

**On the  $\pi$ -Donating Abilities of Sulfur and Oxygen. A Comparative Quantum Chemical Investigation of the Static and Dynamic Properties and Gas Phase Acidities of  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  and  $\overset{+}{\text{C}}\text{H}_2\text{SH}$**

FERNANDO BERNARDI

*Istituto di Chimica Organica, Università di Bologna, Italy*

IMRE G. CSIZMADIA

*Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1*

AND

H. BERNHARD SCHLEGEL<sup>1</sup> AND SAUL WOLFE

*Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6*

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Nonempirical SCF-MO computations have been performed on  $\text{CH}_2\text{O}$ ,  $\text{CH}_2\text{S}$ , and their protonated derivatives  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  and  $\overset{+}{\text{C}}\text{H}_2\text{SH}$ . The methylene group of  $\text{CH}_2\text{O}$  is strongly positive and that of  $\text{CH}_2\text{S}$  is slightly negative, because oxygen in  $\text{CH}_2\text{O}$  behaves towards carbon as a  $\pi$ -donor and  $\sigma$ -acceptor, but sulfur in  $\text{CH}_2\text{S}$  behaves as both a  $\pi$ - and  $\sigma$ -donor. The total  $\pi$ -overlap in  $\text{CH}_2\text{O}$  is greater than that in  $\text{CH}_2\text{S}$ .

The stable conformations of  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  and  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  correspond in each case to a structure in which all atoms lie in the same plane. In this conformation, both the C—O and C—S bond lengths are substantially shorter than those of methanol and methanethiol, indicative of conjugative interaction between the cationic center and the adjacent heteroatom. From the results of a Mulliken-type population analysis it is found that, relative to hydrogen, OH and SH behave towards an adjacent  $\overset{+}{\text{C}}\text{H}_2$  group as electron-withdrawing and electron-releasing ligands, respectively. When  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  is considered to form from  $\overset{+}{\text{C}}\text{H}_2$  and OH fragments,  $\pi$ -donation from O to C amounts to 0.38 electron, but  $\sigma$ -donation in the opposite direction amounts to 0.35 electron; the  $\pi$ -overlap population is 0.1496. A similar analysis of  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  reveals  $\pi$ - and  $\sigma$ -donation from S to C of 0.53 and 0.15 electron, respectively, and a  $\pi$ -overlap population of 0.1734, so that sulfur forms a stronger  $\pi$ -bond to the adjacent cationic center.

Geometrical isomerization of  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  proceeds by linear inversion at oxygen, with a barrier of 13.98 kcal/mol; but that of  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  proceeds by rotation about the C—S bond, with a barrier of 36.47 kcal/mol. This latter value is substantially higher than that (23 kcal/mol) computed for  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  with a rigid rotor model, and reflects the greater strength of the  $\pi$ -bond between sulfur and the adjacent cationic center.

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On a effectué des calculs non-empiriques SCF-MO sur le  $\text{CH}_2\text{O}$ , le  $\text{CH}_2\text{S}$  et leurs dérivés protonés  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  et  $\overset{+}{\text{C}}\text{H}_2\text{SH}$ . Le groupe méthylène du  $\text{CH}_2\text{O}$  est fortement positif et celui du  $\text{CH}_2\text{S}$  est faiblement négatif; ces résultats proviennent du fait que l'oxygène dans le  $\text{CH}_2\text{O}$  agit vis-à-vis le carbone comme un donneur d'électrons  $\pi$  et un accepteur d'électrons  $\sigma$  mais que le soufre du  $\text{CH}_2\text{S}$  agit comme donneur d'électrons  $\pi$  et d'électrons  $\sigma$ . Le recouvrement total d'orbitales  $\pi$  dans le  $\text{CH}_2\text{O}$  est plus grand que dans le  $\text{CH}_2\text{S}$ .

Les conformations stables de  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  et  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  correspondent dans chaque cas à une structure dans laquelle tous les atomes sont dans le même plan. Dans cette conformation, les longueurs de liaison C—O et C—S sont passablement plus courtes que les liaisons correspondantes du méthanol et du méthanethiol indiquant une interaction conjugative entre le centre cationique et l'hétéroatome adjacent. On trouve, à partir des résultats d'une analyse de population du type Mulliken, que par rapport à l'hydrogène, les groupes OH et SH agissent respectivement vis-à-vis un groupe  $\overset{+}{\text{C}}\text{H}_2$  adjacent comme des groupes électro-affinitaires et électro-répulsifs. Lorsque l'on

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considère que  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  se forme à partir de fragments  $\overset{+}{\text{C}}\text{H}_2$  et OH, on calcule qu'il y a eu don d'électrons  $\pi$  de l'oxygène au carbone de 0.38 électrons mais un don d'électrons  $\sigma$  dans la direction opposée correspondant à 0.35 électrons; la population de recouvrement d'électrons  $\pi$  est de 0.1496. Une analyse similaire de  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  révèle qu'il y a des dons d'électrons  $\pi$  et  $\sigma$  du S vers le carbone qui équivalent respectivement à 0.53 et 0.15 électrons et que la population de recouvrement d'électrons  $\pi$  est de 0.1734 ce qui implique que le soufre forme un lien  $\pi$  plus fort avec le centre cationique adjacent.

L'isomérisation géométrique de  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  se produit par une inversion linéaire à l'oxygène avec une barrière de 13.98 kcal/mol; celle de  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  se produit toutefois par une rotation autour du lien C—S avec une barrière de 36.47 kcal/mol. Cette dernière valeur est considérablement plus élevée que celle (23 kcal/mol) calculée pour  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  avec un modèle de rotor rigide et implique une plus grande force du lien  $\pi$  entre le soufre et le centre cationique adjacent.

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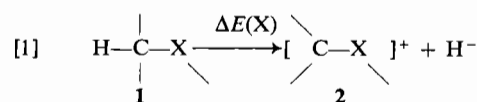
## Introduction

There is an extensive literature concerning the relative effects of oxygen and sulfur upon the properties of adjacent cationic, radical, and anionic centers (e.g. ref. 1). It seems that, in solution, it is easier to generate a carbanion (e.g. ref. 2) or radical (e.g. ref. 3) adjacent to sulfur than to oxygen, but the reverse is observed in the case of carbonium ions (ref. 4 and references cited therein). These various trends have usually been rationalized (2–4) in terms of appropriate conjugative interactions: ( $p \rightarrow d$ ) $_{\pi}$  conjugation in the case of anions and radicals, with the ability of the heteroatom to enter into such conjugation being possible only for the second row atom (sulfur);  $p_{\pi}$ - $p_{\pi}$  conjugation in the case of cations, with the magnitude of this interaction inversely proportional to the internuclear separation and, thus, favored for the system having the shorter bond length (oxygen).

It is noteworthy that, in all such rationalizations, it is the  $\pi$ -type interactions which are emphasized; the possible role of  $\sigma$ -interactions and steric effects is ignored. In addition, these rationalizations have tended to assume that the observed effects are caused by differences in the interactions between the carbon center and the adjacent heteroatom, and not by differential solvation effects. However, it now seems well established that solvation effects cannot be ignored, at least in some cases (2, 5). In the gas phase, where solvation effects are not present, the dissociation energies of CH bonds adjacent to oxygen and to sulfur are identical (6), indicating no difference in the ease of formation of a radical center adjacent to oxygen and to sulfur; and, on the basis of appearance potential measurements (6, 7), there also seems to be no significant difference in the ease of formation of cationic centers adjacent to oxygen and to sulfur.

It is inappropriate to conclude from such observations that one heteroatom "stabilizes" an adjacent reactive center better than or as well as the other, because in one case what is being observed is the breaking of a CH bond adjacent to sulfur to form a reactive center adjacent to sulfur; and in the other case, a CH bond adjacent to oxygen is broken to form a reactive site adjacent to oxygen.

There is no simple theoretical solution to this problem because, in addition to the point just raised, a theoretical treatment introduces two additional difficulties. Consider, for example, the heterolytic bond breaking or bond making process shown in reaction 1, in which the electron



pairing scheme is formally unchanged, so that both the initial and final states have closed electron shells. The first problem is that, if we were to define stabilization energy (s.e.) in terms of the double energy difference shown in eq. 2,

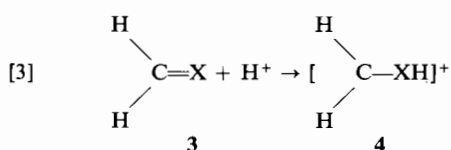
$$[2] \quad \text{s.e.} \equiv \Delta\Delta E = \Delta E(\text{S}) - \Delta E(\text{O})$$

it would be necessary to compute four different energy values. Even in the ideal situation of a reaction such as [1], only computations performed very close to the Hartree-Fock limit would allow us to hope for a minimum of two significant figure accuracy in  $\Delta\Delta E$ . The second problem is that, even if  $\Delta\Delta E$  were considered to be reliable, it is not clear what are the relative contributions to this quantity of  $\pi$ -conjugative effects,  $\sigma$ -effects, steric effects, etc. However, what the theoretical analysis allows is a determination of the changes in bonding which take place between the heteroatom and the adjacent

carbon as a result of the chemical reaction 1 and, therefore, of the nature of the effects exerted by the heteroatoms in each case.

In previous work, we have found that a variety of the static, dynamic, and chemical properties of carbanions (8) and radicals (9) adjacent to oxygen and to sulfur are reproduced faithfully by nonempirical quantum chemical calculations, but that 3d-orbital conjugation in the case of sulfur (*i.e.*, a  $\pi$ -type effect) is not responsible for differences between the two systems. Rather, it is the differences in the sizes of the two heteroatoms and, therefore, differences in their electronegativities, polarizabilities, and energies of the atomic lone pair orbitals that cause these conformational and chemical differences.

The subject of the present work is a comparative quantum chemical investigation of the reaction represented by reaction 3 in which X = oxygen and sulfur. Protonated aliphatic



aldehydes, including formaldehyde (reaction 3, X = O), and protonated aliphatic ketones have been observed experimentally by Olah *et al.* (10) to display geometrical isomerism about the carbon-oxygen bond. However, the barrier to interconversion of geometrical isomers was not determined by these workers, and experimental data concerning the protonation of thioaldehydes and thioketones (reaction 3, X = S) have not yet been reported.

If the magnitude of the barrier to *rotation* about the C—X bond of **4** were to constitute a rough measure of the  $\pi$ -conjugative stabilization afforded by X, then current chemical intuition would suggest that hydroxymethylcarbonium ion should have the higher rotational barrier. Therefore, a prime objective of the present work was the computation of the energetics and mechanisms of geometrical isomerization of the cations **4** (for previous investigations of  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  see ref. 11), and the changes in bonding that occur in the formation of these species from **3**. In disagreement with expectation, we find  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  to have the higher rotational barrier, *i.e.*, that the  $\pi$ -conjugative effects are greater for the second

row atom than for the first row atom. In agreement with this conclusion is the finding that the computed amount of  $\pi$ -charge transfer from the heteroatom to the  $\overset{+}{\text{C}}\text{H}_2$  center and the  $\pi$ -overlap populations are greater for sulfur than for oxygen.

### Method

The method employed was the single-determinant LCAO-MO-SCF procedure, in which each molecular orbital  $\psi_i$  is expressed as a linear combination of a set of contracted Gaussian type functions (eq. 4).

$$[4] \quad \psi_i = \sum_j C_{ij} \phi_j$$

A split valence shell basis set (4-31G) has been used throughout the work (12a, b). In this basis set each inner shell is represented by a four term Gaussian expansion, and the valence shell is split into three- and one-term expansions of the inner and outer parts, respectively. The molecular orbitals were determined by solution of the Roothaan-Hartree-Fock equations using the Gaussian 70 program system (12c) with full optimization of the geometries of each of the four species **3** (X = O, S) and **4** (X = O, S). All computations were performed on a CDC 6600 computer at the University of Bologna.

### Results and Discussion

#### Geometry Optimization of $\text{CH}_2\text{O}$ and $\text{CH}_2\text{S}$

Table 1 lists the computed optimized geometries of formaldehyde (12a) and thioformaldehyde, together with the experimentally determined (13) geometries of these molecules. Formaldehyde has been investigated previously by a number of workers (11a, 11c, 14, 15), but with the exception of ref. 12a, the objectives were different from those of the present work, and full geometry optimization was not performed. It is evident that the optimized geometries of **3** agree well with the experimental values in both cases; this provides some confidence that the basis set employed in the work can also provide accurate geometries of the species **4**, for which experimental data are not available.

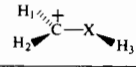
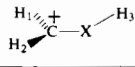
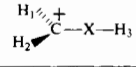
#### Geometry Optimization of $\overset{+}{\text{C}}\text{H}_2\text{OH}$ and $\overset{+}{\text{C}}\text{H}_2\text{SH}$

The most stable conformation in each case is the fully planar structure **5**. In each case, the energy was optimized with respect to all geometrical parameters except the C—H bond length of  $\overset{+}{\text{C}}\text{H}_2\text{OH}$ , kept constant at the value 1.0835 Å previously computed at the minimal basis set level (16). The optimized value of the C—H bond length for  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  is 1.0677 Å, and this value was kept constant in all subsequent computations

TABLE 1. The theoretically optimized and experimentally determined geometries of  $\text{CH}_2\text{O}$  and  $\text{CH}_2\text{S}$ 

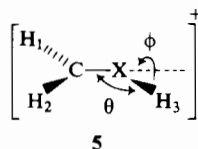
	$\text{CH}_2\text{O}$		$\text{CH}_2\text{S}$	
	Theoretical	Experimental	Theoretical	Experimental
$r(\text{C}-\text{X})$	1.21 Å	1.21 Å	1.63 Å	1.61 Å
$r(\text{C}-\text{H})$	1.08 Å	1.12 Å	1.07 Å	1.09 Å
$\angle \text{HCH}$	116.8°	116.3°	115.6°	116.8°

TABLE 2. Optimum energies (Hartree a.u.), bond lengths (Å), and bond angles (deg) for various conformations of  $\text{CH}_2\text{OH}^+$  and  $\text{CH}_2\text{SH}^+$ 

						
	X = O	X = S	X = O	X = S	X = O	X = S
$r(\text{C}-\text{H})^*$	1.0835	1.0677				
$r(\text{C}-\text{X})$	1.25	1.65	1.27	1.81	1.23	1.63
$r(\text{X}-\text{H}_3)$	0.96	1.36	0.96	1.37	0.96	1.35
$\angle \text{H}_1\text{CH}_2$	122.1	117.3	122.4	117.6	122.4	120.5
$\angle \text{H}_2\text{CX}$	122.2	119.6	—	—	—	—
$\angle \text{CHX}_3$	124.7	100.9	124.7	96.2	180	180
$E$	-113.97905	-436.27448	-113.94325	-436.21639	-113.95671	-436.16782

\*See text.

reported here for this species. The computed geometrical parameters of structure 5 in the two cases are summarized in Table 2. In both protonated systems



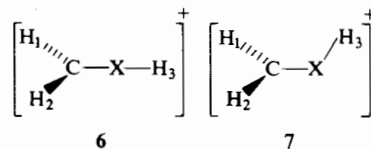
the C—X bonds are longer than those of the parent molecules 3 (0.04 and 0.02 Å for X = O and X = S, respectively). However, these bond lengths are substantially shorter than those of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{SH}$  (1.428 and 1.819 Å, respectively (17)), so that significant double bond character remains following protonation.

The  $\text{H}_2\text{CX}$  and  $\text{CXH}_3$  bond angles (see Table 2) are of some interest, and have important consequences for the mechanisms of geometrical isomerization of the two species. Compared to  $\text{CH}_3\text{OH}$ , whose COH angle is 105.9° (17),  $\text{CH}_2\text{OH}^+$  has a COH angle of 124.76°. In contrast, the CSH angle of  $\text{CH}_2\text{SH}^+$  is only 4.4° larger than that of  $\text{CH}_3\text{SH}$  (17). We suggest that the origin of this large COH bond angle is the small (2.07 Å) internuclear separation that would

otherwise have been present between  $\text{H}_2$  and  $\text{H}_3$ . The movement of these nuclei away from each other leads to an opening not only of the COH angle but also of the  $\text{H}_2\text{CO}$  angle which is now greater than 120°. The  $\text{H}_2\text{CS}$  angle in  $\text{CH}_2\text{SH}^+$  is less than 120°.

#### Geometrical Isomerization of $\text{CH}_2\text{OH}^+$ and $\text{CH}_2\text{SH}^+$ SCF Computations

As pointed out by others (11a, b), two mechanisms are possible for the geometrical isomerization of a species such as 4. In the first, the transition state has the structure 6, and the process may be termed "linear inversion" (18). In the second, the transition state has the structure 7, and the process is one of torsion along the C—X bond.



Linear inversion in  $\text{CH}_2\text{OH}^+$  was studied by computation of the total energy as a function of  $\theta = \angle \text{COH}$ ; at  $\theta = 124.76^\circ$  (the energy minimum) and  $\theta = 180^\circ$  (the transition state) the geometry was optimized with respect to the CO

and OH bond lengths and the HCH angle. The results of these calculations are found in the first and fifth columns of Table 2, and they give a value of the barrier to linear inversion of 13.98 kcal/mol. Linear inversion in  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  was studied in the same way, and the results for  $\theta = 100.9^\circ$  (the energy minimum) and  $\theta = 180^\circ$  (the transition state) are collected in the second and sixth columns of Table 2. The barrier to linear inversion in this case is 66.95 kcal/mol. It will be noted that, in both cations, the optimized CX bond length in the transition state for linear inversion is slightly shorter than that of  $\text{CH}_2\text{X}$ .

The barriers to linear inversion in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  are 26.4 and 37.0 kcal/mol, respectively (19). The simplest interpretation of this difference is that the bond angle of  $\text{H}_2\text{O}$  changes from  $105$  to  $180^\circ$  but that of  $\text{H}_2\text{S}$  changes from  $96.4$  to  $180^\circ$ . On this basis, the substantial decrease in the barrier to linear inversion at oxygen on going from  $\text{H}_2\text{O}$  to  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  is a direct consequence of the geometry relaxation in the ground state of the latter species, already discussed.

We were unable to compute an accurate value for the rotational barrier of  $\overset{+}{\text{C}}\text{H}_2\text{OH}$ . Optimization of the molecular geometry as a function of the dihedral angle  $\phi$  between the HCH and COH planes led to a COH angle of  $180^\circ$  for  $\phi = 90^\circ$ . This means that the rotation is disfavored with respect to linear inversion. An approximate value of the rotational barrier of 23 kcal/mol was obtained (*cf.* Table 2, columns one and three) by maintaining the COH angle at  $124.76^\circ$ , the same value as in the planar conformation. Our results parallel those of Ros (11*a*), in whose study of  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  rotation was found to be disfavored with respect to linear inversion with a rigid rotor model, and those of Lehn *et al.* (11*b*), who found linear inversion to be the favored process in  $\text{CH}_2=\text{NH}$  and  $\text{CH}_2=\text{CH}^-$ .

In contrast, rotation is the favored process in  $\overset{+}{\text{C}}\text{H}_2\text{SH}$ . Table 2, column 4 lists the optimized geometry and energy of the transition state (7) for this process, from which the barrier is computed to be 36.47 kcal/mol. Two features of the geometry of this transition state are of interest: the C—S bond length is now 1.81 Å indicating that conjugation between carbon and sulfur has been completely destroyed; and the angle between the HCH plane and the CS bond is not zero, so that attachment of a nonconjugating SH ligand to the carbonium ion makes this center

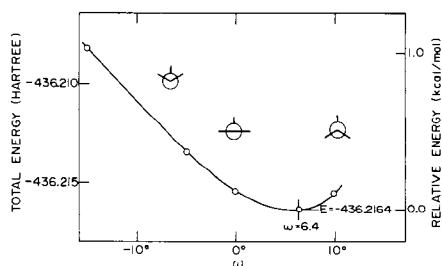
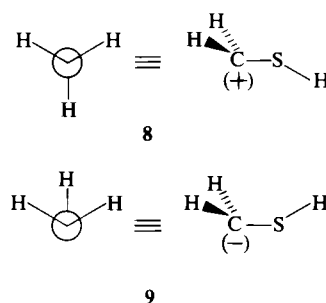


FIG. 1. The total energy of 7 ( $\text{X} = \text{S}$ ) as a function of  $\omega$ , the angle between the HCH plane and the C—S bond.

nonplanar. Figure 1 displays the total energy of 7 ( $\text{X} = \text{S}$ ) as a function of the angle  $\omega$  between the HCH plane and the CS bond, from which it is evident that, in this rotational conformation, the cation adopts the Y conformation 8, in contrast to the corresponding anion, which adopts the W conformation 9 (8).



For the analysis of effects such as the relative stabilities of Y and W conformations, it is useful to consider the relative contributions to the total energy of nuclear and electronic effects (8, 20–22). When electronic effects dominate, the more crowded conformation (W in this case) is the more stable. On this basis, the greater stability of the W conformation in the case of the anion 9 is the result of the increased electronic interactions associated with the additional electron pair.

#### A Configuration Interaction Study

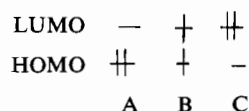
Closed shell restricted Hartree–Fock theory is sometimes unable to provide accurate results because of the overrestrictive nature of the wavefunction. Thus, in the computation of rotational barriers about a bond containing a significant amount of double bond character, a single determinantal approach may not be sufficient (23*a*). For example, in the computation of the rotational barrier of ethylene, unacceptably high values are obtained from a single determinantal

TABLE 3. Total energies (a.u.) computed with a single determinantal (SCF) approach and with a CI procedure for  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  in conformation 7 at different C—S bond lengths

Bond length (Å)	$E_{\text{SCF}}$	$E_{\text{CI}}$	CI eigenvectors
1.70	-436.21147	-436.21150	0.9999 $0.86 \times 10^{-18}$ $-0.7476 \times 10^2$
1.75	-436.21499	-436.21501	0.9999 $0.85 \times 10^{-18}$ $0.6124 \times 10^{-2}$
1.8136	-436.21639	-436.21640	0.9999 $0.81 \times 10^{-18}$ $-0.4755 \times 10^{-2}$

approach, but the inclusion of one additional configuration is sufficient to afford much improved results (23b).

Since the results just described, of rotation in  $\overset{+}{\text{C}}\text{H}_2\text{SH}$ , are highly significant if correct, it seemed desirable to check the role of configuration interaction. The rotational barrier was, therefore, recomputed using a limited CI procedure.<sup>2</sup> The configurations taken into account are the three illustrated in the following Scheme 1, where HOMO refers to the highest occupied molecular orbital, and LUMO to the lowest unoccupied molecular orbital obtained in the single determinant SCF calculation.



SCHEME 1

The CI energy of 7 (X = S) was computed by solving a  $3 \times 3$  secular determinant at three C—S bond lengths: 1.6, 1.7, and 1.8136 Å, the latter corresponding to the optimized value afforded by the single determinantal approach. The results of this study are shown in Table 3. They reveal that the CI procedure does not change the energy of 7 significantly as compared to the value computed by the single determinantal approach. In addition, the eigenvectors show that the ground electronic configuration predominates. This suggests that a single configuration SCF wavefunction can be used with confidence to study rotation along a polarized bond such as C—O and C—S, even when this bond has appreciable double bond character.

<sup>2</sup>We thank Professor W. J. Hehre for providing us with the program.

The higher rotational barrier in  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  therefore seems to be real. Since as noted above,  $\pi$ -conjugation between carbon and sulfur is completely destroyed during rotation, we must conclude that  $\pi$ -conjugation in  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  is greater than in  $\overset{+}{\text{C}}\text{H}_2\text{OH}$ . Quantitative support for this interpretation is provided by the Mulliken-type population analysis, discussed later.

#### The Rotation—Linear Inversion Surfaces of $\overset{+}{\text{C}}\text{H}_2\text{OH}$ and $\overset{+}{\text{C}}\text{H}_2\text{SH}$

The dynamic properties of the two cations can be represented conveniently in the form of rotation-inversion surfaces. Equations for such surfaces were obtained by "least squares" fittings of the expression.

$$[5] \quad E = E_0 + C_1\phi^2 + C_2\phi^4 + C_3\phi^2 \cos 2\theta + C_4\phi^4 \cos 2\theta$$

to the SCF computed energies of a number of conformations. The inversion coordinate  $\phi$  and the rotation coordinate  $\theta$  are as defined previously. The energies of the conformations used in the fitting procedure are summarized in Table 4. Each of the entries in Table 4 has been fully optimized with respect to geometrical parameters other than rotation and inversion. The constants for eq. 5 are given in Table 5.

Plots of the surfaces are shown in Figs. 2 and 3. In both cations, the inversion process is energetically allowed, as indicated by paths A in the figures, and proceeds via the linear transition state. However, in the sulfur cation, an alternate isomerization mechanism is favored. Path B of Fig. 3 shows that rotation is the lower energy process. As indicated by the broken path in Fig. 2, a similar rotation in protonated formaldehyde is energetically not allowed, because any attempt to rotate  $\text{H}_3$  about the C=O axis

TABLE 4. Data employed for the computation of the rotation - linear inversion surfaces of  $\overset{\oplus}{\text{C}}\text{H}_2\text{OH}$  and  $\overset{\oplus}{\text{C}}\text{H}_2\text{SH}$ 

Cation	Rotation (deg)	Inversion (deg)	Energy (a.u.)
$\overset{\oplus}{\text{C}}\text{H}_2\text{OH}$	0	0	-113.956707
	0	56.46	-113.979014
	0	66.00	-113.976466
	90	32.04	-113.953336
	90	40.48	-113.950638
$\overset{\oplus}{\text{C}}\text{H}_2\text{SH}$	0	0	-436.167817
	0	79.02	-436.274482
	0	82.56	-436.273962
	90	83.83	-436.216389
	90	86.83	-436.215939
	0	76.56	-436.274234

TABLE 5. Parameters of the rotation - linear inversion surfaces of  $\overset{\oplus}{\text{C}}\text{H}_2\text{OH}$  and  $\overset{\oplus}{\text{C}}\text{H}_2\text{SH}$ 

Parameter	$\overset{\oplus}{\text{C}}\text{H}_2\text{OH}$	$\overset{\oplus}{\text{C}}\text{H}_2\text{SH}$
$E_0$	-113.956518	-436.167818
$C_1$	-0.021762	-0.078980
$C_2$	0.022422	0.020098
$C_3$	-0.023077	-0.032452
$C_4$	—	0.008962

results in a path proceeding through the linear transition state, as shown by path *B* of Fig. 2. Since the endpoints of paths *A* and *B* are identical ( $\text{H}_3$  *anti* to  $\text{H}_1$ ), these paths are indistinguishable experimentally. Hence, inversion is the only energetically allowed mechanism of geometrical isomerization in protonated formaldehyde, whereas both rotation and inversion are allowed in protonated thioformaldehyde, with rotation being the favored process.

#### Proton Affinities of $\overset{\oplus}{\text{C}}\text{H}_2\text{O}$ and $\overset{\oplus}{\text{C}}\text{H}_2\text{S}$

In the quantum mechanical convention, proton affinity is defined as the difference between the energies of the protonated ( $\text{MH}^+$ ) and deprotonated (*M*) species (eq. 6), since the energy of the proton is zero, by definition. This value is also a measure of the gas phase

$$[6] \quad \text{p.a.}(M) = E(\text{MH}^+) - E(M)$$

basicity of the species *M* and the gas phase acidity of the species  $\text{MH}^+$ . The proton affinity values computed for formaldehyde and thioformaldehyde are shown in Table 6. The two values are of the same order of magnitude, with that of formaldehyde slightly greater.

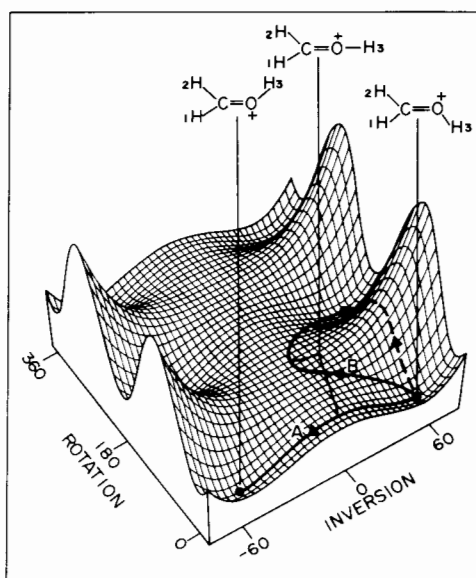


FIG. 2. The rotation-linear inversion surface of  $\overset{\oplus}{\text{C}}\text{H}_2\text{OH}$ .

#### Mulliken Population Analyses of 3 and 4

Table 7 summarizes the net atomic charges and gross orbital populations of the valence orbitals of  $\overset{\oplus}{\text{C}}\text{H}_2\text{O}$  and  $\overset{\oplus}{\text{C}}\text{H}_2\text{S}$ . Table 8 lists the same data for  $\overset{\oplus}{\text{C}}\text{H}_2\text{OH}$  and  $\overset{\oplus}{\text{C}}\text{H}_2\text{SH}$ .

The two parent molecules have opposite charge distributions. In formaldehyde the methylene group has a net charge of +0.51 electron, and in thioformaldehyde the net charge of this group is -0.08 electron. Alternatively, we may state that oxygen is strongly negative in formaldehyde, but sulfur is slightly positive in thioformaldehyde. Inspection of the data of

TABLE 6. Computed proton affinities (p.a.) of  $\text{CH}_2\text{O}$  and  $\text{CH}_2\text{S}$ 

	Total energy (a.u.)	Proton affinity (kcal/mol)
$\text{CH}_2\text{O}$	-113.69252	-179.86 (-161 $\pm$ 3)*
$^+\text{CH}_2\text{OH}$	-113.97905	—
$\text{CH}_2\text{S}$	-435.99186	-177.4
$^+\text{CH}_2\text{SH}$	-436.27448	—

\*Experimental value.

TABLE 7. Net atomic charges ( $q$ ) and gross orbital populations of the valence atomic orbitals for  $\text{CH}_2\text{O}$  and  $\text{CH}_2\text{S}$ \*

	$\text{CH}_2\text{O}$			$\text{CH}_2\text{S}$		
	H	C	O	H	C	S
$q$	+0.16	+0.17	-0.49	+0.22	-0.52	+0.08
$s$	0.84	1.22	1.96	0.78	1.42	1.89
$p_x$	—	1.10	1.90	—	1.19	1.97
$p_y$	—	0.73	1.27	—	0.83	1.20
$p_z$	—	0.79	1.36	—	1.08	0.93

\*The coordinate system is

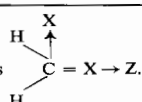
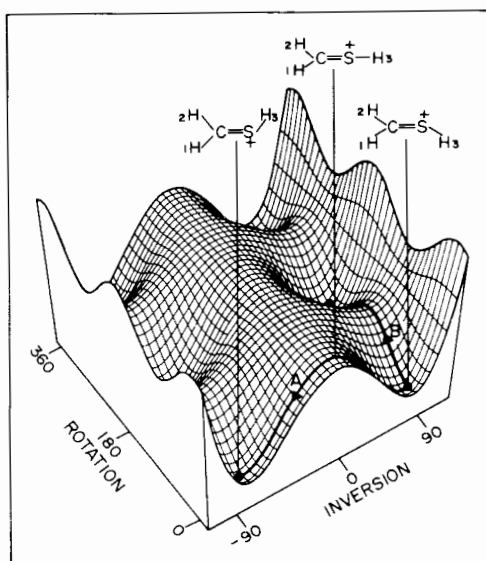

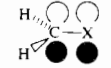


† FIG. 3. The rotation-linear inversion surface of  $\text{CH}_2\text{SH}$ .

Table 7 reveals that oxygen in formaldehyde behaves as a  $\pi$  and a  $\sigma$  acceptor towards carbon, but in thioformaldehyde sulfur behaves as a  $\pi$  acceptor and a  $\sigma$  donor.

Both molecules belong to the  $C_{2v}$  symmetry point group. If we define two reference planes,

one of which is the plane of the molecule and the other is perpendicular and bisects the HCH angle, then two types of  $\pi$  molecular orbitals can be distinguished, as shown below.

Structure	Orbital symmetry type	Orbital energy	
		X = O	X = S
	$b_1$	-0.4421	-0.3461
	$b_2$	-0.5283	-0.4062
	$b_1$	-0.7064	-0.6466

In terms of this representation, the total  $\pi$ -overlap population in formaldehyde is 0.2357 (0.2149 from  $b_1$  and 0.0208 from  $b_2$ ); and in thioformaldehyde it is 0.2257 (0.2119 from  $b_1$  and 0.0138 from  $b_2$ ), so that  $\pi$ -bonding between carbon and oxygen is slightly stronger than  $\pi$ -bonding between carbon and sulfur.

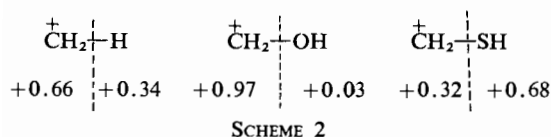
The situation is different in the protonated species. Scheme 2 displays the charge on the methylene group in  $\text{CH}_3^+$ ,  $\text{CH}_2\text{OH}^+$ , and  $\text{CH}_2\text{SH}^+$ .



TABLE 8. Net atomic charges ( $q$ ) and gross orbital populations of the valence atomic orbitals for  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  and  $\overset{+}{\text{C}}\text{H}_2\text{SH}^*$ 

	$\overset{+}{\text{C}}\text{H}_2\text{OH}$					$\overset{+}{\text{C}}\text{H}_2\text{SH}$				
	H <sub>1</sub>	H <sub>2</sub>	C	O	H <sub>3</sub>	H <sub>1</sub>	H <sub>2</sub>	C	S	H <sub>3</sub>
$q$	+0.35	+0.33	+0.31	-0.53	+0.54	+0.36	+0.35	-0.39	+0.45	+0.23
s	0.65	0.67	1.31	1.88	0.46	0.64	0.65	1.47	1.87	0.77
p <sub>x</sub>			0.37	1.63				0.53	1.50	
p <sub>y</sub>			1.29	1.69				1.34	1.32	
p <sub>z</sub>			0.71	1.33				1.05	0.04	

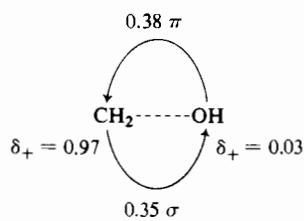
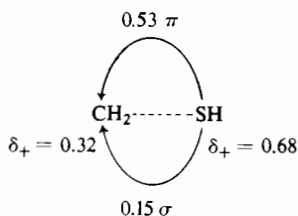
\*The coordinate system is  $\text{H}_1 \cdots \overset{+}{\text{C}} \cdots \text{X} \cdots \text{Z}$ .



With respect to hydrogen we see that OH behaves towards  $\overset{+}{\text{C}}\text{H}_2$  as an electron-withdrawing ligand by 0.31 electron, but SH behaves as an electron-releasing ligand by 0.34 electron.

Perhaps the most informative way to discuss the population analyses of these protonated species is to consider the interaction of the two fragments  $\overset{+}{\text{C}}\text{H}_2$  and XH. Reference to the p<sub>x</sub> and p<sub>z</sub> overlap populations listed in Table 6 shows that, if  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  is considered to be formed by the combination of the fragments  $\overset{+}{\text{C}}\text{H}_2$  and OH,  $\pi$ -donation from oxygen amounts to 0.38 electron. This corresponds to a charge transfer from the 2p<sub>x</sub> oxygen lone pair to the vacant  $\pi$  orbital of  $\overset{+}{\text{C}}\text{H}_2$ , with the consequent formation of a relatively strong  $\pi$  bond between C and O. The  $\pi$ -overlap population is now 0.1496, less than that in  $\overset{+}{\text{C}}\text{H}_2\text{O}$ , so that the C—O bond in  $\overset{+}{\text{C}}\text{H}_2\text{OH}$  is longer than that in  $\text{CH}_2\text{O}$ . As shown in **10**, the  $\pi$ -donation of 0.38 electron from O to C must be counterbalanced by a  $\sigma$ -donation from C to O of 0.35 in order to account for the total charge distribution  $\delta_+$ .

In  $\overset{+}{\text{C}}\text{H}_2\text{SH}$ , a similar analysis reveals that  $\pi$ -donation from S to C amounts to 0.53 electron and that  $\sigma$ -donation from S to C amounts to an additional 0.15 electron. These are shown schematically in **11**. The important finding is that the  $\pi$ -donation from S to C (0.53 electron) is greater than that from O to C (0.38 electron).

**10****11**

The  $\pi$ -overlap population in  $\overset{+}{\text{C}}\text{H}_2\text{SH}$  is, therefore, also larger (0.1734), indicating a stronger  $\pi$ -bond between C and S than between C and O.

These analyses are thus in agreement with the interpretations given earlier of the rotational barriers. We must conclude that, in contrast to the current view of the nature of the interactions between first row and second row heteroatoms and an adjacent carbonium ion center,  $\pi$ -conjugative effects are greater for the second row atom. This result can be rationalized in terms of the interaction between the 2p<sub>x</sub> heteroatom lone pair and the vacant carbon 2p<sub>x</sub> orbital. The charge transfer associated with such an interaction is inversely proportional to the energy difference between the interacting orbitals so that greater stabilization is afforded by a sulfur lone pair than by an oxygen lone pair, because

the ionization potential of a second row atom is always less than that of the corresponding first row atom (e.g. ref. 24:  $\text{H}_2\text{O}$ , 12.61 eV;  $\text{H}_2\text{S}$ , 10.48 eV). A detailed account of this rationalization is presented elsewhere (25).

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