ SO ₂ Ph	23.4	7.4	-0.677	89.7	7.5
3	Ph ₂ CHSPh	26.8	(0.0)	-1.187	82.6 ^g	(0.0)
	Ph ₂ CHSOPh	24.5	2.3		85.4 ^b	2.8
	Ph ₂ CHSO ₂ Ph	22.3	4.5		87.4 ^h	4.8
4	PhCOCH ₂ SPh	17.1	(0.0)	-0.649	81.7 ⁱ	(0.0)
	PhCOCH ₂ SOPh	14.0 ^b	3.1	0.036	93.3 ^b	11.6
	PhCOCH ₂ SO ₂ Ph	12.5	5.6		96.7 ⁱ	14.9
5	PhNHSPh	22.6 ^c	(0.0)	-0.943	82.6	(0.0)
	PhNHSOPh	17.3 ^c	5.3	-0.293	90.2	7.6
	PhNHSO ₂ Ph	12.0 ^c	10.6	-0.151	93.2	10.6

^a Data from Ref. 3 unless indicated otherwise.

^b Measured by X.-M. Zhang.

^c Table 7.

^d Irreversible oxidation potentials measured in DMSO with 0.1 M Et₄N⁺BF₄⁻ at a sweep rate of 100 mV s⁻¹, and referred to the ferrocene/ferrocenium couple.

^e Estimated from Eqn (1), this work, unless indicated otherwise.

^f Ref. 6b.

^g Ref. 9.

^h Ref. 5e.

ⁱ Ref. 7.

example, substitution of MeO and BzO groups for an N—H bond in CH₃CONH₂ decreases the BDE of the remaining N—H bond from 107 to 89 and 90 kcal, respectively.²³

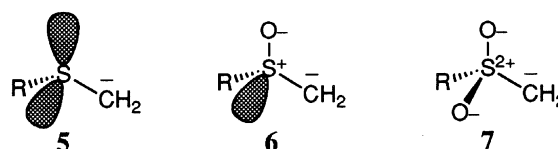
Effects of increasing the oxidation state of sulfur on acidities and BDEs of α -C—H and N—H bonds

The acidities of several series of sulfur-containing C—H and N—H acids with increasing oxidation state of sulfur are summarized in Table 3.

Examination of Table 3 shows that oxidation of the sulfinyl group to sulfinyl and oxidation of the sulfinyl group to sulfonyl increase the acidity by 10 and 6 pK_{HA} units in the MeSCH₃ series (entry 1), 3.6 and 3.8 pK_{HA} units in the PhCH₂SPh series (entry 2), 2.3 and 2.2 pK_{HA} units in Ph₂CHSPh series (entry 3) and 3.1 and 2.5 pK_{HA} units in the PhCOCH₂SPh series (entry 4), respectively. The size of the acidifying effect decreases as the acidity of the parent acid increases, showing a leveling effect. Oxidation of PhNHSPh to form PhNHSOPh and PhNHSO₂Ph increases the acidity of the N—H bond by 5.3 and 5.3 pK_{HA} units (entry 5), respectively. The effects for PhNHSPh series are each about 1.4 times that of the effect for the corresponding isoelectronic isomer PhCH₂SPh series (entry 2), indicating a larger effect for N—H acids than for C—H acids.

Increasing the oxidation state of sulfur can increase the stability of the anion by (a) increasing both the field/inductive effect [cf. the order of F values: MeS

(0.23) < MeSO (0.52) < MeSO₂ (0.53)] and the resonance effect [cf. the order of R values: MeS (-0.23) < MeSO (-0.03) < MeSO₂ (0.19)] and (b) increasing the static charge interaction between the negative charge on the carbon atom and the positive charge on the sulfur atom (5–7).^{12a}



Examination of Table 4 also shows that adjacent C—H bonds are strengthened on increasing the oxidation of sulfur, e.g. the oxidation state of MeS to MeSO, and of MeSO to MeSO₂ strengthens (a) the MeSCH₂—H bond by 2 and 7 kcal, respectively, (b) the PhSCH(Ph)—H bond by 6.6 and 0.9 kcal, respectively, (c) the Ph₂CH(SPh)—H bond by 2.8 and 2.0 kcal, respectively, (d) the PhCOCH(SPh)—H bond by 11.6 and 3.3 kcal, respectively, and (e) the PhNH(SPh)—H bond by 7.6 and 3.0 kcal, respectively. These bond-strengthening effects, which are associated with increasing oxidation state of sulfur, occur for several reasons: (a) the non-bonded electron pairs on sulfur are eliminated, thus removing the possibility of forming three-electron, two-centered bonds which would stabilize the radical and weaken the bond, (b) the increasing positive charge developed on the sulfur atom^{12a} destabilizes the electron-deficient radicals being formed and (c) the S⁺—O⁻ dipole interacts with the C^{δ-}—H^{δ+} dipole to stabilize the acids (8), i.e. the

Table 4. Comparisons of the substituent effects of carbonyl, sulfinyl and sulfonyl groups on acidities and BDEs of α -C—H and α -N—H bonds

Entry	Acid	pK_{HA}^a	ΔpK_{HA}	$E_{ox}(A^-)^d$	BDE_{HA}^e	ΔBDE_{HA}
1	CH ₃ —H	~56	(0.0)		105 ^f	(0.0)
	MeCOCH ₂ —H	26.5	29.5		94 ^g	11
	MeSOCH ₂ —H	35	21	-1.140	94	11
	MeSO ₂ CH ₂ —H	31.1	25	-0.733	99	6
2	PhCH ₃	43	(0.0)		87.5 ^f	(0.0)
	PhCH ₂ COPh	17.7	25.3		82.6 ^g	+4.9
	PhCH ₂ SOPh	27.2	15.8	-0.943	88.8	-1.3
	PhCH ₂ SO ₂ Ph	23.4	19.6	-0.677	89.7	-2.2
3	Ph ₂ CH ₂	32.2	(0.0)		81.5 ^h	(0.0)
	Ph ₂ CHCOPh	18.75	13.45		83 ^g	-1.5
	Ph ₂ CHSOPh	24.5	7.7		85.4 ^b	-3.9
	Ph ₂ CHSO ₂ Ph	22.3	9.9		87.3 ⁱ	-5.9
4	PhCOCH ₃	24.7	(0.0)		93.1 ^g	(0.0)
	PhCOCH ₂ COPh	13.4	11.3		93.3 ^g	-0.2
	PhCOCH ₂ SOPh	14.0 ^b	10.7	0.036	93.3 ^b	-0.2
	PhCOCH ₂ SO ₂ Ph	12.5	12.2		96.7 ^g	-3.6
5	PhNH ₂	30.6	(0.0)		92.0 ^h	(0.0)
	PhNHCOPh	20.0	10.6		97.0 ^g	-5.0
	PhNHSOPh	17.25 ^c	12.6	-0.293	90.2	+1.8
	PhNH ₂ SO ₂ Ph	11.96 ^c	18.6	-0.151	93.2	-1.2

^a Data from Ref. 3 unless indicated otherwise.

^b Measured by X.-M. Zhang.

^c Table 7.

^d Irreversible oxidation potentials measured in DMSO with 0.1 M Et₄N⁺BF₄⁻ at a sweep rate of 100 mV s⁻¹, and referred to the ferrocene/ferrocenium couple.

^e Estimated from Eqn (1), this work, unless indicated otherwise.

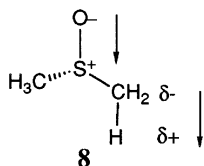
^f Ref. 6.

^g Ref. 8.

^h Ref. 7.

ⁱ Ref. 5e.

ground-state energy of the acid is decreased, which strengthens the C—H bond.²⁴



Comparison of the substituent effects of sulfinyl and sulfonyl groups with that of carbonyl groups on acidities and BDEs of α -C—H and α -N—H bonds

The sulfinyl group has a superficial resemblance to a carbonyl group in that the electronegativity of sulfur is close to that of carbon (2.64 vs 2.60),¹⁹ and the σ_p values of the two groups are nearly the same (0.50 vs 0.49).¹⁵ It is therefore expected that the two groups might have similar effects on the acidities and BDEs of adjacent C—H and N—H bonds. Comparisons of the substituent effects for the two groups together with those for the RSO₂ group on the acidities and BDEs of adjacent C—H and N—H bonds are summarized in Table 4.

Examination of Table 4 shows that the BDEs of

MeCOCH₂—H and MeSOCH₂—H bonds (entry 1) are identical within experimental error (± 1 kcal). In entry 4 the BDEs of the acidic C—H bond of PhCOCH₂COPh and PhCOCH₂SOPh are again within experimental error of one another.

Despite these similarities, the chemistry of CH₃CO and CH₃SO functions differ greatly. The principal characteristic of the carbonyl function is its propensity to undergo nucleophilic addition, whereas the principal characteristic of the sulfinyl group function is its ease of oxidation. In addition, the CH₃SO function has a pyramidal structure^{1c} in which delocalization of the negative charge from the anion center to oxygen atom is prohibited,^{12–14} unlike the CH₃CO function which has a planer structure which allows the negative charge to be delocalized from the anion center to oxygen atom by resonance.

As is apparent from Table 4, despite their much larger F values (0.52 vs 0.33), α -sulfinyl groups usually have smaller acidifying effects than do α -carbonyl groups on carbon acids. The RC=O function wins out because of its much larger R value (0.17 vs -0.03), which is due, in part, to its greater ability to stabilize the carbanion via resonance. The difference in acidities between carbonyl and sulfinyl acids is large in entries 1 and 2 in Table 3 (8.5 and 9.5 pK_{HA} units), but smaller in entry 3 (5.7 pK_{HA} units) where steric inhibition of resonance curtails the R

Table 5. Equilibrium acidities and homolytic BDEs of a series of *para*-substituted benzyl phenyl sulfones, phenylsulfenylsulfonamides and phenylsulfonamides

Substrate	G	p <i>K</i> _{HA} ^a	<i>E</i> _{ox} (A ⁻) ^c	BDE _{HA} ^d
<i>p</i> -GC ₆ H ₄ CH ₂ SO ₂ Ph	MeO	25.0 ^b	-0.807 ^b	89.1 ^b
	H	23.4 ^b	-0.652 ^b	90.3 ^b
	Br	22.3 ^b	-0.582 ^b	90.4 ^b
	CN	18.5 ^b	-0.299 ^b	91.8 ^b
<i>p</i> -GC ₆ H ₄ NH SPh	MeO	23.9	-1.060	81.6
	H	22.6	-0.943	82.6
	Br	21.6	-0.862	83.0
	CN	18.5	-0.625	84.2
<i>p</i> -GC ₆ H ₄ NHSO ₂ Ph	MeO	12.98	-0.086	89.1
	H	12.0	0.151	93.2
	Br	11.26	0.244	94.4
	CN	9.32	0.457	96.6

^a Table 7 unless indicated otherwise.^b Ref. 5a.^c Irreversible oxidation potentials measured in DMSO with 0.1 M Et₄N⁺BF₄⁻ at a sweep rate of 100 mV s⁻¹, and referred to the ferrocene/ferrocenium couple.^d Estimated from Eqn (1), this work, unless indicated otherwise.**Table 6.** Correlation analyses of acidities and homolytic BDEs of C—H and N—H bonds in a series of *para*-substituted benzyl phenyl sulfones, phenylsulfenylsulfonamides and phenylsulfonamides

Substrate	σ^a	p <i>K</i> _{HA} ^b <i>R</i> ²	BDE _{HA} ^b	<i>R</i> ²	<i>R</i> ²
<i>p</i> -GC ₆ H ₄ CH ₂ SO ₂ Ph	σ_p^-	0.998	-5.1	0.920	1.9
	σ_p^+	0.982	-7.0	0.951	2.7
	σ_p^-	0.870	-4.3	0.973	1.8
<i>p</i> -GC ₆ H ₄ NHSPh	σ_p^-	0.999	-4.2	0.955	3.9
	σ_p^+	0.984	-5.8	0.988	4.5
	σ_p^-	0.868	-3.6	0.964	2.8
<i>p</i> -GC ₆ H ₄ NHSO ₂ Ph	σ_p^-	0.992	-2.8	0.819	5.2
	σ_p^+	0.994	-3.9	0.910	7.6
	σ_p^-	0.904	-2.5	0.995	5.3

^a σ values selected from Ref. 11a.^b Linear correlation results (*R* = correlation coefficient, ρ = slope). Data taken from Table 5.

effect of PhCO. The acidity order is reversed by 2 p*K*_{HA} units in entry 5 for a nitrogen acid, where the *F* effect apparently becomes dominant.

The greater acidifying effect of a sulfonyl group than a carbonyl group is expected since both *R* and *F* values for the MeSO₂ group (0.19 and 0.53, respectively) are greater than those for MeCO group (0.17 and 0.33, respectively). This is observed in entries 4 and 5 but not in entries 1, 2 and 3. In fact, a greater acidifying effect for the sulfonyl group is observed in the gas phase (dimethyl sulfone is more acidic than acetone by 2.6 p*K*_{HA} units). The smaller acidifying effect for a sulfonyl group than a carbonyl group in DMSO is therefore due to a solvent effect, possibly because the dipole moment of Me₂SO₂ (4.4 D)²⁰ is much greater than that of Me₂CO (2.9 D),^{18c,d} which leads to a greater solvation energy for dimethyl sulfone than acetone in DMSO. The Me₂SO₂ acid is therefore more stabilized by solvation than acetone, and the acidifying effect for a sulfonyl group is decreased in DMSO. The smaller acidifying effects observed for

PhSO₂CH₂Ph (entry 2) and PhSO₂CHPh₂ (entry 3) in DMSO are possibly due to a similar reason.

Examination of the effects of RC=O, RSO and RSO₂ functions on the BDEs of adjacent C—H bonds in Table 4 shows that the RC=O function weakens the bond by 11 kcal when substituted into methane (entry 1) and by 5 kcal when substituted into toluene (entry 2). The RSO function appears from entry 1 to have a bond-weakening effect similar to that of RC=O on methane. The BDE of 88.8 for PhCH₂SOPh (entry 2) suggests, however, a 1.3 kcal strengthening of the C—H bond in toluene, which is supported by the 0.2 and 3.9 kcal strengthening effects recorded in entries 3 and 4. The data for RSO₂ in entry 1 indicates a 6 kcal bond-weakening effect, relative to methane. On the other hand, the data for the substrates in entries 2, 3 and 4 all point to bond-strengthening effects.

The BDEs in sterically congested diphenylmethane show that the introduction of even the PhCO function into Ph₂CH₂ is bond strengthening by 1.5 kcal because of

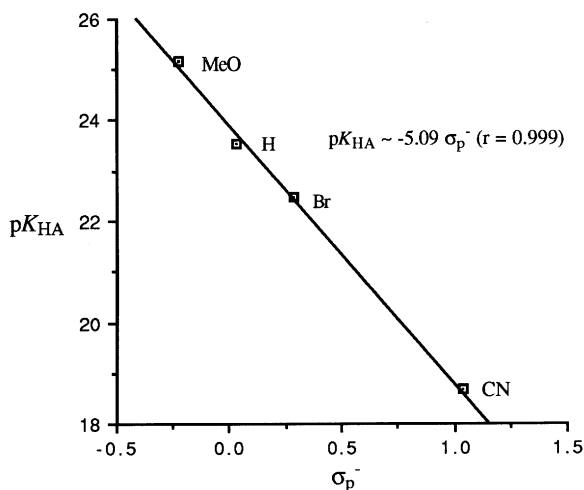


Figure 1.

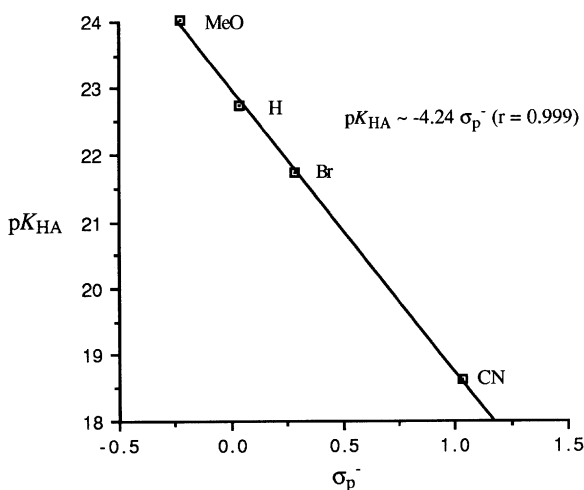


Figure 2.

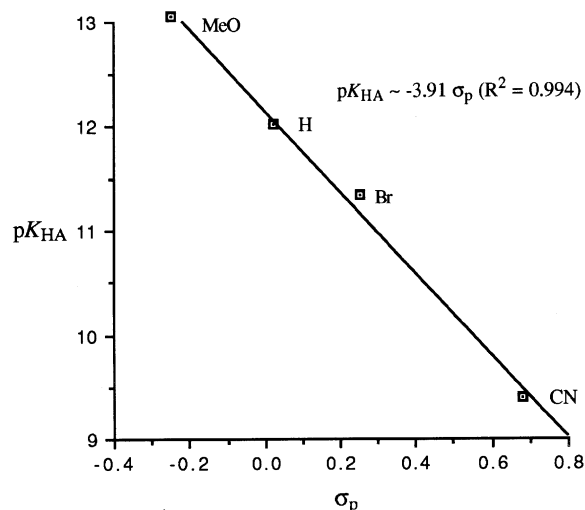


Figure 3.

steric inhibition of resonance in the radical. Introduction of PhSO and PhSO₂ groups causes 3.9 and 5.9 kcal bond strengthening effects, respectively.

The effects on BDE of the PhNH—H bond are varied. Introduction of a PhCO group into aniline strengthens the remaining N—H bond by 5 kcal, but introduction of a PhSO group weakens the remaining N—H bond by 1.8 kcal and introduction of a PhSO₂ group strengthens the remaining N—H bond by 1.2 kcal.

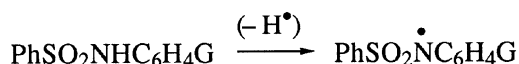
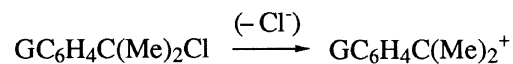
Remote substituent effects on acidities and BDEs of N—H bonds in sulfenamidides and sulfonamidides

The equilibrium acidities and BDEs of a series of 4-substituted benzyl phenyl sulfones (4-GC₆H₄CH₂SO₂Ph), benzenesulfenamidides (4-GC₆H₄NHSPH) and benzenesulfonamidides (4-GC₆H₄NHSO₂Ph) (G = OMe, H, Cl, CN) are summar-

ized in Table 5. The results of linear correlation analyses of the pK_{HA} and BDE values with corresponding σ^+ , σ and σ^- values for these sulfones, sulfenamidides and sulfoamidides are summarized in Table 6.

Examination of Table 6 shows that the acidities of remotely substituted benzyl phenyl sulfones, *p*-GC₆H₄CH₂SO₂Ph, substituted phenylsulfenamidides, *p*-GC₆H₄NHSPH, and substituted phenylsulfonamidides, *p*-GC₆H₄NHSO₂Ph, are well correlated by σ_p^- with a slope of -5.1 (Fig. 1), -4.2 (Fig. 2) and -2.8 (Fig. 3). The slope for the limited plot of pK_{HA} values for *para*-substituted benzyl phenyl sulfones is only slightly higher than that for *meta*-substituted benzyl phenyl sulfones (-4.76).^{4a} The acidities of the *para*-substituted phenylsulfonamidides are also well correlated with σ_p with a slope of -3.9 (possibly because the appropriate scale for this set of acidities lies between the σ_p and σ_p^- scales).

The BDEs of the *para*-substituted phenylsulfonamidides plot well with σ^+ (Fig. 4), however. This can be rationalized since Brown's σ_p^+ scale is based on the solvolysis of cumyl chlorides and the radicals formed on homolysis of the phenylsulfonamidides also have appreciable cationic character since they are attached to the strongly electron-withdrawing sulfonyl group.



Good linear correlations were not observed between the BDEs of *para*-substituted benzyl phenyl sulfones and phenylsulfenamidides, possibly owing to the small size of the substituent effects on BDEs (2.7 and 2.6 kcal, respectively), which are not much larger than the experimental uncertainties of BDE values (± 2 kcal).

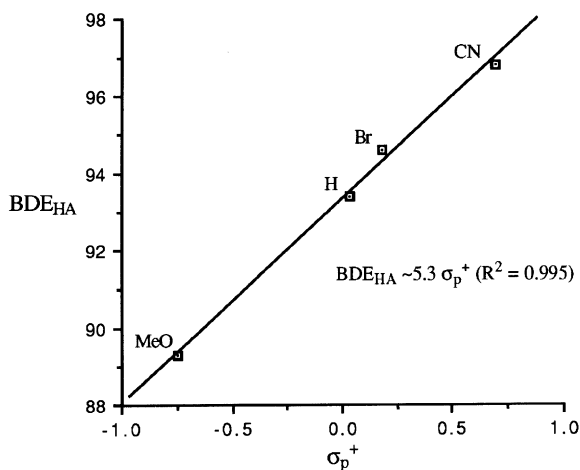


Figure 4.

In terms of Eqn (1), BDEs depend on pK_{HA} and $E_{ox}(A^-)$. Also, within a family, pK_{HA} and $E_{ox}(A^-)$ are often linearly related.²⁵ It is perhaps not surprising, then, to find that the BDEs plot linearly with $E_{ox}(A^-)$ (Fig. 5) for 4-substituted benzyl phenyl sulfones, phenylsulfenani- lides and phenylsulfonani- lides.

Examination of Fig. 5 shows that the plot of the BDEs of the carbon acid family of 4-substituted benzyl phenyl sulfones vs $E_{ox}(A^-)$ has a slope close to that of the nitrogen acid family of 4-substituted phenylsulfenani- lides, although the BDEs of the latter are about 6 kcal smaller. The 4-substituted phenylsulfonani- lides have appreciably larger N—H BDEs because of the electron- withdrawing effect in destabilizing the radical being formed. Linear correlations between BDEs and $E_{ox}(A^-)$ values in H—A acids occur because the oxidation of A^- and the homolysis of the H—A bond give the same radical.

CONCLUSION

Introduction of an α -PhS group greatly increases the acidities of adjacent C—H and N—H bonds and also weakens the adjacent C—H and N—H bonds appreciably. The effect of introducing an α -PhS group into PhCOCH₃ to give PhCOCH₂SPh weakens the acidic C—H bond by 11 kcal, whereas the effect of introducing an α -PhS group into Ph₂CH₂ to give Ph₂CHSPh *strengthens* the acidic C—H bond by 1 kcal. The striking difference in the α -PhS effect on the BDE in these two substrates is attributed to a strong stabilizing acceptor–donor ('captodative') effect on the corresponding PhCOCH(SPh)[•] radical and a strong destabilizing steric effect on the Ph₂C(SPh)[•] radical. The much greater bond-weakening effect of the α -PhS group on the N—H bond in PhN(SPh)H (9.7 kcal) than on the C—H bond in PhCH₂SPh (5 kcal) is attributed to the greater

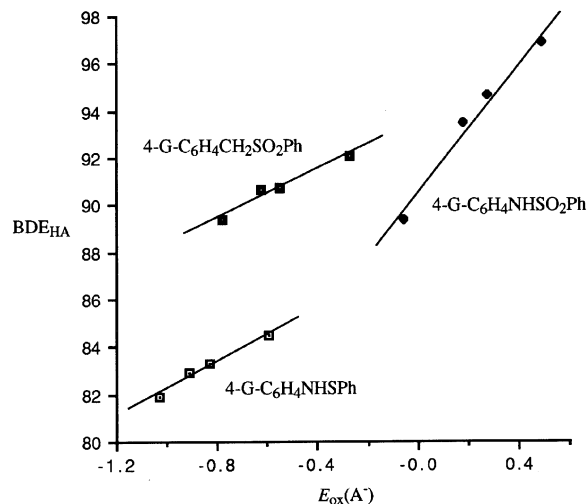


Figure 5.

stability of the $RS^{+\bullet} - N^-R$ contributor (a nitranion) than the $RS^{+\bullet} - C^-HR$ contributor (a carbanion).

α -Alkylsulfenyl groups have greater acidifying effects on C—H bonds than do an α -alkoxy groups, but have similar effects on N—H bonds (Table 2). On the other hand, an α -BzO group weakens the N—H bond in aniline to a much greater degree than does an α -PhS group (16 vs 9.5 kcal) because the three-electron, two-center N—O in the corresponding radical **4a** \longleftrightarrow **4b** is unusually strong.

Oxidations of sulfenyl functions to sulfinyl functions and of sulfinyl functions to sulfonyl functions cause progressive increases in acidities (amounting to 2.2–7 pK_{HA} units) and increases in the BDEs (amounting to 1–12 kcal). Sulfinyl groups usually have smaller acidifying effects than do carbonyl groups on C—H acids, but have larger acidifying effects than do carbonyl groups on N—H acids.

The pK_{HA} values of 4-GC₆H₄CH₂SO₂Ph, 4-GC₆H₄NHSPH and 4-GC₆H₄NHSO₂Ph (G = MeO, H, Br, CN) were found to be well correlated with the σ_p^- scale and The BDE_{HA} values for 4-GC₆H₄NHSO₂Ph were found to be well correlated with the σ_p^+ scale. Good linear correlations were also found for the BDEs of 4-GC₆H₄CH₂SO₂Ph, 4-GC₆H₄NHSPH and 4-GC₆H₄NHSO₂Ph with the corresponding $E_{ox}(A^-)$ values. These linear correlations are in accord with a general rule that when quantities for two series of compounds are correlated well with one other, there must be an underlying molecular cause. For example, the BDE_{HA} values for 4-GC₆H₄NHSO₂Ph were found to be best correlated with the σ_p^+ scale because the latter is based on the solvolysis of cumyl chlorides in which a cumyl cation is formed, and in the homolysis of the N—H bonds in sulfonamides wherein the *p*-GC₆H₄N(SO₂Ph)[•] radical is formed, both the cumyl cation and the *p*-GC₆H₄N(SO₂Ph)[•] radical are highly electron-deficient species. Good linear correlations between BDEs and the

Table 7. Equilibrium acidities of benzenesulfenilides, benzenesulfinilide and benzenesulfonilides determined by the overlapping indicator method^a

Acid	Indicator (pK_{In}^b)	$pK_{HA} \pm SD^l$
BzNHSPH	TH (30.6) ^c	30.6 \pm 0.1
<i>t</i> -BuNHSPH	TH (30.6) ^c	30.8 \pm 0.2
PhNHSPH	FIH (22.6) ^d	22.63 \pm 0.03
<i>p</i> -MeOC ₆ H ₄ NHSPH	BzN=CPh ₂ (24.3)	23.9 \pm 0.1
<i>p</i> -BrC ₆ H ₄ NHSPH	2NPANH (20.66) ^e	21.6 \pm 0.1
<i>p</i> -NCC ₆ H ₄ NHSPH	CNAH (18.9) ^f	18.5 \pm 0.1
PhNHSOPH	FMY30 (18.1) ^g	17.25 \pm 0.05
BzNHSO ₂ Ph	MCIPFH (16.8) ^h	16.21 \pm 0.02
<i>t</i> -BuNHSO ₂ Ph	FMY30 (18.1) ^g	18.05 \pm 0.01
PhNHSO ₂ Ph	HZFO2P (11.98) ⁱ	11.96 \pm 0.01
<i>p</i> -MeOC ₆ H ₄ NHSO ₂ Ph	HZFO2 (12.95) ^j	12.98 \pm 0.03
<i>p</i> -BrC ₆ H ₄ NHSO ₂ Ph	HZFO2P(11.98) ⁱ	11.26 \pm 0.05
<i>p</i> -NCC ₆ H ₄ NHSO ₂ Ph	MeO2CFH(10.35) ^k	9.32 \pm 0.02

^a Ref. 33.^b Indicators or standard acids used with their pK_{HA} values.^c Triphenylmethane.^d Fluorene.^e 2-Naphthylacetonitrile.^f 4-Chloro-2-nitrophenol.^g 2-(Phenylsulfonyl)fluorene.^h 9-(3-Chlorophenyl)fluorene.ⁱ 9-Fluorenone 2,4-dichlorophenylhydrazone.^j 9-Fluorenone 2-chlorophenylhydrazone.^k 9-Methoxycarbonylfluorene.^l Measured pK_{HA} and standard deviation.

corresponding $E_{ox}(A^-)$ values are observed because both the oxidation of the anion (A^-) and the homolysis of the H—A bond form the same radical.

EXPERIMENTAL

NMR spectra were recorded on a Gemini XL-300 (300 MHz) or an XLA 400 (400 MHz) spectrometer. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Materials. Aniline, *p*-bromoaniline, *p*-cyanoaniline, *p*-methoxyaniline, benzenesulfonyl chloride and thiophenol were purchased from Aldrich and used as received. Benzenesulfonyl chloride was prepared by reaction of thiophenol and sulfonyl chloride²⁶ in 83% yield as a red liquid, b.p., 48–50 °C/2 Torr (lit.²⁶ 41–42 °C/1.5 Torr). Benzyl phenyl sulfide, benzyl phenyl sulfoxide and benzyl phenyl sulfone were available from previous work in our laboratory.²⁷

Benzenesulfenilides, *N*-tert-butylbenzenesulfenamide and *N*-benzylbenzenesulfenamide. These were prepared by the method of Miura and Kinoshita.²⁸ Benzenesulfenilide, m.p. 108–109 °C (lit.²⁸ 109–110 °C); 4'-methoxybenzenesulfenilide, m.p. 69–70 °C (lit.²⁸ 69–70 °C); 4'-bromobenzenesulfenilide, m.p. 94–95 °C (lit.²⁸ 94–95 °C); 4'-cyanobenzenesulfenilide, m.p. 98–100 °C. *N*-tert-Butylbenzenesulfena-

mid²⁹ and *N*-benzylbenzenesulfenamide³⁰ were obtained as colorless liquids.

Benzenesulfinilide. Benzenesulfinilide was obtained by reaction of thionylaniline (PhN=S=O) and phenylmagnesium bromide in 70 % yield, m.p. 53–55 °C (lit.³¹ 54–56 °C).

Benzenesulfonilides, *N*-tert-butyl benzenesulfonamide and *N*-benzylbenzenesulfonamide. These were prepared by the method of Ludwig *et al.*³² Benzenesulfonilide, m.p. 108–109 °C (lit.³² 109–110 °C); 4'-methoxybenzenesulfonilide, m.p. 94–95 °C (lit.³² 95–96 °C); 4'-bromobenzenesulfonilide, m.p. 134–135 °C (lit.³² 134–136 °C); 4'-cyanobenzenesulfonilide, m.p. 171–172 °C (lit.³² 172–173 °C).

Equilibrium acidities and oxidation potentials measurements. The equilibrium acidities in DMSO solution were determined by the indicator overlapping titration method as described previously.³³ The results are summarized in Table 7.

Oxidation potentials were measured with a conventional cyclic voltammetric instrument as described previously.⁵ The working electrode consisted of a 1.5 mm diameter platinum disk embedded in a cobalt glass seal. The counter electrode was platinum wire (0.3 mm in diameter). The reference electrode was Ag/AgI, and the redox potentials reported were referenced to the ferrocene/ferrocenium couple. In general,

tetraethylammonium tetrafluoroborate was used as the electrolyte. When the pK_a of the weak acid to be measured was higher than 30, tetrabutylammonium hexafluorophosphate was used as the electrolyte. The redox potential values measured in several different runs were usually within a range of 50 mV. The uncertainties of BDE values estimated using Eqn (1) were estimated to be less than 2 kcal based on the experimental errors of oxidation potential values and equilibrium acidity values.

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