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Effects of Adjacent Acceptors and Donors on the Stabilities of Carbon-Centered Radicals

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Abstract: The radical stabilization energies (RSEs) for 21 radicals, $GCH_2^•$, where G is an electron donor or acceptor group, were estimated from differences in homolytic C–H bond dissociation energies (ΔBDEs relative to that of methane). These RSEs were found to agree reasonably well in *order* with theoretically calculated RSEs that have been reported and with those obtained by averaging RSEs from nine different methods (a literature RRS_x scale). But the RSEs estimated from ΔBDEs were almost without exception larger because the theoretical calculations and RRS_x method greatly underestimate the *size* of most RSEs. The RSEs for $GCH_2^•$ radicals were found to be enhanced to the extent that G is able to delocalize an odd electron on an adjacent carbon atom and were diminished by the presence of electron-withdrawing properties in G. Most groups stabilize the radical, but when the electron-withdrawing effect of the group is large, as in $F_3C^•$ and $Me_3N^+CH_2^•$ radicals, the net effect is to destabilize the radical relative to the methyl radical. The RSEs of 12 radicals of the type $RSC^•HG$ or $PhSC^•HG$, relative to that of the $GCH_2^•$ radical, were found to increase progressively as the acceptor group G was changed along the series Ph, fluorenyl (Fl), CO_2Et, CN, COMe, and COPh. The RSEs of these donor–acceptor radicals were all smaller than the sum of the RSEs of the singly-substituted radicals, $GCH_2^•$ and $PhSCH_2^•$ (or $RSCH_2^•$). The effects of a second PhS or like donor and of a second acceptor on the RSEs were also determined. Examination of the RSEs of $GC^•(Ph)CN$ radicals indicates that the interactions of G and CN in the $GC^•CN$ moieties, with G = MeO, EtS, or c-$C_5H_{10}N$, are not synergistic as has been claimed from ESR studies.

The gas-phase homolytic bond dissociation energies (BDEs) of hydrocarbons bearing heteroatom substituents, such as substituted methanes, GCH_2–H, have long been considered to provide the best estimates for the stabilities of the corresponding radicals, $GCH_2^•$.[1] The determination of gas-phase BDEs has been limited for experimental reasons largely to bonds in small molecules, however. Recently we developed a simple method of estimating the BDEs of the acidic H–A bonds in weak acids, HA, that are strong enough to allow acidity measurements to be made in DMSO, i.e., acids in the pK_{HA} range 2–32, by means of a semiempirical equation (eq 1).[2] The pK_{HA} values of the acids

$$\mathrm{BDE_{HA}} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.1E_{\mathrm{ox}}(\mathrm{A}^-) + 73.3 \qquad (1)$$

are believed to be accurate to ±0.2 kcal/mol, and the oxidation potentials of the conjugate bases (A^-) of the acids, although usually irreversible,[3] are believed to be accurate to ±2 kcal/mol. In fact, for 18 compounds where literature values were available, BDEs estimated by this method have recently been shown to agree with the best gas-phase values to within ±2 kcal/mol, or better, in all but three instances (PhO–H, PhNH–H, and Ph_3C–H), and the literature values for PhNH–H and Ph_3C–H were shown to be in error.[2] This method is capable of providing BDE data for hundreds of H–A bonds that would be difficult or impossible to obtain by other means.

It has been of interest to measure the BDEs of the C–H bonds of carbon atoms attached to both a donor (*D*) and an acceptor (*A*) group in order to compare the effects of this combination on the radical stabilization energies (RSEs) of radicals of the type $DC^•A$.[5] The expectation is that the RSEs usually will be greater for such radicals than for either of the individual effects of $DC^•$ or $C^•A$ radicals. Indeed, there is considerable qualitative evidence to support this expectation, as has been brought out by Sustmann and Korth in their recent review titled "The Captodative Effect".[6]

In our laboratory we have made estimates of the BDEs of the acidic C–H bonds in several molecules of the type DCH_2A, where the donor is RO or R_2N and the acceptor is PhCO, RCO, or $(CN)_2$. In every instance, we have found that the combined effects are larger than the individual effects. The combined effects are additive or nearly additive when *D* is RO or R_2N and *A* is PhCO or RCO, but less than additive by 5 kcal/mol when *D* is R_2N and *A* is $(CN)_2$. (Henceforth, kcal/mol will be abbreviated as kcal.) The additive effects observed when *D* is RO or NR_2 and *A* is PhCO have been interpreted to mean that the combined effects are actually synergistic because we assume that they have been diminished by a saturation effect.[7] When the effects of MeO and CN groups on the C–H BDE act through the π system of the central ring of anthracene, they have been found to be more than additive, i.e., synergistic.[8] On the other hand, when R_2N and CN groups interact in a donor–acceptor system where a Ph group is also attached to the central carbon atom, i.e., in $R_2NCH(Ph)CN$, their effects are much less than additive because of the presence of saturation and steric effects.[9]

The combined effects of donors and acceptors on the BDEs of N–H bonds in a few molecules of the type *D*NH*A* have also been examined. PhCO and MeCO acceptors were found to have negligible effects on the BDEs of the N–H bonds in $PhCONH_2$ and $MeCONH_2$, relative to the BDE of H_2N–H.[10] This is in sharp contrast to the 11–12 kcal decreases in the BDEs for the C–H bonds in $PhCOCH_2$–H and $MeCOCH_2$–H.[11] Introduction of MeO, HO, and NH_2 groups into the NH group of $PhCONH_2$ to give PhCONHOMe, PhCONHOH, and $PhCONHNH_2$ caused decreases in BDEs of 17, 19, and 25 kcal, respectively.[10] These

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† Northwestern University.
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[3] Comparisons of irreversible oxidation potentials measured under our usual conditions (scan rate of 100 mV/s) with reversible potentials measured under fast scan conditions have shown that the difference in $E_{ox}(A^-)$ values is usually 50 mV or less.[4]

[4] (a) Bausch, M. J.; Gostowski, R. *J. Org. Chem.* **1991**, *56*, 6260–6262. (b) Satish, A. V.; Zion, D. A.; Hupp, J. T. Unpublished results.

[5] These radical stabilization energies are defined as ΔBDE = BDE(CH_3–H) – BDE($^{D}_{A}$C–H) = RSE, where the BDE of the C–H bond in methane is 105 kcal/mol[1] and that for the C–H bond in *D*CH*A* is estimated from eq 1.

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Table I. Radical Stabilization Energies (RSEs) of Substituted Methyl Radicals

no.	substituent	ΔBDE ref 1^{a} ($GCH_2^{\bullet}$)	RRS_x ref 15 ($GCH_2^{\bullet}$)	ΔBDE ref 12 ($G\text{-}Fl^{\bullet}$)^{j}	RSE_{calcd} ref 13 ($GCH_2^{\bullet}$)	RSE_{calcd} ref 14 ($GCH_2^{\bullet}$)
	H	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
1	F	3	−1.4	0.5	1.6	0.6
2	Cl	4	2.4	2.4	2.6	0.05
3	Me	7	2.3	4.5	3.3	3.2
4	PhSe	8^{b}				
5	MeO	12	4.5	7	5.3	6.1
6	HO	11	3.1		5.7	5.2
7	PhO		4.9	5.5		
8	RS	12^{c}	10.7	5.4	5.7 (SH)	3.3 (SH)
9	PhS	12^{d}	10.7	5.2		
10	Me_3Si	6^{e}	3.5	1.5		
11	Ph	17	11.2	5.9		14.3
12	$H_2C{=}CH$	19^{c}	12.8		7.8	15.8
13	H_2N	22^{f}	8.4	15	10.3	10.2
14	HMeN	18	10.9	14	9.7	
15	Me_2N	21	8.9	8		
16	Me_3N^+			−5	−4 (H_3N^+)	
17	Ph_2P			4.8	4.3 (H_2P)	
18	Ph_3P^+			−1	−0.4 (H_3P^+)	
19	F_3CSO_2	2^{g}				
20	PhSO		5.9	−0.5	1.1 (HSO)	
21	$c\text{-}C_5H_5N^+$			−1		
22	$PhSO_2$	6^{g}	4.5	−2	−0.8 (HSO_2)	
23	NO_2	7^{g}	9.4		1.7	3.7
24	$^+N{\equiv}C^-$			5.3		
25	$N{\equiv}C$	12 (10^{h})	8.6	5.7	5.3	7.2
26	H_2NCO		9.1	2.3	5.5	
27	MeOCO	10	7.9	3.9	5.7 (CO_2H)	3.5 (CO_2H)
28	MeCO	11				
29	PhCO	12^{i}			5.7 (HCO)	7.3 (HCO)

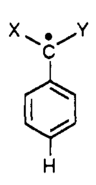
[a] Reference 1 unless otherwise noted; ΔBDE = BDE(CH_3–H, 105 kcal/mol) − BDE(GCH_2–H). [b] Assumed to be the same as GCH_2COPh (see text). [c] Reference 18a. [d] Assumed to be the same as RS (see text). [e] Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–252. [f] Reference 7. [g] Bordwell, F. G.; Harrelson, J. A., Jr.; Zhang, X.-M. *J. Org. Chem.* **1991**, *56*, 4448–4450. [h] Kanabus-Kaminska et al. (Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311–3314) have recently reported a BDE value of 95 kcal/mol. [i] Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714–1718. [j] BDE(FlH_2) = 80 kcal/mol.

effects are larger than those in the analogous ketones, $PhCOCH_2OMe$ (ΔBDE = 13 kcal) and $PhCOCH_2NH_2$ (ΔBDE ≅ 22 kcal), but appear to be caused solely by the presence of the $NHNH_2$ or NHOR moieties. The acceptor function appears to play little or no role since PhCO can be replaced by $PhSO_2$.

In the present paper, we examine the effects of PhS and RS donors interacting with acceptors in $PhSC^{\bullet}HA$ and $RSC^{\bullet}HA$ type radicals, where A is Ph, fluorenyl (Fl), CO_2Et, CN, MeCO, or PhCO. The results are then compared with those for $DC^{\bullet}HCOPh$ type radicals, (where D is Ph, Me, $c\text{-}C_5H_5N^+$, MeO, RS, PhS, PhSe, and R_2N), $DC^{\bullet}(Ph)CN$ type radicals (where D is R, MeO, PhO, RS, PhS, and R_2N), and a few double-donor radicals of the type $D_2C^{\bullet}A$.

Results and Discussion

Effects of Individual Donors and Acceptors on Radical Stabilization Energies (RSEs). Before attempting to evaluate RSEs for carbon-centered radicals attached to both a donor and an acceptor substituent, we will examine the individual effects of donors and acceptors on these radicals. Table I compares RSEs for donors and acceptors as estimated by various methods. The RSEs in column 1 of Table I are ΔBDEs relative to CH_3–H (BDE = 105 kcal) taken from the review of McMillen and Golden[1] or other sources. The RSEs in column 3 are ΔBDEs for 9-G-fluorenes relative to fluorene (BDE = 80 kcal).[12] The RSEs in column 4 are from calculations of Pasto,[13] and the RSEs in column 5 are from calculations by Leroy.[14] In column 2 the RRS_x values of Merényi[15] are an average of RSEs derived by the following nine methods: (a) calculations by Leroy;[14] (b) thermolysis of azo compounds $GC(Me)_2N{=}NC(Me)_2G$;[16] (c) rates of rearrangements of 1,2-disubstituted cyclopropanes; (d) enthalpies of cleavage of strained C–C bonds;[17] (e) barriers to rotation;[18] (f) the $\sigma_\alpha^{\bullet}$ scale;[19a] (g) the $\sigma_{sec}^{\bullet}$ scale;[20] (h) the rates of rearrangement of methylenecyclopropanes;[21] and (i) the $\Delta S(\%)$ scale.[6] The last scale is based on delocalization spin density parameters derived from ESR hyperfine coupling constants for benzyl radicals of types **1** and **2**. (We will discuss these effects further in a later section.)



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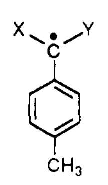

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ΔBDEs were listed in the Merényi tables[15] as possible measures of RSEs, but were not included in the averaging because comparisons indicated that "for substituents such as *t*-Bu and MeO

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the radical stabilizing power would be *overestimated* by BDEs".

Estimates of the effects of para donor substituents on the ΔBDEs for fluorenes have shown that the RSEs (relative to HFl$^•$) on these carbon-centered radicals are small, i.e., 0.1, 0.4, 1.0, 1.1, and 0.6 kcal for 3-F, 3-Me, 3-MeO, 3-MeS, and 3-PhS, respectively.[12] The same is true for para donor substituents in phenylacetonitrile radicals (relative to PhC$^•$HCN), i.e., 4-F (0.1), 4-PhS (0.3), 4-Me (0.4), 4-Ph (0.8), 4-MeO (1.4), and 4-Me_2N (4 kcal).[22] Equilibrium radical–dimer measurements by ESR on substituted triphenylmethane radicals have also revealed small radical stabilizing effects, e.g., log (K/K_0) values for para substituents were found: *t*-Bu (0.38), MeO (0.66), Ph (0.93), CF_3 (0.33), CN (0.82), and PhCO (1.0). Either two donors or two acceptors were found to act additively. No specific synergism of a donor with an acceptor was observed.[23] Similar small effects have been observed for RSEs for para-substituted triphenylmethanes: *t*-BuO (0), Cl (0.9), Ph (0.5), and PhS (0 kcal).[24] Examination of Table I shows that, almost without exception, the RSEs obtained from ΔBDEs relative to $CH_3^•$ (column 1) are larger than the RRS_x values (column 2). This is no doubt due to the inclusion of para substituent effects [$\sigma_\alpha^•$, $\sigma_{sec}^•$, and $\Delta S(\%)$] in the RRS_x averaging. Also, the inclusion of substituent data based on secondary, tertiary, benzylic, or allylic radicals will lower the average value because of the presence of saturation effects. It follows that RRS_x values must greatly *underestimate* RSEs.

The use of ΔBDEs as measures of RSEs has been questioned by several investigators on the basis that ground-state effects on the radical precursors have not been taken into consideration.[6,15,25] It is true that ground-state effects can exert appreciable effects on the BDEs of polar bonds such as those in benzyl bromides[25] and C–C bonds in strained molecules,[17] but for the nonpolar C–H bonds in unstrained systems such as GCH_2–H, where only one type of bond is broken, we believe that substituent effects on ground states are likely to be small compared to the substituent effects on most $GCH_2^•$ radicals.

The *order* of the RSEs derived from ΔBDEs of GCH_2–H agrees reasonably well for the most part with the RRS_x values, but there are a few discrepancies in the order, as well as the size. For example, RSE values for $PhSCH_2^•$ and $RSCH_2^•$ radicals (entries 8 and 9) are about twice the size of those for $PhOCH_2^•$ and $ROCH_2^•$ radicals (entries 5–7) according to the RRS_x scale, whereas they are of about the same size according to the ΔBDE scale. The *much* larger RSE values for $R_2NCH_2^•$ groups (entries 13–15) indicated by the ΔBDE scale than by the RRS_x scale are also noteworthy. The large size of these RSEs for MeO, H_2N, and R_2N type groups indicated by the ΔBDE scale has been confirmed by the ΔBDEs observed for the acidic C–H bonds in $MeOCH_2COPh$, H_2NCH_2COPh, and R_2NCH_2COPh.[7]

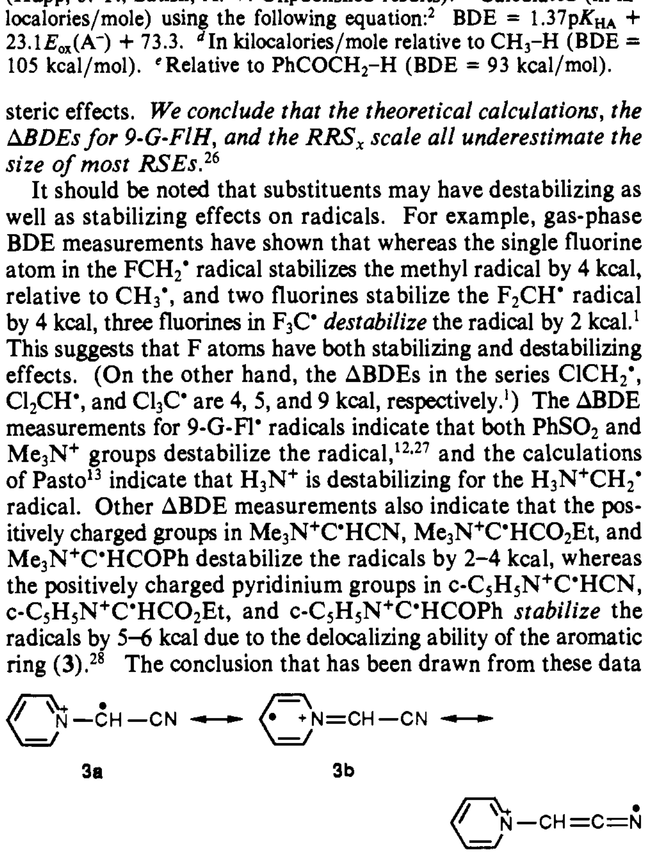
The sizes of the RSEs for $GCH_2^•$ given by the calculations of Pasto[13] and Leroy[14] (columns 4 and 5, respectively, in Table I) agree reasonably well with one another and also agree fairly well with the ΔBDE values for 9-G-Fl$^•$ radicals in column 3. The latter agreement is significant, since the BDEs of 9-G-FlH compounds are subject to appreciable saturation and often to steric effects. The RSEs of the 9-G-Fl$^•$ radicals where G is a small group, such as Me, H_2N, or CN (calculated from ΔBDE, relative to 9-H-FlH, BDE = 80 kcal), are 4.5, 15, and 5.7 kcal, respectively, i.e., about 50–65% as large as those for the corresponding $GCH_2^•$ radicals calculated from ΔBDE, relative to CH_3–H, because of saturation. On the other hand, when G is larger in size, such as Ph, Me_2N, or MeCO, their steric demands are greater and the RSEs are 6, 8, and 4 kcal, respectively, i.e., only about 40% of the size of ΔBDE for the corresponding $GCH_2^•$ radicals, because of saturation *and* steric effects. *We conclude that the theoretical calculations, the ΔBDEs for 9-G-FlH, and the RRS_x scale all underestimate the size of most RSEs.*[26]

Table II. Estimates of Radical Stabilizing Energies (RSEs; RSE = ΔBDE) for the PhCO Acceptor with Various Donors

DCH_2COPh	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[c]	RSE[d]	ΔBDE[e]
HCH_2COPh	24.7	−0.607	93	12	(0.0)
$MeCH_2COPh$	24.4	−0.815	88	17	5
c-$C_5H_5N^+CH_2COPh$	10.7	−0.036	87	18	6
$PhSeCH_2COPh$	18.6	−0.599	85	20	8
$PhCH_2COPh$	17.7	−0.645	82.5	22.5	10.5
$PhSCH_2COPh$	17.1	−0.649	81.5	23.5	11.5
$MeOCH_2COPh$	22.8	−1.050	80.5	24.5	12.5
c-$C_5H_{10}NCH_2COPh$	23.5	−1.439	72	33	21

[a] Measured in DMSO against two indicators. [b] Irreversible potentials (E_{pa}) measured in DMSO by cyclic voltammetry relative to the Fc/Fc$^+$ couple, as previously described.[2] Oxidation potentials for 28 organic anions measured by fast scan CV have been found to be reversible with $E_{1/2}$ values within 50 mV of the irreversible potentials (Hupp, J. T.; Satish, A. V. Unpublished results). [c] Calculated (in kilocalories/mole) using the following equation:[2] BDE = 1.37pK_{HA} + 23.1$E_{ox}(A^-)$ + 73.3. [d] In kilocalories/mole relative to CH_3–H (BDE = 105 kcal/mol). [e] Relative to $PhCOCH_2$–H (BDE = 93 kcal/mol).

It should be noted that substituents may have destabilizing as well as stabilizing effects on radicals. For example, gas-phase BDE measurements have shown that whereas the single fluorine atom in the $FCH_2^•$ radical stabilizes the methyl radical by 4 kcal, relative to $CH_3^•$, and two fluorines stabilize the $F_2CH^•$ radical by 4 kcal, three fluorines in $F_3C^•$ *destabilize* the radical by 2 kcal.[1] This suggests that F atoms have both stabilizing and destabilizing effects. (On the other hand, the ΔBDEs in the series $ClCH_2^•$, $Cl_2CH^•$, and $Cl_3C^•$ are 4, 5, and 9 kcal, respectively.[1]) The ΔBDE measurements for 9-G-Fl$^•$ radicals indicate that both $PhSO_2$ and Me_3N^+ groups destabilize the radical,[12,27] and the calculations of Pasto[13] indicate that H_3N^+ is destabilizing for the $H_3N^+CH_2^•$ radical. Other ΔBDE measurements also indicate that the positively charged groups in $Me_3N^+C^•HCN$, $Me_3N^+C^•HCO_2Et$, and $Me_3N^+C^•HCOPh$ destabilize the radicals by 2–4 kcal, whereas the positively charged pyridinium groups in c-$C_5H_5N^+C^•HCN$, c-$C_5H_5N^+C^•HCO_2Et$, and c-$C_5H_5N^+C^•HCOPh$ *stabilize* the radicals by 5–6 kcal due to the delocalizing ability of the aromatic ring (**3**).[28] The conclusion that has been drawn from these data and from data on remote substituent effects[29] is that *substituents play a dual role toward radicals, i.e., destabilizing by virtue of their group electronegativities and stabilizing to the extent of their ability to delocalize an odd electron.* (Since radicals are electron deficient, it is reasonable for electron withdrawal to cause destabilization.)



Donor–Acceptor Effects on Radical Stabilities. When donor and acceptor groups are both attached to a carbon-centered radical, the RSE is almost always greater than that of either of the individual RSEs and increases progressively with increasing donor ability when the acceptor is kept contant (Table II). Examination of Table II shows that the donor properties of the selected groups increase in the order (H) < Me < c-$C_5H_5N^+$ < PhSe < Ph < PhS < MeO < c-$C_5H_{10}N$. This order suggests that

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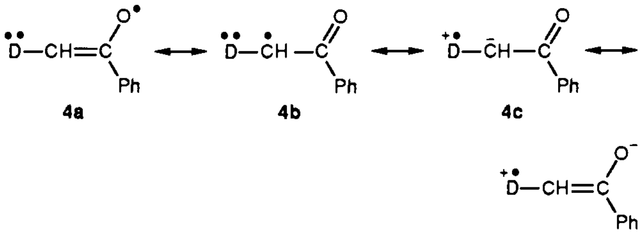
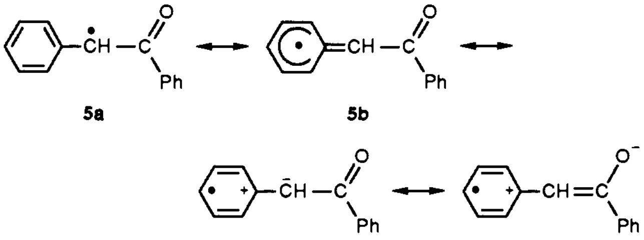
(29) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736–1743.

delocalization of negative charge in polar contributors of the type **4c** and **4d** is important in determining the size of the RSE in these radicals. The best donors, c-$C_5H_{10}N$, MeO, and PhS, all benefit from this type of radical stabilization. The discrepancy in size between the p orbital on carbon containing the odd electron and the adjacent p orbitals on S and Se causes successive decreases in the effects of PhS and PhSe groups, relative to MeO, despite their greater polarizability. Ph is less effective than PhS as a donor, despite the 5 kcal higher RSE for the $PhCH_2^•$ radical than for the $PhSCH_2^•$ radical in Table I, because the resonance contributor analogues of **4c** and **4d**, i.e., **5c** and **5d**, are of much higher energy due to loss of aromaticity. The small effects of Me and c-$C_5H_5N^+$ groups can be rationalized in a similar manner.



4a **4b** **4c** **4d**



5a **5b** **5c** **5d**

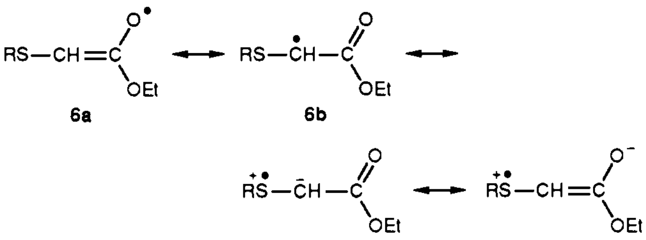
Donor Effects of PhS and RS Groups Interacting with Various Acceptors. There is still some uncertainty about the size of the RSEs of $RSCH_2^•$ and $PhSCH_2^•$ radicals. The BDEs of the C–H bonds in (1-adamantyl)SCH_2–H and t-$BuSCH_2$–H have each been estimated to be 93 kcal, i.e., ΔBDE = RSE = 12 (Table I), from a correlation of barriers of rotation with known BDEs.[18a] We favor this value over that of 96.6 kcal reported by Shum and Benson[18] for CH_3SCH_2–H, because in our work there appears to be little or no difference in the BDEs for ROC–H and RSC–H type bonds[12] and the BDE for $ROCH_2$–H bonds appears to be firmly established in the 92–93 kcal range.[1,18c] We note, on the other hand, that the spin density in RSC• and ROC• type radicals, as determined by ESR, is greater on S than on O.[19] In Table III we have assumed that the RSE of the $PhSCH_2^•$ radical is the same as that of the $RSCH_2^•$ radical because the BDEs of the acidic C–H bonds in $RSCH_2CN$ vs $PhSCH_2CN$ and 9-RSFlH vs 9-PhSFlH in Table III are within 0.5 kcal of one another.

Table III. Estimates of Radical Stabilizing Energies (RSEs; RSE = ΔBDE) for PhS and RS Donors with Various Acceptors

no.	DCH_2A	pK_{HA}[a]	$E_{ox}(A^-)$[d]	BDE[e]	RSE[g]	ΔBDE[h]
std	CH_3–H	~56[b]		105	(0.0)	
std	$RSCH_2$–H	~43[b]		~93	12	
std	H–CH_2Ph	~43[b]		88	17	(0.0)
1	$PhSCH_2$–Ph	30.8	−1.353	84	21	4
std	HFl–H	22.6	−1.069	80	25	(0.0)
2	9-PhSFl–H	15.4	−0.852	74.5	30.5	5.5
3	9-MeSFl–H	18.0	−1.011	74.5	30.5	5.5
std	H–CH_2CO_2Et	~29[b]		~95[b]	~10	(0.0)
4	$PhSCH_2$–CO_2Et	21.2[c]	−0.715	86	19	9
5	EtS–CH_2CO_2Et	24.3[c]	−0.842	87	18	8
std	H–CH_2CN	31.3		95[f]	10	(0.0)
6	PhS–CH_2CN	20.8[c]	−0.700	85.5	17.5	9.5
7	MeS–CH_2CN	24.3[c]	−0.885	86	19	9
8	EtS–CH_2CN	24.0[c]	−0.858	86	19	9
std	H–CH_2COMe	26.5	−0.674	94	11	(0.0)
9	PhS–CH_2COMe	18.85[c]	−0.649	84	21	10
std	H–CH_2COPh	24.7	−0.607	93	12	(0.0)
10	PhS–CH_2COPh	17.1	−0.649	81.5	23.5	11.5
11	PrS–CH_2COPh	19.8[c]	−0.854	80.5	24.5	12.5
12	$PhCH_2SCH_2$–COPh	19.0[c]	−0.787	81	24	12

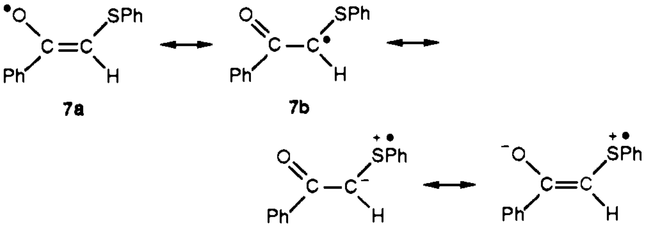
[a] Measured in DMSO against two indicators (Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463, unless otherwise noted). [b] Estimated. [c] Present work. [d] Irreversible potentials (E_{pa} measured by cyclic voltammetry under the conditions previously described[2] and referenced to the Fc/Fc^+ couple. Oxidation potentials for 28 organic anions measured by fast scan CV have been found to be reversible with $E_{1/2}$ values within ±50 mV of the irreversible potentials (Hupp, J. T.; Satish, A. V. Unpublished results). [e] Estimated using eq 1. [f] Kanabus-Kaminska, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311–3314. [g] Relative to CH_3–H (BDE = 105 kcal/mol). [h] Relative to the parent indicated.

Examination of Table III shows that in entry 1 introduction of an α-PhS group into the $PhCH_2^•$ radical increases the RSE of the corresponding radical by only 4 kcal compared to about a 12 kcal increase in RSE for the $RSCH_2^•$ radical, relative to the $CH_3^•$ radical. The smaller effect is due to a saturation effect caused by the large stabilizing effect of the Ph group in the $PhCH_2^•$ radical, which has an increased stability of 17 kcal relative to the methyl radical (Table III). Similarly, the HFl• radical is 25 kcal more stable than the $CH_3^•$ radical (Table III), so that introduction of a 9-PhS (or 9-MeS) group into the HFl• radical (entries 2 and 3) results in only a 5.5 kcal increase in RSE. In contrast, the RSE of the $^•CH_2CO_2Et$ radical is about 15 kcal smaller than that of the HFl• radical, so that the introduction of an α-PhS (or α-RS) group into HCH_2CO_2Et (entry 4) is subject to a smaller saturation effect. In addition, the polar resonance contributors **6c** and **6d** assist in lowering the energy of the $RSC^•HCO_2Et$ radical relative to the RSFl• radical. The result is a 2–3 kcal increase in the stabilizing effect of PhS (or RS), relative to that observed for HFlH. The effects of introducing α-PhS or α-RS groups into HCH_2CN (entries 6–8) on the RSEs are similar to those observed for HCH_2CO_2Et for the same reasons.



6a **6b** **6c** **6d**

The presence of a ketonic carbonyl acceptor and an RO or R_2N donor group on a carbon-centered radical has been shown to give rise to $DC^•HA$ radicals of unusually high stability.[7] It is not surprising then to find that the RSEs of the radicals of this type derived from $PhSCH_2COPh$ and $RSCH_2COCH_3$ compounds are among the highest in Table III. The RSEs of the $PhSC^•HCOPh$, $ROC^•HCOPh$,[7] and $R_2NC^•HCOPh$[7] radicals, relative to that of the $PhCOCH_2^•$ radical, are all about as large as those of the $PhSCH_2^•$, $MeOCH_2^•$, and $Me_2NCH_2^•$ radicals relative to that of the $CH_3^•$ radical. We suggested earlier that this apparent lack of a saturation effect for $DC^•HCOPh$ type radicals can be rationalized in terms of a compensating intramolecular electrostatic effect in such enolate type radicals (note contributor **7d**).[30]



7a **7b** **7c** **7d**

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[30] Bordwell, F. G.; Gallagher, T.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 3495–3497.

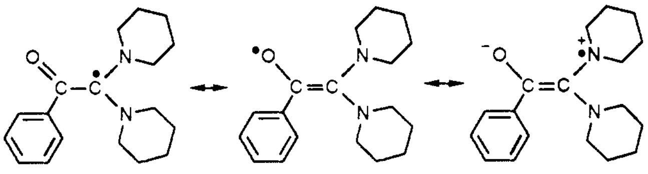
Table IV. Estimates of Radical Stabilization Energies (RSEs; RSE = ΔBDE) in D_2C$^\bullet$$A$ Type Radicals

D_2CHA	pK_{HA}^{a}	E_{ox}(A$^-$)^f	BDE^g	RSE^h	ΔBDE^i
HCH_2Ph	~43		88	17	(0.0)
$PhSCH_2Ph$	30.8	−1.353	84	21	4
$(PhS)_2CHPh$	23.0^b	−1.006	81.5	23.5	6.5
HCH_2COPh	24.7	−0.607	93	12	(0.0)
$MeCH_2COPh$	24.4^c	−0.815	88	17	5
$Me_2CHCOPh$	26.3^c	−1.003	86	19	7
$PhSCH_2COPh$	17.1	−0.649	81.5	23.5	11.5
$(PhS)_2CHCOPh$	12.1^d	−0.345	81.5	23.5	11.5
c-$C_5H_{10}NCH_2COPh$	23.5^e	−1.314	75	30	18
(c-$C_5H_{10}N)_2CHCOPh$	25.6^e	−1.506	73.5	31.5	19.5
(c-$OC_4H_8N)_2CHCOPh$	24.4^e	−1.360	75	30	18

[a] Measured in DMSO against two indicators (Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463 unless otherwise noted). [b] Bordwell, F. G.; Drucker, G. E.; Andersen, N. H.; Denniston, A. D. *J. Am. Chem. Soc.* **1986**, *108*, 7310–7313. [c] Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714–1718. [d] Present work. [e] Zhang, X.-M.; Bordwell, F. G. *J. Org. Chem.*, in press. [f] Measured by cyclic voltammetry relative to the Fc/Fc$^+$ couple. [g] Calculated (in kilocalories/mole) by eq 1. [h] Relative to CH_3–H (BDE = 105 kcal/mol[1]). [i] Relative to the indicated parent.

The near identity of the donor atom effects on GCH_2–H and PhCOCH(G)–H ΔBDEs makes possible estimates of RSE values for $GCH_2^\bullet$ radicals where RSEs are not known. For example, the ΔBDE for the acidic C–H bond in the $PhSeCH_2COPh$ molecule, relative to the H–CH_2COPh ΔBDE of 8 kcal, was used in Table I to estimate the RSE for the $PhSeCH_2^\bullet$ radical. (This method is restricted to donors; it fails for Ph or other acceptors.)

Double-Donor Effects in D_2C$^\bullet$$A$ Type Radicals. In Table IV we see that successive substitutions of α-PhS groups into the $PhCH_2^\bullet$ radical cause 4 and 6.5 kcal increases, respectively, in RSE. The smaller increase in RSE for the introduction of the second α-PhS substitution is a consequence of increased saturation and steric effects. A similar pattern is observed for successive α-Me substitution into acetophenone, where the increases in RSEs are 5 and 7 kcal, respectively. The powerful stabilizing effects of α-PhS and α-c-$C_5H_{10}N$ groups observed in the PhSC$^\bullet$HCOPh and c-C_5H_{10}NC$^\bullet$HCOPh radicals are completely damped out for a second substitution by a saturation effect and a large steric effect between the second substituent and the resident phenyl substituent in enolate type contributors (e.g., **8a** ↔ **8c**).



8a 8b 8c

Donor and Acceptor Effects in Other Trisubstituted Radicals. In the previous section we saw that introduction of an α-PhS group into the PhSC$^\bullet$HPh radical causes only a 2.5 kcal increase in RSE because of saturation and steric effects. Introduction of an α-Ph group into the PhSC$^\bullet$HPh radical causes an even smaller increase in RSE (1.5 kcal) because of the greater stereoelectronic demands of the Ph than the PhS group. Additional examples of substituent effects in trisubstituted radicals are shown in Table V. The comparisons of the effects of donors in the GCH(Ph)CN compounds listed at the bottom half of Table V show that the phenyl group, becase of its large stabilizing effect and strong steric demands, exerts a dominant effect on the RSEs of the corresponding GC$^\bullet$(Ph)CN radicals. Phenyl substitution into the $^\bullet CH_2CN$ radical to give the PhC$^\bullet$HCN radical increases the RSE by 13 kcal. Further substitutions at the radical center to give C_6H_5C$^\bullet$(G)CN radicals cause increases in the RSEs in the order c-C_6H_{11} (1) < Me, PhO (3) < MeO, EtS, CN (5) < c-C_5H_{10}N (7 kcal). It is clear from these results that the major part of the electron density in most, if not all, of these radicals is on the phenyl ring.

Table V. Estimates of Radical Stabilization Energies (RSEs; RSE = ΔBDE) in Trisubstituted Radicals

DCHA_2	pK_{HA}^{a}	E_{ox}(A$^-$)^f	BDE^g	RSE^h	ΔBDE^i
H–CH_2Ph	~43		88	17	(0.0)
$PhSCH_2Ph$	30.8	−1.353	84	21	4
$PhSCHPh_2$	26.8^b	−1.187	82.5	22.5	5.5
H–CH_2CN	31.3		95	10	(0.0)
H–CH(Ph)CN	21.9	−0.909	82	23	13
c-C_6H_{11}–CH(Ph)CN	24.2^c	−1.090	81	24	14
Me–CH(Ph)CN	23.0	−1.070	80	25	15
PhO–CH(Ph)CN	20.1^d	−0.928	79.5	25.5	15.5
MeO–CH(Ph)CN	23.0^d	−1.180	77.5	27.5	17.5
EtS–CH(Ph)CN	16.9^d	−0.823	77.5	27.5	17.5
CN–CH(Ar)CN^e	3.1	−0.012	77	28	18
c-C_5H_{10}N–CH(Ph)CN	23.1^c	−1.260	76	29	19

[a] Measured in DMSO against two indicators (Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463 unless otherwise noted). [b] Reference 35. [c] Reference 9. [d] Present work. [e] Data for *p*-$ClC_6H_4CH(CN)_2$, a model for $PhCH(CN)_2$. [f] Irreversible oxidation potentials (E_{pa}) measured in DMSO relative to the Fc/Fc$^+$ couple, as described previously.[2] [g] Calculated by eq 1. [h] In kilocalories/mole relative to CH_3–H (BDE = 105 kcal/mol). [i] Relative to the parent indicated.

Table VI. Delocalization Parameters for the HC_6H_4C$^\bullet$XY Radical[a]

X	Y	S^{exp}	S^{calcd}	ΔS(%)
H	H	0		
Me	H	0.034		
MeO	H	0.074		
H_2N	H	0.187		
MeS	H	0.199		
Me	MeO	−0.010	0.105	−109
MeO	MeO	0.026	0.143	−82
CO_2Me	CO_2Me	0.115	0.236	−51
CN	CO_2Me	0.168	0.257	−35
CN	CN	0.187	0.278	−33
MeS	MeS	0.323	0.358	−10
CN	Me	0.241	0.179	+35
CO_2Me	MeO	0.313	0.191	+64
CO_2Me	MeS	0.32	0.30	+7
CN	MeO	0.339	0.213	+59
CN	H_2N	0.375	0.309	+21
CO_2Me	H_2N	0.378	0.289	+31
CN	EtS	0.405	0.316	+28

[a] Adapted from Table 6 in ref 6.

The RSEs of the $GCH_2^\bullet$ radicals taken from column 1 in Table I are $PhCH_2^\bullet$ (17), $CNCH_2^\bullet$ (10), $MeOCH_2^\bullet$ (12), and $EtSCH_2^\bullet$ (12 kcal). If we assume that these groups have proportionate radical stabilizing effects in the PhC$^\bullet$(MeO)CN and PhC$^\bullet$(EtS)CN radicals, we can estimate that, of the total RSE of 27.5 kcal observed for each of these radicals (Table V), the relative stabilization due to the Ph, MeO (or EtS), and CN groups will be 12, 8.5, and 7 kcal, respectively. The sum of the radical stabilizing effects of the groups in the MeOC$^\bullet$CN and EtSC$^\bullet$CN moieties will then be 15.5 kcal rather than the 22 kcal calculated from the sum of the $GCH_2^\bullet$ values. This nonadditivity is consistent with the nonadditivities observed for the RSCH$^\bullet$CN radicals in Table III (with R = Ph, Me, or Et), but is at odds with the synergistic interpretation of the ESR data given[6] for the results summarized in Table VI. The RSE for the c-C_5H_{10}NC$^\bullet$CN moiety in Table V is also nonadditive, rather than synergistic as would be expected from the interpretation of the ESR data for this type of radical.[6] Also, the data in Table V for the RSE of the CNC$^\bullet$CN moiety in ArC$^\bullet$(CN)$_2$ radical point to some additivity, rather than the "antagonism" expected from the ESR data.[6]

Conclusions Concerning Donor–Acceptor Effects and the Question of Synergism. The unusual stability inherent in radicals of the type DC$^\bullet$HA was recognized by a number of early workers.[31]

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(31) (a) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3353–3354. (b) Balaban, A. T. *Rev. Roum. Chim.* **1971**, *16*, 725. (c) Baldock, R. W.; Hudson, P.; Katritzky, A. R.; Soti, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1422–1427.

The later extensive investigations of such radicals by Viehe and his colleagues provided many new examples and a new name for the phenomenon, the captodative effect. The captodative effect was defined as one that always leads to synergism, i.e., an effect that is always greater than the sum of the individual effects.[32] Most of the evidence concerning the size of such effects has been qualitative in nature. In their recent review,[6] Sustmann and Korth (a) question the usefulness of our C–H BDEs[7] in the context of captodative substitution because of a lack of knowledge concerning ground-state effects, (b) question the usefulness of the theoretical calculations of Pasto[13] and of Leroy[14] because insufficient electron correlations have been carried out, and (c) conclude that the only unambiguous confirmation of synergistic substituent effects comes from their ESR measurements.[33] They rely on $\Delta S(\%)$ values (eq 2) derived from substituent-induced spin density variations of PhC$^{\bullet}$XY type radicals (**1**), using the unsubstituted radicals (X = Y = H) as reference systems.[6] Some of their data for radical **1** are reproduced in Table VI.

$$\Delta S(\%) = 100[S_{xy}^{\text{exp}} - S_{xy}^{\text{calcd}}]/S_{xy}^{\text{calcd}} \qquad (2)$$

Examination of Table VI reveals that the $\Delta S(\%)$ values are negative when X and Y are either both donors or both acceptors, which the authors interpret as antagonistic effects. The positive values of $\Delta S(\%)$ donor–acceptor combinations upon which Sustmann and Korth base their case for synergism increase in the following order: MeS, CO_2Me (+7) < H_2N, CN (+21) < EtS, CN (+28) < H_2N, CO_2Me (+31) < Me, CN (+35) < MeO, CN (+59) < MeO, CO_2Me (+64). The RSE values in column 1 of Table I indicate that the H_2N group is the most powerful donor on the list, but the order in Table VI places both the H_2N,CN and H_2N,CO_2Me donor–acceptor combinations below the Me,CN combination, which includes the weak Me donor. The most powerful donor from the standpoint of spin densities is MeS (Table VI and ref 19), but the MeS,CO_2Me combination has the lowest positive $\Delta S(\%)$ value in Table VI. Furthermore, the evaluation of the RSE data in Table V for the GC$^{\bullet}$CN moieties in the MeOC$^{\bullet}$(Ph)CN, EtSC$^{\bullet}$(Ph)CN, and c-C_5H_{10}NC$^{\bullet}$(Ph)CN radicals does not support the claim from ESR that extra stabilization, beyond that attributable to the individual effects, is present. Also, our data indicate that the second CN group in the HC$^{\bullet}$(CN)$_2$ or ArC$^{\bullet}$(CN)$_2$ radical enhances the RSE, rather than being antagonistic.[34]

Finally, Rüchardt has pointed out that no clear relationship between the spin delocalization, as detected by ESR, and thermochemical stabilization energies has been formulated,[17b] and Sustmann and Korth state in their review[6] that "it should be stressed that spin delocalization as measured by ESR spectroscopy can be related to the overall thermodynamic stabilization of a radical only if the interaction of the substituent with the radical center constitutes the only or, at least the dominant contribution to the stabilization of the radical species as a whole." Since we have presented evidence in the previous section that the interaction of the phenyl group rather than the X and Y substituents in PhC$^{\bullet}$XY radicals is the dominant one, we conclude that the Sustmann–Korth case for synergism is weak.

Summary and Conclusions

In the present paper we have used PhS and RS functions as donors for *D*C$^{\bullet}$H*A* type radicals and have found that the radical stabilization energies (RSEs) estimated from BDEs of the acidic C–H bonds increase progressively as the acceptor, *A*, is changed along the series Ph < Fl < CO_2Et, CN < COMe < COPh. The RSEs are less than additive, but for the latter four they conceivably could be synergistic if saturation and steric effects are taken into account. In any event, synergism does not appear to amount to more than a few kilocalories per mole in these radicals, at best. The extent to which a given radical is stabilized, as judged by its RSE value, relative to the $CH_3^{\bullet}$ radical appears to be a more important question, and ΔBDEs appear to be the best way to answer this question for carbon-centered radicals. The RSE values presented in column 1 of Table I are designed to answer this question for 21 radicals, $GCH_2^{\bullet}$. When more than one substituent is present, answers are provided in Tables II–V under the heading RSE. A study of the RSEs of GC$^{\bullet}$(Ph)CN radicals has shown that the donor–acceptor interactions of the G and CN functions, with G = MeO, EtS, or c-C_5H_{10}N, are not synergistic, as has been claimed from ESR studies.

Experimental Section

General. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian VXR-300 spectrometer with TMS as the internal standard. When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet; t, triplet, m, multiplet. Gas chromatography–mass spectrometry (GC–MS) was obtained on a Hewlett-Packard Model 5890 chromatograph interfaced to a 5970 mass selective detector. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Equilibrium acidities were determined by the overlapping indicator method described previously using a Perkin-Elmer 442A spectrometer. Oxidation potentials of the conjugate anions were measured in DMSO solution with 0.1 M tetraethylammonium tetrafluoroborate as supporting electrolyte by cyclic voltammetry. The working and auxiliary electrodes were Pt, and the reference electrode was Ag/AgI. The sweep rate was 100 mV/s, and the oxidation potentials were referred to ferrocene/ferrocenium couple ($E_{1/2}$ = 0.875 V).[2]

Materials. Analytical grade dimethyl sulfoxide (DMSO) was distilled from sodium amide at reduced pressure prior to use and stored under a blanket of argon. Gold label anhydrous acetonitrile was obtained from Aldrich and was used as received. Bis(phenylthio)methane, benzyl phenyl sulfide, and fluorene (Aldrich) were recrystallized from methanol. The high purity of all samples used for pK_{HA} and CV measurements were established by melting points, GC, GC–MS, NMR, and/or elemental analyses.

A sample of PhOCH(Ph)CN was supplied by Professor M. Makosza, Institute of Organic Chemistry, Warsaw, Poland. Samples of $EtSCH_2CO_2Et$, $PhSCH_2CO_2Et$, PhCH(OMe)CN, and PhCH(SEt)CN were kindly provided by Professor H. G. Viehe and Dr. J. Penelle, University of Louvain, Belgium. The synthesis, properties, and acidities of 9-(phenylthio)fluorene, $MeOCH_2COPh_2$, $(PhS)_2CHPh$, and c-$C_5H_{10}NCH_2COPh$ have been previously reported.[7,35] The other compounds were commercially available except for $PrSCH_2COPh$, $PhSeCH_2COPh$, $PhSCH_2COCH_3$, $PhCH_2SCH_2COPh$, and $(PhS)_2CHCOPh$, the preparations of which are described below.

α-(Propylthio)-, α-(Phenylthio)-, and α-(Benzylthio)acetophenones ($RSCH_2COPh$). To 200 mL of degassed methanol containing 100 mmol of α-chloroacetophenone was added slowly 200 mL of a 0.5 M methanolic solution of RSNa (prepared by adding metallic sodium to the thiol in methanol). The solution was allowed to stir for 30 min under argon, quenched with dilute HCl, and extracted with CH_2Cl_2. The organic extracts were combined, dried over $MgSO_4$, and concentrated. The residues were purified as described below: when R = Pr, the yellow oil was distilled at 0.10 mmHg, bp 110–113 °C (lit.[36] bp 120–121 °C at 2 mmHg). Further purification by flash chromatography on aluminum oxide using a mixture of pentane/ether (80/20 v/v) as the eluent yielded 35% of product: ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.51–1.62 (m, 2 H), 2.48 (t, 2 H), 3.71 (s, 2 H), 7.36–7.54 (m, 3 H), 7.89–7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.31, 22.21, 34.20, 36.93, 128.56, 128.70, 133.21, 135.14, 194.44. When R = phenyl, the residue was recrystallized from methanol, yielding 72.4% of $PhSCH_2COPh$: mp 53–55 °C (lit.[36] mp 54 °C); ^1H NMR ($CDCl_3$) δ 4.27 (s, 2 H), 7.15–7.6 (m, 8 H), 7.90–7.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 41.18, 127.09, 128.66, 129.05, 130.48, 133.47, 134.68, 135.31, 194.05. When R = benzyl, the residue was also recrystallized from methanol, yielding 64% of product: mp 87–89 °C (lit.[36] mp 87 °C).

α-(Phenylthio)acetone ($PhSCH_2COCH_3$). The procedure for synthesizing α-(phenylthio)acetone is similar to that described above for α-(phenylthio)acetophenone. A desired quantity of α-chloroacetone was dissolved in methanol and added slowly to a methanolic solution of sodium thiophenoxide. Normal workup followed by distillation (bp 82–84 °C/1.00 mmHg) and recrystallization of the yellow oil from a pentane/benzene mixture (90/10 v/v) gave white crystals of

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$PhSCH_2COCH_3$ in 40% yield: mp 36–38 °C (lit.[37] mp 34–35 °C); ^1H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 3.65 (s, 2 H), 7.14–7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 28.01, 44.65, 126.84, 129.17, 129.47, 134.63, 203.61.

α-(Phenylseleno)acetophenone ($PhSeCH_2COPh$). The compound was prepared according to the procedure of Detty and Wood.[38] After distillation, the residual oil was found to be contaminated with a small amount of diphenyl diselenide. The impurity was removed by flash chromatography using pentane as the eluent. The selenium compound was eluted with diethyl ether and recrystallized from methanol to give white crystals of $PhSeCH_2COPh$: mp 42–44 °C (lit.[38] bp 162–164 °C, 0.8 mmHg); ^1H NMR ($CDCl_3$) δ 4.20 (s, 2 H), 7.31–7.56 (m, 8 H), 7.85–7.93 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.85, 127.99, 128.52, 128.60, 129.06, 129.15, 133.18, 133.88, 135.27, 194.71.

Bis(phenylthio)acetophenone ($(PhS)_2CHCOPh$). A mixture of 40 mmol of *N*-chlorosuccinimide and 40 mmol of α-(phenylthio)acetophenone in 100 mL of CCl_4 was refluxed for 30 min and then allowed to stir at room temperature for 6 h. After filtration, the solvent was removed under vacuum, and the oil residue was used without further purification in the preparation of bis(phenylthio)acetophenone: ^1H NMR ($CDCl_3$) δ 6.42 (s, 1 H), 7.20–7.65 (m, 8 H), 7.89–8.10 (m, 2 H).

A solution of α-chloro-α-(phenylthio)acetophenone (25 mmol) in 100 mL of methanol was added to a methanolic solution of sodium benzenethiolate under argon. After the normal workup, the oil residue was recrystallized repeatedly from methanol to provide bis(phenylthio)acetophenone in 50% yield: mp 101–103 °C (lit.[39] mp 99–100 °C); ^1H NMR ($CDCl_3$) δ 5.74 (s, 1 H), 7.25–7.62 (m, 13 H), 7.92–7.96 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 62.71, 128.54, 128.72, 128.985, 129.01, 132.21, 133.47, 133.86, 134.32, 191.21.

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Secondary β-Deuterium Isotope Effects on the Rates and Equilibria of Organometallic Oxidative Addition/Reductive Elimination Reactions

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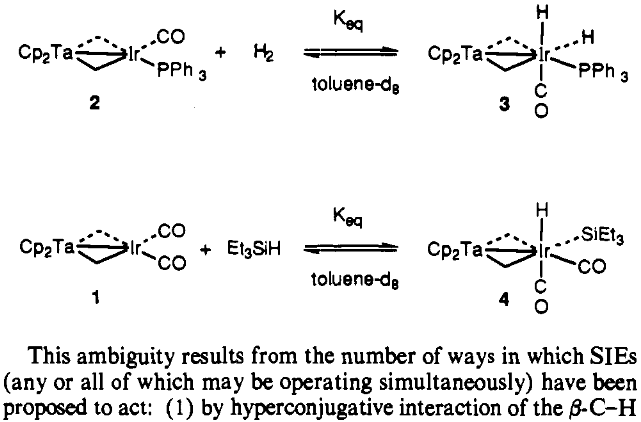
Abstract: We report a study of β-deuterium isotope effects on the rate and equilibrium of an organometallic transformation: the oxidative addition of silane R_3SiH (R = Et) and the corresponding deuteride R_3SiD to the iridium center in the heterodinuclear complex $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ (**1**) and to its tetradeuterated analogue $Cp_2Ta(\mu\text{-}CD_2)_2Ir(CO)_2$ (**1-*d*₄**). The Si–H(D) bond contributes only a small normal isotope effect to the forward rate constant k_1 ($k_1^H/k_1^D = 1.13 \pm 0.06$). An *inverse* effect ($k_1^H/k_1^D = 0.875 \pm 0.022$) is caused by isotopic tetrasubstitution at the bridging methylenes. For the reductive elimination of Et_3SiX from $Cp_2Ta(\mu\text{-}CX_2)_2Ir(X)(SiEt_3)(CO)_2$ (X = H, D), the Si–H(D) bond again contributes a small normal isotope effect to the rate constant k_{-1} ($k_{-1}^H/k_{-1}^D = 1.45 \pm 0.08$). However, a *normal* effect ($k_{-1}^H/k_{-1}^D = 1.25 \pm 0.03$) is caused by the secondary isotopic substitution. The combined primary and secondary *equilibrium* isotope effect on the silane oxidative addition/reductive elimination equilibrium constant $K_{eq}^H/K_{eq}^D = [k_1/k_{-1}]^H/[k_1/k_{-1}]^D$ is 0.53 ± 0.04 at 0 °C. A kinetic isotope effect analogous to that observed with **1** is measured for the oxidative addition of methyl iodide to $(PPh_3)_2Ir(CO)(CX_3)$ (X = H, D) ($k_1^H/k_1^D = 0.922 \pm 0.030$ in THF at 0 °C). This suggests that the inverse β-deuterium isotope effect on oxidative addition is a general phenomenon. Kinetic isotope effects of similar direction and magnitude were also observed for oxidative addition of CH_3I ($k_1^H/k_1^D = 0.752 \pm 0.018$ in THF at 0 °C) and Ph_3SiH ($k_1^H/k_1^D = 0.898 \pm 0.077$ in THF at 10 °C) to the tantalum/iridium complex **1**, indicating that steric effects are not the source of the measured difference in rate behavior. The tendency of deuterium to act as an inductive electron donor relative to hydrogen is suggested to account for its ability to enhance the rate of oxidative addition reactions that convert iridium(I) to iridium(III).

The use of isotope effects to study the mechanism of organic reactions is a well-established technique.[1,2] Primary hydrogen/deuterium isotope effects are in general the most straightforward to interpret, usually indicating the degree of C–H bond-breaking in the transition state. On the other hand, secondary isotope effects (SIE)[3] and their analyses[4-6] are still the basis for active research. Their proper interpretation requires extensive experimentation in order to properly describe their effect on a reaction.

Scheme I



This ambiguity results from the number of ways in which SIEs (any or all of which may be operating simultaneously) have been proposed to act: (1) by hyperconjugative interaction of the β-C–H bond with a developing intermediate carbocation; (2) by a change

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