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Thermochemistry of Small Organosulfur Compounds from ab Initio Calculations

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Gas-phase standard enthalpies of formation, S−H bond dissociation enthalpies, and gas-phase acidities, at $T = 298.15$ K, for a large number of small sulfur-containing molecules were calculated by means of B3LYP, CBS-Q, G3MP2B3, and G3 approaches. The computed values are compared with available experimental results for these quantities. It is shown that the DFT approach is well-suited to predict S−H bond dissociation enthalpies and gas-phase acidities but fails completely in the estimation of enthalpies of formation from atomization enthalpies. However, three selected reactions, describing the fragmentation of larger molecules into small portions, show that the combination of the enthalpies of those reactions computed at the B3LYP level and the enthalpies of formation of the smaller molecules coming from the most economic composite approach yield excellent estimates of the gas-phase enthalpy of the larger molecules.

Introduction

The chemistry of sulfur-containing compounds assumes an important role in atmospheric, combustion, industrial, and biological reactions. Therefore, it is not surprising that their reactions and structural parameters have been strongly investigated in recent years.[1−14] Likewise, in the literature it is possible to find works devoted to their thermodynamic properties, but unfortunately, they are still not fully determined, or in some cases, the experimental values are associated with large uncertainties.[15,16] In general, these problems are associated with the high instability of these gaseous molecules, which makes it difficult to determine or even prevents the determination of precise or even reliable thermodynamic data. However, the high development of computational chemistry seems to allow the determination of precise data. Thus, in recent years a strong effort has been made to obtain more knowledge about the thermochemistry of sulfur-containing compounds.[17−24] Accurate thermodynamic information is highly demanded since, for example, accurate enthalpies of formation of small compounds are widely used to derive the enthalpies of formation of larger molecules by using isodesmic reaction or similarly derived reactions. Further, since the main source of atmospheric sulfur comes from fossil fuel burning, thermodynamic knowledge on sulfur-containing compounds is also crucial for the development of new environmentally friendly combustion techniques. The environmental problems appear since gas-phase sulfur-containing molecules formed during fuel burning may react with other atmospheric components. For example, it may yield sulfur oxide that is later washed to form sulfuric acid.[25] Other important reactions in which gas-phase sulfur compounds appear are those related to industrial desulfurization processes. In solution, organic sulfur compounds assume importance in several biological reactions including S-oxygenation and metabolic activation.[26] These reactions may involve a series of *S*-oxide and *S*,*S*-dioxide compounds, oxyanions, thioamides, etc., due to the several possible oxidation states of the sulfur atom and, thus, due to the sulfur atom ability to expand electronically into the empty d orbitals.[26]

Despite the rather interesting chemistry of sulfur compounds in both gas and condensed phases, less attention was given to the thermochemistry of small sulfur-containing molecules except in the recent works of Denis and co-workers[17,23] devoted essentially to diatomic and triatomic sulfur-containing molecules. These authors used different theoretical approaches to estimate the enthalpies of formation in the gas phase for 25 different small molecules.[17,23] Recently, other authors focused their study on the thermochemistry of other sulfur compounds, namely, sulfine,[18] nitrogen sulfide,[20] hydrogen sulfide, and dihydrogen sulfide.[21]

The known difficulties in direct application of experimental techniques to gain thermodynamic knowledge about light sulfur-containing species led us to engage a computational study on the estimation of their standard enthalpies of formation in the gas phase. The compounds studied have at least one sulfur and one carbon atom and a maximum of three carbon atoms. They may present different molecular structures, noncyclic or small-ring heterocyclic, which depend also on the sulfur neighboring molecular environment, due to different double R═S or single R−S bonds. These molecules have the chemical formulas H_2CS, H_4CS, H_4C_2S, H_6C_2S, H_6C_3S, and H_8C_3S and include the small strained heterocyclic thiirane, methylthiirane, and thiethane molecules. Four different computational approaches were used to estimate the gas-phase enthalpies of formation, and three of them were further used in the calculation of S−H bond dissociation energies and gas-phase acidities for some of the compounds considered in the present work. Our aim is to test the different computational schemes, to know which yields the best results when compared with experimental data.

As a case study, the standard enthalpies of formation for the small sulfur compounds were used to estimate the enthalpies of formation of larger molecules that also contain a single sulfur atom. The compounds tested are dibenzothiophene, diphenyl sulfide, and *N*,*N*-diethyl-*N*′-isobutanoylthiourea, and their gas-phase enthalpies of formation were estimated by application of

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suitable working equations and the much more economic B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) level of theory.

Theoretical Calculations

Three different composite theoretical procedures were used to carry out a series of calculations on small sulfur-containing compounds. These standard ab initio MO calculations were performed by means of the GAUSSIAN 98 suite of programs.[27] The composite methods employed were the CBS-Q,[28] G3,[29] and G3MP2B3[30] approaches. These composite methods combine a series of separately performed standard ab initio calculations that are aimed to successively introduce corrections to the enthalpy initially calculated with a less expensive computational approach. This is possible since HF, MP2, and DFT methods combined with a reasonable basis set are known to be capable of predicting molecular geometries which often are in good agreement with experiment. Then, for these frozen but previously optimized geometries, several calculations are performed at higher levels of theory.

The CBS-Q composite procedure was proposed by Ochterski and co-workers.[28] This complete basis set method was found to give a mean absolute deviation of 4.2 kJ/mol between calculated and experimental energies of the G2 set. Essentially, in this method higher order contributions are done at the QCISD(T)/6-31+G(d′), MP2/6-311++G(3d2f,2df,2p), and MP4(SDQ)/6-31+G(d(f),d,p) levels on an MP2(FC)/6-31G(d′)-optimized geometry. Zero-point energies, ZPEs, are obtained by the HF/6-31G(d′) approach and using a scale factor of 0.9184.

The G3 method is assumed to provide an accurate approximation to the final energies calculated at the QCISD(T)/G3large//MP2/6-31G(d) level of theory.[29] The G3 energy incorporates ZPEs from HF/6-31G(d) vibrational wavenumber calculation with a scale factor of 0.8929. A variation of the G3 method, the G3MP2B3 composite approach, was also used in the present work. It introduces ZPEs from B3LYP/6-31G(d) calculations and a second-order Moller−Plesset perturbation, MP2, instead of MP4. The high-order corrections are performed on a B3LYP/6-31G(d)-optimized geometry.[30]

The energies computed by each of these composite approaches, at $T = 0$ K, were thermally corrected for $T = 298.15$ K by introducing the vibrational, translational, rotational, and the pV terms. The vibrational term is based on the vibrational wavenumbers calculated by each of the composite models as explained above. Finally, the enthalpies of formation in the gas phase for the different sulfur compounds were estimated by considering their atomization reactions as used with standard Gaussian-N theories. The following atomic experimental gas-phase enthalpies of formation were used: hydrogen, 218.00 kJ/mol; carbon, 716.67 kJ/mol; nitrogen, 472.68 kJ/mol; oxygen, 249.17 kJ/mol; and, finally, sulfur, 276.98 kJ/mol.[31]

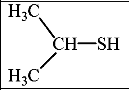
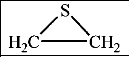
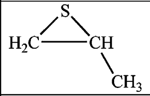
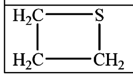
A separate set of calculations was performed with the B3LYP method,[32] a semiempirical DFT-based approach, together with the 6-311++G(3df,3pd) basis set.[33,34] These calculations involving full optimization plus frequency runs were used to extract total energies corrected for $T = 298.15$ K, which were then used to calculate enthalpies of formation, S−H bond dissociation energies, and gas-phase acidities of the sulfur molecules under study.

Results and Discussion

The carbon−sulfur bond lengths of all compounds together with C−S−C, C−S−H, and X−C−S (X = H or C) angles computed at the B3LYP/6-311++G(3df,3pd) level of theory are summarized in Table 1. For comparison purposes, MP2/6-31G(d)-optimized geometries computed within the G3 approach and available experimental numbers are also reported in this table. The MP2/6-31G(d′) distances (CBS-Q) are +0.002 to +0.006 Å longer than MP2/6-31G(d) bond lengths, while MP2/6-31G(d′) bond angles vary by −0.3° to +0.1° when compared with the G3-optimized values. The B3LYP/6-31G(d)-optimized bond lengths (G3MP2B3 composite method) are ~0.01 Å longer than those optimized at the B3LYP/6-311++G(3df,3pd) level. The B3LYP/6-31G(d) bond angles are similar to those computed with the other approaches. The analysis of this table shows that the B3LYP C−S or C═S bond lengths are, in general, larger than those computed with the MP2 approach, with the maximum difference, 0.019 Å, observed for 2-propanethiol. However, it is possible to find four exceptions to this behavior, namely, H_2CS, CH_3CHS, CH_3SCH_3, and CH_2CHSH, for which the computed DFT values are smaller than those obtained with the Moller−Plesset approximation. Further, the comparison with available experimental data shows a better agreement in the case of the MP2/6-31G(d) values. This is also true in the case of bond angles, but for methanethiol, there is a significant difference between the experimental value, 100.3°, and the computed values, ~97°. The present set of results suggests that the use of diffuse functions and extended basis sets with the B3LYP methods does not significantly improve the geometrical results for the species under study. This finding is deeply interesting since it shows why it is possible to obtain excellent energies with the composite methods. Instead of losing computer time with geometry optimization carried out with large basis sets, it is more advisable to correct the energy of the system with single-point runs performed with more accurate theoretical approximations.

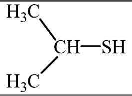
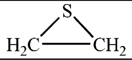
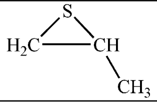
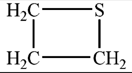
The enthalpies of formation computed for the 16 sulfur compounds considered in the present work are reported in Table 2. This table collects computed data from B3LYP, CBS-Q, G3MP2B3, and G3 calculations together with available experimental information. The enthalpies of formation were estimated from the computed atomization enthalpies and the experimental enthalpies of formation for H, C, N, O, and S atoms given in the preceding section. The enthalpies of atomization are not given but may be easily calculated from data reported in Table 2 and the experimental enthalpies of formation of the atomic species. As expected, it is not possible to estimate accurate enthalpies of formation with the hybrid approach combined with the reaction of atomization. This is due to the fact that current DFT methods cannot provide accurate enthalpies of atomization, and thus, even for the smallest species, thioformaldehyde, the calculated value is far from the highest experimental number (118 ± 8.4 kJ/mol) and far from the estimated values based on the three different composite procedures. A closer inspection of Table 2 shows that the deviation between the B3LYP- and the composite-estimated enthalpies of formation is generally of 8−10 kJ/mol per carbon atom in the compound. It is also interesting to find that, if the enthalpy of formation is positive, the G3MP2B3 values are always lower than those obtained with the CBS-Q or G3 procedure and that, if the enthalpy of formation is negative, the G3MP2B3 values lie between those from CBS-Q and G3 calculations. Further, the G3MP2B3 and G3 methods seem to be the best approaches to estimate standard enthalpies of formation for this family of compounds. It is worth pointing out that this conclusion is based only on the better agreement with experimental data and considering only enthalpies of formation from the compounds with well-determined

TABLE 1: Selected Bond Lengths (Å) and Bond Angles (deg) for the Different Sulfur Compounds Computed at the B3LYP/6-311++G(3df,3pd), Normal Text, and MP2/6-31G(d), Italic Text, Levels of Theory[a]

Compound	C-S	C=S	C-S-C	X-C-S[b] C-S-H[c]
H_2CS	—	1.606 / *1.616* (1.611)	—	122.2 / *122.0*[b] (121.6)
CH_3CHS	—	1.615 / *1.620* (1.610)	—	119.0 / *119.0*[b] (119.4)
$(CH_3)_2CS$	—	1.627 / *1.627*	—	122.6 / *122.7*[b]
CH_3CH_2CHS	—	1.616 / *1.621*	—	119.0 / *119.0*[b]
CH_3SCH_3	1.812 / *1.804*	—	99.9 / *98.5*	—
$CH_3CH_2SCH_3$	1.813 / *1.805* (1.804) 1.824 / *1.812* (1.804)	—	100.1 / *98.8* (99.0)	—
CH_2CHSCH_3	1.815 / *1.808* 1.757 / *1.759*	—	101.0 / *99.7*	—
CH_3SH	1.824 / *1.814* (1.818)	—	—	97.3 / *96.9*[c] (100.3)
CH_3CH_2SH	1.837 / *1.822* (1.820)	—	—	97.4 / *97.0*[c] (96.2)
$CH_3CH_2CH_2SH$	1.836 / *1.822* (1.820)	—	—	97.3 / *96.9*[c] (96.2)
CH_2CHSH	1.764 / *1.766*	—	—	96.9 / *96.4*[c]
	1.847 / *1.828*	—	—	97.2 / *96.7*[c]
CH_2CHCH_2SH	1.836 / *1.823*	—	—	97.0 / *96.6*[c]
	1.824 / *1.814* (1.815)	—	47.8 / *48.1* (48.3)	—
	1.827 / *1.818* 1.836 / *1.822*	—	47.6 / *47.9*	—
	1.850 / *1.838* (1.847)	—	76.9 / *76.1* (76.8)	—

[a] Available experimental values are given in parentheses. Experimental data taken from ref 49. [b] X−C−S bond angle with X = H or C. [c] C−S−H bond angle.

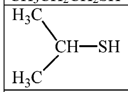
TABLE 2: Gas-Phase Enthalpies of Formation (kJ/mol) for the Sulfur Compounds Calculated from Atomization Enthalpies Computed by Four Different Theoretical Approaches (See the Text)

Compound	B3LYP	CBS-Q	G3MP2B3	G3	Exptl.
H_2CS	127.3	113.6	111.1	115.8	90. ± 8.[a] 118. ± 8.4[a]
CH_3CHS	86.6	68.7	66.6	70.5	50. ± 8.[a]
$(CH_3)_2CS$	54.9	26.3	23.7	26.6	—
CH_3CH_2CHS	78.4	49.5	47.2	50.6	—
CH_3SCH_3	-20.6	-38.7	-37.8	-35.8	-37.5 ± 2.0[a] -37.6 ± 0.6[a]
$CH_3CH_2SCH_3$	-31.4	-62.1	-60.5	-59.1	-60.3 ± 1.1[a]
CH_2CHSCH_3	83.4	61.7	58.8	64.4	—
CH_3SH	-15.1	-24.4	-23.7	-20.5	-22.8 ± 0.6[a]
CH_3CH_2SH	-26.6	-47.0	-46.4	-43.5	-46.1 ± 0.6[b]
$CH_3CH_2CH_2SH$	-36.1	-68.7	-67.5	-64.8	-68.58 ± 0.63[a] -67.8 ± 0.7[b]
	-42.4	-78.8	-78.8	-76.3	-76.94 ± 0.63[a] -76.2 ± 0.7[b]
CH_2CHSH	91.1	77.0	72.2	79.3	—
CH_2CHCH_2SH	94.8	70.2	66.3	73.2	—
	98.9	76.8	76.3	80.0	82.1 ± 1.3[b]
	75.9	41.9	40.9	43.8	46.0 ± 4.2[a] 45.8 ± 2.0[b]
	98.0	62.3	62.3	65.4	61.1 ± 1.3[a] 60.6 ± 1.3[b]

[a] Experimental result taken from ref 15. [b] Experimental result taken from ref 16.

experimental values. Thus, the enthalpies of formation of thioformaldehyde and thioacetaldehyde are not considered due to the large uncertainty associated with the experimental results. In fact, this is supported by the large difference between estimated enthalpies of formation from the composite approaches and experimental numbers. The enthalpies of formation coming from G3MP2B3 calculations are comparable, and in some cases compare better with experiment, to those coming from the much more demanding G3 method. However, these findings seem fortuitous and may come from a cancellation of errors since, as

TABLE 3: S−H Bond Dissociation Energies (kJ/mol) for Some of the Compounds Considered in the Present Work

Compound	B3LYP	G3MP2B3	G3	Exptl.
SH	363.9	356.9	353.5	365.3±2.9[a]
H_2S	385.1	379.3	377.9	381.2±4.2[b] ; 381.6±2.9[c] ; 388.7±8.4[d] ; 381.4±0.5[b]
CH_3SH	368.6	363.5	360.7	369.6[b] ; 361.5±9.2[b] ; 365.7[b] ; 364.0±1.7[b] ; 368.6±8.4[d] ; 365.7±2.1[c]
CH_3CH_2SH	369.6	361.5	359.7	365.3[c] ; 370.7±8.4[d]
$CH_3CH_2CH_2SH$	368.6	365.7	381.0	365.7[c] ; 371.1±8.4[d]
 $(H_3C)_2CH{-}SH$	372.2	366.7	364.6	365.7[c] ; 369.9±8.4[d]
CH_2CHSH	372.6	342.3	336.8	—

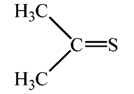
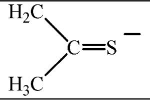
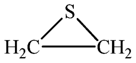
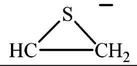
[a] Experimental value taken from ref 41. [b] Experimental value taken from ref 42. [c] Recommended experimental value in ref 42. [d] Experimental value taken from ref 44.

pointed out before, MP2 geometries computed within CBS-Q and G3 procedures are in better agreement with available experimental structural data than those coming from B3LYP (G3MP2B3) calculations. In the case of thiirane and methylthiirane, the G3MP2B3 approach is less efficient with deviations from experimental data larger than 5 kJ/mol. This failure cannot be attributed to strain effects since the G3MP2B3 enthalpy of formation for thiethane is closer to the available experimental values than those from G3 calculations. The computationally derived enthalpies of formation suggest that the experimental results available for thioformaldehyde and thioacetaldehyde should be remeasured. Also, from the analysis of Table 2 it seems that the G3MP2B3-estimated values may be employed safely on the estimation of enthalpies of formation of bigger molecules from a combination of an isodesmic reaction or a similarly derived reaction and a less CPU demanding theoretical approach. The results coming from a few tests with this methodology will be reported below.

To find if some differences between G3 and G3MP2B3 values are due to the use of MP2/6-31G(d) or B3LYP/6-31G(d) geometries, G3MP2 calculations were also performed for comparison purposes. The G3MP2-derived enthalpies of formation are not presented in Table 2 since the computed values are very similar to the G3MP2B3 values. The largest difference between G3MP2B3 and G3MP2 gas-phase enthalpies of formation is found for 2-propanethiol and, it is only 1.1 kJ/mol, whereas the mean deviation is 0.5 kJ/mol. Thus, despite significant differences between the MP2/6-31G(d)- and B3LYP/6-31G(d)-optimized geometries, the final computed enthalpies of formation are essentially affected by the high-order corrections to the enthalpy initially calculated at these geometries.

S−H bond dissociation enthalpies, S−H BDEs, of the thiols considered in the present work and also of SH and H_2S species are listed in Table 3. These enthalpies have been computed by means of the (RO)B3LYP/6-311++G(3df,3pd)//(U)B3LYP/6-311++G(3df,3pd) approach and also by G3MP2B3 and G3 calculations. The restricted open formalism was used to obtain the energy of the open-shell thioxy species previously optimized at the unrestricted B3LYP level of theory. The UB3LYP approach was used to correct these energies for $T = 298.15$ K. In the case of the thiol neutral molecules, all calculations, optimization plus calculation of frequencies, were performed with the restricted B3LYP/6-311++G(3df,3pd) method. The enthalpy of the hydrogen atom is that coming from the exact energy, −0.500000 au, to which the term $5/2RT$ was added (pV and translational contributions). This procedure initially introduced by Wright et al.[35] is known to yield BDEs in very good agreement with experimental results.[36−40] In the case of the composite methods, the enthalpy of the hydrogen atom is that computed by the G3MP2B3 and G3 approaches. As a test case, the S−H BDE in SH was calculated by both the composite methods and the (RO)DFT methodology referred to above. The computed BDEs are 353.5, 356.9, and 363.9 kJ/mol from G3, G3MP2B3, and (RO)B3LYP/6-311++G(3df,3pd) calculations, respectively. The DFT value compares excellently with the photodissociation experimental value, 365.3 ± 2.9 kJ/mol,[41] and with the most accurate computed BDE, 365.8 kJ/mol, obtained from CCSD(T) extrapolated to complete basis set limit calculations.[21] The BDE in H_2S was also computed by means of the (RO)DFT methodology and the composite G3MP2B3 and G3 procedures; the results are 385.1, 379.3, and 377.9 kJ/mol, respectively. The (RO)DFT value is still in excellent agreement with the experimental data available, which vary between 381.2 and 381.6 kJ/mol.[42] More recently, Shiell et al. have remeasured this quantity at $T = 0$ K, by using threshold ion-pair production spectroscopy (TIPPS), and reached a value of 376.24 ± 0.05 kJ/mol.[43] This value turns out to be 381.1 kJ/mol by conversion to $T = 298.15$ K. Another value, 388.7 ± 8.4 kJ/mol,[44] is also found in the literature, but it seems unreliable. The (RO)DFT approach yields excellent results even if smaller basis sets are used, which may be appropriate for the determination of S−H BDEs in larger molecules. For example, when the (RO)B3LYP/6-311+G(2d,2p)//(U)B3LYP/6-31G(d) approach is used, the S−H BDEs for H_2S and SH are 382.3 and 360.4 kJ/mol, respectively. These values are in better agreement with experimental data than those obtained directly with the composite procedures. With this much less computing resource demanding procedure, the S−H BDE in methanethiol is calculated to be 367.3 kJ/mol. For the other compounds listed in Table 3, it is shown that the G3 method gives less accurate S−H BDEs when compared with the DFT and G3MP2B3 approaches. It is also important to note that the composite methods give a too small S−H BDE for the CH_2CHSH species when compared with the application of the DFT approach within the restricted open formalism, which gives 372.6 kJ/mol. This is due to strong spin contamination noticed in the HF, QCISD(T), and MPn calculations from the composite approaches. It should be pointed out here that some spin contamination is found in composite calculations on the similar CH_2CHOH species. However, due to less extension of spin contamination or due to a fortuitous cancellation of this spin contamination in the latter compound, the O−H BDEs were calculated to be 351.7, 353.2, and 355 kJ/mol with the DFT, G3MP2B3, and G3 approaches, respectively. These numbers may be compared with the experimental result, which is 355.6 kJ/mol. Also surprising, the S−H BDEs for propanethiol computed by the G3 and G3MP2 approaches are 381.0 and 382.1 kJ/mol, respectively, far from the experimental values recommended for the alkanethiols and also far from the DFT- and G3MP2B3-computed numbers; cf. Table 3. This contrasts with the G3- and G3MP2-computed BDEs for buthanethiol (not shown), respectively 359.4 and 360.9 kJ/mol, which are identical to those computed for ethanethiol. It should be pointed out here that no significant geometric differences were found for these alkanethiols and their corresponding radicals. Further, in these G3 and G3MP2 calculations, several starting geometries have been considered including those coming from different computational approaches and from optimized ethanethiol plus a methyl group and from optimized butanethiol with the terminal $-CH_3$ substituted by −H. The comparison

TABLE 4: Gas-Phase Acidities (kJ/mol) for Some of the Sulfur Compounds Considered in the Present Work[b]

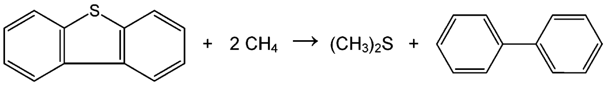
Reactants	Products (-H$^+$)	B3LYP	G3MP2B3	G3	Exptl.
H_2S	HS^-	1469.1	1470.8	1469.3	1468. ± 12. 1469.0 ± 8.8 1469.8 ± 0.4 1473.0 ± 8.8
$(CH_3)_2S$	$CH_3SCH_2^-$	1640.0	1648.6	1652.2	1633.0 ± 6.3 1645.0 ± 8.8
H_2CS	HCS^-	1610.2	1612.6	1613.2	—
CH_3CHS	CH_3CS^-	1610.0	1612.5	1612.8	1456. ± 14.
	CH_2CHS^-	1444.6	1450.9	1453.3	
$CH_3CH_2CH{=}S$	$CH_3CH_2C{=}S^-$	1609.0	1607.6	1605.3	—
	$CH_3CHCH{=}S^-$	1435.3	1440.7	1443.9	
	$CH_2CH_2CH{=}S^-$	1512.9	1512.5	1513.6	
		1455.7	1457.7	1460.2	1469.±14.
CH_3SH	CH_3S^-	1496.0	1496.5	1496.2	1493 ± 9.2 1496. ± 8.4
	CH_2SH^-	1656.8	1660.0	1663.1	1648.5±12.6
CH_3CH_2SH	$CH_3CH_2S^-$	1486.2	1486.0	1485.6	1488.±8.8 1486.±9.2
	CH_3CHSH^-	1661.9	1666.9	1670.8	
	$CH_2CH_2SH^-$	—[a]	—[a]	—[a]	
CH_2CHSH	CH_2CHS^-	1444.5	1445.3	1440.1	—
	CH_2CSH^-	1623.2	1622.0	1618.0	
	$CHCHSH^-$	1663.6	1661.6	1653.9	
		1649.3	1648.8	1651.0	—

[a] The $CH_2CH_2SH^-$ species is not stable; it yields ethylene and SH^-. [b] Experimental data taken from ref 15.

with the G3MP2B3-computed values shows that the S−H BDE for propanethiol is also slightly increased with respect to that computed for ethanethiol. Thus, it seems that the problem still exists but the variation is less noticed in this case. This explanation is supported by the use of B3LYP instead of MP2 geometries in the Gaussian-3-modified G3-RAD and G3X-RAD procedures specially designed for the prediction of some thermochemical properties of radicals.[45]

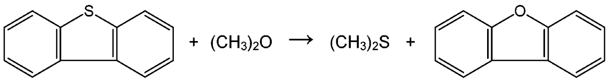
The three theoretical approaches used to compute S−H BDEs were also used to calculate gas-phase acidities for some of the sulfur compounds considered in the present work. The calculated acidities are reported in Table 4 together with available experimental results. A direct comparison of computed and experimental data is difficult because of the rather large uncertainty intervals associated with the experimental results. However, it seems that the DFT approach is capable of predicting this thermodynamic quantity, and the larger differences from experimental values are found only for the cases with larger error bars, namely, for thioacetaldehyde, propanethione, and the reaction yielding the CH_2SH^- species. Also important is that, in some cases, the three methodologies yield practically identical gas-phase acidities for a specific reaction but, in other cases, there are differences of up to 9 kJ/mol among the three theoretical approaches. One important point is that, generally, the less computing resource demanding G3MP2B3 approach gives gas-phase acidities in good agreement with experiment and may be the first choice to obtain this thermodynamic quantity when applied to larger molecules. Similarly to what was written above for the enthalpies of formation, negligible differences were found between G3MP2B3 and G3MP2 gas-phase acidities for the compounds that appear in Table 4.

Finally, and as a test case, gas-phase enthalpies calculated with the G3MP2B3 approach for some sulfur-containing molecules were used to estimate, by means of an appropriate working reaction, the enthalpy of formation of dibenzothiophene, diphenyl sulfide, and *N*,*N*-diethyl-*N*′-isobutanoylthiourea compounds. The working reactions used to estimate the enthalpy of formation of these compounds are



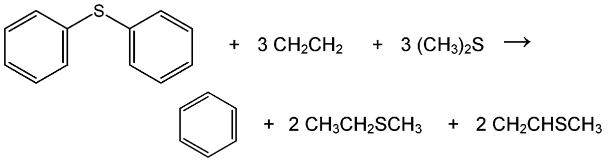
(1)

and



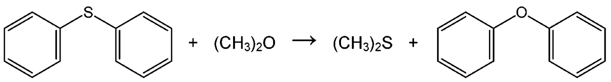
(2)

for dibenzothiophene,



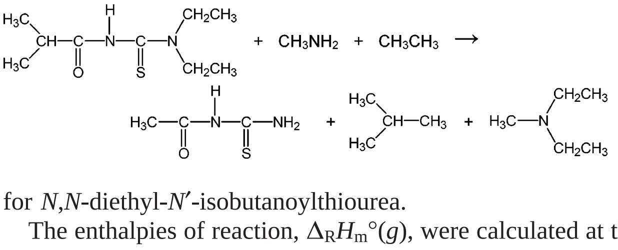
(3)

and



(4)

for diphenyl sulfide, and

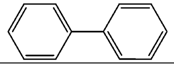
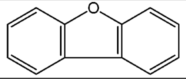
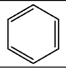
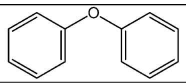
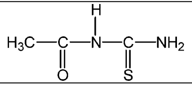
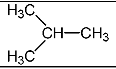
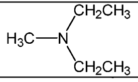


(5)

for *N*,*N*-diethyl-*N*′-isobutanoylthiourea.

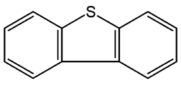
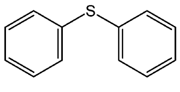
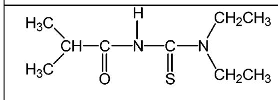
The enthalpies of reaction, $\Delta_R H_m°(g)$, were calculated at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) level of theory. The enthalpies of formation of dibenzothiophene, diphenyl sulfide,

TABLE 5: Experimental and G3MP2B3 Enthalpies of Formation (kJ/mol), $T = 298.15$ K, for the Auxiliary Species That When Combined with Eqs 1−5 Are Used To Estimate the Enthalpies of Formation of Dibenzothiophene, Diphenyl Sulfide, and *N*,*N*-Diethyl-*N*′-isobutanoylthiourea Compounds

Compound	G3MP2B3	Exptl.	Δ
CH_4	-73.3	-74.4 ± 0.4[a]	-1.1
$(CH_3)_2S$	-37.8	-37.6 ± 0.6[b]	+0.2
	—	+181.4 ± 2.0[a]	—
$(CH_3)_2O$	-182.5	-184.1 ± 0.5[b]	-1.6
	—	47.3 ± 4.8[c] 55.2 ± 4.8[d]	—
CH_2CH_2	50.0	52.5 ± 0.3[a]	+2.5
	—	82.6 ± 0.7[a]	—
$CH_3CH_2SCH_3$	-60.5	-60.3 ± 1.1[b]	+0.2
CH_2CHSCH_3	58.8 64.4[e]	—	—
	—	52.0 ± 1.8[a]	—
CH_3NH_2	-17.5	-23.4 ± 1.0[a]	-5.9
CH_3CH_3	-82.3	-83.8 ± 0.3[a]	-1.5
 $H_3C-C(=O)-N(H)-C(=S)-NH_2$	-181.7	—	—
	-131.8	-135.6 ± 0.5[b]	-3.8
	-69.3	—	—

[a] Taken from ref 16. [b] Taken from ref 15. [c] Taken from refs 50 and 51. [d] Taken from refs 51 and 52. [e] G3 value.

TABLE 6: Estimated Enthalpies of Formation (kJ/mol), $T = 298.15$ K, for the Dibenzothiophene, Diphenyl Sulfide, and *N*,*N*-Diethyl-*N*′-isobutanoylthiourea Compounds

Compound	Reaction	Calcd.	Exptl.
	1	218.5	213.2 ± 0.7[e]
	2	216.0[a] 224.0[b]	205.1 ± 1.5[f] 189.3 ± 4.5[g]
	3	217.9[c] 229.1[d]	232. ± 3.[h] 231.2 ± 2.9[f]
	4	236.6	
	5	-235.0	-240.4 ± 3.9[i]

[a] The enthalpy of formation of dibenzofuran from refs 50 and 51 was used. [b] The enthalpy of formation of dibenzofuran from refs 51 and 52 was used. [c] The G3MP2B3 enthalpy of formation of CH_2CHSCH_3 was used. [d] The G3 enthalpy of formation of CH_2CHSCH_3 was used. [e] Value taken from ref 53. [f] Value taken from ref 16. [g] Value taken from ref 51. [h] Value taken from ref 54. [i] Value taken from ref 55.

and *N*,*N*-diethyl-*N*′-isobutanoylthiourea were estimated by combination of the computed enthalpies (reactions 1−5) and the experimental gas-phase enthalpies of formation included in Table 5. When not available, the calculated enthalpies of formation coming from G3MP2B3 atomization enthalpies and reported in Table 5 were used. The derived enthalpies of formation for the larger molecules considered in this work are compiled in Table 6. Starting with dibenzothiophene, reactions 1 and 2 yield almost the same numbers, which are somewhat larger than the available experimental results. However, the computed enthalpies of formation are close to the highest experimental results due to Chirico and co-workers.[53] Therefore, the theoretical calculations seem to suggest that the Chirico et al. result is the best estimate for the enthalpy of formation of the dibenzothiophene species. However, an independent experimental determination of the enthalpy of formation for this species is still required. Turning our attention to what happens with the diphenyl sulfide species, it is found that the calculated and experimental values are in good agreement. However, if the G3MP2B3 enthalpy of formation of CH_2CHSCH_3 is considered, the estimated enthalpy of formation of the diphenyl sulfide species significantly differs from the available experimental results. This probably suggests that the G3MP2B3 method gives wrong estimations for the enthalpy of formation of vinyl-based sulfur compounds, and this may be extended to compounds with C=C bonds adjacent to the sulfur atom. Finally, for the *N*,*N*-diethyl-*N*′-isobutanoylthiourea species, the experimental and computational enthalpies of formation are in excellent agreement and show that this theoretical approach may be used to estimate enthalpies of formation of similar molecules. This is an important result for us since one of the research lines in our group of investigation is devoted to the study of the thermodynamic properties of ML_2 complexes with L = *N*,*N*-alkyl-*N*′-acylthiourea or L = *N*,*N*-alkyl-*N*′-alkylthiourea.[46−48]

Conclusions

Several different computational approaches (B3LYP, CBS-Q, G3MP2B3, and G3) were used to compute the gas-phase enthalpies of formation of small sulfur-containing molecules, $T = 298.15$ K. Experimental results for several of these small molecules were not available in the literature, or in some cases, they are not accurate, probably due to their instability, which prevented accurate experimental measurement. Other thermodynamic properties were calculated for some of these molecules, such as S−H bond dissociation enthalpies and gas-phase acidities. When compared with available experimental data, it is shown that the enthalpies of formation calculated from atomization enthalpies computed with the G3MP2B3 or G3 composite methods deviate less from the experimental results than those coming from B3LYP or CBS-Q calculations. In some cases, the less demanding computer resource method, G3MP2B3, yields the best estimates. As expected, the B3LYP/6-311++G-(3df,3pd) approach gives the worst estimates due to the problems associated with the calculation of atomization enthalpies. However, the B3LYP approach is competitive in terms of accuracy when it is combined with selected working reactions and experimental gas-phase enthalpies for the other species considered in those reactions. This is also verified even if an economic B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) level is used. Further, this DFT-based approach proved also to be well-suited for the calculation of S−H bond dissociation energies and gas-phase acidities, especially when a restricted open formalism is applied to the radicals. Finally, another important conclusion retrieved from the present work is that it is possible to obtain rather accurate enthalpies of formation for large molecules if one considers an adequate working reaction and G3MP2B3 or G3MP2 gas-phase enthalpies of formation for the smaller molecules that appear in this reaction. This was tested for three compounds, namely, dibenzothiophene, diphenyl sulfide and *N*,*N*-diethyl-*N*′-isobutanoylthiourea.

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