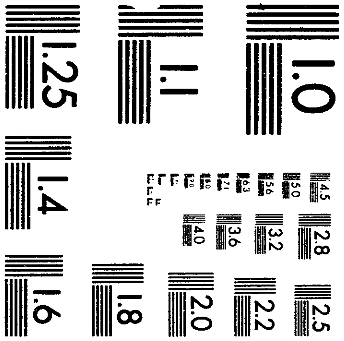
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HOMOLYTIC BOND DISSOCIATION ENERGIES FOR C-H BONDS ADJACENT TO SULFUR AND AROMATIC MOIETIES: THE EFFECTS OF SUBSTITUENTS ON C-H BOND STRENGTHS OF THE BENZYLIC POSITIONS IN COAL MODEL COMPOUNDS

M. S. Alnajjar
J. A. Franz
G. J. Gleicher
S. Truksa
F. Bordwell[a]
X. Zhang[a]

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Pacific Northwest Laboratory
Richland, Washington 99352

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[a] Northwestern University
Evanston, Illinois

HOMOLYTIC BOND DISSOCIATION ENERGIES FOR C-H BONDS ADJACENT TO SULFUR AND AROMATIC MOIETIES: THE EFFECTS OF SUBSTITUENTS ON C-H BOND STRENGTHS OF THE BENZYLIC POSITIONS IN COAL MODEL COMPOUNDS

Mikhail Alnajjar,*,[1] James Franz,[1] Gerald Gleicher,[2] Scott Truksa,[2] Frederick Bordwell,[3] and Xian-Man Zhang,[3]
[1]Pacific Northwest Laboratory, P. O. Box 999, Richland, Wa USA 99352-0999 [2]Department of Chemistry, Oregon State University, Corvallis, OR USA 97331-4003 and the [3]Department of Chemistry, Northwestern University, Evanston, IL USA 60201

Summary: The radical stabilization energies (RSEs) of PhSCH(·)-Acceptor type radicals are larger than the RSEs of the corresponding $PhSCH_2(\cdot)$ or $(\cdot)H_2C$-Acceptor radicals, but smaller than the sum of the RSEs of the two radicals.

Introduction: Sulfur-containing compounds are precursors for thiyl radicals at coal liquefaction temperatures due to the weakness of the S-C and S-S bonds. Thiyl radicals play important roles in hydrogen atom shuttling between benzylic positions and catalyze the cleavage and the formation of strong C-C bonds. Although many reactions of thiyl and other sulfur-containing radicals are qualitatively understood, the homolytic bond dissociation energies (BDE's) and the thermochemistry associated with many key high molecular weight hydrocarbon and sulfur-containing organic structures important to coal is lacking because they are inappropriate for gas-phase techniques. The measurement of BDE's has been proven to be difficult[4,5] even in the simplest of molecules.[6-8]

Recently, we have used the electrochemical method to estimate BDEs of the acidic H-A bonds in weak acids, H-A. The method (eq.1) requires that the acids be strong enough to allow acidity measurement to be made in dimethyl sulfoxide (DMSO) solutions. Equation (1) is based on a thermochemical cycle in which the factors **1.37** and **23.1** are used to convert pK_{H-A} units and oxidation potential (eV)

$$BDE = 1.37pK_{HA} + 23.1E_{OX}(A^-) + 56 \qquad (1)$$

units to kcal/mol.[9-11] The constant **56** is needed to relate the free energies in solution to gas-phase ΔH° values. The oxidation potential values of the conjugate bases (A^-) are obtained from cyclic voltammetric measurements in dilute DMSO relative to the standard hydrogen electrode (SHE).[12] This electrochemical method is very powerful as it provides BDEs for large numbers of compounds that otherwise would be difficult or impossible to obtain.

In this paper we have examined the effects of PhS, RS, and aromatic donors on radical stabilization energies (RSEs) in PhS-CH(·)-**A**, RS-CH(·)-**A**, and ArCH(.)-**A** type radicals, where conjugation involves both substituents[13] and **A** is phenyl, CO_2Et, and COPh, and compared them to the effects obtained from radicals of the type $\mathbf{D}_2$-(·)-**A**.

Results and Discussion: The radical stabilization energies (RSEs)[14] of carbon-centered radicals attached to sulfur, alkyl and aromatic groups are presented in Tables I and II. Our studies of the effects of substituents on homolytic C-H bond dissociation energies provide new bond strengths and new insights into structural features controlling stabilization energies.

RSEs for PhCH(·)-SPh. Examination of the data in Table I shows that the BDE of the acidic C-H in $PhCH_2$-SPh is 84 kcal/mole (referred to hereafter as kcal). Comparison with the known BDE value for toluene (88 kcal/mol) leads to 4 kcal extra stabilization relative to the $PhCH_2(\cdot)$ or 21 kcal compared to the $CH_3(\cdot)$ radical.[15,16] The sum of the RSEs for the $PhSCH_2(\cdot)$ radical (12 kcal, 105 -93) and $PhCH_2(\cdot)$ radical (17 kcal, 105 - 88) is 8 kcal larger than the RSE of PhCH(·)-SPh (29 vs. 21 respectively).

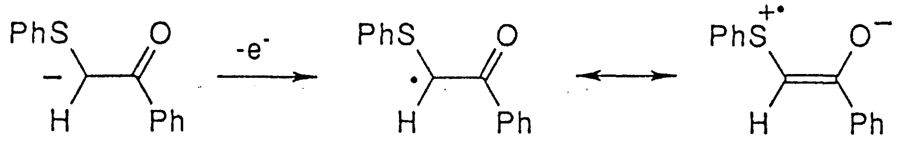
Table I. Acidities and Bond Dissociation Energies (BDEs) for the α-C-H Bonds in Sulfur Containing Systems.

Entry	Substrates	pK_{HA}[a]	$E_{OX}(A^-)$[b]	BDE[c]	RSE[d]
1.	$PhCH_2$-H			88	0.0
2.	$PhCH_2$-SPh	30.8	-0.603	84	4
3.	$PhCH(SPH)_2$	23.0	-0.260	81.5	6.5
4.	H-CH_2CO_2Et	29.0	-0.032	95	0.0
5.	PhS-CH_2CO_2Et	21.1	0.035	86	9
6.	EtS-CH_2CO_2Et	24.3	-0.092	87	8
7.	H-CH_2COPh	24.7	0.143	93	0.0
8.	PhS-CH_2COPh	17.1	0.090	81.5	11.5
9.	$(PhS)_2$-CHCOPh	12.0	0.405	82	11
10.	PrS-CH_2COPh	19.8	-0.100	81	12
11.	$PhCH_2S$-CH_2COPh	19.0	-0.037	81	12

[a] Measured in DMSO against two indicators. [b] In volts; irreversible oxidation potentials (E_p) measured in DMSO by cyclic voltammetry and referenced to the standard hydrogen electrode (SHE). [c] Calculated(in kcal/mol)using eq 1. [d] Radical stabilization energy (RSE).[14]

RSEs for PhS-CH(·)CO_2Et and PhS-CH(·)COPh: The BDE of the C-H bond in PhS-CH_2CO_2Et is 86 kcal (Table I, entry 5). The RSE for the corresponding radical is 3 kcal lower than the sum of the RSEs of the $PhSCH_2(\cdot)$ radical (12 kcal) and $(\cdot)CH_2CO_2Et$ radical (10 kcal)[17].

The acidic C-H bond in PhS-CH_2COPh is 81.5 kcal. The RSE is 23.5 kcal relative to $CH_3(\cdot)$ radical. This value is 0.5 kcal lower than the combined values for $PhSCH_2(\cdot)$ and $(\cdot)CH_2COPh$ radicals (24 kcal, 12 + 12). Table I shows clearly that RSEs for sulfur containing radicals increase progressively as the acceptors change along the series: Ph, CO_2Et, and COPh with the latter being the most stabilizing acceptor (12 kcal relative to acetophenone). The special electronic effects of the carbonyl in combination with the sulfur substituents is probably due to the conjugative and electrostatic interactions between the negatively charged oxygen and the positively charged sulfur (2c).



2a 2b 2c

The effect of a second PhS substitution into already doubly substituted methane (entries 3, and 9) is negligible. The small decrease in BDE compares well with the third phenyl substitution into methane (ΔBDE = 1 kcal) and is probably due to a large steric effect.[4,8]

Also from Table I (compare entries 5 & 6, and 8, 10, & 11), it appears that the sulfur atom is acting as an insulator thereby preventing the conjugation between the radical center and the group attached to the sulfur donor.

Table II. Acidities and Bond Dissociation Energies (BDEs) for the α-C-H Bonds in Ketones.

Entry	Substrates	pK_{HA}[a]	$E_{OX}(A^-)$[b]	BDE[c]	RSE[d]
1.	CH_3COCH_3	26.5	0.076	94	0.0
2.	$PhCOCH_3$	24.7	0.143	93	1.0
3.	$p\text{-}MePhCOCH_3$	25.0	0.153	94	0.0
4.	$p\text{-}MeOPhCOCH_3$	25.7	0.092	93	1.0
5.	$p\text{-}CNPhCOCH_3$	22.0	0.314	93	1.0
6.	$PhCOCH_3$	24.7	0.143	93	0.0
7.	$PhCOCH_2Me$	24.4	-0.065	88	5.0
8.	$PhCOCH_2Ph$	17.7	0.110	83	10.0
9.	$PhCOCH_2$Naph-2	17.1	0.150	83	10.0
10.	$PhCOCH_2$Anth-2	16.4	0.130	81.5	11.5
11.	$PhCOCH_2$Phen-3	17.2	0.170	83.5	9.5
12.	$PhCOCH_2$Py-1	15.65	0.135	80.5	12.5

[a]Measured in DMSO against two indicators. [b]In volts; irreversible oxidation potentials (E_p) measured in DMSO by cyclic voltammetry and referenced to the standard hydrogen electrode (SHE). [c]Calculated(in kcal/mol)using eq 1. [d]Radical stabilization energy (RSE).[14]

Substituent Effects on BDE's of Ketones: Examination of entries 1-5 of table II show that remote electron donating and electron accepting groups make the ketone less or more acidic, but have no effect on BDE's of the α-C-H bonds. The changes in acidities of the ketones are offset in eq.1 by shifts of $E_{OX}(A^-)$ to less or more positive potentials. The result is no change in BDE. This observation indicates that the remote substituent is not interacting directly with the incipient radical to provide additional stabilization. However, substitution of an α-hydrogen in acetophenone by methyl groups lowers the BDE of the α-C-H bond by 5 kcal/mol (entries 6 and 7). Introduction of an aryl groups into the α-position of acetophenone provides substantial increase in

RSE's (9.5 - 12.5 kcal/mol; entries 8-12). This increase in RSE's can be attributed to the delocalization of the unpaired electron into the large aromatic systems, an effect comparable in magnitude to that of aryl methyl radicals.[18]

Summary and Conclusion: Homolytic bond dissociation energies in DMSO for C-H bonds in aryl and sulfur-containing compounds have been measured using pK_{HA} and $E_{OX}(A^-)$ data in eq 1. In every case, the radical stabilization energies (RSEs) of PhSCH(·)-**A** , RSCH(·)-**A** or ArylCH(.)-**A** estimated from the BDEs, relative to the BDE for C-H bond in methane are larger than the RSEs estimated from the individual radicals, but are equal or smaller than the sum of RSEs of the two radicals, indicating the apparent absence of synergism in the systems studied.

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1. Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute, under contract DE-AC06-76RL0 1830.
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15. The BDE of CH_3-H = 105 kcal[3]. The RSE of PhCH(·)-SPh relative to methyl radical is 21 kcal (105 - 84).
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