

Thermochemistry of Sulfenic Esters (RSOR'): Not Just Another Pretty Peroxide

Daniel D. Gregory and William S. Jenks*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

Received November 4, 1997

A computational study on the thermochemistry of several simple sulfenic acids (RSOH) and esters (RSOR') is reported. The enthalpies of R–S, S–O, and O–R' homolytic cleavage are calculated at the G2 level of theory and compared to related peroxides and disulfides. Less expensive B3LYP calculations were unsatisfactory. When R and R' are both alkyl, the O–C bond is expected to be the weakest in the molecule; for CH₃SOCH₃, C–S, S–O, and O–C bond dissociation enthalpies of 67, 64, and 49 kcal/mol are predicted by G2. Compared to peroxides, sulfenic esters are predicted to have weaker O–C bonds and S–O bonds that are stronger than the analogous O–O bonds. The C–S bonds of sulfenic esters are predicted to be somewhat stronger than those of disulfides. A rationalization is given for the observation that radical stabilization is greater for RSO• than ROO•, RSS•, or ROS•.

Introduction

During the course of our investigation into the photochemistry of sulfoxides, we encountered a less common but nonetheless intriguing functional group, the sulfenic ester (RSOR').^{1,2} This class of compounds is isomeric to the sulfoxide, but with a linear connectivity that reminds one of peroxides or disulfides. As a point of nomenclature, however, they are esters of sulfenic acids (RSOH). More commonly known organic sulfur acids are the sulfonic (RSO₃H) and sulfinic (RSO₂H) classes, in which sulfur is at a higher oxidation state.

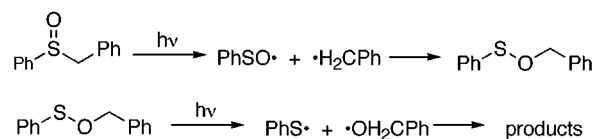
Sulfenic acids are not especially common in natural products, but they are extraordinarily important in the kitchen, being the first enzymatically produced compounds on crushing or slicing of onions, garlic, and other members of the *Allium* genus.³ The actual onion lacrymator is a sulfine, CH₃CH₂CH=S=O, formed by an electrocyclic isomerization of the enzymatically produced 1-propenesulfinic acid.⁴

As another point of interest, the sulfenic acid is essentially unique among organic acids in that the equilibrium in aqueous solution favors its anhydride, called a thiosulfinic ester.⁵ As a result, less is known about sulfenic acids than about the more highly oxidized sulfur acids.



Sulfenic esters are also relatively uncommon despite their obvious relationship to peroxides and disulfides. Even though they have been theoretically predicted to be thermodynamically more stable than the ubiquitous

Scheme 1



sulfoxides,⁶ sulfenic esters can be more difficult to handle than their more common sulfoxide isomers. Without strong electron-withdrawing groups on the sulfur substituent, they are often relatively unstable to hydrolysis and/or radical attack.

Products isolated after photolysis of a number of different sulfoxides appeared to be actually derived from the radical pair or biradical obtained by homolytic cleavage of the S–O bond of a sulfenic ester.^{7,8} At first, the mechanism of S–O bond scission was not clear, but it was established that secondary photolysis of the sulfenic ester resulted in S–O homolysis (Scheme 1).^{1,2} Meanwhile, in the early 1990s, it had also been established that direct photolysis of alkyl esters of *p*-nitrobenzenesulfinic acid was an outstanding source of alkoxy radicals for various studies.^{9–13} The nitro group makes the sulfenic ester easier to handle in the laboratory and shifts the absorption into a more convenient range.⁹

These results all seemed reasonable enough; by analogy to peroxides, the S–O bond was expected to be weak and was likely to be broken by photochemical excitation. Indeed, it seemed intuitively reasonable to use peroxides as a starting point when predicting many properties of

(6) Wolfe, S.; Schlegel, H. B. *Gazz. Chim. Ital.* **1990**, *120*, 285–290.

(7) Jenks, W. S.; Gregory, D. D.; Guo, Y.; Lee, W.; Tetzlaff, T. In *Organic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1997; Vol. 1; pp 1–56.

(8) Still, I. W. J. In *The Chemistry of Sulfoxides and Sulfoxides*; Patai, S., Rappaport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons Ltd.: New York, 1988; pp 873–887.

(9) Pasto, D. J.; Hermine, G. L. *J. Org. Chem.* **1990**, *55*, 5815–5816.

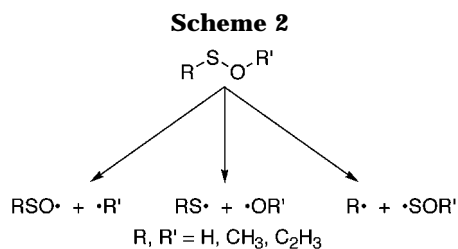
(10) Pasto, D. J.; Cottard, F.; Horgan, S. *J. Org. Chem.* **1993**, *58*, 4110–4112.

(11) Pasto, D. J.; Cottard, F. *Tetrahedron Lett.* **1994**, *35*, 4303–4306.

(12) Pasto, D. J.; Cottard, F. *J. Am. Chem. Soc.* **1994**, *116*, 8973–8977.

(13) Pasto, D. J.; Cottard, F. *J. Org. Chem.* **1994**, *59*, 4642–4646.

(1) Guo, Y.; Jenks, W. S. *J. Org. Chem.* **1995**, *60*, 5480–5486.
 (2) Guo, Y.; Jenks, W. S. *J. Org. Chem.* **1997**, *62*, 857–864.
 (3) Block, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1135–1178.
 (4) Block, E.; Gillies, J. Z.; Gillies, C. W.; Bazzi, A. A.; Putman, D.; Rebelle, L. K.; Wang, D.; Zhang, X. *J. Am. Chem. Soc.* **1996**, *118*, 7492–7501.
 (5) de Maria, P. In *The Chemistry of Sulphenic Acids and their Derivatives*; S. Patai, Ed.; John Wiley & Sons: Ltd.: New York, 1990; pp 293–310.



sulfenic esters. However, a look at bond dissociation enthalpies (BDEs) taken from known and estimated heats of formation brought forth a surprise. Consider benzyl benzenesulfonate (PhSOCH₂Ph, Scheme 1), which is an intermediate in the photolysis of benzyl phenyl sulfoxide.¹ Estimates of the heats of formation for all of the appropriate radicals suggested that the S–O bond was in fact about 20 kcal/mol *stronger* than the O–C bond, despite the photochemical results. This piqued our interest in the thermochemistry of this functional group whose peroxide and disulfide analogues we thought we understood.

Reports of unimolecular thermochemistry on sulfenic esters are rare, but a few have been made for sulfenic esters in solution. Several highly substituted sulfonates have been shown to undergo heterolysis in solution.^{14–17} By contrast, it was proposed that the solution-phase thermal decomposition of benzyl *p*-toluenesulfonate mainly to the sulfoxide went by a concerted mechanism.¹⁸ To the best of our knowledge, no gas-phase data regarding thermolysis of sulfenic esters exist. The experimental heat of formation is known for CH₃SO·,¹⁹ but not for any other sulfinyl radical. Similarly, only one heat of formation is known for radicals of the form ROS·, where R = H.²⁰ Finally, ΔH_f° is only known for HSOH, among sulfenic acids and esters.²⁰

We report a computational study of several sulfenic esters, acids, and the corresponding radicals formed by homolysis of R–S, S–O, and O–R' bonds. A series of representative sulfenic acids and esters was chosen (Scheme 2), and energies were calculated for the closed shell molecules and the radicals which result from the homolytic cleavages of interest. We compare the sulfenic ester to its closest analogues, the peroxide and disulfide, and summarize trends for bond energies as a function of structure in these systems. It is shown that the RSO group causes a dramatic decrease of the BDE of O–H or O–C, compared to alcohols and ethers, while the ROS, ROO, and RSS groups show smaller but real bond destabilizations. It is also shown that the S–O bond of sulfenic acids and esters is much stronger than the O–O bond of peroxides and is rather similar in strength to the S–S bond.

Methods

All computations were carried out with the Gaussian 92/DFT²¹ or GAMESS²² suites of programs. Because absolute enthalpies for the reactions shown in Scheme 2 were desired, levels of theory which did not produce accurate absolute energies for both singlet and doublet species were not acceptable. The Gaussian-2 (G2) method is a protocol advanced by Curtiss et al. that has had success in predicting heats of formation of small molecules within 2–3 kcal/mol.^{23–25} It is a demanding set of calculations, and therefore the substituents R in this study were limited to H, CH₃, and CH=CH₂.

The G2 theory uses an approach designed to approximate the result of a QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) calculation. Molecular geometries are obtained at the MP2(full)/6-31G(d) level. Correlation corrections are obtained with MP2, MP4, and QCISD(T) runs, and basis set corrections are also obtained. After the properly scaled zero point energy is included, an empirical correction based on the number of electrons in the system is applied to obtain the final absolute energy. The method is limited to molecules with five or six non-hydrogen atoms, depending on available computational resources. Variations on the G2 theory have been introduced in which lower correlation methods, G2(MP2),²⁶ and smaller basis sets G2(MP2,SVP),²⁷ are used in the additivity approximations. However, it has been shown that care must be exercised with larger molecules for all G2 methods, as an accumulation of noncanceling errors can be significant.²⁸

Recent experimental work by Pasto and ourselves has involved alkyl esters of arenesulfenic esters.^{9,11,13,29,30} G2 calculations on molecules of this size are not currently practical, so a less demanding computational method was sought that could be extended to larger molecules. The Becke3LYP hybrid density functional was investigated as an alternative.^{31,32} These efforts were not satisfactory; details are given in Supporting Information.

Results

Thermochemistry. Absolute energies were obtained for the series of sulfenic acids and esters and radicals using the G2, G2(MP2), and G2(MP2,SVP) protocols.^{23–27,33} The G2 energies and the optimized geometries are available in the Supporting Information. Spin contamination on all radicals not containing the vinyl group was quite modest ($S^2 \leq 0.76$). For the vinyl-substituted radicals, however, the spin contamination was more significant ($S^2 \sim 0.80$), and the spin-projected energies

(14) Hogg, D. R.; Smith, J. H.; Vipond, P. W. *J. Chem. Soc. (C)* **1968**, 2713–2716.

(15) Hogg, D. R.; Vipond, P. W. *J. Chem. Soc. (C)* **1970**, 60–63.

(16) Braverman, S. In *The Chemistry of Sulfenic Acids and Their Derivatives*; Patai, S., Ed.; John Wiley & Sons: New York, 1990; pp 311–359.

(17) Braverman, S. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons Ltd.: New York, 1988; pp 717–757.

(18) Miller, E. G.; Rayner, D. R.; Thomas, H. T.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4861–4868.

(19) Zhao, H.-Q.; Cheung, Y.-S.; Heck, D. P.; Ng, C. Y.; Tetzlaff, T.; Jenks, W. S. *J. Chem. Phys.* **1997**, *106*, 86–93.

(20) O'Hair, R. A. J.; DePuy, C. H.; Bierbaum, V. M. *J. Phys. Chem.* **1993**, *97*, 7955–7961.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. In *Gaussian, Inc.*: Pittsburgh, PA, 1993.

(22) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, N.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(23) Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030–9034.

(24) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221–7230.

(25) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063–1079.

(26) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293–1298.

(27) Curtiss, L. A.; Redfern, P. C.; Smith, B. J.; Radom, L. *J. Chem. Phys.* **1996**, *104*, 5148–5152.

(28) Nicolaidis, A.; Radom, L. *Mol. Phys.* **1996**, *88*, 759–765.

(29) Pasto, D. J.; Cottard, F.; Picconatto, C. *J. Org. Chem.* **1994**, *59*, 7172–7177.

(30) Pasto, D. J.; L'Hermine, G. *Tetrahedron* **1993**, *49*, 3259–3272.

(31) Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974–12980.

(32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(33) Raghavachari, K.; Stefanov, B. B.; Curtiss, L. A. *J. Chem. Phys.* **1997**, *106*, 6764–6767.

Table 1. Heats of Formation ΔH_f° (298 K), kcal/mol

species	G2	G2(MP2) ^c	G2(MP2,SVP) ^d	experiment ^a
H•	51.6	51.6	51.6	52.1 ± 0.0
HO•	9.1	8.9	9.3	9.4 ± 0.1
HS•	34.6	32.9	32.9	34.2 ± 0.7
HSO•	-4.0	-7.6	-6.4	
HOS•	-0.3	-2.7	-1.7	-0.5 ± 2 ^b
CH ₃ •	35.1	35.6	35.8	35.0 ± 0.1
CH ₃ O•	4.7	4.9	5.0	4.1 ± 0.9
CH ₃ S•	30.0	28.6	28.4	29.8 ± 0.4
CH ₃ SO•	-15.5	-18.8	-17.8	-14.8 ± 2 ^c
CH ₃ OS•	2.6	0.4	1.4	
C ₂ H ₃ •	72.7	73.5	71.7	71.6 ± 0.8
CH ₂ =CHO•	4.1	3.8	3.5	2.5 ± 2.2
CH ₂ =CHS•	49.3	48.1	46.4	
CH ₂ =CHSO•	9.5	7.1	6.3	
CH ₂ =CHOS•	26.6	24.7	23.7	
HSOH	-26.4	-29.5	-26.4	-27. ± 3.5 ^b
CH ₃ SOH	-33.6	-36.4	-35.6	
HSOCH ₃	-23.2	-26.1	-25.1	
CH ₃ SOCH ₃	-29.5	-32.1	-31.4	
CH ₂ =CHSOH	-8.1	-10.9	-11.8	
HSOCH=CH ₂	-1.1	-3.8	-4.6	

^a Experimental heats of formation taken from ref 47 unless otherwise noted. ^b Reference 20. Reference 19. ^c The average deviation between G2 and G2(MP2) was -1.7 kcal/mol, and the average absolute deviation was 1.9 kcal/mol. ^d The average deviation between G2 and G2(MP2,SVP) was -1.6 kcal/mol, and the average absolute deviation was 1.7 kcal/mol.

were used, though the variation between the projected and unprojected G2 energies was less than 0.5 kcal/mol.

Though not necessary to calculate BDEs, heats of formation are quite useful for comparison of theory and experiment, and computed ΔH_f° values were obtained. Different methods have been advocated for arriving at computed heats of formation, generally using either atomization^{25,34} or bond separation^{28,33} approaches. The bond separation method, which uses isodesmic reactions and molecular rather than atomic reference compounds, has some advantages, but it requires that there be appropriate reference compounds with experimentally known ΔH_f° values. Among the sulfenic acids and esters, there is only one experimental estimate of ΔH_f° (for HSOH), so the atomization method was used instead. The calculated heats of formation, shown in Table 1, were corrected to 298 K.³⁴ They are compared to available experimental values and all three models perform well.³⁵ It was found that G2 ΔH_f° values reproduced previous reports to within less than 1 kcal/mol for species which did not contain sulfur. Such minor differences were attributed to slightly different geometries obtained from structural optimizations. The G2 heats of formation obtained for sulfur-containing compounds varied slightly more (<1.5 kcal/mol) when compared to previous computations than did the others.³⁶

Bond dissociation energies, obtained by the three G2-type methods are shown in Table 2, and agreement is generally very good. Nonetheless, only the G2 values will be used in the Discussion section.

Computing resource limitations did not allow for calculation of G2 energies for the largest sulfenic esters:

(34) Nicolaidis, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460-17464.

(35) Several radicals are members of the standard test set for the G2 methods, but we have reproduced the calculations here.

(36) The 6-311G basis set for sulfur has been modified in the Gaussian programs to conform to those of McLean and Chandler.⁵⁰ Variation between current and previous ΔH_f° calculations on sulfur-containing molecules was not systematic.

Table 2. Computed Cleavage Enthalpies for Sulfenic Acids and Esters (298 K, kcal/mol)

		R-SOR'	RS-OR'	RSO-R'
HSOH	G2	77	70	73
	G2(MP2)	74	71	69
	G2(MP2,SVP)	74	71	70
HSOCH ₃	experiment	79 ± 3.5 ^a		
	G2	76	63	54
	G2(MP2)	74	64	54
	G2(MP2,SVP)	74	63	54
CH ₃ SOH	G2	68	73	69
	G2(MP2)	69	74	65
	G2(MP2,SVP)	70	73	65
CH ₃ SOCH ₃	G2	67	64	49
	G2(MP2)	68	66	49
	G2(MP2,SVP)	69	65	49
HSOCH=CH ₂	G2	78	40	70
	G2(MP2)	76	41	70
	G2(MP2,SVP)	76	41	70
CH ₂ =CHSOH	G2	81	67	68
	G2(MP2)	82	68	66
	G2(MP2,SVP)	82	68	66
CH ₃ SOC ₂ H ₃ ^b	G2	(27) 67	(0) 40	(23) 63
C ₂ H ₃ SOCH ₃ ^b	G2	(21) 80	(0) 59	(-10) 49
C ₂ H ₃ SOC ₂ H ₃ ^b	G2	(46) 80	(0) 34	(29) 63

^a Reference 20. ^b Values in parentheses are G2 relative cleavage energies in kcal/mol, with the S-O cleavage arbitrarily set to 0, derived only from the radical energies. Values in italics are crude estimates of the absolute BDEs, based on absolute H-S and C-S cleavage energies for the related species. This assumption was justified based on previous collections of data.³⁷

CH₃SOC₂H₃, C₂H₃SOCH₃, and C₂H₃SOC₂H₃. Relative BDEs were obtained by comparing the sums of energies of the three pairs of products; these are reported in parentheses in Table 2. Examination of the rest of the table (and previous work on sulfur thermochemistry³⁷) suggested that C-S bond enthalpies would be nearly stable for these larger sulfenic esters. This allowed estimation of the S-O and O-C bond enthalpies for the largest sulfenic esters, and the results are shown in italics.

In addition to those necessary for the sulfenic ester BDEs, heats of formation for a few other species were obtained. A few are as noted in Table 3 for the standards. Also calculated were energies of dimethyl sulfoxide, the sulfoxide isomer of H₂SO, and the transition state which connects dimethyl sulfoxide and CH₃SOCH₃ in a concerted rearrangement.

It is important to establish what is to be considered a significant effect when comparing BDEs for similar bonds in different compounds, and a lower limit of 4 kcal/mol is rationalized here. The absolute average deviation for heats of formation in the expanded G2 test set, which includes many molecules of this size, is 1.6 kcal/mol. The spread of BDEs calculated by the three G2 variants is generally small (≤ 2 kcal/mol), but ranges up to 4 kcal/mol. Further, three compounds are used to calculate any given BDE. Therefore, it is concluded that 4 kcal/mol is probably a reasonable limit below which BDE differences were not considered significantly different.

Photochemistry. The photochemistry of esters of aromatic sulfenic acids (i.e., Ar-S-O-R) observed by Pasto^{9,11,13,29,30} and by us^{1,2} involves S-O homolysis, despite the fact that this bond is stronger than the O-R bond. Photoheterolysis has also been observed for certain systems, but this was with very highly substituted compounds which were clearly biased toward that path.³⁸

(37) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23-35.

Table 3. Bond Dissociation Energies^a

compound	BDE, kcal/mol					
	O-H	O-C- (sp ³)	O-C- (sp ²)	S-H	S-C- (sp ³)	O-O, S-S, S-O
HOH	119	—	—	—	—	—
CH ₃ OH	104	93	—	—	—	—
CH ₂ =CHOH	85	—	103	—	—	—
CH ₃ OCH ₃	—	83	—	—	—	—
CH ₂ =CHOCH ₃	—	62	91	—	—	—
CH ₂ =CHOCH=CH ₂	—	—	69	—	—	—
HOOH ^b	87	—	—	—	—	51
CH ₃ OOH ^c	85	67	—	—	—	44
CH ₃ OOCH ₃ ^d	—	67	—	—	—	37
HSH	—	—	—	90	—	—
CH ₃ SH	—	—	—	91	74	—
PhSH	—	—	—	80	—	—
CH ₃ SCH ₃	—	—	—	—	77	—
PhSCH ₃	—	—	—	—	67	—
HSSH ^b	—	—	—	76	—	71
CH ₃ SSH ^g	—	—	—	79	64	68
CH ₃ SSCH ₃	—	—	—	—	57	72
HSOH	73	—	—	79, ^b 77 ^f	—	70
CH ₃ SOH	69	—	—	—	68	73
HSOCH ₃	—	54	—	76	—	63
CH ₂ =CHSO-H	68	—	—	—	—	67
HSOCH=CH ₂	—	—	70	78	—	40
CH ₃ SOCH ₃	—	49	—	—	67	64
CH ₃ SOCH=CH ₂ ^e	—	—	63	—	67	40
CH ₂ =CHSOCH ₃ ^e	—	49	—	—	—	59
CH ₂ =CHSOCH=CH ₂ ^e	—	—	63	—	—	34

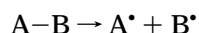
^a Unless otherwise indicated, BDEs for sulfenic acids and esters are G2 values from Table 2. Unless otherwise noted, all others are taken from ΔH_f° values from the NIST database.^{47a} ^b Reference 20. ^c ΔH_f° of CH₃OO• taken as the G2 value of 1.7 kcal/mol. ^d ΔH_f° of CH₃OO• = 1.7 kcal/mol taken from G2 calculation. ^e See Table 3 and text. ^f This work. ^g ΔH_f° for CH₃SSH from ref 49.

A first step in understanding of the photochemistry is to generate a picture of the initially obtained excited states. Based on both ROHF calculations on the lowest triplet of CH₃SOCH₃ and CASSCF calculations on the lowest excited singlet and triplet, it was concluded that these states of purely alkyl sulfenic esters are a repulsive surface reached by an $n_s \rightarrow \sigma_{s-o}^*$ transition. A nonrepulsive $\pi \rightarrow \pi^*$ excited state was found for PhSOCH₃, a model for the alkyl arenesulfenates. More detail is given in the Supporting Information. A more detailed theoretical investigation of PhSOR photochemistry is necessary before any further conclusions can be drawn.

Discussion

A major portion of this discussion is dedicated to the BDEs of the sulfenic acids and esters, compared to other related compounds, with the object of assessing the bond strengthening or weakening by particular structural units. To facilitate this comparison, the G2 BDEs for the current compounds are collected in Table 3 along with experimental BDEs for representative standard compounds. A very useful compilation of measured and estimated bond enthalpies for many other types of sulfur-containing compounds has been published previously.³⁷

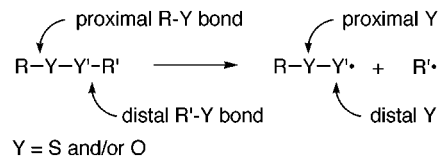
Any given homolytic bond dissociation can be described by the following equation:



Though this is self-evident, it is useful to consider when discussing BDEs, because it makes the following point clear. Structural effects that stabilize one or more of the product radicals to an extent greater than the starting material lower the BDE. (This could also be put as destabilizing the products *less* than the starting material.) This is illustrated in Table 3, for instance, in the O-H BDEs for CH₃OH and CH₂=CHOH.

Conversely, structural effects that selectively stabilize A-B lead to increased BDEs. An example of this type of interaction is electronegativity differences between the bonding atoms in A-B. When the electronegativity difference is large, a stabilizing bond dipole ensues in response. Of course, this bond dipole is unavailable to the separated radicals A• and B•. As a result, a larger electronegativity difference between two bonded atoms generally leads to a stronger bond than for analogous compounds whose atoms of interest have more similar electronegativity. This, for instance, contributes to the extraordinary bond strength for O-H.

Comparison of the Weakening of the O-H, O-C, S-H, and S-C bonds by Peroxides, Disulfides and Sulfenic Esters. The three functional groups under consideration (now designated RYY'R' where Y is S and/or O) are isoelectronic, and their respective homolytic cleavages yield isoelectronic radicals. All are expected to have weakened H-Y or C-Y bonds, relative to RYR', because the RYY• radicals have a new electronic structure that is stabilized, compared to alkoxy or thiyl radicals. For purposes of discussion, we define "proximal" and "distal" bonds and atoms in relationship to the alkyl group of RYY' as shown below.



In RYY•, the orbital containing the unpaired electron on Y' (which used to be involved in the distal σ bond) overlaps with a lone pair orbital on Y, giving a three-electron π system consisting of a doubly occupied π orbital and singly occupied π^* orbital. Overall, this stabilizes the system. In support of this interpretation, peroxy, perthiyl, and sulfinyl radicals are all known experimentally to be π -type radicals.

It is reasonable to inquire whether the radical stabilization exerted by this π interaction will be the same for peroxy radicals, perthiyl radicals, and the two radicals available from sulfenic ester cleavage, RSO• and ROS•. This can be addressed by examination of resonance forms. Under this analysis, there are two important structures that can be drawn for each of the four radicals, one neutral, and one dipolar (Figure 1). The extent to which the dipolar form contributes to the correct overall structure is an expression of the extent to which the three-electron π stabilization is effective. An expectation of no dipolar contribution is related to the expectation that the three-electron π system does not stabilize the radical at all.

Underneath the dipolar structures in Figure 1 are qualitative judgments on their value as contributing structures. Charge separation in the peroxy case is expected to be energetically expensive. Sulfur, on the other hand, is more polarizable than oxygen, so the

(38) Horspool, W. M. In *The Chemistry of Sulphenic Acids and their Derivatives*; Patai, S., Ed.; John Wiley & Sons Ltd.: New York, 1990; pp 517-547.

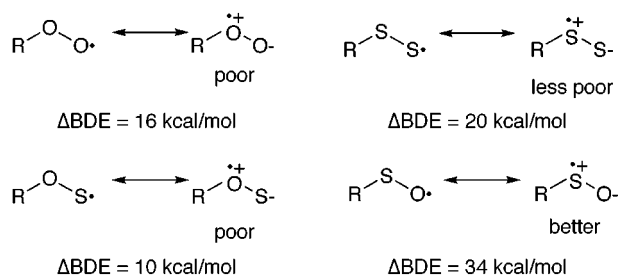


Figure 1. Resonance forms for the RYY'• radicals. Δ BDE represents the difference in O–C or S–C BDE between CH_3OCH_3 or CH_3SCH_3 and the appropriate molecule $\text{CH}_3\text{-YY}'\text{CH}_3$ which produces the given radical.

Table 4. Natural Population Analysis for $\text{CH}_3\text{YY}'$ Radicals^a

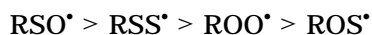
species	proximal spin density	distal spin density
$\text{CH}_3\text{OO}^\bullet$	0.10	0.90
$\text{CH}_3\text{SS}^\bullet$	0.18	0.82
$\text{CH}_3\text{SO}^\bullet$	0.39	0.62
$\text{CH}_3\text{OS}^\bullet$	0.10	0.91

^a All data taken from UMP2(full)/6–31(d) optimized structures.

charge separated species is seen as more viable for the perthiyl radical. Oxygen is more electronegative than sulfur; thus, it is expected that the dipolar structure for ROS^\bullet will probably be the least important among all four radicals.

However, the dipolar resonance form will be important for the sulfinyl radical RSO^\bullet , where both polarizability and electronegativity are favorable for the charge-separated form. Thus we arrive at the expectation that, while all four systems should cause weakening of the distal Y'–R' bond, the greatest destabilization should be for the O–R' bond of sulfenic acids and esters. The least bond destabilization is expected for the R–S bond of these same compounds. Confirming this expectation are the Δ BDE data shown in Figure 1, which compare the C–O or C–S BDE of the $\text{CH}_3\text{-Y-Y}'\text{-CH}_3$ compound to that of dimethyl ether or dimethyl sulfide as appropriate.

The best surrogate to probe for the contribution of the dipolar resonance forms in the electronic structure calculations is the amount of unpaired spin on the proximal and distal Y atoms for all four radicals. This is shown in Table 4, using the Natural Population Analysis of Reed and Weinhold. The delocalization is qualitatively smaller for ROO^\bullet and ROS^\bullet than for the other two, and is clearly the greatest for RSO^\bullet . Thus the sulfinyl radical (RSO^\bullet) appears to be the best radical stabilizing group of the four, with the rest in the following order:



Other effects impinge on the BDEs as well. The O–H bond of hydrogen peroxide is weaker than that of water and alcohols. However, the fraction of the weakening due to the fractional π bond of HOO^\bullet is difficult to extract because of the large electronegativity contribution to the bond strength changes. However, this is less difficult for the destabilization of O–C(sp^3) bonds by the ROO function compared to RO . A value of about 16 kcal/mol is probably reasonable for any simple alkyl system.^{37,39}

Since the H–S BDE differs so much less for H_2S and CH_3SH , we can presume that the 12–20 kcal/mol BDE drop observed on substitution of SS for S in Table 3 is due largely to the partial bond in the perthiyl radical. Benson had estimated a nearly universal bond destabilization for $\text{RS}_{n-1}\text{-H}$ of about 21 kcal/mol, but the recent results of O'Hair et al. make revision of ΔH_f° of HSS^\bullet seem necessary, and the O'Hair value is used to calculate the H–S bond strength in Table 3.²⁰ Our G2 calculations on HSS^\bullet (data not shown) are in very good agreement with the O'Hair datum. A further consequence of this revision is an increase in the HSS-CH_3 bond strength, compared to the Benson value. The BDE of 57 kcal/mol and bond destabilization of about 20 kcal/mol (relative to the corresponding sulfide) for the distal alkyl–SS bond is probably still general as long as the proximal substituent is also an ordinary alkyl group.

Now the sulfenic esters are considered. Compared to $\text{CH}_3\text{O-CH}_3$, the $\text{CH}_3\text{SO-CH}_3$ bond is weaker by some 34 kcal/mol. A similarly astounding O–H bond weakening of 35 kcal/mol is observed for methanesulfenic acid, relative to methanol. On the other hand, the BDEs for $\text{CH}_3\text{S-CH}_3$, $\text{CH}_3\text{SS-CH}_3$, and $\text{CH}_3\text{OS-CH}_3$ are 77, 57, and 67 kcal/mol, respectively. They suggest a bond weakening of 20 and 10 kcal/mol for the disulfide and S face of the sulfenic ester. For S–H bonds, similar bond destabilizations of 12 and 15 kcal/mol are observed for disulfides and HSOR.

Finally, examination of Table 3 yields the conclusion that distal RYY'–R' BDEs are less sensitive to the proximal substituent than are the single heteroatom functional analogues. Because of the extra "insulation" of the proximal Y atom, proximal substituents have less influence on the effective electronegativity of the distal Y' atom. Since larger electronegativity differences lead to higher BDEs, it stands to reason that such "insulation" will decrease variability in the proximal Y'–R' bond BDE. Furthermore, the aforementioned radical stabilization occurs whether the peroxide, disulfide, or sulfenic ester is conjugated on the proximal side.

Comparison of O–O, S–S, and S–O Bond Enthalpies. Among peroxides, disulfides, and sulfenic esters, peroxides have the weakest Y–Y' bonds (Table 3). The destabilization of these bonds is usually ascribed to lone pair repulsion. This effect is smaller for the second row elements than for the first row elements because the lone pairs are more diffuse.

The S–O bond enthalpies for HSOH and CH_3SOCH_3 are much closer to those of the analogous disulfides than the peroxides. It can reasonably be assumed that the inherent lone pair repulsion energy for S–O will be larger than that of S–S and smaller than that of O–O, leading to an intermediate BDE. However, the electronegativity difference between S and O is expected to increase the bond strength. No quantitative expectation can be given, but the observed values similar to the disulfide BDEs are certainly reasonable.

The peroxide BDEs are sensitive to H/ CH_3 substitution, much more so than the disulfides.⁴⁰ The O–O BDE drops about 7 kcal/mol for each H that is substituted by CH_3 . This effect is virtually negligible for disulfides. This

(40) A related correlation between electronegativity and heats of formation of H and CH_3 derivatives has been well documented by Benson and co-workers. Luo, Y.-R.; Benson, S. W. *Acc. Chem. Res.* **1992**, *25*, 375–381.

(39) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419–2438.

contrast between S and O behavior carries over into the sulfenic compounds. Substitution of CH₃ for H on the sulfur terminus has a small effect on the S–O enthalpy, perhaps slightly increasing it. The effect of the same substitution on the oxygen atom is more dramatic, lowering the S–O BDE by about 10 kcal/mol.

Last, there is the effect of substituting vinyl groups for methyls. Such substitutions will be reflected in the special stability of the allyl-like C₂H₃S• and C₂H₃O• radicals, causing a weakening in the S–O bond. Benson has estimated the allylic stabilization energy for C₂H₃S• to be about 8 kcal/mol.³⁷ A stabilization of 5–6 kcal/mol is observed here, but the magnitude is clearly comparable. A much larger allylic stabilization is observed for C₂H₃O•, approximately 24 kcal/mol. The larger allylic stabilization for C₂H₃O• than for C₂H₃S• is also qualitatively in line with trends for PhO• versus PhS• and C–O versus C–S π -bonds in general.³⁷

RSO• vs ROS• Isomers. There has been in the literature some question as to whether HSO• or HOS• is the more stable isomer of that triatomic radical.^{20,37,41–44} Several computational studies have been completed, and all but the most recent agreed that HOS• was more stable than HSO• by a few kcal/mol.^{41,42,45}

The best purely experimental measurement ΔH_f° for HSO• appears to be -1.5 ± 2 kcal/mol,⁴⁶ but other kinetic evidence suggests that it must be below -2 kcal/mol.^{43,44} Most recently, by combining experimental heats of formation and very large multireference configuration interaction calculations, ΔH_f° for HSO was placed at -6.1 ± 1.3 kcal/mol by Xantheas and Dunning.^{43,44} The G2 value of -4.0 (Table 1) is in reasonable agreement.

Xantheas used the same experimental–computational combination to obtain a value of $\Delta H_f^\circ = -0.7 \pm 1.3$ kcal/mol for HOS•. This is in outstanding agreement with the nearly simultaneously published experimental value of -0.5 ± 2 kcal/mol, and is about 5 kcal/mol higher than the value for HSO•.²⁰ The G2 value of -0.3 for HOS• is also in very good agreement. The convergence of these experimental and theoretical data seem to finally resolve that HSO• is the more stable isomer.

That being so, it is only because of the extraordinary O–H bond energies that HSO• and HOS• are even particularly close in energy. Substituting CH₃ or C₂H₃ for H gives a gap between the isomers of about 18 kcal/mol favoring the sulfinyl radical. Because of the bigger difference in BDE between HO and CO than between HS and CS, there is little doubt that when R is any ordinary carbon substituent, the sulfinyl radical will be the significantly more stable isomer than the corresponding ROS• radical.

A similar phenomenon involving H and C substitution is seen for the isomerism of sulfenic esters and sulfoxides. Heats of formation (298 K) for the sulfoxides H₂SO and (CH₃)₂SO were calculated at the G2 level, and values of -8.9 and -35 kcal/mol were obtained. (The experimental value for (CH₃)₂SO is -36.2 kcal/mol.⁴⁷) Thus, while

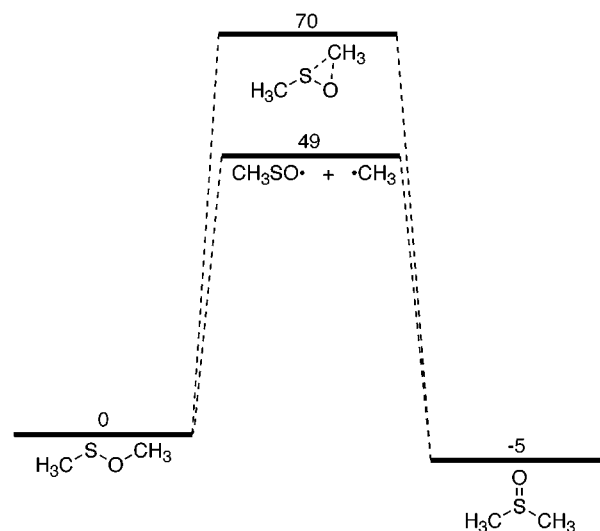


Figure 2. Relative energies of CH₃SOCH₃ structures. All energies are in kcal/mol relative to the sulfenic ester CH₃SOCH₃ and are G2 values at 298 K.

dimethyl sulfoxide is favored by 6 kcal/mol, the sulfoxide isomer of H₂SO is less stable than HSOH by nearly 20 kcal/mol! This trend is in line with previous calculations at lower levels of theory, though the absolute values differ substantially.⁶

According to previous work, disulfides are always more stable than the corresponding thiosulfoxides. At the MP2/6-311G(d,p) level, the separation is 34 kcal/mol for the H₂S₂ isomers and 20 kcal/mol for the (CH₃)₂S₂ isomers.⁴⁸ As with other effects observed in this paper, the direction of the H/CH₃ substitution effect is the same for the purely sulfur system as for the SO, but the effect is smaller.

Isomerization of Sulfenic Esters to Sulfoxides. Mislow and co-workers experimentally studied the isomerization of benzyl *p*-toluenesulfonate to benzyl *p*-tolyl sulfoxide in benzene.¹⁸ They obtained $\Delta H^\ddagger = 30$ kcal/mol and $\Delta S^\ddagger = -2$ eu. Isotopic labeling experiments indicated a partial retention of configuration at the benzyl carbon during the rearrangement. Thus, it was proposed that the reaction was concerted.

Calculations at the G2 level are out of the question for molecules of that size, but a transition state was obtained for the concerted conversion of CH₃SOCH₃ to dimethyl sulfoxide. Its geometry, if not energy, is quite similar to that obtained at lower levels of theory.⁶ As shown in Figure 2, the concerted transition state is expected to be about 21 kcal/mol above the radical cleavage pathway in this case. Thus, a concerted rearrangement pathway does not seem likely for any simple alkyl case.

Summary

The thermochemistry of the peroxide, disulfide, and sulfenic ester functional groups has been compared. G2

(41) Luke, B. T.; McLean, A. D. *J. Phys. Chem.* **1985**, *89*, 4592–4596.

(42) Plummer, P. L. M. *J. Chem. Phys.* **1990**, *92*, 6627–6634.

(43) Xantheas, S. S.; Dunning, T. H., Jr. *J. Phys. Chem.* **1993**, *97*, 18–19.

(44) Xantheas, S. S.; Dunning, T. H., Jr. *J. Phys. Chem.* **1993**, *97*, 6616–6627.

(45) Hinchliffe, A. *J. Mol. Struct.* **1980**, *66*, 235.

(46) Davidson, F. E.; Clemo, A. R.; Duncan, G. L.; Browett, R. J.; Hobson, J. H.; Grice, R. *Mol. Phys.* **1982**, *46*, 33–40.

(47) Stein, S. E.; Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. *NIST Structures and Properties: NIST Standard Reference Database 25*; U.S. Department of Commerce, NIST: Gaithersburg, MD, 1994.

(48) The absolute differences between H₂SS and HSSH is overestimated by several kcal/mol at this level, which can be recovered by a more flexible basis set. Nonetheless, the reported trend is expected to be verified. Steudel, R.; Drozdova, Y.; Miakiewicz, K.; Hertwig, R. H.; Koch, W. *J. Am. Chem. Soc.* **1997**, *119*, 1990–1996.

(49) Downard, K. M.; Bowie, J. H.; O'Hair, R. A. J.; Krempp, M.; DePuy, C. H. *Int. J. Mass Spectrosc. Ion Proc.* **1992**, *120*, 217–229.

(50) McLean, A. C.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639–5648.

calculations were shown to reproduce the experimental ΔH_f (298 K) data for the sulfur-containing species when available and were used to generate data for sulfenic esters and several radicals whose heats of formation are unknown. In the instance of HSO^\bullet and HOS^\bullet , the G2 method reasonably reproduced an energy separation previously only predicted by multireference CI calculations with enormous basis sets.

When compared to $\text{RY}'\text{-R}'$ bonds, $\text{RYY}'\text{-R}'$ are weaker for the peroxide, disulfide, and sulfenic ester. This is due to the reorganization of the electronic structure of the remaining RYY'^\bullet radical by placement of three electrons into a new set of π and π^* orbitals. The sulfinyl radical (RSO^\bullet) is the most stabilized of the four types of radicals, and its O-C bond is the most destabilized among the set. For any simple alkyl sulfenate, the weakest bond is expected to be the O-C bond. For vinyl or aryl sulfenates, a strong stabilization of the O-centered radical resulting from S-O homolysis is expected to make the S-O bond the most labile. The S-O and O-H bonds of sulfenic acids are expected to have comparable BDEs, depending somewhat on substitution.

The extraordinarily low BDE for O-O bonds in peroxides (~ 37 kcal/mol) is not reproduced in the sulfenic esters. The S-O bond is much closer to the S-S bond strength (ca. 64 kcal/mol for CH_3SOCH_3). This is attributed to less effective lone pair repulsions and the

difference in electronegativity between S and O, both of which increase bond enthalpy relative to O-O.

In short, while sulfenic esters are isoelectronic to peroxides, the thermochemistry of the two species stands in distinct contrast. Without allyl-type stabilization of the putative alkoxy radical provided by vinyl or aryl substitution on the O terminus, the O-C bond of a sulfenic ester will be markedly weaker than the central S-O bond. This makes the photochemistry of sulfenic esters seem all the more interesting.

Acknowledgment. The authors would like to acknowledge many helpful discussions with Mark Gordon, Mike Schmidt, and other members of the Gordon group. This research was supported by the National Science Foundation (CHE 9708237) and the Research Corporation.

Supporting Information Available: Coordinates and absolute G2 energies are available for all compounds calculated in this paper. Also given are additional details on the Becke3LYP studies and calculations on excited states (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9720243