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Correcting the experimental enthalpies of formation of some members of the biologically significant sulfenic acids family

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ABSTRACT: Sulfenic acids are important intermediates in the oxidation of cysteine thiol groups in proteins by reactive oxygen species. The mechanism is influenced heavily by the presence of polar groups, other thiol groups, and solvent, all of which determines the need to compute precisely the energies involved in the process. Surprisingly, very scarce experimental information exists about a very basic property of sulfenic acids, the enthalpies of formation. In this paper, we use high level quantum chemical methods to derive the enthalpy of formation at 298.15 K of methane–, ethene–, ethyne– and benzenesulfenic acids, the only ones for which some experimental information exists. The methods employed were tested against well–known experimental data of related species and extensive CCSD(T) calculations. Our best results consistently point out to a much lower enthalpy of formation of methanesulfenic acid, CH_3SOH, ($\Delta_f H^0(298.15K) =$ –35.1 ± 0.4 kcal mol^{-1}) than the one reported in the NIST thermochemical data tables. The enthalpies of formation derived for ethynesulfenic acid, HC≡CSOH, +32.9 ± 1.0 kcal/mol, and benzenesulfenic acid, C_6H_5SOH, –2.6 ± 0.6 kcal mol^{-1}, also differ markedly from the experimental values, while the enthalpy of formation of ethenesulfenic acid CH_2CHSOH, not available experimentally, was calculated as –11.2 ± 0.7 kcal mol^{-1}.

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1. INTRODUCTION

Earth's atmosphere was originally reductive until the introduction of oxygen, presumably by cyanobacteria, about 3 billion years ago. After that, oxygen became crucial for the life of most animals, including ourselves. An unwanted side effect was the appearance of reactive oxygen species (ROS), which can react with essential molecules, mainly cysteine containing proteins, turning them useless. Paradoxically, those same ROS can also act as messengers in intracellular reaction pathways, making thus mandatory for the organisms to develop redox homeostasis mechanisms that keep unwanted oxidations under control.[1–3]

The oxidation reactions caused by ROS produce an effect known as oxidative stress,[4,5] mainly produced by the reaction of one– and two–electron oxidants with the thiol groups of cysteine and methionine. Abstraction of the hydrogen atom from the –SH groups of those aminoacids produces thiyl radicals ($RS^{\cdot}$ species), which can react with $HO^{\cdot}$ radicals[6,7] to form sulfenic acids (RSOH).[8–12] These species can be also formed through the reaction of thiols with other molecules like peroxynitrites (ROONO), or hypohalogenous acids (HOCl, HOBr). Sulfenic acids are involved in neurodegenerative disease mechanisms[13] and their reversible formation is a requirement for the T–cell activation and function within the immunological system. In these times of COVID–19 pandemic, it is interesting to point out some attempts to use allicin (a simple thiosulfinate derived from sulfenic acids and present in garlic)[14] to attack the cysteine free thiol at the active site of the SARS–CoV–2 main protease enzyme.[15] In fact, species of the genius *Allium*, like garlic (*A. sativum*) or onion (*A. cepa*) do contain sulfenic acids and their derivatives, believed to be crucial for their beneficial effects on human health (and also, due to the action of the enzyme lachrymatory–factor synthase, responsible for the tears formed when cutting onions) .[16–18]

Due to the widespread sulfenic acid formation in tissues, in response to hydrogen peroxide acting as an intracellular signaling species,[19,20] researchers have tried to study those species for many years. However, sulfenic acids are extremely reactive and difficult to study experimentally. Only recently, for instance, a clever method for isolating the cysteine sulfenic acid was devised, protected by a molecular cradle to avoid fast reactions.[21] This method may be useful in the future as a way to study other small molecule sulfenic–acid species but, at the moment, the best procedure for studying them is to apply the tools of computational chemistry. For this purpose, it is important to use methods that can accurately reproduce geometries, energies and other molecular characteristics of the species.

We have studied in the past several instances of compounds which exhibit SO bonds. Sulfur and oxygen are valence isoelectronic, but the former is much larger, less electronegative and more polarizable than the latter. Moreover, sulfur exhibits different oxidation states due to the accessible *d* orbitals, and we showed a long time ago that it is difficult to describe at the same level of accuracy molecules with S(II), S(IV) and S(VI) atoms.[22] For this reason, it is important to have accurate benchmarks where the results of theoretical calculations are compared to experimental data. In the realm of energies, one of the most exacting challenges is to obtain accurate enthalpies of formation from the atomization energies of these species.

In the course of the above–mentioned studies, we came across sulfenic acids as species that we would like to describe accurately, because of their importance in the biochemical processes we pointed out before. Not surprisingly, in view of the difficulties to isolate those species, there is very scarce information on their enthalpies of formation. Only three sulfenic acids are present in the NIST thermochemical data tables[23] to our knowledge: methane–, ethyne– and benzenesulfenic acid, all of them determined by Tureček et al.[24] Ethenesulfenic acid was studied in that work also, but its enthalpy of formation was not determined accurately. Surprisingly, our initial simple calculations showed a remarkable difference between those experimental results and the theoretical ones. Therefore, we decided to perform a more in–depth study of this problem. In this paper, we report the determination of the standard enthalpy of formation of the four sulfenic acids reported before, using atomization energies, energies of dissociation to diatomic molecules, and isodesmic reactions for that purpose. The results strongly suggest that the values present in the NIST thermochemical tables for these species should be revised, and that additional experimental studies should be performed to corroborate our theoretical predictions.

2. CHEMICAL MODELS AND METHODS

The standard enthalpy of formation $\Delta_f H^0(298.15K)$ is one of the thermochemical properties crucial for the development of accurate kinetic models of chemical reactions. Experimental methods do provide accurate information in relatively few cases and it is customary to resort to computational methods for obtaining them accurately.[25] Normally, the method employed is semi–experimental: quantum chemical calculations of the enthalpies of the species of interest are performed with a variety of methods, and error cancellation chemical equations are built to calculate the $\Delta_f H^0(298.15K)$ from species for which experimental data are accurately known. These reactions may be those of atomization (since the $\Delta_f H^0(298.15K)$ of most atoms are experimentally known) or of other types, like dissociation into diatomic molecules in their standard states. Other types of error cancellation equations are isogyric (equal spin states on both sides of the equation), isodesmic (same atoms and bonds) or homodesmotic (a subclass of the former). The accuracy obtained depends on several factors, one of which is the accuracy with which the enthalpy of the species can be calculated.

2.1. *Computational methods*

Individual enthalpies for the species can be calculated with density functional (DFT) methods, perturbation procedures (second–order Møller–Plesset theory, MP2[26] for instance) or more refined post–Hartree–Fock methods, like CCSD(T).[27–29] Generally, large basis sets must be used and the ideal situation, when the basis set is large and balanced enough, is known as complete basis set (CBS) limit. For many years, the CCSD(T)/CBS calculations were considered the 'gold standard' for obtaining what is called 'chemical accuracy' (i.e., discrepancies with experiment below 1 kcal mol^{-1}).[27,30] Several approximations do exist to the CCSD(T)/CBS limit that normally is not reachable for medium size molecules. These methods receive the name of 'composite' because the procedures imply the calculation of additive contributions that address the incompleteness of the basis set, different approximations to the dynamical correlation energies, the one and N–electron errors, and include empirical correction factors in some cases.

Well–known procedures in this area are the complete basis set methods developed by Peterson and coworkers[31–35] (of which the most popular is CBS–QB3[34,35]), the Gn methods developed by Pople and collaborators[36–44] (which latest version are G4 and G4MP2[39,43]), the Weizmann–n (Wn) methods of Martin and coworkers[45–48] (the most accurate and expensive of which is W4[48]) and the correlation consistent composite approach (ccCA) method of Wilson et al.[49–54] Other more accurate or more purpose specific composite procedures, like the HL,[55] HEAT,[56, 57] and focal point analysis (FPA)[58, 59] methods, have also been proposed but used less frequently in the literature. Wn, HEAT and FPA are methods used normally for benchmarking, due to their high accuracy (maximum errors of less than 1 kJ mol^{-1}), but commensurate high demand of computer resources.

In this paper we have used two DFT methods, featuring the M06–2X,[60] and rev–DSDPBEP86[61] functionals, with Dunning's aug–cc–pV(T+*d*)Z and Truhlar's jun–cc–pV(T+*d*)Z[62] basis sets, plus several composite methods of progressively larger degree of accuracy (and, of course, increasing demand of computational resources). The extension of the basis set with tight *d* functions is known to be important for a quantitative description of the electronic structure of third–row atoms (sulfur in our case).[63–67] In order to account for dispersion interactions, M06–2X and rev–DSDPBEP86 were augmented by Grimme's DFT–D3 semiempirical dispersion,[68,69] which has been applied with considerable success to a large number of different systems, including dimers, large supramolecular complexes and reaction energies/barriers.[70–72]

The extensively employed CBS–QB3,[34,35] and G4,[39] composite methods were used in their original implementations, along with the more recent jun–ChS[73,74] and SVECV–f12[75] models. The jun–ChS approach employs rev–DSDPBEP86–D3(BJ)/jun–cc–pV(T+*d*)Z geometries and corrects CCSD(T)/jun–cc–pV(T+*d*)Z energies for the CBS error and core–correlation effects. These are evaluated by a two–point extrapolation[76] of MP2 energies using the jun–cc–pV(T+*d*)Z and jun–cc–pV(Q+*d*)Z basis sets, and as the difference between MP2/cc–pwCVTZ results obtained by correlating all and only valence electrons, respectively. The improvements with respect to the previously mentioned CBS–QB3 and G4 methods lies both in the use of a more accurate DFT method for obtaining optimum geometries and frequencies (CBS–QB3 and G4 use B3LYP for this purpose), and the calculation of the CBS limit and core–valence contributions at the MP2 level, thus providing a reduction of the computational burden.

SVECV–f12, in the implementation used in this paper, employs M06–2X–D3/aug–cc–pV(T+*d*)Z optimum geometries to perform CCSD(T,fc)–F12b(3C/FIX)[77] complete basis set (CBS) single–point calculations (obtained by extrapolation of cc–pVDZ–F12 and cc–pVTZ–F12 results), augmented by core–valence correlation corrections at the MP2/cc–pwCVTZ level. As such, this method includes more correlation energy than the jun–ChS method but is considerably more resource demanding and, therefore, of a more restricted application. Previous works have shown that both methods are equivalent in a number of situations.[66,67]

Required geometry optimizations at the DFT level were performed with very tight criteria. Analytical frequency calculations were performed using the DFT methods, and the thermochemical properties calculated using the rigid–rotor/harmonic oscillator approximation. Since no thermal contributions were calculated at the CCSD(T) or CCSD(T)–F12 levels, the individual enthalpies necessary for the calculation of $\Delta_f H^0(298.15K)$ were obtained adding the difference $H_{298} - E_T$ at the corresponding DFT level to the ab initio total energies (E_T is the sum of electronic and fixed nuclei energy). All calculations were performed using the Gaussian 16[78] and Molpro 20.1[79–81] computer packages.

2.2. *Chemical models*

This work aims to evaluate the $\Delta_f H^0(298.15K)$ of the four species considered in the experimental determination of Tureček et al.[24] and shown in Fig. 1, namely methanesulfenic acid (MSA), ethenesulfenic acid (ESA, vinylsulfenic acid), ethynesulfenic acid (YSA) and benzenesulfenic acid (BSA). For this purpose, we used atomization energies, energies of dissociation into diatomic molecules, and several isodesmic reactions for some special cases. Three well–known anchors, dimethylsulfide (DMS), dimethylsulfoxide (DMSO) and diethylsulfoxide (DESO) that are also presented in Fig.1 and for which enthalpies of formation are known accurately, were used as benchmark to assess the quality of the computational procedures. Two other species, dihydrogensulfoxide (DHSO) and sulfine (see

Fig. 1), which enthalpies of formation were calculated using accurate theoretical procedures, were included to further discuss the accuracy and precision of the composite methods.

Three protocols were used for the calculation of the $\Delta_f H^0(298.15K)$. Taking DMSO as an example, the enthalpy of formation using enthalpies of atomization was calculated as[82]

$$\Delta_f H^o(\mathrm{DMSO}) = \Delta_r^{theor} H^{at} + \sum_{atoms} \Delta_f^{exptl} H^o$$

$$= [(H(DMSO) - H(O) - \mathrm{H}(S) - 2H(C) - 6H(H)]^{theor} +$$

$$+ \Delta_f^{exptl} H^o(O) + \Delta_f^{exptl} H^o(S) + 2\Delta_f^{exptl} H^o(C) + 6\Delta_f^{exptl} H^o(H)$$

In this expression, *theor* refers to enthalpies calculated theoretically and *exptl* to experimental values. The subscripts *f* and *r* refer to formation and reaction respectively, and all values are calculated or measured at 298.15K. Atoms are considered in their standard state and their enthalpies of formation taken from reference 23 (H(^{1}S), 218.00±0.01 kcal mol^{-1}; C(^{3}P), 171.29±0.11 kcal mol^{-1}; O(^{3}S), 59.555±0.024 kcal mol^{-1}; S(^{3}P), 66.245±0.036 kcal mol^{-1}).

The calculation starting from diatomic molecules was performed in a similar way but taking diatomic molecules as reference

$$\Delta_f H^o(\mathrm{DMSO}) = \Delta_r^{theor} H^{at} + \textstyle\sum_{diatomics} \Delta_f^{exptl} H^o$$

$$= [(H(DMSO) - 1/2H(O_2) - 1/2H(S_2) - 1/2H(C_2) - 3H(H_2)]^{theor}$$

$$+ 1/2\Delta_f^{exptl} H^o(S_2) + \Delta_f^{exptl} H^o(C_2)$$

In this case, there is no component for H_2 or O_2 because the enthalpies of formation of these species in their standard state are exactly zero. The $\Delta_f H^0(298.15K)$ of $S_2(^3\Sigma_g)$ is 30.376±0.072 kcal mol^{-1} and that of $O_2(^3\Sigma_g)$ is 49.033±0.001 kcal mol^{-1}.

Finally, isodesmic reactions (i.e., those in which the number and type of different bonds in the species in the right–hand side and left–hand side of the chemical equation match as closely as possible) were also considered in some cases. The general formulation for a reaction A + B + D … → X + Y + Z … would be

$$\Delta_f H^0\,(\mathrm{A}) = -\Delta_r^{theor} H - \textstyle\sum_{B,C,D,\ldots} \Delta_f^{exptl} H^0 + \textstyle\sum_{X,Y,Z,\ldots} \Delta_f^{exp} H^0$$

where A is the species which enthalpy of formation one wants to obtain and B, C, …, X, Y, … etc., the other species that participate in the isodesmic reaction. This procedure is expected to reduce greatly any error in the calculation of the enthalpies of reaction but requires that the experimental (or high–accuracy theoretical) enthalpy of formation of the species B, C, etc. are known with the desired accuracy.

The following (quasi)isodesmic reactions were used in this work (species in bold characters are the ones for which the chemical equation was used to determine the enthalpy of formation).

$$\mathbf{(CH_3)_2S} + H_2S \rightarrow 2\ CH_3SH \tag{1a}$$

$$\mathbf{(CH_3)_2S} + (CH_3CH_2)_2O \rightarrow (CH_3CH_2)_2S + (CH_3)_2O \tag{1b}$$

$$\mathbf{(CH_3)_2S{=}O} + CH_3CH_2CH_3 \rightarrow (CH_3CH_2)_2S{=}O + CH_4 \tag{2a}$$

$$\mathbf{(CH_3)_2S{=}O} + (CH_3CH_2)_2O \rightarrow (CH_3CH_2)_2S{=}O + (CH_3)_2O \tag{2b}$$

$$\mathbf{(CH_3CH_2)_2S{=}O} + CH_4 \rightarrow (CH_3)_2S{=}O + CH_3CH_2CH_3 \tag{2c}$$

$$\mathbf{(CH_3CH_2)_2S{=}O} + (CH_3)_2O \rightarrow (CH_3)_2S{=}O + (CH_3CH_2)_2O \tag{2d}$$

$$\mathbf{H_2S{=}O} + (CH_3)_2S \rightarrow (CH_3)_2S{=}O + H_2S \tag{3a}$$

$$\mathbf{H_2S{=}O} + (CH_3CH_2)_2S \rightarrow (CH_3CH_2)_2S{=}O + H_2S \tag{3b}$$

$$\mathbf{H_2S{=}O} + (CH_2{=}CH)_2S \rightarrow (CH_2{=}CH)_2S{=}O + H_2S \tag{3c}$$

$$\mathbf{HSOH} + (CH_3)_2S \rightarrow (CH_3)_2S{=}O + H_2S \tag{4a}$$

$$\mathbf{HSOH} + (CH_3CH_2)_2S \rightarrow (CH_3CH_2)_2S{=}O + H_2S \tag{4b}$$

$$\mathbf{H_2C{=}S{=}O} + H_2S \rightarrow H_2S{=}O + H_2C{=}S \tag{5a}$$

$$\mathbf{H_2C{=}S{=}O} + H_2C{=}O \rightarrow H_2COO + H_2C{=}S \tag{5b}$$

$$\mathbf{CH_3{-}SOH} + (CH_3)_2S \rightarrow (CH_3)_2S{=}O + CH_3SH \qquad (6a)$$

$$\mathbf{CH_3{-}SOH} + (CH_3CH_2)_2S \rightarrow (CH_3CH_2)_2S{=}O + CH_3SH \qquad (6b)$$

$$\mathbf{CH_3{-}SOH +} H_2S \rightarrow HSOH + CH_3SH \qquad (6c)$$

$$\mathbf{CH2{=}CH{-}SOH} + CH_4 \rightarrow CH_3{-}SOH + H_2C{=}CH_2 \qquad (7a)$$

$$\mathbf{CH2{=}CH{-}SOH} + CH_4 \rightarrow HSOH + H_2C{=}CH_2CH_3 \qquad (7b)$$

$$\mathbf{HC{\equiv}C{-}SOH} + CH_4 \rightarrow CH_3{-}SOH + HC{\equiv}CH \qquad (8a)$$

$$\mathbf{HC{\equiv}C{-}SOH} + CH_4 \rightarrow CH_3{-}SOH + HC{\equiv}CH \qquad (8a)$$

$$\mathbf{C_6H_5{-}SOH} + CH_4 \rightarrow CH_3{-}SOH + C_6H_6 \qquad (9a)$$

$$\mathbf{C_6H_5{-}SOH} + CH_4 \rightarrow HSOH + C_6H_5{-}CH_3 \qquad (9b)$$

$$\mathbf{C_6H_5{-}SOH} + (CH_3)_2S \rightarrow (CH_3)_2S{=}O + C_6H_5{-}SH \qquad (9c)$$

$$\mathbf{C_6H_5{-}SOH} + (CH_3CH_2)_2S \rightarrow (CH_3CH_2)_2S{=}O + C_6H_5{-}SH \qquad (9d)$$

Isodesmic reactions (1a) and (1b) were used to determine the enthalpy of formation of DMS with respect to methylthiol and diethylsulfide respectively. Reactions (2a) and (2b) were employed to determine the enthalpy of formation of DMSO with respect to DESO and the pairs propane/methane and diethyl ether/dimethyl ether respectively. The reverse reactions (2c) and (2d) were employed alternatively to calculate the enthalpy of DESO from the experimental enthalpy of formation of DMSO and the aforementioned pairs. The purpose of all this procedure is to assess the accuracy of the methodology using species which $\Delta_f H^0(298.15K)$ is well–known experimentally.

Isodesmic reactions (3a–3c) were used to calculate the $\Delta_f H^0(298.15K)$ of DHSO (dihydrogen sulfoxide), a molecule that has been difficult to identify. In fact, DHSO is one of the three possible isomers with global structure [H_2SO], namely hydrogen thioperoxide HSOH (also known as sulfenic acid or sulfur hydride hydroxide) and H_2OS (thiooxonium ylide or thioformaldehyde *S*–oxide), for both of which there is some experimental evidence of existence,[83] and the simplest of all the sulfoxides, DHSO itself. Although studied theoretically several times (most recently in ref. 84, while the most recent study of HSOH is in ref. 85), it has never been isolated. In a recent experimental study[86] the fleeting DHSO sulfinyl structure seemed to be trapped by consecutive Knövenagel and Michael additions with dimedone. However, a very recent experimental study of successive hydrogenation of SO and SO_2 in solid para–H_2[87] did not find any trace of the elusive DHSO. We will talk later about the sulfenic acid isomer HSOH.

The theoretically determined $\Delta_f H^0(298.15K)$ of DHSO was used in reaction (4a) to obtain the enthalpy of formation of the simplest possible sulfine, $CH_2=S=O$, a molecule first observed in 1976.[88] The only experimentally derived value for $\Delta_f H^0(298.15K)$ is –1.9 ± 2.4 kcal mol^{-1}, published by Bouchoux and Salpin.[89] Theoretical studies by Ventura et al.,[22,90–92] Ruttink et al.[93,94] and Nagy et al.[95] gave discrepant values in quite an extended range. The apparent consensus nowadays is that the $\Delta_f H^0(298.15K)$ should be between –7 and –9 kcal mol^{-1}. A second isodesmic reaction, 4b, was introduced to calculate the $\Delta_f H^0(298.15K)$ of $CH_2=S=O$ using formaldehyde, thioformaldehyde and the simplest Criegee intermediate as anchors.

Reactions (5a)–(5b) and (6a)–(6b) were used to calculated the enthalpies of formation of HSA and MSA with respect to experimental anchors. Notice in passing that these reactions are not truly isodesmic. Therefore, the truly isodesmic reaction (6b) was used in the same way, but in this case one of the chaperons is HSOH for which we have no experimental value. Therefore, we used the previously determined $\Delta_f H^0(298.15)$, obtained as a weighted average of the values from the quasi–isodesmic reactions (5).

Regretfully, there are no experimental data for designing isodesmic reactions for ESA and YSA independently, but we used the previous theoretical determinations of the $\Delta_f H^0$ (298.15) for HSA and MSA to formulate the isodesmic reactions (7) and (8), which allowed us to calculate the enthalpies of formation of ESA and YSA. In the same way, we used the isodesmic reactions (9a) and (9b), which use the previously calculated enthalpies of reaction of HSA and MSA, and the quasi–isodesmic reactions (9b) and (9c), analogs to reactions (5) and (6), to calculate the enthalpy of formation of the largest sulfenic acid BSA.

It must be noticed that, because of error cancellation, the most trustable results are those derived from the isodesmic reactions. All reasonably sophisticated methods should give similar results in this case. They have one drawback however: it is not always simple to find appropriate reactions where the necessary experimental values are known with enough accuracy. Some less than perfect quasi–isodesmic reactions had to be used instead. In the second place come atomization reactions. Atomization energies are very difficult properties to describe computationally, and one should be careful to include spin–orbit and scalar–relativistic corrections. Moreover, for large molecules with many atoms, accumulative errors may be important. Finally, using diatomic molecules as reference is a very trustable and better method than the others for molecules containing elements which standard state is the diatomic (H_2, O_2, N_2, F_2) but less trustable when the species include elements (like C and S) which standard state in the gaseous phase is not the diatomic.

Unless specifically mentioned otherwise, the experimental enthalpies of formation for atoms, diatomic molecules and other species used in the isodesmic reactions were taken from the NIST Chemistry Webbook[23] where the references to the original sources can be found. The spin–orbit (S–O) correction for the atoms were taken from the paper by Curtiss et al.[96]

3. RESULTS AND DISCUSSION

3.1. Reference isodesmic reactions

As mentioned before, DMS, DMSO and DESO (see images of these species in Figure 1) were used as a benchmark set to see which chemical models would be more precise to calculate their enthalpies of formation, which experimentally[23] are –8.96 ± 0.48, –35.97 ± 0.36, and –49.1 ± 0.4 kcal mol^{-1} respectively. The results obtained using spin–orbit corrected atomization energies, energies of dissociation to diatomic molecules, and the isodesmic reactions (1a), (1b), (2a) and (2b), are collected in Table 1. We do not show here the isodesmic reactions (2c) and (2d) since they are simply the reverse of reactions (2a) and (2b) (see the Supplementary Information, Table S1). The results obtained for the enthalpies of formation of DESO will be mentioned later.

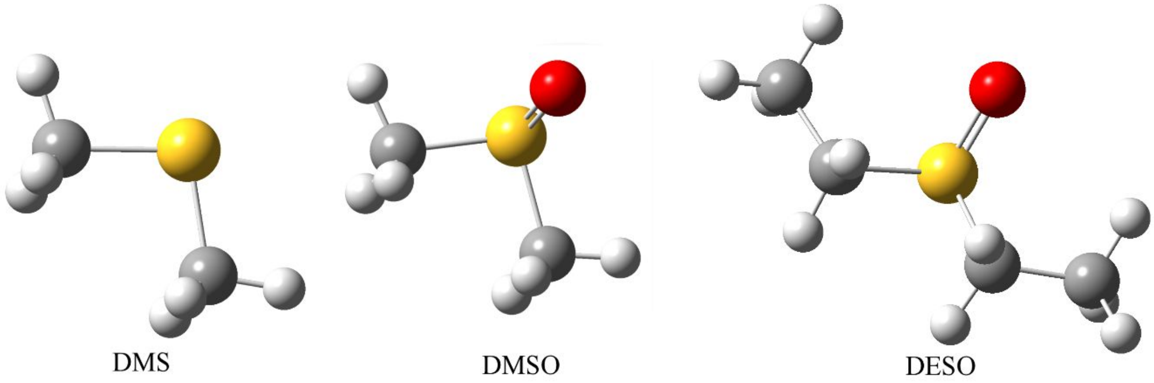

Figure 1. Structure of the three species used as test for the determination of enthalpies of formation of the sulfides and sulfoxides with the methods employed in this paper.

The $\Delta_f H^0(298.15K)$ was obtained from the enthalpy of reaction for each isodesmic reaction, itself calculated as the average of the enthalpies of reaction afforded by each method (except M06–2X–D3 which was not used). The uncertainty in this averaged enthalpy of reaction was expressed as ±2σ. The final uncertainty of the enthalpy of formation was calculated, following the procedure in ref. 97, as $\Sigma(u_i^2)^{1/2}$ where u_i are the uncertainties in the experimental values and in the average theoretical enthalpy of reaction. The enthalpy of formation for each isodesmic reaction *j*, x_j, obtained from the average over all methods of the enthalpy of reaction, are averaged as

$$\bar{x} = \sum(x_j/u_j^2)/\sum(1/u_j^2)$$

where the uncertainties u_j are $u_j = \Sigma(u_i^2)^{1/2}$ with u_i the uncertainties in the experimental values and in the average theoretical enthalpy of reaction. Simultaneously, the final uncertainty of the enthalpy of formation is derived as

$$\bar{u} = 1/[\sum(1/u_j^2)]^{1/2}$$

and the final estimation for the enthalpy of formation is $\Delta_f H^0(298.15K) = \bar{x} \pm \bar{u}$.

It is worth to observe that the dispersion of values of $\Delta_f H^0$(298.15) obtained using the isodesmic reactions with the four composite methods employed for the three molecules are similar to the experimental error (the average values for DMS, DMSO and DESO are –9.20 ± 0.23, –37.12 ± 0.44 and –487.95 ± 0.58 using a 95% confidence interval). This fact supports the case for error compensation, implicit in the isodesmic reactions protocol. A much larger dispersion is observed when the enthalpies of formation are calculated using atoms or diatomic molecules as reference values, underlying the need to be careful when employing those for accurate quantitative computations. For the three species, however, the enthalpies of formation obtained at the SVECV–f12 level using atoms or molecules as references are very similar to the averages obtained using the isodesmic reactions.

Considering the average of the r.m.s. errors for these molecules, we will express the probable error using isodesmic reactions as 1.0 kcal mol^{-1}, although in some cases this value is probably larger than the actual error of the calculations.

Table 1. $\Delta_f H^0$(298.15), in kcal mol^{-1}, for the test molecules DMS, DMSO and DESO, using isodesmic reactions (1) and (2), atomization energies, and dissociation to diatomic molecules.

		isodesmic reactions					w.r.t. atoms		w.r.t. diatomics	
Reaction (1a)	**Exptl**	**$(CH_3)_2S$** +	H_2S =	CH_3SH		ΔH(rxn)	ΔH(rxn)	ΔH_f	ΔH(rxn)	ΔH_f
rev–DSDPBEP86		–477.510154	–399.080448	–438.292817		3.12				
CBS–QB3		–477.370600	–398.931131	–438.148272		3.25	–731.67	–10.23	–218.20	–2.79
G4		–477.799870	–399.254705	–438.524761		3.17	–731.20	–9.75	–218.43	–3.02
jun–ChS		–477.797377	–399.249820	–438.521076		3.17	–734.60	–11.81	–222.79	–7.39
SVECV–f12		–477.781776	–399.244775	–438.510693		3.24	–731.37	–9.92	–225.08	–9.67
$\Delta_f H^0$(298.15)	**–8.96**	**–9.21**	–4.90	–5.46		3.19[a]		**–10.43[a]**		**–5.72[a]**
±	**0.48**	**0.24[b]**	0.10	0.14		0.10[c]		**2.78[c]**		**5.86[c]**
Reaction (1b)	**Exptl**	**$(CH_3)_2S$** +	$(CH_3CH_2)_2O$ =	$(CH_3CH_2)_2S$ +	$(CH_3)_2O$					
rev–DSDPBEP86		–477.510154	–233.170134	–555.949657	–154.722216	5.28				
CBS–QB3		–477.370600	–233.205875	–555.820886	–154.746915	5.44				
G4		–477.799870	–233.473641	–556.354673	–154.910225	5.40				
jun–ChS		–477.797377	–233.492711	–556.355614	–154.925805	5.44				
SVECV–f12		–477.781776	–233.464203	–556.328751	–154.908144	5.70				
$\Delta_f H^0$(298.15)	**–8.96**	**–9.04**	–60.40	–20.00	–43.99	5.45[a]				
±	**0.48**	**0.78**	0.47	0.55	0.12	0.27[c]				
Reaction (2a)		**$(CH_3)_2S{=}O$** +	$CH_3CH_2CH_3$ =	$(CH_3CH_2)_2S{=}O$ +	CH_4	ΔH(rxn)	ΔH(rxn)	ΔH_f	ΔH(rxn)	ΔH_f
rev–DSDPBEP86		–552.626878	–118.828698	–631.068011	–40.394700	–4.48				
CBS–QB3		–552.493069	–118.850359	–630.945219	–40.406194	–5.01	–818.00	–37.00	–244.45	–29.05
G4		–552.979409	–119.010264	–631.535885	–40.461492	–4.83	–817.01	–36.02	–244.70	–29.29
jun–ChS		–552.992639	–119.013473	–631.552563	–40.460808	–4.56	–821.38	–40.38	–249.98	–34.57
SVECV–f12		–552.971921	–118.995769	–631.520953	–40.453878	–4.48	–817.73	–36.73	–252.13	–36.72
$\Delta_f H^0$(298.15)	**–35.97**	**–37.21**	–25.02	–49.10	–17.80	–4.67[a]		**–37.53[a]**		**–32.41[a]**
±	**0.36**	**0.60[b]**	0.12	0.40	0.07	0.43[c]		**3.37[c]**		**6.66[c]**

Reaction (2b)		**$(CH_3)_2S{=}O$**	+ $(CH_3CH_2)_2O$ =	$(CH_3CH_2)_2S{=}O$ +	$(CH_3)_2O$	ΔH(rxn)
rev–DSDPBEP86		–552.626878	–233.170134	–631.068011	–154.722216	4.26
CBS–QB3		–552.493069	–233.205875	–630.945219	–154.746915	4.27
G4		–552.979409	–233.473641	–631.535885	–154.910225	4.35
jun–ChS		–552.992639	–233.492711	–631.552563	–154.925805	4.38
SVECV–f12		–552.971921	–233.464203	–631.520953	–154.908144	4.41
$\Delta_f H^0$(298.15)	**–35.97**	**–37.03**	–60.40	–49.10	–43.99	4.34[a]
±	**0.36**	**0.64[b]**	0.47	0.40	0.12	0.12[c]

[a] Average of the enthalpies obtained with each method. [b] composition of the uncertainties in the enthalpies of formation of the reference species and of the enthalpy of reaction (see text). [c] ±2σ.

3.2. Enthalpies of formation of DHSO, HSOH and CH_2SO

These three species, displayed in Figure 2, were also used to test the methodology. Differently from DMS, DMSO and DESO, no experimental values for the enthalpies of formation exist. However, there are several accurate theoretical studies, which can be used to test our present methods.

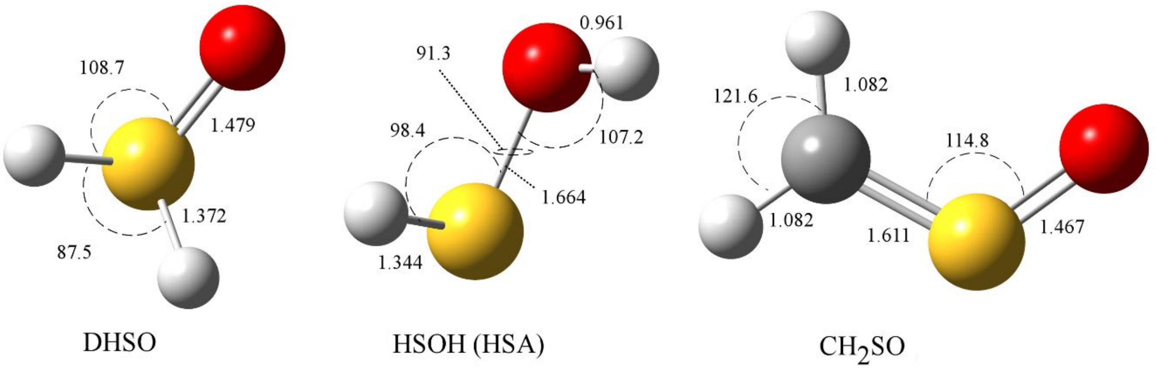

Figure 2. Structure of DHSO, HSA and CH_2SO used as further testing species. Bond distances (in Å) and angles (in deg) were calculated at the CCSD(T)–F12/cc–VTZ–F12 level.

3.2.1 DHSO

The results obtained for this species using reactions (3a)–(3c) are shown in Table 2. The $\Delta_f H^0$ $(298.15K)$ of DHSO was calculated as a weighted grand average over the three isodesmic reactions as done before. Values derived from the atomization reactions and the dissociation to diatomic molecules are also shown, averaged over the four more precise methods and assigned an error bar of $\pm 2\sigma$.

The work by Denis[84] gave the most recent theoretical value to our knowledge for the enthalpy of reaction of this species, –12.3 kcal mol^{-1}. In that work, CCSD(T) calculations were extrapolated with a two–point formula from the cc–pVTZ and cc–pVQZ to the CBS limit, supplemented by corrections of the zero–point energy (ZPE) by anharmonicity, the energy by the core–valence contribution, and including both spin–orbit and scalar–relativistic contributions.

Table 2 also shows the calculation of the enthalpy of formation using either the atoms or the molecules as chaperons. In these two cases, the dispersion is three or four times larger than that we obtained using the isodesmic reactions. The average value over the four methods considered for the atomization reactions is slightly outside the error interval. For the diatomic molecules instead, the average value is very near to that obtained using the isodesmic reactions. Notice specifically that the value of Denis[84], obtained from the energy of atomization, is quite like the one we got with the same procedure, lending some support to the lower value we got using the isodesmic reactions. However, notice that the three isodesmic reactions give results which are significantly different. On one side, the most noticeable difference occurs if the divinyl sulfide and sulfoxide are used as reference species. In this case, the $\Delta_f H^0(298.15K)$ is much less negative, almost 3 kcal mol^{-1} below the weighted average, but with a large error. If this isodesmic reaction is excluded from the calculation, the enthalpy of formation shifts from –11.12 ± 0.58 to –11.68 ± 0.64 kcal mol^{-1}, not a very large difference (the averaged data are shown in the Table S3).

The results of our calculations are then a bit inconclusive. If the atomization reactions are used, Denis' results and ours are well in agreement. If the isodesmic reactions are used (in principle more trustable) then the value should be almost exactly 1 kcal mol^{-1} lower. Until further experiments of more accurate theoretical calculations are available, we will favor our $\Delta_f H^0(298.15K) = -11.12 \pm 0.58$ kcal mol^{-1}.result.

3.2.2 HSA (Sulfenic acid, HSOH)

Grant et al.[85] did not study DHSO but the more stable isomer HSOH (HSA), at the same level of calculation that Denis[84] used, and obtained an enthalpy of formation of –28.0

kcal mol^{-1}, in agreement with that of ref. 79, –28.1 ± 1 kcal mol^{-1}. From the two isodesmic reactions (4a) and (4b) shown in Table 3 (see Table S4 for the weighted average calculation), we obtained a $\Delta_f H^0(298.15K) = -28.00 \pm 0.60$ kcal mol^{-1}, a value which is in excellent agreement with that of Grant et al.[85]

In the same way as with the previous cases, the dispersion of the enthalpies of formation calculated with respect to the atoms or the diatomic molecules are larger than the one obtained with the isodesmic reactions. The values themselves, however, are within the error range obtained from the isodesmic reactions. In particular, the value obtained using the atomization energy, -28.39 ± 1.25 kcal mol^{-1}, is indistinguishable (given the errors in all the calculations) from the previous values. Notice however that (4a) and (4b) are not truly isodesmic, since on one side of the equation we have an S(II)–OH bond and in the other an S(IV)=O bond. We will examine later this aspect of the question after we determine the enthalpy of formation of MSA.

Reactions (3a)–(3b) and (4a)–(4b) are essentially the same, the only substitution being the replacement of CH_2SO by HSOH. Therefore, one can inquire whether the isomerization conversion between this species is well represented at the levels of calculation we are using. Therefore, we calculated both molecules at an accurate level of theory, CCSD(T)–F12/cc–VMZ–F12, with M= D, T and Z. Full geometry optimization and thermochemical calculations were performed at each level. The results (see Table S5 in the Supplementary Information) show a small dispersion (the maximum difference between the largest and lowest values is 1.58 kcal mol^{-1}) and the average isomerization enthalpy is 16.08 ± 1.02 kcal mol^{-1} if all calculations are considered, and 16.37 ± 0.82 kcal mol^{-1} if the least accurate rev–DSDPBEP86, CBS–QB3 and CCSD(T)–F12/cc–VDZ–F12 are excluded.

3.2.3 CH_2SO (Sulfine))

As said before, the enthalpy of formation of sulfine was much discussed some years ago.[22,89–94,98] Ruttink's[94] best value was –7.6 ± 1.5 kcal mol^{-1}, Ventura et al.[22] obtained –9.1 ± 2.4 kcal mol^{-1}. Williams and Wilson[98] obtained –7.9 ± 2.4 kcal mol^{-1}, and the best value up to date, relying on atomization energies and large CCSDT(Q)/CBS calculations, was obtained by Grant et al.[85] as –8.4 ± 1.5 kcal mol^{-1}.

Isodesmic chemical reactions employed to determine the enthalpy of formation of H_2CSO include thioformaldehyde, a molecule which experimental $\Delta_f H^0(298.15K)$ exhibits a large error margin. Moreover, reaction (5a) includes DHSO, which $\Delta_f H^0(298.15K)$ is unknown. Therefore, we used our previously determined theoretically enthalpy of formation. Finally, reaction (5b) includes the Criegee intermediate CH_2OO, for which the experimental data is not present in the NIST–JANAF data tables. We employed instead the value present in the Active Thermochemical Tables (ATcT)[99–101]. Because of consistency, we also used the ATcT value for formaldehyde and we note that the experimental value used for thioformaldehyde is the one determined by Ruscic and Berkowitz[102], Ruscic himself being responsible for the ATcT.

The results obtained from the isodesmic reactions exhibit large error spans providing a weighted average of $\Delta_f H^0(298.15K)$ = –7.15 ± 1.87 kcal mol^{-1} (see Table S6), which is in agreement with all previous theoretical determinations, as can be seen in Figure S1. On the other side, the value we obtained using the atomization energies, $\Delta_f H^0(298.15K)$ = –8.31 ± 0.90 kcal mol^{-1}, is actually very close to the best one calculated by Grant et al.[85] as –8.4 ±

1.5 kcal mol^{-1}. It can be seen in Figure S1 that the largest errors come from our old calculation using DFT methods[22] (too low) and the present one using diatomic molecules as anchors (two high). Even so, there is enough overlap among the different methods to attempt a grand average (assigning equal weights to all methods). If all the results from different publications are used, the predicted enthalpy of formation of CH_2SO would be –7.99 ± 0.59 kcal mol–1, while if we exclude the worse results, the enthalpy of formation would be –8.05 ± 0.62 kcal mol^{-1}. A mean value of –8.0 ± 0.62 kcal mol^{-1} would then be appropriate for this species.

Table 2. Enthalpies (in Hartrees), $\Delta_{rxn}H^0$ and $\Delta_f H^0$ (in kcal mol^{-1}) at 298.15 K for DHSO obtained from the isodesmic reactions (3a)–(3c), enthalpies of atomization and dissociation to diatomic molecules.

Reaction (3a)	H_2S=O	+	$(CH_3)_2S$	=	$(CH_3)_2S$=O	+	H_2S	□*H*(rxn)	w.r.t. atoms		w.r.t. diatomics	
rev–DSDPBEP86	–474.164779		–477.510154		–552.626878		–399.080448	–20.33	*ΔH*(rxn)	*ΔH*(rxn)	ΔH_f	*ΔH*(rxn)
CBS–QB3	–474.021272		–477.370600		–552.493069		–398.931131	–20.29	–242.28	–13.06	–25.53	–10.34
G4	–474.401163		–477.799870		–552.979409		–399.254705	–20.76	–240.54	–10.54	–25.38	–10.19
jun–ChS	–474.411849		–477.797377		–552.992639		–399.249820	–20.85	–243.76	–13.75	–27.31	–12.12
SVECV–f12	–474.401403		–477.781776		–552.971921		–399.244775	–21.03	–241.81	–11.81	–27.06	–11.88
$\Delta_f H^0$(298.15)	**–11.26**		–8.96		–35.97		–4.90	**–20.65**^{a}		**–12.29**^{a}		**–11.13**^{a}
±	**0.85**^{b}		0.48		0.36		0.10	**0.59**^{c}		**2.30**^{c}		**1.74**^{c}
Reaction (3b)	H_2S=O	+	$(CH_3CH_2)_2S$	=	$(CH_3CH_2)_2SO$	+	H_2S	*ΔH*(rxn)				
rev–DSDPBEP86	–474.164779		–555.949657		–631.068011		–399.080448	–21.35				
CBS–QB3	–474.021272		–555.820886		–630.945219		–398.931131	–21.46				
G4	–474.401163		–556.354673		–631.535885		–399.254705	–21.81				
jun–ChS	–474.411849		–556.355614		–631.552563		–399.249820	–21.91				
SVECV–f12	–474.401403		–556.328751		–631.520953		–399.244775	–22.32				
$\Delta_f H^0$(298.15)	**–12.23**		–20.00		–49.10		–4.90	**–21.77**^{b}				
±	**0.98**^{b}		0.55		0.40		0.10	**0.69**^{c}				
Reaction (3c)	H_2S=O	+	$(CH_2{=}CH)_2S$	=	$(CH_2{=}CH)_2S$=O	+	H_2S	*ΔH*(rxn				
rev–DSDPBEP86	–474.164779		–553.540756		–628.649397		–399.080448	–15.25				
CBS–QB3	–474.021272		–553.404662		–628.519646		–398.931131	–15.59				
G4	–474.401163		–553.933605		–629.104956		–399.254705	–15.62				
jun–ChS	–474.411849		–553.937092		–629.124645		–399.249820	–16.02				
SVECV–f12	–474.401403		–553.912522		–629.095074		–399.244775	–16.27				
$\Delta_f H^0$(298.15)	**–8.50**		25.33		5.98		–4.90	**–15.75**^{b}				
±	**1.40**^{b}		0.96		0.72		0.10	**0.71**^{c}				

[a] Average of the enthalpies obtained with each method. [b] composition of the uncertainties in the enthalpies of formation of the reference species and of the enthalpy of reaction (see text). [c] ±2σ.

Table 3. Enthalpies (in Hartrees), $\Delta_{rxn}H^0$ and $\Delta_f H^0$ (in kcal mol^{-1}) at 298.15 K for HSOH obtained from the isodesmic reactions (4a) and (4b), enthalpies of atomization and dissociation to diatomic molecules.

Reaction (4a)	HSOH	+ $(CH_3)_2S$	= $(CH_3)_2SO$	+ H_2S	*ΔH*(rxn)	w.r.t. atoms		w.r.t. diatomics	
rev–DSDPBEP86	–474.189745	–477.510154	–552.626878	–399.080448	–4.66	*ΔH*(rxn)	ΔH_f	*ΔH*(rxn)	ΔH_f
CBS–QB3	–474.046538	–477.370600	–552.493069	–398.931131	–4.43	–258.92	–28.92	–41.39	–26.20
G4	–474.427988	–477.799870	–552.979409	–399.254705	–3.93	–257.38	–27.37	–42.21	–27.02
jun–ChS	–474.438464	–477.797377	–552.992639	–399.249820	–4.15	–258.90	–28.89	–44.01	–28.82
SVECV–f12	–474.427806	–477.781776	–552.971921	–399.244775	–4.46	–258.38	–28.38	–43.63	–28.44
$\Delta_f H^0$(298.15)	**–27.58**	–8.96	–35.97	–4.90	**–4.33**[a]		**–28.39**[a]		**–27.62**[a]
±	**0.80**[b]	0.48	0.36	0.10	**0.52**[c]		**1.25**[c]		**2.12**[c]
Reaction (4b)	HSOH	+ $(CH_3CH_2)_2S$	= $(CH_3CH_2)_2SO$	+ H_2S	*ΔH*(rxn)				
rev–DSDPBEP86	–474.189745	–555.949657	–631.068011	–399.080448	–5.68				
CBS–QB3	–474.046538	–555.820886	–630.945219	–398.931131	–5.60				
G4	–474.427988	–556.354673	–631.535885	–399.254705	–4.98				
jun–ChS	–474.438464	–556.355614	–631.552563	–399.249820	–5.21				
SVECV–f12	–474.427806	–556.328751	–631.520953	–399.244775	–5.75				
$\Delta_f H^0$(298.15)	**–28.55**	–20.00	–49.10	–4.90	**–5.45**[a]				
±	**0.91**[b]	0.55	0.40	0.10	**0.60**[c]				

[a] Average of the enthalpies obtained with each method. [b] composition of the uncertainties in the enthalpies of formation of the reference species and of the enthalpy of reaction (see text). [c] ±2σ.

Table 4. Enthalpies (in Hartrees), $\Delta_{rxn}H^0$ and $\Delta_f H^0$ (in kcal mol^{-1}) at 298.15 K for $CH_2=S=O$ obtained from the isodesmic reactions (5a) and (5b), enthalpies of atomization and dissociation to diatomic molecules.

Reaction (5a)	$H_2C=S=O$	+	H_2S	=	$H_2S=O$	+	$H_2C=S$	*ΔH*(rxn)	w.r.t. atoms		w.r.t. diatomics	
rev–DSDPBEP86	–512.212523		–399.080448		–474.164779		–437.080419	29.98	*ΔH*(rxn)	ΔH_f	*ΔH*(rxn)	ΔH_f
CBS–QB3	–512.070569		–398.931131		–474.021272		–436.934301	28.95	–410.25	–8.95	–120.04	–4.75
G4	–512.501373		–399.254705		–474.401163		–437.308567	29.08	–409.06	–7.76	–119.86	–4.56
jun–ChS	–512.513962		–399.249820		–474.411849		–437.304570	29.72	–409.78	–8.48	–122.30	–7.00
SVECV–f12	–512.499489		–399.244775		–474.401403		–437.295281	29.86	–409.35	–8.06	–122.53	–7.23
$\Delta_f H^0$(298.15)	**–7.44**		–4.90		*–11.12*[a]		28.30	**29.52**[b]		**–8.31**[b]		**–5.88**[b]
±	**2.25**[c]		0.60		*0.58*[a]		2.00	**0.84**[d]		**0.90**[d]		**2.47**[d]
Reaction (5b)	$H_2C=S=O$	+	$H_2C=O$	=	H_2COO	+	$H_2C=S$	*ΔH*(rxn)				
rev–DSDPBEP86	–512.212523		–114.326099		–189.315179		–437.080419	89.75				
CBS–QB3	–512.070569		–114.340350		–189.338867		–436.934301	86.44				
G4	–512.501373		–114.449379		–189.505166		–437.308567	85.98				
jun–ChS	–512.513962		–114.464923		–189.534844		–437.304570	87.52				
SVECV–f12	–512.499489		–114.453759		–189.517265		–437.295281	88.29				
$\Delta_f H^0$(298.15)	**–6.52**		–27.70		25.08		28.30	**87.60**[b]				
±	**3.36**		0.02		0.02		2.00	**2.69**[d]				

[a] Since there is no experimental value available for the enthalpy of formation of DHSO, we used our previously determined theoretical value (Table 2). [b] Average of the enthalpies obtained with each method. [c] composition of the uncertainties in the enthalpies of formation of the reference species and of the enthalpy of reaction (see text). [d] ±2σ.

3.3. Geometries and bond dissociation energies of the sulfenic group

Before looking into the enthalpies of formation of the sulfenic acids we are mostly interested in, there are two characteristics that can be evaluated with the data produced in this work. On one side, we can investigate how does the substituent affect the structure of the –SOH group and, on the other, how well do the methods in this paper perform with respect to the Bond Dissociation Energy (BDE) of both the O–H and S–O bonds in the group. For this purpose we calculated also the structure of the radicals R–SO$^\bullet$ and R–S$^\bullet$, with CH_3–, H_2C=CH–, HC≡C– and C_6H_5– (the structure of the sulfenic acid HSA was shown already in Figure 2 and the radicals are trivial). The general structure of the sulfenic acids and their radicals are shown in Figure 3.

3.3.1 Geometries

Due to the size of the last member of the series, BSA, geometry optimization at the CCSD(T) or CCSD(T)–F12 levels with sufficiently large basis sets is a daunting task and hence one has to resort to the use of DFT. In this respect, a comprehensive assessment of the performances of different density functionals in the prediction of geometrical parameters has already been performed.[64,103–106] While results for species linked to the present investigation like DMS, DMSO and sulfine can be found in the work by Ceselin et al.[106], here the attention is focused on the structures of HSA, MSA, ESA, YSA and BSA (see Figure 3) in order to explore the effects, if any, that the substituent on the S atom has on the SOH group structure.

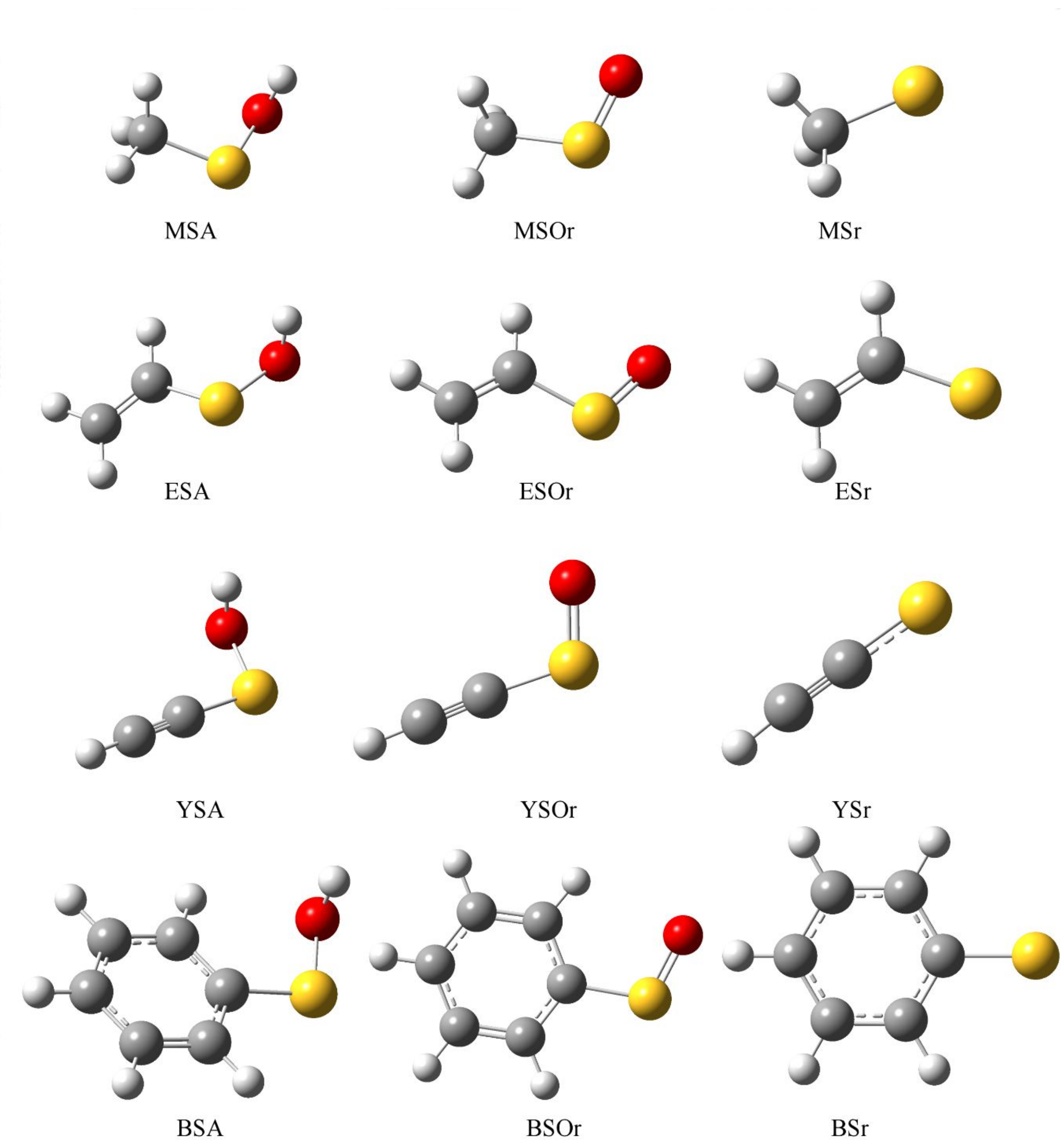

Figure 3. Structure of the sulfenic acids studied and their sulfinyl and thiyl radicals. Cartesian coordinates for all species studied are collected in the Supplementary Information.

The structural parameters of HSA and MSA, the smallest members of the series, are reported in Tables S6 and S7, respectively, where they are compared to theoretical literature data and to the available experimental information.[107–110] As expected, HSA has been studied with more sophisticated methods than MSA and, most importantly, its semi–experimental (SE) equilibrium geometry has been determined from the rotational constants measured for different isotopic species augmented through theoretical vibrational corrections.[108] Inspection of Table S6 reveals that bond lengths and valence angles are well reproduced at CCSD(T)–F12 and CCSD(T) levels of theory, even if frozen–core calculations residual deviations from the SE structure might be further reduced accounting for core–valence contributions The two density functionals also show a fair accuracy for bond distances and angles, with the exception of the SOH angle obtained at the M06–2X level of theory, which deviates by about 1.2° from the SE value. While an overall good agreement is observed for bond lengths and valence angles, all the methods underestimate the torsional HSOH angle by about 1 degree.

In the case of MSA, the structural parameters determined experimentally[109] cannot be employed to benchmark theoretical results because they represent vibrationally averaged values, whereas computations provide equilibrium structures. Unsurprisingly then, the deviations between experimental and calculated values are larger than for HSA. Due to the lack of usable experimental data for the equilibrium geometry, that obtained at the CCSD(T)–F12/cc–VQZ–F12 level can be employed, a solution workable only for the smallest molecules. Alternatively, the nano–LEGO tool can be used to improve rev–DSDPBEP86 geometries,[106] and these values are also reported in Table S7. It can be appreciated that the bond lengths obtained at the CCSD(T)–F12/cc–VQZ–F12 and nano–LEGO augmented rev–DSDPBEP86 levels coincide perfectly (the maximum difference being 1×10^{-3} Å for the C–S bond), and even for bond and torsional angles the predictions agree within 0.2–0.3 degree. It is therefore possible to conclude that rev–DSDPBEP86/jun–cc–pV(T+*d*)Z corrected through the nano–LEGO approach delivers structural parameters of almost the same quality as the much more expensive explicitly correlated methods, and hence it can be safely employed to produce high–quality data for the larger molecules. That said, on comparing M06–2X and rev–DSDPBEP86 geometries to CCSD(T)–F12/cc–pVQZ–F12 (or equivalently rev–DSDPBEP86 + nano–LEGO) structures, bond distances and angles are reproduced with an average accuracy of 0.005 Å and 0.6 degree, respectively. Therefore, it is safe to assume that a comparison of the R–SOH geometry as a function of R with these methods is appropriate. Such a comparison is presented in Table S8.

The general conclusion of these calculations is that the sulfenic acid group is barely influenced by the substituent on the sulfur atom, with the exception of the C–S distance The C–S distance is clearly affected, and the variation is not easy to rationalize in terms of conjugative effects, but it can be better understood in terms of bond–orders. Looking at MSA, ESA and YSA, the conclusion is that the more unsaturated the substituent group is, the shortest the C–S distance, which makes sense. However, the C–S bond in BSA comes closer to the value in the vinylsulfine YSA, a fact that perhaps can be attributed to the size of the conjugated system. The S–O distance, in turn, is very slightly affected by the increase in conjugation and the O–H distance is not influenced at all, a fact that is significant given the biological importance of the sulfinyl radicals ($RSO^{\bullet}$) generated by the loss of the hydrogen in the sulfenic acids of cysteine.[111]

3.3.1 Bond dissociation energies

Sulfinyl radicals themselves, are important species in biochemistry[112,113], and in the case of HSO• and CH_3SO• also in atmospheric chemistry.[114] One of the important characteristics of these compounds is the bond dissociation energy (BDE) (or enthalpy, in case the ZPE and temperature effects are included). Since, as we saw previously, the –OH group is mostly unaffected by the substituent, one could obtain a good appraisal of the BDE for these species by subtracting the respective energies of the sulfenic acid and the sulfinyl radical (plus the H atom, of course). Vaidya et al.[18] calculated the BDE for some sulfenic acids, including HSO• and CH_3SO•, using the CBS–QB3 method and obtained a value of around 68 kcal mol^{-1}, except for HSO• that was larger, 73.1 kcal mol^{-1}. Later, McGrath et al.[12] studied experimentally the BDE of a sulfenic acid derived from triptycene (a much larger molecule) and determined a value of 71.9 ± 0.3 kcal mol^{-1}. We have calculated the BDE for the O–H bond of the five sulfenic acids studied in this paper, collecting them in Table 5 together with the BDE for the S–O bond. The values have been calculated at several theoretical levels for all the species. Additionally, the BDEs for HSO• and CH_3SO• were calculated at the CCSD(T)–F12 level using progressively large basis sets, cc–pVDZ–F12, cc–pVTZ–F12 and cc–pVQZ–F12. In this case, full geometry optimization for the thiyl radical, the sulfenyl radical, and the sulfenic acid were performed in order to obtain the respective energies. The ZPE and thermal corrections were calculated at the M06–2X–D3 and added to the CCSD(T)–F12 energies.

Considering first the O–H BDE, the values calculated with different methods are all within the range of [67.0–75.0] kcal mol^{-1}. Only the smallest molecules HSOH and CH_3SOH could be calculated at the large CCSD(T)–F12/cc–pVQZ–F12 level, including geometry optimization and frequency calculation. SVECV–f12 uses instead the DFT optimized geometries and frequencies, with a single point calculation of the energies, then extrapolated to the CBS limit. The agreement between the composite method results and the extensive CCSD(T)–F12/cc–pVQZ–F12 level calculations validate the approximate procedure and these results can be used for a comparison of all the BDE in the case of the species which cannot be calculated at the exceedingly expensive full level.

Table 5. Bond dissociation enthalpy (kcal mol^{-1}) for the O–H and S–O bonds in the five sulfenic acids studied in this work.

	H–SOH		CH_3–SOH		H2C=CH–SOH		HC≡SOH		C_6H_5–SOH	
Method	OH	SO	OH	SO	OH	SO	OH	SO	OH	SO
M06–2X–D3	75.3	78.8	70.7	72.5	70.3	72.9	74.6	62.0	69.6	74.3
rev–DSDPBEP86	73.1	69.1	68.3	71.1	69.0	71.6	72.8	63.1	69.5	72.9
CBS–QB3	73.1	70.8	68.4	72.6	68.4	73.5	71.7	61.2	69.2	74.4
G4	73.3	69.6	68.2	71.3	68.2	71.9	71.8	60.7	67.1	65.1
jun–ChS	75.8	71.4	71.1	73.5	71.4	70.6	75.2	64.2	72.7	75.2
SVECV–f12	74.4	72.2	69.7	74.1	69.2	69.4	73.0	63.6	68.1	68.4
CCSD(T)–F12/DZ–F12	73.6	72.1	68.9	74.0	68.4	67.7	72.1	63.5		
CCSD(T)–F12/TZ–F12	74.1	71.9	69.3	73.8	68.9	67.6	72.6	63.4		
CCSD(T)–F12/QZ–F12	74.4	72.2	69.6	74.1						

HSOH and HC≡SOH OH BDEs are in the upper limit of the range, 74.4 and 73.0 kcal mol^{-1}, which we think is a result of the special nature of the substituent on sulfur, H– and HC≡C– respectively. Notice that the results obtained with full geometry optimization at the CCSD(T)–F12/cc–pVDZ–F12 and CCSD(T)–F12/cc–pVTZ–F12 levels agree also reasonably well with the SVECV–f12 results (that are based on the CBS extrapolation of CCSD(T)–F12 energies on top of M06–2X geometries), thus highlighting again that DFT optimized structures can be safely used in place of more expensive coupled–cluster ones. In this respect, however, it should be stressed that the functional has to be carefully chosen, in fact it has been shown that the popular B3YLP functional may leads to geometries that prevent reaching accurate thermochemical and kinetic predictions.[115] The O—H BDEs for CH_3S–OH, H_2C=CHS–OH and C_6H_5S–O–H of 69.7, 69.2 and 68.4 kcal mol^{-1} at the SVECV–f12 level, and 71.1, 71.4 and 72.7 kcal mol^{-1} at the jun–ChS level respectively, are very close among them. While these results are outside the error range obtained by McGrath et al. for triptycene sulfenic acid (TSA)[12], for which their lowest value is 71.6 kcal mol^{-1}, the difference can very well be understood on the basis of the large size difference of the molecules. Regretfully, TSA has 36 atoms and is outside the range of what we can calculate accurately.

The more than 2 kcal mol^{-1} difference between the SVECV–f12 value for MSA and the experimental value for TSA may be a real effect, produced perhaps by the size and the crowded arrangement of the TSA skeleton, or an insufficiency of the theoretical description of the sulfenic acid/sulfinyl radical pair. This is a feature we cannot elucidate at present, although one may notice that the jun–ChS method gives values closer to the experimental ones than the SVECV–f12 method. Notice however, that for MSA at least, the best

CCSD(T)–F12/cc–pVTQZ–F12 fully optimized result is well in line with SVECV–f12, suggesting that the geometrical and electronic structure are well represented. A point we did not investigate, however, is whether the ZPE and thermal contributions (which we obtained from the DFT calculation) are correct at the CCSD(T)–F12 level.

The S–O BDEs show another peculiarity of the species HSOH and HC≡SOH. While in the SVECV–f12 calculations of CH_3SOH, $H_2C{=}CSOH$ and C_6H_5SOH (and the jun–ChS calculations on CH_3SOH and C_6H_5SOH), the BDE of S–O is larger than that of O–H, the opposite is true for HSOH and HC≡SOH, implying a larger preference for the breaking of the S–O bond than the H–O bond in these compounds, i.e., $RSOH \rightarrow RS^{\bullet} + {}^{\bullet}OH$ instead of $RSOH \rightarrow RSO^{\bullet} + {}^{\bullet}H$. This deserves a further accurate study that is currently being undertaken in our laboratories. Incidentally, notice that there is a larger dispersion among the methods with respect to the S–O BDEs than in the case of the O–H BDEs, which may be related to the importance of representing more accurately the structure of the thiyl radical.

As a final consideration, one can compare the results we obtained for the sulfenic acids hydrogen dissociation toward sulfinyl radicals with the similar reaction of dissociation of hydroperoxides toward peroxyl radicals. Blanksby et all[116], for instance, determined experimentally the BDE of $CH_3OO–H$ and $CH_3CH_2OO–H$ as 87.9 ± 1.1 kcal mol^{-1} and 84.8 ± 2.2 kcal mol^{-1} showing then also a small variation with the substituent, about 10–15 kcal mol^{-1} more endergonic than the values we obtained for the sulfenic/sulfinyl pair. This can be explained by the resonance structure of the S–O group where the unpaired electron can profit from the low–lying *d*–orbitals on sulfur to get stabilization through the resonant structures $R–S–O^{\bullet} \leftrightarrow R–S^{\bullet}{=}O$. Since this is a general phenomenon, we expect the sulfinyl radicals to be more stable than the peroxyl radicals. Consequently, while the hydroperoxyl species will suffer homolytic breaking of the O–O bond to form the alkoxyl radical, the sulfenic acids will preferentially lose the hydrogen to form the sulfinyl radical. This is illustrated in Table 6 where the theoretical average values of the BDE for RSOH and ROOH species (the latter calculated in this work by the same procedures that we used for the sulfenic acids, see Table S9) are compared among them and with experimental results taken from the ATcT tables.

Table 6. Comparison of the bond dissociation enthalpies (kcal mol^{-1}) for the O–H and S–O/O–O bonds in the sulfenic acids and hydroperoxides.

		RSOH		ROOH	
R Group		O–H	S–O	O–H	O–O
H–	Theoretical[a]	74.16	72.06	87.09	51.23
	Experimental[b]			87.39	50.30
CH_3–	Theoretical[a]	69.34	72.86	86.26	44.89
	Experimental[b]			85.80	44.67

C_6H_5–	Theoretical[a]	69.36	68.43	86.39	24.59
	Experimental[b]			86.20	26.68

[a] Average of the theoretical BDEs shown for each species in Table 5. [b]Obtained from the enthalpies of formation of the sepecies in the ATcT tables.

3.4. Enthalpies of formation of the sulfenic acids and their radicals

Considering the previous discussions, we can now examine the results obtained for all the sulfenic acids of interest. HSOH was already considered, thus we will focus here on the rest of the sulfenic acids.

In the case of MSA, we used reactions (6a) and (6b), analogous to the (5a) and 5b) employed in the case of HSA and reaction (7) where we resorted to the theoretical enthalpy of formation of HSA, –28.00 ± 0.60 kcal mol^{-1}, determined in the previous steps of this work. We show these data in Table 7.

There is a very good agreement between the enthalpies of formation obtained from the isodesmic reactions, –35.06 ± 0.44 kcal mol^{-1} and that derived from the atomization reaction, –35.94 ± 2.78 kcal mol^{-1}, not so much with the one derived from the diatomic molecules. However, considering the error intervals, the values overlap. As we said before, we will keep the value derived from the isodesmic reactions as the recommended one.

Isodesmic reactions (8), (9), and (10) as well as atomization reactions and dissociation to diatomic molecules for ESA, YSA and BSA are collected in Tables 8–10. Notice that in the case of ESA (Table 8), YSA (Table 9), and BSA (Table 10) we used HSA and MSA as chaperons. In both cases we considered as its enthalpy of formation the value that we calculated theoretically as the weighted average of the individual isodesmic reactions. The best results obtained then with the isodesmic reactions are –11.22 ± 0.74, +32.88 ± 0.96, and –2.58 ± 0.56 kcal mol^{-1}, for ESA, YSA and BSA respectively. This last case resulted to be the most problematic, with some of the isodesmic reactions, the atomization reactions and especially the dissociation to diatomic molecules showing very large error bars. For that reason, in the case of BSA we considered four isodesmic reactions instead of the two or three we used for the other cases studied. The final error bar for the weighted average is reasonable.

The final results of our calculations for all the sulfenic acids are summarized in Table 11. Clearly the results obtained with the isodesmic and quasi–isodesmic reactions have a much lower spread than those calculated using the atoms or the diatomic molecules as anchors. Nevertheless, when one considers the intervals, there is overlapping of the results from the three sources of enthalpies of formation, and we will propose the values obtained from the isodesmic reactions as the most accurate ones. As mentioned before, only three of them were determined experimentally.[24] The results obtained in our work for MSA, ESA and YSA differ by about 10, 8 and 4 kcal mol^{-1}, respectively, from the experimental ones. In no case does the experimental values fall into the 95% significance error interval (±2σ) for the theoretically determined values. Given the precision of present calculations and the accuracy supported by the analysis done in this work, it is then forcefully concluded that the experimental results have some flaw and should be revised.

Table 7. Enthalpies (in Hartrees), $\Delta_{rxn}H^0$ and $\Delta_f H^0$ (in kcal mol^{-1}) at 298.15 K for MSA obtained from the isodesmic reactions (6a)–(6c), enthalpies of atomization, and dissociation to diatomic molecules.

Reaction (6a)	CH_3SOH	+	$(CH_3)_2S$	=	$(CH_3)_2S{=}O$	+	CH_3SH	*ΔH*(rxn)	w.r.t. atoms		w.r.t. diatomics	
rev–DSDPBEP86	–513.412296		–477.510154		–552.626878		–438.292817	1.73	*ΔH*(rxn)	ΔH_f	*ΔH*(rxn)	ΔH_f
CBS–QB3	–513.274139		–477.370600		–552.493069		–438.148272	2.13	–541.18	–35.68	–145.64	–30.34
G4	–513.708276		–477.799870		–552.979409		–438.524761	2.49	–540.07	–34.57	–146.33	–31.03
jun–ChS	–513.720058		–477.797377		–552.992639		–438.521076	2.33	–543.75	–38.25	–149.82	–34.52
SVECV–f12	–513.704185		–477.781776		–552.971921		–438.510693	2.10	–540.77	–35.27	–150.59	–35.29
$\Delta_f H^0$(298.15)	**–34.63**		–8.96		–35.97		–5.46	**2.16**[a]		**–35.94**[a]		**–32.80**[a]
±	**0.80**[b]		0.48		0.36		0.14	**0.52**[c]		**2.78**[c]		**4.29**[c]
Reaction (6b)	CH_3SOH	+	$(CH_3CH_2)_2S$	=	$(CH_3CH_2)_2SO$	+	CH_3SH	*ΔH*(rxn)				
rev–DSDPBEP86	–513.412296		–555.949657		–631.068011		–438.292817	0.71				
CBS–QB3	–513.274139		–555.820886		–630.945219		–438.148272	0.96				
G4	–513.708276		–556.354673		–631.535885		–438.524761	1.45				
jun–ChS	–513.720058		–556.355614		–631.552563		–438.521076	1.28				
SVECV–f12	–513.704185		–556.328751		–631.520953		–438.510693	0.81				
$\Delta_f H^0$(298.15)	**–35.60**		–20.00		–49.10		–5.46	**1.04**[a]				
±	**0.89**[b]		0.55		0.40		0.14	**0.56**[c]				
Reaction (6c)	CH_3SOH	+	H_2S	=	HSOH	+	CH_3SH	*ΔH*(rxn)				
rev–DSDPBEP86	–513.412296		–399.080448		–474.189745		–438.292817	6.39				
CBS–QB3	–513.274139		–398.931131		–474.046538		–438.148272	6.56				
G4	–513.708276		–399.254705		–474.427988		–438.524761	6.42				
jun–ChS	–513.720058		–399.249820		–474.438464		–438.521076	6.49				
SVECV–f12	–513.704185		–399.244775		–474.427806		–438.510693	6.56				
$\Delta_f H^0$(298.15)	**–35.05**		–4.90		*–28.00*[d]		–5.46	**6.49**[a]				
±	**0.64**[b]		0.10		*0.60*		0.14	**0.14**[c]				

[a] Average of the enthalpies obtained with each method. [b] composition of the uncertainties in the $\Delta_f H^0$(298.15) of the reference species and the ΔH(rxn). [c] ±2σ. [d] Since there is no experimental value available for the enthalpy of formation of HSA, we used our previously determined theoretical value.

Table 8. Enthalpies (in Hartrees), $\Delta_{rxn}H^0$ and $\Delta_f H^0$ (in kcal mol^{-1}) at 298.15 K for CH$_2$=CHSOH obtained from the isodesmic reactions (7a) and (7b), enthalpies of atomization and dissociation to diatomic molecules.

Reaction (7a)	CH$_2$=CH–SOH +	CH$_4$ =	CH$_3$SOH +	H$_2$C=CH$_2$	*ΔH*(rxn)	w.r.t. atoms		w.r.t. diatomics	
rev–DSDPBEP86	–551.425579	–40.394700	–513.412296	–78.396304	7.33	*ΔH*(rxn)	ΔH_f	*ΔH*(rxn)	ΔH_f
CBS–QB3	–551.289376	–40.406194	–513.274139	–78.412644	5.51	–686.99	–10.20	–218.78	–3.37
G4	–551.773235	–40.461492	–513.708276	–78.517878	5.38	–686.46	–9.67	–218.68	–3.28
jun–ChS	–551.787947	–40.460808	–513.720058	–78.517683	6.91	–690.03	–13.24	–223.34	–7.93
SVECV–f12	–551.767560	–40.453878	–513.704185	–78.509402	4.93	–686.52	–9.73	–224.28	–8.87
$\Delta_f H^0$(298.15)	**–10.73**	–17.80	–35.06^{c}	12.54	**6.01**^{a}		**–10.71**^{a}		**–5.86**^{a}
±	**1.92**^{b}	0.07	0.44^{c}	0.10	**1.87**^{d}		**2.95**^{d}		**5.12**^{d}
Reaction (7b)	CH$_2$=CH–SOH +	CH$_4$ =	HSOH	+ H$_2$C=CHCH3	*ΔH*(rxn)				
rev–DSDPBEP86	–551.425579	–40.394700	–474.189745	–117.620964	6.01				
CBS–QB3	–551.289376	–40.406194	–474.046538	–117.639050	6.26				
G4	–551.773235	–40.461492	–474.427988	–117.796733	6.28				
jun–ChS	–551.787947	–40.460808	–474.438464	–117.801213	5.70				
SVECV–f12	–551.767560	–40.453878	–474.427806	–117.784608	5.66				
$\Delta_f H^0$(298.15)	**–11.31**	–17.80	–28.00^{c}	4.88	**5.98**^{a}				
±	**0.81**^{b}	0.07	0.60^{c}	0.05	**0.53**^{d}				

[a] Average of the enthalpies obtained with each method. [b] composition of the uncertainties in the $\Delta_f H^0$(298.15) of the reference species and the ΔH(rxn). [c] Since there is no experimental value available for the enthalpy of formation of HAS and MSA, we used our previously determined theoretical value. [d] ±2σ.

Table 9. Enthalpies (in Hartrees), $\Delta_{rxn}H^0$ and $\Delta_f H^0$ (in kcal mol^{-1}) at 298.15 K for HC≡CSOH obtained from the isodesmic reactions (8a) and (8b), enthalpies of atomization and dissociation to diatomic molecules.

Reaction (8a)	HC≡C–SOH	+	CH_4	=	CH_3SOH	+	HC≡CH	ΔH(rxn)	w.r.t. atoms		w.r.t. diatomics	
rev–DSDPBEP86	–550.200372		–40.394700		–513.412296		–77.174770	5.02	ΔH(rxn)	ΔH_f	ΔH(rxn)	ΔH_f
CBS–QB3	–550.059736		–40.406194		–513.274139		–77.183653	5.11	–539.70	32.89	–176.82	38.59
G4	–550.541079		–40.461492		–513.708276		–77.290351	2.47	–539.60	32.98	–176.36	39.04
jun–ChS	–550.556854		–40.460808		–513.720058		–77.291484	3.84	–542.12	30.47	–180.13	35.28
SVECV–f12	–550.537294		–40.453878		–513.704185		–77.280700	3.95	–539.06	33.52	–180.17	35.24
$\Delta_f H^0$(298.15)	**32.86**		–17.80		–35.06[c]		54.19	**4.08[a]**		**32.47[a]**		**37.04[a]**
±	**1.97[b]**		0.07		0.44[c]		0.10	**1.92[d]**		**2.36[d]**		**3.57[d]**

Reaction (8b)	HC≡C–SOH	+	CH_4	=	HSOH	+	$HC≡CCH_3$	ΔH(rxn)
rev–DSDPBEP86	–550.200372		–40.394700		–474.189745		–116.403356	1.24
CBS–QB3	–550.059736		–40.406194		–474.046538		–116.416680	1.70
G4	–550.541079		–40.461492		–474.427988		–116.571775	1.76
jun–ChS	–550.556854		–40.460808		–474.438464		–116.578043	0.72

SVECV–f12	–550.537294	–40.453878	–474.427806	–116.562184	0.74
$\Delta_f H^0$(298.15)	**32.88**	–17.80	–28.00[c]	44.32	**1.23[a]**
±	**1.10[b]**	0.07	0.60[c]	0.21	**0.89[d]**

[a] Average of the enthalpies obtained with each method. [b] composition of the uncertainties in the $\Delta_f H^0$(298.15) of the reference species and the ΔH(rxn). [c] Since there is no experimental value available for the enthalpy of formation of HAS and MSA, we used our previously determined theoretical value. [d] ±2σ.

Table 10. Enthalpies (in Hartrees), $\Delta_{rxn}H^0$ and $\Delta_f H^0$ (in kcal mol^{-1}) at 298.15 K for C_6H_5SOH obtained from the isodesmic reactions (9a)–(9d), enthalpies of atomization and dissociation to diatomic molecules.

Reaction (9a)	C_6H_5–SOH	+	CH_4	=	CH_3SOH	+	C_6H_6	*ΔH*(rxn)	w.r.t. atoms		w.r.t. diatomics	
									ΔH(rxn)	*ΔH$_f$*	*ΔH*(rxn)	*ΔH$_f$*
rev–DSDPBEP86	–704.792374		–40.394700		–513.412296		–231.765850	5.60				
CBS–QB3	–704.662509		–40.406194		–513.274139		–231.784345	6.41	–1469.32	–3.16	–605.09	10.76
G4	–705.345192		–40.461492		–513.708276		–232.094014	2.76	–1469.06	–2.91	–600.60	15.24
jun–ChS	–705.371518		–40.460808		–513.720058		–232.099261	8.16	–1473.86	–7.70	–611.39	4.45
SVECV–f12	–705.334096		–40.453878		–513.704185		–232.075541	5.18	–1468.95	–2.79	–615.06	0.79
$\Delta_f H^0$(298.15)	**–3.08**		–17.80		–35.06[c]		19.80	**5.62[a]**		**–4.14[a]**		**7.81[a]**
±	**3.55[b]**		0.07		0.44[c]		0.20	**3.52[d]**		**4.12[d]**		**11.16[d]**
Reaction (9b)	C_6H_5–SOH	+	CH_4	=	HSOH	+	C_6H_6–CH3	*ΔH*(rxn)				
rev–DSDPBEP86	–704.792374		–40.394700		–474.189745		–270.990349	4.38				
CBS–QB3	–704.662509		–40.406194		–474.046538		–271.014056	5.09				
G4	–705.345192		–40.461492		–474.427988		–271.371097	4.77				
jun–ChS	–705.371518		–40.460808		–474.438464		–271.387305	4.11				

SVECV–f12	–705.334096		–40.453878		–474.427806		–271.352607	4.74
$\Delta_f H^0$(298.15)	**–2.92**		–17.80		–28.00^{c}		12.00	**4.62^{a}**
±	**0.94^{b}**		0.07		0.60^{c}		0.26	**0.68^{d}**
Reaction (9c)	C_6H_5–SOH	+	$(CH_3)_2S$	=	$(CH_3)_2S$=O	+	C_6H_5–SH	*ΔH*(rxn)
rev–DSDPBEP86	–704.792374		–477.510154		–552.626878		–629.673400	1.41
CBS–QB3	–704.662509		–477.370600		–552.493069		–629.536732	2.08
G4	–705.345192		–477.799870		–552.979409		–630.162126	2.21
jun–ChS	–705.371518		–477.797377		–552.992639		–630.173084	1.99
SVECV–f12	–705.334096		–477.781776		–552.971921		–630.142017	1.21
$\Delta_f H^0$(298.15)	**–1.93**		–8.96		–35.97		26.86	**1.78^{a}**
±	**1.01^{b}**		0.48		0.36		0.21	**0.79^{d}**
Reaction (9d)	C_6H_5–SOH	+	$(CH_3CH_2)_2S$	=	$(CH_3CH_2)_2SO$	+	C6H5–SH	*ΔH*(rxn)
rev–DSDPBEP86	–704.792374		–555.949657		–631.068011		–629.673400	0.39
CBS–QB3	–704.662509		–555.820886		–630.945219		–629.536732	0.91
G4	–705.345192		–556.354673		–631.535885		–630.162126	1.16
jun–ChS	–705.371518		–556.355614		–631.552563		–630.173084	0.93
SVECV–f12	–705.334096		–556.328751		–631.520953		–630.142017	–0.08
$\Delta_f H^0$(298.15)	**–2.90**		–20.00		–49.10		26.86	**0.66^{a}**
±	**1.14^{b}**		0.55		0.40		0.21	**0.90^{d}**

[a] Average of the enthalpies obtained with each method. [b] composition of the uncertainties in the $\Delta_f H^0$(298.15) of the reference species and the ΔH(rxn). [c] Since there is no experimental value available for the enthalpy of formation of HAS and MSA, we used our previously determined theoretical value. [d] ±2σ.

The weighted averages obtained from the isodesmic reactions in Tables 7 to 10 are shown in Tables S10–S13 in the Supporting Information.

Table 11. Summary of $\Delta_f H^0$ (in kcal mol^{-1}) at 298.15 K for the five sulfenic acids studied in this paper, obtained from isodesmic reactions, enthalpies of atomization and dissociation to diatomic molecules.

Source	H — SOH	CH_3 — SOH	CH_2=CH — SOH	HC≡C — SOH	C_6H_5 — SOH
Isodesmic	–28.0 ± 0.6	− 35.1 ± 0.4	–11.2 ± 0.7	− 32.9 ± 1.0	− 2.6 ± 0.6
Atomization	–28.4 ± 1.3	–35.9 ± 2.8	–10.7 ± 3.0	− 32.5 ± 2.4	− 4.1 ± 4.1
Dissociation	–27.6 ± 2.1	–32.8 ± 4.3	–5.9 ± 5.1	− 37.0 ± 3.6	+ 7.8 ± 11.2
NIST/JANAF[23,24]		**45.4**		**24.8**	**–8.1**

The procedure used for the experimental determination[24] relied on flash–vacuum pyrolysis of the corresponding sulfoxides and characterization of the ions using mass spectrometry. The heats of formation were then obtained indirectly from those of the radical cations $[RSOH]^{\bullet+}$ and the threshold ionization energy (IE), using the equation

$$\Delta_f H^o(\mathrm{RSOH}) = \Delta_f H^o[\mathrm{RSOH}]^{\bullet+} - \mathrm{IE}(\mathrm{RSOH})$$

The authors[24] mentioned that they used the additivity method to determine the enthalpies of formation of the sulfoxides, needed to assess the $\Delta_f H^o$[RSOH]$^{•+}$, and recognized that they were aware that possible errors may be introduced in the values through this approximation. Our theoretical results in this paper seem to support this warning and we conclude that more experimental studies are needed to resolve this discrepancy.

The previous assertion could benefit from some additional support, taking advantage of the calculations we performed on the thiyl and sulfinyl radicals. We calculated the enthalpies of formation of such radicals using the same procedures we employed for the sulfenic acids, using isodesmic reactions when possible, enthalpies of atomization and enthalpies of dissociation into diatomic molecules. To avoid an excessive length of the paper, we show in Table 12 only the average values, while the full data used to obtain them are compiled in the Supplementary Information (Table S14).

Table 12. $\Delta_f H^o_{298}$ (kcal mol^{-1}, T=298.15K) for thiyl and sulfinyl radicals of the species studied in this work. Values in italic bold corresponds to a full (optimization + frequencies) calculation at the CCSD(T)–F12/cc–VTZ–F12 level.

Parent	Radical	isodesmic	w.r.t. atoms	w.r.t. diatomics	other

H–SOH	$HS^{\bullet}$	+33.5 ± 2.5	+33.3 ± 0.6	+34.2 ± 0.7	33.301[a]
		+33.5 ± 2.5	***34.2***	***34.0***	+33.56 ± 0.84[b]
	$HSO^{\bullet}$	–6.0 ± 1.6[c]	–6.8 ± 1.4	–5.9 ± 0.3	–5.2 ± 0.5[e]
		–8.2 ± 1.6[d]	***–4.6***	***–5.6***	–3.7[f]
CH_3–SOH	$CH_3S^{\bullet}$	+29.6 ± 0.5[g]	+28.00 ± 1.0	+30.9 ± 2.6	+31.04 ± 0.42[i]
		+29.6 ± 3.2[h]	***30.9***	***30.4***	+29.9 ± 0.5[j]
					+34.2 ± 2.0[k]
					+30.8 ± 2.4[l]
					+29.7[m]
	$CH_3SO^{\bullet}$	–18.5 ± 3.3[n]	–18.7 ± 1.4	–15.7 ± 2.0	–16.8[m]
			–14.5	***–15.8***	
CH_2=CHSOH	$CH_2=CHS^{\bullet}$	+50.7 ± 3.2	+51.7 ± 5.0	+56.3 ± 8.0	
		+48.9 ± 3.1	***51.6***	***51.3***	
	$CH_2=CHSO^{\bullet}$	+5.1 ± 4.1	+6.1 ± 1.7	+10.8 ± 2.6	
			11.9	***10.7***	
HC≡CSOH	$HC{\equiv}CS^{\bullet}$	+86.0 ± 4.9	+85.9 ± 1.4	+90.3 ± 1.7	
		+86.3 ± 4.8	***90.6***	***90.7***	
	$HC{\equiv}CSO^{\bullet}$	+54.9 ± 4.0	+53.3 ± 1.5	+57.7 ± 1.5	
		+55.2 ± 3.8	***58.7***	***58.0***	
C_6H_5–SOH	$C_6H_5–S^{\bullet}$	+59.7 ± 5.6	+57.7 ± 7.0	+69.4 ± 12.0	
	$C_6H_5–SO^{\bullet}$	+13.2 ± 3.4	+12.7 ± 1.0	+24.6 ± 10.5	

[a] NIST/JANAF[23]. [b] ref 117. [c] using the ATcT value of the enthalpy of formation of HOO•. [d] using the NIST/JANAF value of the enthalpy of formation of HOO•. [e] ref. 118. [f] ref. 119. [g] using ATcT values for CH_3OH and CH_3O. [h] using NIST/JANAF values for CH_3OH and CH_3O. [i] Reference 120. [j] ref. 121. [k] ref. 122. [l] Ref. 123. [m] ref. 124. [n] With respect to ATcT values because the NIST/JANAF experimental value for CH_3OO is not reported.

In general, the agreement between the enthalpies of formation obtained using different references depends heavily on the method and the structure of the molecule. It must be noticed that at least two sources of experimental data can be used for the isodesmic reactions, the NIST/JANAF data tables[23] (our current preference) or the ATcT[99–101] values. They are normally not so different but sometimes it is substantial. For instance, the experimental enthalpy of formation of the $HOO^{\bullet}$ radical amounts to 0.50 kcal mol^{-1} in the first database and to 2.94 ± 0.06 kcal mol^{-1} in the latter. This is especially relevant for radicals and in Table 14 we list both results, obtained with respect to both references, in the case of the isodesmic reactions (see the Supporting Information).

In the case of the smallest radicals, we have several sources of information to discuss. The enthalpy of formation of $HS^{\bullet}$ is coincident with the experimental one considering the error bars. For the isodesmic reaction used ($HS^{\bullet} + H_2O \rightarrow H_2S + HO^{\bullet}$) there is no difference between the NIST/JANAF and ATcT results. The atomization and dissociation energies provide also numbers coincident with experiment within the error bars, and the accurate CCSD(T)–F12/cc–VTZ–F12 calculation (full geometry optimization and thermochemical properties at the post–Hartree–Fock level but no core–valence correction) also agrees with all the other theoretical and experimental values.

For $HSO^{\bullet}$ we employed the isodesmic reaction $HSO^{\bullet} + H_2O_2 \rightarrow HSOH + HOO^{\bullet}$, which requires our previously calculated enthalpy of formation of HSA and shows the problem indicated before with respect to the experimental data. The enthalpies of formation calculated from both isodesmic reactions differ in 1.3 kcal mol^{-1}, but given the error bar, both results are possible. The smallest one, –6.0 ± 1.6 kcal mol^{-1}, is reasonably in agreement with the experimental one, as well as the averages obtained using atoms and diatomic molecules as reference. The accurate CCSD(T)–F12/cc–VTZ–F12 calculation with respect to atoms and diatomics are also reasonably in agreement with the experimental value of Gurvich et al.[117] and larger than the theoretical value calculated with atoms as reference by Denis[118].

For $CH_3S^{\bullet}$ we have both experimental and theoretical information. Bise et al.[120] determined experimentally a value of 31.0 ± 0.4 kcal mol^{-1}, Hynes and Wine[121] reported 29.9 ± 0.5 kcal mol^{-1}, and an older work by Colussi and Benson[122] afforded 34.2 ± 2.4 kcal mol^{-1}. Giving equal weight to the two more modern measurements, and using the weighted average as described before, we conclude an approximate experimental value of 30.6 ± 0.3 kcal mol^{-1}. The results employing the isodesmic reaction $CH_3S^{\bullet} + CH_3OH \rightarrow CH_3SH + CH_3O^{\bullet}$ and the atomization reaction are reasonably in agreement and consistent with the experimental one. Notice that although the results of the isodesmic using NIST/JANAF and ATcT anchor values are the same, the error is larger for the former, because the experimental enthalpy of formation of methanol has a much larger error there. In the case of using the atoms as references, the average is much too low, and this fact cannot be adscribed particularly to the results of any one of the methods averaged (see the SI). The accurate CCSD(T)–F12/cc–VTZ–F12 calculation, however, gives a value concordant with the experimental one, both when using the atoms and the diatomic molecules as reference. Previous theoretical calculations agree with these values. Nobes and Radom,[123] obtained 30.8 ± 2.4 kcal mol^{-1} at the G2 level using several reactions, and in a more recent work, Resende and Ornellas,[124] obtained 29.7 kcal mol^{-1} at the CCSD(T)/CBS–R3 level of theory.

We used the isodesmic reaction $CH_3SO^\bullet + CH_3OOH \rightarrow CH_3SOH + CH_3OO^\bullet$. Since the methyl peroxide enthalpy of formation is not present in the NIST/JANAF tables, we used only the ATcT value for this anchor. We used also the $\Delta_f H^0(298.15K)$ that we determined previously for MSA as an anchor. The results for the three types of anchors overlap when errors bars are considered, and they also encompass the other theoretical value determined by Resende and Ornellas[124]. Some recent papers have studied the MSOr[125–127] and YSr sulfinyl radicals[128] but, to the best of our knowledge, there is no further information about their enthalpies of formation, neither about those of ESOr and BSOr. The results we obtained seem to be then the only available for these species, although the errors are large, and the values do not have chemical accuracy.

Special consideration must be given to the enthalpies of formation of BSr and BSOr. As we said in the case of BSA, this is a more difficult compound. We used two sets of anchor species for both BSr and BSOr, namely

$$C_6H_5{-}S^\bullet + C_6H_5{-}OH \rightarrow C_6H_5{-}SH + C_6H_5{-}O^\bullet \qquad (11a)$$

$$C_6H_5{-}S^\bullet + C_6H_5{-}OOH \rightarrow C_6H_5{-}SH + C_6H_5{-}OO^\bullet \qquad (11b)$$

$$C_6H_5{-}SO^\bullet + C_6H_5{-}OH \rightarrow C_6H_5{-}SOH + C_6H_5{-}O^\bullet \qquad (12a)$$

$$C_6H_5{-}SO^\bullet + C_6H_5{-}OOH \rightarrow C_6H_5{-}SOH + C_6H_5{-}OO^\bullet \qquad (12b)$$

We used also the previously determined enthalpy of reaction of BSA (the weighted average from isodesmic reactions) in reactions (12). The results are a bit discouraging, with very large error bars, but at least there is a reasonable coincidence between the values obtained using the isodesmic reactions and the atomization energies. Not so for the dissociation into diatomic molecules, which gives an unreasonable large value for both species. To the extent of our knowledge, the enthalpy of formation of BSr and BSOr have not been measured experimentally, but an estimation of the BDE doing some experimental acidities was published by Bordwell et al.[129] as 79.1 kcal mol^{-1}. Our average value is much lower (69.1 kcal mol^{-1}), a fact that claims for a more in–depth study of the radicals of the benzenesulfenic acid. In particular, the phenylsulfenyl radical photo–induced isomerization has been studied very recently by Liu et al.[119] and a comparison with our data is in order for future work. The results produced in this paper for the radicals should then be considered as a tentative appraisal of these values until further experimental and theoretical work is performed.

4. CONCLUSIONS

High quality quantum composite methods have been employed to study the enthalpy of formation of the four sulfenic acids experimentally investigated by Tureček et al.,[24] MSA, ESA, YSA, BSA. The values obtained for them, except ESA, are the only ones quoted in the NIST thermochemical tables as experimental data for these compounds.

Enthalpies of formation were determined using atomization energies, dissociation reactions toward diatomic molecules and isodesmic reactions. Validation of the methodology was performed by calculation of the experimentally well–known enthalpies of formation of DMS, DMSO and DESO. It was found that, using the isodesmic reactions described, the weighted averages for these species reproduce the experimental enthalpies of formation at

298K within an error limit of 1.0 kcal mol^{-1}. These methods were then used to calculate the enthalpies of formation of the sulfenic acids of interest and other two species, which have been experimentally elusive and difficult to describe theoretically, H_2SO and CH_2SO. The best results obtained in this work, averaging the theoretical values for the isodesmic reactions are

(1) $\Delta_f H^o(H_2SO)$ –11.2 ± 0.6 kcal mol^{-1}

(2) $\Delta_f H^o(CH_2SO)$ –7.2 ± 1.9 kcal mol^{-1}

(3) $\Delta_f H^o(HSOH)$ -28.0 ± 0.6 kcal mol^{-1}

(4) $\Delta_f H^o(CH_3SOH)$ –35.1 ± 0.4 kcal mol^{-1}

(5) $\Delta_f H^o(CH_2CHSOH)$ –11.2 ± 0.7 kcal mol^{-1}

(6) $\Delta_f H^o(HCCSOH)$ +32.9 ± 1.0 kcal mol^{-1}

(7) $\Delta_f H^o_{298}(C_6H_5SOH)$ –2.6 ± 0.6 kcal mol^{-1}

The errors presented include a 2σ□dispersion for the average of the enthalpies of reaction calculated at the rev–DSDPBEP86, CBS–QB3, G4, jun–ChS and SVECV–f12 levels, as well as the errors in the experimental enthalpies of formation of the chaperon molecules.

Concerning the values obtained with the atomization reactions and the dissociation to diatomic molecules, errors are in generally larger, especially for the diatomics, with the notable exception of BSA, for which the values derived using these molecules as references differe markedly from those obtained from the isodesmic or atomization reactions.

These results, which we believe are the best state–of–the–art theoretical values, show that the experimental data contained in the NIST thermochemical tables for these species are too low by at least 6 and up to 11 kcal mol^{-1}.

We therefore recommend not to use the NIST values as they are presently recorded, employing those given in this paper instead, until new experiments are performed. In particular, the singularity of BSA must be noticed, and more work is needed to fully characterize its properties.

NOTES

The authors declare no competing financial interest.

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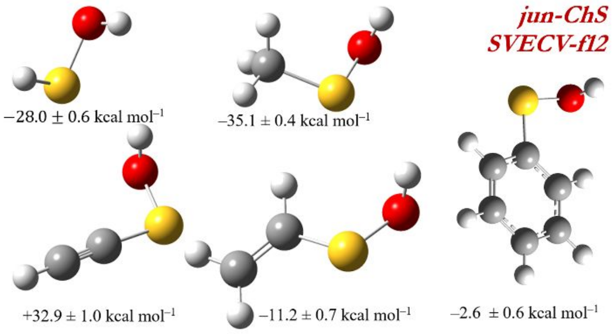
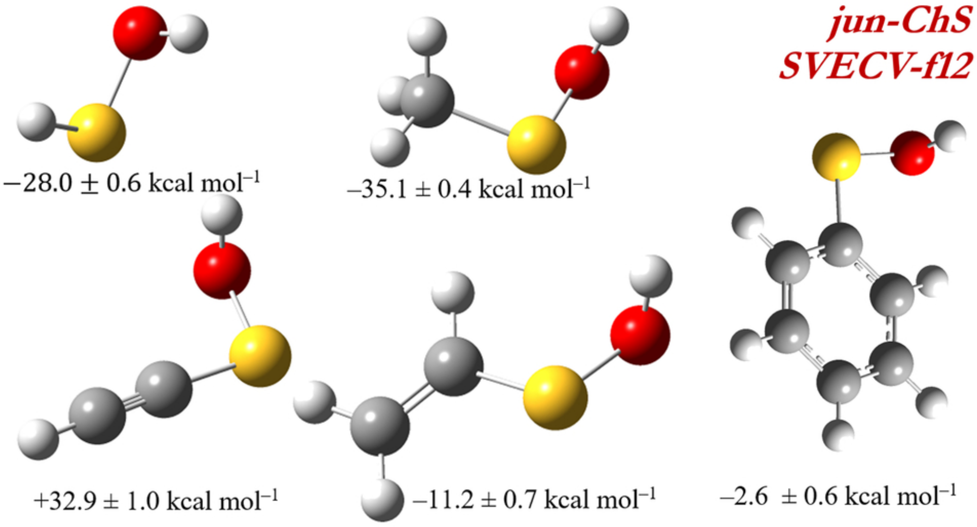
TOC Graphic


jun-ChS
SVECV-f12
−28.0 ± 0.6 kcal mol^{-1}
−35.1 ± 0.4 kcal mol^{-1}
+32.9 ± 1.0 kcal mol^{-1}
−11.2 ± 0.7 kcal mol^{-1}
−2.6 ± 0.6 kcal mol^{-1}



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