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Stereoelectronic Effects of Divalent Sulfur Functions on Radical Stabilities

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The stabilization of carbon-centered radicals by adjacent sulfur atoms has important consequences in bond-breaking, condensation, and complex rearrangement reactions.[1,2a,b] However, homolytic thermochemistry of C−H bonds substituted with divalent sulfur functions is lacking or of limited accuracy.[2c,d] In this paper we present homolytic bond dissociation energies (BDEs) of C−H bonds adjacent to one and two sulfur atoms and demonstrate that the presence of two donor MeS groups in the acetophenone $(MeS)_2CHCOPh$ leads to no greater weakening of the acidic C−H bond than the presence of one MeS group in the acetophenone $(MeS)CH_2COPh$. When, however, the two sulfur atoms are incorporated into five-, six-, and seven-membered rings, the acidic C−H bond is dramatically weakened, depending on the size of the ring.

Measurement of BDEs has historically been a difficult exercise: only in recent years has a consensus regarding accurate thermochemical properties of simple alkyl radicals been reached[3,4a−c] and uncertainties in C−H bond strengths remain large for many polyaromatic and heteroatom substituted alkanes.[4d−f] Recently, however, many new bond strengths have become accessible through measurement of pK_{HA} values of organic acids and one-electron oxidation potentials of the corresponding anions. Equation 1 provides a means of estimating BDE values of the acidic C−H bonds for weak acids in DMSO solution for comparison with gas-phase values. The factors 1.37

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

and 23.1 in eq 1 convert the pK_{HA} and $E_{ox}(A^-)$ units to kcal/mol. When the value 73.3 kcal/mol for the constant C is used in eq 1, the BDE values obtained usually agree to within ±2 kcal/mol with gas-phase literature values.[5,6]

In a previous paper,[6] we compiled values of BDEs for C−H bonds in substituted methanes (GCH_2−H) based on gas-phase results, values estimated from eq 1, and values from other sources. The values of ΔBDEs obtained relative to that of CH_3−H (105 kcal/mol) were interpreted to provide estimates of relative radical stabilization energies (RSEs) for radicals.[3,7,8] The approximate RSEs of the $GCH_2^{\bullet}$ radicals that are pertinent to this paper are $c\text{-}C_5H_{10}NCH_2^{\bullet}$ (21 kcal/mol),[9] $RSCH_2^{\bullet}$ (12 kcal/mol),[6] and $PhSCH_2^{\bullet}$ (12 kcal/mol).[6] The RSEs for the combination of these donor groups with the benzoyl acceptor group, $PhCOCH_2^{\bullet}$ (12 kcal/mol), to give donor-$C^{\bullet}HCOPh$ type radicals have been found to be appreciably enhanced compared to the RSEs of the individual radicals. The combined RSEs relative to that of methane are $c\text{-}C_5H_{10}NC^{\bullet}HCOPh$ (33 kcal/mol),[9] $RSC^{\bullet}HCOPh$ (24 kcal/mol),[6] and $PhSC^{\bullet}HCOPh$ (24 kcal/mol).[6] In the latter three cases, the combined RSEs appear to be additive. On the other hand, results in Table 1 (entries 1 and 2) show that the RSE of the $(PhCO)_2CH^{\bullet}$ radical,[10] where the radical bears two acceptor groups, is 13 kcal/mol, only one kcal/mol greater than that of the $PhCOCH_2^{\bullet}$ radical. The RSE for the $(PhS)_2CH^{\bullet}$ radical, where the radical bears two donor groups, is 17 kcal/mol, only 5 kcal/mol greater than that of the $PhSCH_2^{\bullet}$ radical (entries 11 and 12). Addition of a second donor to a donor−acceptor combination appears to produce radicals with little or no enhanced stability. For example, the RSE of the $(PhS)_2C^{\bullet}COPh$ radical differs little from that of the $PhSC^{\bullet}HCOPh$ radical (entries 8 and 9 of Table 1). The RSE of the $(c\text{-}C_5H_{10}N)_2C^{\bullet}COPh$ radical was previously found[6] to be 1.5 kcal/mol smaller than that of the $c\text{-}C_5H_{10}NC^{\bullet}HCOPh$ radical. In these tertiary radicals the effect of the second substituent is clearly attenuated by steric interactions between substituents that prevent optimum orbital overlap with the radical center, reminiscent of the trityl radical.[3,4a]

The present results shown in Table 1 reveal that incorporation of two S-substituents at a radical site into five-, six-, or seven-membered rings *substantially reduces* the C−H BDE relative to the open chain analogues, $(MeS)_2C^{\bullet}COPh$ and $(PhS)_2C^{\bullet}COPh$. Removing the conformational effects of steric repulsion between substituents of the tertiary open chain radicals by ring closure improves the orbital overlap between the two sulfur atoms and the adjacent radical center.

Examination of Table 1 (entry 3) shows that an α-MeS function weakens the acidic C−H bond by 12.0 kcal/mol. A second α-MeS function (entry 4) causes no further weakening of this C−H bond. On the other hand, incorporation of the two divalent sulfur functions into a five-, six-, or seven-membered ring results in further weakening of the acidic C−H bond by 3.1−7.1 kcal/mol

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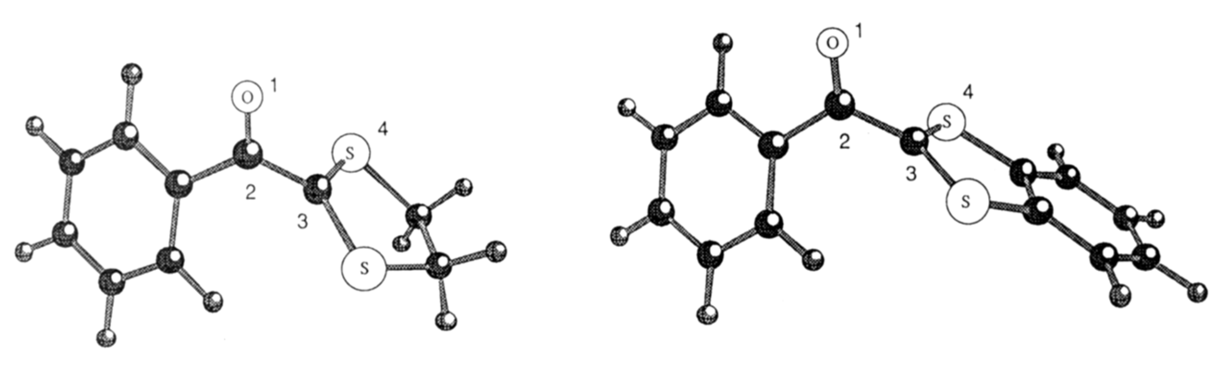
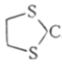
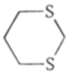
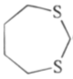
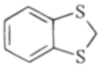


1• 2•

Figure 1. ROHF-MNDO-PM3 Calculations show that the most stable confomers for radicals **1**• and **2**• correspond to dihedral angle 1-2-3-4 of 87° and 90°, respectively (radical site, C3).

Table 1. Effects of Acyclic and Cyclic Divalent Sulfur Functions on Acidities and BDEs in Acetophenones

Entry	Acetophenone[a]	pK_{HA}[b]	$E_{ox}(A^-)$[c]	BDE[d]	ΔBDE[e]
1	CH_3COPh	24.7	-0.607	93[f]	(0.0)
2	$CH_2(COPh)_2$	13.3	0.032	92	(1.0)
3	$MeSCH_2COPh$	19.6	-0.834	81.0	12.0
4	$(MeS)_2CHCOPh$	17.8	-0.709	81.3	11.7
5	 CHCOPh	18.0	-1.027	74.2	18.8
6	 CHCOPh	17.7	-0.842	78.0	15.0
7	 CHCOPh	16.5	-0.817	77.0	16.0
8	$PhSCH_2COPh$	17.1	-0.656	81.5	11.5
9	$(PhS)_2CHCOPh$	12.0	-0.345	81.8	11.2
10	 CHCOPh	15.2	-0.993	71.2	21.8
11	$PhSCH_3$	~43		~93[f,g]	(0.0)
12	$(PhS)_2CH_2$	30.8	-1.144	89 (88)[h]	5.0[i]

[a] pK_{HA} values in DMSO solution for entries 1, 2, 8, 9, and 12 were determined elsewhere.[6,11] [b] pK_{HA} values in entries 3−7 and 10 were obtained by the indicator overlapping titration method previously described.[11a,b] [c] Irreversible oxidation potentials[12a,b] were measured as previously described[5a,6] and are referenced to the Fc/Fc$^+$ couple. [d] Estimated using eq 1. [e] Radical stabilization energies (RSEs), defined as ΔBDE, relative to that of CH_3COPh. [f] The RSE relative to that of methane is 12 kcal/mol (105−93). [g] Estimated.[6] [h] The BDE in parentheses is the average value between 89 (present work) and 87 (obtained by the photoacoustic calorimetry technique); Alnajjar, M. S., unpublished results. [i] RSE relative to that of $PhSCH_3$.

(entries 5−7). The largest effect is observed for the five-membered ring as shown in radical **1**• (Figure 1), pointing to a more favorable overlap between the orbitals of the two sulfur atoms and the orbital of the radical center than those in the six- or seven-membered rings or those in the acyclic analogues. Entries 8 and 9 in Table 1 also show that the introduction of a second α-PhS group into $PhSCH_2COPh$ to give $(PhS)_2CHCOPh$ produces no change in the methine C−H bond strength, reflecting steric inhibition of orbital overlap in the corresponding radicals. However, incorporating the two sulfur atoms (entry 10) into a five-membered ring, as in radical **2**• (Figure 1), leads to even greater radical stabilization than that of radical **1**• (10.6 kcal/mol vs 7.1 kcal/mol). The overall effect is to weaken the acidic C−H bonds in the acetophenones as shown in entries 5 and 10, by 18.8 and 21.8 kcal/mol, respectively. Entry 6 of Table 1 shows that for the six-membered ring dithiane, the RSE is 15 kcal/mol, i.e., 3.8 kcal/mol and 6.8 kcal/mol smaller than that of the five-membered ring systems (entries 5 and 10, respectively). These observations illustrate the remarkable sensitivity of the stabilization of the radical center to ring conformation.

Examination of the geometries obtained from ROHF-MNDO-PM3 calculations[13,14] for radicals **1**• and **2**• show that the plane of the carbonyl group is orthogonal to that of the five-membered dithiane ring, minimizing steric interactions with the adjacent phenyl group. Thus, delocalization of the unpaired spin on the carbon atom does not involve the π-system of the carbonyl. The large RSEs for radicals **1**• and **2**• are therefore attributed to π-delocalization of the radical centers with the adjacent sulfur atoms.

Table 1 also shows that replacement of a methyl by a phenyl group at sulfur to give $PhSCH_2COPh$ and $(PhS)_2CHCOPh$ increases the acidities by 2.5 (3.4 kcal/mol) and 5.8 (7.9 kcal/mol) pK_{HA} units, respectively (entries 3 vs 8, and 4 vs 9), reflecting field/inductive effects. The bond weakening effects that might accompany these increases in acidities (eq 1) are equally offset, however, by the less negative values of the oxidation potentials of the conjugate anions. As a consequence, C−H bond strengths remain unaffected.

We conclude that the much greater stabilizing effects of the two sulfur atoms in radicals **1**• and **2**• than those in the larger rings or acyclic analogues are due to stereoelectronic effects that lead to more effective orbital overlap between the radical center and the adjacent sulfur atoms.

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Supporting Information Available: Experimental procedures, full characterization of new compounds, and pK_{AH}s of indicators used in titrations (3 pages).

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(13) The structural information for radicals **1**• and **2**• were obtained using semiempirical MNDO-PM3[14] calculations (Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, IN: QCPE No. 455 ver. 6.0). The geometries were optimized using the spin-restricted open shell Hartree−Fock (ROHF) (half-electron) Hamiltonian. Energy minima were located using either the default optimizer or the eigen following optimizer with the option hess = 1.

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