

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244436668>

Ab initio study of hypervalent sulfur hydrides as model intermediates in the interconversion reactions of compounds containing sulfur-sulfur bonds

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · FEBRUARY 1987

Impact Factor: 12.11 · DOI: 10.1021/ja00237a012

CITATIONS

32

READS

13

3 AUTHORS, INCLUDING:



Risto S. Laitinen

University of Oulu

258 PUBLICATIONS 1,968 CITATIONS

SEE PROFILE



Ralf Steudel

Technische Universität Berlin

357 PUBLICATIONS 4,465 CITATIONS

SEE PROFILE

Table V. Promotion Energies of WL_5 Fragments from Hartree-Fock Calculations

electronic configuration	rel energy (kcal/mol)	
	$W(CO)_3(PH_3)_2$	$W(PH_3)_5$
singlet— $d_{xy}^2 d_{yz}^2 d_{xz}^2$	0 ^a	0 ^b
triplet— $d_{xy}^2 d_{yz}^2 d_{xz}^1 d\sigma^1$	+1	-8
triplet— $d_{xy}^2 d_{yz}^1 d_{xz}^2 d\sigma^1$	+12	-8

^a Total energy = -357.315 16 au. ^b Total energy = -47.851 59 au.

terms of exciting to a d^9s^1 configuration which favors cis-dihydride formation.

Promotion Energies. As discussed in the preceding sections, the stability of the $d\pi$ orbital will reduce its propensity to form the dihydride. Examining the $d\pi \rightarrow d\sigma$ promotion energy in the WL_5 fragment can provide an indication of this propensity. In Table V we show the results of SCF calculations on the low-spin d^6 singlet state of the two WL_5 fragments— $W(CO)_3(PH_3)_2$ and $W(PH_3)_5$ —and the high-spin d^6 triplet state where the $d\pi$ orbital has been promoted to the $d\sigma$ orbital (Figure 1). The promotion energies are 9–12 kcal/mol larger in the $W(CO)_3(PH_3)_2$ fragment compared to the $W(PH_3)_5$ fragments, which is consistent with the lower stability of the dihydrides in the former case relative to the η^2 -dihydrogen species. In the SCF calculations the triplet is actually predicted to lie below the singlet for the $W(PH_3)_5$ fragment, but electron correlation effects not included at the SCF level would stabilize the singlet relative to the triplet. These effects have been discussed for the electronic states of $Cr(CO)_5$, for example.¹⁶ It is interesting that the promotion energy from the d_{xz} orbital, which lies in the plane containing the phosphines, is lower than that for the d_{yz} orbital, which lies in the plane of the CO ligands. This is consistent with the fact that formation of the cis dihydride by bonding back the phosphines (which will involve the d_{xz} orbital in W–H bonding) is favored over the dihydride formed by bonding back the CO ligands (involving the d_{yz} orbital).

IV. Summary

The η^2 -dihydrogen and dihydride forms of $d^6 ML_5-H_2$ complexes have been investigated for the specific cases of H_2 bound

to $W(CO)_3(PR_3)_2$ and $W(PR_3)_5$ fragments. Using optimized geometries from ab initio calculations, the six-coordinate η^2 -dihydrogen form is found to be the most stable species for the case of $W(CO)_3(PR_3)_2(H_2)$ while the seven-coordinate dihydrides $W(PR_3)_5(H)_2$ are found to be most stable. The stability of η^2 -dihydrogen complexes can be traced to the stabilization of the d orbitals by the π -acceptor CO ligands which prevents the oxidative addition from continuing on to the dihydride complex.

V. Details of the Calculations

The calculations employed ab initio effective core potentials (ECP) on the P atoms⁵ and relativistic ECP's (RECP) on the W atom¹⁷ to replace the effect of the core electrons and, in the case of W, to incorporate the effects of the relativistic mass-velocity and Darwin terms on the valence electrons. A flexible primitive (3s 4p) and (3s 3p 3d) Gaussian basis set contracted to [2s 2p] and [2s 2p 2d] was used to represent the valence orbitals of P and W, respectively.⁵ (4s) and (5s 1p) primitive bases contracted to [2s] and [3s 1p] were used for the hydrogens in PH_3 and H_2 , respectively. The latter basis set provides a balanced description of the H_2 molecule and H atom. STO-3G minimal basis sets were used for C and O.

The bond lengths (Å) of the WL_5 fragment were fixed using the experimental values from the X-ray structure¹ of $W(CO)_3(PR_3)_2(H_2)$ as follows (in Å): W–P (2.492), W–C_{ax} (1.969), C_{ax}–O_{ax} (1.119), W–C_{eq} (1.989), and C_{eq}–O_{eq} (1.148). The P–H distance of 1.421 Å in PH_3 was adopted with tetrahedral bond angles. For the $W(PH_3)_5(H)_2$ complex with the hydrogens staggered relative to each other in the equatorial plane, the following bond angles (in degrees) were taken from the $Mo(PMe_3)_5(H)_2$ structure of Lyons et al.¹⁰: P_a–M–H (68), H–M–P_b (63), and P_b–M–P_b (99).

Calculations were carried out using (1) the BIGGMOLI-GVBTO programs of R. C. Raffanetti and F. W. Bobrowicz, respectively, and (2) the CRAY version of GAUSSIAN 82 by S. Binkley and R. L. Martin. Gradient optimization of the geometrical parameters not fixed in the ML_5 fragment was performed using the GAUSSIAN 82 program.

Acknowledgment. I thank G. J. Kubas, H. J. Wasserman, and R. R. Ryan for helpful discussions over the course of this work and for sharing experimental results prior to publication.

Registry No. 1, 106017-60-1; 5, 106017-61-2; 8, 89230-44-4; 11, 106017-62-3; H_2 , 1333-74-0.

(16) Hay, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 2411.

(17) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 220.

Ab Initio Study of Hypervalent Sulfur Hydrides as Model Intermediates in the Interconversion Reactions of Compounds Containing Sulfur–Sulfur Bonds

Risto S. Laitinen,^{*1a} Tapani A. Pakkanen,^{1b} and Ralf Steudel^{1c}

Contribution from the Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo, Finland, Department of Chemistry, University of Joensuu, SF-80100 Joensuu, Finland, and Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-1000 Berlin 12, Federal Republic of Germany. Received June 12, 1986

Abstract: Ab initio MO calculations involving the 4-31G* basis set have been used to predict the equilibrium geometries of the hypervalent sulfur hydrides H_2SS , $(HS)_2SS$, $H_2S(SH)_2$, $H_2S(SSH)_2$, and the cyclic H_4S_4 . The energy changes in their formation from appropriate sulfanes H_2S_n ($n = 1-4$) have been studied with the 6-31G* basis set including the correction for the electron correlation by the second- and third-order Møller-Plesset perturbation theory. The results are used to discuss the possible pathways in the interconversion reactions between various sulfur compounds containing cumulated SS bonds, for example, the formation of S_7 from S_8 for which hypervalent intermediates have been proposed recently. Comparison with experimental evidence is made whenever possible.

The structural features of the SS bonds in various environments are well-established.² It has also been observed that many

compounds containing cumulated SS bonds easily undergo interconversion reactions. Some of the more common examples are

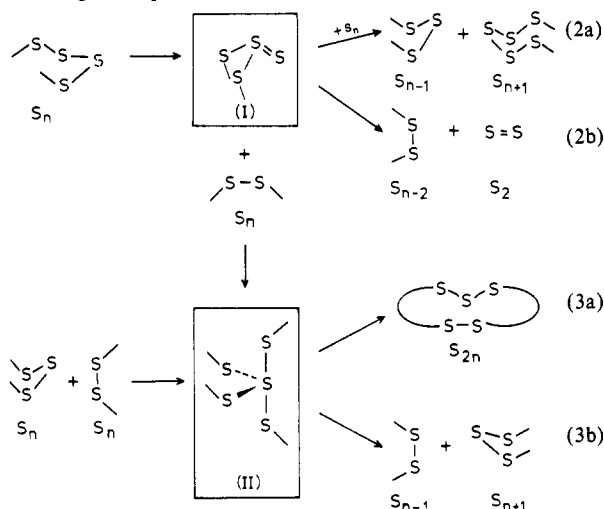
listed below: (1) decomposition of unstable sulfur allotropes in the solid state with the formation of stable S_8 ; ^{3a} (2) decomposition of S_8 in the sulfur melt or in organic solvents with the formation of S_6 , S_7 , and other homocyclic sulfur molecules; ^{3b,c} (3) polymerization and depolymerization of liquid sulfur; ^{3a} and (4) decomposition of organic polysulfanes R_2S_n on heating, resulting in the formation of homologous molecules with larger and smaller values of n . ⁴

Though extensive investigations have been carried out to elucidate the mechanism of such reactions and several models have been suggested, ^{2a,5} lack of rigorous experimental evidence renders all of them speculative. It also seems probable that there are several competing mechanisms depending on the reaction conditions. ^{2c}

The early workers favored the formation of free radicals as primary intermediates: ⁴



Steudel, ^{2a} however, has recently suggested that the hypervalent species I and II could be involved as intermediates in the interconversion reactions as shown in the reaction schemes eq 2 and 3. Although compounds containing the structural units I or II



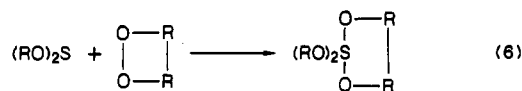
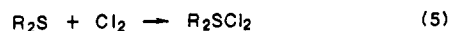
are unknown, a number of related species have been prepared or identified spectroscopically. For instance, F_2SS , ⁶ Cl_2SS , ⁷ Br_2SS , ^{7a} and $(RO)_2SS$ ⁸ are all related to structure I, and the sulfuranes R_2SCl_2 , ⁹ $FSSF_3$, ^{10a} $FSSF_3$, ^{10b} and many others ¹¹ are clearly related to structure II as they all contain a central sulfur atom

with a trigonal-bipyramidal coordination.

Species of type I can be obtained by photochemical isomerization from the unbranched molecules, e.g., ⁷



Compounds with type II structure have been synthesized by the insertion of a monosulfane R_2S into covalent single bonds as shown by the following examples: ^{9,11}



Reactions of this type are allowed by the orbital symmetry considerations and are in principle reversible. The insertion of $(RO)_2S$ into the O-O bond as shown in eq 6 proceeds easily at $-78^\circ C$, and it could be expected that a reaction between two molecules of elemental sulfur proceeds in an analogous manner as shown in eq 3. The unstable intermediate II can undergo pseudorotation at the central sulfur atom and dissociate in the two different fashions. Reaction 3b is in effect a "sulfur atom transfer" from one molecule to another and could therefore explain the formation of S_7 from S_8 and vice versa.

To investigate the plausibility of the hypervalent structures I and II as compared to other possible intermediates which have been reviewed by Steudel, ^{2a} we have performed ab initio MO calculations with the goal of estimating the energies of formation of the intermediates from the unbranched sulfur species. As the calculations with the existing homocyclic sulfur molecules or organic chain-like polysulfanes would be prohibitively time consuming, the model reactions between the sulfane molecules H_2S_n ($n = 1-4$) have been studied. Ionic intermediates are not considered in this work as the discussion is restricted to the reactions in nonpolar environments.

Calculations

All calculations were carried out with the GAUSSIAN 82 series of programs ¹² using a CRAY-1M computer. The gradient techniques were employed in the geometry optimization. As it is well-established that the correct geometry prediction of the molecules containing SS bonds requires the addition of the 3d-polarization functions to the basis set of sulfur, ¹³ we utilized the polarized 4-31G* basis set (the 4-31G basis ¹⁴ augmented with the 3d-functions for sulfur) in the geometry optimization of all molecules included in this study. Single-point calculations using the 6-31G* basis set ¹⁵ and including the second- and third-order Møller-Plesset correction for the electron correlation ¹⁶ were performed using the optimized geometries. ¹⁷

The hypervalent species which serve as model intermediates are shown in Figure 1. The symmetry and the conformation restrictions of the species are based on the following considerations.

- (1) (a) Helsinki University of Technology. (b) University of Joensuu. (c) Technische Universität Berlin.
 (2) (a) Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 149. (b) Steudel, R. *Angew. Chem.* **1975**, *87*, 683; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655. (c) Steudel, R. In *Sulfur—Its Significance for Chemistry, for the Geo-, Bio- and Cosmospere and Technology*; Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, 1984; p 3.
 (3) (a) Steudel, R.; Passlack-Stephan, S.; Holdt, G. *Z. Anorg. Allg. Chem.* **1984**, *517*, 7. (b) Steudel, R.; Strauss, R.; Koch, L. *Angew. Chem.* **1985**, *97*, 58; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 59. (c) Steudel, R.; Strauss, R. *Z. Naturforsch., Teil B* **1982**, *37*, 1219.
 (4) (a) Kende, I.; Pickering, T. L.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1965**, *87*, 5582. (b) Pickering, T. L.; Saunders, K. J.; Tobolsky, A. V. *Ibid.* **1967**, *89*, 2364.
 (5) Pryor, W. A. *Mechanisms of Sulfur Reactions*; McGraw-Hill: New York, 1963.
 (6) Kuczkowski, R. L.; Wilson, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 2028.
 (7) (a) Feuerhahn, M.; Vahl, G. *Chem. Phys. Lett.* **1979**, *65*, 322. (b) Chadwick, B. M.; Grzybowski, J. M.; Long, D. A. *J. Mol. Struct.* **1978**, *48*, 139.
 (8) (a) Harpp, D. N.; Steliou, K.; Cheer, C. J. *J. Chem. Soc., Chem. Commun.* **1980**, 825. (b) Harpp, D. N., personal communication to R. S.
 (9) (a) Baenzinger, N. C.; Buckles, R. E.; Maner, R. J.; Simpson, T. D. *J. Am. Chem. Soc.* **1969**, *91*, 5749. (b) Wilson, G. E.; Chang, M. M. Y. *Tetrahedron Lett.* **1971**, 875.
 (10) (a) Haas, A.; Willner, H. *Z. Anorg. Allg. Chem.* **1980**, *462*, 57. (b) Willner, H. *Ibid.* **1984**, *514*, 171.
 (11) Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemistry: Theoretical and Experimental Advances*; Csizmadia, I. G., Mangini, A., Bernardi, F., Eds.; Elsevier: Amsterdam, 1985; p 1.

- (12) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University.

- (13) (a) Hinchliffe, A. *J. Mol. Struct.* **1979**, *55*, 127. (b) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. (c) Marsden, C. J.; Smith, B. J. *J. Mol. Struct. (THEOCHEM)* **1983**, *105*, 385.

- (14) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

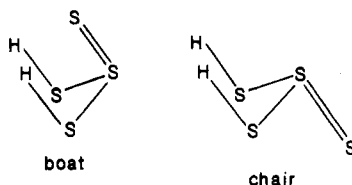
- (15) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

- (16) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229. (c) Pople, J. A.; Binkley, J. S.; Seeger, R. *Ibid.* **1976**, *10*, 1.

- (17) The notation used in this work follows the recommendations of Binkley et al.: ¹² HF, the Hartree-Fock calculations; MP2 and MP3, the second- and third-order Møller-Plesset Perturbation evaluation ¹⁶ of electron correlation effects, respectively. The single point calculations are denoted by HF/6-31G*//4-31G*, MP2/6-31G*//4-31G*, and MP3/6-31G*//4-31G*. The symbol /6-31G* indicates the basis set used in the calculations and the symbol //4-31G*, the basis set yielding the optimum geometry.

H₂SS (1). The molecule was expected to assume a pyramidal conformation with both HS bond lengths equivalent and with the SS bond bisecting the HSH angle. Thus the molecule was assigned to the point group C_s.

(HS)₂SS (2). There are several alternative isomers even when the geometry around the three-coordinated sulfur atom is assumed to be similar to that in 1. The two main alternatives are the following:

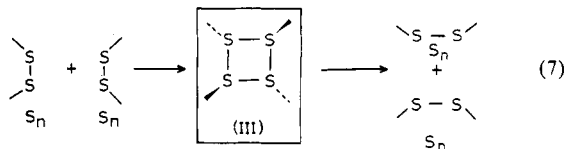


The hydrogen atom positions were chosen to simulate the conformation in homocyclic sulfur molecules, thus restricting the molecular symmetry to C_s in both cases. The geometry optimization was carried out for both the boat and the chair forms. The optimizations yielded practically identical bond parameters and total energies for both forms (see Table II). The boat form was chosen to exemplify this type of intermediate because of the anomeric effect observed in cyclic sulfur oxides S_nO and in organic sulfoxides.¹⁸ Therefore, the single-point energy calculations at HF/6-31G*//4-31G*, MP2/6-31G*//4-31G* and MP3/6-31G*//4-31G* levels were performed only with the boat form of 2.

H₂S(SH)₂ (3). The species involving a four-coordinated sulfur atom are expected to show structural characteristics similar to those of SF₄¹⁹ and other well-known σ-sulfuranes.¹¹ The coordination polyhedron around the central sulfur atom in 3 is a trigonal bipyramid with the axial positions occupied by sulfur atoms and the two equatorial positions by hydrogen atoms. The third equatorial position is occupied by a lone pair of the central sulfur atom. To minimize the repulsion between this lone pair and the p lone pairs of the axial sulfur atoms, the central sulfur atom and all axial atoms in 3 are expected to lie in the same plane.²⁰ The crystal structures of some organic sulfuranes are in agreement with this model.²¹ These structures also show that it is reasonable to set the equatorial plane perpendicular to the axial plane. Therefore, the geometry optimization of 3 was carried out by constraining the molecule to a point group C_{2v}.

H₂S(SSH)₂ (4). Following analogous considerations as in the case of 3, the geometry optimization of 4 was performed by constraining the molecule to a point group C₂. The symmetry of the H₂S(SS)₂-fragment of 4 is identical with that of 3. The axial hydrogen atoms in 4, however, will not lie in the plane of other axial atoms since the SS bond which is not directly originating from the central sulfur atom can be expected to exhibit normal torsional angles of ca. 90° as a consequence of minimized lone-pair repulsion (see Figure 1).

H₄S₄ (5). The square-planar arrangement of sulfur atoms (structure type III) is a reasonable midpoint in the reaction coordinate where two SS bonds belonging to different molecules approach each other and then break up at right angles forming two new molecules (eq 7). H₄S₄ (5) serves as a model for this



(18) Steudel, R. *Phosphorus Sulfur* **1985**, 23, 33.

(19) (a) Tolles, W. M.; Gwinn, W. D. *J. Chem. Phys.* **1962**, 36, 1119. (b) Kimura, K.; Bauer, S. H. *Ibid.* **1963**, 39, 3172.

(20) This implies that the torsional angle connected with the axial SS bonds has the value of 180°. To test the hypothesis this torsional angle was allowed to vary in connection with the geometry optimization. It was found that 3 had a true energy minimum with the axial torsional angles at 180°.

(21) (a) Paul, I. C.; Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1972**, 94, 5010. (b) Perozzi, E. F.; Martin, J. C. *Ibid.* **1979**, 101, 1155. (c) Schomburg, D.; Mir, Q.-C.; Shreeve, J. M. *Ibid.* **1981**, 103, 406.

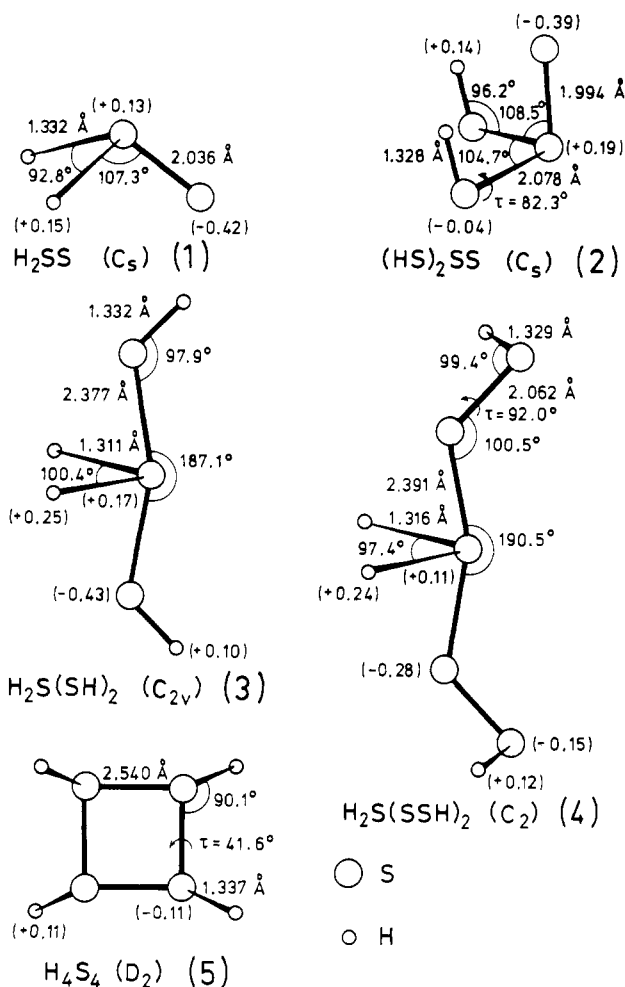


Figure 1. The optimum geometries of the selected hypervalent sulfur hydrides have been calculated using the 4-31G* basis set. The net atomic charges from the single-point calculations with the 6-31G* basis set are indicated in parentheses.

type of intermediate. Initially the optimization was carried out without any symmetry constraints except that all SS bonds were kept of equal length. However, it was observed that the optimum geometry of the intermediate had nearly the molecular symmetry D₂, and therefore final optimization was carried out with the appropriate symmetry constraints.

It can also be thought that the two SS bonds approach each other perpendicular to each other. The resulting intermediate would therefore have a tetrahedral arrangement of the four sulfur atoms in question. However, as neither the square-planar nor the tetrahedral intermediate can be expected to be energetically plausible,^{2a,22} the latter was not included in this study and the square-planar arrangement of the sulfur atoms exemplifies this type of intermediate.

Results and Discussion

The optimized geometries of the first four members of the sulfane series H₂S_n which have been used as starting materials in our reactions are shown in Table I. It can be seen that the bond parameters agree closely with the experimental information

(22) The model calculations on (HSSH)₂²⁺^{23a} indicate that in the neutral square-planar arrangement the two highest occupied molecular orbitals are antibonding.^{23b}

(23) (a) Gleiter, R. *Angew. Chem.* **1981**, 93, 442; *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 444. (b) Laitinen, R.; Pakkanen, T. *J. Mol. Struct.(THEOCHEM)* **1983**, 91, 337.

(24) Cook, R. L.; De Lucia, F. C.; Helminger, P. *J. Mol. Struct.* **1975**, 28, 237.

(25) Winnewisser, G.; Winnewisser, M.; Gordy, W. *J. Chem. Phys.* **1968**, 49, 3465.

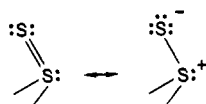
Table I. 4-31G* Optimized Geometries of HS_nH ($n = 1-4$), HS^* , and HSS^*

molecule	parameter	value	exptl
HSH	r_{HS} (Å)	1.326	1.3356 ^a
	α_{HSH} (deg)	93.8	92.11
HSSH	r_{SS} (Å)	2.066	2.055 ^b
	r_{HS} (Å)	1.327	1.327
	α_{HSS} (deg)	98.6	91.3
	τ_{HSSH} (deg)	89.9	90.6
HSSSH	r_{SS} (Å)	2.063	
	r_{HS} (Å)	1.327	
	α_{SSS} (deg)	106.3	
	α_{HSS} (deg)	98.5	
	τ_{HSSS} (deg)	84.3	
	r_{SS1} (Å)	2.061	
	r_{SS2} (Å)	2.064	
HSSSSH ^c	r_{HS} (Å)	1.327	
	α_{SSS} (deg)	106.2	
	α_{HSS} (deg)	98.3	
	τ_{SSSS} (deg)	84.1	
	τ_{HSSS} (deg)	79.5	
	r_{HS} (Å)	1.330	1.345 ^d
	r_{SS} (Å)	1.996	
	r_{HS} (Å)	1.329	
HS^* HSS^*	α_{HSS} (deg)	100.5	

^a From ref 24. ^b From ref 25. ^c The bonds in HSSSSH are denoted as follows: SS1, the central bond; SS2, the adjacent bond (the symmetry of the molecule is C_2). ^d From ref 27.

where available and are well in accord with the values expected for the unstrained SS single bonds ($r = 2.066$ Å, $\alpha = 106^\circ$, and $\tau = 85^\circ$).^{2b,26} Also the radicals HS^* and HSS^* which are included in Table I show reasonable structures which agree with the experimental structure of HS^* ²⁷ and with the results of an earlier SCF-MO study of HSS^* .²⁸

The optimized geometries of the five hypervalent species studied in this work are shown in Figure 1. The SS bond in H_2SS (1) and the corresponding bond in $(\text{HS})_2\text{SS}$ (2) show some double-bond character similar to the SS bonds in the two structurally characterized thiosulfoxides F_2SS ($r_{\text{SS}} = 1.86$ Å)⁶ and $(\text{RO})_2\text{SS}$ ($r_{\text{SS}} = 1.901$ Å),⁸ and the bonding situation can therefore be represented by the two canonical structures:



The conformation at the three-coordinated sulfur atom is similar in all four compounds X_2SS (local symmetry C_3).²⁹

The axial SS bonds in $\text{H}_2\text{S}(\text{SH})_2$ (3) and $\text{H}_2\text{S}(\text{SSH})_2$ (4) originating from the central sulfur atoms are significantly longer than the normal single bond length of 2.05 Å.^{2b} All other internuclear distances in both molecules correspond to the single bond values. The bond angles around the four-coordinated sulfur atoms deviate from the idealized values of 180° for the axial bonds and of 120° for the equatorial bonds in a manner expected from the simple VSEPR model and agree with those in SF_4 ($F_{\text{ax}}\text{-S-F}_{\text{ax}} = 183.2^\circ$, $F_{\text{eq}}\text{-S-F}_{\text{ax}} = 89^\circ$, and $F_{\text{eq}}\text{-S-F}_{\text{eq}} = 103.8^\circ$)¹⁹ and in R_2SCl_2 .^{9a}

The SS bond in the intermediate 5 having the square-planar arrangement of sulfur atoms is expectedly very long. The formation of this molecule forces the hydrogen atoms of the original HSSH molecules nearer to the plane of the sulfur atoms, and therefore the torsional angles τ_{HSSH} are smaller than in the original HSSH molecules (see Table I and Figure 1).

The total energies obtained from the singlet point calculations using the 6-31G* basis set have been summarized in Table II. These energies have been used to estimate the energy changes in the selected processes which simulate the interconversion reactions shown in eq 1-3 and 7. Though all hypervalent species are stable with respect to the atoms they are composed of, energy must be spent in order to form them from the appropriate sulfanes as has been shown in Table III. It is seen that the calculated value of the energy required for the homolytic cleavage of the SS bond changes considerably when the electron correlation is taken into account. This is due to the fact that restricted Hartree-Fock theory is used for the reactant molecules, while unrestricted Hartree-Fock theory is applied to the products. A reasonable agreement with the experimental data is reached when the total energies are corrected for the electron correlation effects. In the case of hypervalent species 1-5 the electron correlation yields smaller, but still significant effects in the energetics of the formation reactions (see Table III). Thus, the discussion of the formation of the hypervalent species is done at the MP2 or MP3 levels of theory.

The calculated homolytic cleavage of HSSH provides an estimate on the dissociation energy of the SS bonds, the experimental value of which is 66 kcal mol⁻¹ (see Table III).³⁰ However, with longer sulfur chains the energy needed to form a pair of free radicals is lowered to ca. 35 kcal mol⁻¹ as indicated by the ESR and magnetic susceptibility measurements.³¹ The cleavage of the SS bond of HSSH and of the central SS bond in HSSSSH, which have been used as models in this work, show that the experimental trend is reproduced by the calculated energy values (see Table III). A very recent ab initio study of Baird³² is in agreement with these findings. It is reasonable to conclude that the MP2 and MP3 calculations can be used to study the energetics of the interconversion reactions in a semiquantitative way.

From the calculated formation energies of Table III the interconversion reactions could be expected to involve homolytic SS cleavage (reaction 1). However, no free radicals have been detected in organic solutions of sulfur or in liquid sulfur below 170 °C.³³ It has therefore been suggested^{2a} that the interconversion at moderate temperatures proceeds via hypervalent intermediates which do not require radical formation.

The energy required for the isomerization of the sulfanes to produce thiosulfoxides of structure type I amounts to ca. 32 kcal mol⁻¹ regardless of the level of sophistication in the calculations. It also seems that this energy is independent on the length of the sulfur chain in the original sulfane. The values obtained are somewhat higher than those indicated by the earlier ab initio and CNDO calculations on H_2SS ^{13a,34} (these treatments also included the polarization functions for sulfur). However, it is obvious that structure I is energetically the most favorable intermediate of the hypervalent species 1-5 considered in this work (see Figure 1). Such compounds have very often been discussed as possible intermediates in the reactions of compounds containing SS bonds.³⁵ Our results provide support for these arguments.

Experimental evidence for the structural unit I at low temperatures comes from the vibrational spectroscopic investigations of sulfur deposits obtained by the condensation of S_2 vapor at 77 K or below.³⁶ An infrared absorption near 680 cm⁻¹ has been interpreted as the stretching vibration of the SS double bond of structure I. This wavenumber is in agreement with the SS stretching vibrations of Cl_2SS (698 cm⁻¹)⁷ and of Br_2SS ^{7a} when the dependence of the wavenumbers on the electronegativity is allowed for. Above the temperature of 170 K the thiosulfoxides

(26) Meyer, B. *Chem. Rev.* **1976**, *76*, 367.

(27) Rosen, B. *International Tables of Selected Constants; Data Relative to Diatomic Molecules*; Pergamon Press: London, 1970.

(28) (a) Sannigrahi, A. B. *J. Mol. Struct.* **1978**, *44*, 223. (b) Luke, B. T.; McLean, A. D. *J. Phys. Chem.* **1985**, *89*, 4592.

(29) F_2SS : $\alpha_{\text{FSS}} = 107.5^\circ$, $\alpha_{\text{FSF}} = 92.5^\circ$.⁶ $(\text{RO})_2\text{SS}$: $\alpha_{\text{OSS}} = 106.4$, 110.6° , $\alpha_{\text{OSO}} = 94.3^\circ$.⁸ For the corresponding values in H_2SS and $(\text{HS})_2\text{SS}$, see Figure 1.

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

(31) Steudel, R. *Phosphorus Sulfur* **1983**, *16*, 251 and references therein.

(32) Baird, N. C. *J. Mol. Struct. (THEOCHEM)* **1986**, *137*, 1.

(33) (a) Koningsberger, D. C.; Neef, T. *Chem. Phys. Lett.* **1970**, *4*, 615.

(b) Koningsberger, D. C.; Neef, T. *Ibid.* **1972**, *14*, 453. (c) Gardner, D. M.; Fraenkel, G. F. *J. Am. Chem. Soc.* **1956**, *78*, 3279.

(34) Solouki, B.; Bock, H. *Inorg. Chem.* **1977**, *16*, 665.

(35) Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 333.

(36) (a) Steudel, R. *Z. Naturforsch., Teil B* **1972**, *27*, 469. (b) Steudel, R. *Z. Anorg. Allg. Chem.* **1968**, *361*, 180.

Table II. Total Energies of the Molecules (in au)

molecule	4-31G*	6-31G**/4-31G*		
	HF	HF	MP2	MP3
HSH	-398.257 69	-398.667 31	-398.788 23	-398.806 54
HSSH	-795.359 95	-796.174 37	-796.411 04	-796.440 69
HSSSH	-1192.465 77	-1193.684 60	-1194.042 17	-1194.081 44
HSSSSH	-1589.571 36	-1591.194 92	-1591.674 05	-1591.722 48
HS*	-397.654 86	-398.064 40	-398.161 83	-398.178 68
HSS*	-794.773 32	-795.587 09	-795.807 86	-795.834 80
H ₂ SS	-795.302 00	-796.122 02	-796.358 80	-796.386 97
(HS) ₂ SS	-1589.515 33 ^a	-1591.141 45	-1591.627 05	-1591.672 07
H ₂ S(SH) ₂	-1193.516 02	-1194.737 91	-1195.119 41	-1195.162 10
H ₂ S(SSH) ₂	-1987.737 27	-1989.767 45	-1990.390 12	-1990.450 71
H ₄ S ₄	-1590.559 87	-1592.177 72	-1592.689 70	-1592.748 49

^a The optimized geometry of the chair form of (HS)₂SS has the total energy of -1589.509 53 with the 4-31G* basis sets. The optimization yielded practically identical bond parameters for both the boat and the chair forms.

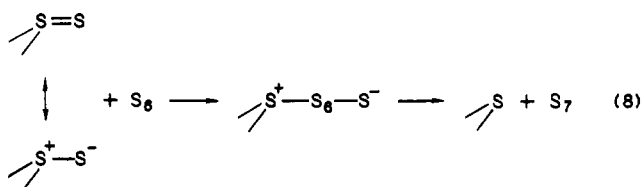
Table III. Energy Change (kcal mol⁻¹) during the Formation of the Selected Hypervalent Sulfur Species^a

reaction	HF	MP2	MP3	exptl
HSSH → 2HS*	28.6	54.8	52.3	66.0 ^b
HSSSH → HS* + HSS*	20.8	45.5	42.6	
HSSSSH → 2HSS*	13.0	36.6	33.2	35.4 ^c
HSSH → H ₂ SS	32.8	32.8	33.7	
HSSSSH → (HS) ₂ SS	33.6	29.5	31.6	
HSH + H ₂ SS → H ₂ S(SH) ₂	32.3	17.3	19.7	
HSH + (HS) ₂ SS → H ₂ S(SSH) ₂	25.9	15.8	17.5	
HSH + HSSH → H ₂ S(SH) ₂	65.1	50.1	53.4	
HSH + HSSSSH → H ₂ S(SSH) ₂	59.5	45.3	49.1	
2HSSH → H ₄ S ₄	107.3	83.1	83.4	

^a The values are based on the single-point energy calculations using the 6-31G* basis set and 4-31G* optimized geometries. ^b From ref 30. ^c From ref 31.

of type I seem to isomerize to the unbranched chain of sulfur atoms.³⁶

The consecutive reactions of the thiosulfoxide intermediate could be the following: (1) additions to the double bond (see eq 2 and 3 and Table III); (2) nucleophilic attack on other molecules owing to the considerable negative charge of ca. -0.4 e on the terminal sulfur atoms (see Figure 1), e.g.,



The attack leads to a bond scission of the attacked molecule and finally to a net sulfur atom transfer.

The formation of the sulfuranes H₂S(SH)₂ (3) and H₂S(SSH)₂ (4) from H₂S and HS_nSH (*n* = 1 or 2) requires energy which is comparable to the dissociation energy of the central SS bond in the starting sulfanes (see Table III). The actual numerical value depends on the level of the treatment of the electron correlation. Taking into account the absence of free sulfur radicals in organic sulfur solutions or in sulfur melts at moderate temperatures, the hypervalent species of type II formed by the insertion of a sulfane to another sulfane molecule is also a possible intermediate of the

interconversion to consider. The present results also indicate that the energy required for the insertion is lowered as the sulfur chains get longer. This is consistent with the fact that the homolytic dissociation of the longer sulfur chains is considerably lower than that of the disulfanes (see Table III).

The σ -sulfuranes of type II are stabilized by the electronegative substituents. It can therefore be expected that the insertion of, for instance, H₂S₃ into the central bond of H₂S₄ with the formation of (HS)₂S(SSH)₂ would increase the positive charge on the central sulfur atom and stabilize the two otherwise very weak axial SS bonds. A similar relation is seen between the structures and the charge distributions of H₂SS (1) and (HS)₂SS (2). The SS "double" bond of the latter is stronger (shorter), and the positive charge on the central sulfur atom is higher than in the former (see Figure 1). Therefore, the formation of the intermediate of type II from H₂S₃ and H₂S₄ may require approximately the same amount of energy as (or even less energy than) the formation of two radicals HSS* from H₂S₄.

The energy of formation of the homocyclic H₄S₄ (5) from two disulfane molecules is very large as compared with the other processes listed in Table III. This reflects the very long SS bonds shown in Figure 1 and indicates that four-center reactions are unlikely candidates for the interconversion of sulfur compounds.

The charge distribution of species 1-5 shown in Figure 1 allows speculation on the solvent effects. The polar species 1 and 2 can be expected to be stabilized by polar solvents, rendering it possible that the interconversion takes a different pathway depending on the solvent used.

The energy changes of the reactions reported in Table III give only a limited possibility to discuss the plausibility of the various interconversion pathways, and additional information must be sought. However, the results presented in this work indicate that hypervalent species of type I and II may play an important role in the chemistry of polysulfur and polyselenium compounds.

Acknowledgment. The research fellowship from the Alexander von Humboldt Foundation to R.L. as well as financial support from the Technical University of Berlin (MIT-Sondermittel) and from the Academy of Finland are gratefully acknowledged.

Registry No. 1, 63344-86-5; 2, 105943-93-9; 3, 105943-94-0; 4, 105943-95-1; 5, 105943-96-2; S₇, 21459-04-1; S₈, 10544-50-0; S, 7704-34-9.