
Density Functional Investigation of Atmospheric Sulfur Chemistry. I. Enthalpy of Formation of HSO and Related Molecules

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ABSTRACT: The enthalpy of formation of several species intervening in the atmospheric chemistry of sulfur compounds (SH, H₂S, SO, HSO, SOH) have been calculated using density functional theory with correlation consistent basis sets and extrapolation to the complete basis set limit. Excellent agreement with experiment is found for the species of which the enthalpy of formation are well determined. The values predicted for HSO [$\Delta_f H_{298K}^\circ(\text{HSO}) = -27.8 \pm 2.1$ kJ/mol] and SOH [$\Delta_f H_{298K}^\circ(\text{SOH}) = -6.8 \pm 2.1$ kJ/mol] agree well with previous multireference configuration interaction (MR-CI) calculations. Based on these results, it is determined that the reaction of HSO with ozone is endothermic at all temperatures but spontaneous above 220 K because of entropic effects. Both the reactions of dissociation SOH \rightarrow H + SO and isomerization HSO \rightarrow SOH are studied in detail, and the transition states located. The results are also in agreement with the much more costly MR-CI results. © 2000 John Wiley & Sons, Inc. *Int J Quantum Chem* 80: 439–453, 2000

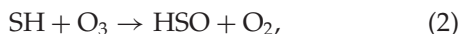
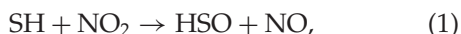
Key words: HSO; SOH; atmospheric chemistry; sulfur compounds; density functional calculations; computational thermochemistry

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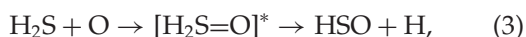
Introduction

Sulfur is one of the most abundant elements on earth. Great amounts of effort and money are invested in problems such as desulfurization of coal, oil, and fuels and removal of sulfur-containing species from exhaust stacks of power plants and factories. On the other side, the chemistry of atmospheric sulfur oxides is central to environmentally important processes such as the production and precipitation of sulfuric acid (acid rain) and the conversion into visibility-reducing aerosol particles [1–4]. A more sophisticated understanding of the thermochemistry and kinetics of sulfur compounds, especially the oxides, has become necessary and much work has been dedicated in latter years to this subject [5, 6].

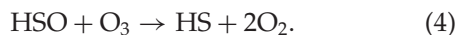
One of the radicals involved in atmospheric sulfur chemistry is HSO, which has been the subject of experimental and theoretical studies in recent years. HSO is formed very fast in atmospheric conditions through the reaction of the SH radical with NO₂ and O₃ [2, 7, 8]:



and eventually, also in the reaction with oxygen atoms [9, 10]:



which seems to be much slower than (1) or (2). Reaction (2) is especially interesting since experimental studies [2, 7, 11, 12] have shown that the radical HSO can catalytically destroy ozone through a cycle involving reactions (2) and (4):



Several experiments have been performed to determine the rate constant of reaction (4). Friedl et al. [2] used a low-pressure discharge flow reactor with laser induced fluorescence (LIF) detection of SH for studying the reaction of this species with O₃, among others. They determined a value of $3.2 \pm 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate constant of reaction (2) (other authors gave values of 3.5×10^{-12} [13], 2.9×10^{-12} [14], and 4.5×10^{-12} [15] $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and a value of $1.0 \pm 0.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the regeneration of SH through reaction (4). Wang and Howard [1] later confirmed the presence of the SH regeneration reaction (4) and estimated a value of $7.0 \pm 2.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate constant. Roughly

speaking, then, reaction (4) seems to be about 40 times slower than reaction (2) but still of significance in the overall process, at least in the laboratory conditions.

A minor controversy exists about the thermochemistry of reaction (4) due essentially to the discrepancy about the enthalpy of formation of HSO. Experimentally, the first estimation of $\Delta_f H_{298\text{K}}^\circ$ (HSO) was made by Schurath et al. [8] in a study on the chemiluminescence from O₃-O-H₂S systems originating from electronically excited HSO. They established an upper limit of 62.4 kJ/mol and concluded that the high enthalpy of formation of HSO would make reaction (3) too endothermic to be of importance relative to the competitive exothermic abstraction route



The upper limit determined by Schurath et al. [8] was shifted downwards in 1978 by Slagle et al. [10], who used thermochemical arguments for suggesting -12.6 kJ/mol as the most probable value of $\Delta_f H_{298\text{K}}^\circ$ (HSO). They also pointed out that if one would use the thermochemical data on sulfur compounds compiled by Benson [6], one would obtain a value of about -21 kJ/mol for the enthalpy of formation. Later, Davidson et al. [15] made another study of reaction (3) and determined a larger value of $-5.9 \pm 8.0 \text{ kJ/mol}$ for $\Delta_f H_{298\text{K}}^\circ$ (HSO). Finally, the latest experimental determination we are aware of was performed by Balucani et al. [16], measuring a slightly less negative value of $-4.7 \pm 2.9 \text{ kJ/mol}$. In none of these latter experiments was it determined that the structure of the isomeric form was present, but it was assumed to be HSO on the basis of the study by Schurath et al. [8] and other spectroscopic work [17, 18]. Until recently [19] the SOH isomer had not been observed experimentally.

Theoretically, Sannigrahi et al. [20] determined some molecular constants of the HSO radical employing self-consistent field (SCF) and configuration interaction (CI) methods. Luke and McLean in 1985 [21] estimated a value of $-1.7 \pm 12.6 \text{ kJ/mol}$ on the basis of MP4/6-31 G(d,p) calculations corroborated by multiconfiguration SCF (MCSCF) geometry optimizations and CI calculations of the energies of both isomers HSO and SOH. The methods used incorrectly predicted SOH to be the most stable isomer by more than 10 kJ/mol. Later, Xantheas and Dunning [22, 23] performed extensive multireference configuration interaction (MR-CI) calculations consisting of all the single and double excitations arising from a complete active space (CASSCF) wave

function obtained using the correlation consistent polarization valence (cc-pV) basis sets developed previously by Dunning et al. [24]. A unique feature of these basis sets is that each set improves on the previous one by systematically enlarging the orbital space. As a consequence, properties calculated with these basis sets can be fitted to a simple function of their size and extrapolated toward a “complete basis set” limit. Xantheas and Dunning in this way derived a value of -25.6 ± 5.4 kJ/mol for $\Delta_f H_{298\text{K}}^\circ(\text{HSO})$, much more negative than Luke and McLean’s [21] result, and correctly predicted HSO to be the more stable isomer. Finally, three studies appeared almost simultaneously in 1994. Espinosa-García and Corchado [25] performed fourth-order Møller–Plesset (MP4) and Pople’s quadratic configuration interaction [QCISD(T)] calculations using a 6-311++G(3df,2p) basis set on MP2/6-31G(d,p) optimum geometries, to obtain a value of -8.8 kJ/mol for the enthalpy of formation of HSO, in disagreement with the MR-CI result of Xantheas and Dunning [22, 23]. Esseffar et al. [26] employed the Pople’s G2 model chemistry theory [27], as well as QCISD(T) calculations, to derive a value of -17.6 ± 5.4 kJ/mol for $\Delta_f H_{0\text{K}}^\circ(\text{HSO})$ (Xantheas and Dunning’s [22, 23] value at 0 K was -22.6 ± 5.4 kJ/mol). Finally, Wilson and Hirst [28] performed modified G2 calculations on the reaction of H_2S with OH and determined the enthalpy of formation of HSO as -21.9 ± 2.6 kcal/mol. Both studies [26, 28] also predicted HSO as more stable than SOH, although by a smaller amount than Xantheas and Dunning [23]. A more recent study is available in a work by Goumri et al. [29], but the methodology used is similar to that employed by Esseffar et al. [26] and by Wilson and Hirst [28] (G2) and the enthalpy of formation of HSO at 298 K, -19.9 kJ/mol, is also similar. To our knowledge, no further computational studies of this problem are present in the literature.

Clearly, the most recent experimental and theoretical values present a serious discrepancy. Moreover, among the experimental determinations themselves (i.e., [10] vs. [15, 16]) and among the theoretical determinations themselves (i.e., [22, 23] vs. [25, 26, 28, 29]), there are discrepancies. For that reason, we decided to reinvestigate this problem using an alternative theoretical procedure, density functional theory (DFT) [30–32]. DFT is based on a completely different set of assumptions than the Hartree–Fock and post–Hartree–Fock methods that had been applied up to now to this problem. Thus, we can have an independent theoretical

assessment of $\Delta_f H_{298\text{K}}^\circ(\text{HSO})$ to compare with the ab initio results already present in the literature. We have shown previously [33–39] that density functional methods using large basis sets and isodesmic reactions can produce very accurate thermochemical results, bettering G2 and even coupled cluster singles and doubles calculations with perturbative inclusion at triple excitation [CCSD(T)] methods in many cases. We expect that the results obtained for HSO employing this methodology will be of the same quality as those obtained before.

Computational Details

Density functional methods [30–32] were used throughout this work for geometry optimizations and evaluation of molecular properties. The standard adiabatically coupled [40] functionals were employed, using Becke’s exchange potential [41] and either Lee–Yang–Parr [42] or Perdew–Wang [43] correlation potentials (respectively, B3LYP and B3PW91 methods). Dunning’s augmented correlation consistent polarized valence double- ζ basis sets [24] aug-cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z were chosen in order to investigate the convergence of the results in the way advocated by Dunning, and to compare with Xantheas and Dunning’s work [22, 23]. The smallest set employed, aug-cc-pVDZ, is Dunning’s standard valence double- ζ augmented by an extra set of diffuse (*s, p, d*) functions. The largest set employed, cc-pV5Z, is a valence quintuple- ξ basis set including *h* functions on the main atoms and *g* functions on hydrogens. Contrary to what Xantheas and Dunning did [23], we were not forced to remove the *g* functions for hydrogens. Properties were plotted as a function of the ordinal number of the basis set (i.e., $n = 1$ for aug-cc-pVDZ, $n = 2$ for cc-pVTZ, $n = 3$ for cc-pVQZ, and $n = 4$ for cc-pV5Z), following Dunning’s standard procedure. According to experience, it is possible to fit several properties that depend on the size of the basis set (the enthalpy, for instance) using an equation of the form

$$P(n) = A + B \exp(-Cn) \quad (6)$$

where $P(n)$ is the property of interest, A , B , C are constants determined by a least-squares fit, and n is the number referred to above that characterizes the basis set. We also performed calculations employing Pople’s 6-311+(3df,2p) [44], to compare its performance with respect to that of Dunning’s basis sets.

Several reactions were employed to derive the enthalpy of formation of HSO. On one side, we used

the same reaction employed by Xantheas and Dunning [22, 23]:

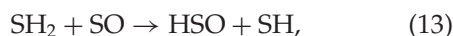
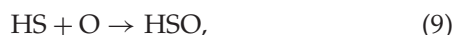


Analogously to Xantheas and Dunning's study [23], we calculated the dissociation reaction path and located the saddle point for the reaction. For the purpose of calculating the enthalpy of formation of HSO, we consider also the reaction

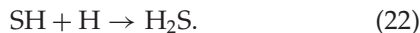
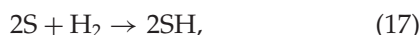


to minimize the error in the calculated enthalpy of formation of the hydrogen atom.

On the other side, we chose also the reactions employed by Esseffar et al. [26], namely



In the case of reaction (14) we studied also the reaction path for the isomerization and determined the saddle point. Some other reactions were also employed for the study of the enthalpy of formation of other species whose values are well established experimentally (SH, H₂S, and SO). These reactions were



Geometry optimizations of all the species involved in reactions (7)–(22) were performed using adequate thresholds so as to obtain a precision of 0.0001 Å in distances and 0.01° in angles. Minima and saddle points were characterized as usual by calculating the Hessian. Standard statistical thermodynamics equations were used for calculating thermodynamic functions. All the calculations were performed employing Gaussian 94 [45].

Results and Discussion

STRUCTURAL DATA

A comparison of some of the available structural data for HSO and SOH is presented in Table I. No experimental determinations are available for the geometry of SOH, while both Schurath et al. [8] and Ohashi et al. [18] have determined geometrical data for HSO. The experimental data in Ref. [18], obtained through Doppler-limited dye laser excitation spectroscopy, are the most accurate and will be used for the comparison with the theoretical results. A first striking observation is the accuracy of the MP2/6-311+G(d) calculations. There are no theoretical grounds to justify why these calculations have to be more accurate than coupled cluster singles and doubles (CCSD) or CISD calculations, and thus we are led to conclude that this effect is only a consequence of a casual error cancellation. On the other side, the best theoretical methods show reasonable agreement among themselves. The increase in the size of the basis set within any of the methods leads to a decrease of the H–S and S–O bond lengths and a small increase in the HSO angle. There is perfect agreement between MR-CI and DFT methods with the same basis set concerning the S–O bond length and a small discrepancy with respect to the H–S bond length. The DFT methods give this length at about 0.01 Å larger than the MR-CI method and more in agreement with the experimental result. Notice that the basis set effect is more noticeable in the description of the S–O bond than in the description of the H–S bond; the variation with the improvement of the basis set is five times larger in the former case. The extrapolation to the complete basis set limit gives SO bond lengths of 1.498 Å at the B3LYP level and 1.492 Å at the B3PW91 level.

In the case of SOH there is again good agreement between the calculations at different levels, although the discrepancy between the complete basis set limits of B3LYP (1.636 Å) and B3PW91 (1.627 Å) is a little bit larger. All in all, one can say that there is good agreement between the MR-CI and DFT calculations and among them and the experimental determination, at least for the SO bond.

In Table II we list the harmonic vibrational frequencies of both HSO and SOH calculated at the DFT level. There are two important points to notice in this table.

In the first place, the convergence of the DFT results with the improvement of the basis set is excellent in general, but the fact remains that in the

TABLE I
Optimal geometries of the isomers HSO and SOH.

Method	Basis set	Error ^a	HSO			SOH			Ref.
			$r(\text{SH})$ (Å)	$r(\text{SO})$ (Å)	$\theta(\text{HSO})$ (deg)	$r(\text{SO})$ (Å)	$r(\text{OH})$ (Å)	$\theta(\text{SOH})$ (deg)	
UHF	aug-cc-pVDZ	0.040	1.350	1.554	101.14	1.640	0.946	109.87	[23]
	6-311+G(d)	0.037	1.341	1.534	101.46				This work
CASSCF	aug-cc-pVDZ	0.034	1.361	1.571	103.40	1.690	0.973	105.50	[23]
	cc-pVTZ	0.020	1.355	1.528	104.69	1.656	0.969	106.34	[23]
	cc-pVQZ	0.018	1.354	1.519	104.86	1.650	0.968	106.79	[23]
MP2	6-311+G(d)	0.007	1.394	1.480	105.98				This work
CI SD	6-311+G(d)	0.020	1.362	1.503	103.73				This work
	cc-pVTZ	0.017	1.364	1.487	104.34				This work
CCSD	6-311+G(d)	0.022	1.375	1.527	103.51				This work
QCISD	6-311G(d,p)	0.020	1.369	1.533	104.40				[26]
MR-CI	cc-pVTZ	0.017	1.363	1.518	104.75	1.655	0.965	105.81	[23]
	cc-pVQZ	0.015	1.361	1.506	104.95	1.645	0.963	106.37	[23]
B3LYP	aug-cc-pVDZ	0.030	1.387	1.555	103.08	1.676	0.971	108.03	This work
	cc-pVTZ	0.017	1.379	1.518	104.24	1.648	0.967	108.42	This work
	cc-pVQZ	0.015	1.376	1.509	104.47	1.642	0.966	108.89	This work
	cc-pV5Z	0.014	1.375	1.502	104.60	1.638	0.966	109.20	This work
	6-311+G(3df,2pd)	0.015	1.374	1.504	104.43	1.645	0.966	109.19	This work
B3PW91	aug-cc-pVDZ	0.027	1.386	1.547	103.22	1.666	0.969	107.71	This work
	cc-pVTZ	0.016	1.378	1.512	104.29	1.639	0.965	108.16	This work
	cc-pVQZ	0.014	1.376	1.503	104.47	1.633	0.964	108.60	This work
	cc-pV5Z	0.013	1.375	1.496	104.69	1.629	0.964	108.88	This work
	6-311+G(3df,2pd)	0.015	1.370	1.498	104.51	1.632	0.965	108.87	This work
Exp.			1.389 ± 0.005	1.494 ± 0.005	106.6 ± 0.5				[18]
			1.35	1.54	102				[8]

^aThe average error was calculated as the root mean square (rms) of the three calculated geometrical parameters of HSO with respect to the experimental data of Ref. [19]; angles were expressed in radians for this calculation.

TABLE II
Harmonic vibrational frequencies of the isomers HSO and SOH at different theoretical levels, in cm^{-1} .

Method	Basis set	HSO			SOH			Ref.
		SO stretch	HSO bend	HS stretch	SO stretch	SOH bend	HO stretch	
CASSCF	aug-cc-pVDZ	941	1094	2634	795	1220	3692	[23]
	cc-pVTZ	959	1121	2620	820	1230	3723	[23]
	cc-pVQZ	939	1115	2651	802	1226	3713	[23]
QCISD(T)	6-311G(d,p)	951	1092	2481				[26]
MR-CI	cc-pVTZ	1013	1099	2625	844	1220	3806	[23]
	cc-pVQZ	966	1078	2620	821	1202	3729	[23]
B3LYP	aug-cc-pVDZ	951	1048	2420	819	1158	3737	This work
	cc-pVTZ	999	1080	2399	841	1176	3746	This work
	cc-pVQZ	1010	1088	2404	841	1174	3746	This work
	cc-pV5Z	1018	1093	2418	842	1170	3749	This work
	6-311+G(3df,2pd)	1015	1092	2418	840	1170	3761	This work
B3PW91	aug-cc-pVDZ	971	1058	2445	842	1163	3764	This work
	cc-pVTZ	1016	1092	2422	865	1179	3776	This work
	cc-pVQZ	1025	1099	2423	864	1176	3775	This work
	cc-pV5Z	1032	1106	2437	864	1173	3777	This work
Exp.	6-311+G(3df,2pd)	1028	1104	2437	863	1174	3790	This work
		1026 1013 \pm 5	1164 1064	2271 2570				[18] [8]

case of the HS stretch the aug-cc-pVDZ results are as good as the pV5Z ones. We attribute this to some kind of error compensation between the optimum geometry at this level and the electron density distribution. This is supported by the observation that in passing from aug-cc-pVDZ to cc-pvTZ the result becomes worse, and later improvements in the basis set bring it back to the aug-cc-pVDZ value.

In the second place, notice that the DFT harmonic frequencies are nearer to the experimental results than the MR-CI ones, especially for the bond stretchings. The H-S bond stretching presents the largest discrepancy, with a difference of about 200 cm^{-1} between both methods. Notice that there is also a large discrepancy in this frequency between both experimental determinations. Ohashi et al. [18] had some trouble to derive this frequency and had to resort to data on the SH radical to obtain the value proposed. The force field employed to derive the fundamental frequencies was a simple valence force field with three diagonal elements. Their value for the HS stretching must be taken therefore with some care, and probably a better one would be intermediate between those of Ohashi et al. [18] and Schurath et al. [8]. In any case, the DFT results would be always much nearer to the experimental result than the MR-CI calculations.

In conclusion we can say that both for the geometrical parameters and the vibrational frequencies DFT gives well-converged results that are as good as or better than the MR-CI results obtained with the same basis sets. A final test of the goodness of the methodology is provided by the comparison of optimum geometries and harmonic frequencies of other molecules presenting the same type of bonds (S-H, S-O) in particular the radical SH and the closed-shell molecules H_2S and SO. A summary of these data and the comparison with experiment is shown in Table III. The results are clearly in line with what we said before and allow us to consider DFT as the most exact methodology of those employed on this problem up to now.

THERMOCHEMISTRY

Total energies, zero-point energy corrections, and absolute enthalpies for all the species calculated in this work at all levels of theory are available from the authors on request. These energies were employed to calculate the enthalpies of formation of the species SH, H_2S , and SO, whose experimental values are well determined, and the results shown in Table IV. The striking aspect of this table is that

TABLE III
Optimum geometries and harmonic vibrational frequencies for HS, SH_2 , and SO calculated at different theoretical levels.

Molecule	Method	$r(\text{S-O})$ (Å)	$r(\text{S-H})$ (Å)	$\theta(\text{HSH})$ (deg)	SO stretch (cm^{-1})	SH stretch (cm^{-1})	SH stretch (cm^{-1})	SH stretch (cm^{-1})	HSH bend (cm^{-1})	Ref.
SO	MRCI/cc-pVQZ	1.491			1135					[22]
	B3LYP/cc-pV5Z	1.486			1158					This work
	B3PW91/cc-pV5Z	1.481			1182					This work
	exp.	1.481			1151					[46]
SH	B3LYP/cc-pV5Z		1.346			2671				This work
	B3PW91/cc-pV5Z		1.345			2694				This work
	exp.		1.340			2711				[46]
H_2S	B3LYP/cc-pV5Z		1.341	92.52		2690		2703	1212	This work
	B3PW91/cc-pV5Z		1.341	92.30		2711		2725	1202	This work
	exp.		1.336			2615		2626	1182	[46]

TABLE IV
Enthalpies of formation of SH, H₂S, and SO at 298 K using the different theoretical levels employed in this work, in kJ/mol.

Method	Basis set	SO		SH		H ₂ S			
		React. (15)	React. (16)	React. (17)	React. (18) ^a	React. (19) ^a	React. (20)	React. (21)	React. (22) ^a
B3LYP	aug-cc-pVDZ	45.7	42.4	141.8	147.0	-1.2	-12.8	-11.7	-8.9
	cc-pVTZ	21.4	14.8	142.7	141.6	-12.0	-11.8	-9.9	-14.2
	cc-pVQZ	12.9	5.6	141.0	139.7	-15.4	-13.1	-12.8	-15.7
	cc-pV5Z	5.8	-1.1	139.7	138.4	-17.8	-15.2	-15.2	-16.8
	6-311+G(3df,2p)	7.6	-0.4	139.8	138.7	-17.4	-15.2	-15.1	-16.6
B3PW91	aug-cc-pVDZ	45.2	38.5	139.2			-17.9	-19.3	
	cc-pVTZ	21.1	11.8	139.4			-17.7	-18.8	
	cc-pVQZ	12.7	2.4	137.9			-18.6	-21.4	
	cc-pV5Z	5.6	-4.3	136.6			-19.7	-23.7	
	6-311+G(3df,2p)	6.8	-3.3	136.7			-19.9	-24.0	
Exp. [47]		5.02		139.42					-20.52

^a No B3PW91 calculations were performed for these reactions because it is known that this method fails in reactions where the H atom is involved.

the enthalpy of formation of the three molecules can be accurately predicted using DFT theory, provided the reactions employed are well chosen. In fact, considering the cc-pV5Z or 6-311+G(3df,2p) results for all reactions except (16), the calculated and experimental enthalpies of formation do not differ in more than 6 kJ/mol in the worst case. The exception is reaction (16), and this is related to the fact that the DFT calculations with these basis sets have a large error of about 10 kJ/mol in the enthalpy of atomization of the oxygen molecule and, therefore, in the enthalpy of formation of the oxygen atom. Our conclusions with respect to the small molecules which will be involved in the calculation of the enthalpy of formation of HSO and SOH is that DFT methods are accurate enough for the purpose.

In Table V we have finally collected the data concerning the enthalpy of formation of HSO. Let us consider first the isodesmic reaction (13), which should show the largest error cancellation and thus give the most accurate results. The values of $\Delta_f H_{298K}^\circ(\text{HSO})$ calculated with the five different basis sets and two different exchange correlation potentials exhibit differences not larger than 4.3 kJ/mol (i.e., about 1 kcal/mol). These results lend credibility to our belief that errors in the calculation of the enthalpy of formation of HSO through the use of Eq. (13) are largely canceled out. We have included in Table V the extrapolated complete basis set (CBS) limits in the manner calculated by Dunning. For that purpose, we obtained the CBS limit for the enthalpies of each species in reaction (13) and then calculating the enthalpy of reaction at the CBS limit. As we will show later, we consider this to be an upper limit while the values calculated at the cc-pV5Z are our lower limit. Using these two limits, we would derive slightly more negative value than those derived with other theoretical methods. This might be due to the acceptance of Dunning's extrapolation method, which may not be adequate for the DFT calculations. To test this aspect of the question we used the data calculated for reaction (7), the one used by Xantheas and Dunning [23], Esseffar et al. [26], and Wilson and Hirst [28]. As one can see in the table, the enthalpy of formation of HSO calculated from the enthalpy of reaction (7) shows a strong basis set dependency at the complete active space SCF (CASSCF) and MR-CI levels (17 and 25 kJ/mol, respectively). This effect is not so evident in the DFT calculations (only 9 kJ/mol), but it is clearly larger than in the data obtained from the isodesmic reaction (13). When the data are plotted as we did in Figure 1, one can see that the DFT cal-

TABLE V
Enthalpy of formation of HSO at 0 K calculated using different theoretical methods, in kJ/mol.

Method	Basis set	React. (13)	React. (7)	React. (8)	React. (9)	React. (10)	React. (11)	React. (12)	Ref.
CASSCF	aug-cc-pVDZ		13.8						[23]
	cc-pVTZ		5.03						[23]
	cc-pVQZ		0.42						[23]
	cc-pV5Z		-3.35						[23]
QCISD(T)	6-311++G(5d2f,2p)	-19.7	-19.7		-18.4		-18.0		[26]
CASSCF + 1 + 2	aug-cc-pVDZ		7.54						[23]
	cc-pVTZ		-9.64						[23]
	cc-pVQZ		-14.2						[23]
	cc-pV5Z		-17.2						[23]
	CBS limit		-17.6						[23]
FCI	CBS limit		-22.6						[23]
G2		-22.6	-23.5		-13.0		-12.6		[26]
G2*		-23.5	-24.7		-10.5		-10.1		[26]
		-22.6	-24.6		-24.7		-19.1		[28]
B3LYP	6-311+G(3df,2p)	-26.2	-18.7	-17.3	-19.1	-11.4	-24.6	-15.4	This work
	aug-cc-pVDZ	-25.3	-10.0	-15.0	22.3	27.1	25.1	25.0	This work
	cc-pVTZ	-22.7	-12.7	-11.3	-1.70	5.50	-4.2	4.40	This work
	cc-pVQZ	-25.0	-16.6	-15.0	-12.8	-4.90	-17.3	-7.30	This work
	cc-pV5Z	-26.7	-19.3	-17.7	-21.0	-13.5	-26.7	-17.6	This work
	CBS limit	-26.5	-23.9						This work
B3PW91	6-311+G(3df,2p)	-24.9	-21.7	-21.7	-24.0	-13.3	-20.6	-20.6	This work
	aug-cc-pVDZ	-24.3	-19.0	-19.0	17.8	25.2	20.5	20.5	This work
	cc-pVTZ	-22.0	-16.4	-16.4	-6.40	3.40	-1.00	-1.00	This work
	cc-pVQZ	-24.1	-19.6	-19.6	-17.3	-6.60	-12.5	-12.5	This work
	cc-pV5Z	-25.6	-22.1	-22.1	-25.5	-15.1	-22.2	-22.2	This work
	CBS limit	-25.5							This work

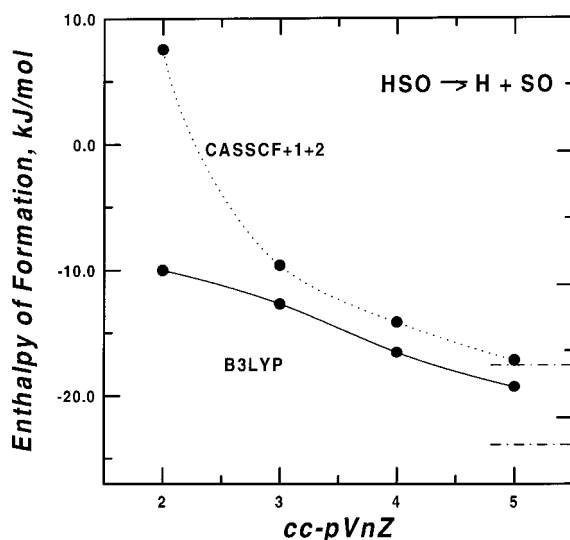


FIGURE 1. Enthalpies of formation calculated at the MR-CI and B3LYP levels of theory employing the cc-pVnZ basis sets. Fill lines are spline interpolation of the calculated data. The dotted lines show the complete basis set limits in each case, calculated according to Dunning's formula.

culations show a much smoother behavior than the MR-CI ones: the aug-cc-pVDZ calculation gives a much better value at the B3LYP level. The extrapolation leads to a value that is in good agreement with the full configuration interaction/CBS (FCI/CBS) limit (a correction of the MR-CI/CBS limit obtained by estimating the remaining error in MR-CI/CBS calculations because of dynamical correlation energy) of Xantheas and Dunning [23], and with the G2 and G2* estimations [26, 28]. All the other methods used with this reaction give a lower value.

Considering then this previous exercise, as well as the lower and upper limits obtained for reaction (13), we suggest the values of $\Delta_f H_{0K}^\circ = -24.9 \pm 2.1$ kJ/mol and $\Delta_f H_{298K}^\circ = -27.8 \pm 2.1$ kJ/mol for the enthalpy of formation of HSO.

With respect to the other reactions, one can observe that the $\Delta_f H_{0K}^\circ(\text{HSO})$ calculated using the largest basis set, cc-pV5Z, are reasonable. The largest difference with our predicted value is about 8 kJ/mol. However, for all the smaller basis sets the behavior is much worse. It must be noticed also that Pople's 6-311+G(3df,2p) basis set behaves almost as well as cc-pV5Z in most cases, a remarkable fact since it includes less functions and, more important, of smaller angular quantum numbers than the cc-pV5Z set.

In Table VI we show the results obtained for the energy difference between the isomers HSO and HOS. There is a clear convergence of the basis sets employed toward an extrapolated value of $\Delta \Delta_f H_{298K}^\circ = 21.0 \pm 2.1$ kJ/mol, in agreement with the CASSCF and MR-CI results of Xantheas and Dunning [23] (predicted value of 22.6 ± 5.4 kJ/mol), and about 7 kJ/mol higher than the result of Esseffar et al. (at 0 K) [26] and Wilson and Hirst [28]. Our final proposed value for $\Delta_f H_{298K}^\circ(\text{SOH})$ is -6.8 ± 2.1 kJ/mol, in agreement with Xantheas and Dunning's result [23] of -2.9 ± 5.4 kJ/mol, Wilson and Hirst [28] -7.7 ± 2.6 kJ/mol, and O'Hair et al. [48] combined experimental and theoretical study which predicted a $\Delta_f H_{0K}^\circ(\text{SOH})$ of -2.1 ± 8.4 kJ/mol.

We conclude then that for the enthalpy of formation of both HSO and HOS, the density functional results are entirely in agreement with the MR-CI ones of Xantheas and Dunning [23], while they are larger than those calculated at the G2 or modified G2 levels, especially if nonisodesmic reactions are employed.

As a final consideration, if one accepts the theoretically proposed value for the $\Delta_f H_{298K}^\circ(\text{HSO})$, there exists a large difference with the experimental result. All high-level theoretical methods are reasonably in agreement in predicting $\Delta_f H_{298K}^\circ(\text{HSO})$ below -21 kJ/mol at least, instead of the -5 kJ/mol measured by Davidson et al. [15] and Balucani et al. [16]. Since the theoretical methods have been, repeatedly proved to be accurate enough, one has to conclude that the experimental information concerns HOS and not HSO as thought before. The $\Delta_f H_{298K}^\circ(\text{SOH})$ calculated in this work, -6.8 ± 2.1 kJ/mol, is entirely in agreement with this hypothesis and with the experiments of Iraqi et al. [19].

Moreover, accepting the proposed theoretical value of $\Delta_f H_{298K}^\circ(\text{HSO})$, then reaction (4) is clearly endothermic at room temperature. Using the accepted enthalpies of formation at 298 K of HS (139.42 kJ/mol) and O₃ (142.88 kJ/mol) [46] and our value of -27.8 kJ/mol for HSO, one obtains a $\Delta_r H_{298K}^\circ$ of about 24.3 kJ/mol. The important point concerning this reaction, however, is that the entropy has a large contribution to the free energy of the reaction because three molecules are produced after the collision of HS and O₃. Using the experimental entropies for O₂, HS, and O₃ [46], and the one calculated at the B3LYP/cc-pV5Z level for HSO, the $-T\Delta S$ term contributes -37.5 kJ/mol to the $\Delta_r G^\circ$ of the reaction at 298 K for a final $\Delta_r G^\circ$ value of -13.1 kJ/mol at the B3LYP/cc-pV5Z level. This means that the reaction should be spontaneous

TABLE VI
Energy and enthalpy difference for the reaction $\text{HSO} \rightarrow \text{SOH}$ calculated using different theoretical methods, in kJ/mol.

Method	Basis set	ΔE_e	ΔE_0	$\Delta \Delta_r H_{298K}^\circ$	Ref.
CASSCF	aug-cc-pVDZ	-13.8	-7.96		[23]
	cc-pVTZ	1.68	7.96		[23]
	cc-pVQZ	9.21	15.5		[23]
	cc-pV5Z	10.9	19.3 ^a		[23]
	CBS limit		22.7		[23]
CASSCF + 1 + 2	aug-cc-pVDZ	-18.4	-12.6 ^a		[23]
	cc-pVTZ	-3.35	4.19		[23]
	cc-pVQZ	6.29	13.0		[23]
	cc-pV5Z	13.0	17.6 ^a		[23]
	CBS limit		22.7	22.6	[23]
G2*				14.9	[26]
B3LYP	aug-cc-pVDZ	-12.9	-5.20		This work
	cc-pVTZ	-1.10	6.49		This work
	cc-pVQZ	5.90	13.4		This work
	cc-pV5Z	12.0	19.4		This work
	6-311+G(3df,2p)	10.9	19.2		This work
B3PW91	aug-cc-pVDZ	-9.81	-2.10		This work
	cc-pVTZ	-1.70	9.80		This work
	cc-pVQZ	8.39	16.0		This work
	cc-pV5Z	14.5	21.9		This work
	6-311+G(3df,2p)	22.7	21.8	21.9	This work

^a The ZPE energy necessary for these calculations was taken from the values calculated at a lower level of theory.

TABLE VII
Geometric structure of the saddle point for the isomerization HSO → SOH and barrier calculated at different theoretical levels.

Method	Basis set	r(SO) (Å)	r(SH) (Å)	θ (HSO) (deg)	ω_1 (cm ⁻¹)	ω_2 (cm ⁻¹)	ω_3 (cm ⁻¹)	ΔE_0 (kJ/mol)	Ref.
CASSCF	aug-cc-pVDZ	1.733	1.477	50.30	1834 <i>i</i>	726	2317	180.0	[23]
	cc-pVTZ	1.696	1.361	54.63	1862 <i>i</i>	742	2377	197.0	[23]
	cc-pVQZ	1.668	1.430	49.92	1591 <i>i</i>	611	2929	208.1	[23]
MR-CI	aug-cc-pVDZ	1.677	1.355	54.92	1858 <i>i</i>	778	2407	186.3	[23]
	cc-pVTZ	1.630	1.426	49.93	1544 <i>i</i>	609	2946	194.7	[23]
B3LYP	aug-cc-pVDZ	1.695	1.450	50.56	1860 <i>i</i>	807	2321	175.8	This work
	cc-pVTZ	1.665	1.435	50.99	1906 <i>i</i>	817	2364	190.8	This work
	cc-pVQZ	1.656	1.434	50.88	1919 <i>i</i>	822	2356	196.4	This work
	6-311+G(3df,2p)	1.653	1.439	50.68	1936 <i>i</i>	823	2344	201.2	This work
B3PW91	aug-cc-pVDZ	1.684	1.443	50.93	1837 <i>i</i>	833	2367	173.4	This work
	cc-pVTZ	1.653	1.429	51.32	1884 <i>i</i>	848	2412	188.3	This work
	cc-pVQZ	1.645	1.431	51.25	1892 <i>i</i>	851	2401	193.4	This work
	6-311+G(3df,2p)	1.642	1.433	50.98	1910 <i>i</i>	854	2390	198.2	This work
G2*								192.7 ^a	[28]

^a Value of the enthalpy of activation at 298 K.

at room temperature, no matter that it is endothermic. One has to take care, however, because the temperature at which these reactions occur in the atmosphere is not 298 K. Assuming a temperature of -50°C (223 K) as more appropriate, $\Delta_r G^{\circ}$ amounts to about -1.4 kJ/mol. Therefore, one can conclude that the reaction would be spontaneous above around 220 K, as observed in all the experiments mentioned above, which were performed mostly at room temperature but not necessarily in atmospheric conditions.

REACTION PATHS

The first experimental studies on HSO were able to detect only one isomeric form. However, Iraqi et al. [19] showed that both isomeric anions HSO^- and SOH^- can be prepared experimentally as different species. These anions suffer oxidation in a one-electron process and are subsequently reionized to the corresponding cations. Therefore, it is clear that both isomeric radicals are accessible. However, the presence of only one of the isomers in the previous experiments led Luke and McLean [21] and Xantheas and Dunning [23] to predict the existence of a large barrier for the interconversion of the isomers. Xantheas and Dunning [23] calculated a barrier of 194.8 kJ/mol at the MR-CI/cc-pVQZ level. In Table VII we show our own results obtained using DFT methods for the isomerization saddle point. Although in some cases [49] B3LYP has been found to give inadequate values for the barrier of three-atom saddle points, we find in this case that the values of the isomerization barrier are perfectly in agreement with other values found in the literature. The same can be said with respect to the geometrical structure of the saddle point, although the frequencies do present some major deviations.

The dissociation of both HSO and SOH to $\text{H} + \text{SO}$ was also studied at the DFT level. In agreement with Xantheas and Dunning [23], no saddle point was found for the decomposition of HSO and one saddle point was located for the decomposition of SOH. The data associated to this saddle point are displayed in Table VIII. As in the previous case, the saddle point located with B3LYP has a quite similar geometrical structure than the one located at the MR-CI level. The same happens with the barrier, whose value agrees well with the one calculated by Xantheas and Dunning [23]. Therefore, we can conclude that DFT is behaving quite reasonably for the description of these two saddle points and shows no

TABLE VIII
Geometric structure of the saddle point for the decomposition $\text{SOH} \rightarrow \text{SO} + \text{H}$ and barrier calculated at different theoretical levels.

Method	Basis set	$r(\text{SO})$ (Å)	$r(\text{SH})$ (Å)	$\theta(\text{HSO})$ (deg)	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	ΔE_0 (kJ/mol)	Ref.
CASSCF	cc-pVTZ	1.898	1.564	120.3	721/	456	959	13.4	[23]
	cc-pVQZ	1.834	1.534	120.4	527/	508	1000	15.1	[23]
MR-CI	cc-pVTZ	1.906	1.513	121.9	643/	424	1072	9.64	[23]
B3LYP	6-311+G(3df,2p)	2.010	1.496	123.8	394/	308	1114	12.1	This work

^a Value of the enthalpy of activation at 298 K.

sign of inadequacy like the one previously reported for other transition state [49].

Conclusions

B3LYP and B3PW91 methods with correlation consistent basis sets have been applied to the study of the enthalpy of formation of HSO and related species, as well as to the isomerization and decomposition reactions of HSO. It was found that from the point of view of structure, as reflected in the geometries and fundamental vibrational frequencies, DFT gives results completely in agreement with the much more demanding MR-CI calculations. From the point of view of the thermochemistry of the processes, DFT was shown to be very precise in the evaluation of the enthalpy of formation of several species related to HSO, whose values have been experimentally determined with great accuracy. Concerning HSO and SOH, the proposed values in this work, $\Delta_f H_{298\text{K}}^\circ(\text{HSO}) = -27.8 \pm 2.1$ kJ/mol and $\Delta_f H_{298\text{K}}^\circ(\text{SOH}) = -6.8 \pm 2.1$ kJ/mol, agree well with those determined at the MR-CI level, -25.6 ± 5.4 kJ/mol and -2.9 ± 5.4 kJ/mol, respectively. As a consequence, we subscribe to the idea [20] that the experimentally determined enthalpy of formation is not that of HSO but may well be that of SOH, since the measurements done by Balucani et al. [16] could have produced this latter isomer, as done in the experiments by Iraqi et al. [19]. Moreover, the enthalpy of formation of HSO makes the reaction with ozone clearly endothermic at room temperature, although the entropic component makes the reaction spontaneous at temperatures above 220 K. The barrier for the isomerization reaction $\text{HSO} \rightarrow \text{SOH}$ and the decomposition $\text{SOH} \rightarrow \text{SO} + \text{H}$ were located and both the geometrical structure and the barriers do agree well with the MR-CI results.

As a general conclusion, it was shown once more that DFT methods do compete with very high level post-Hartree-Fock calculations, giving results that are of high accuracy when they can be compared to experiment. In those cases where the experimental results do not exist, DFT computational thermochemistry should be the method of choice.

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