Density Functional Computational Thermochemistry: Isomerization of Sulfine and Its Enthalpy of Formation

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Density functional (DFT), second-order perturbation theory (MP2), and coupled-cluster [(CCSD(T)] calculations using Pople's basis sets up to 6-311++G(3df,2pd) and Dunning's correlation consistent basis sets have been employed to determine the enthalpy of formation of sulfine, CH_2SO, **1**, using the isodesmic reaction $CH_2S + SO_2 \rightleftharpoons CH_2SO + SO$. Previous calculations showed an inconsistency between the enthalpy of formation obtained using this methodology, $\Delta_f H^o_{298.15}(\mathbf{1}) = -52 \pm 10$ kJ/mol, and the value obtained employing the isomerization reaction CH_2SO (**1**) $\rightleftharpoons$ HC(=O)SH (**2**) if Benson's estimate for the enthalpy of formation of isomer **2** (thioformic acid) was employed. This result was particularly vexing, since the computed enthalpy of formation of **1** was reasonably in agreement with Benson's own estimate. In this paper we extended our previous study using the reactions HC(=O)−XH + RH $\rightleftharpoons$ H_2CO + R−XH with R = H, Me, Et, Pr, and i-Pr. X was either sulfur, to obtain the enthalpy of formation of **2**, or oxygen, to assess the errors to be expected in the use of these reactions for the evaluation of $\Delta_f H^\circ$. The result, $\Delta_f H^o_{298.15}(\mathbf{2}) = -121 \pm 8$ kJ/mol, arrived at after a critical assessment of B3LYP, MP2, and CCDSD(T) results, is in complete agreement with the value of −126 ± 4 kJ/mol estimated by Benson. This implies that the isomerization reaction cannot be employed for the determination of the enthalpy of formation of sulfine. We ascribe this inadequacy to the errors introduced due to the change in the oxidation state of sulfur.

Introduction

Density functional theory (DFT)[1−4] was successfully employed in recent years for the study of thermochemical properties of species which bonding patterns are difficult to describe with traditional ab initio techniques. Examples are not only radicals, like FO, FO_2, or HCO_2, but also closed-shell molecules, like FOOF. We have discussed several of these compounds in previous papers in this series.[5−11] In our search for testing the limits of applicability of DFT for the computation of thermochemical properties, we became recently interested in sulfur compounds,[10,11] especially in relation to atmospheric chemistry reactions.[10] One class of compounds in which we are interested are sulfines, of the general formula $R_1R_2C{=}S{=}O$. Many of these compounds, which parent molecule is methanethial S-oxide (or sulfine), $CH_2{=}S{=}O$, **1**, have been prepared in the past.[12] The parent molecule was prepared in gas phase in 1976[13] by flash vacuum pyrolysis of 1,3-dithiethane 1-oxide and identified by its microwave[13] and photoelectron[14,15] spectra.

As far as we are aware, no direct experimental data are available on the enthalpy of formation of **1**. Bouchoux and Salpin[16] 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[17] to 755.1 ± 1.5 and 798.9 ± 2.6 kJ/mol, respectively). The enthalpy of formation of sulfine was derived then from the enthalpy difference

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

where $\mathbf{1}H^+$ represents protonated sulfine. The enthalpy of formation of $\mathbf{1}H^+$ was obtained from the appearance energy of $[DMSO{-}CH_3]^+$ ions measured by Zha et al.[18] 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 $[CH_{3-}S{=}O^+]$. This hypothesis was supported by experimental and theoretical data from Terlouw's group.[19]

Ruttink et al.[19] employed 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 six anchors: the thioformic acid isomer HC(=O)SH, **2**; the protonated form $\mathbf{1}H^+$**;** 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.[20] In fact, Benson estimated a value of −51 ± 22 kJ/mol, but on the basis of a comparison of bond lengths and bond strengths in **1** and $H_2C{=}S$, he argued that the actual value should be even more negative.

Although these theoretical and experimental determinations are in agreement, there are reasons to think that none are

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TABLE 1: Values of the Theoretical Absolute Enthalpies (in hartrees, at 298.15 K) of the Molecules Participating in Reaction 3, as Well as the Enthalpy of Reaction and the Deduced Enthalpy of Formation for Sulfine (in kJ/mol)

method	basis set[a]	CH_2SO	SO	SO_2	CH_2S	$\Delta_rH^o_{298}$	$\Delta_fH^o_{298}$
B3LYP	6-311++[11]	−512.720 26	−473.421 03	−548.704 94	−437.483 01	−122.7	−61.0
	aug-DZ	−512.660 87	−473.385 13	−548.621 83	−437.460 36	−95.1	−88.6
	TZ	−512.714 12	−473.420 70	−548.693 99	−437.485 28	−116.9	−66.8
	QZ	−512.733 94	−473.433 96	−548.720 63	−437.492 91	−120.0	−63.7
	5Z	−512.746 04	−473.441 95	−548.736 70	−437.498 16	−123.2	−60.5
B3PW91	6-311++[11]	−512.621 32	−473.336 54	−548.591 69	−437.412 31	−121.3	−62.4
MP2	aug-DZ	−511.833 46	−472.682 27	−547.773 30	−436.795 41	−139.3	−44.4
	TZ	−512.027 89	−472.819 23	−547.995 87	−436.912 65	−161.4	−22.3
	QZ	−512.144 64	−472.904 39	−548.131 20	−436.981 07	−166.3	−17.4
	5Z		−473.043 65		−437.114 65		
CCSD(T)	6-311++[11]	−512.001 14	−472.792 79	−547.951 27	−436.896 41	−141.3	−42.4
	aug-DZ	−511.860 96	−472.696 72	−547.777 32	−436.824 32	−115.6	−68.1
	TZ	−512.059 45[b]	−472.821 44[b]	−547.990 89[b]	−436.941 79[b]	−135.8[b]	−47.9[b]

[a] Acronyms used for the basis sets: 6-311++ = 6-311++G(3df,2pd); aug-DZ = aug-ccpVDZ; TZ = cc-pVTZ, QZ = cc-pVQZ, 5Z = cc-pV5Z. [b] Due to lack of computational resources, $\Delta_rH^o_{298}$ in this case was obtained using the cc-pVTZ total energies listed in the table and correcting to the enthalpy of reaction using the difference $\Delta_rH^o_{298} \angle \Delta_rE_0$ obtained at the CCSD(T)/aug-cc-pVDZ level (0.23 kJ/mol).

accurate. On the experimental side, the enthalpy of formation found by Bouchoux and Salpin[16,17] depends on the experimental determination of the proton affinity of sulfine plus an estimate of the enthalpy of formation of the protonated form, $\Delta_fH°(\mathbf{1}H^+)$, deduced from the appearance energy of $[DMSO{-}CH_3]^+$ ions. It is well-known that appearance energies may only give upper limits for the enthalpy of formation of the products for several reasons, some of them present in the case of $DMSO^+$. For instance, methyl loss is not the lowest energy process, but H elimination is; thus, a competitive shift is expected. Moreover, methyl loss cannot be a direct process and ab initio calculations show that the isomerization barrier to $CH_2{=}S(OH)CH_3^+$ lies 50 kJ/mol below the threshold for methyl loss.[21] Therefore, a reaction barrier higher than the energy of the products, or slowing-down effects due to the existence of an intermediate, may be expected. If so, then probably the enthalpy of formation of $\mathbf{1}H^+$ is overestimated and the enthalpy of formation of **1** suffers from this error.

On the theoretical side, Ruttink et al.[19] calculated the enthalpy of formation employing reactions that involve molecules with very different chemical bonds. Therefore, it is not sure whether there is appropriate error cancellation in these calculations, and actually we showed[11] that the situation is precisely the opposite. For instance, if one considers reactions among the decomposition products employed in Ruttink's paper,[19] namely

$$H_2O + CS \rightleftharpoons H_2S + CO \qquad (1)$$

$$H_2 + \mathbf{SCO} \rightleftharpoons \mathbf{H_2O} + \mathbf{CS} \qquad (2)$$

and uses Ruttink's calculations for obtaining the enthalpy of reaction at 0 K, one finds a discrepancy with experiment of only 1 kJ/mol (0.6%) for reaction 1 (where the bonding patterns are quite similar) but an error of 25 kJ/mol (13%) for reaction 2.

Consequently, we found it advisable to perform further computational research into the problem of the enthalpy of formation of **1** trying to avoid the drawbacks mentioned. To that end, we employed the isodesmic reaction

$$CH_2{=}S{=}O + S{=}O \rightleftharpoons CH_2{=}S + O{=}S{=}O \qquad (3)$$

Our previous results[11] showed 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, a bothersome discrepancy was present in those calculations. This same enthalpy of formation of sulfine, calculated at the generally good B3LYP/ 6-311++G-(3df,2pd) level of theory, employing the isomerization reaction

$$CH_2{=}S{=}O \rightleftharpoons HC({=}O)SH \qquad (4)$$

(which $\Delta_rH^o_{298.15}$ at that computational level was calculated as −108 kJ/mol) was obtained as −18 kJ/mol by Ventura et al.,[11] quite a different value from the −52 ± 10 kJ/mol of our more precise estimation. This −18 kJ/mol enthalpy just mentioned was deduced employing the enthalpy of formation for **2** estimated by Benson[20] on the basis of group additivity arguments, −126 ± 4 kJ/mol (notice that the value in Table 1 of Ventura et al.[11] is actually $\Delta_fH^o_0$ and not $\Delta_fH^o_{298.15}$, thus introducing a small error in Table 3 for the isomerization reaction). Therefore, one has to decide between alternative hypothesis: either Benson's estimate of the enthalpy of formation of **2** is wrong or one cannot use reaction 4 to estimate the enthalpy of formation of sulfine. In this paper, we have performed further calculations on reaction 3 to confirm our preliminary conclusions on the enthalpy of formation of sulfine, and we performed independent calculations on the reactions

$$HC({=}O)SH + RH \rightleftharpoons CH_2O + RSH(5a{-}e)$$

$$R = \text{(a) H, (b) Me, (c) Et, (d) Pr, (e) i-Pr}$$

to determine the enthalpy of formation of **2** and help us to decide between the alternative hypothesis. We obtained $\Delta_fH^o_{298.15}(\mathbf{2})$ = −121 ± 8 kJ/mol, substantially in agreement both with Benson's estimate,[20] −126 ± 4 kJ/mol, and the Le et al.[22] ab initio value, −124 kJ/mol, which demonstrates that the isomerization reaction cannot be used to estimate the enthalpy of formation of sulfine.

Methods

As we did in our previous paper,[11] we chose reaction 3 for the calculation of enthalpy of formation of sulfine. We chose reactions 5a−e for the calculation of the enthalpy of formation of **2**. All these reactions except (5a) are formally isodesmic; i.e., the number of lone pairs and the number and type of bonds are conserved in both sides of the equation. However, the fact that in one case the sulfur atom is bound to a carbonyl carbon and in the other to an aliphatic carbon (in reactions 5b−e) may introduce an unknown error in the calculation. Thus, we chose to perform the same calculations for reactions 5 but substituting

TABLE 2: Absolute Enthalpies (in hartrees) Calculated for the Molecules Intervening in Reaction 4 Both for Sulfur and Oxygen[a] and Experimental Enthalpies of Formation According to the Most Modern Value Available Usually, but Not Always, the One Recommended by Chase[32]

species			B3LYP		MP2		
formula	X	R	base I	base II	base I	base II	$\Delta_f H^o_{298}$(expt)
H_2CO			−114.472 66	−114.515 74	−114.159 78	−114.319 10	−108.6 ± 0.46[b]
HCOXH	O		−189.724 12	−189.796 81	−189.232 22	−189.497 18	−378.6[c]
	S		−512.680 50	−512.757 54	−511.819 06	−512.212 96	
RH		H	−1.165 06	−1.166 64	−1.143 86	−1.151 02	0.00
		Me	−40.475 18	−40.488 96	−40.319 44	−40.384 37	−74.48 ± 0.42[d]
		Et	−79.759 39	−79.783 72	−79.471 78	−79.593 43	−83.85 ± 0.29[d]
		Pr	−119.046 17	−119.081 24	−118.628 27	−118.807 55	−104.7 ± 0.50[d]
RXH	O	H	−76.394 59	−76.428 98	−76.196 77	−76.311 21	−241.826 ± 0.040[e]
		Me	−115.668 32	−115.733 28	−115.332 58	−115.503 98	−201[f]
		Et	−154.960 83	−155.016 33	−154.494 24	−154.722 77	−235.3 ± 0.50[g]
	S	Pr	−194.247 44	−194.313 56	−193.650 42	−193.936 69	255.59 ± 1.30[h]
		i-Pr	−194.254 11	−194.319 74	−193.658 03	−193.944 08	−272.8[i]
		H	−399.372 72	−399.410 10	−398.801 41	−399.045 13	−20.6 ± 0.5[e]
		Me	−438.654 89	−438.702 57	−437.951 39	−438.256 30	−22.8 ± 0.59[j]
		Et	−477.942 14	−478.000 64	−477.109 01	−477.466 55	46.15[k]
		Pr	−517.228 81	−517.298 04	−516.266 05	−516.681 26	−68.58 ± 0.63[l]
		i-Pr	−517.231 58	−517.300 65	−516.270 79	−516.686 52	−76.94 ± 0.63[l]

[a] Base I is 6-31G(d,p), base II is 6-311G(3df,2pd) [b] Fletcher, R. A.; Pilcher, G. *Trans. Faraday Soc.* **1970**, *66*, 794. [c] Guthrie, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 3608. [d] Pittam, D. A.; Pilcher, G. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2224. [e] Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Group: New York, 1984; p 1. [f] Hine, J.; Arata, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3089. [g] Green, J. H. S. *Chem. Ind. (London)* **1960**, 1215. [h] Connett, J. E. *J. Chem. Thermodyn.* **1972**, *4*, 233. [i] Buckley, E.; Herington, E. F. G. *Trans. Faraday Soc.* **1965**, *61*, 1618. [j] Good, W. D.; Lacinta, J. L.; McCullough, J. P. *J. Phys. Chem.* **1961**, *65*, 2229. [k] McCullough, J. P.; Hubbard, W. N.; Frow, F. R.; Hossenlopp, I. A.; Waddington, G. *J. Am. Chem. Soc.* **1957**, *79*, 561. [l] Hubbard, W. N.; Waddington, G. *Rec. Trav. Chim.* **1954**, *73*, 910.

TABLE 3: Enthalpy of Formation of HC(═O)OH and HC(═O)SH Obtained from Reaction 4 Using Different Methods and Basis Sets[a] (in kJ/mol)

		B3LYP		MP2	
X	R	base I	base II	base I	base II
O	H	−408.1	−399.7	−401.8	−397.5
	Me	−388.4	−384.3	−391.0	−388.9
	Et	−391.6	−387.5	−391.5	−388.2
	Pr	−391.4	−387.7	−391.7	−388.2
	i-Pr	−391.1	−388.6	−388.9	−386.0
exptl[b]		−378.6 ± 2[f]	−378.6 ± 2[f]	−378.6 ± 2[f]	−378.6 ± 2[f]
corr Me[c]		9.8	5.7	12.4	10.3
av Et−i-Pr[d]		391.4	387.9	390.7	387.5
corr av[e]		12.8	9.3	12.1	89
S	H	−129.6	−124.8	−133.7	−128.5
	Me	−130.9	−131.0	−128.8	−128.6
	Et	−136.8	−136.3	−128.9	−125.4
	Pr	−138.7	−138.2	−129.0	−125.5
	i-Pr	−139.7	−139.7	−124.8	−120.0
corr Me[c]		−121.1	−125.3	−116.4	−118.3
corr av[e]		−125.6	−128.8	−115.5	−114.7

[a] Base I is 6-31G(d,p); base II is 6-311G(3df,2pd). [b] Chase.[32] [c] Difference between the experimental and calculated values of the enthalpy of formation of HC(═O)OH calculated using reaction 4 with X = O and R = Me; this value is used to correct the computed value of the enthalpy of formation of HC(═O)SH except in the last row of the table. [d] Average of the values obtained with R = Et, Pr, and i-Pr, respectively. [e] Difference between the experimental value of the enthalpy of formation of HC(═O)OH and the average above; this value is used to correct the computed value of the enthalpy of formation of HC(═O)SH in the last row of the table. [f] Error estimated by propagation of the experimental errors in the enthalpies of formation of the species intervening in reaction 4 with X = O.

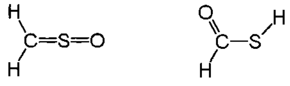
1. sulfine 2. thioformic acid

Figure 1. Structure of the two isomers considered in this work, sulfine (**1**) and thioformic acid (**2**).

oxygen for sulfur. Since the enthalpy of formation of formic acid is well-known, we can obtain an estimate of the incompleteness of error cancellation in reactions 5 when we compare the experimental and computed values.

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[23−25] and B3PW91[23,24,26] functionals for the calculations reported in this paper. As a conventional check, we also performed MP2 calculations on the same structures. In all cases we employed Pople's basis sets[27,28] 6-31G(d,p) and 6-311G(3df,2pd), called I and II in the following. We also used Dunning's basis sets[29] to obtain a better estimation of the enthalpy of formation of sulfine than the one obtained previously employing Pople's basis sets.[11]

Geometry optimization on all the molecules at the DFT and CCSD(T) levels were performed using tight thresholds, so that bond lengths were precise up to 10^{-4} Å and angles up to 10^{-2} deg. Second derivatives of the energy with respect to the nuclear coordinates were performed analytically (for DFT calculations) or numerically (for CCSD(T) calculations). Thermodynamic functions were obtained employing the usual approximations of statistical thermodynamics (ideal gas, harmonic oscillator, and rigid rotor). All the calculations reported were performed employing the Gaussian 94 set of computer codes.[30]

Results and Discussion

The optimum geometry of sulfine was presented already.[11] All sufficiently sophisticated calculations are coincident, and the computed parameters agree well with the existing microwave experimental determination. To our knowledge there are no experimental data on thioformic acid, i.e., isomer **2** (see Figure 1 for the structure of both isomers considered). A recent theoretical calculation of the gas-phase structure of **2** was published by Delaere et al.[31] at the MP2/6-311++G(d,p) and B3LYP/6-31G(d,p) levels, while Le et al.[22] published an MP2/

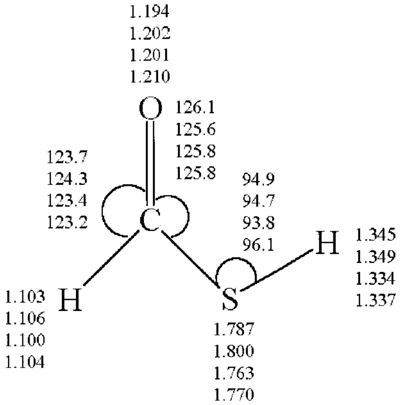

Figure 2. Structure of thioformic acid, **2,** obtained at different levels of theory. The four entries correspond to the following levels of calculation (from top to bottom): B3LYP/6-311G(3df,2pd); B3LYP/6-31G(d,p);[30] MP2/6-311G(3df,2pd); MP2/6-311++G(d,p).[30]

6-31G(d,p) structure as part of their study on thioxyhydroxycarbene. A compendium of these geometries is shown in Figure 2. As was the case with sulfine,[11] no unexpected discrepancies arise among the calculated values.

Table 1 shows the values obtained at different theoretical levels for reaction 3 and the enthalpy of formation deduced for sulfine at each level. MP2 calculations show a very poor performance. Improvement of the basis set actually worsens the agreement with the CCSD(T) calculation, which presumably is near the actual value. DFT calculations, on the other hand, converge toward a limit value of −60 ± 1 kJ/mol (using different extrapolation methods). Although still in disagreement with the CCSD(T) results, the B3LYP/Dunning result is consistent with our previous estimation, which seems to demonstrate that the error, if any, does not lie with the basis sets employed in the previous paper. Moreover, further CCSD(T) calculations performed with the aug-cc-pVDZ and cc-pVTZ basis set are also in agreement with the CCSD(T)/6-311++G(3df,2p) results of Ventura et al.[11]

The data for the second reaction studied, reaction 5, are collected in Table 2. Experimental values of the enthalpies of formation of the compounds were taken from the most modern sources available, according to the *NIST-JANAF Thermochemical Data Tables*.[32] The corresponding enthalpies of reaction obtained for formic acid and its sulfur-substituted analogue are displayed in Table 3.

Reaction 5 with X = O serves as our benchmark. One observes that the calculation for the reaction with R = H shows a larger error than with the rest of the substituents. Consequently, we can ignore this case and concentrate on the other ones. Even with the larger basis sets, the errors are still considerable. If we consider only the reaction with R = Me, the B3LYP calculations have still almost a 6 kJ/mol error with respect to experiment. MP2 calculations are even worse. Considering the average value of the reactions with substituents Et, Pr, and i-Pr, the errors are of the order of 9 kJ/mol for both types of calculations. Considering these errors as corrections for the calculations with X = S, we obtain a value of about −125 kJ/mol for B3LYP and −117 kJ/mol for MP2. In principle, it is to be expected that the B3LYP value is nearer to the correct result, because MP2 values for second-row atoms have a much larger error than for first-row ones, while this is not the case for DFT. At any rate, one can average both values to obtain −121 kJ/mol with an error bar of 8 kJ/mol, generous enough to include possible errors caused by the methodology, the basis sets, and the errors intrinsic to the reactions employed.

TABLE 4: Enthalpy of Formation of HC(=O)XH Obtained Using Reaction 4 with R = Me for X = O and X = S (in kJ/mol)

X	basis set	$\Delta_r H^o_{298}$	$\Delta_f H^o_{298}$
O	cc-pVDZ	147.4	−382.5
	cc-pVTZ	143.7	−378.8
	∞[a]	142.3	−377.4
	exptl[b]		−378.6
	corr[c]		−1.2
S	cc-pVDZ	68.4	−125.3
	cc-pVTZ	66.2	−123.1
	∞[a]	65.0	−121.9
	corr[d]		−123.1

[a] Extrapolated using the two-point formula $A + B/n^3$; see Martin.[33] [b] Taken from Chase.[32] [c] Difference between the corrected and experimental enthalpies of formation of HC(=O)OH. [d] Adding the correction calculated for HC(=O)OH.

CCSD(T) calculations using Dunning's cc-pVDZ and cc-pVTZ were performed also for reaction 5 with R = Me. The results are collected in Table 4. It is seen that, after extrapolation to infinite basis set,[33] the result for the enthalpy of formation of HC(=O)OH is only 1.2 kJ/mol apart from the experimental value. Correcting for this error the enthalpy of formation obtained from reaction 5 for HC(=O)SH with R = Me, we obtained a value of −123.1 kJ/mol, essentially in agreement with the B3LYP calculation. Therefore, we feel justified to propose a value of −121 ± 8 kJ/mol for the enthalpy of formation of this species.

The proposed value is entirely in agreement with Benson's estimate. Taking then the values of −60 and −125 kJ/mol as the more precise enthalpies of formation of sulfine and HC(=O)SH at the B3LYP level, we obtain an enthalpy of isomerization of −65 kJ/mol. However, if the calculation is done directly using the results of Ventura et al.,[11] the result at either the B3LYP or B3PW91 level with the 6-311++G(3df,2pd) basis set is −108 kJ/mol, i.e., a 66% error! This was the reason the enthalpy of formation evaluated using the isomerization reaction, −12.2 kJ/mol, significantly differed from the more accurate results. It is then obvious that the isomerization reaction cannot be employed to calculate the enthalpy of formation of sulfine, and one should inquire into the reasons for such a failure.

The main problem seems to be the change in the oxidation state of the sulfur atom. We have observed in the case of SO, SO_2, and SO_3[34] that the convergence of properties with the enlargement of the basis set is much poorer for S with oxidation state VI than IV and in turn more with IV than with II. In other words, the description of sulfine with a given basis set is always poorer than the description of the HC(=O)SH isomer with the same basis set, unless a very extended one is used (not even cc-pV5Z seems to be sufficient[34]). This problem seems to be similar to the one observed for the MP2 method in the case of the isomerization of formaldehyde to hydroxymethylene and related molecules;[35] i.e., the method of calculation was recovering a different amount of correlation energy for each isomer.

Conclusions

The enthalpy of formation of sulfine at 298 K has been confirmed to be within the range previously reported,[11] −52 ± 10 kJ/mol, while the enthalpy of formation of the HC(=O)SH isomer was found to be −121 ± 8 kJ/mol, also at 298 K. Both results are in close agreement with Benson's previous estimates and reinforce our previous conclusions regarding the enthalpy of formation of sulfine.[11] The enthalpy of isomerization can be computed in two ways. On one side, one can calculate the absolute enthalpies of both isomers and obtain the enthalpy of isomerization by direct subtraction, i.e., the usual procedure. On the other, one can use independent isodesmic reactions to evaluate the enthalpies of formation of both isomers and subtract them to obtain the enthalpy of isomerization. This second procedure is more accurate, since errors tend to cancel when isodesmic reactions are employed. The discrepancy between the former and latter values, a 66% error, supports our assertion that this reaction cannot be used to evaluate the enthalpy of formation of sulfine. The reason for the error in the direct calculation of the enthalpy of reaction is attributed to the change in the oxidation state of the sulfur atom. The calculations are not homogeneously converged to the limit with the type of basis set employed; i.e., the representation of the electronic structure of $HC({=}O)SH$ is much better than that of $H_2C{=}S{=}O$, causing an overstabilization of the former. This effect has been previously observed by Ventura et al.[11] in the very large basis-set effect on the isomerization energy.

In conclusion, what has been formerly thought to be a discrepancy with our evaluation of the enthalpy of formation of sulfine is shown to be only a basis-set effect, very difficult to correct. On the other hand, both the enthalpy of formation of sulfine and thioformic acid predicted by Benson were put on firmer ground through the set of calculations presented here and in Ventura et al.[11]

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