Density Functional Computational Thermochemistry: Determination of the Enthalpy of Formation of Methanethial-*S*,*S*-dioxide (Sulfene)

Oscar N. Ventura,* Martina Kieninger, and Pablo A. Denis

CCPG, DEQUIFIM, Facultad de Química, UDELAR, CC 1157, 11800 Montevideo, Uruguay

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The enthalpy of formation of methanethial-*S*,*S*-dioxide (CH_2SO_2) has been determined by the use of isodesmic and nonisodesmic reactions, with individual enthalpies calculated by employing density functional methods and the CBS-QB3 model chemistry. After assessing the possible errors in the methodology, it was concluded that this value can be expressed as $\Delta_f H°_{298}(CH_2SO_2) = -144.7 \pm 8.4$ kJ/mol.

Introduction

Density functional theory (DFT)[1−4] has been successfully employed in recent years to the study of thermochemical properties of species for which bonding patterns are difficult to describe with traditional ab initio techniques. Examples include not only radicals such as FO, FO_2, or HCO_2 but also closed-shell molecules such as FOOF. We have discussed several of these compounds in previous papers in this series.[5−11] In testing the limits of applicability of DFT for the computation of thermochemical properties, we recently became interested in sulfur compounds,[10−13] especially in relation to atmospheric chemistry reactions.

We recently became interested in the S-oxides of thioaldehydes and thioketones[14] (also known by the IUPAC deprecated name of sulfines), with the general formula $R_1R_2C{=}S{=}O$. The parent molecule, methanethial S-oxide (sulfine, $CH_2{=}S{=}O$, **1**), was prepared in the gas phase in 1976[15] by flash vacuum pyrolysis of 1,3-dithiethane 1-oxide and was identified by its microwave[15] and photoelectron[16,17] spectra.

As far as we are aware, no direct experimental data are available on the enthalpy of formation of **1** yet. Bouchoux and Salpin[18] in 1996 measured the gas-phase basicity (GB) and proton affinity (PA) of sulfine, obtaining values of GB = 758.5 ± 1.8 kJ/mol and PA = 786.3 ± 1.9 kJ/mol (recently corrected[19] to 755.1 ± 1.5 kJ/mol and 798.9 ± 2.6 kJ/mol, respectively). The enthalpy of formation of sulfine was derived then from the enthalpy difference

$$\mathrm{PA}(\mathbf{1}) = \Delta_f H°(\mathbf{1}) + \Delta_f H°(\mathrm{H}^+) - \Delta_f H°(\mathbf{1}\mathrm{H}^+)$$

where $\mathbf{1}\mathrm{H}^+$ represents protonated sulfine. The enthalpy of formation of $\mathbf{1}\mathrm{H}^+$ was obtained from the appearance energy of $[\mathrm{DMSO}-CH_3]^+$ ions measured by Zha et al.[20] The underlying hypothesis necessary for using these data is that the appearance energy corresponds to the presence of $[CH_2{=}S{=}OH^+]$ ions and not $[CH_3{-}S{=}O^+]$ and that the dissociation is the energy-determining step. This hypothesis was supported by experimental and theoretical data from Terlouw's group.[21] Very recently, however, Bouchoux et al.[22] published in this same journal a further study of the subject, concluding that the low-energy dissociation processes of ionized DMSO are preceded by the *energy-determining* isomerization to the aci isomer. This renders the use of the appearance energies of the corresponding ions to derive their enthalpies of formation erroneous.

The support of the previous determination by Ruttink et al.[21] relied on CAS-SDCI energy calculations on top of CASSCF/DZ(2df,2d,p)+f(S) geometry optimizations to obtain the enthalpy of formation of **1** relative to that of six anchors: the thioformic acid isomer HC(=O)SH, the protonated form $\mathbf{1}\mathrm{H}^+$, and the decomposition products CH_2 + SO, H_2S + CO, H_2O + CS, and H_2 + SCO. They obtained values ranging from −21 to +13 kJ/mol, from which they averaged a value of −3 ± 14 kJ/mol at 0 K and a recommended value of −9 kJ/mol at 298 K. As they properly noticed in that paper, this value is a significant revision upward from the value estimated by Benson in 1978,[23] −51 ± 22 kJ/mol. On the basis of a comparison of bond lengths and bond strengths in **1** and $H_2C{=}S$, Benson[23] argued that the actual value should be even more negative.

In previous papers,[12,13] we have studied the problem employing the almost isodesmic reaction

$$CH_2{=}S{=}O + S{=}O \rightleftharpoons CH_2{=}S + O{=}S{=}O \qquad (1)$$

and concluded that the enthalpy of formation of sulfine should be about −52 ± 10 kJ/mol, allowing a large enough error interval to encompass the DFT and CCSD(T) results obtained. However, we warned about the possibility of errors in the determination due to the presence of the open-shell, triplet SO molecule on the lhs of the reaction whereas the molecules on the rhs were all closed-shell singlets. In fact, further studies by Terlouw and co-workers[24,25] showed this to be the case. They used the reaction

$$CH_2{=}S{=}O + SO_2 \rightleftharpoons CH_2{=}S + SO_3 \qquad (2)$$

which is isodesmic and isogyric, and a different method of calculation (CBS-QB3[26]). They got a better estimation of the enthalpy of formation of **1** as −30 ± 6 kJ/mol. Following their idea, we were recently able to show that DFT calculations employing the same isodesmic reaction lead to a similar enthalpy of formation, −38 ± 10 kJ/mol, and that the error is in fact connected to the inclusion of SO in reaction 1.[27] Our own best estimation of this enthalpy of formation at present is −29.7 ± 8.4 kJ/mol,[27] and we will use this value in the following discussion.

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* Corresponding author. E-mail: oscar@bilbo.edu.uy. Fax. (5982)924-1906 or (5982)924-8396.

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TABLE 1: Geometry Parameters Calculated for CH_2SO_2 at Different Levels

method	basis set	r(CS)/Å	r(SO)/Å	r(CH)/Å	θ(CSO)/deg	θ(HCS)/deg
B3LYP	6-311++G(3df,2pd)	1.435	1.586	1.076	119.1	117.8
	aug-cc-pVDZ	1.485	1.613	1.085	118.9	117.2
	cc-pVTZ	1.450	1.596	1.076	119.1	117.6
	cc-pVQZ	1.441	1.590	1.075	119.1	117.7
B3PW91	6-311++G(3df,2pd)	1.431	1.582	1.077	119.1	117.8
	aug-cc-pVDZ	1.479	1.607	1.085	118.9	117.2
	cc-pVTZ	1.445	1.591	1.077	119.1	117.6
	cc-pVQZ	1.437	1.586	1.077	119.1	117.7
MP2	6-311++G(3df,2pd)	1.433	1.585	1.074	118.9	117.3
	aug-cc-pVDZ	1.485	1.622	1.087	118.8	116.6
	cc-pVTZ	1.447	1.595	1.071	118.9	116.9
CBS-QB3		1.442	1.592	1.078	118.8	117.6

Contrary to the case of **1**, the methylthial-*S*,*S*-dioxide (**2**, sulfene) has been much less studied. To our knowledge, a handful of papers have been published on the reactivity (mainly Diels−Alder) of this species, a representative recent example being the paper by Manoharan and Venuvanalingam.[28] With respect to the structure of **2** itself, only the group of Lyashchuk in Ukraine seems to have published recently (IR experimental determinations and semiempirical calculations).[29] We were unable to find any experimental or theoretical evaluation of the enthalpy of formation of **2**; therefore, we thought it worthwhile to apply the aforementioned methodology to obtain a first approximation to this value. Our efforts in this direction are described in this paper.

Methods

We chose reaction 3 for the calculation of the enthalpy of formation of **2**.

$$CH_2{=}S{=}O + SO_3 \rightarrow CH_2{=}SO_2 + SO_2 \qquad (3)$$

Although this reaction is clearly isodesmic and isogyric, and therefore should lead to almost complete error cancellation, an independent assessment of the error to be expected was desirable. Therefore, we chose to study the following reactions, to which reaction 3 is formally similar:

$$R_1R_1S{=}O + SO_3 \rightarrow R_1R_1SO_2 + SO_2$$

$$R_1 = F \qquad (4a)$$

$$R_1 = CH_3 \qquad (4b)$$

$$R_1 = CH_2CH_3 \qquad (4c)$$

Experimental data are available for the enthalpy of formation of all of the molecules involved in reactions 4, allowing us to estimate the errors to be expected in the calculation of the enthalpy of reaction for each substituent and the theoretical method employed. Experimental data were taken from ref 30 except in the case of $R_1 = F$, for which the experimental data of ref 31 were employed instead.

It has been noted before that the higher the valence of sulfur compounds the harder it is to attain the basis set limit for the enthalpy of formation.[12] We expect this error to be compensated in reaction 3 because there are S(VI) and S(IV) species on both sides of the reaction. It would be interesting to know if there is a large error associated with the change in the sulfur valence. Therefore, we also studied the results obtained for the enthalpy of formation of CH_2SO_2 using reaction 5,

$$CH_2{=}S{=}O + CH_2{=}S{=}O \rightarrow CH_2{=}S + CH_2{=}SO_2 \qquad (5)$$

Although we can write symbolically that reaction 3 is a IV + VI → VI + IV reaction, reaction 5 could be written as IV + IV → II + VI (i.e., a disproportionation). We expect that there may be severe errors connected to the less accurate description of some of the oxidation states of sulfur, which will show up in full in the results obtained from eq 5.

Finally, but not less important, we included the atomization reaction

$$CH_2SO_2(g) \rightarrow C(g) + 2H(g) + S(g) + 2O(g) \qquad (6)$$

As mentioned in the Introduction, there is sufficient experience on the high quality of DFT for predicting thermochemical properties of molecules, especially those with difficult bonding patterns.[5−11] Therefore, we chose the well-known semiempirical B3LYP[32−34] and B3PW91[32,33,35] functionals for the calculations reported in this paper. Pople basis sets 6-31G(d,p) and 6-311++G(3df,2pd)[36,37] were used for exploration and production purposes, respectively. Also, Dunning's basis sets[38] were employed to obtain better precision. Finally, the CBS-QB3 model chemistry[26] was used because of its demonstrated quality in the determination of the enthalpy of formation of **1**.[24] Conventional MP2 calculations were performed using the 6-311++G(3df,2pd) basis set for comparative purposes.

Geometry optimizations on all of the molecules at the DFT and MP2 levels were performed using tight thresholds so that bond lengths were precise up to 10^{-4} Å and angles, up to 10^{-2} degrees. Second derivatives of the energy with respect to the nuclear coordinates were performed analytically, and it was verified that the structures obtained were true minima on the global potential energy surface (all positive eigenvalues of the Hessian). In the case that some of the initial structures turned out to be conformational transition states, the structure was relaxed in the direction of the eigenvector(s) with negative eigenvalue(s) and reoptimized. Thermodynamic functions were obtained by employing the usual approximations of statistical thermodynamics (ideal gas, harmonic oscillator, and rigid rotor). All of the calculations reported were performed employing the Gaussian 94 set of computer codes.[39]

Results and Discussion

Structure of H_2CSO_2. Table 1 presents a collection of the geometrical parameters that define the structure of **2** at the different levels employed in the calculations. The important thing to observe here is that the structure depends quite considerably on the size and quality of the basis set used, but it does not depend markedly on the method of calculation. This implies that there are no problems connected to nondynamical correlation (i.e., it is not necessary to use multiconfiguational methods) in this molecule. One can analyze the variation in geometry produced by the addition of the second oxygen atom. In the case of SO_2/SO_3 at the B3LYP/6-311++G(3df,2pd) level

TABLE 2: Absolute Theoretical Enthalpies and Experimental Enthalpies of Formation of the Species Included in Reactions 3 and 4

species	B3LYP[a,b]	B3PW91[a,b]	CBS-QB3[b]	exptl[c]
H	−0.499897	−0.501705	−0.497457	217.998 ± 0.006
C	−37.855111	−37.833139	−37.783025	716.68 ± 0.45
O	−75.088554	−75.057303	−74.985273	249.18 ± 0.10
S	−398.132138	−398.077503	−397.655005	277.17 ± 0.15
SO_2	−548.704936	−548.591685	−548.033595	−296.81 ± 0.20[d]
SO_3	−623.919508	−623.781275	−623.150824	−395.765 ± 0.71
CH_2S	−437.483009	−437.412301	−436.934273	118 ± 8.4[g]
CH_2SO	−512.720260	−512.621317	−512.070537	−29.7 ± 8.4[e]
CH_2SO_2	−587.940997	−587.816493	−587.194151	
F_2SO	−673.212234	−673.055153	−672.402630	−584.952[f]
F_2SO_2	−748.447655	−748.266612	−747.548563	−760.000[f]
$(CH_3)_2SO$	−553.220579	−553.109463	−552.493033	−150.5 ± 1.5[h]
$(CH_3)_2SO_2$	−628.477558	−628.340149	−627.657760	−373. ± 3.[i]
$(CH_3CH_2)_2SO$	−631.817361	−631.676864	−630.945146	−205. ± 2.[j]
$(CH_3CH_2)_2SO_2$	−707.073919	−706.907010	−706.109988	−429.3 ± 2.6[k]

[a] Calculations made using the 6-311++G(3df/2pd) basis set. [b] Enthalpies in hartrees. [c] Taken from ref 30a and b unless otherwise stated; if no error is quoted, it is absent in the original reference; units are kJ/mol. [d] CODATA value. [e] Value obtained theoretically.[24,27] [f] Experimental values taken from ref 31 because the value for the enthalpy of formation of F_2SO in ref 30b is an estimation only. [g] Value from ref 30b and c. [h] Value from ref 30b and d. [i] Value from ref 30b and e. [j] Value from ref 30b and f. [k] Value from ref 30b, e, and f.

TABLE 3: Enthalpies of Reaction for Reactions 3−6 at the Different Computational and Experimental Levels (kJ/mol)

reaction	exptl	B3LYP[a]	B3PW91[a]	CBS-QB3[a]
4a	−75.89	−54.82	−57.50	−75.47
4b	−123.34	−111.50	−108.05	−124.88
4c	−125.14	−110.39	−106.63	−125.19
3		−16.2	−14.7	−16.8
5		43.4	36.4	33.3
6		2042.5	2071.4	2078.9

[a] Calculations made using the 6-311++G(3df/2pd) basis set.

(the situation is similar at other computational levels), the SO bond in SO_3 is 0.012 Å shorter than in SO_2. In the case of CH_2SO/CH_2SO_2, the contraction is 0.021 Å, almost double. From the point of view of the charges, on the other side, the sulfur atom in CH_2SO is less positive than in SO_2, but the opposite is true for the CH_2SO_2 molecule with respect to SO_3.

Precision of the Calculations. As we said before, our intention was to estimate the precision with which one can calculate the enthalpy of formation of CH_2SO_2 using reaction 3. For this purpose, we calculated the enthalpy of reaction in the case of the species in reactions 4. The necessary data for these calculations are contained in Table 2, including the results for CH_2SO and CH_2SO_2. The enthalpy of reaction for reactions 3 and 4 are given in Table 3.

The results show that density functional methods do not behave well for these reactions. Considered globally, one can say that there is an error of about 20 kJ/mol. This error is not random but systematically makes the DFT result too small with respect to the experimental one. Quite a different situation is seen with the CBS-QB3 method. In this case, the three results are less than 2 kJ/mol apart from the experimental ones. We can expect that the DFT results for reaction 3 are at most 20 kJ/mol off the better CBS-QB3 value, and in turn, we can expect that these results are better than or equal to the ones obtained using reactions 5 and 6.

The somewhat surprising results are collected in Table 4. When employed with reaction 3, the three computational methods are in agreement within 2 kJ/mol. Here, DFT methods do not exhibit the same error that was noticed with reactions 4. We cannot explain this fact at present beyond the obvious fact that all species in reaction 3 are planar whereas neither the sulfoxides nor the sulfones included in reactions 4 are. At any rate, the results are better than expected and lend support to the actual number assigned to the enthalpy of formation of CH_2SO_2.

TABLE 4: Enthalpy of Formation of CH_2SO_2 Derived from Reactions 3, 5, and 6 According to the Different Computational Methods (kJ/mol)

reaction	B3LYP[a]	B3PW91[a]	CBS-QB3[a]
3	−145.1	−143.6	−145.7
5	−134.0	−141.0	−144.1
6	−114.3	−143.2	−150.6

[a] Calculations made using the 6-311++G(3df/2pd) basis set.

Another surprising fact is the behavior of the different functional methods with respect to reactions 5 and 6. In both cases, B3LYP exhibits an error that is not too large in the case of reaction 5 but quite considerable in the case of reaction 6. This was the expected behavior, thus it came as a surprise that B3PW91 is very much in agreement both with the results obtained with the CBS-QB3 method and with the results obtained using the isodesmic reaction 3. These results support our previous belief, used normally as a rule of thumb, that in the case where the B3LYP and B3PW91 results differ significantly B3PW91 is usually closer to the correct answer. This observed fact is undoubtedly related to the derivation of these hybrid methods, since Becke originally derived the parameters employing the Perdew−Wang correlation-energy functional and not the Lee−Yang−Parr functional. Using the parameters of B3PW91 in B3LYP, as is usually done, is normally of no consequence except in some notorious cases in which the second method should be preferred.

Taking into account the discussion in the previous paragraphs, we estimated the enthalpy of formation of methanethial-*S*,*S*-dioxide by averaging the B3PW91 and CBS-QB3 results for reactions 3, 5, and 6 given in Table 4. The B3LYP results were not used because the lack of precision among the results for the three reactions leads us to believe that the result obtained with the B3LYP method are not accurate. We estimated the error bar of the estimated theoretical result as 2 times the standard deviation of the 6 values obtained to find the average. In this way, we came to the final conclusion that the enthalpy of formation of methanethial-*S*,*S*-dioxide, CH_2SO_2, is −144.7 ± 8.4 kJ/mol.

Conclusions

The yet unpublished enthalpy of formation of methanethial-*S*,*S*-dioxide has been determined by the use of isodesmic and nonisodesmic reactions, with individual enthalpies calculated by employing density functional methods and the CBS-QB3 model chemistry. After assessing the possible errors in the methodology, it was concluded that this value can be expressed as $\Delta_f H^\circ_{298}(CH_2SO_2) = -144.7 \pm 8.4$ kJ/mol.

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