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Density functional investigation of atmospheric sulfur chemistry II. The heat of formation of the XSO₂ radicals X = H, CH₃

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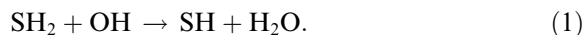
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Abstract

The $\Delta_f H^0$ (298 K) of HSO₂ is estimated as -42.6 ± 2 kcal/mol through calculations using Dunning's basis sets up to cc-pV6Z and Pople's 6-311+G(3df,2p). This estimation differs from previous G2 calculations and from our own G3 result of -37.1 kcal/mol. Similarly, the $\Delta_f H^0$ (298 K) CH₃SO₂ is estimated as -56.3 kcal/mol, in good agreement with Benson's prediction, -55.0 kcal/mol, and again in disagreement with the G2 value, -47.6 kcal/mol. Finally, we propose a revision of the enthalpy of formation of the CH₃S radical. On the basis of the density functional theory (DFT) calculations, we propose a value of 28.8 ± 1 kcal/mol, slightly lower than the presently accepted value of 29.78 ± 0.44 kcal/mol. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Oxidation of sulfur compounds present in the atmosphere is central to environmentally important processes such as acid rain and pollution [1]. Unfortunately the mechanism for the oxidation of hydrogen sulfide, one of the largest components in the total emission of reduced sulfur compounds, is not yet well understood [2]. It is clear that the process starts with the reaction of the SH₂ and the OH radical [2]:



The nascent SH radical reacts with ozone or NO₂ [2], giving the HSO radical; but it is not clear how

the mechanism proceeds forward. Several experiments have been performed to study the reactivity of HSO. It was concluded that its most significant reactions are with NO₂ [3,4], to give HSO₂, and with ozone [3,5,6]. The products of this latter reaction are not well known as yet although Wang and Howard [3] proposed two channels of reaction, one giving also the HSO₂ radical, as with NO₂, and another that regenerates the SH radical and produces molecular oxygen.

The knowledge of the enthalpy of formation of the HSO₂ radical is important to address the reaction mentioned in the previous paragraph. However, to our knowledge, only two theoretical studies have been performed to determine $\Delta_f H^0(\text{HSO}_2)$. The first of them was performed by Boyd et al. [7] in 1980. They derived a value of -52.7 kcal/mol using the Hartree–Fock method and STO-3G basis sets. Many years later, Laakso

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et al. [8] calculated a value of -34.0 kcal/mol using the G2 theory [9]. The only experimental estimation of $\Delta_f H^0(\text{HSO}_2)$, -44.0 kcal/mol, based on the S–H bond energy obtained from flame experiments [10–12], is in disagreement with both computed values.

Due to the discrepancy between the experimental and calculated values, we decided to reinvestigate this problem using density functional theory (DFT). As shown by us previously [13,14], DFT methods using modest basis sets and isodesmic reactions can produce very accurate thermochemical information, bettering G2 and even CCSD(T) results in many cases.

2. Theoretical methods

We used the adiabatically coupled B3LYP and B3PW91 methods [15,16], which include Becke's 1993 exchange potential [17] and either Lee–Yang–Parr [18] or Perdew–Wang [19] correlation potentials, with Dunning's correlation consistent basis sets [20] cc-pVxZ ($x = 2, 3, 4, 5, 6$). We also performed some calculations employing Pople's 6-311+(3df,2p) [21] basis set for comparative purposes and for the larger molecules. DFT calculations were performed with GAUSSIAN 98 [22] and the CASSCF ones using Gamess [23]. Geometry optimization of all the species considered were performed at each level of calculation except CASSCF. DFT optimum geometries were employed for these calculations.

Several computational experiments were done. Firstly, we studied the performance of DFT to describe the electronic environment of the sulfur atom in the case of three well known molecules where sulfur is present with different oxidation states, namely SO, SO₂ and SO₃. For this purpose, we calculated $\Delta_f H^0$ for the three molecules, using mainly atomization reactions.

Secondly, we derived $\Delta_f H^0(\text{HSO}_2)$ employing one of the reactions in [8]



To increase the accuracy of our model predictions, we added three other reactions from which we can obtain $\Delta_f H^0(\text{HSO}_2)$, namely



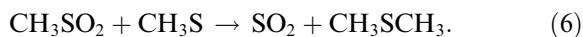
the isodesmic reaction:



and the atomization reaction:

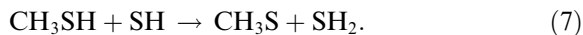


In the third place, we determined $\Delta_f H^0(\text{CH}_3\text{SO}_2)$. This value has not been determined experimentally as yet, although it is one of the key intermediates in the oxidation process of dimethylsulfide (DMS). Again, Boyd et al. [7] and Marshall and co-workers [8] performed the only two quantum-chemical calculations known to us, obtaining values of -62.7 and -47.6 kcal/mol, respectively. On the other hand, Benson [24] in his review of 1978 proposed a value of -55 kcal/mol. Due to the dispersion of these three theoretical estimations, we decided to determine $\Delta_f H^0(\text{CH}_3\text{SO}_2)$ employing the reaction:



The enthalpies of formation of DMS and sulfur dioxide have been determined experimentally several times with sufficient accuracy, but there have been some discrepancies in the values determined for the CH₃S radical [25]. Benson [24] proposed a value of 34.2 ± 2 kcal/mol in 1978. Other estimates are quoted in the paper by Nicovich et al. [25], who themselves determined a value of 29.78 ± 0.44 kcal/mol, the one accepted nowadays.

In view of these discrepancies in the enthalpy of formation of CH₃S and that we need it for reaction (6), our final experiment consisted in determining this value. For that purpose we used the isodesmic reaction:



Due to the size of the molecules, especially those of reaction (6), we calculated $\Delta_f H^0(\text{CH}_3\text{SO}_2)$ with Pople's basis set only. In some of the cases studied, we employed also the recently developed G3 theory [26], an improvement of the G2 theory.

3. Results and discussion

3.1. SO, SO₂ and SO₃

In Table 1 are summarized the enthalpies of formation calculated for these three molecules employing the atomization reactions. One notices that the convergence with the enlargement of the basis set is slower as the valence of sulfur rises (Fig. 1). Differences can be better appreciated if we compare the results obtained with Duninng's cc-pV6Z and Pople's 6-311+G(3df,2p) basis sets. The discrepancies between these are 1, 2 and 3 kcal/mol for SO, SO₂ and SO₃, respectively. Aside from these differences with the best basis set used, the performance of Pople's basis set is excellent, being better than cc-pVQZ and slightly worse than cc-pV5Z, a remarkable fact if we consider that Pople basis is very small compared with Duninng basis set. For instance, Pople's basis set for SO₃ contains 164 contracted basis functions, while cc-pV5Z contains 368 and cc-pV6Z contains 564 (1024 primitives), respectively. Moreover, these basis sets include *g*, *h* and *i* functions which are not present in Pople's basis set. This observation serves as a basis for the use of Pople's basis set for large molecules, for which use of cc-pV6Z or cc-pV5Z is impractical.

The slow basis set convergence has been noted previously by Bauschlicher and Partridge [27] and

Martin [28,29], and they attributed this behavior to an SCF effect inbred into the DFT calculations. We have shown in other cases that modest basis sets and isodesmic reactions can produce very accurate thermochemical data. It is tempting to verify this process in this case, where such a marked basis set effect is present. For that purpose, we constructed the isodesmic reaction:



to estimate the enthalpy of formation of SO₂. The values obtained are in excellent agreement with experiment, with an error smaller than 1 kcal/mol (especially with B3PW91). To our knowledge, there is only one better theoretical estimation of this property. It was performed by Martin [29] using CCSD(T) and very extended basis sets followed by extrapolation to the complete basis set limit, a procedure clearly prohibitive for molecules even slightly larger. B3PW91 performs even better than G3. The G3 error for the atomization reaction is 3.8 kcal/mol and it is 2.5 kcal/mol employing the G3B3LYP modification. G3 and G3B3LYP are also outperformed by B3PW91 in the case of sulfur trioxide, by roughly 3 and 2 kcal/mol, respectively.

Another important point in this study is the comparative performance of B3LYP and B3PW91. The results indicate B3PW91 outperforms B3LYP for sulfur compounds where the S

Table 1
Calculated enthalpy of formation of SO, SO₂ and SO₃ at 298.15 K, in kcal/mol

Method	Basis set	SO	SO ₂	SO ₃	
		SO → S + O	SO ₂ → S + 2O	SSO + SO → SO ₂ + SS	
B3LYP	6-311+G(3df,2p)	0.1	−62.8	−70.2	−82.3
	aug-cc-pVDZ	9.9	−32.0		
	cc-pVTZ	3.5	−52.1		
	cc-pVQZ	1.3	−58.8		
	cc-pV5Z	−0.3	−64.0		
	cc-pV6Z	−1.1	−64.9		
B3PW91	6-311+G(3df,2p)	−0.8	−65.3	−70.5	−88.7
	aug-cc-pVDZ	9.2	−34.7		−41.8
	cc-pVTZ	2.8	−54.4		−74.0
	cc-pVQZ	0.6	−60.9		−82.2
	cc-pV5Z	−1.0	−66.2		−89.6
	cc-pV6Z	−1.8	−67.2		−91.4
G3		1.7	67.1	−70.4	−88.7
G3B3LYP			68.4		−89.5
Expt.		1.2	−70.9	−70.9	−95.5

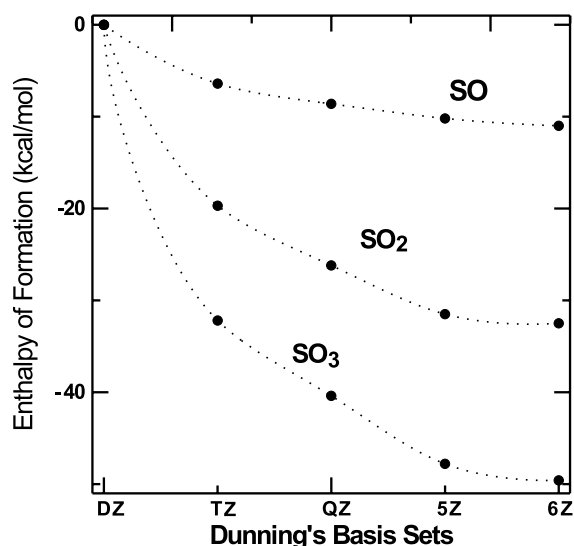


Fig. 1. Enthalpies of formation at 298.15 K calculated with the B3PW91 method and different Dunning basis sets for SO, SO₂ and SO₃. The curves were displaced by −9.2, 34.7 and 41.8 kcal/mol, respectively, so that all of them start at 0.0 kcal/mol for the cc-pVDZ basis set value. The curves drawn are spline interpolations of the calculated values.

valence is larger than 2. In the case of SO, B3LYP is nearer to the experimental value than B3PW91 by about 1 kcal/mol. This situation is reversed in the case of SO₂, for which B3PW91 is now better, by 2.5 kcal/mol. Finally, this situation is even worse for SO₃, since the B3PW91 value is 6 kcal/mol better than the B3LYP one. Therefore, one can conclude that B3PW91 with modest basis sets

and isodesmic reactions is the method of choice for the study of sulfur compounds of varying oxidation state of the S atom.

3.2. Enthalpy of formation of the CH₃S radical

As we said previously, there have been several changes in the accepted enthalpy of formation of the CH₃S radical through the years. In Table 2 we compare the DFT results obtained employing reaction (7) with all the experimental determination known to us. The effect of using the isodesmic reaction is reflected in a very small basis set dependency (compare the 0.3 kcal/mol difference between the results obtained with the aug-cc-pVDZ and the 6-311+(3df,3p) basis sets). The CH₃S radical is included in the G297 test set with which G3 was fine-tuned. Therefore, the result obtained employing the atomization reaction is not useful, but one can apply the G3 theory to the isodesmic reaction (7). The result obtained is 28.5 kcal/mol. Our recommended conservative value for the enthalpy of formation of the CH₃S radical is obtained from the DFT and G3 results as 28.8 ± 1 kcal/mol, slightly lower than the value determined by Nicovich et al. [25] 29.78 ± 0.44 kcal/mol, although they overlap if one accounts for the error bars in both estimations.

3.3. Enthalpy of formation of the CH₃SO₂ radical

No isodesmic reaction for this radical could be used, because the enthalpy of formation of the

Table 2

Enthalpy of formation at 298.15 K calculated for CH₃S with different methods and estimated experimentally, in kcal/mol

Determination	Value	Reference
Experimental	29.78 ± 0.44	^a
Experimental	29.4 ± 2.1	^a
Experimental	34.2 ± 2.0	^a
Experimental	31.4 ± 2.0	^a
Experimental	33.2 ± 1.5	^a
Experimental	30.5 ± 2.0	^a
Experimental	$>29.5 \pm 2.0$	^a
Experimental	33.0 ± 2	^a
B3LYP/6-311+G(3df,2p)	27.5 ± 1	This work
B3LYP/aug-cc-pvdz	27.7 ± 1	This work
B3PW91/6-311+G(3df,2p)	27.4 ± 1	This work
G3(isodesmic reaction)	28.5	This work

^a Ref. [25] and references therein.

HSO₂ radical is not well known. We decided then to check Benson's [24] value with that obtained employing reaction (6). Using our previously determined value for the enthalpy of formation of the CH₃S radical and the JANAF Thermochemical Table's [30] values for sulfur dioxide and DMS, we calculated an enthalpy of formation for the CH₃SO₂ radical of −55.8 kcal/mol (B3LYP) and −56.8 kcal/mol (B3PW91) using the 6-311+G(3df,2p) basis set. These values are in good agreement with Benson's estimate, −55.0 kcal/mol. We then propose a value of -56.3 ± 2 kcal/mol for the enthalpy of formation of the CH₃SO₂ radical. This value is quite different from Marshall's estimate [8], −47.6 kcal/mol, or Boyd's value [7], −62.7 kcal/mol.

3.4. Enthalpy of formation of the HSO₂ radical

The results obtained for all the reactions are summarized in Table 3. Let us consider first reaction (4), which shows the largest error cancellation (the results obtained using aug-cc-pVDZ and 6-311+G(3df,2p) show again differences no larger than 0.2 kcal/mol). These results confirm our hypothesis that possible errors in the calculation of $\Delta_f H^0(\text{HSO}_2)$ largely canceled out, although one

cannot forget that $\Delta_f H^0(\text{CH}_3\text{SO}_2)$ is not known precisely. We are using here our own estimate, given previously.

Due to the eventual uncertainty in $\Delta_f H^0(\text{CH}_3\text{SO}_2)$, we also employed reactions (3)–(5). Neither of these reactions is isodesmic, but the results can be very helpful if critically assessed. For instance, only one of those reactions shows a large basis set dependency, the atomization reaction. For reactions (3) and (4) this dependency is small: 0.3 kcal/mol passing from aug-cc-pVDZ to cc-pV5Z for reaction (3), and 1.6 kcal/mol for the same variation in the case of reaction (4). A remarkable fact is the agreement among the results obtained with reactions (3) and (4) and with the isodesmic reaction, differences being smaller than 2 kcal/mol for both functionals employed. The whole set of data lends support to our estimated value for the enthalpy of formation of CH₃SO₂ and CH₃S.

Notice also the good B3PW91 results from the atomization reaction, only 2 kcal/mol lower than the enthalpy of formation obtained with the isodesmic reaction. The behavior of B3LYP and B3PW91 is similar as that observed for SO₂ and SO₃. B3PW91 outperforms B3LYP because the valence of sulfur in HSO₂ is intermediate between

Table 3
Calculated enthalpy of formation for HSO₂, at 298.15 K, in kcal/mol

Molecule	Method	Basis Set	Reaction 5	Reaction 3	Reaction 2	Reaction 4	Distance S–O
HSO ₂	B3LYP	6-311+G(3df,2p)	−33.1	−41.3	−41.2	−41.6	1.455
		aug-cc-pVDZ	−2.3	−43.9	−41.1	−41.3	1.509
		cc-pVTZ	−21.8	−42.0	−40.5		1.470
		cc-pvqz	−28.8	−42.2	−41.0		1.461
		cc-pv5z	−34.5	−42.3	−41.4		1.453
		cc-pv6z	−35.6				1.452
	B3PW91	6-311+G(3df,2p)	−37.0	−42.8	–	−41.6	1.450
		aug-cc-pVDZ				−41.4	
		cc-pVTZ					
		cc-pvqz	−32.7 ^a				1.456
		cc-pv5z	−38.1 ^a	−43.1	−43.2 ^a		1.448
		cc-pv6z	−39.6 ^a				1.447
	G2	–			−34.0		1.480
	G3	–	−32.8	−37.1	−37.1		1.476
	G3B3LYP		−32.9		−35.9		1.485
	G3(modif.) ^b			−38.1	−38.1		1.447

^a For these calculations the H has been changed to 1/2 H₂ in the chemical reaction.

^b G3 calculation performed at the B3PW91/6-311+G(3df,2p) geometry.

4 and 5. We suggest then a value of -42.6 ± 2 kcal/mol for $\Delta_f H^0(\text{HSO}_2)$. This value is in excellent agreement with the flame experimental determination, but very different from Marshall's G2 value [8], and our G3 and G3B3LYP results obtained using reaction (2). Although the enthalpy of formation is improved by these methods with respect to the G2 value, differences are still substantial, 5.5 and 6.7 kcal/mol, respectively. The question then arises of why the Gn ($n = 2, 3$)

models fail in this way. On the one hand, one must realize that HSO_2 has a strong multiconfigurational character. This can be seen in the number of resonant forms one can write for this radical, and is supported by CASSCF(5,5) calculations we performed on this species. Several configurations with coefficients greater than 0.2 are present in these calculations, while the reference configuration has a coefficient of less than 0.9. The multiconfigurational character of HSO_2 is also

Table 4
Geometries of the molecules studied in this Letter

Method	Basis Set	Parameter	SO	SO ₂	SO ₃	HSO ₂	CH ₃ S	CH ₃ SO ₂
B3LYP	cc-pV6Z	R(SO)	1.485	1.435		1.452		
		R(SC)						
		R(SH)				1.382		
		R(CH)						
		$\theta(\text{OSO})$		119.1		123.0		
		$\theta(\text{HSO})$				105.5		
		$\phi(\text{HSOO})$				120.7		
	6-311+G(3df,2p)	R(SO)	1.489	1.437	1.425	1.455		1.458
		R(SC)					1.798	1.824
		R(SH)				1.381		
		R(CH)					1.094	1.088
							1.088	1.085
		$\theta(\text{OSO})$		119.2	120.0	123.2		146.0
		$\theta(\text{HSO})$				105.3		
		$\theta(\text{CSO})$						107.0
		$\theta(\text{HCS})$					111.7	107.7
							106.5	106.2
B3PW91	cc-pV6Z	$\phi(\text{HSOO})$				120.3		
		$\phi(\text{CSOO})$						131.4
		R(SO)	1.480	1.431	1.420	1.447		
		R(SC)						
		R(SH)				1.381		
		R(CH)						
		$\theta(\text{OSO})$		119.1	120.0	123.2		
		$\theta(\text{HSO})$				105.6		
		$\phi(\text{HSOO})$				121.1		
	6-311+G(3df,2p)	R(SO)	1.483	1.433	1.422	1.450		1.453
		R(SC)					1.786	1.807
		R(SH)				1.380		
		R(CH)					1.095	1.089
							1.090	1.086
		$\theta(\text{OSO})$		119.2	120.0	123.4		145.6
		$\theta(\text{HSO})$				105.5		
		$\theta(\text{CSO})$						107.2
		$\theta(\text{HCS})$					111.8	107.8
							106.3	106.3
B3LYP	cc-pV6Z	$\phi(\text{HSOO})$				124.0		
		$\phi(\text{CSOO})$						132.0

Units are Å and degrees.

supported by a T1 diagnostic [16] of 0.026, larger than the recommended limit of 0.018 for the application of CCSD(T).

Another problem can be the inadequacy of the basis set employed in the G2 model. The basis set dependency of the methods for compounds of second-row elements is very large [27–29], much larger than what is observed in DFT calculations. For this reason, the final energy is calculated with a larger basis set in the new G3 approach (although apparently not extended enough for this type of compounds).

A third drawback can be found in the geometry employed in the Gaussian theory approach. The optimum S–O bond distances in HSO_2 at each level of calculation are listed in Table 3 (optimum geometries for the molecules studied are collected in Table 4). MP2(full)/6-31G* and B3LYP/6-31G* bond distances, employed in the G2 and G3 models, are very bad, 0.026 and 0.035 Å larger than the B3LYP and B3PW91 results with the more complete and larger basis sets. The effect is also noticeable in the calculation of $\Delta_f H^0(\text{SO}_2)$: using the experimental geometry instead of the optimized one within G2 or G3, the results are greatly improved. G3 results are better than G3B3LYP ones because the MP2/6-31G(d) geometry for HSO_2 is better than the B3LYP/6-31G(d) one. We also performed a G3 calculation using the B3PW91/6-311+G(3df,2p) optimum geometry instead of the default method, and the new result, –38.1 kcal/mol, is already 1 kcal/mol better. This result shows the importance of the use of adequate basis sets in the geometry optimization procedure for second row compounds, especially those with elements in extended valence states.

It must be pointed out that to eliminate the extra 4.5 kcal/mol error exhibited by the G3 result with respect to the DFT one, the calculation of single-point energies should be done with Dunning correlation consistent basis sets, and extrapolate to the complete basis set limit, if possible. As a final example of these considerations, we calculated the enthalpy of formation of SSO at the G3 level. The result for this molecule, which is not included in the training set of G3, is –9.4 kcal/mol, 4.12 kcal/mol lower than the –13.5 kcal/mol experimental

result. This result reinforces the suggestion that the G3 calculation of enthalpies of formation via the atomization procedure fails for compounds containing sulfur with a valence larger than 2.

4. Conclusions

The enthalpy of formation of the HSO_2 radical at 298 K has been estimated. Our recommended value is –42.6 kcal/mol, in excellent agreement with the experimental determination and in disagreement with the values of the G2, G3, and G3B3LYP model chemistries. For the CH_3SO_2 radical we estimated a value of –56.3 kcal/mol, in good agreement with Benson's prediction of –55 kcal/mol, but again in disagreement with the G2 value. The basis sets employed in the G2 and G3 approaches for second row compounds such as SO_2 , HSO_2 , SSO, SO_3 should be revised, both within the optimization procedure and in the single-point energy calculations. A final point to notice is that, as we remarked before, B3PW91 tends to be a better method for the study of thermochemical magnitudes of sulfur compounds than B3LYP, especially for higher oxidation states of the S atom.

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- [30] Values taken from the NIST Web site, <http://webbok.nist.gov/Chemistry>.