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An ab Initio Molecular Orbital Study of the Rearrangement of α-Disulfoxide to Thiosulfonate

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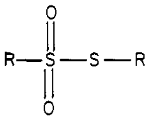
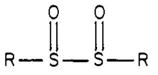
Abstract: The structures of hydrogen persulfide (HSSH, **18**) and its monoxide (HS(O)SH, **3**), dioxides (HSO_2SH, **1**, HS(O)S(O)H, **2**), and tetraoxide (HSO_2SO_2H, **17**) derivatives were examined by ab initio molecular orbital calculations at the HF/3-21G* and 6-31G* levels. The energetics of the rearrangement of α-disulfoxides (**2**) to thiosulfonates (**1**) via sulfenyl sulfinate (HS(O)OSH, **11**), sulfinyl radical, thiyl radical, and/or sulfonyl radical were investigated. The calculated relative energies agree with proposed mechanisms and experimental results.

The possible structures of disulfide dioxides have generated considerable controversy, the question being whether they have the thiosulfonate structure **1** or the isomeric α-disulfoxide structure **2**. Infrared and Raman spectra[1] and X-ray diffraction data[2] indicate that **1** is the preferred structure for thiosulfonates.



$\mathrm{R{-}\overset{O}{\underset{O}{S}}{-}S{-}R}$

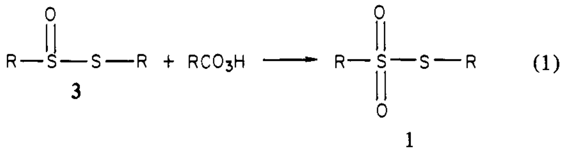
1



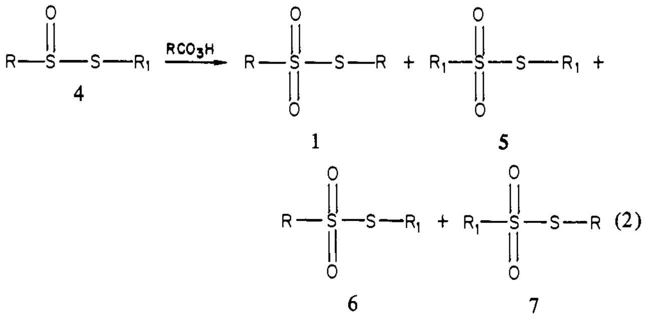
$\mathrm{R{-}\overset{O}{S}{-}\overset{O}{S}{-}R}$

2

Thiosulfinates (**3**) are oxidized by peroxy acids to thiosulfonates (**1**). Although the mechanism of oxidation has not been fully elucidated, it appears to vary with the structure of the thiosulfinate.[3-10] Oxidation of unsymmetrical thiosulfinates (**4**) such as 4-fluorophenyl benzenethiosulfinate[8] and methyl benzenethiosulfinate[9,10] led to the formation of four different thiosulfonates, respectively (eq 2). These products, kinetic studies,[7] ^{19}F NMR experiments,[8] and ^{18}O labeling experiments[9,10] are consistent with an α-disulfoxide intermediate (**2**, **8**) and show that the S–S bond has undergone cleavage during the course of the reaction.

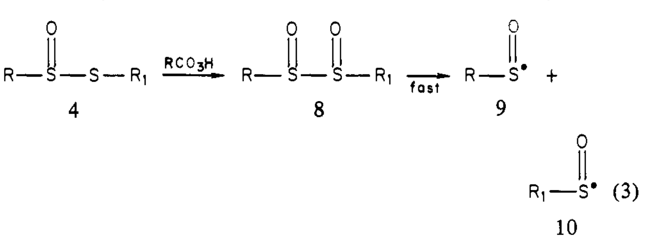


$$\underset{\mathbf{3}}{\mathrm{R{-}\overset{O}{S}{-}S{-}R}} + \mathrm{RCO_3H} \longrightarrow \underset{\mathbf{1}}{\mathrm{R{-}\overset{O}{\underset{O}{S}}{-}S{-}R}} \quad (1)$$



$$\underset{\mathbf{4}}{\mathrm{R{-}\overset{O}{S}{-}S{-}R_1}} \xrightarrow{\mathrm{RCO_3H}} \underset{\mathbf{1}}{\mathrm{R{-}\overset{O}{\underset{O}{S}}{-}S{-}R}} + \underset{\mathbf{5}}{\mathrm{R_1{-}\overset{O}{\underset{O}{S}}{-}S{-}R_1}} + \underset{\mathbf{6}}{\mathrm{R{-}\overset{O}{\underset{O}{S}}{-}S{-}R_1}} + \underset{\mathbf{7}}{\mathrm{R_1{-}\overset{O}{\underset{O}{S}}{-}S{-}R}} \quad (2)$$

Homolytic scission of the S–S bond in **8** leads to sulfinyl radicals **9** and **10**. A head to tail recombination of radicals **9** and **10** can lead to four different sulfenyl sulfinates (**11**–**14**),[11] which can rearrange to thiosulfonates **1**, **5**, **6**, and **7** respectively, via sulfonyl (**15**, $R\dot{S}O_2$) and thiyl (**16**, $R\dot{S}$) radicals.[12]



$$\underset{\mathbf{4}}{\mathrm{R{-}\overset{O}{S}{-}S{-}R_1}} \xrightarrow{\mathrm{RCO_3H}} \underset{\mathbf{8}}{\mathrm{R{-}\overset{O}{S}{-}\overset{O}{S}{-}R_1}} \xrightarrow[\text{fast}]{} \underset{\mathbf{9}}{\mathrm{R{-}\overset{O}{S}{\bullet}}} + \underset{\mathbf{10}}{\mathrm{R_1{-}\overset{O}{S}{\bullet}}} \quad (3)$$

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(1) Block, S. S.; Weldner, J. P. *Appl. Spectrosc.* **1966**, *20*, 73 and references therein.

(2) Noordik, J. H.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 156.

(3) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1981**, *103*, 6232.

(4) Freeman. F.; Angeletakis, C. N. *J. Am. Chem. Soc.*, in press.

(5) Freeman, F.; Angeletakis, C. N.; Maricich, T. J. *Tetrahedron Lett.* **1981**, *22*, 1867.

(6) Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1981**, *45*, 3991.

(7) Marangeli, V.; Modena, G.; Todesco, P. E. *Gazz. Chim. Ital.* **1960**, *90*, 681; *Chem. Abstr.* **1961**, *55*, 16510.

(8) Chau, M. M.; Kice, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7711.

(9) Oae, S.; Kim, Y. H.; Takata, T.; Fukushima, D. *Tetrahedron Lett.* **1977**, 1195.

(10) Oae, S., personal communication.

(11) Howard, J. A.; Furimsky, E. *Can. J. Chem.* **1974**, *52*, 555.

(12) Gilbert, B. C.; Gill, B.; Ramsden, M. J. *Chem. Ind.* (*London*) **1979**, 283.

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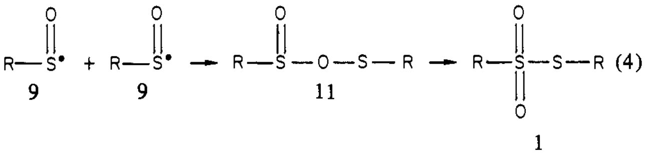
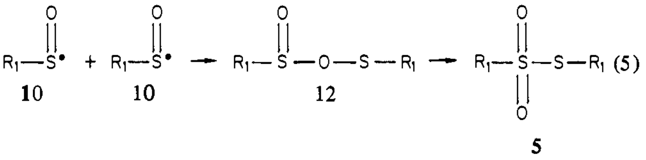
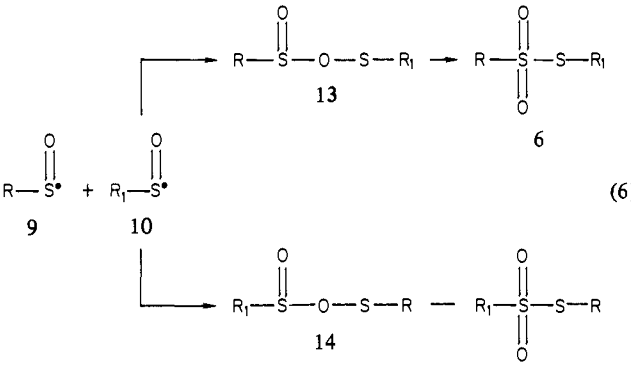


$$\underset{9}{R{-}\overset{O}{\overset{\|}{S}}{\cdot}} + \underset{9}{R{-}\overset{O}{\overset{\|}{S}}{\cdot}} \rightarrow \underset{11}{R{-}\overset{O}{\overset{\|}{S}}{-}O{-}S{-}R} \rightarrow \underset{1}{R{-}\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}{-}S{-}R} \quad (4)$$



$$\underset{10}{R_1{-}\overset{O}{\overset{\|}{S}}{\cdot}} + \underset{10}{R_1{-}\overset{O}{\overset{\|}{S}}{\cdot}} \rightarrow \underset{12}{R_1{-}\overset{O}{\overset{\|}{S}}{-}O{-}S{-}R_1} \rightarrow \underset{5}{R_1{-}\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}{-}S{-}R_1} \quad (5)$$

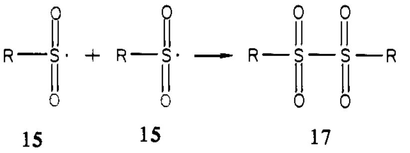


$$\underset{9}{R{-}\overset{O}{\overset{\|}{S}}{\cdot}} + \underset{10}{R_1{-}\overset{O}{\overset{\|}{S}}{\cdot}} \begin{cases} \rightarrow \underset{13}{R{-}\overset{O}{\overset{\|}{S}}{-}O{-}S{-}R_1} \rightarrow \underset{6}{R{-}\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}{-}S{-}R_1} \\ \rightarrow \underset{14}{R_1{-}\overset{O}{\overset{\|}{S}}{-}O{-}S{-}R} - R_1{-}\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}{-}S{-}R \end{cases} \quad (6)$$

α-Disulfoxides (**2**, **8**)[3,4] and sulfenyl sulfinates (**11**–**15**)[3–6] have been neither isolated nor trapped. Although sulfinyl radical intermediates have not been detected by ESR in the peroxy acid oxidation of thiosulfinates, spin-trapping experiments support the hypothesis that sulfonyl and thiyl radicals are actually formed during the peroxydation.[13–15]

Sulfinyl radicals have been characterized as relatively delocalized and unreactive π radicals in comparison to σ-type sulfonyl radicals.[15,16] Kice[13] has ascribed the "bond-weakening effect" of SO on adjacent bonds to the stability of sulfinyl radicals. In contrast, Benson,[17] using thermodynamic arguments, concluded that $\mathrm{Ar\dot{S}O_2}$ possesses greater resonance stabilization than $\mathrm{Ar\dot{S}O}$ and proposed that the "bond-weakening effect" of SO arises from the low $\Delta H_f{}^{\circ}$ of the parent molecule owing to the "principle of alternating polarity". However, the "principle of alternating polarity" does not appear to explain the unusual stability of α-disulfones (**17**).

Considering the stability of α-disulfones (**17**) and disulfides (**18**),

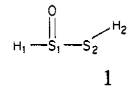
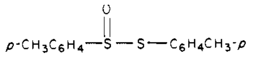


$$\underset{15}{R{-}\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}{\cdot}} + \underset{15}{R{-}\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}{\cdot}} \rightarrow \underset{17}{R{-}\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}{-}\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}{-}R} \quad (7)$$

possible alternative pathways for recombination of sulfonyl (**15**) and thiyl (**16**) radicals are shown in eq 7 and 8. However, **17** and **18** are not generally observed as peroxydation products of thiosulfinates.[3–6,18,19]

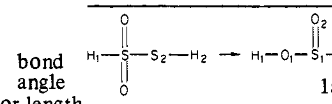
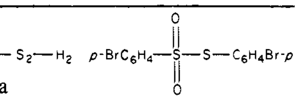
$$\underset{16}{R\dot{S}} + \underset{16}{R\dot{S}} \rightarrow \underset{18}{R{-}S{-}S{-}R} \quad (8)$$

Table I. A Comparison of Observed and Calculated Bond Angles (Deg) and Bond Lengths (Å) in Thiosulfinates 3[a] and 19[25]

bond angle or length	thiosulfinate	
	 1	 19
$\angle S_2S_1H_1$ (C_1)	87.9	93.1
$\angle OS_1H_1$ (C_1)	109.1	108.3
$\angle OS_1S_2$	113.5	111.3
S_2-H_2 (C)	1.326	1.771
S_1-H_1 (C)	1.335	1.782
S_1-O	1.473	1.457
S_1-S_2	2.104	2.108

[a] Calculated values.

Table II. A Comparison of Observed and Calculated Bond Angles (Deg) and Bond Lengths in Thiosulfonates 1[a,b] and 20[2]

bond angle or length	thiosulfonates	
	 1 1a	 20
$\angle S_1S_2H_2$ (C_2)	94.29	99.6 (0.9)[c]
$\angle S_2S_1O_1$	88.38	104.2 (0.7)
$\angle S_1S_1O_2$	110.51	110.9 (0.7)
$\angle C_1S_1O_2$		109.5 (1.2)
$\angle(C_1)H_1S_1O_1$	1.19	107.8 (1.1)
$\angle(C_1)H_1S_1S_2$	111.94	103.6 (0.9)
$\angle O_1S_1O_2$	109.8	119.7 (1.1)
S_1H_1 (C_1)		1.763 (0.015)
S_2H_2 (C_2)	1.328	1.782 (0.015)
S_1O_1	1.624	1.443 (0.011)
S_1O_2	1.447	1.448 (0.011)
S_1S_2	2.084	2.091 (0.006)
H_1O_1	0.971	
H_1O_2	2.86	

[a] Calculated values. [b] 1a is calculated structure. [c] Standard deviation in parentheses.

The purpose of this investigation is to examine the following points by means of a initio molecular orbital calculations: (1) the structures of α-disulfoxides (**2**) and sulfenyl sulfinates (**11**, **12**); (2) the relative energies of α-disulfoxides (**2**), sulfenyl sulfinates (**11**, **12**) and thiosulfonates (**1**); and (3) the relative stabilities of sulfinyl (**9**, **10**), sulfonyl (**15**), and thiyl (**16**) radicals. The simplest homologues, where R = R_1 = H, were chosen for this study for ease of computation and in order to exclude substituent effects.

Theoretical Methods

The equilibrium structures of all molecules and radicals considered in this study were fully optimized at the HF/3-21G* level.[20–23] Single point calculations utilizing the more extensive 6-31G* basis set were performed by using these structures. Both theoretical methods have been shown to be relatively successful in reproducing known geometries and relative stabilities of a variety of normal and hypervalent molecules incorporating second-row elements.[20,21] All calculations were carried out with the Gaussian 77 program system[24] on a Harris Slash 6 computer.

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(13) Kice, J. L., In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 24.

(14) Topping, R. M.; Kharasch, N. *J. Org. Chem.* **1962**, *27*, 4353.

(15) da Silva Correa, C. M. M.; Waters, W. A. *J. Chem. Soc.* C **1968**, 1874.

(16) Chatgiliaboglu, C.; Gilbert, B. C.; Kirk, C. M.; Norman, B. O. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1084.

(17) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(18) Barnard, D.; Percy, E. J. *Chem. Ind.* (*London*) **1960**, 1332.

(19) Disulfide (**18**) was observed during the peroxydation of an aryl thiosulfinate.[18] However, other workers[7,8] have attributed the formation of disulfide (**18**) to the decomposition of the thiosulfinate (**3**).

(20) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.*, submitted for publication. This basis set is used in conjunction with the 3-21G* representation for first-row elements.

(21) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(22) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.

(23) Francl, M. M.; Pietro, W. J.; Hehre, W. J., Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.*, submitted for publication.

(24) DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Blurock. E. S.; Hout R. F., Jr.; Pietro, W. J. Hehre, W. J., to be submitted to Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.

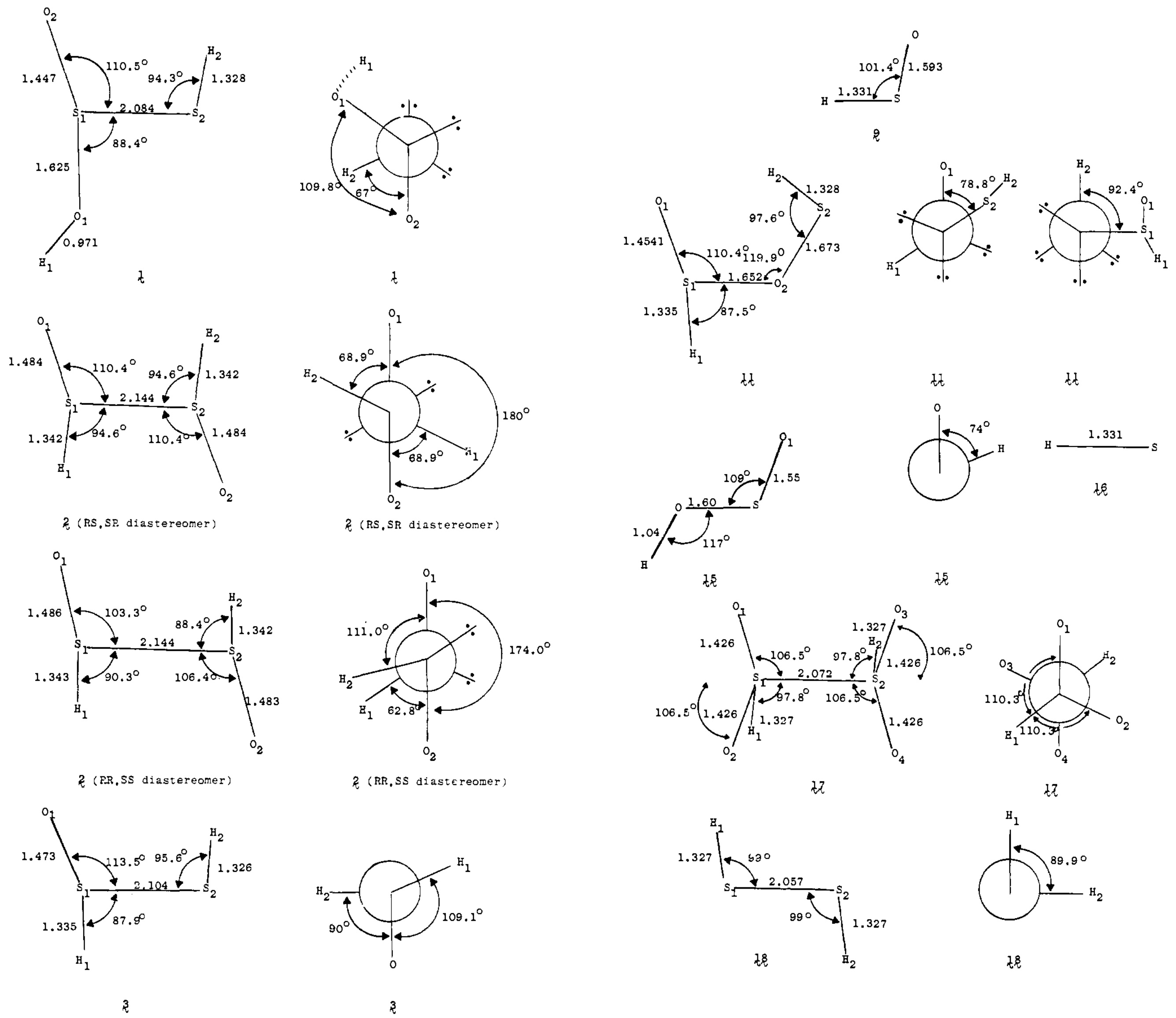


Figure 1. Calculated equilibrium geometries of hydrogen persulfide (18), its oxide derivatives, and related species.

Table III. A Comparison of Observed and Calculated Bond Angles (Deg) and Bond Lengths (Å) in α-Disulfones 17[a] and 21[26]

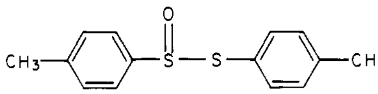
	α-disulfone	
	$H_1{-}S(=O_2)(=O_1){-}S(=O_2)(=O_1){-}H_1$	$C_6H_5{-}S(=O)(=O){-}S(=O)(=O){-}C_6H_5$
bond angle or length	17	21
$S_1S_1O_1$	106.5	105.5 (0.1)[b]
$S_1S_1O_2$	106.5	105.9 (0.1)
$S_1S_1H_1$ (C_1)	97.8	101.5 (0.1)
$O_1S_1O_1$		120.3 (0.1)
$O_1S_1H_1$ (C_1)	110.2	111.5 (0.1)
$O_2S_1H_1$ (C_1)	110.2	118.0 (0.1)
S_1H_1 (C_1)	1.327	1.753 (0.001)
S_1O_1	1.426	1.428 (0.001)
S_1O_2	1.426	1.428 (0.001)
S_1S_2	2.072	2.193 (0.001)

[a] Calculated values. [b] Standard deviations in parentheses.

Results and Discussion

The calculated equilibrium geometries of hydrogen homologues ($R = R_1 = H$) 1–3, 9, 11, and 15–18 are shown in Figure 1. Structures 1–3, 11, and 17 were calculated by using the anti conformation initially. No energy minimum could be found for 1 with the hydrogens anti to each other and for 15 with the hydrogen bonded to sulfonyl sulfur. Indeed, the hydrogen is bonded to oxygen when 1 is optimized in the anti conformation.

Table I shows a comparison of the calculated bond angles and bond lengths of 3 (R = H) with the observed values of *p*-tolyl *p*-toluenesulfinate (19).[25]



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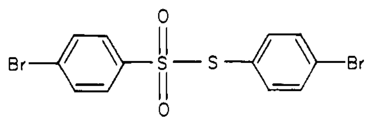

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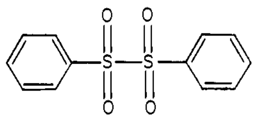
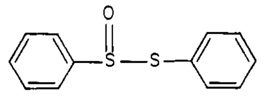


21



22

Table II shows a comparison of the calculated bond angles and bond lengths of 1 (R = H) with the observed values of *p*-

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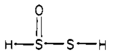
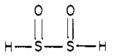
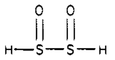
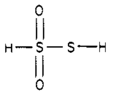
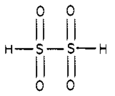
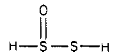
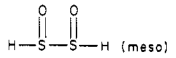
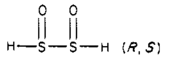
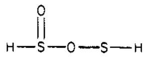
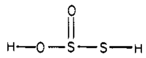
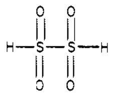
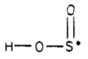
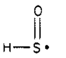
(25) Kiers, C. Th.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 166.

Table IV. A Comparison of Calculated and Observed Bond Angles (Deg) and Bonds Lengths (A) of Hydrogen Persulfide (H-S-S-H, 18) and Its Corresponding Oxide Derivatives[a]

sulfur compd	structure no.	$\angle O_1S_1H_1$ (C_1)	$\angle$OSS	$\angle S_2S_1H_1$ (C_1)	r_{SO}, A	$r_{S_1S_2}$, A
H-S-S-H	18	...	...	99.0 (91.3)[23]	...	2.057 (2.055)
 $\mathrm{H{-}S({=}O){-}S{-}H}$	3	109.1 (108.3)[21]	113.5 (111.3)	87.9 (93.1)	1.473 (1.457)	2.104 (2.108)
 $\mathrm{H{-}S({=}O){-}S({=}O){-}H}$	2 (meso)	110.4	104.8	89.4	1.484	2.144
 $\mathrm{H{-}S({=}O){-}S({=}O){-}H}$	2 (*R,S*)	...	103.3, 106.4	90.3, 88.4	1.486, 1.483	2.144
 $\mathrm{H{-}S({=}O)_2{-}S{-}H}$	1		110.5 (110.9)[2,6]	110.5 (99.6)[b]	1.447 (1.448)[b]	2.084 (2.091)[b]
 $\mathrm{H{-}S({=}O)_2{-}S({=}O)_2{-}H}$	17	110.2 (111.5)[22] (118.0)	106.5 (105.5) (105.9)	97.8 (101.5)	1.426 (1.428)	2.072 (2.193)

[a] Values from this work, literature values in parentheses. [b] The monodentate oxygen atom in 1 used for comparison.

Table V. Total Energies of Some Organosulfur Derivatives

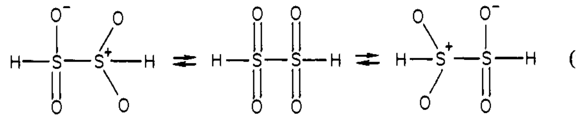
organosulfur compd	structure no.	total energy (au)	
		3-21G*	6-31G*
H-S-S-H	18	−792.4832	
 $\mathrm{H{-}S({=}O){-}S{-}H}$	3	−866.8485	
 $\mathrm{H{-}S({=}O){-}S({=}O){-}H}$ (meso)	2	−941.2084	−945.7345
 $\mathrm{H{-}S({=}O){-}S({=}O){-}H}$ (*R, S*)	2	−941.2084	−945.7344
 $\mathrm{H{-}S({=}O){-}O{-}S{-}H}$	11	−941.2806	−945.7796
 $\mathrm{H{-}O{-}S({=}O){-}S{-}H}$	1a	−941.3111	−945.8189
 $\mathrm{H{-}S({=}O)_2{-}S({=}O)_2{-}H}$	17	−1090.0692	
 $\mathrm{H{-}O{-}S({=}O)\cdot}$	15	−545.0897 −541.43082[15]	
 $\mathrm{H{-}S({=}O)\cdot}$	9	−470.6430	
$\mathrm{H{-}\dot{S}}$	16	−396.2180	

bromophenyl *p*-bromobenzenethiosulfonate (**20**).[2]

Table III shows a comparison of the calculated bond angles and bond lengths of **17** (R = H) with the observed values of phenyl disulfone (**21**).[26]

A comparison of calculated and observed bond angles and bond lengths of hydrogen persulfide (**18**, R = H)[27] and its corresponding oxide derivatives is shown in Table IV. The calculated equilibrium geometries in this study for **1**, **3**, **17**, and **18** agree well with the literature values.[2,21-23] The only exception is the shorter r_{SS} of **17** (2.072 Å) in comparison with **21** (2.193 Å). At least part of the difference (0.121 Å) in the calculated S–S length of **21** can probably be attributed to substituent effects.

The small value for the S–S bond length in **17** does not appear to agree with Benson's "principle of alternating polarity"[17] and suggests appreciable double bond character between the sulfur atoms (eq 9).


(9)

17b 17a 17c

The S–S bond lengths decrease in the series **2** > **3** > **1** > **17** > **18** (Table IV), which correlates quite well with the ease of S–S bond homolysis of the corresponding known aryl analogues.[8,13,28] It is known that aryl thiosulfinates undergo homolysis of the S–S bond several orders of magnitude faster than the corresponding α-disulfones.[28,29] Thus, the S–S bond lengths in **21** and in its corresponding thiosulfinate (**22**) do not parallel this ordering of S–S bond homolysis.

The decrease in $S_2S_1H_1$ bond angles in the series **2** > **3** > **17** > **18** (Table I) also correlates fairly well with the ease of S–S bond homolysis.

The contraction of the S(O)S bond angle relative to tetrahedral has been interpreted in terms of increasing s character of the lone pair of electrons on sulfur and the strong, repulsive character of the partial SO double bond.[25,30]

Although the conformations of α, β, and γ disulfoxides would not necessarily be expected to be closely related, the calculated anti conformation of α-disulfoxide **2** is consistent with the preferred conformations of β and γ disulfoxides.[32-34] α-Disulfoxide **2** has an unusually long S–S bond, an expected characteristic of this unstable structure. However, comparison of the S–S bond length of **2** (2.144 Å) with that of dithionite ion ($^-O_2SSO_2^-$, 2.39 Å)[34] shows that they are quite different and suggests **2** probably does not undergo S–S bond homolysis as readily as dithionite ion.[35]

The decrease in SO bond distance in the series **2** > **3** > **17** also correlates with the ease of S–S bond homolysis. This could also suggest increasing *d* orbital participation by sulfur.

Calculated total energies of **1**, **2**, **3**, **9**, **11**, and **15–18** at the 3-21G* and 6-31G* levels are given in Table V. Equations 10 and 11 summarize the energy differences among **1**, **2**, and **11**.

The alternative reaction pathway (dimerization) for the sulfonyl (**15**) and thiyl (**16**) radicals shown in eq 7 and 8 is not observed experimentally.[6,8,12,13,15,19] These calculations agree, suggesting that disproportionation of **1** to **17** and **18** (i.e., eq 12) is endo-

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$$H-\overset{O}{\overset{\|}{S}}-\overset{O}{\overset{\|}{S}}-H \longrightarrow H-\overset{O}{\overset{\|}{S}}-O-S-H \qquad (10)$$

2 11

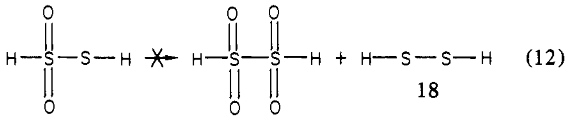
-45 kcal mol^{-1} (3-21G*), -28 kcal mol^{-1} (6-31G*)

$$H-\overset{O}{\overset{\|}{S}}-O-S-H \longrightarrow H-O-\overset{O}{\overset{\|}{S}}-S-H$$

11 10

-19.1 kcal mol^{-1} (3-21G*), -24.6 kcal mol^{-1} (6-31G*)

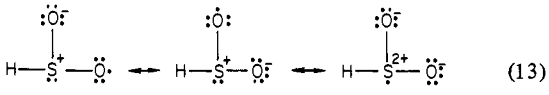
thermic by 43.8 kcal mol^{-1} at the 3-21G* level.



$$H-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-S-H \not\leftarrow H-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-H + H-S-S-H \qquad (12)$$

1 17 18

The sulfonyl radical (**15**), which is generally represented by three principal resonance contributors (eq 13), has been found



$$H-\underset{\cdot\cdot}{\overset{:\ddot{O}:^-}{\overset{|}{S^+}}}-\ddot{O}\cdot \longleftrightarrow H-\underset{\cdot\cdot}{\overset{:\dot{O}:}{\overset{|}{S^+}}}-\ddot{O}:^- \longleftrightarrow H-\underset{\cdot}{\overset{:\ddot{O}:^-}{\overset{|}{S^{2+}}}}-\ddot{O}:^- \qquad (13)$$

15

to have hydrogen bonded to oxygen.[17,36-38] Moreover, although both $HOS\dot{O}$ and $ROS\dot{O}$ are known, alkyl sulfonyl radicals generally possess a carbon-sulfur single-bonded structure RSO_2.[36]

Although sulfinyl radicals (**9**) are considered as stable, relatively

$$\underset{\mathbf{9}}{2HS\dot{O}} \rightarrow \underset{\mathbf{15}}{HS\dot{O}_2} + \underset{\mathbf{16}}{H\dot{S}} \qquad (14)$$

-13.6 kcal mol^{-1} (3-21G*)

delocalized, and unreactive π-type radicals,[13,16] the disproportionation of **9** to **15** and **16** appears to be thermodynamically favorable.

Conclusions

1. Although other reasonable mechanisms are possible, these theoretical calculations support the mechanism proposed for the rearrangement of α-disulfoxides (**2**) via sulfinyl radicals to thiosulfinates (eq 3-6). These calculations also suggest that α-disulfoxides (**2**) are sufficiently stable to be observed and/or isolated at low temperatures.[3,4]

2. The variation of the S-S bond lengths in **1-3**, **15**, and **16** agrees with the observed order of S-S bond homolysis for **1-3**, **15**, and **16**.

Recent low-temperature ^1H NMR and ^{13}C NMR studies show that the *m*-chloroperoxybenzoic acid oxidation of 2-methyl-2-propyl 2-methyl-2-propanethiosulfinate (**23**)[3] and 2,2-dimethylpropyl 2,2-dimethylpropanethiosulfinate (**24**)[4] involves the corresponding α-disulfoxides (**25** and **26**) as intermediates. These resports represent the first direct observation of α-disulfoxide (**2**) intermediates.

$$R-\overset{O}{\overset{\|}{S}}-S-R \qquad R-\overset{O}{\overset{\|}{S}}-\overset{O}{\overset{\|}{S}}-R$$

23, R = *t*-Bu 25, R = *t*-Bu

24, R = *neo*-C_5H_{11} 26, R = *neo*-C_5H_{11}

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Registry No. 1, 80375-33-3; 1a, 15060-43-2; 2, 80375-34-4; 3, 80375-36-6; 9, 62470-71-7; 11, 80375-38-8; 15, 64255-60-3; 16, 13940-21-1; 17, 80375-39-9; 18, 13465-07-1; 19, 6481-73-8; 20, 3347-03-3; 21, 10409-06-0.

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Al Atom-Ethylene and Al Atom-Acetylene Complexes: Matrix Isolation Electron Spin Resonance Study

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Abstract: Al atom-ethylene and Al atom-acetylene complexes generated and/or trapped in rare-gas matrices at ~4 K were examined by ESR spectroscopy. The Al-monoethylene complex has a π-coordinated structure with a dative bond of donation from a semifilled p orbital of Al into the antibonding π orbital of ethylene. The Al atom and acetylene, in contrast, interact to form a σ-bonded adduct of vinyl structure. Photoirradiation of matrices containing Al-monoethylene complexes causes spectral changes suggesting the formation of Al-bis(ethylene) complexes. Photoirradiation of matrices containing the Al-acetylene adduct causes the cis-trans isomerization of the vinyl form.

Reactions between vaporized metal atoms and organic or inorganic molecules co-condensed at cryogenic temperature have been the subject of many recent investigations.[1] Skells and Wolf[2] demonstrated the formation of organoaluminum compounds when the aluminum atoms were co-condensed with excess propene or propyne at liquid-nitrogen temperature. Based upon the product analysis of the hydrolysis (by deuterium oxide) of the resultant organoaluminum compounds they concluded that the primary reaction between free aluminum atoms and alkene or alkyne molecules is an addition of one aluminum atom to the unsaturated bond. The structural feature of the primary product was not elaborated.

Recently we communicated to this journal the generation and detection by electron spin resonance (ESR) spectroscopy of Al atom-ethylene and Al atom-acetylene complexes in rare gas matrices.[3,4] The spectral analyses revealed that the Al atom-

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