Theor Chem Acc (1999) 101:388–395
DOI 10.1007/s00214990m183

Theoretical
Chemistry Accounts

Regular article

Gas-phase properties and Fukui indices of sulfine (CH_2SO). Potential energy surface and maximum hardness principle for its protonation process. A density functional study

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Received: 12 October 1998 / Accepted: 24 November 1998 /

Abstract. Gas-phase thermochemical properties of sulfine (CH_2SO) and the potential energy surface of its protonation process were studied by the density functional method employing different exchange-correlation potentials. All calculations showed that the most stable protonated isomer is planar with the proton bonded to the oxygen atom in a trans arrangement of the skeleton. Three transition states were located that allow interconversion between the different isomers. Hardnesses and Fukui indices were calculated to follow the reactivity trend along the protonation path and to explain the preference for a particular protonation site on neutral sulfine. Proton affinity, gas-phase basicity and heat of formation values, obtained for the first time fully quantum mechanically, agree well with those derived by a recent mass spectrometry experimental study. Good agreement between density functional theory and previous high-level theoretical and experimental data was also found for the heat of formation of sulfine and its most stable protonated form.

Key words: Thermochemical properties – Reactivity indices – Maximum hardness principle – Potential energy surface – Density functional theory

1 Introduction

Sulfines (thiocarbonyl S-oxides, $R_1R_2C{=}S{=}O$) and related compounds are a class of important organic systems and occur naturally in garlic and onions [1]. Many sulfines have been prepared and most of them appear to be stable species [2]. The simplest molecule of this class, thioformaldehyde S-oxide (CH_2SO), was obtained in the gas-phase by flash vacuum pyrolysis of 1,3-dithiethane 1-oxide and was characterized by microwave [3] and photoelectron [4] spectroscopy; however, due its short life-time, most of its thermochemical and spectroscopic properties are not known. This is the reason for the current experimental interest. Benson [5] estimated the sulfine heat of formation (ΔH_f°) to be -51 ± 22 kJ/mol. A recent Fourier transform-ion cyclotron resonance (FT-ICR) experiment, on the basis of the ΔH_f° of CH_2SOH^+, proposed a new value of -8 ± 10 kJ/mol at 298 K [6]. A similar value was obtained theoretically at the CAS-SDCI level (-9 ± 14 kJ/mol at 298 K) while standard G2 and G2(MP2) calculations gave -18 and -30 kJ/mol, respectively, at 0 K [7]. Improvement of the basis set in the G2(MP2) procedure reduces the value to -2 kJ/mol [7].

In principle neutral sulfine can be protonated at carbon, oxygen and sulfur, but its protonation process is still the subject of controversy. From a mass spectrometry measurement it was proposed that the dimethyl sulfoxide (DMSO) radical cation cleaves off CH_3 to produce the CH_3SO^+ sulfinyl cation [8]. Subsequently, different ab initio computations [7, 9] demonstrated that the measured appearance energy for the loss of CH_3 from DMSO [10, 11] does not correspond to the sulfinyl but rather to the oxygen protonated cation (CH_2SOH^+). This isomer was found to be more stable than that protonated on the carbon in several ab initio studies employing different levels of theory [7, 9, 10, 12].

Proton affinity (PA) and gas-phase basicity (GB) were first obtained through an FT-ICR experiment [6]. The suggested values are PA = 786 kJ/mol and GB = 758 kJ/mol [6]. Ruttink et al. [7] derived a theoretical CAS-SDCI PA of 787 kJ/mol at 298 K, using the calculated (ΔH_f°) for $CH_2{=}S{=}O$ and the measured heat of formation of the corresponding most stable protonated form (CH_2SOH^+) [11]. Using the value suggested by Lias et al. [13] of -50 ± 21 kJ/mol for the ΔH_f° of neutral sulfine, an MR-SDCI study predicted a PA of 744 kJ/mol [9].

Notwithstanding these studies, no work has been devoted to the characterization of the entire potential

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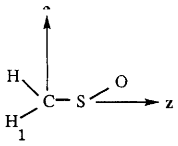
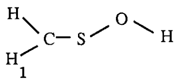


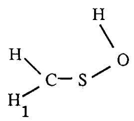
	PWP	B3LYP	EXP
C-H	1.096	(1.081)	[1.081]
C-S	1.645	(1.615)	[1.610]
S-O	1.523	(1.487)	[1.469]
H-C-S	122.5	(123.0)	[122.5]
H_1-C-S	116.5	(115.9)	[115.6]
C-S-O	114.3	(114.5)	[114.7]

1



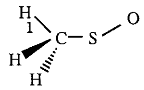
	PWP	B3LYP	MP2
C-H	1.099	(1.085)	1.08
C-S	1.621	(1.597)	1.60
S-O	1.645	(1.604)	1.61
O-H	0.995	(0.975)	0.98
H-C-S	122.2	(123.1)	121.6
H_1-C-S	116.1	(115.6)	/
C-S-O	102.9	(103.8)	102.7
S-O-H	109.8	(111.0)	110.7

2



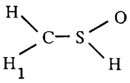
	PWP	B3LYP
C-H	1.099	(1.084)
C-H_1	1.100	(1.087)
C-S	1.623	(1.599)
S-O	1.630	(1.590)
O-H	0.996	(0.975)
H-C-S	125.6	(125.0)
H_1-C-S	114.8	(114.4)
C-S-O	111.9	(111.9)
S-O-H	115.7	(117.4)

3



	PWP	B3LYP	MP2
C-H_1	1.102	(1.088)	1.09
C-H	1.114	(1.101)	/
C-S	1.788	(1.763)	1.76
S-O	1.485	(1.448)	1.49
H-C-S	106.9	(106.2)	/
H_1-C-S	111.5	(111.4)	110.7
C-S-O	109.4	(109.9)	108.9

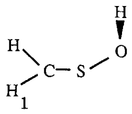
4



	PWP	B3LYP
C-H	1.097	(1.084)
C-H_1	1.098	(1.085)
C-S	1.615	(1.590)
S-O	1.478	(1.444)
S-H	1.378	(1.363)
H-C-S	119.9	(120.4)
H_1-C-S	116.1	(115.8)
C-S-O	132.1	(131.4)
C-S-H	110.2	(110.9)

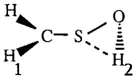
a

TS1



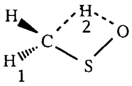
	PWP	B3LYP
C-H	1.100	(1.085)
C-H_1	1.100	(1.087)
C-S	1.629	(1.607)
S-O	1.641	(1.601)
O-H	0.996	(0.978)
H-C-S	122.9	(123.9)
H_1-C-S	116.9	(108.5)
C-S-O	107.9	(108.5)
S-O-H	114.1	(115.2)
H-O-S-C	73.3	(69.9

TS3



	PWP	B3LYP
C-H	1.101	(1.087)
C-S	1.674	(1.641)
S-O	1.585	(1.536)
S-H_2	1.434	(1.429)
O-H_2	1.658	(1.629)
H-C-S	121.2	(121.7)
H_1-C-S	116.0	(116.0)
C-S-O	117.3	(118.3)
C-S-H_2	114.5	(114.7)
S-O-H_2	52.4	(51.8)
H-C-S-O	-19.4	(-20.1)
C-S-O-H	75.7	(75.6)

TS2



	PWP	B3LYP	MP2
C-H	1.116	(1.104)	/
C-H_1	1.100	(1.085)	1.08
C-H_2	1.462	(1.438)	1.44
C-S	1.694	(1.661)	1.64
S-O	1.575	(1.524)	1.48
O-H_2	1.423	(1.421)	1.39
H-C-S	112.5	(112.8)	/
H_1-C-S	122.7	(123.7)	123.1
C-S-O	92.3	(94.9)	94.9
S-O-H_2	81.0	(79.0)	80.6
H-C-S-O	66.0	(60.7)	/
H1-C-S-O	-31.0	(-30.0)	/
C-S-O-H_2	7.4	(8.0)	/

b

Fig. 1. **a** Labels and geometrical parameters of neutral sulfine and its protonated isomers. Distances are in Å and angles in degrees. **b** Labels and geometrical parameters of transition states connecting the protonated isomers of sulfine. Distances are in Å and angles in degrees

energy surface (PES) for the protonation process of sulfine. Previous ab initio calculations were carried out especially on isomers **1** and **3** (see Fig. 1a). Gozzo and Eberlin [10] also studied isomer **4** and the transition state for going from **1** to **3** at MP2 and G2 levels of theory.

In this study we analyze the PES for the sulfine protonation process including the most stable minima and the transition states connecting one isomer to another.

Fukui indices are calculated in order to identify the preferred site for the attachment of the proton on the neutral species. In order to verify the maximum hardness principle, global hardness were computed along the reaction path governing protonation.

Because of the increasing interest of the scientific community in density-functional-based methods [14, 15] we have undertaken a systematic study employing some of the most used exchange-correlation functionals including those derived by the generalized gradient approximation [16–21] and one of the so-called "hybrid" [22, 23] functionals in which a fixed amount of Hartree–Fock exchange is included.

The main goal of this paper is to provide further insight into the physico-chemical properties of sulfine and of its protonated forms through the determination of reactivity indices. Another aim is to test the reliability of density functional methods in the study of these charged systems in view of their possible use for larger molecular systems for which traditional ab initio methods, including correlation energy, become computationally prohibitive.

2 Method

All calculations were carried out using the GAUSSIAN 94 [24] and a modified version of the deMon [25] codes. Full geometry optimization of sulfine and its protonated minima was performed using the following local, gradient-corrected and hybrid functionals:

Vosko-Wilk and Nusair [26] (VWN),
Perdew and Wang [16] and Perdew [17] (PWP),
Becke [18] and Perdew [17] (BP),
Perdew [19] and Perdew [20] (PP91),
Becke [18] and Proynov [21] (BPROY),
Becke3-Lee Yang and Parr [22, 23] (B3LYP).

As is customary, in the above list, the first term of each model represents the exchange functional and the second term its correlation counterpart.

In addition these species were optimized at the Møller–Plesset second-order perturbation [MP2/6-31G(d)] level. QCISD(T)/6-31G(d,p) single-point computations were also carried out at the MP2/6-31G(d,p) optimized geometry.

Triple-zeta orbital and the corresponding auxiliary basis sets were employed in the case of all local and gradient-corrected computations [27] whilst the internal 6-31G(d,p) [28], 6-311++G(d,p) [28, 29] and aug-cc-PVTZ [30] basis sets were employed for the B3LYP ones.

Transition states and vibrational analysis were respectively located and computed at PWP/TZVP, B3LYP/6-31G(d,p) and B3LYP/aug-cc-PVTZ levels of theory. Transition states at the PWP level were determined by the Abaskhin and Russo [31] algorithm.

Harmonic frequencies (v_i) computed at the above levels were used directly without any scaling factor.

The PA was obtained as the negative of the variation of the enthalpy for the reaction

$$\mathrm{A} + \mathrm{H}^+ \rightarrow \mathrm{AH}^+ \ .$$

ΔH_T^0 was computed as

$$\Delta H_{298}^0 = \Delta E_{\mathrm{SCF}} + RT + \Delta(\mathrm{ZPE}) + \frac{3}{2}RT + \Delta\left(\sum_i \frac{hv_i \exp(-hv_i/kT)}{1-\exp(-hv_i/kT)}\right) \ , \qquad (1)$$

where ΔE_{SCF} is the variation in internal energy which arises directly from the self-consistent field (SCF) procedure, RT substitutes the $\Delta(PV)$ term necessary to convert internal energy into enthalpy (if reagents and products can be considered as ideal gases), and Δ(ZPE) is the variation in zero-point vibration energies derived by computed harmonic frequencies.

The changes in the population of the vibrational states, occurring when the system is brought from 0 K to room temperature, are evalued through the last term of ΔH_{298}^0 (Eq. 1). The remaining corrections due to translation and rotation were treated classically, using the equipartition theorem. Because the proton has only translational degrees of freedom and considering the quite similar rotational contribution of A and AH$^+$ species it was necessary to add only the $\frac{3}{2}RT$ term.

GB was obtained as the negative of the Gibbs free energy.

The entropic contribution to ΔG_T^0 was calculated as follows:

$$-T\Delta S_T^0 = -T\left[S(\mathrm{AH}^+) - S(\mathrm{A}) - S(\mathrm{H}^+)\right] \ . \qquad (2)$$

The entropies of neutral and protonated systems, in the case of PWP computations, were obtained from thermochemical calculations by using the theoretical harmonic frequencies and the equilibrium geometries, while for the proton entropy we employed the experimental value of 7.76 kcal/mol at 298 K [32].

Heats of formation (ΔH_{f}) for neutral sulfine, $\mathrm{CH_2SOH^+}$ and $\mathrm{CH_3SO^+}$ protonated species were calculated on the basis of the following expression:

$$\sum \Delta H_{\mathrm{f}}(\text{products}) = \sum \Delta H_{\mathrm{f}}(\text{reactants}) - \Delta H_{\mathrm{r}} \ , \qquad (3)$$

where ΔH_{r} represents the heat of the reaction considered.

In density functional theory (DFT) the hardness η can be calculated as the second derivative of the total energy or as the first derivative of the chemical potential μ with respect to the number of electrons N at constant external potential $\upsilon(\mathbf{r})$ [33, 34]. Softness S is defined as the inverse of hardness.

While the chemical potential is constant everywhere within the molecule, the hardness is a function of the position, thus, in addition to the global definition of η, the local hardness η_{ij} [35] and the local softness s_{ij} [36] were introduced. These latter quantities allow the reactivity of specific molecular sites to be studied.

In order to compute local quantities for a particular site in a molecule, an approach based on the Janak theorem [37], in the framework of DFT, allows η_{ij} to be calculated as the first derivative of the Kohn–Sham orbital eigenvalues ε_i with respect to the orbital occupation numbers n_i [38–40]:

$$\eta_{ij} = \frac{\partial \varepsilon_i}{\partial n_j} \ . \qquad (4)$$

Numerically, the derivatives can be computed using the finite difference approximation [41]:

$$\eta_{ij} = \frac{\varepsilon_i(n_j - \Delta n_j) - \varepsilon_i(n_j)}{\Delta n_j} \ . \qquad (5)$$

This expression takes into account the response of the ith orbital to the change in the occupation number of the jth orbital.

The softness matrix is the inverse of the hardness one [39]:

$$[s_{ij}] = [\eta_{ij}]^{-1} \ . \qquad (6)$$

The previous formula holds for a nonsingular η_{ij} matrix.

The total softness S is an additive function [39] approximated by

$$S = \sum_{ij} s_{ij} \ . \qquad (7)$$

Thus the total hardness becomes

$$\eta = \frac{1}{S} = \frac{1}{\sum_{ij} s_{ij}} \ . \qquad (8)$$

Another local quantity which is significant for the reactivity study is the Fukui function defined as follows [39]:

$$f(\mathbf{r}) = \left[\frac{\partial \mu}{\partial \upsilon(\mathbf{r})}\right]_N = \left[\frac{\partial \rho}{\partial N}\right]_\upsilon \ . \qquad (9)$$

$f(\mathbf{r})$ involves the electron density ρ of the atom or molecule in proximity of its frontier orbitals [39]. This function measures how the chemical potential μ reacts to an external perturbation (variation of electron number) of the system.

The approximation to the Fukui function is computed in the following way:

$$f_i = \frac{\partial n_i}{\partial N} = \frac{\Delta n_i}{\Delta N} = \left(\frac{\partial n_i}{\partial \mu}\right)\left(\frac{\partial \mu}{\partial N}\right) = \eta \sum_j s_{ij} \ , \qquad (10)$$

with $\sum_i f_i = 1$.

Thus, the change in the number of electrons (ΔN) implies the occurrence of the so-called reactivity indices f_i and s_{ij}, which indicate the preference of the reagent for a particular molecular site.

The chemical potential is related to the Fukui indices by the expression

$$\mu = -\sum_i \varepsilon_i f_i \ , \qquad (11)$$

in which ε_i are the Kohn–Sham orbital energies.

The η value is directly related to the system stability and the softness is associated with the reactivity indices [39, 42]. Then, for Pearson's principle [43] of maximum hardness, η values along the reaction path should be maxima in correspondence of energy minima and vice versa. The principle holds only if the chemical potential μ is kept constant through the whole reaction path [34].

The calculations of the hardness matrix elements and, consequently, of the absolute hardness values were carried out by taking into account the occupied valence orbitals, the LUMO and varying the occupation numbers n_i by 0.1.

3 Results and discussion

3.1 Geometrical parameters

As a first step, we performed a search of the stationary points on the PES for the protonation process of sulfine. Geometry optimizations at all theoretical levels specified in the preceding section were followed by PWP/TZVP, B3LYP/6-31(d,p) and B3LYP/aug-cc-PVTZ vibrational analyses to identify minima and transition states on the PES.

In Fig. 1 we show the two most significant complete sets of equilibrium geometrical parameters for neutral, protonated forms and transition states of sulfine.

In agreement with experimental determinations [3, 4], CH_2SO was found to be planar both at PWP/TZVP and B3LYP/aug-cc-PVTZ levels as well as in all other computations. Bond lengths and valence angles computed by different methods are similar, but B3LYP values are closer to experimental data.

The PWP calculation overestimates C—S and S—O distances; however, the error is not due to the use of this particular exchange-correlation potential, because all other gradient corrected functionals give almost the same values for these same parameters. VWN local computation yields, instead, two better values [1.621 Å for C—S and 1.498 Å for S—O). This fact suggests that the correlation contribution in the gradient-corrected computations improves, generally, the energy values but does not have the same positive effect on the geometrical parameters. The present hypothesis is similar to that advanced by Ruttink et al. [9] to justify the same discrepancy, in CH_2SOH^+, between RHF and CASSCF calculations, although, in their case, the dependence of the results on the basis set must be considered.

PWP and B3LYP/aug-cc-PVTZ dipole moments for neutral sulfine are 3.287 and 3.238 D, respectively; the experimental value is 2.99 D [6].

For the **1**, **2**, **3** and **4** protonated forms (Fig. 1a) and the **TS1**, **TS2** and **TS3** transition states (Fig. 1b), the largest differences between PWP and B3LYP calculations occur again for C—S and S—O bond lengths, but the spatial disposition is essentially the same in the two methods as confirmed by valence and torsional angle values.

3.2 Potential energy surface

The relative stabilities of the sulfine protonated isomers and of the transition states connecting them are reported in Table 1 together with previous theoretical data [10]. The PWP/TZVP and B3LYP/aug-cc-PVTZ protonation paths are compared in Fig. 2.

All computations indicate that isomer **1** is the most stable followed by isomers **2**, **3** and **4**. The stabilization effect on the carbenium ion due to the electron-donating S—O—H group accounts well for the preference for the oxygen protonation site.

Despite the stability order being the same, differences are evident in the relative energy values provided by the different methods. Comparison of our data with the available G2 results seems to indicate that B3LYP sets of values are more reliable than PWP ones, but are still underestimated in the case of the **TS2** species.

All the methods agree in suggesting that only the isomerization process **1** → **2** is relatively easy, because in this case a small barrier of 15.6–19.5 kJ/mol must be overcome: the interconversion **1** → **2** occurs through a simple rotation around the O—H bond. An imaginary frequency of $-321\,\mathrm{cm}^{-1}$ (PWP/TZVP) and $260\,\mathrm{cm}^{-1}$ [B3LYP/6-31G(d,p)] is associated with this vibrational mode.

In contrast, the 1,2 and 1,3 shifts needed to go from isomer **1** to **4** and from isomer **2** to **3**, respectively, are much less probable according to all methods considered.

Table 1. Relative energies (kJ/mol) at 0 K of the sulfine protonated isomers and of their connecting transition states

System	PWP/ TZVP	B3LYP/ 6-31G(d,p)	B3LYP/ aug-cc-PVTZ	MP2/ 6-31G(d)[a]	G2/ 631G(d,p)[a]
1[b]	0.0	0.0	0.0	0.0	0.0
2	13.8	14.2	12.8	/	/
3	77.6	93.0	95.5	83.2	93.7
4	197.9	227.5	210.0	217.3	/
TS1	19.5	15.6	16.0	/	/
TS2	292.4	317.6	316.7	311.6	354.4
TS3	342.3	375.6	366.9	/	/

[a] Ref. [10]

[b] Absolute energy values can be found in Table 3

TS2 and **TS3** transition states are characterized by the following imaginary frequencies at PWP/TZVP and B3LYP/6-31G(d,p) levels, respectively: −2196 and −1306 cm^{-1} and −2290 and −1417 cm^{-1}.

The dependence on the basis set in the B3LYP calculations is very small and does not significantly change the energy of the protonation reaction.

3.3 Thermochemical properties

Sulfine is preferentially protonated at the oxygen atom and consequently the determination of its PA as well as its GB involves the CH_2SOH^+(1)/CH_2SO acid/base couple.

The values computed in the present study for the PA and GB of CH_2SO are compared in Table 2 with previous CAS-SDCI [7] and experimental [6] results.

Our best results are those derived by PWP/TZVP and PP91/TZVP gradient-corrected density functional computations. The worse values obtained at the levels BP/TZVP and BPROY/TZVP demonstrate simply that the choice of the exchange-correlation potential is crucial for obtaining reliable information. B3LYP hybrid calculations underline, instead, the importance of the basis sets for reproducing these parameters.

As in the case of the work of Ruttink et al. [7], the MP2/6-31G(d,p) method does not reproduce the experimental structure of neutral sulfine and thus the total energy value, for this species, is unreliable as well as that obtained by single-point QCISD/MP2/6-31G(d,p) [7].

CAS-SDCI/DZ(2df,2d,p) + f(S) [7] PA, although obtained from the calculated ΔH_f of CH_2SO and the experimental ΔH_f of CH_2SOH^+, demonstrates indirectly the accuracy of the theoretical value used. Because the $T\Delta S$ term is practically the same at all levels of theory, the previous discussion on the reliability of the methods remains valid for explaining the GB trend.

The fact that PA and GB values are well reproduced at the PWP level, also revalorizes the PWP relative energies shown in Table 1 with respect to B3LYP ones, because a good theoretical method should treat both neutral and charged systems equally well. If this is true we should expect similar reliability for the data given in Tables 1, 2, but this is not the case for B3LYP results.

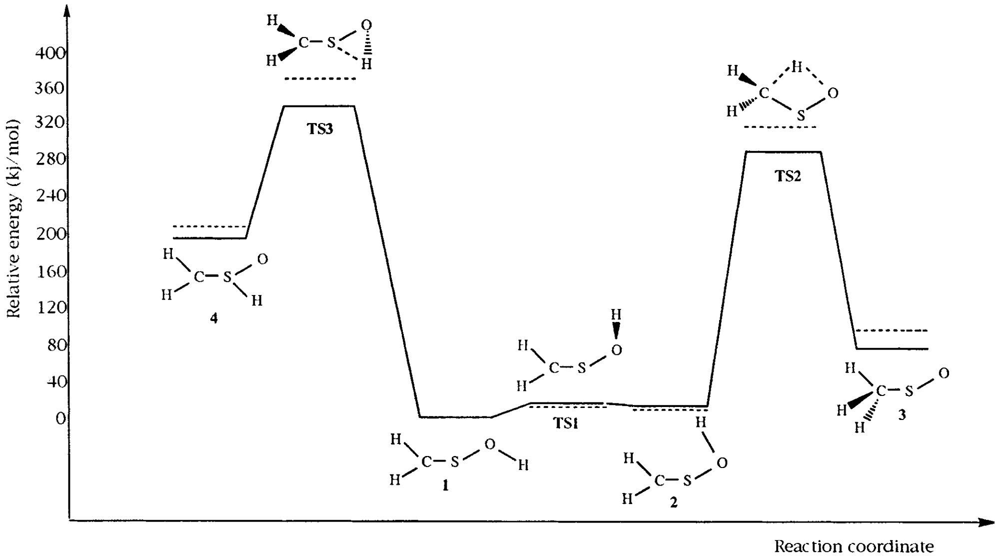


Fig. 2. Potential energy surface for the protonation process of sulfine. *Dashed* and *solid lines* indicate B3LYP and PWP paths respectively

Table 2. Proton affinity (*PA*) and gas-phase basicities (*GB*) (kJ/mol) at 298 K for sulfine at different levels of theory

	PA	ΔZPE	ΔPA	GB	$T\Delta S$	ΔGB
VWN/TZVP	773.9	29.7	−12.1	737.9	36.0	−20.1
PWP/TZVP	785.9	29.7	−0.1	749.9	36.0	−8.1
BP/TZVP	869.6	29.7	83.6	833.6	36.0	75.6
PP91/TZVP	787.5	29.7	1.5	751.5	36.0	−6.5
BPROY/TZVP	882.2	29.7	96.2	846.2	36.0	88.2
B3LYP/6-31G(d,p)	827.3	29.9	41.3	791.7	35.6	33.7
B3LYP/TZVP	811.8	29.7	25.8	775.9	35.9	17.9
B3LYP/TZVP//PWP/TZVP	813.4	29.9	27.4	777.5	35.9	19.5
B3LYP/6-311G + + (d,p)	808.6	29.9	22.6	773.0	35.6	15.0
B3LYP/aug-cc-PVTZ	804.4	29.9	18.4	768.8	35.6	10.8
MP2/6-31G(d,p)	815.8	31.2	29.8	780.3	35.5	22.3
QCISD(T)/6-31G(d,p)//MP2/6-31G(d,p)	839.4	31.2	53.4	803.9	35.5	45.9
CAS-SDCI/DZ(2df,2d,p) + f(S)^a	787.0	/	1.0	/	/	/
EXP^b	786.0	/	/	758.0	28	/

^{a} Ref. [7]
^{b} Ref. [6]

Table 3. Total energy values (a.u.) of sulfine, its $\mathrm{CH_2SOH^+}$ and $\mathrm{CH_3SO^+}$ protonated isomers and some dissociation fragments at different level of theory

System	PWP/TZVP	B3LYP/ 6-31G(d,p)	B3LYP/TZVP	B3LYP/6-311++G(d,p)	B3LYP/aug -cc-PVTZ	MP2/6-31G(d,p)
$\mathrm{CH_2SO}$	−512.949200	−512.653577	−512.705466	−512.718852	−512.752469	−511.779194
$\mathrm{CH_2SOH^+}$ (**1**)	−513.258103	−512.978279	−513.024206	−513.036407	−513.068447	−512.099996
$\mathrm{CH_3SO^+}$ (**3**)	−513.227539	−512.942029	−512.985994	−512.997260	−513.031270	−512.072418
$\mathrm{CH_3^+ + SO^{\cdot\cdot}}$	−513.111086	−512.837162	−512.885327	−512.898002	−512.925504	−511.964809
$\mathrm{CH_3^{\cdot} + SO^{+\cdot}}$	−513.089630	−512.810006	−512.859223	−512.870628	−512.900703	−511.932737

On the other hand, if we take the G2 computations [7] as a reference, we should know how this method reproduces the PA value of neutral sulfine before deciding if relative energy values of sulfine protonated isomers are reliable.

The total energy values for $\mathrm{CH_2SO}$, $\mathrm{CH_2SOH^+}$, $\mathrm{CH_3SO^+}$ and some dissociation fragments are reported in Table 3. These values are used to calculate their ΔH_f for which other theoretical and experimental [5–7] data are available. The ΔH_f obtained are collected in Table 4.

The following most favorable (see Table 3) dissociation processes have been considered for $\mathrm{CH_2SO}$, $\mathrm{CH_2SOH^+}$ and $\mathrm{CH_3SO^+}$ formation, respectively.

$$\mathrm{CH_2SOH^+ \rightarrow CH_2SO + H^+}$$

$$\mathrm{CH_3^+ + SO^{\cdot\cdot} \rightarrow CH_2SOH^+}$$

$$\mathrm{CH_3^+ + SO^{\cdot\cdot} \rightarrow CH_3SO^+}$$

Calculations were performed using the experimental values of $\Delta H_f(\mathrm{H^+}) = 1532$ kJ/mol [13] and $\Delta H_f(\mathrm{CH_3^+ + SO^{\cdot\cdot}}) = 1093$ kJ/mol [13] at 298 K.

The ΔH_f values obtained for the $\mathrm{CH_2SOH^+}$ species are all in reasonable agreement with the experimental result of 736 ± 8 kJ/mol [11] and suggest that the ΔH_f measured for the $[\mathrm{H_3, C, S, O}]^+$ ion generated from ionized DMSO, actually corresponds to isomer **1**. This fact is also confirmed by the much higher values found for the $\mathrm{CH_3SO^+}$ protonated form.

For neutral sulfine only the B3LYP/aug-cc-PVTZ and PWP/TZVP values fall in the ranges proposed by other theoretical and experimental works (-9 ± 14 kJ/mol [7], -8 ± 10 kJ/mol [6] and -51 ± 22 kJ/mol [5]). In particular the PWP/TZVP computation gives a negative value of −30.3 kJ/mol. The data in Table 4 were obtained from the ΔH_f value for the $\mathrm{CH_2SOH^+}$ species and from the heat of reaction $-\Delta H_r = \mathrm{PA(CH_2SO)}$ computed at the same level of theory. Following the same practice of previous theoretical work [7], if the experimental ΔH_f of $\mathrm{CH_2SOH^+}$ is used in the calculation of the ΔH_f of $\mathrm{CH_2\ SO}$, the PWP value becomes −10.1 kJ/mol, in agreement with the most recent experimental estimate of -8 ± 10 kJ/mol [6]. All the other theoretical results remain out of the range of the proposed values and this is also the case for MP2 computations.

This last fact again reflects some problems of the B3LYP and MP2 methods in the treatment of neutral sulfine, but it is also possible that in our calculations the basis set convergence is not reached. This latter conclusion is supported by the work of Bauschlicher et al. [44] on compounds containing sulfur in which the importance of the basis set is widely discussed. On the other hand previous determinations of ΔH_f, performed by density functional methods for a series of neutral species [45, 46], demonstrate that the PWP functional reproduces well this thermochemical parameter.

Table 4. Heats of formation (ΔH_f)(kJ/mol) for sulfine $\mathrm{CH_2SOH^+}$ and $\mathrm{CH_3SO^+}$ protonated forms at different levels of theory. Data are given at 298 K. Data in *parentheses* for $\mathrm{CH_2SO}$ are obtained using the experimental value of ΔH_f of $\mathrm{CH_2SOH^+}$

Method	$\mathrm{CH_2SO}$	$\mathrm{CH_2SOH^+}$(1)	$\mathrm{CH_3SO^+}$(3)
PWP/TZVP	−30.8 (−10.1)	715.3	793.3
B3LYP/6-31G(d,p)	29.2 (31.3)	733.9	827.5
B3LYP/TZVP	19.6 (15.8)	739.8	838.5
B3LYP/ 6-311++G(d,p)	17.7 (12.6)	741.1	842.1
B3LYP/aug -cc-PVTZ	2.2 (8.4)	729.8	825.8
MP2/6-31G(d,p)	19.7 (19.8)	735.9	806.7
Exp	-8 ± 10[a]	736 ± 8[b]	/

[a] Ref. [6]

[b] Ref. [11]

3.4 Reactivity indices

The behavior of neutral sulfine with respect to $\mathrm{H^+}$ electrophilic attachment has been rationalized in terms of the reactivity of the possible protonation sites and has been expressed by the orbital Fukui indices. The computations are performed using the PWP exchange-correlation functional in the deMon code. The values of the Fukui indices for the valence occupied and the lowest unoccupied orbitals, together with the main orbital coefficients from a Mulliken population analysis are collected in Table 5. According to Pearson's hard-soft-acid-base principle [47] in the proton attachment process the hardest orbital would be the most reactive. The hardest orbital is of low polarizability and is associated with the lowest Fukui index. From the results in Table 5 it can be seen that the orbital $15A'$, i.e. the oxygen lone-pair, is characterized by the smallest Fukui index (0.04 eV), followed by the value of 0.19 eV of the $16A''$ orbital (of predominantly C character). This means that the tendency of the oxygen atom to accept $\mathrm{H^+}$ during the electrophilic attachment on sulfine is stronger than that of the carbon atom. The molecular orbitals characterized by large contributions of sulfur have higher values of the Fukui indices. Thus, one can conclude that the protonation should occur preferentially at the oxygen site. The SCF calculations at the different levels of theory presented here confirm that CH_2SOH^+ is the most stable protonated isomer, while the isomers protonated at C and S sites are significantly higher in energy (Fig. 2). The LUMO orbital does not contribute in the protonation process, but from the orbital reactivity analysis ($f_i = 0.08$ eV) one can predict that it should be active in reactions with hard nucleophiles.

The global hardness η and the chemical potential μ values for all minima and transition states along the protonation path of sulfine (Fig. 2) are given in Table 6. Following Pearson's maximum hardness principle [43] the relative stability should correlate with the hardness of the system, i.e. the more stable isomer is hardest. This principle was proved by Chattarraj et al. [48] assuming a constant chemical potential during the reaction. Our calculations of the chemical potential show that μ can be considered constant during the **1** → **2** isomerization. Indeed, in going from species **1** to species **2**, μ varies by only 0.3 eV and the more stable isomer **1** is found to be harder than **2**. The **TS1** species is softer than the two minima. The other two isomerization processes studied **1** → **4** and **1** → **3** are accompanied by more pronounced oscillation of the chemical potential and in fact μ varies by 0.8 and by 1.3 eV, respectively. In these parts of the protonation path the energetically lower isomers **3** and **4** are found to be softer than the transition states **TS2** and **TS3**. The energy and hardness profiles along the reaction coordinate are drawn in Fig. 3. It can be seen that the hardness profile is nearly the perfect mirror image of the energy one for **1** → **2** isomerization, while the locations of the other two local energy maxima do not coincide with those of the local hardness minima.

Thus, the relation between the stability of the species on the PES and their hardness is found to be well respected when the chemical potential does not change.

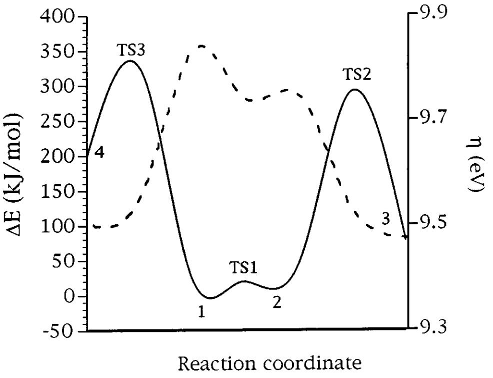


Fig. 3. Comparison between the energy (*solid line*) and hardness (*dashed line*) profiles for the protonation path of sulfine

Table 5. Valence orbital Fukui indices (f_i) for neutral sulfine in eV, orbital energies (ε_i) in eV and main molecular orbital (*MO*) coefficients from Mulliken population analysis. H denotes the HOMO orbital and L the LUMO one

N_{orb}	Sym_{orb}	ε_i	Main MO coefficients	f_i
11	A'	−12.099	p_x(C), s(H) 0.49, 0.32	0.26
12	A'	−11.427	p_x(C), p_z(C), p_z(S) 0.33, 0.23, 0.35	−0.06
13	A''	−10.280	p_y(S), p_y(O) 0.58, 0.32	0.21
14	A'	−9.578	p_x(S), p_x(O) 0.40, 0.37	0.28
15	A'	−6.746	p_x(O), p_z(O) 0.20, 0.53	0.04
16H	A''	−6.709	p_y(C), p_y(O) 0.48, 0.43	0.19
17L	A''	−3.536	p_y(C), p_y(S), p_y(O) 0.44, 0.38, 0.18	0.08

Table 6. Global hardness (η) and chemical potential (μ) values for minima and transition states in the protonation path of sulfine

System	η (eV)	μ (eV)
1	9.834	12.2
2	9.741	12.3
3	9.473	13.6
4	9.499	12.2
TS1	9.736	12.5
TS2	9.522	13.2
TS3	9.561	13.0

4 Conclusions

In this work we have explored the PES for the protonation process for sulfine and computed some of its thermochemical properties for which experimental information was available.

The results concerning the most favorable protonation sites of neutral sulfine and the stability order of protonated isomers and their connecting transition states have been rationalized on the basis of Fukui indices and hardness values.

Our data show that:

1. The geometrical parameters and dipole moment for neutral sulfine obtained by gradient-corrected or hybrid potentials are similar and are close to experimental values.
2. All computations give the same stability for the protonated isomers although the relative energy values are different.
3. Experimental PA and GB are better reproduced by PWP and PP91 gradient-corrected potentials.
4. All methods give accurate values of ΔH_f for the most stable protonated isomer, but only PWP computations seem to be able to yield a good value of this quantity for neutral sulfine.
5. PA, GB and ΔH_f show that PWP and PP91 gradient-corrected computations treat neutral and charged species with the same level of accuracy.
6. Fukui indices for neutral sulfine indicate and/or confirm that the most favorable protonation site in the molecule is the oxygen atom.
7. The global hardness profile for the protonation process is exactly specular to the energy path only in the part in which the chemical potential does not change.

Acknowledgements. This work was supported by the Universita' della Calabria (60%) and MURST (40%). We thank CINECA for its generous gift of computer time.

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