Theoretical Investigations of the Protonation of Dihydrogen Sulphoxide and Intramolecular Interconversion of the Protonated Sulphoxide and Hydrogen Thioperoxide

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Protonation on dihydrogen sulphoxide (H_2SO) and intramolecular interconversion of H_2S^+OH and HSOH have been examined by means of *ab initio* MO calculations with STO-3G and 4-31G basis sets. The results imply that H_2SO forms a more striking pyramidal conformation upon protonation, and that the *trans*-staggered form of H_2S^+OH is more stable than the *cis*-staggered one. The difference can be correlated with the change of the polarization of the S-O bond and/or the π-electron density on the SO fragment. The intramolecular interconversion of H_2S^+OH proceeds *via* pseudo-rotation but not *via* oxygen inversion or sulphur-pyramidal inversion. This behaviour is quite different from that of protonated carbonyl compounds. The intramolecular interconversion of hydrogen thioperoxide (HSOH) is also predicted to proceed *via* the transition state of the *trans*-conformation on the rotational path with lower energy barrier than the case of H_2S^+OH. The relative stability of the transition states for interconversion is also discussed in connection with the changes in some particular MO energy levels.

SINCE the variable character of a terminal sulphur-oxygen bond was recognized, efforts to clarify the nature of this bond, especially in sulphoxides ($R_2S{=}O$), have been attempted by various methods.[1] Owing to the strong electronegativity of oxygen atom and the location of negative charge on this atom in sulphoxides,[2] they function as electron donors towards electrophilic reagents such as metal ions [3] and Lewis acids [4] and form molecular complexes with them.[†] In these reactions, protonation of the sulphoxide is a typical electrophilic reaction by the important electrophile H^+. Indeed, spectroscopic and acid-base equilibra studies [6,7] confirm that protonation of the sulphoxide occurs on the oxygen atom (R_2S^+OH) in strong acids. In contrast to this experimental work, there have been few theoretical studies concerning protonated sulphoxides, except the semiempirical MO calculations performed by Olah *et al.*[7] Thus, it is of interest to elucidate theoretically changes in the electronic structure and geometry upon protonation of sulphoxides.

The interesting aspect is the conformational behaviour of a protonated sulphoxide (R_2S^+OH) during intramolecular interconversion, and concerns the dynamic behaviour of a molecule in the electronic ground state. In connection with this, Ros [8] predicted that protonated formaldehyde and acetaldehyde (R_2COH^+) undergo *cis-trans* isomerization not *via* rotation around the C=O bond but by motion in the molecular plane. The dependence of the barrier to intramolecular interconversion on the carbon-oxygen bond order is thus emphasized. This prediction has recently been supported by detailed theoretical calculations by Jost *et al.*[9] The possible mechanisms for intramolecular interconversion in a protonated sulphoxide with a three-co-ordinate sulphur atom, include sulphur pyramidal inversion,[10] as well as internal rotation and oxygen inversion (the motion of the hydroxy hydrogen in the S^+-OH plane) as in the case of protonated carbonyl compounds. This may be understood from the calculated result that the most stable conformation of R_2S^+OH is a pyramid with sulphur at the top as is also the case for the sulphoxide before protonation (see Figure 1); this is quite different from the planar conformation of the protonated carbonyl compounds. Furthermore, it is necessary to consider simultaneous (or coupled) conversion and/or the intermediates in the fundamental mechanisms mentioned above, *i.e.*, distorted (pseudo) rotation, coupling [11] of rotation and sulphur-pyramidal inversion, and of oxygen and sulphur-pyramidal-inversion (see Figure 2).

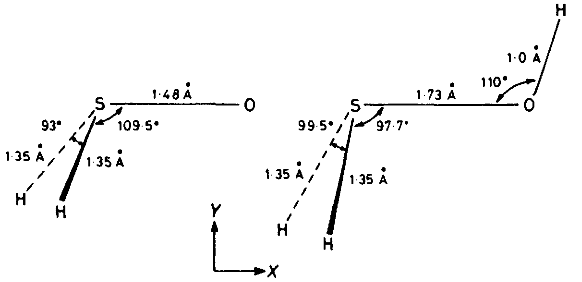

FIGURE 1 Optimized geometries of H_2SO and H_2S^+OH

While RSOR,[12] the structural isomer of R_2SO, is expected to have a different conformational behaviour for the intramolecular interconversion such as sulphur inversion, *etc.*, since it is composed of two-co-ordinate sulphur atom. This drives us to include consideration of RSOR in the present study.

From these points of view, the purpose of the present investigation is to elucidate the following points by means of *ab initio* calculations: (1) the changes of the electronic structure and the geometry due to protonation of R_2SO; (2) the determination of the pathway of intramolecular interconversion; and (3) the differences of the energy barrier and mechanism between R_2SO and/or R_2S^+OH and RSOR.

[†] It should be noted that the sulphoxide is also capable of co-ordinating to some kinds of metal cations not *via* oxygen but *via* sulphur,[3] which is characteristic behaviour for a sulphoxide with unshared pairs of electrons on both sulphur and oxygen. Thus it is urgent to elucidate the origin of the property of the sulphoxide in forming complexes with metal ions or electrophiles. A study concerning this aspect will be reported elsewhere. See also ref. 5.

In order to simplify the discussion and to exclude substituent effects, H_2SO and HSOH, being the simplest homologues, are therefore chosen as the models for R_2SO and RSOR, respectively.

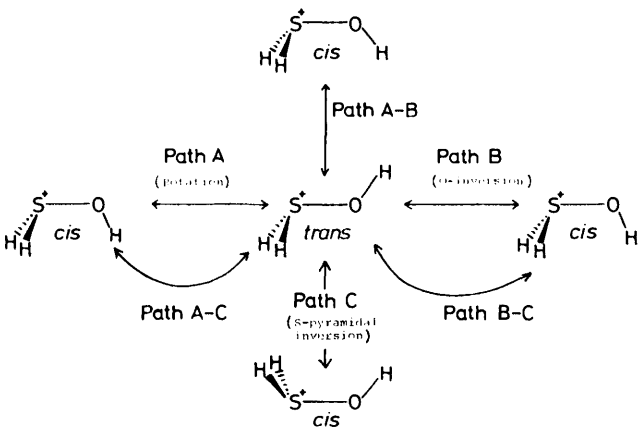

FIGURE 2 Schematic presentation of intramolecular interconversion in H_2S^+OH

METHODS

Ab initio LCAO-SCF-MO calculations were performed with the split-valence 4-31G basis set,[13] with the standard scale factors and also the STO-3G basis set [14] using the Gaussian 70 program.[15] Since the total energy calculated by the 4-31G basis set is in general more reliable than that of STO-3G basis set, we stress the calculated results from the former.[*] The geometries of H_2SO, H_2S^+OH, and HSOH in the ground state are fully optimized with the 4-31G basis set, except that the S–H bond length is 1.35 Å, the experimentally determined value for H_2S.[18] Since we do not know the conformation in each transition state for the intramolecular interconversion in H_2S^+OH and HSOH, a few particular paths are assumed and the geometry of maximum energy configuration is optimized with respect to each path by the use of the geometry of the most stable configuration with some symmetrical restrictions.

It should be noted that the energy and energy difference shown in the Tables and Figures are throughout expressed as a.u. (hartree) and kcal mol^{-1}, respectively, *i.e.*, 1 a.u. of energy (hartree) = 27.21 eV = 627.7 kcal mol^{-1} = 2 628.72 kJ mol^{-1}.

RESULTS AND DISCUSSION

(I) *Protonation of* H_2SO.—The geometries of both H_2SO and H_2S^+OH optimized by the 4-31G basis set are illustrated in Figure 1. The calculated results, that H_2SO is nonplanar as is H_2S^+OH with the S^+OH portion being bent, are in accord with the molecular shapes deduced from the simple MO correlation diagrams of H_2AB and H_2ABH structures with 14 valence electrons.[19] The sulphur-pyramidal shape of H_2SO and the S–O bond length (1.48 Å) in H_2SO are in agreement with those in dimethyl sulphoxide (S–O 1.47 Å).[20] The protonated sulphoxide, H_2S^+OH, which possesses a *trans*-staggered conformation, shows a remarkable difference, in that the S–O bond distance is lengthened by 0.25 Å and the HS^+O angle becomes smaller by *ca.* 12°, leading to a more striking pyramidal conformation compared with H_2SO. The lengthening of the S–O bond upon protonation is strongly supported by the experimental fact that the S–O stretching frequency (ν_{SO}) is lowered by 170 cm^{-1} in the *O*-protonated dimethyl sulphoxide, Me_2S^+OH.[6d]

The protonation energy is calculated to be 240.0 kcal mol^{-1}, which is larger than those for the protonation of carbonyl compounds (*ca.* 137—199 kcal mol^{-1} at 4-31G level [10,21]). For instance, the protonation energy of H_2CO is calculated to be 179.2,[21] or 178.6 kcal mol^{-1} [10] with the 4-31G basis set. This trend in protonation energy is also found by the STO-3G basis set, *i.e.*, 327.9 kcal mol^{-1} for H_2SO and 217.2 [21] or 222.7 kcal mol^{-1} [10] for H_2CO, although protonation energies (hence proton affinities) are overestimated throughout owing to the nature of STO-3G basis set.[21,22]

These results demonstrate that H_2SO is a stronger base towards an electrophile such as a proton than are carbonyl compounds. This can also be understood from the argument that a high n_O orbital energy (low ionization potential as approximated by Koopmans theorem) corresponds a larger proton affinity of the base (high basicity through increased n_O donor ability).[21,23] In fact, the n_O orbital energies are -10.44 (-5.93) and -11.97 (-9.58) eV [10] for H_2SO and H_2CO, respectively, using the 4-31G (STO-3G) basis set.

The *cis*-staggered conformation of H_2S^+OH is metastable in the electronic ground state and is further stabilized by 0.6 kcal mol^{-1} (4-31G) at an S^+OH angle of 116° in order to decrease the internuclear repulsion between two hydrogens attached to sulphur and the hydroxy-hydrogen, compared with the conformation obtained by pure rotation around the S–O bond (dihedral angle 0 and S^+OH angle 110°, see Figure 3).

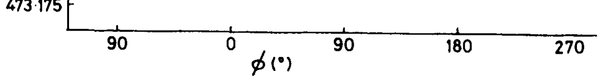

FIGURE 3 Potential curve calculated as a function of the dihedral angle ϕ and the S^+OH angle (θ) for the barrier to internal rotation

Thus, the energy difference between the *trans*- (more stable) and *cis*-staggered conformation in H_2S^+OH is 7.7 and 7.2 kcal mol^{-1} with the 4-31G and STO-3G basis sets, respectively. It should be noted here that although

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[*] Although some *ab initio* calculations [16] stress that the role of the *d* function in predicting accurate geometries of molecules containing sulphur is important, the present calculations using the 4-31G basis set yield satisfactory optimum geometries for H_2SO and H_2S^+OH (see text). Hence, the results of these calculations cannot be expected to have a bearing on the conclusions. See also ref. 17.

the semiempirical MINDO/3 calculation[7] yields the result that in protonated dimethyl sulphoxide the *cis*-staggered form is more stable by 3.1 kcal mol^{-1} than the *trans*-staggered one, the preference for the *trans*-staggered form in H_2S^+OH is evident from our *ab initio* calculations.

Table 1 shows Mulliken population analyses[24] of H_2SO and the *trans*- and *cis*-staggered forms of H_2S^+OH with the two basis sets. Before discussing the electronic distribution, we must examine the basis set dependence for the present systems.

The important difference between two basis sets is the is greater electron loss from the SO fragment than from the SH_2 hydrogen, indicating that the charge transfer from H_2SO to H^+ mainly occurs through the σ electron system of the SO fragment. The comparison between *trans*- and *cis*-staggered H_2S^+OH implies that the increasing stability of the cation correlates with the decreasing polarization of the S–O bond and/or the increasing π-electron density on the SO fragment, *i.e.* π (perpendicular to the S^+OH plane)-back donation taking place from the molecular orbital 2*a*″ (see Figure 4). These relationships are also found in the results of calculation by the 4-31G basis set.

TABLE 1

Gross atomic charges, overlap populations, and changes of electron density[a] in H_2SO and H_2S^+OH

	STO-3G			4-31G		
	H_2SO	H_2S^+OH (*trans*)	H_2S^+OH (*cis*)	H_2SO	H_2S^+OH (*trans*)	H_2S^+OH (*cis*)
S	+0.616	+0.608	+0.646	+0.735	+0.581	+0.670
O	−0.556	−0.204	−0.195	−0.913	−0.686	−0.702
H	−0.030	+0.150	+0.135	+0.089	+0.294	+0.263
H		+0.296	+0.278		+0.517	+0.506
S–O	0.137	0.164	0.163	−0.003	0.083	0.091
H–S	0.233	0.294	0.288	0.226	0.296	0.290
O–H		0.249	0.246		0.239	0.238
E. T. to H^+		0.704	0.722		0.483	0.494
E. L. on SO		0.344	0.391		0.073	0.146
π–E. G. on SO		0.197	0.176		0.215	0.171
E. L. on H		0.180	0.165		0.205	0.174
Dipole moment[b]	3.548			4.995		

[a] Electron transfer (E.T.), electron loss (E.L.), and electron gain (E.G.) are relative to H_2SO; π refers to the S($2p_z$, $3p_z$) and O($2p_z$) atomic orbitals (see Figure 1). [b] In debye. Experimental value is 3.9 D for Me_2SO.[3a]

overlap population of the S–O bond. That is, the S–O overlap population is 0.137 at the STO-3G level and −0.003 at the 4-31G level, where the latter is associated with the very large polarization such as $S^{+0.735}$–$O^{-0.913}$, yielding an unreasonable bonding in H_2SO. This trend in the 4-31G basis set is also found in H_2S^+OH.* In practice, it is known that the 4-31G basis set tends to overestimate the electronegativities of the more electronegative elements, while a minimal basis set such as STO-3G tends to underestimate them.[13,14,21] Under such conditions, the dipole moment is a helpful means of examining which electronic distribution given by these two basis sets is the more reliable. As expected, while the dipole moment of H_2SO by 4-31G (4.995 D) is much overestimated, that by STO-3G (3.548 D) is closer to the experimental value (3.9 D for Me_2SO). Hence it can be said that the STO-3G basis set affords a more reliable electronic distribution in the electronic ground state rather than 4-31G basis set, at least for the present systems. We therefore stress the results of the STO-3G calculations for the electronic distribution.

It is evident from Table 1 (STO-3G) that the electron density tends to be delocalized over the molecule upon protonation, associated with the decrease in polarization of the S–O bond, by which the cation is stabilized. This

(II) *Intramolecular Interconversion of* H_2S^+OH.—In the intramolecular interconversion from the *trans*- to the *cis*-staggered conformation of H_2S^+OH the following six

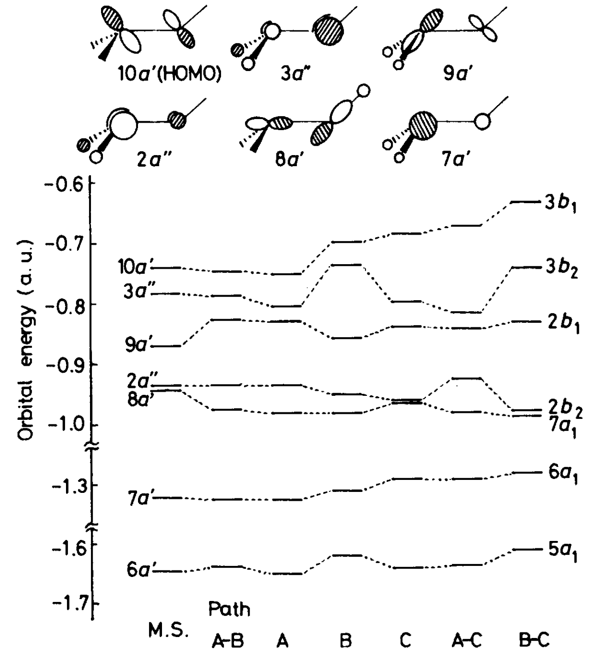

FIGURE 4 Some MOs of the most stable (M.S.) conformations and relationships between MO energy levels with respects to the most stable conformation in H_2S^+OH

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* For comparison, we calculated H_2SNH by the 4-31G basis set, with the geometry used by Mezey *et al.*,[11] and found a similar trend from this basis set for the S–N bond, *i.e.*, the gross atomic charges on S and N are +0.493 and −1.115, respectively, and overlap population between them is −0.098.

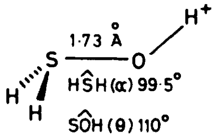
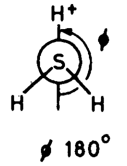
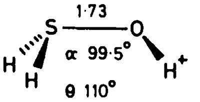
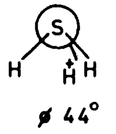
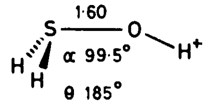
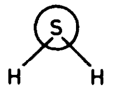
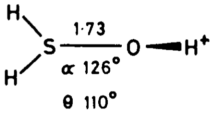
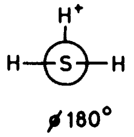
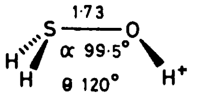
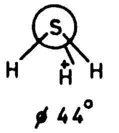
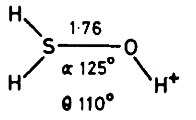
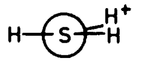
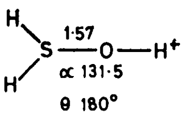
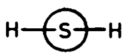
possible mechanisms are chosen as shown in Figure 2: Path A, rotation of the hydroxy hydrogen around the S–O bond, also called torsion; Path B, motion of hydroxy hydrogen in the S^+OH plane, also called oxygen inversion; Path C, sulphur-pyramidal inversion; Path A–B, distorted or pseudo-rotation, a combination of Paths A and B; Path A–C, simultaneous rotation and sulphur-pyramidal inversion, a combination of Paths A and C; and Path B–C, simultaneous motion in the S^+OH plane and sulphur-pyramidal inversion, a combination of Paths B and C.

The conformations of the transition states on the corresponding pathways were calculated by limited optimization with the 4-31G basis set. Table 2 summarizes the energy barriers relative to the most stable (*trans*-staggered) conformation of H_2S^+OH, together with some optimized bond lengths and angles. Comparison of the energy barriers thus obtained by the 4-31G basis set shows that the most favoured path is not motion in the S^+OH plane (Path B) but distorted rotation around the S–O bond (Path A–B) although at the STO-3G level pure rotation (Path A) is preferred over the distorted rotation. Hence, we examine in some detail the geometries of the transition states and the corresponding barriers (4-31G) with respect to Paths A and A–B.

Path A. The dihedral angle of the transition state is found to be 44°, as shown in Figure 3. The potential curve calculated as a function of the dihedral angle shows that the *trans*-staggered form is more stable by 8.3 kcal mol^{-1} than the *cis*-staggered form and that barriers towards *trans*- and *cis*-staggered forms are 8.7 and 0.4 kcal mol^{-1}, respectively. (It should be noted that the *cis*-

TABLE 2

Optimized geometries and energy barriers (kcal mol^{-1}) in H_2S^+OH

			H_2S^+OH		H_2SNH [b]
			4-31G	STO-3G	4-31G
Most stable conformation (*trans*)					
Path A			8.7	7.5	9.6
Path B			26.3	30.5	(31.5) [c]
Path C			32.4 (34.4) [a]	41.5 (45.9) [a]	24.4
Path A–B			8.3	12.8	
Path A–C			38.6	46.8	44.5
Path B–C			66.1	121.2	

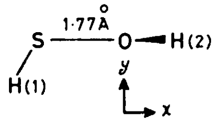
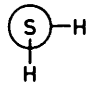
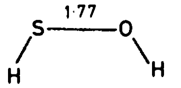
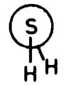
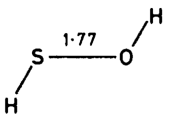
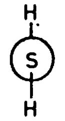
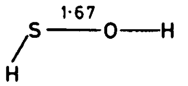
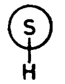
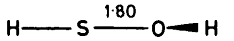
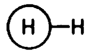
[a] Calculated value of sulphur-pyramidal inversion in H_2SO. Corresponding experimental value is 39.7 kcal mol^{-1} obtained from adamantyl methyl sulphoxide (D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854). [b] See ref. 11. [c] Calculated result for comparison of H_2S^+OH with H_2SNH.

staggered form dealt with here is that obtained by pure rotation around the S–O bond, keeping the S^+OH angle constant at 110°.) The barrier thus obtained for Path A (8.7 kcal mol^{-1}) is much smaller than that in H_2COH^+ (28.5 kcal mol^{-1} [8]).

Path A–B. The geometry of the transition state is determined by optimization of the S^+OH angle, based on the geometry of the transition state for Path A. The optimum bond angle is 120°, an increase of 10° compared with that for the transition state of Path A. From the change in this angle, it follows that Path A–B can be regarded as distorted rotation along Path A rather than a combination of Paths A and B. In this sense, it may be said that the S^+OH bond angle dependence for the barrier in Path A is 0.4 kcal mol^{-1}, since the barriers at 110 and 120° are 8.7 and 8.3 kcal mol^{-1}, respectively.

TABLE 3

Optimized geometries and energy barriers (kcal mol^{-1}) in HSOH

			4-31G	STO-3G
Most stable conformation [a]				
Path a	 *cis*		5.96	4.37
	 *trans*		2.73	2.58
Path b			28.9	67.7
Path c			110.6	141.2

[a] The optimized O–H bond length is 1.0 Å, and the H(1)SO and SOH(2) angles are 96 and 110°, respectively.

According to the more reliable results from the 4-31G basis set, a pathway for intramolecular interconversion from the *trans-* to the *cis*-staggered conformation in H_2S^+OH may be drawn. That is, H_2S^+OH proceeds towards the transition state (Path A–B), with rotation of the dihedral angle ϕ (180° $\longrightarrow$ 44°) and expansion of the S^+OH angle θ (110° $\longrightarrow$ 120°), and, *via* the transition state, subsequently reaches the metastable state of the *cis*-staggered form (ϕ 44° $\longrightarrow$ 0°, θ 120° $\longrightarrow$ 116°). The results from both 4-31G and STO-3G basis sets differ from the case of protonated formaldehyde and acetaldehyde, where motion in the plane is more energetically favourable than pure or distorted rotation around the C–O bond. Based on the arguments of Ros,[8] it may be that the difference is mainly due to the difference of the bond orders of the S–O and C–O bonds in the protonated conformations. The C–O bond in H_2COH^+, for example, retains the nature of the double bond,[8,9] while the S–O bond in H_2S^+OH has almost single bond nature, which makes rotation around the S–O bond (Path A) easier than the oxygen inversion (Path B).

Furthermore, the relative preference for intramolecular interconversion in H_2S^+OH is found to be: Path A–B $\geqslant$ A $>$ B $>$ C $>$ A–C $>$ B–C (4-31G). It is clear that the paths involving distortion of the hybridization on the sulphur atom (*e.g.*, Paths C and A–C) brings about more destabilization of the corresponding transition state than those for the oxygen atom (*e.g.*, Path B). This trend is understood by the changes in orbital energies of the 10*a'* (sulphur lone pair, n_S) and 3*a''* (oxygen lone pair, n_O) orbitals which are HOMO and next-to-HOMO, respectively, in H_2S^+OH (Figure 4). Although one can find no definite relationship between the stability of the cation and a given orbital energy, the sum of orbital energies of 10*a'*, 3*a''*, and 9*a'* seems to reflect, to some extent, the relative stability of the cations in the transition states.

Here, it is interesting to compare H_2S^+OH with H_2SO and H_2SNH,[11] which have also 14 valence electrons (see Table 2). The small difference, 2.0 kcal mol^{-1} of the energy barrier for the sulphur-pyramidal inversion (Path C) between H_2S^+OH (32.4 kcal mol^{-1}) and H_2SO (34.4 kcal mol^{-1}) seems, to predict that the barrier to this kind of inversion is not so affected by protonation on the terminal oxygen atom. Meanwhile, although it is reverse of the case for H_2S^+OH that sulphur-pyramidal inversion is preferred in energy to nitrogen-inversion (Path B) in H_2SNH, the preference for internal rotation (and/or pseudo-rotation) in H_2SNH is in agreement with the result for H_2S^+OH. Furthermore, that the barrier to Path A in H_2S^+OH is smaller by *ca.* 1.0 kcal mol^{-1} than that in H_2SNH seems to be ascribed to the condition that the single (double) bond character of the S–O bond in H_2S^+OH is stronger (weaker) that that of the S–N bond in H_2SNH.

(III) *Hydrogen Thioperoxide* HSOH.—The optimized geometry of HSOH in the ground state using the 4-31G basis set is illustrated in Table 3, with a dihedral angle ϕ of 90°. This geometry is the same in energy as that with ϕ −90° (= 270°) (see Figure 6). Thus in the intramolecular interconversion from ϕ 90 to −90°, there arise three fundamental mechanisms as shown in Figure 5: Path a, internal rotation around the S–O bond, where there are two transition states with *cis*- (ϕ 0°) and *trans*- (ϕ 180°) conformations; Path b, oxygen inversion, *i.e.* motion of the hydroxy hydrogen in the SOH(1) plane; and Path c, sulphur inversion, *i.e.* motion of the hydrogen of the thiol in the H(2)SO plane. Here it should be noted that simultaneous motion or coupling of two mechanisms as considered in the case of H_2S^+OH is neglected for HSOH. Figure 6 shows the potential curve calculated as function of the dihedral angle ϕ. The resultant geometry of the transition state on each path is also shown in Table 3, as well as the corresponding energy barrier. It is clear from Table 3 that the most favourable route is Path a *via* the transition state of *trans*-conformation (ϕ 180°), not *via* that of *cis*-conformation (ϕ 0°). The difference in barrier between the *trans*- and *cis*-conformations is easily understood in terms of the difference in internuclear repulsion between H(1) and H(2). The order of preference in HSOH, Path a > b > c, obtained by the 4-31G basis set, is consistent with the results calculated by the STO-3G basis set.

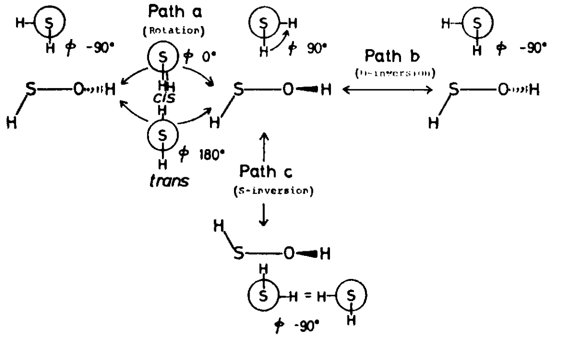


FIGURE 5 Schematic presentation of intramolecular interconversion in HSOH

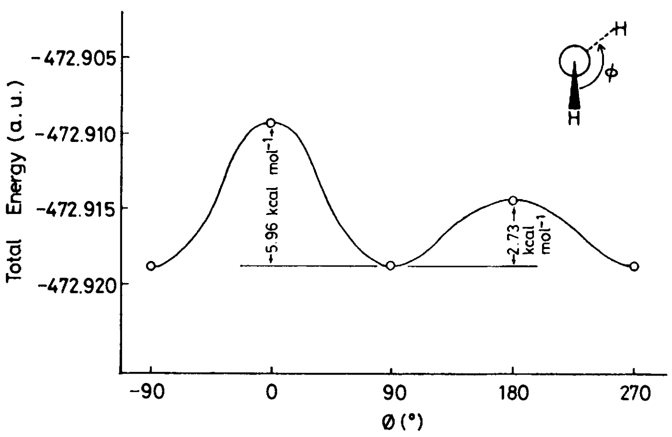


FIGURE 6 Potential curve calculated as a function of the dihedral angle ϕ in HSOH

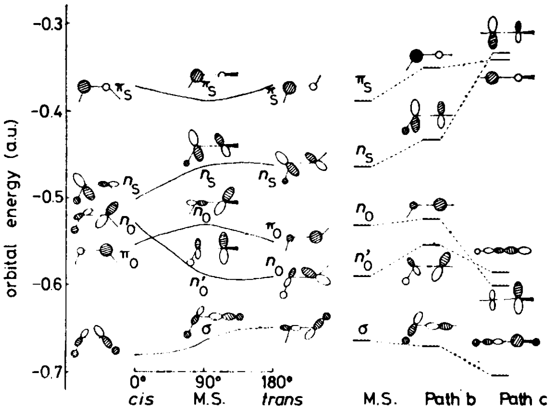


FIGURE 7 Relationship between MO energy levels with respect to the most stable (M.S.) conformation in HSOH

Figure 7 shows the relationship of MO energy levels to the most stable conformation of HSOH. It is remarkable that there is crossing between the π_S and n_S orbitals* in the transition state on Path c, *i.e.*, the π_S and n_S orbitals, which are HOMO and next-to-HOMO in the most stable conformation, becomes next-to-HOMO and HOMO, respectively, in the above transition state. This is because the H(1) 1*s* orbital is pulled out of overlap with the $3p_x$ orbital on the sulphur atom during sulphur inversion, and disappears from the n_S orbital because H(1) lies on the nodal plane of the $2p_y$ orbital at the transition state on Path c. Rotation *via* the *cis*-transition state on Path a is found to encounter the crossing of two oxygen lone pair orbitals, which may require the rearrangement of the electronic distribution centred at the oxygen atom in HSOH. It can also be demonstrated from this argument that rotation *via* the *cis*-transition state on Path a is less favourable than that *via* the *trans*-transition state, as mentioned above.

Lastly, it is worthwhile to compare the pathways between HSOH and H_2S^+OH. It is apparent that the trend in HSOH is in accord with that in H_2S^+OH, since rotation (including distorted rotation) around the S–O bond is easier than other motions and furthermore oxygen inversion requires less energy than sulphur inversion in both systems. While the energy barriers to oxygen inversion in HSOH and H_2S^+OH are almost the same, *i.e.* 28.9 and 26.3 kcal mol^{-1}, respectively, that for sulphur inversion in the former is three or more times larger than for the latter, *i.e.* 110.6 and 32.4 kcal mol^{-1} for HSOH and H_2S^+OH, respectively (at the 4-31G level in Tables 2 and 3). These results indicate that sulphur inversion at a two-co-ordinate sulphur atom yields more

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* To distinguish two kinds of lone pair orbitals on sulphur, the lone pair orbital in the *x*–*y* and *z*-planes are designated as n_S and π_S, respectively. A similar designation is made also for the oxygen lone pair orbitals, *i.e.* n_O and π_O.

geometrical destabilization of a molecule than at a three-co-ordinate sulphur atom (sulphur-pyramidal inversion), where the latter destabilization is energetically comparable with oxygen inversion.

Conclusions.—Dihydrogen sulphoxide H_2SO is a much stronger base towards a proton than carbonyl compounds R_2CO, as is shown by the protonation energy, 240.0 kcal mol^{-1}, the small ionization potential of the oxygen lone pair orbital, and the large electron transfer to the proton. Protonation makes the sulphoxide take up a more striking pyramidal conformation with a *trans*-staggered form.

Intramolecular interconversion from the *trans* to the *cis*-staggered conformation in H_2S^+OH is predicted to proceed *via* pseudorotation but not *via* oxygen inversion or *via* sulphur-pyramidal inversion. This is quite different behaviour than protonated formaldehyde and acetaldehyde. The relative stability of the transition states on the pathways is reflected by the sum of the orbital energies for the HOMO and next-to-HOMO, *etc*. The preference for internal rotation including pseudorotation rather than other motions seems to be general in H_2ABH molecules with 14 valence electrons.

Intramolecular interconversion in HSOH is thought to occur preferably *via* the *trans*-transition state on the rotational path. Sulphur inversion at a two-co-ordinate sulphur atom is confirmed to be the least favoured path and the corresponding energy barrier is three or more times larger than those for sulphur-pyramidal inversion and oxygen-inversion.

Throughout the present study, it can be said that the procedure based on fundamental intramolecular motions is useful in determining the energetically favoured path for intramolecular interconversion. Further investigation in the course of the present study, especially dynamic n.m.r. investigations, would be desirable.

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