Proton Affinity of Dimethyl Sulfoxide and Relative Stabilities of C_2H_6OS Molecules and $C_2H_7OS^+$ Ions. A Comparative G2(MP2) ab Initio and Density Functional Theory Study

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Relative energies of several C_2H_6OS molecules and $C_2H_7OS^+$ ions were obtained by ab initio and density functional theory calculations. Geometry optimizations with Becke's hybrid functional (B3LYP) and the 6-31+G(d,p) basis set gave good-quality equilibrium structures which did not improve significantly by B3LYP calculations using the larger 6-311+G(2df,2p) basis set. Among C_2H_6OS isomers with S−O bonds, dimethyl sulfoxide (DMSO, **1**) was the most stable species, followed by methyl methanesulfenate (**3**), *S*-hydroxy-*S*-methyl-*S*-methylenesulfurane (DMSO enol, **2**), *S*-methoxy-*S*-methylene-*S*-(H)sulfurane (**4**), and (*S*,*S*-H_2)2-oxa-1-thietane (**5**). O-protonated dimethyl sulfoxide (**1aH**$^+$) was the most stable $C_2H_7OS^+$ isomer of those studied. Ion **1aH**$^+$ was separated from the less stable isomers by substantial potential energy barriers. The G2(MP2) proton affinity of DMSO (885 kJ mol^{-1}) was in excellent agreement with the value from equilibrium measurements. DMSO-enol (**2**) was predicted to be a strong gas-phase base for protonation at the methylene and hydroxyl groups. S-protonation in **3** was 44 kJ mol^{-1} more exothermic than O-protonation. In general, proton affinities were overestimated by B3LYP calculations and underestimated by MP2 calculations with all basis sets used. Empirical averaging of the B3LYP and MP2 values, obtained from calculations with the 6-311+G(2df,2p) basis set, provided an improved agreement with experimental or accurate G2(MP2) proton affinities.

Introduction

Proton affinity is one of the fundamental properties of gaseous atoms and molecules.[1] Defined as the standard heat of ion dissociation to a proton and the conjugate base (eq 1),[2] proton affinities connect the gas-phase energetics of cations with those of neutral atoms and molecules. Experimental proton affinities have been obtained from equilibrium measurements,[3]

$$HB^+ \rightarrow H^+ + B \qquad PA(B) = \Delta H^\circ_{r,298} \qquad (1)$$

bracketing,[2a,3] competitive dissociations (kinetic method),[4] or proton-transfer kinetics[5] for a large series of molecules as compiled recently.[6] In addition, computational methods have been employed to calculate proton affinities according to eq 1.[7] Proton affinities accurate to within 5−10 kJ mol^{-1} are often obtained at sufficiently high levels of ab initio theory,[8] as represented for example by the Gaussian 1[9] and Gaussian 2 schemes,[10] their modifications,[11] and the complete basis set schemes.[12] Density functional theory methods,[13] in particular those employing hybrid functionals,[14] have been shown to give reasonably accurate proton affinities, typically within 20 kJ mol^{-1} of reliable experimental values.[15,16]

The major difference between the experimental and computed proton affinities is in the structural information they provide. In particular, in polyfunctional molecules the experimental data bring thermodynamic values at equilibrium corresponding to protonation at the most basic site(s). Isomerizations in ions and neutral molecules due to proton exchange are not probed directly in these measurements. In contrast, computational methods permit and often mandate that several ion isomers differing in the proton position be investigated. Hence, relative energies of isomers and energy barriers to ion isomerization can be obtained and used to evaluate proton-transfer equilibria.

In the present work we address the protonation of dimethyl sulfoxide (DMSO) in the gas phase. In addition to being an important dipolar aprotic solvent,[17] DMSO is a bifunctional molecule with valence electron pairs on sulfur and oxygen that both can serve as protonation sites. The experimental proton affinity (PA) deduced from equilibrium measurements is 884 kJ mol^{-1}.[18] A recent study using competitive dissociations of proton-bound dimers (the kinetic method)[4] reported that PA(DMSO) = 882 kJ mol^{-1}.[20] Protonated DMSO is known to be a stable ion in the gas phase.[21] In the condensed phase, the crystal structure of a hexachlorotellurate complex was interpreted as being due to an O-protonated DMSO isomer, **1aH**$^+$, hydrogen bonded to the oxygen atom of another DMSO molecule.[22] Hence O-protonation appears to be preferred in the condensed phase. A recent ab initio study of Bagno and Scorrano[23] indicated preferential protonation on oxygen in DMSO. However, compared with the experimental value, the calculated proton affinity of DMSO was overestimated by 64 kJ mol^{-1} at the MP2/6-31G(d,p) level of theory used,[23] which was of the same order as the energy difference between the isomers.

Ab initio studies of sulfur-containing molecules are notoriously difficult and often show large basis set effects.[24] For example, in their study of protonation of sulfine, $CH_2{=}S{=}O$, Ruttink and co-workers found that standard G1 and G2 calculations did not provide accurate relative energies because of an inadequate basis set (6-31G(d)) that was used for geometry optimizations.[25] Larger split-valence basis sets, e.g., 6-311+G(2df,2p), were required for obtaining reliable equilibrium structures. In a recent study of SO_2H^+ isomers,[26] we obtained a proton affinity and ionization energy for SO_2 that were in excellent agreement with experimental values using the G2-

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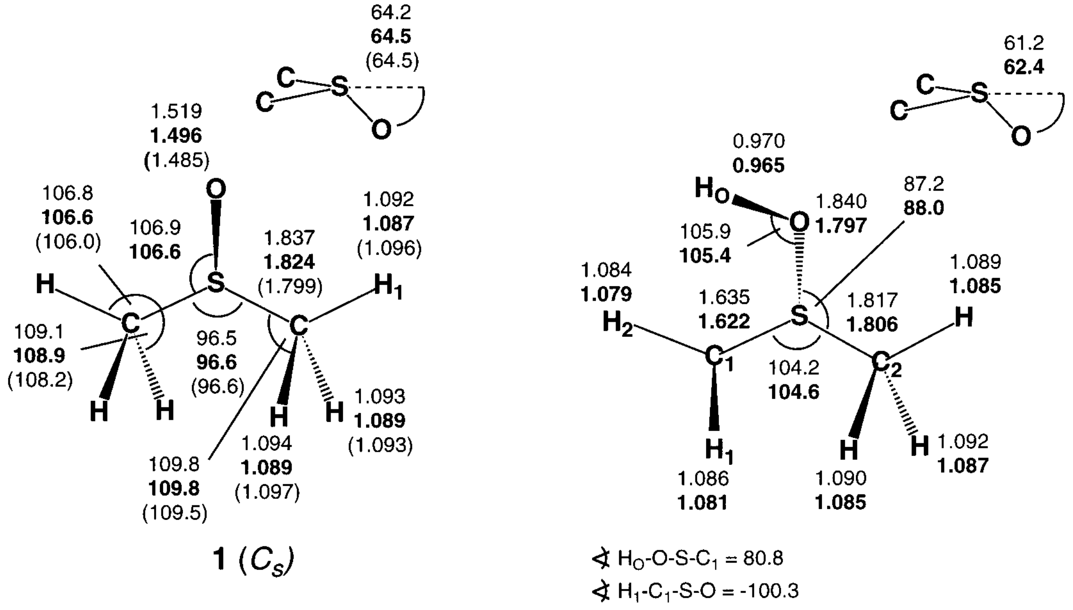


1 (C_s)

2 (C_1)

Figure 1. B3LYP/6-31+G(d,p) optimized geometries of **1** and **2**. Bond lengths in angstroms, bond and dihedral angles in degrees. Bold values are from B3LYP/6-311+G(2df,2p) optimizations. Values in parentheses are from ref 34.

(MP2) scheme, which was based on MP2(FULL)/6-31+G(d,p) optimized geometries. Density functional theory methods have been shown recently to provide accurate equilibrium geometries and good harmonic vibrational frequencies for a number of molecules and ions.[27] One advantage of DFT methods is that they scale only with the 2.7−3.5 power of the number of basis set functions and thus allow one to use larger basis sets for geometry optimizations and frequency calculations even in polyatomic systems. In this study we combine geometry optimizations using Becke's hybrid functional (B3LYP)[14] with single-point ab initio energy calculations to obtain relative energies of several C_2H_6OS molecules and $C_2H_7OS^+$ ions pertinent to DMSO protonation. A similar approach has been used successfully by Partridge and Bauschlicher for a series of molecules.[28] We also address the isomerization barriers and dissociation energies of $C_2H_7OS^+$ ions. Calculations that employed the frequently used 6-31+G(d,p) and 6-311G(d,p) basis sets[29] (hereinafter referred to as "smaller" basis sets) will be compared with those using the 6-311G(2df,p) and 6-311+G-(2df,2p) basis sets (referred to as "larger" basis sets). The B3LYP and MP2 relative energies will be compared with benchmark G2(MP2) data.

Calculations. Calculations were performed using the Gaussian 94 suite of programs.[30] Geometries were optimized with B3LYP using the 6-31+G(d,p) basis set.[29,31] Only singlet states were considered. Harmonic vibrational frequencies were obtained from B3LYP/6-31+G(d,p) calculations and used to characterize local energy minima (all frequencies real) and first-order saddle points (one imaginary frequency). The calculated frequencies were scaled by 0.961[27] and used to calculate zero-point vibrational energies (ZPVE), enthalpies, and entropies. Thermal enthalpy and entropy corrections were obtained from standard thermodynamic formulas using the rigid-rotor-harmonic-oscillator approximation. To compare with DFT calculations, the Moller−Plesset perturbation theory[32] truncated at second order (MP2(FULL)) was also used to obtain optimized geometries of selected species with the 6-31+G(d,p) basis set. Single-point energies on the MP2 and B3LYP/6-31+G(d,p) optimized geometries were calculated by MP2(frozen core) and B3LYP with the larger 6-311G(2df,p) and 6-311+G(2df,2p) basis sets. The latter include the McLean−Chandler (63111) contracted basis set for sulfur[33] and the standard triply split valence basis set for C, H, and O.[29,31] Basis set effects on equilibrium structures and energies were examined with B3LYP/6-311+G-(2df,2p) geometry optimizations for several selected species. At the highest level of theory, effective QCISD(T)/6-311+(3df,2p) energies were calculated using the additive Gaussian 2(MP2) scheme[11] to provide reference proton affinities and relative energies. These modified G2(MP2) calculations used the B3LYP/6-31+G(d,p) optimized geometries, ZPVE, and thermal corrections. The empirical energy corrections, inherent to the G2(MP2) scheme,[11] canceled out in the calculated relative energies of isoelectronic systems. The calculated total energies, harmonic frequencies, ZPVE corrections, and complete geometries (Cartesian atomic coordinates) are given as Supporting Information.

Results and Discussion

Optimized Structures of C_2H_6OS Isomers. Five C_2H_6OS valence-bond isomers containing S−O bonds were identified as local energy minima, i.e., dimethyl sulfoxide (**1**), its enol-form (**2**) (Figure 1), methyl methanesulfenate (**3**), its tautomer (**4**), and the four-membered ring sulfurane, (*S*,*S*-H_2)2-oxa-1-thietane (**5**) (Figure 2). An attempted geometry optimization with B3LYP/6-31+G(d,p) of a three-membered ring sulfurane, *S*-methyl-*S*-(H)thiaoxirane, resulted in ring cleavage and dissociation to CH_3SH and $CH_2{=}O$. Optimized structures were also obtained for syn and anti rotamers of 2-hydroxyethanethiol (**6** and **7**, respectively), methylthiomethanol (**8**), and methoxymethanethiol (**9**).

DMSO (**1**) is the only C_2H_6OS isomer whose molecular structure has been determined experimentally by microwave spectroscopy[34] as recently revised by Typke.[35] Figure 1 shows the bond lengths and angles from the present B3LYP optimizations compared with those from the reassigned rotational spectra of DMSO isotopomers.[35] B3LYP optimizations with both the 6-31+G(d,p) and 6-311+G(2df,2p) basis sets gave bond angles in good agreement with the experimental parameters. The

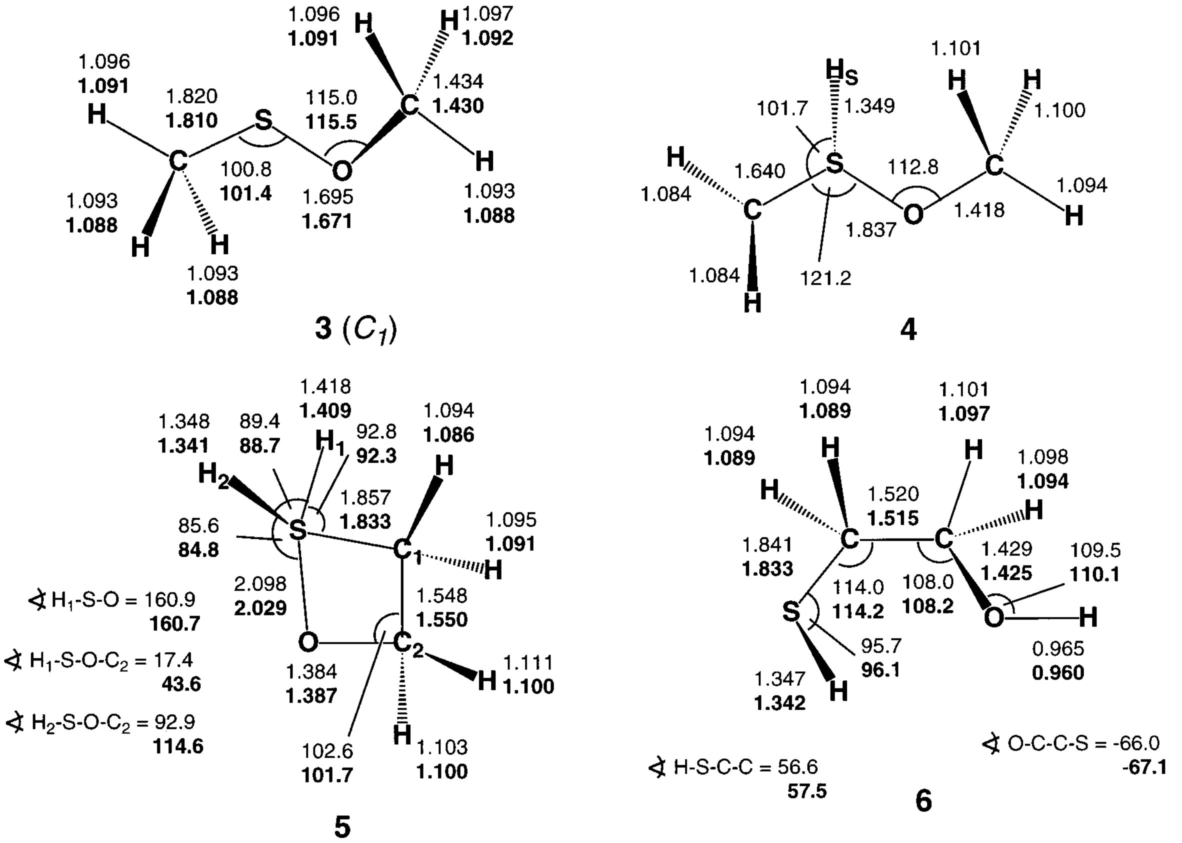


Figure 2. B3LYP/6-31+G(d,p) optimized structures of **3**, **4**, **5**, and **6**. Bold values are from B3LYP/6-311+G(2df,2p) optimizations.

B3LYP/6-31+G(d,p) calculations overestimated the S−O and S−C bond lengths by 0.03 and 0.04 Å, respectively. The B3LYP/6-311+G(2df,2p) calculations showed a better agreement with experimental data for the S−O and S−C bond lengths, but underestimated the C−H bond lengths by 0.06−0.09 Å (Figure 1). However, the total energies were *insensitive* to these small variations in geometry parameters, as the B3LYP/6-311+G(2df,2p) single-point energy for **1** optimized with the 6-31+G(d,p) basis set was only 0.6 millihartree (1.6 kJ mol^{-1}) higher than for **1** fully optimized with the larger 6-311+G-(2df,2p) basis set. The optimized structures of **2** (Figure 1), **3**, **5**, and **6** (Figure 2) were also rather insensitive to the basis set used. The B3LYP/6-311+G(2df,2p) optimized structures in general showed slightly shorter bond lengths than did those optimized with B3LYP/6-31+G(d,p), with the largest differences (0.02−0.04 Å) being obtained for the S−O bonds. The B3LYP/6-311+G(2df,2p) energies calculated for fully optimized geometries were lower than the single-point energies by 0.2−0.6 millihartrees for **2**, **3**, **5**, and **6**. This indicated that the economical 6-31+G(d,p) basis set was adequate for B3LYP geometry optimizations of oxygenated sulfur-containing molecules of this type, in keeping with our previous results for [S,O_2,H_n] molecules, radicals, and ions.[26] The B3LYP/6-31+G-(d,p) optimized geometries were therefore used for all single-point calculations, including those in the G2(MP2) scheme.

The structures of **6**−**9** were unexceptional and showed standard C−S, C−C, and C−O bond lengths. The structures of **2**−**5** deserve a brief comment. The DMSO-enol (**2**) showed a short S−CH_2 bond (1.62−1.63 Å, Figure 1), whose length was similar to that of the S−CH_2 bond in sulfine.[25,36] The CH_2 group in **2** was slightly pyramidal and the C-1−H bonds were twisted out of the C-1−S−O plane. The S−O bond was unusually long, and the O−H bond was twisted almost perpendicular to the O−S−C-1 plane.

Structure **3** showed a perpendicular dihedral angle of the C−S and O−C bonds (Figure 2), which was analogous to the C−S−O−H dihedral in methanesulfenic acid.[37,38] The ene−thiol tautomer **4** showed a short C−S bond and a long S−O bond, which were analogous to the corresponding bonds in **2** (Figure 2). The CH_2 group in **4** was slightly pyramidized and twisted out of the C-1−S−O plane. The H_S and methyl carbon atoms were also out of the C−S−O plane (Figure 2). According to Mulliken population analysis of the HF/6-311+G(2df,2p) wave functions, the methylene carbon atoms in both **2** and **4** carried substantial negative charges, −0.42 and −0.44, respectively, whereas the sulfur atoms were close to electroneutral (+0.07 and −0.01, respectively). Despite the short H_2C−S bonds, the top three occupied molecular orbitals in **2** and **4** had nodal properties that did not indicate the formation of $H_2C{=}S$ double bonds.

The cyclic sulfurane **5** had a long S−O bond, which was substantially polarized. The calculated total atomic charges on S and O were +0.37 and −0.62, respectively. The structure resembled a zwitterionic complex, $H_2S^+CH_2CH_2O^-$, rather than a covalent cyclic molecule with a tetracoordinated sulfur atom in a regular oxathietane ring.

C_2H_6OS Energies. The relative energies of the C_2H_6OS isomers were investigated with B3LYP and MP2 calculations for the whole set and with modified G2(MP2) calculations for **1**, **2**, **3**, **6**, and **7**. The G2(MP2) energies were anchored to the $\Delta H°_f$ scale through the atomization energies of DMSO, which were calculated as 3420.3 and 3374.4 kJ mol^{-1} at 298 and 0 K, respectively. Combined with the standard heats of formation of C, H, O, and S,[39] the heats of formation of DMSO were obtained as −152.6 and −134.3 kJ mol^{-1} at 298 and 0 K, respectively. The 298 K value was in excellent agreement with the tabulated $\Delta H°_{f,298}$(DMSO) = −151.3 ± 0.8 kJ mol^{-1}.[40] It should be noted that this level of agreement was achieved only

TABLE 1: G2(MP2)-Calculated Relative Energies of C_2H_6OS Isomers

	relative enthalpy (kJ mol^{-1})			
species	MP2/6-311+G(3df,2p)	MP2/6-311G(d,p)	QCISD(T)/6-311G(d,p)	G2(MP2)
$(CH_3)_2SO$ (**1**)	0^a	0	0	0^a
				0^b
$CH_3S(OH){=}CH_2$ (**2**)	107.9	86.4	92.4	114.0
				115.1
$CH_3S{-}OCH_3$ (**3**)	29.5	−19.2	−26.5	22.2
				23.0
syn-$HSCH_2CH_2OH$ (**6**)	−54.3	−128.7	−129.6	−55.2
				−55.4
anti-$HSCH_2CH_2OH$ (**7**)	−51.4	−125.3	−127.0	−53.2
				−53.0

[a] 0 K values. [b] 298 K valaues.

TABLE 2: B3LYP- and MP2-Calculated Relative Energies of C_2H_6OS Isomers

	relative enthalpy (kJ mol^{-1})				
	B3LYP	6-311G(2df,p)		6-311+G(2df,2p)	
species	6-31+G(d,p)	B3LYP	MP2	B3LYP	MP2
$(CH_3)_2SO$ (**1**)	0^a	0	0	0	0
	0^b	0	0	0	0
$CH_3S(OH){=}CH_2$ (**2**)	96.7	109.3	110.3	107.0	104.4
	97.8	110.4	111.4	108.1	105.5
$CH_3S{-}OCH_3$ (**3**)	−15.0	3.8	15.3	12.5	24.1
	−14.2	4.5	16.0	13.3	24.9
$CH_2{=}S(H){-}OCH_3$ (**4**)	151.6	160.6	171.3	164.4	173.9
	152.5	161.4	172.2	165.2	174.8
cyc-$H_2SCH_2CH_2O$ (**5**)	175.3	192.0	199.2	189.8	194.7
	173.2	189.9	197.1	187.8	192.6
syn-$HS{-}CH_2CH_2{-}OH$ (**6**)	−91.7	−59.7	−63.9	−56.1	−60.7
	−91.9	−59.9	−64.1	−56.4	−60.9
anti-$HS{-}CH_2CH_2{-}OH$ (**7**)	−89.0	−57.5	−59.9	−54.8	−57.6
	−88.8	−57.3	−58.7	−54.7	−57.4
CH_3SCH_2OH (**8**)	−82.8	−51.1	−52.4	−48.9	−49.9
	−82.2	−50.5	−51.8	−48.3	−49.3
CH_3OCH_2SH (**9**)	−52.5	−25.5	−18.7	−18.2	−11.1
	−52.4	−25.4	−18.6	−18.1	−10.9

[a] 0 K values. [b] 298 K values.

after including the empirical "high-level" corrections in the calculated total energies.[11b] These corrections cancel out in the calculations of relative energies for isomers of the same spin state. Hence, the excellent heat of formation of DMSO from modified G2(MP2)[11b] does not necessarily guarantee the same level of accuracy for the relative energies of other C_2H_6OS isomers. Nevertheless, we show below that the modified G2(MP2) scheme did provide very good relative energies for the molecules and ions under study and can be used as a benchmark for comparison of relative energies calculated by other methods.

DMSO was more stable than any other C_2H_6OS isomer with an S−O bond. In particular, isomers **2**, **4**, and **5** were substantially less stable than DMSO at all levels of theory (Tables 1 and 2). For **2**, the MP2 and B3LYP relative energies calculated with the larger basis sets agreed within 10 kJ mol^{-1} with the G2(MP2) value. The energy of **3** relative to **1** depended on the basis set used. Calculations with the smaller basis sets preferred **3** as the most stable isomer. This result was consistent with the previous Hartree−Fock-level calculations of Wolfe and Schlegel.[41] However, increasing the basis set by adding diffuse sp shells and f shells, and splitting the d shells resulted in reversed relative stabilities which preferred **1** as the more stable isomer (Tables 1, 2). This basis set effect was observed for both B3LYP and MP2 calculations. Introduction of the diffuse and outer d and f functions clearly had a greater stabilizing effect on DMSO, which had a short S−O bond, than on **3**, in which the S and O atoms were farther apart. At the modified G2(MP2) level of theory, which was based on a MP2 calculation with the largest basis set, **3** was 23 kJ mol^{-1} less stable than **1** at 298 K and had a $\Delta H^\circ_{f,298} = -129.6$ kJ mol^{-1}.

To compare the S−O bond containing isomers **1**−**4** with other structures, four standard C_2H_6OS molecules were also investigated by B3LYP and MP2 calculations, e.g., *syn*- and *anti*-2-hydroxyethanethiol (**6** and **7**, respectively), methylthiomethanol (**8**), and methoxymethanethiol (**9**). Although experimental heats of formation of these compounds are unknown, they can be estimated within ±5 kJ mol^{-1} by Benson's group equivalent method,[42] as recently reviewed by Domalski and Hearing.[43]

syn-2-Hydroxyethanethiol (**6**) was calculated to be the most stable isomer (Tables 1, 2). The *anti* rotamer **7** was only marginally less stable than **6** at all levels of theory used. It may be noted that the higher stability of **6** is probably due to the more favorable arrangement of the $C^{(-)}{-}S^{(+)}$ and $C^{(+)}{-}O^{(-)}$ bond dipoles in **6** than in **7**. The distance between H_S and O in **6** (2.64 Å) was too long to justify the existence of an intramolecular hydrogen bond (Figure 2). The calculated $\Delta G^\circ_{298}(\mathbf{6}\rightarrow\mathbf{7})$, 2.7−3.7 kJ mol^{-1} by MP2 and 0.9−2.3 kJ mol^{-1} by B3LYP, indicated 59−81% of **6** at thermal equilibrium. G2(MP2) gave $\Delta G^\circ_{298}(\mathbf{6}\rightarrow\mathbf{7}) = 1.6$ kJ mol^{-1}. The energies of **6**−**9** relative to that of **1** depended on the basis set used (Table 2). MP2 and B3LYP calculations using the smaller basis sets gave relative energies for DMSO that were 30−70 kJ mol^{-1} higher than those obtained with the larger basis sets or G2(MP2) (Table 1, 2). Increasing the basis set resulted in gradually diminishing differences between **1** and **6**−**9** for both MP2 and B3LYP energies. This effect can be attributed to the improved

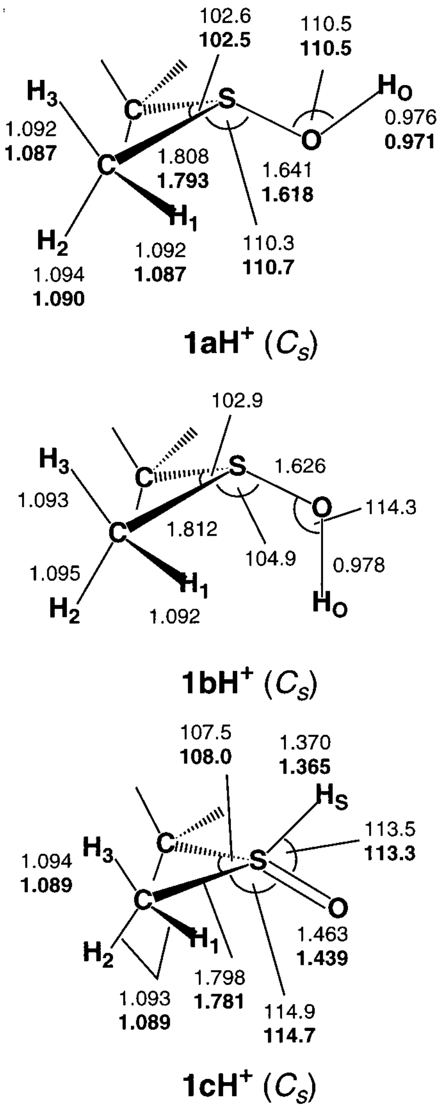


Figure 3. Optimized geometries of **1aH**$^+$, **1bH**$^+$, and **1cH**$^+$. Bond parameters as in Figure 1.

description of the S−O electronic system with calculations using both diffuse and multiple polarization functions. The 6-31+G(d,p) basis set did better in estimating the relative energies within the **6**−**9** subset, where the differences were within 10 kJ mol^{-1} of the values calculated with the larger basis sets (Table 2).

Using Benson's additivity rules, one can estimate that $\Delta H°_{f,298}$(**6**,**7**) = −196.8 kJ mol^{-1}. The Boltzmann-averaged $\Delta H°_{f,298}$ for the 298 K equilibrium mixture of **6** and **7** from the G2(MP2) atomization energies was −207.2 kJ mol^{-1}. The agreement was only fair. Since the MP2 calculations showed convergence of the C_2H_6OS relative energies with increasing size of the basis set, it is possible that the calculated $\Delta H°_{f,298}$(**6**,**7**) could be further improved by employing a basis set larger than 6-311+G(3df,2p). It is interesting to note that the G2(MP2) scheme underestimated the heats of formation of aliphatic alcohols and ethers by 4−10 kJ mol^{-1},[44] which was consistent with the difference found for 2-hydroxyethanethiol.

Optimized Structures of $C_2H_7OS^+$ Isomers. Geometry optimization of O-protonated DMSO gave two stable rotamers of C_s symmetry, **1aH**$^+$ and **1bH**$^+$ (Figure 3). The S-protonated isomer, **1cH**$^+$, was also calculated to be a stable structure. Additional structures (**3aH**$^+$ and **3bH**$^+$) were obtained by geometry optimizations which corresponded to O- and S-protonated methyl methanesulfenate (**3**), respectively (Figure 4). Ions **1aH**$^+$−**3bH**$^+$ represent the various permutations of the proton and methyl groups on the S−O backbone. In addition, two structures, **10**$^+$ and **11**$^+$, corresponding to combined backbone and hydrogen rearrangements in protonated DMSO, were found as local energy minima (Figure 4). Ions **10**$^+$ and **11**$^+$ can be viewed as ion−molecule complexes[45] of $CH_3SCH_2^+$ with water, the latter being loosely bound to the sulfur atom and CH_2 groups, respectively (Figure 4).

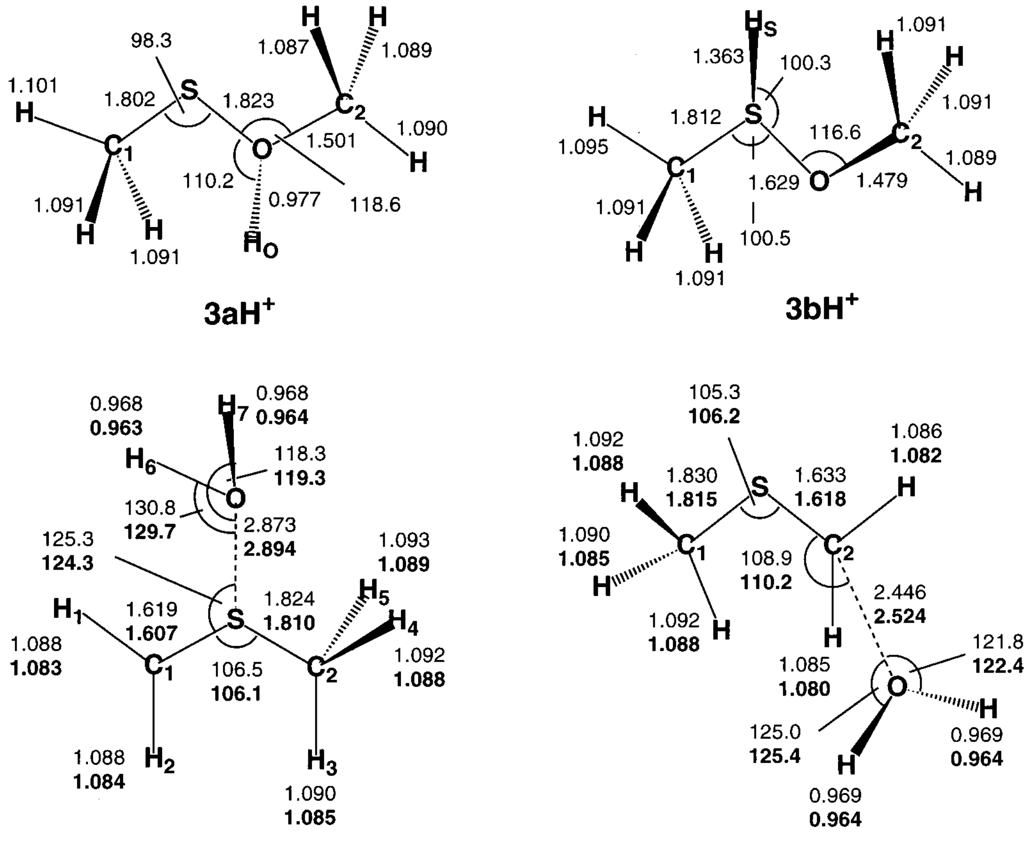
Since there are no experimental ion structures to compare the calculated geometries with, the quality of the latter was checked by optimizations with B3LYP/6-311+G(2df,2p) for **1aH**$^+$, **1cH**$^+$, **10**$^+$, and **11**$^+$. The structures obtained with the two basis sets showed only small differences, which mostly concerned the S−O bond lengths (Figures 3, 4). In particular, the more flexible 6-311+G(2df,2p) basis set allowed for slightly longer S−O bonds in the ion−molecule complexes **10**$^+$ and **11**$^+$, where the differences were 0.02 and 0.08 Å, respectively. The B3LYP/6-311+G(2df,2p) total energies for **10**$^+$ and **11**$^+$ obtained from single-point calculations and those from full optimizations differed by less than 0.4 millihartree (Supporting Information, Table S3). It appeared from these comparisons that the 6-31+G(d,p) basis set provided reasonably good estimates of molecular structures for the neutral molecules and ions under study.

$C_2H_7OS^+$ Energies. The calculated energies of $C_2H_7OS^+$ ions allowed one to compare the relative stabilities of the ion isomers, barriers to their unimolecular isomerizations, and dissociation energies. Combination of the energy data for C_2H_6OS and $C_2H_7OS^+$ provided proton affinities for the neutral molecules. The relative energies are summarized in Tables 3 and 4.

According to G2(MP2), B3LYP, and MP2 calculations with the larger basis sets, O-protonated DMSO (**1aH**$^+$) was the most stable ion isomer. The calculated energies of **1aH**$^+$ were therefore used as references for the other $C_2H_7OS^+$ isomers. The syn rotamer **1bH**$^+$ was found by G2(MP2) to be 12.3 kJ mol^{-1} less stable than **1aH**$^+$ (Table 3), so that the latter is expected to constitute >99% of the rotamer mixture at 298 K. The other calculations gave the same order of relative stabilities and similar relative energies for the rotamers (Table 4). The S-protonated isomer **1cH**$^+$ was substantially less stable than **1aH**$^+$ at all levels of theory. The G2(MP2) relative energy (115.4 kJ mol^{-1}, Table 3) was reasonably well approximated by the MP2 and B3LYP calculations using the larger basis sets (Table 4). Calculations with the smaller basis sets made **1cH**$^+$ less stable by an additional 30−40 kJ mol^{-1}. In addition to the energy difference, **1aH**$^+$ and **1cH**$^+$ were separated by a large energy barrier to unimolecular isomerization, E_a = 313 kJ mol^{-1} by G2(MP2) (Table 3). The O- and S-protonated forms of DMSO therefore exist as separate, noninterconverting isomers. The calculated activation energies for **1aH**$^+$ → **1cH**$^+$ were similar for G2(MP2), B3LYP, and MP2 using the larger basis sets and converged to ca. 309 kJ mol^{-1} upon increasing the basis set.

Protonated methyl methanesulfenate isomers (**3aH**$^+$ and **3bH**$^+$) were less stable than **1aH**$^+$ at all levels of theory. Compared with the G2(MP2) values (Table 3), the MP2 relative energies for **3aH**$^+$ and **3bH**$^+$ were 5−8 kJ mol^{-1} higher, while the B3LYP relative energies were 2−4 kJ mol^{-1} lower. Calculations with the smaller basis sets performed well for **3bH**$^+$ but poorly for **3aH**$^+$ (Table 4).

The energies of the ion−molecule complexes **10**$^+$ and **11**$^+$ relative to **1aH**$^+$ depended on the basis set used. The smaller basis sets slightly preferred the ion−molecule complexes,



10$^+$ **11**$^+$

Figure 4. Optimized geometries of **3aH**$^+$, **3bH**$^+$, **10**$^+$, and **11**$^+$. Bond parameters as in Figure 1.

TABLE 3: G2(MP2) Relative Energies of $C_2H_7OS^+$ Ions

species	relative enthalpy[a] MP2/6-311+G(3df,2p)	MP2/6-311G(d,p)	QCISD (T)/6-311G(d,p)	G2(MP2)
$(CH_3)_2S{-}OH^+$ anti (**1aH**$^+$)	0	0	0	0[b] 0[c]
$(CH_3)_2S{-}OH^+$ syn (**1bH**$^+$)	12.7	13.0	12.9	12.6 *12.3*
$(CH_3)_2S(H^+){=}O$ (**1cH**$^+$)	107.7	149.2	158.2	116.7 *115.4*
$CH_3S^+(\cdots OH_2)CH_2$ (**10**$^+$)	18.3	−16.1	−22.5	11.9 *16.7*
$CH_3SCH_2^+\cdots OH_2$ (**11**$^+$)	24.3	−10.1	−18.4	16.0 *20.6*
$CH_3S{-}O(H^+)CH_3$ (**3aH**$^+$)	137.6	104.6	97.6	130.6 *131.1*
$CH_3S(H^+){-}OCH_3$ (**3bH**$^+$)	93.0	89.4	83.1	86.8 *86.8*
TS(**1aH**$^+$ → **1cH**$^+$)	309.4	351.1	354.9	313.1 *312.7*
TS(**1aH**$^+$ → **10**$^+$)	250.3	230.7	236.9	256.5 *255.9*
TS(**10**$^+$ → **11**$^+$)[d]	5.5	5.7	4.3	4.2 *2.3*
1aH$^+$ → $CH_3SCH_2^+ + H_2O$	65.0	40.4	31.2	55.7 *60.9*
10$^+$ → $CH_3SCH_2^+ + H_2O$	46.6	56.5	53.7	43.8 *44.2*
11$^+$ → $CH_3SCH_2^+ + H_2O$	40.7	50.5	49.6	39.8 *40.4*

[a] Enthalpies relative to **1aH**$^+$ including zero-point energy and thermal corrections in kJ mol^{-1}. [b] 0 K values. [c] 298 K values. [d] Relative to **10**$^+$.

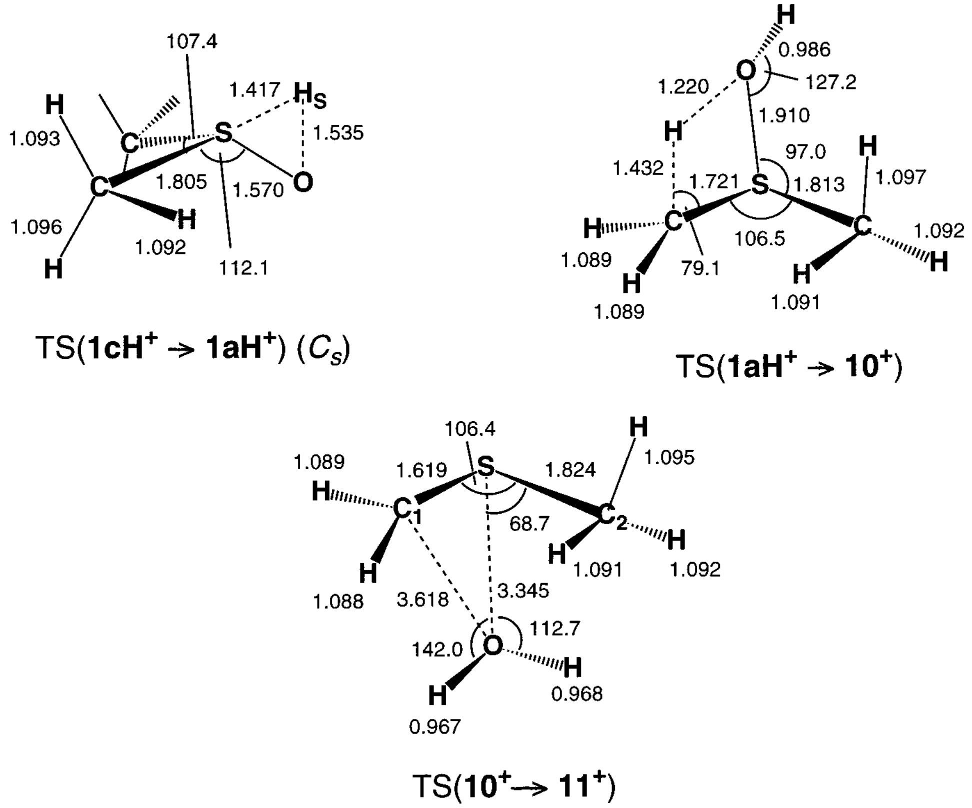
whereas calculations with the larger basis sets gave **1aH**$^+$ as the most stable isomer.

Transition states were also located for the isomerizations **1aH**$^+$ → **10**$^+$ and **10**$^+$ → **11**$^+$. The former isomerization showed a four-membered cyclic transition state (Figure 5) with a partially extended S−O bond. This required an activation energy of 256 kJ mol^{-1} (G2(MP2), Table 3), which was approximated within 10 kJ mol^{-1} by B3LYP and MP2 calcula-

TABLE 4: B3LYP- and MP2-Calculated Relative Energies of $C_2H_7OS^+$ Ions

	relative enthalpy[a]				
		6-311G(2df,p)		6-311+G(2df,2p)	
species/reaction	B3LYP/6-31+G(d,p)	B3LYP	MP2	B3LYP	MP2
anti-$(CH_3)_2S{-}OH^+$ (**1aH**$^+$)	0[b]	0	0		
	0[c]	0	0	0	0
syn-$(CH_3)_2S{-}OH^+$ (**1bH**$^+$)	15.4	11.2		12.8	13.0
	15.1	10.9		12.5	12.7
$(CH_3)_2S(H){=}O^+$ (**1cH**$^+$)	155.7	121.7	111.3	126.4	118.6
	154.4	120.3	109.9	125.1	117.2
$CH_3S(\cdots OH_2)CH_2^+$ (**10**$^+$)	−1.7	22.7	25.3	14.8	16.3
	3.1	27.5	30.1	19.6	21.1
$CH_3SCH_2\cdots OH_2^+$ (**11**$^+$)	−4.8	23.5	31.2	14.0	20.8
	−0.2	28.1	35.8	18.6	25.4
$CH_3S{-}O(H)CH_3^+$ (**3aH**$^+$)	98.2	119.1	133.1	122.2	136.2
	98.6	119.5	133.5	122.7	136.6
$CH_3S(H){-}OCH_3^+$ (**3bH**$^+$)	82.3	81.9	91.9	83.8	95.1
	82.3	81.9	91.9	83.8	95.1
$CH_3SCH_2^+ + H_2O$	41.5	76.8	82.5	53.5	62.0
	46.6	81.8	87.7	58.6	67.1
TS(**1aH**$^+$ → **1cH**$^+$)	333.5	318.7	318.3	316.2	316.4
	333.1	318.2	317.9	315.8	316.0
TS(**10**$^+$ → **11**$^+$)[d]	3.5	6.9	6.6	4.2	4.5
	1.5	5.0	4.7	2.3	2.5
TS(**1aH**$^+$ → **10**$^+$)	234.1	246.1	246.7	248.3	249.5
	233.5	245.5	246.1	247.7	248.9

[a] Relative to **1aH**$^+$ in kJ mol^{-1}. [b] 0 K values. [c] 298 K values. [d] Relative to **10**$^+$.



TS(**1cH**$^+$ → **1aH**$^+$) (C_s)

TS(**1aH**$^+$ → **10**$^+$)

TS(**10**$^+$ → **11**$^+$)

Figure 5. Optimized geometries for transition states of ion isomerizations. Bond parameters as in Figure 1.

tions using the larger basis sets (Table 4). The lower levels of theory in general underestimated the activation energy by 23−25 kJ mol^{-1}. The isomerization, **10**$^+$ → **11**$^+$, involved a migration of the water molecule along the $CH_2{-}S$ bond (Figure 5). The isomerization had a very low activation energy at all levels of theory (Tables 3 and 4). This finding was consistent with the fact that the ion−molecule complexes **10**$^+$ and **11**$^+$ were loosely bound against dissociation to water and $CH_3SCH_2^+$, which required only 40−44 kJ mol^{-1} (Table 3).

Loss of water was the lowest energy dissociation of **1aH**$^+$. The G2(MP2) threshold energy was 61 kJ mol^{-1} at 298 K (Table 3). The B3LYP and MP2 calculated energies oscillated about the G2(MP2) value depending on the basis set used (Table 4). An experiment-based estimate of the dissociation energy in **1aH**$^+$ was obtained from the standard heats of formation of protonated DMSO (494 kJ mol^{-1}), water (−241.8 kJ mol^{-1}), and $CH_3SCH_2^+$.[19] It should be noted, however, that the tabulated $\Delta H_f(CH_3SCH_2^+) = 812$ kJ mol^{-1} refers to 0 K[46] and

TABLE 5: G2(MP2)-Calculated Proton Affinities of Auxiliary Molecules

	proton affinity (kJ mol^{-1})[a]			
species	MP2/6-311+G(3df,2p)	MP2/6-311G(d,p)	QCISD(T)/6-311G(d,p)	G2(MP2)
$(CH_3)_2S$	816.8	826.9	837.9	827.7[b]
				833.3[c]
				(830.9)[d,e]
				(839)[f]
2-methylpropene	784.6	796.5	808.5	796.7
				800.6
				(802.1)[d,e]
				(802.0)[f]
$(CH_3)_2C{=}O$	795.7	809.0	820.1	806.7
				812.9
				(811.7)[d,e]
				(823)[f]
				(810.9)[g]

[a] Reaction enthalpies for $BH^+ \rightarrow B + H^+$. [b] 0 K values. [c] 298 K values. [d] G2 calculations, ref 8. [e] From ref 6b. [f] Experimental data from ref 2b. [g] Experimental data from ref 49.

TABLE 6: B3LYP- and MP2-Calculated Proton Affinities of Auxiliary Molecules

	proton affinity[a] (kJ mol^{-1})						
		6-311G(2df,p)		6-311+G(2df,2p)			
species	B3LYP 6-31+G(d,p)	B3LYP	MP2	B3LYP	MP2	B3LYP + MP2	
$(CH_3)_2S$	818.6[b]						
	824.2[c]	832.5	818.8	833.6	820.9	825.7[d]	827.2[e]
2-methylpropene	825.7						
	829.6	827.7	790.7	825.7	789.6	809.2	807.7
$(CH_3)_2C{=}O$	814.5						
	820.7	829.4	807.8	823.2	804.0	818.6	813.6

[a] Reaction enthalpies for $BH^+ \rightarrow B + H^+$. [b] 0 K values. [c] 298 K values. [d] From averaged B3LYP and MP2 energies calculated with the 6-311G(2df,p) basis set. [e] From averaged B3LYP and MP2 energies calculated with the 6-311+G(2df,2p) basis set.

must be converted to 298 K to give $\Delta H^\circ_{f,298}(CH_3SCH_2^+) = 799$ kJ mol^{-1}. The corrected 298 K endothermicity for **1aH**$^+$ $\rightarrow CH_3SCH_2^+ + H_2O$, $\Delta H^\circ_{r,298} = 63$ kJ mol^{-1}, was thus reproduced very well by G2(MP2). The G2(MP2) heats of formation of $CH_3SCH_2^+$, calculated from the atomization energies as 812.4 and 799.4 kJ mol^{-1} at 0 and 298 K, respectively, were also in an excellent agreement with experiment.[47]

Direct S−O bond cleavage in **1aH**$^+$ to give $(CH_3)_2S^{\bullet+}$ and $OH^\bullet$ is a high-energy process. The G2(MP2)-calculated enthalpy for this dissociation, $\Delta H^\circ_{r,298} = 344$ kJ mol^{-1}, was in an excellent agreement with an estimate (345 kJ mol^{-1}) based on the experimental heats of formation of the reactant and products.[19] The thermochemical threshold for the S−O bond cleavage in **1aH**$^+$ was about 109 kJ mol^{-1} above the transition state for the isomerization to **10**$^+$. Note that the latter is 196 kJ mol^{-1} above the dissociation threshold for the formation of CH_3SCH_2+ by elimination of water (Table 3), so that when formed from **1aH**$^+$, complex **10**$^+$ must dissociate rapidly. Interestingly, formation of both $(CH_3)_2S^{\bullet+}$ and $CH_3SCH_2^+$ was observed upon collisionally activated dissociation of **1aH**$^+$ in the gas phase.[21] This implied that the *k(E)* curves[48] for the hydrogen rearrangement and S−O bond cleavage crossed at ion vibrational excitations > 345 kJ mol^{-1} and that significant populations of ions with internal energies exceeding this threshold were produced by collisional activation.

Proton Affinities. The relative energies of the C_2H_6OS and $C_2H_7OS^+$ species allowed the proton affinities (PA) of the neutral molecules to be assessed. To test the performance of the computational methods used, we also calculated proton affinities of three auxiliary molecules, dimethyl sulfide, acetone, and isobutene, for which there are both experimental data[2b,49] and previous G2 calculations.[8] The G2(MP2)-calculated PA of the auxiliary molecules are summarized in Table 5; the B3LYP and MP2 values are given in Table 6. G2(MP2) gave PA values that agreed well with those reported previously. The calculated PA of dimethyl sulfide from both G2(MP2) and G2 were 6−8 kJ mol^{-1} lower than the previously listed value from equilibrium measurements (839 kJ mol^{-1}),[2b] but in a good agreement with the most recent revised value (831 kJ mol^{-1}).[6b] It is worth noting that the G2(MP2) atomization energy of dimethyl sulfide gave $\Delta H^\circ_{f,298} = -38.9$ kJ mol^{-1}, which was very close to the experimental value of -37.5 kJ mol^{-1}.[40] The G2(MP2) PA of isobutene was in close agreement with the G2 and experimental values (Table 5). The $\Delta H^\circ_{f,298}$ of isobutene from the G2(MP2) atomization energy was -8.7 kJ mol^{-1}, which was in only fair agreement with the experimental value (-16.9 kJ mol^{-1}).[39] The G2(MP2) PA value for acetone agreed closely with that from G2 and revised experimental data[6b,49] (Table 5). The $\Delta H^\circ_{f,298}$ of acetone from the G2(MP2) atomization energy was -220.7 kJ mol^{-1}, in good agreement with the experimental value of -217.2 kJ mol^{-1}.[40]

The B3LYP- and MP2-calculated PA of the auxiliary molecules showed only weak dependence on the basis set used (Table 6). Small systematic deviations from the G2(MP2) values were found for the B3LYP and MP2 calculations using the larger basis sets. The B3LYP calculations mostly overestimated the proton affinities, whereas the PA values from MP2 were too low. The same trend was observed for the PA of C_2H_6-OS isomers as discussed below. The physical meaning of these deviations is not clear because the methods use quite different approximations to treat the correlation energy,[50] and the PAs are relative energies combining calculations on two different species. It was suggested previously that the MP2-calculated proton affinities can be improved by correcting for the basis set superposition error.[8b] We found empirically that averaging the B3LYP and MP2 proton affinities gave an excellent fit to the G2(MP2) and/or experimental data.

TABLE 7: G2(MP2)-Calculated Proton Affinities of C_2H_6OS

	proton affinity (kJ mol^{-1})^a			
species	MP2/6-311+G(3df,2p)	MP2/6-311G(d,p)	QCISD(T)/6-311G(d,p)	G2(MP2)
$(CH_3)_2S-O\mathbf{H}^+$(**1aH**$^+$)	871.2	919.8	930.0	881.5^b *886.1*^{c}
$(CH_3)_2S-O\mathbf{H}^+$(**1bH**$^+$)	858.7	906.9	917.2	869.0 *873.9*
$(CH_3)_2S\mathbf{H}^+{=}O$ (**1cH**$^+$)	763.6	770.6	771.8	764.7 *771.1*
$CH_3S(OH)CH_2-\mathbf{H}^+$ (**1aH**$^+$)	979.2	1006.2	1022.5	995.5 *1001.2*
$CH_3S(\cdots O\mathbf{H}_2{+})CH_2$ (**10**$^+$)	960.9	1022.3	1045.0	983.6 *984.5*
$CH_3S-O(\mathbf{H}^+)CH_3$ (**3aH**$^+$)	763.1	796.0	805.9	773.1 *778.0*
$CH_3S(\mathbf{H}^+)-OCH_3$ (**3bH**$^+$)	807.8	811.2	820.4	817.0 *822.3*

[a] Reaction enthalpies for $BH^+ \rightarrow B + H^+$. [b] 0 K values. [c] 298 K values.

TABLE 8: B3LYP- and MP2-Calculated Proton Affinities of C_2H_6OS

	proton affinity (kJ mol^{-1})^a						
	B3LYP	6-311G(2df,p)		6-311+G(2df,2p)			
species	6-31+G(d,p)	B3LYP	MP2	B3LYP	MP2	B3LYP + MP2	
$(CH_3)_2S-O\mathbf{H}^+$ (**1aH**$^+$)^b	897.3^c						
	902.0^d	903.4	890.8	892.9	881.7	897.1^e	887.3^f
$(CH_3)_2S-O\mathbf{H}^+$ (**1bH**$^+$)	881.9						
	886.8	892.4	879.6	880.4	869.0	886.0	874.7
$CH_3S(OH)CH_2-\mathbf{H}^+$	994.0						
	999.8	1013.8	1002.2	1001.0	987.2	1008.0	994.1
$CH_3S(\cdots O\mathbf{H}_2){=}CH_2^+$	995.8						
	996.7	986.3	972.2	981.3	966.2	979.2	973.8
$(CH_3)_2S\mathbf{H}{=}O^+$ (**1cH**$^+$)	741.6						
	747.6	783.1	780.9	767.8	764.5	782.0	766.2
$CH_3S-O(\mathbf{H})CH_3^+$ (**3aH**$^+$)	784.1						
	789.1	788.4	773.3	783.5	770.0	780.8	776.7
$CH_3S(\mathbf{H})-OCH_3^+$ (**3bH**$^+$)	800.0						
	805.4	826.0	814.9	822.4	811.4	820.4	816.9

[a] Reaction enthalpies for $BH^+ \rightarrow B + H^+$. [b] Protonation sites denoted with bold **H**. [c] 0 K values. [d] 298 K values. [e] From averaged B3LYP and MP2 energies calculated with the 6-311G(2df,p) basis set. [f] From averaged B3LYP and MP2 energies calculated with the 6-311+G(2df,2p) basis set.

The oxygen atom was the most basic site in **1**. This followed from both G2(MP2) and B3LYP or MP2 calculations (Tables 7 and 8). The 298 K proton affinity of **1** to give **1aH**$^+$ was calculated at 886 kJ mol^{-1} by G2(MP2), which was bracketed by the B3LYP and MP2 calculations with the larger basis sets (Table 8). The average of the latter two calculations (887 kJ mol^{-1}, Table 8) gave a very good fit with the G2(MP2) value. When comparing the calculated PA of **1** with the experimental value (884 kJ mol^{-1}),[2b] one has to consider that the equilibrium measurement was performed at 600 K, which affected the populations of **1aH**$^+$ and **1bH**$^+$ in the gas phase. The G2(MP2) value for the isomerization free energy, ΔG°_{600}(**1aH**$^+$→**1bH**$^+$) = 13.5 kJ mol^{-1}, indicated 6.2% of the less stable conformer at 600 K. To obtain the equilibrium-based PA of **1**, the G2(MP2)-calculated PA for the formation of the major ion isomer **1aH**$^+$, denoted as PA(**1**→**1aH**$^+$), must be Boltzmann-averaged for the 600 K rotamer populations, according to eq 2, where x(**1aH**$^+$) is the molar fraction of **1aH**$^+$ at 600 K.

$$\mathrm{PA}(\mathbf{1}) = \mathrm{PA}(\mathbf{1}\rightarrow\mathbf{1aH}^+) + RT\ln x(\mathbf{1aH}^+) \qquad (2)$$

The Boltzmann-averaged value, 885 kJ mol^{-1}, was in excellent agreement with experiment.

The topical proton affinity of the sulfur atom in **1** was low, PA = 771 kJ mol^{-1} by G2(MP2) (Table 7). The B3LYP and MP2 values were 3−7 kJ mol^{-1} lower (Table 8). Hence, gas-phase protonation on sulfur in **1** cannot proceed competitively with common chemical-ionization reagents of medium basicity, such as acetone (PA = 812 kJ mol^{-1}), 2-methylpropene (PA = 802 kJ mol^{-1}), or dimethyl ether (PA = 793 kJ mol^{-1}).[49] In contrast, S-protonation with H_3O^+/H_2O in **1** was calculated to be 75−81 kJ mol^{-1} exothermic, based on the experimental proton affinity of water,[2b,49] and therefore energetically possible. Likewise, protonation with CH_5^+/CH_4 was estimated to be 220−226 kJ mol^{-1} exothermic. However, the latter energy exceeded the barrier to unimolecular isomerization to the more stable **1aH**$^+$, which was 197 kJ mol^{-1} above **1cH**$^+$ (Table 3). Hence, a fraction of CH_5^+-protonated **1cH**$^+$ may rearrange to the more stable **1aH**$^+$. It appears that H_3O^+ may be the best acid for coformation of the less stable isomer **1cH**$^+$ upon gas-phase protonation of DMSO.

The G2(MP2) and combined B3LYP and MP2 calculations suggested that the DMSO-enol (**2**) was extremely basic toward protonation at both the methylene and hydroxyl groups. The calculated PA for protonation of **2** at the methylene group, 1001 kJ mol^{-1} by G2(MP2) (Table 7), approached those of the strongest gas-phase bases, e.g., aliphatic diamines and 1,8-bis(dimethylamino)naphthalene (proton sponge).[2b] Protonation at the hydroxyl group was slightly less exothermic, having PA = 985 kJ mol^{-1}. It can be inferred from these PA values that neutral **2** should be extremely sensitive to acid−base-catalyzed isomerization to the more stable **1**, due to interactions with solvent or surface. This prediction is in perfect agreement with the unsuccessful attempt at preparation of **2** by flash-vacuum pyrolysis, which resulted in the formation of **1** instead and which was tentatively attributed to surface-catalyzed isomerization.[51]

The calculations further predicted that the sulfur atom should be the preferred protonation site in methyl methanesulfenate (**3**) to give **3bH**$^+$ (Tables 7 and 8). The G2(MP2)-calculated topical proton affinities of **3** (Table 7) were reasonably well reproduced by both the B3LYP and MP2 calculations with the larger basis sets (Table 8).

Conclusions

G2(MP2) calculations based on B3LYP/6-31+G(d,p) optimized geometries provided accurate heats of formation and proton affinities for C_2H_6OS isomers with S−O bonds. Geometry optimizations with the larger 6-311+G(2df,2p) basis set did not result in significant changes in the calculated energies. The less expensive B3LYP and MP2 energy calculations required basis sets furnished with diffuse and multiple polarization functions in order to provide data of acceptable quality. Energy data obtained for this group of compounds with the smaller 6-31+G(d,p) and 6-311G(d,p) basis sets were unreliable and sometimes qualitatively incorrect. It appeared that the deficiencies in proton affinity calculations inherent to the B3LYP and MP2 formalisms can be compensated empirically by averaging the calculated values. Protonation of DMSO is predicted to occur exclusively on the oxygen atom for gas-phase acids of PA > 770 kJ mol^{-1}. Deprotonation of the most stable isomers **1aH**$^+$ and **1bH**$^+$ is predicted to yield DMSO. O-protonated DMSO is separated from the other valence-bond isomers by large potential energy barriers. **1aH**$^+$ and **1bH**$^+$ are the only ions accessible by protonation with moderate gas-phase acids.

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Supporting Information Available: Tables of ab initio total energies (2 pages), B3LYP and MP2 total energies (2 pages), B3LYP/6-31+G(d,p) and 6-311+G(2df,2p) optimized geometries, and B3LYP/6-31+G(d,p) harmonic frequencies (15 pages).

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