J. Phys. Chem. A **2009,** *113,* 11343–11353

Heats of Formation of the $H_{1,2}O_mS_n$ (m, n = 0−3) Molecules from Electronic Structure Calculations

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Received: June 22, 2009; Revised Manuscript Received: August 21, 2009

Atomization energies at 0 K and heats of formation at 0 and 298 K are predicted from high level ab initio electronic structure calculations using the coupled cluster CCSD(T) method with augmented correlation-consistent basis sets extrapolated to the complete basis set (CBS) limit for the $H_{1,2}O_mS_n$ (m, n = 0−3) compounds, as well as various radicals involved in different bond breaking processes. To achieve near chemical accuracy (±1.0 kcal/mol), additional corrections were added to the CBS binding energies based on the frozen core CCSD(T) energies including corrections for core−valence, scalar relativistic, and first-order atomic spin−orbit effects. Geometries were optimized up through the CCSD(T)/aV(T+d)Z level. Vibrational zero point energies were computed at the MP2/aV(T+d)Z level. The calculated heats of formation are in excellent agreement with the available experimental data and allow the prediction of adiabatic bond dissociation energies (BDEs) to within ±1.0 kcal/mol. The decomposition mechanisms were largely determined by a preference to maintain a strong S═O bond in the dissociated products as opposed to O═O and S═S bonds, exactly matching the ordering of the BDEs in the diatomics. For the H_2X_2 and H_2X_3 systems, as well as the HX_3 radicals, the energetically favorable decomposition pathway leads to the formation of XH radicals and breaking the X−X bond as opposed to breaking the X−H bond. For the HX_2 radicals, however, the more thermodynamically favorable pathway leads to a breaking of the H−X bond and forming X_2 molecules.

Introduction

The chemistry of atmospheric sulfur has received renewed interest in terms of understanding how the present day sulfur cycle interacts with current anthropogenic emissions, as well as in terms of understanding differences in sulfur chemistry between now and that of the early Earth.[1−4] One of the most important sources of natural emissions of sulfur into the atmosphere is from volcanoes and the two most abundant sulfur gases are SO_2 and H_2S. The photochemistry of these gases in the atmosphere is a source of elemental sulfur, sulfur particles, sulfuric acid, and oceanic sulfate. Figure 1 illustrates some of the chemical processes suggested to be important in the photochemical oxidation of volcanogenic sulfur species in the early atmosphere of Earth.[5] Mass-independent sulfur isotope data support the importance of sulfur chemical reactions in the atmosphere influencing sulfur cycles.[6,7] In photochemical models of sulfur,[8] chemical species that are considered short-lived are H_2S, HS, S, SO, SO_2, HSO, and H_2SO_4. Subsequent atmospheric reactions of these species with atmospheric radical species are not well characterized, nor are all of the intermediate radical species produced by these reactions well understood. Sulfur and sulfur oxides also are important in developing chemical models for the combustion of fuels containing sulfur.[9] Various sulfur radical species including those containing oxygen and hydrogen can play an important role in the modeling of such species.

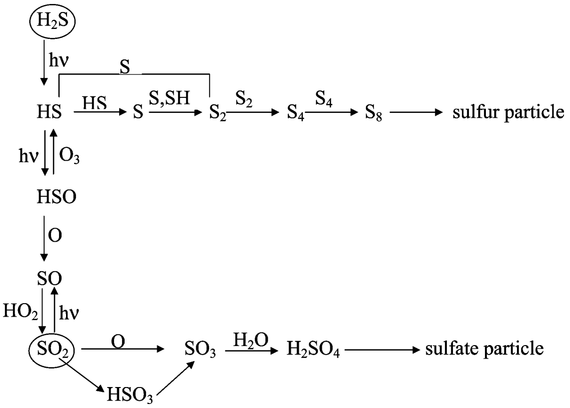

Figure 1. Atmospheric sulfur photochemistry.

There is considerable interest in the chemistry of compounds of the form $H_{1,2}O_mS_n$ (m, n = 0−3) that are formed from these photochemical reactions with respect to their identification and decomposition pathways in the atmosphere. There is a limited quantity of experimental[10−16] and theoretical[17,18] thermodynamic data available for these compounds, specifically their heats of formation and bond dissociation energies (BDEs). Although the heats of formation of the diatomic and triatomic species and of

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10.1021/jp905847e CCC: $40.75

HOOH are known experimentally,[10−16] there are no experimental heats of formation for H_2OS, the H_2X_3 compounds, and the various radicals involved in several of the bond breaking processes studied. One exception is HO_3 for which there has been recent experimental and computational studies of its structure, vibrational structure and energetics, which have been recently summarized by Lester and co-workers.[19] There have been a number of high level theoretical studies of this radical at the CCSD(T) and MRCI levels, including its structure and its energetics, and the results are discussed in detail later.[20−25] Denis and Ornellas have reported high level calculations on HOOOH.[24] The second exception is HOSO for which Wheeler and Schaefer recently published highly accurate calculations of the structures and energetics at the complete basis set (CBS) limit CCSD(T) level with additional energetic corrections, including higher level correlation up through the CCSDT(Q) level.[26] These authors summarize prior experimental and computational work on this radical. Other authors have reported computational results on some of these compounds as part of studies on the properties of sulfuric acid,[27] the atmospheric oxidation of CS_2,[28] and chirality changing modes of H_2O_2 and its derivatives.[29] The enthalpies of formation of HSO and SOH have been reported from high level calculations.[30−32] Balacuni et al.[33] estimated a lower bound of −3.0 kcal/mol for the heat of formation of HSO at 0 K from crossed molecular beam scattering experiments of the reaction $O + H_2S$, but this value is outside the computational limits. The heats of formation of HOSO and HOSOH have been reported at the G3B3 and G3/MP2 levels in a study of the atmospheric chemistry of dimethyl sulfide.[34] The heat of formation of HOSH has been reported at the CCSD(T)/CBS level with additional corrections to be −28.1 ± 1 kcal/mol.[35] Steudel and co-workers have reported MP2 calculations on the relative energies of the H_2S_2O isomers.[36] Troiani et al.[37] detected HSSS by gas-phase mass spectrometry and studied its dissocation pathways by using ab initio calculations. High level calculations are available from Denis[38] on HSS and HSSH in terms of the structure and heats of formation, and from Peterson and co-workers[39] on the structure, vibrational frequencies, and energetics of HSS. There is also limited experimental BDE data available from Luo's compilation.[40] Accurate thermodynamic data is essential to assess the thermochemistry involved in the various decomposition pathways occurring in the atmosphere. The heats of formation of these simple model compounds are also needed accurately for use in isodesmic reaction schemes to treat larger molecules.

In the present work, a detailed high level ab initio electronic structure analysis of the energetics of the $H_{1,2}O_mS_n$ ($m, n = 0-3$) molecules including the various radicals formed during bond breaking processes, has been performed.

Computational Approach

Modern computational chemistry methods implemented on high performance computer architectures can now provide reliable predictions of chemical BDEs to within about 1 kcal/mol for most compounds that do not have substantial amounts of multireference character in the wave function. We can use the approach that we have been developing with collaborators at Washington State University for the prediction of accurate molecular thermochemistry[41] to determine the heats of formation and BDEs of these molecules. Our approach is based on calculating the total atomization energy (TAE) of a molecule and using this value with known heats of formation of the atoms to calculate the heat of formation at 0 K. The approach starts with coupled cluster theory with single and double excitations and including a perturbative triples correction (CCSD(T)),[42−44] combined with the correlation-consistent basis sets[45,46] extrapolated to the CBS limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core−valence interactions and relativistic effects, both scalar and spin−orbit. The zero point energy can be obtained from experiment, theory, or a combination of the two. Corrections to 298 K can then be calculated by using standard thermodynamic and statistical mechanics expressions in the rigid rotor-harmonic oscillator approximation[47] and appropriate corrections for the heat of formation of the atoms.[48]

For the current study, we used the augmented correlation consistent basis sets aug-cc-pVnZ for H, O and S (n = D, T, Q, 5).[45,46] For the sake of brevity, we abbreviate the names to aVnZ. Only the spherical components (5d, 7f, 9g, 11h) of the Cartesian basis functions were used. It has recently been found that tight d functions are necessary for calculating accurate atomization energies for second row elements,[49] so additional tight d functions were included in our calculations. Basis sets containing extra tight d functions are denoted aug-cc-pV(n+d)Z in analogy with the original augmented correlation consistent basis sets. We use aug-cc-pV(n+d)Z to represent the combination of aug-cc-pV(n+d)Z (on the second row atom S) and aug-cc-pVnZ (on H and O) basis sets and abbreviate this as aV(n+d)Z. All of the current work was performed with the MOLPRO suite of programs.[50] The open-shell CCSD(T) calculations for the atoms were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[51−53]

The geometries were optimized numerically at the frozen core CCSD(T) level with the aV(n+d)Z (n = D, T, Q, 5) basis sets for SOO, SSO, SOS, HOS, HSO, HSS, and HOOOH. For HOSH and HSSH, geometries were optimized up through the CCSD(T)/ aV(Q+d)Z level and were then used in single point CCSD(T)/aV(5+d)Z calculations. For the remaining molecules, geometries were optimized up through the CCSD(T)/aV(T+d)Z level and were then used in single point CCSD(T)/aV(Q+d)Z and aV(5+d)Z calculations.

Frequencies for the molecules were calculated at the MP2/aV(T+d)Z level using the Gaussian program system[54] to obtain zero point energies and thermal corrections at 298 K. For the molecules HSO, SOO, and HOOF, we calculated the frequencies at the CCSD(T)/aV(T+d)Z level. For the remaining molecules, we applied a scaling factor of 0.9767 to the O−H stretches calculated from the MP2/aV(T+d)Z (3824.7 and 3950.6 cm^{-1}) and experimental (3657[55] and 3756 cm^{-1})[55] values of the a_1 and b_1 vibrational modes of H_2O. For the S−H stretches, we obtained a scaling factor of 0.9699 from H_2S (MP2/aV(T+d)Z: $a_1 = 2779.1$ and $b_1 = 2798.1$ cm^{-1}; expt, $a_1 = 2615$[55] and $b_1 = 2626$ cm^{-1}).[55] The scaling factor was obtained by dividing the average of the experimental and theoretical value by the theoretical value.[56] Zero point energies were obtained directly from the experimental values, from an average of the harmonic and experimental values (when experimental frequencies were available), or from the scaled frequencies (when experimental values were not available). For HOOO, we used the UCCSD(T)/aVQZ vibrational frequencies of Denis and Ornellas,[20] plus anharmonic corrections obtained at the B3LYP/VTZ level,[21] for the ν_1 and ν_2 modes, and the experimental frequencies for the remaining modes. For HOSO, we used the predicted fundamental vibrational frequencies of Wheeler and Schaeffer[26] evaluated at the frozen core ROCCSD(T)/V(5+d)Z level, plus anharmonic corrections from a frozen core ROCCSD(T)/

V(T+d)Z full quartic force field. The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form

$$E(n) = E_{\mathrm{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \quad (1)$$

with $n = 2$ (aV(D+d)Z), 3 (aV(T+d)Z), and 4 (aV(Q+d)Z), as first proposed by Peterson et al.[57] This extrapolation method has been shown to yield TAEs in the closest agreement with experiment (by a small amount) as compared to other extrapolation approaches up through $n = 4$.[41] The TAEs for the molecules were also obtained by extrapolating the aV(Q+d)Z and aV(5+d)Z values using the formula

$$E(l_{\max}) = E_{\mathrm{CBS}} + B/l_{\max}^{\ 3} \quad (2)$$

This expression works slightly better when one has values of n larger than 4. We use the values from eq 2 in our discussion below as we found in predicting the heat of formation of H_2SO_4, that basis sets as large as aV(5+d)Z were needed to attain reasonable agreement with experiment.[58] The work on H_2SO_4 showed for compounds containing sulfur atoms in a high oxidation state that convergence in the CBS extrapolation was slow and that the extrapolations with eq 2 gave very good values in comparison with experiment if the quintuple-ζ basis sets were used as the largest basis set. Thus, one cannot just compare the extrapolated values from eqs 1 and 2 to determine if convergence has been attained. We provide both sets of value where possible to show when the quintuple-ζ basis set is needed for the extrapolations. The values from eq 1 for the corresponding heats of formation are given in the Supporting Information.

Core−valence corrections, ΔE_{CV}, were obtained as the difference between frozen-core and all-electrons correlated calculations, (except the S 1s electrons were never correlated) all at the CCSD(T)/cc-pwCVTZ level.[59] Scalar relativistic corrections, ΔE_{SR}, which account for the changes in the relativistic contributions to the total energies of the molecule and constituent atoms, were calculated at the CCSD(T) level with the cc-pVTZ-DK basis set and the spin-free, one-electron Douglas−Kroll−Hess (DKH) Hamiltonian.[60−62] Most calculations using available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state as spin−orbit in the atom is usually not included. Instead, the energy is a weighted average of the available multiplets. Corrections of 0.22 kcal/mol for O and 0.56 kcal/mol for S were taken from the excitation energies of Moore.[63]

By combining our computed TAE (ΣD_0) values with the known heats of formation at 0 K for the elements,[12] $\Delta H_f^0(\mathrm{H}) = 51.63$ kcal mol^{-1}, $\Delta H_f^0(\mathrm{O}) = 58.99$ kcal mol^{-1}, and $\Delta H_f^0(\mathrm{S}) = 65.66$ kcal mol^{-1}, we can derive ΔH_f^0 values for the molecules under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[48]

All of the calculations were done on the Cray XD-1, Altix, and DMC computer systems at the Alabama Supercomputer Center or a Dell Cluster at the University of Alabama.

Results and Discussion

Geometries and Frequencies. The total CCSD(T) energies as a function of the aVnZ and aV(n+d)Z (n = D, T, Q, 5) basis sets are given in the Supporting Information in Table SI-1. The geometry parameters calculated as a function of the basis set are given in the Supporting Information (Table SI-2−4), and are in excellent agreement with the available structural data.[64] Experimental data is available for H_2S,[65] HSO,[66,67] HSS,[68−70] HSOH,[71−74] HSSH,[75,76] SOO,[77] SSO,[78,79] HOOO,[80] HOSO,[81] and HOOOH.[82,83] The electronic states and symmetry types of the molecules are also given in Table 1, and consequently have been excluded from the other tables. The calculated harmonic vibrational frequencies are also given as Supporting Information (Table SI-5).

Our calculated geometry for H_2S at the CCSD(T)/aV(T+d)Z level is in excellent agreement with the experimental one.[65] with the r(S−H) distance too short by 0.005 Å. The vibrational frequencies of HSO have been reported[66,67] for υ_2 and υ_3, and our CCSD(T)/aV(T+d)Z value is too large by 6 cm^{-1} for υ_2 and too small by 106 cm^{-1} for υ_3 consistent with previous calculations.[84] The rotational spectra and molecular structure of HSS has been reported,[68] and our calculated CCSD(T)/aV(5+d)Z geometry parameters are in excellent agreement with the experimental values with the r(S−S) and r(S−H) distances 0.006 Å too long and 0.003 Å too short, respectively. Our values are also in agreement with other high level calculations of the structure of HSS.[38,39] The υ_1 (SH stretch) in an Ar matrix has been reported,[69] and our calculated gas-phase MP2 value is in reasonable agreement considering the differences between harmonic and anharmonic frequencies and the shift expected due to the matrix effect. Gas-phase values for υ_2 and υ_3 of HSS have been reported,[70,85] and our calculated MP2 values are in excellent agreement, too high by ~30 cm^{-1}. The vibrational spectra of HOS has been calculated at the CCSD(T)/aV(T+d) level,[84] and our calculated MP2 values are in good agreement. The infrared absorption of SOO in a solid argon matrix has been reported.[77] Our calculated CCSD(T)/aV(T+d)Z values are in reasonable agreement within 105 and 43 cm^{-1} of υ_1 and υ_2. Our CCSD(T)/aV(5+d)Z values for r(S−S) and r(S−O) in S_2O are in excellent agreement with the equilibrium structure of from diode laser spectroscopy experiments.[78] Our calculated MP2 frequencies are in excellent agreement with the experimental values for SSO,[79] differing by ~10 cm^{-1}.

Baum et al.[71] reported the equilibrium structure of oxadisulfane, HSOH, from gas-phase spectroscopic studies, and our calculated values at the CCSD(T)/aV(Q+d)Z level are in excellent agreement within 0.006 Å. Beckers et al.[73] reported the gas-phase IR vibrational wavenumbers of HOSH together with calculated harmonic and anharmonic values at the CCSD(T)/VQZ level. Our MP2 harmonic frequencies are in good agreement with the reported experimental anharmonic frequencies, except for υ(OH) and υ(SH), which are too large by ~180 cm^{-1}. The remaining experimental modes measured in an Ar matrix are within 35 cm^{-1} of our gas-phase MP2 harmonic frequencies. Our MP2 values are also in good agreement with the CCSD(T) harmonic frequencies within 25 cm^{-1}, except for υ(OH) and υ(SH), which are calculated to be 46 cm^{-1} lower and 69 cm^{-1} higher than the CCSD(T) values. Behrend et al.[75] spectroscopically determined the structure of HSSH, and our CCSD(T)/aV(Q+d)Z values are in excellent agreement as well as in agreement with the older spectroscopic data.[76] The experimental vibrational frequencies have also been reported,[76] and our calculated MP2 harmonic values differ by up to ~180 cm^{-1} for the SH stretches and are within 33 cm^{-1} for the other frequencies.

Endo et al.[82] have reported the rotational spectrum and molecular structure of HOOOH, and our CCSD(T)/aV5Z values are in excellent agreement. The calculated structural parameters[20,24] for HOOOH at the CCSD(T)/V5Z level are in agreement with

TABLE 1: CCSD(T) Atomization Energies in kcal/mol[a]

	ΔE_{CBS}[b]						ΣD_0 (0 K)[g]	
molecule	(DTQ+d)	(Q5+d)	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	(DTQ+d)	(Q5+d)
SH ($^2\Pi$-$C_{\infty v}$)	87.57	87.65	3.95	0.15	−0.18	−0.56	83.03	83.12
SH_2 ($^1A_1$-C_{2v})	183.62	183.80	9.44	0.30	−0.38	−0.56	173.54	173.72
HOS ($^2A''$-C_s)	186.10	186.31	8.18	0.41	−0.38	−0.78	177.18	177.38
HSO ($^2A''$-C_s)	187.95	188.67	6.32	0.45	−0.51	−0.78	180.79	181.50
HSS ($^2A''$-C_s)	164.13	164.90	5.85	0.49	−0.45	−1.12	157.21	157.98
SOO ($^1A'$-C_s)	137.20	137.64	3.12	0.88	−0.28	−1.00	133.68	134.13
SSO ($^1A'$-C_s)	206.23	207.78	3.19	0.73	−0.59	−1.34	201.85	203.40
SOS ($^1A_1$-C_{2v})	140.89	141.46	3.41	0.08	−0.38	−1.34	135.83	136.40
HOOF s. (^1A-C_1)	208.95[h]	209.07[h]	11.23	0.10	−0.27	−0.83	196.71	196.83
HOSH s. (^1A-C_1)	269.06	269.30	14.00	0.47	−0.58	−0.78	254.17	254.41
HOSH c. ($^1A'$-C_s)	262.88	263.10	13.34	0.47	−0.56	−0.78	248.67	248.89
HOSH t. ($^1A'$-C_s)	264.69	264.92	13.44	0.47	−0.58	−0.78	250.36	250.58
HSSH s. (^1A-C_2)	242.37	243.23	12.25	0.53	−0.62	−1.12	228.91	229.77
HSSH c. ($^1A_1$-C_{2v})	234.43	235.21	10.90	0.51	−0.59	−1.12	222.32	223.11
HSSH t. (^1A_g-C_{2h})	236.61	237.43	10.96	0.52	−0.60	−1.12	224.45	225.27
HOOO c. ($^2A''$-C_s)	230.98[h]	231.00[h]	10.90	0.17	−0.29	−0.66	219.30	219.32
HOOO t. ($^2A''$-C_s)	230.81[h]	230.73[h]	9.80	0.18	−0.29	−0.66	220.23	220.15
HOOS c. ($^2A''$-C_s)	229.23	229.69	1.11	0.40	−0.39	−1.00	217.12	217.58
HSOO s. (^2A-C_1)	214.04	214.41	8.63	0.37	−0.43	−1.00	204.35	204.72
HSOO c. ($^2A''$-C_s)	211.76	213.80	8.50	0.38	−0.43	−1.00	202.21	204.25
HSOO t. ($^2A''$-C_s)	213.53	213.87	8.51	0.39	−0.42	−1.00	203.99	204.32
HOSO c. ($^2A''$-C_s)	303.37	304.19	9.98	0.74	−0.71	−1.00	292.43	293.25
HOSO t. ($^2A''$-C_s)	301.17	301.99	10.56	0.73	−0.73	−1.00	289.60	290.43
HOSS c. ($^2A''$-C_s)	266.87	267.74	9.64	0.79	−0.63	−1.34	256.05	256.92
HOSS t. ($^2A''$-C_s)	264.50	265.33	9.49	0.77	−0.64	−1.34	253.79	254.63
HSSO s. (^2A-C_1)	258.68	260.02	8.22	0.76	−0.67	−1.34	249.21	250.55
HSSO c. ($^2A''$-C_s)	257.60	258.94	7.95	0.74	−0.67	−1.34	248.39	249.73
HSSO t. ($^2A''$-C_s)	257.82	259.20	8.26	0.75	−0.66	−1.34	248.32	249.69
HSOS s. (^2A-C_1)	222.24	222.77	7.98	0.60	−0.56	−1.34	212.95	213.48
HSOS c. ($^2A''$-C_s)	220.28	222.59	7.81	0.62	−0.58	−1.34	211.17	213.46
HSOS t. ($^2A''$-C_s)	220.36	222.67	7.98	0.61	−0.56	−1.34	211.09	213.40
HSSS s. (^2A-C_1)	228.72	230.09	7.08	0.80	−0.59	−1.68	220.16	221.54
HSSS c. ($^2A''$-C_s)	227.56	228.92	6.93	0.80	−0.61	−1.68	219.14	220.50
HSSS t. ($^2A''$-C_s)	227.99	229.39	7.08	0.88	−0.64	−1.68	219.48	220.88
HOOOH s. (^1A-C_2)	318.53[h]	318.68[h]	18.51	0.30	−0.43	−0.66	299.23	299.38
HOOSH s. (^1A-C_1)	307.67	309.48	15.90	0.48	−0.61	−1.00	290.64	292.46
HOSOH s. (^1A-C_2)	371.80	372.15	18.20	0.73	−0.76	−1.00	352.57	352.92
HOSSH s. (^1A-C_1)	338.10	338.97	15.44	0.77	−0.78	−1.34	321.32	322.19
HSOSH s. (^1A-C_2)	306.44	307.05	13.55	0.64	−0.78	−1.34	291.42	292.02
HSSSH s. (^1A-C_2)	306.34	307.83	12.79	0.78	−0.78	−1.68	291.86	293.36

[a] The atomic asymptotes were calculated with the R/UCCSD(T) method. Abbreviations s. = skew, c. = cis, and t. = trans. [b] Extrapolated by using eq 1 with the aV(D+d)Z, aV(T+d)Z and aV(Q+d)Z basis sets and eq 2 with the aV(Q+d)Z, and aV(5+d)Z basis sets except as noted for molecules with only H and O. [c] The zero point energies were obtained as described in the text. [d] Core−valence corrections were obtained with the cc-pwCVTZ basis sets at the optimized CCSD(T)/aVTZ geometries. [e] The scalar relativistic correction is based on a CCSD(T)-DK/VTZ-DK calculation and is expressed relative to the CCSD(T) result without the DK correction. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables, ref 63. [g] The theoretical value of ΔD_0(0 K) was computed with the CBS (aV(n+d))Z estimates. [h] The calculations were done with the aVnZ basis sets as there are no S atoms.

our CCSD(T)/aV5Z values within 0.01 Å. Our gas-phase MP2 harmonic frequencies for HOOOH are in good agreement with the anharmonic frequencies from an Ar matrix study[83] within 50 cm^{-1}, except for the υ_1 and υ_6 OH stretches, which are predicted to be ~210 cm^{-1} too large and for the υ_3 OO stretch, which is predicted to be ~90 cm^{-1} too large. Our calculated MP2/aV(T+d)Z harmonic frequencies are in good agreement with the CCSD(T)/VTZ harmonic frequencies[20,24] to within 12 cm^{-1}, except for the υ_1 and υ_6 OH stretches which are predicted to be ~ 25 cm^{-1} smaller.

The HOOO radical product can be best described as a weak complex of OH with O_2 bound by only 4.8 kcal/mol. HO_3 was first observed by Cacace et al.[86] in a mass spectrometry study and the initial energetics were estimated by Speranza[87] from mass spectrometry measurements. Nelander et al.[88] reported a matrix isolation study of the vibrational transitions, and Suma et al.[80] measured the rotational spectrum of HO_3 using Fourier transform microwave spectroscopy. In combination with calculations at the multireference single and double excitation configuration interaction method with the Davidson +Q correction (MRCI+Q) with the aVTZ basis set, they predicted a structure, which fit the experimental data with a long O−O bond length of 1.688 Å.[80] Subsequent infrared measurements of supersonically expanded HO_3 provided vibrational frequencies and an estimate of BDE(HO−OO) = 5.3 kcal/mol.[19,89] There have also been extensive high-level calculations on HO_3.[20−25] Varner et al. recommend an equilibrium bond distance of ~1.59 Å on the basis of their CCSD(T) calculations.[22] An extensive study[20] of the geometry with different high-level methods and basis sets showed that the CCSD(T) method predicts the long r(O−O) = ~1.59 Å whereas the long r(O−O) = ~1.69 Å at the MRCI level. From TAEs, they predicted ΔH_f^{298}(HOOO) = 7.53 kcal/mol and a BDE of 0.96 kcal/mol at 298 K. Using these results in combination with the isodesmic reaction 3,

$$HOO + FOO \rightarrow HOOO + FO \quad (3)$$

Denis and Ornellas[24] predicted ΔH_f^{298}(HOOO) = 5.46 kcal/mol. Fabian et al. predicted a value of 7.9 kcal/mol at the CCSD(T)-CBS(3,4) W1U level and obtained a value of 5.1 kcal/mol at the MR-ACPF-CBS(3,4) + CAS extrapolation level, in good agreement with the isodesmic reaction result.[21] Semes'ko and Khursan[25] at the MRMP2(19 × 11)/aVTZ level obtain a dissociation energy at 0 K of 4.8 kcal/mol.

The minimum energy structure of the HOOO radical is of C_s symmetry in the trans configuration with the cis isomer lying 0.5 kcal/mol higher in energy at the CCSD(T)/CBS (Q5) level including the additional corrections. On the basis of just the valence electronic energies extrapolation, the cis-isomer is predicted to be lower in energy by 0.27 kcal/mol at the CCSD(T)/CBS (Q5) level. The HO—OO bond distance is calculated to be 1.605 Å at the CCSD(T)/aV(T+d)Z level, which is 0.170 Å longer than equivalent bond distance in HOOOH at the same level. In addition to the lengthening of the HO—OO bond, there is a comparable decrease in the HOO—O bond distance of 0.204 Å at the CCSD(T)/aV(T+d)Z level when compared to that of HOOOH, consistent with HOOO being a complex of O_2 and OH. The HOOO radical is characterized by all real harmonic frequencies at the MP2/aV(T+d)Z level, which are in semiquantitative agreement with the experimental values.[89] Our MP2 values are also in good agreement with the reported UCCSD(T)/aVQZ values,[20] with the largest difference being 60 cm^{-1} for the O═O stretching frequency. The HO—OO stretch is predicted to be at 281.0 cm^{-1} in comparison to the experimental value of 244 cm^{-1}.[89]

Wheeler and Schaefer[26] used calculations at the CCSD(T)/cc-pV(T+d)Z level to predict that HOSO has a nonplanar cisoid geometry, which is only 5 cm^{-1} above the cis planar structure, so a planar cis structure is a good approximation for HOSO. The HSO_2 isomers have been studied in rare-gas solids using FTIR spectroscopy.[81] Three modes were reported for *cis*-HOSO in an Ar matrix, and our calculated MP2 values are too high by 174, 100, and 26 cm^{-1} for the OH, SO, and SO stretching frequencies, respectively. Our calculated MP2/aV(T+d)Z harmonic frequencies are in good agreement with the CCSD(T)/V(5+d)Z harmonic vibrational frequencies[26] to within 60 cm^{-1}.

There are three possible structures of essentially the same energy for the HSOO radical. The minimum energy structure is of C_1 symmetry in a skewed configuration with both the cis and trans isomers of C_s symmetry lying slightly higher in energy by less than 0.5 kcal/mol at the CCSD(T)/CBS (Q5) level plus the additional corrections, indicating that there is essentially no barrier to the rotation of the S−H bond. Similar to HOOO, HSOO is weakly bound, 7.1 kcal/mol with respect to SH + O_2. The structural changes for HSOO as compared to HSOOH are consistent with those given for the comparison of HOOO with HOOOH.

HOOS is predicted to be above the OH + SO dissociation limit by 3.7 kcal/mol, showing that when the HOOS−H bond is broken, the radical will further dissociate to the diatomic radicals. The minimum energy structure of the HOOS radical is of C_s symmetry in a cis configuration. The HO−OS distance is calculated to be 1.597 Å at the CCSD(T)/aV(T+d)Z level, which is 0.111 Å longer than the equivalent bond distance in HOOSH at the same level. There is a decrease in the r(S−O) distance of HOOS of 0.056 Å compared to that of HSOOH at the CCSD(T)/aV(T+d)Z level. The HOOS radical is a metastable species characterized by all real harmonic frequencies at the MP2/aV(T+d)Z level with an O−O stretching frequency of 1349.1 cm^{-1}.

Heats of Formation. The energetic components for predicting the total molecular dissociation energies are given in Table 1, and we first describe some trends in the different components. The ΔE_{CV} corrections are all small and positive ranging from 0.15 (SH) to 0.88 (HSSS trans) kcal/mol. The ΔE_{SR} corrections are all small and negative ranging from −0.18 (SH) to −0.78 (HSSSH) kcal/mol. We estimate that the error bars for the calculated heats of formation are ±1.0 kcal/mol considering errors in the energy extrapolation, frequencies, and other electronic energy components except as discussed below. Using even larger basis sets, e.g., aV(6+d)Z and cc-pwCV5Z, plus higher order corrections and an improved treatment of the zero point energy, a best estimate for D_0 of 83.69 ± 0.2 kcal/mol was reported for HS.[17] The difference in the extrapolated TAEs using eqs 1 and 2 are positive in all cases but trans HOOO where it is slightly negative. In general, compounds with a sulfur atom in a normal valency with no more than two bonds have a small difference in the extrapolated TAEs between the two equations of less than 0.5 kcal/mol. A number of compounds with two S atoms have differences between the extrapolated TAEs of 0.7−0.9 kcal/mol. The compounds with three S atoms have differences in the TAEs between 1.3 and 1.5 kcal/mol. Other compounds with differences in the TAEs greater than 1.0 kcal/mol are SSO, HSOO, HSSO, cis and trans HSSO, and HOOSH. A number of these compounds have S atoms with an S═O type bond plus at least one other ligand.

An estimate of the potential for significant multireference character in the wave function can be obtained from the T_1 diagnostic[90] for the CCSD calculation. The T_1 diagnostics (Supporting Information) are small (<0.03) showing that the wave functions are dominated by a single configuration except for the molecules HOOO, HSOO, HOOS, and HSOS, which are like FOO[91] and ClOO.[92] For these molecules, we have originally used the atomization reaction to calculate their heats of formation. However, there remains considerable disagreement between the experimental and theoretical values, which is due to higher order correlation effects. To better predict the heats of formation of these molecules, we used the following isodesmic reactions to account for the higher order correlation effects.

$$HOOOH + FOO \rightarrow HOOF + HOOO \quad (4)$$

$$HOOSH + FOO \rightarrow HOOF + HOOS \quad (5)$$

$$HSOOH + FOO \rightarrow HOOF + HSOO \quad (6)$$

$$HSOSH + FOO \rightarrow HOOF + HSOS \quad (7)$$

For FOO, we used the reported heat of formation value of Feller et al.[17] of 5.8 ± 0.3 at 298 K, and for HOOF, we have calculated the heat of formation at 298 K using our standard TAE approach.

The calculated heats of formation at 0 and 298 K are given in Table 2, and are in excellent agreement with the reported experimental values where available,[10−16] as well as with the previously reported even higher level CCSD(T)/CBS values,[17] to within ±1.0 kcal/mol at a maximum discrepancy. There are a number of sources of the errors in the calculations of which the largest are expected to be the basis set extrapolation and the zero point energies if higher order correlation corrections beyond CCSD(T) are not important. We estimate that the errors in the CBS extrapolation and the zero point energies account for about ±1.0 kcal/mol on the basis of our prior work in this

TABLE 2: Isodesmic Reactions for Calculating Heats of Formation of HOOO, HOOS, HSOO, and HSOS (kcal/mol)

isodesmic reactions	ΔE_{CBS} (DTQ+d)	ΔE_{CBS} (Q5+d)	ΔE_{ZPE}	ΔE_{CV}	ΔE_{SR}	$\Delta E_{\mathrm{total}}$ (DTQ+d)	$\Delta E_{\mathrm{total}}$ (Q5+d)
HO−OOH + FOO → HOOF + HO−OO	10.59	10.50	−1.03	0.05	−0.02	9.59	9.50
HO−OSH + FOO → HOOF + HO−OS	1.32	2.35	2.88	0.01	−0.10	4.10	5.14
HS−OOH + FOO → HOOF + HS−OO	16.50	17.63	0.41	0.03	−0.06	16.88	18.00
HS−OSH + FOO → HOOF + HS−OS	7.08	6.84	2.11	−0.04	−0.10	9.05	8.81

TABLE 3: Calculated and Experimental Heats of Formation (kcal/mol)

molecule	ΔH_f (Q5)[a] (0 K)	ΔH_f (Q5)[a] (298 K)	ΔH_f (Q5+d)[b] (0 K)	ΔH_f (Q5+d)[b] (298 K)	expt (298 K)
OH		9.0 ± 0.1[c]			9.03 ± 0.0[d]
SH	34.0	34.0	34.2	34.2, 33.7 ± 0.2[c]	33.56 ± 0.8[e]
SO				1.0 ± 0.3[c]	1.20 ± 0.3[f]
S_2				29.6 ± 0.3[c]	30.69 ± 0.07[g]
H_2O		−57.8 ± 0.2[c]			−57.83 ± 0.01[d]
H_2S			−4.8	−5.5, −5.3 ± 0.2[c]	−5.33 ± 0.07[h]
HOO		3.0 ± 0.2[c]			2.91 ± 0.05[d]
HOS	−1.5	−2.2	−1.1	−1.8	
HSO	−6.4	−7.1	−5.2	−5.9	−1.5 ± 0.7[i], >−3.7[j]
HSS			25.0	24.3	25.6 ± 2.5[k]
OOO		33.9 ± 0.4[c]			33.82 ± 0.01[g]
SOO			49.5	48.9	
SO_2(OSO)				−71.5 ± 0.6[c]	−71.45 ± 0.05[g]
SSO	−15.5	−16.0	−13.1	−13.6	−13.24 ± 0.26[l]
SOS	53.1	52.7	53.9	53.5	
SSS			34.3[m]	34.0[m]	33.8 ± 1.9[h]
HOOH s.		−32.0 ± 0.3[c]			−32.43 ± 0.02[d]
HOOF s.	−8.8	−10.2			
HOSH s.	−24.6	−26.1	−26.5	−28.0	
HOSH c.			−21.0	−22.6	
HOSH t.			−22.7	−24.3	
HSSH s.			4.8	3.4	
HSSH c.			11.5	10.0	
HSSH t.			9.3	7.8	
HOOO c.	9.3	8.1			
HOOO t.	5.1 (8.5)	4.2 (7.6)			
HOOS c.			14.9 (17.7)	13.7 (16.5)	
HSOO s.			27.8 (30.6)	26.6 (29.4)	
HSOO c.			31.0	29.6	
HSOO t.			30.9	29.5	
HOSO c.			−58.0	−59.1	
HOSO t.			−55.1	−56.2	
HOSS c.	−16.1	−17.1	−15.0	−16.0	
HOSS t.	−13.8	−14.7	−12.7	−13.6	
HSSO s.	−10.1	−11.0	−8.6	−9.5	
HSSO c.	−9.2	−10.5	−7.8	−9.1	
HSSO t.	−9.2	−10.1	−7.8	−8.7	
HSOS s.			25.6 (28.5)	24.6 (27.5)	
HSOS c.			28.5	27.1	
HSOS t.			28.5	27.7	
HSSS s.	25.5	24.7	27.1	26.3	
HSSS c.	26.9	25.8	28.1	27.0	
HSSS t.	26.6	25.9	27.7	27.0	
HOOOH s.	−19.2	−21.3			
HOOSH s.			−5.6	−7.4	
HOSOH s.			−66.0	−68.2	
HOSSH s.			−28.6	−30.5	
HSOSH s.	0.3	−1.4	1.5	−0.1	
HSSSH s.	5.4	3.8	6.9	5.2	

[a] Calculated using the aVnZ basis sets. [b] Calculated using the aV(n+d) Z basis sets. [c] Reference 17. [d] Reference 10. [e] Reference 11. [f] Reference 12. [g] Reference 13. [h] Reference 14. [i] Reference 15. [j] Reference 33. [k] Reference 13. [l] Reference 16. [m] Reference 18.

area[17] and the above agreement with experiment. Thus, we can estimate that our calculated theoretical values for which experimental estimates are not available should be good to ±1.0 kcal/mol, except for HOOO, HSOO, HOOS, and HSOS, which should be good to ±1.5 kcal/mol.

Our current values for the heats of formation of HOOH and HOO are in excellent agreement with the reported experimental values of −32.43 ± 0.02[10] and 2.91 ± 0.05[10] kcal/mol, differing by only 0.09 and 0.43 kcal/mol, respectively. Our values are also in excellent agreement with the W4.2 calculated values of Karton et al.[93] of ΔH_f^{298}(HOOH) = −32.24 ± 0.14 kcal/mol and ΔH_f^{298}(HOO) = 2.96 ± 0.14 kcal/mol, as well as the corrected CCSD(T)/CBS (6,5) value of Denis and Ornellas[24] of $\Delta H^\circ_{f,298}$(HOOH) = −32.46 kcal/mol. Our calculated value

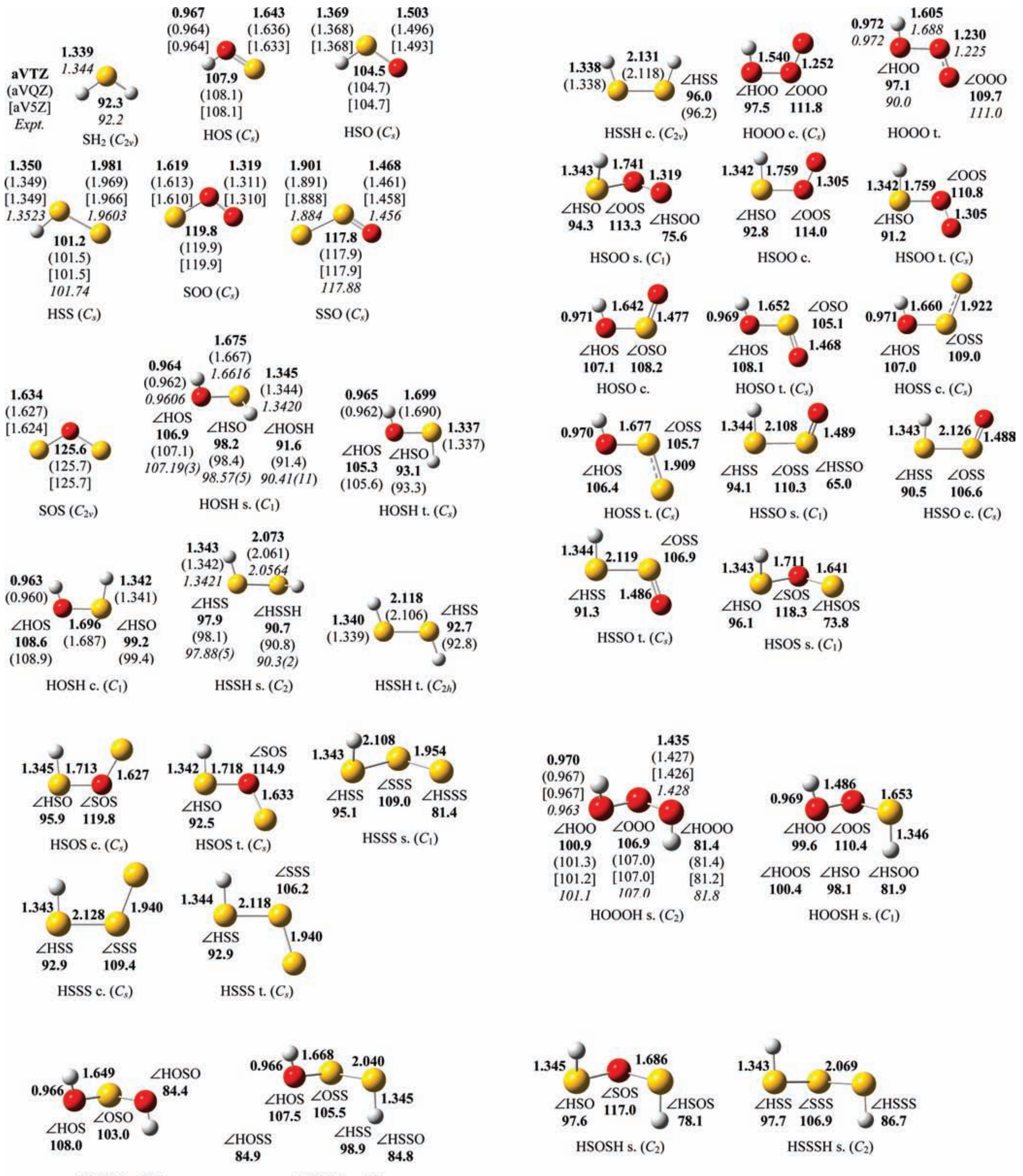

Figure 2. Optimized CCSD(T) geometry paramaters calculated with the aV(T+d) basis set and, where applicable, with the aV(Q+d) and aV(5+d) basis sets. Bond distances are given in angstroms and angles in degrees. Abbreviations are s. = skew, c. = cis, and t. = trans. Hydrogen = white, oxygen = red, and sulfur = yellow. Experimental values are given in italics. H_2S (ref 65). HSS (ref 68). HOSH (ref 71). HSSH (ref 75). SSO (ref 78). HOOO (ref 80). HOOOH (ref 82).

for the heat of formation of HSS is in excellent agreement with the two previous calculated values of 25.0[38] and 25.2[39] kcal/mol at 0 K and in good agreement with the experimental value of 25.6 ± 2.5 kcal/mol.[13]

Our calculated value for the heat of formation of HSO is in excellent agreement within 0.2 kcal/mol with the estimated value of $\Delta H^\circ_{f,0K}(\mathrm{HSO}) = -5.4 \pm 1.3$ kcal/mol[30] obtained at the MR-CI level of theory. HSO is predicted to be more stable than HOS by 5.4 kcal/mol at the MR-CI level, in reasonable agreement with our HOS−SOH isomerization energy of 4.1 kcal/mol. Our calculated values for the heat of formation of HSO and HOS are within 0.7 kcal/mol, of the values of Denis[31]

TABLE 4: Bond Dissociation Energies (BDE) at 298 K

reactant	products	BDE
OH	O + H	102.7
SH	S + H	84.6
O_2	O + O	119.1
S_2	S + S	102.9
SO	S + O	123.0
H_2O	H + OH	118.9
H_2S	H + SH	91.1
HOO	H + O_2	49.1
HOO	O + OH	65.6
HOS	H + SO	54.9
HOS	S + OH	77.0
HSO	H + SO	59.0
HSO	O + SH	99.2
HSS	H + S_2	57.4
HSS	S + SH	75.6
O_3	O + O_2	25.7
OOS	O + SO	11.6
OOS	S + O_2	17.3
OSO	O + SO	132.1
SSO	S + SO	80.8
SSO	O + S_2	102.7
SOS	S + SO	13.8
SSS	S + S_2	61.8
HOOH	H + HOO	87.1
HOOH	OH + OH	50.0
HOSH	H + HSO	74.2
HOSH	H + HOS	78.3
HOSH	OH + SH	70.7
HSSH	H + HSS	73.0
HSSH	SH + SH	64.0
HOOO	H + O_3	81.8
HOOO	OH + O_2	4.8
HOOO	O + HOO	58.4
HOOS	H + SOO	87.3
HOOS	S + HOO	55.6
HOOS	OH + SO	−3.7
HSOO	H + SOO	74.5
HSOO	O + HSO	27.1
HSOO	SH + O_2	7.1
HOSO	HO + SO	69.1
HOSO	H + OSO	39.7
HOSS	H + SSO	54.6
HOSS	S + HOS	80.5
HOSS	OH + S_2	54.6
HSSO	H + SSO	48.0
HSSO	O + HSS	93.4
HSSO	SH + SO	44.2
HSOS	H + SOS	80.9
HSOS	S + HSO	35.7
HSOS	SH + SO	10.1
HSSS	H + S_3	59.8
HSSS	S + HSS	64.3
HSSS	SH + S_2	37.0
HOOOH	H + HOOO	77.6
HOOOH	OH + HOO	33.3
HOOSH	H + HSOO	86.1
HOOSH	H + HOOS	73.2
HOOSH	OH + HSO	10.5
HOOSH	SH + HOO	44.1
HOSOH	H + HOSO	61.2
HOSOH	OH + HOS	75.4
HOSSH	H + HSSO	73.1
HOSSH	H + HOSS	66.6
HOSSH	OH + HSS	63.9
HOSSH	SH + HOS	62.5
HSOSH	H + HSOS	76.9
HSOSH	SH + HSO	27.9
HSSSH	H + HSSS	73.2
HSSSH	SH + HSS	52.8

of $\Delta H^\circ_{f,298K}(HSO) = -5.2 \pm 0.5$ kcal/mol and $\Delta H^\circ_{f,298K}(HSO) = -1.6 \pm 0.5$ kcal/mol calculated in a similar way at the CCSD(T)/CBS level including additional corrections. All of the high level computational values are more negative than the lower bound of −3.7 kcal/mol at 298 K obtained in a crossed molecular beam experiment of the reaction O + H_2S. It has been suggested[31] that there is additional internal energy in the products of the reaction, which would lead to improved agreement of the experiment with the calculated values.

Our calculated value for the heat of formation of HOSO is within a few tenths of a kcal/mol of the calculated values of -58.0 ± 0.4 and -58.8 ± 0.4 kcal/mol at 0 and 298 K, respectively, obtained by Wheeler and Schaefer.[26] The Wheeler and Schaefer values were obtained for two reactions with a focal point analysis up through aV(5+d)Z/CCSD(T) with an anharmonic force field, higher order correlation effects at the UCCSDT(Q) level, and diagonal Born−Oppenheimer corrections. The current experimental estimate of −57.7 kcal/mol at 298 K used in modeling the effects of SO_2 on the oxidation of CO-H_2 mixtures is in good agreement with our value.[94] The G3B3 or G3/MP2 values[34] for HOSO and HOSOH are about 2 kcal/mol more positive than our values. Our best calculated value for $\Delta H_f^{298}(HOSH)$ of −28.0 kcal/mol is in excellent agreement with the calculated value of Denis who obtained -28.1 ± 1 kcal/mol using a comparable approach with the inclusion of an anharmonic force field.

Our value for the heat of formation of HOOOH is within 0.2 kcal/mol of the predicted value of $\Delta H^\circ_{f,298}$ (HOOOH) $= -21.5 \pm 0.5$ kcal/mol obtained by Denis and Ornellas at the CCSD(T)/CBS(5,Q) level of theory (their CCSD(T)/CBS(6,5) calculation gave −21.26 kcal/mol).[24] Our value for the heat of formation of HOOO of 4.2 kcal/mol at 298 K is within 1.3 kcal/mol of the value obtained by Denis and Ornellas[24] of $\Delta H^\circ_{f,298}$ (HOOO) $= 5.5 \pm 1$ kcal/mol using an isodesmic approach. Our CCSD(T)/CBS(Q,5) isodesmic value is also in excellent agreement with the reported value of Fabian et al.[21] $\Delta H_f^{298}(HOOO) = 5.1$ kcal/mol obtained at the MR-ACPF-CBS level of theory. Our value of $\Delta H_f^0(HOOO) = 5.1$ kcal/mol gives an HO-OO BDE of 3.8 kcal/mol at 0 K, which can be compared with the upper limit of 1856 cm^{-1} (5.3 kcal/mol) obtained for DO−OO.[19,89] Denis and Ornellas[24] have estimated the ZPEs for HOOO/OH and DOOO/DO at the B3LYP/6-311+G(3df,2p) level, and find that $\Delta(\Delta ZPE)$ for the binding energy of H(D)O−OO decreases the binding energy of HOOO by 0.56 kcal/mol. Thus, we can estimate that the experimental D_0(HO-OO) is <4.74 kcal/mol and our calculated value is only 0.9 kcal/mol less than experiment, certainly within our estimated error limits.

Bond Dissociation Energies (BDEs). We can predict BDEs to within an accuracy of ±1 kcal/mol for most of these compounds. In predicting and understanding the chemistry of these dihydrogen trioxide and dihydrogen trisulfide molecules in terms of their reactivity and stability, we need to carefully consider the definition of the BDE as described in our recent work on the PF_xO_y and SF_xO_y compounds.[95] We define the adiabatic BDE as dissociation to the ground state of the separated species and the diabatic BDE as the dissociation of the products to the electronic states most closely representing the bonding configuration in the reactant. The adiabatic BDE will always be equal to or less than the diabatic BDE. We use the calculated adiabatic BDE at 298 K in our discussion below.

For the simplest polyatomic hydrides H_2O and H_2S, the H−OH BDE is calculated to be 27.8 kcal/mol larger than the H−SH BDE, showing a stronger O−H bond in H_2O as compared to the S−H bond in H_2S. In S_3, the S−S_2 BDE is calculated to be 36.1 kcal/mol larger than the comparable O—O_2 BDE, showing a much stronger S—S bond in S_3 as compared to the O—O bond in O_3. For OOS, breaking the O—O bond to form O + SO is lower in energy than breaking the O—S bond and forming S + O_2 by 5.7 kcal/mol, indicating a preference for the maintenance of the S═O bond as opposed to the O═O bond. This is exactly the ordering of the BDEs in the diatomics.[17] The O—OS BDE is 14.1 kcal/mol less than the O—O_2 BDE, indicating a large substituent effect of S on the strength of the O—O bond. The centrosymmetric OSO molecule is predicted to have an O—SO BDE comparable to that of S═O, being 9.1 kcal/mol higher in energy, consistent with double bonds in O═S═O and a larger formal charge on the S in SO_2 than in SO. For SSO, the S—SO BDE is predicted to be less than the SS—O BDE by 21.9 kcal/mol, indicating a tendency to retain the S═O as opposed to the S═S bond, consistent with the SO and S_2 BDEs.[17] The SS—O BDE is 29.4 kcal/mol less than the OS—O BDE, indicating the presence of a reasonably strong S═O bond in SSO. The S—SO BDE is 19.0 kcal/mol larger than the equivalent bond in S_3, indicating a large substituent effect of O on the S—S bond in SSO. Decomposition of the centrosymmetric SOS molecule to S + SO is low in energy and comparable to the OOS → O + SO pathway, indicating a preference for the formation of S═O in the product as seen in OOS, OSO, and SSO.

For the tetra-atomic molecules, we start with HOOH. The H—OOH BDE is predicted to be 37.1 kcal/mol larger than the HO—OH BDE, indicating a lower dissociation pathway to two OH radicals. For the radical product HOO, the H—OO BDE is less than the HO-O BDE by 16.5 kcal/mol, consistent with the difference in O_2 and OH BDEs.[17] The H—OO and HO—O BDEs are 38.0 kcal/mol less and 15.6 kcal/mol larger, respectively, than the equivalent BDEs in the parent HOOH.

The various BDEs for HSOH are comparable, within ~8 kcal/mol of each other. The HO—SH BDE is the lowest followed by the H—OSH and HOS—H BDEs, 3.5 and 7.6 kcal/mol higher in energy, respectively. The pathway leading to the formation of the diatomics OH and SH is the most thermodynamically favorable and the respective O—H and S—H BDEs lie within 4 kcal/mol of each other. The H—SO BDE is 40.2 kcal/mol less than the HS—O BDE, indicating a thermodynamic preference for the maintenance of the S═O bond in the product. Our value for the H—SO BDE is in excellent agreement, within 0.8 kcal/mol, of the reported MR-CI value of D_0(H—SO) ≈ 58.2 ± 1.0 kcal/mol.[30] The HS—O BDE is less than the S—O BDEs in SO and OSO by 23.8 and 32.9 kcal/mol, respectively, but 28.5 kcal/mol larger than that in HOSH. The H—OS BDE is 22.1 kcal/mol less than the HO—S BDE, as found for HSO, again consistent with the diatomic BDEs. Although the H—O and H—S BDEs in HOS and HSO are comparable, within 6 kcal/mol, the S—O BDE in HSO is 22.2 kcal/mol higher than in HOS.

For HSSH, the thermodynamically favorable pathway leads to two SH radicals, as found for HOOH, with the pathway leading to H + HSS lying 9.0 kcal/mol higher in energy. The H—SS BDE in HSS is predicted to be 18.2 kcal/mol less than the HS—S BDE, indicating a preference to forming S_2 as opposed to SH, as found for HOO. The HS—S BDE is comparable to that of HSSH being 11.6 kcal/mol higher in energy, as found in HOO.

We next consider the bonding in the penta-atomic molecules. For dihydrogen trioxide, HOOOH, the H—OOOH BDE is predicted to be considerably higher than the HO—OOH BDE by 44.3 kcal/mol. The H—OOOH and HO—OOH BDEs are predicted to be 9.5 and 16.7 kcal/mol less than analogous BDEs in HOOH, indicating a substantial effect of the OH group on the O—O and O—H BDEs. Upon dissociation of the H—OOOH bond, there is only endothermicity to overcome to form OH + O_2. The HOO—O and H—OOO BDEs are predicted to be 53.6 and 77.0 kcal/mol higher in energy than the HO—OO BDE; therefore, the pathways forming HOO and O_3 are thermodynamically unfavorable. Similarly, the H—OOO and HOO—O BDEs are comparable to the H—OOOH and H—OOH and the HO—OH and HO—O BDEs, respectively.

For HOOSH, the OH + HSO pathway is the lowest whereas the HS + HOO pathway is predicted to be 33.6 kcal/mol higher in energy. The H—OOSH and HOOS—H BDEs are predicted to be 75.6 and 62.7 kcal/mol higher in energy than the HO—OSH BDE, respectively. The HO—OSH BDE is predicted to be 39.5 kcal/mol less than the HO—OH BDE, indicating a large substituent effect of the SH group on the O—O BDE. The HSO—O and H—SOO BDEs are 20.0 and 67.4 kcal/mol higher in energy than the HS—OO BDE. The H—SOO BDE is 1.3 kcal/mol above the HOOS—H BDE. The HOO—S and H—OOS BDEs are predicted to be 59.3 and 91.0 kcal/mol higher in energy, respectively, than the HO—OS BDE. The H—OOS and HOO—S BDEs are predicted to be 1.2 and 11.5 kcal/mol higher than the equivalent BDEs in HOOSH.

For the centrosymmetric HOSOH molecule, the H—OSOH BDE is predicted to be 14.2 kcal/mol less than the HO—SOH BDE, showing a thermodynamic preference for breaking an O—H bond as opposed to an S—O bond. The HO—SOH BDE is 4.7 kcal/mol larger and 47.6 kcal/mol less than the HO—SH and S═O BDEs, respectively. For the radical product HOSO, the HO—SO BDE is predicted to be 29.4 kcal/mol higher in energy than the H—OSO BDE. Our values for the two BDEs for HOSO are within 0.5 kcal/mol of those of Wheeler and Schaefer.[26] This is consistent with the trends previously observed that there is a preference to maintain the S═O bond in the dissociated products as indicated by the lower O—H BDE leading to the formation of O═S═O and S═O.

The HOSSH molecule has four possible dissociation pathways with the HOS + SH pathway predicted to be the lowest energetically. The HOS—SH, HO—SSH, and HOSS—H BDEs lie within ~4 kcal/mol of each other. The H—OSSH BDE is predicted to be 10.6 kcal/mol higher than the HOS—SH BDE. The HOS—SH, HO—SSH, HOSS—H, and H—OSSH BDEs are comparable to the HS—SH, HO—SH, HSS—H, and H—OSH BDEs, respectively, within ~7 kcal/mol, showing a minimal substituent effect on the respective BDEs. For the radical HSSO, the H—SSO and HSS—O BDEs are predicted to be 3.8 and 49.2 kcal/mol higher in energy than the HS—SO BDE, respectively. As expected, the HSS—O BDE is the largest consistent with the preference for maintaining the strong S═O bond in the dissociated product. The other radical product, HOSS, resulting from breaking the HOSS—H bond, has three possible decomposition pathways with that leading to the formation of OH + S_2 and H + SSO predicted to essentially have the same energy. The HOS + S pathway is predicted to be the higher by 25.9 kcal/mol. The HO—SS BDE is predicted to be 2.8 kcal/mol less than the H—SS BDE, indicating a minimal substituent effect of the OH group on the pathway forming S_2.

For the centrosymmetric HSOSH molecule, the HS—OSH BDE is predicted to be the lowest followed by the H—SOSH BDE, 49.0 kcal/mol higher in energy, indicating a preference for the formation of SH. The H—SOSH BDE is 1.4 kcal/mol less than the H—SOH BDE, indicating a minimal substituent effect of the OSH group on the S—H BDE. The SH substituent has a considerable substituent effect on the S—O bond as the HS—OSH BDE is calculated to be 42.8 kcal/mol less than the HS—OH BDE. For HSOS, the HSO—S and H—SOS BDEs are predicted to be 25.6 and 70.8 kcal/mol higher than the HS—SO BDE. Again, there is a thermodynamic preference for maintaining the S═O bond in the dissociated product.

For HSSSH, the SH + HSS dissociation pathway is predicted to be the lowest with the H + HSSS pathway lying 20.4 kcal/mol higher in energy. The HS—SSH and H—SSSH BDEs are calculated to be 11.2 kcal/mol lower and 0.2 kcal/mol higher in energy than the equivalent BDEs in HSSH, indicating the effect of the SH substituent on the S—S and S—H BDEs, respectively. For the HSSS radical, the H—SSS and HSS—S BDEs are calculated to be 22.8 and 27.3 kcal/mol higher than the HS—SS BDE, respectively. Both energetically lower pathways favor the formation of S_2 and S_3, unlike the equivalent reaction for the HOOO radical in which the pathway forming O_3 is predicted to be substantially more endothermic than the pathway forming HOO. The S—H BDE of the radicals HS_3 and HS_2 are comparable, within 2.6 kcal/mol. The HS—SS and HSS—S BDEs calculated at the W1[37] and CBS-Q[37] levels are in good agreement to within 1 kcal/mol of our CCSD(T)/CBS value.

Conclusions

The present work provides a complete and comprehensive set of thermochemical data for the HO_xS_{3-x} radicals and $HO_xS_{3-x}H$, where $x = 0-3$, neutrals. These data are essential for evaluating key chemical pathways for kinetic models of sulfur chemistry in the atmosphere. Since similar species are involved in sulfur oxidation reactions in the combustion of fossil fuels, these data are central to being able to understand that chemistry. We have predicted the heats of formation at the CCSD(T)/CBS level plus additional corrections. The calculated values should be good to ±1.0 kcal/mol in most cases and are in excellent agreement with the available experimental data. Our accurately calculated heats of formation allow us to predict the various adiabatic BDEs for all of the dihydrogen trioxide and dihydrogen trisulfide compounds to within ±1.0 kcal/mol, dramatically improving the estimates of these important quantities. When possible, the decomposition mechanisms were largely determined by a preference to maintain the strong S═O bond in the dissociated products as opposed to the O═O and S═S bonds, exactly matching the ordering of the BDEs in the diatomics. For the H_2X_2 and H_2X_3 systems, favorable pathways lead to the formation of XH radicals as opposed to breaking X—H bonds.

Acknowledgment. This work was supported in part by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE), under grant no. DE-FG02-03ER15481 (catalysis center program) and the National Science Foundation. D.A.D. also thanks the Robert Ramsay Chair Fund of The University of Alabama for support. K.A.P. acknowledges the support of the National Science Foundation under grant CHE-0723997.

Supporting Information Available: Total CCSD(T) energies as a function of the aVnZ and aV(n+d)Z basis sets. Optimized bond lengths and angles for the O_mS_n compounds at the CCSD(T) level. Optimized bond lengths and angles for the $H_{1,2}O_m$ and $H_{1,2}S_n$ compounds at the CCSD(T) level. Optimized bond lengths and angles for the $H_{1,2}O_mS_n$ compounds at the CCSD(T) level. Calculated MP2 frequencies. T_1 Diagnostics calculated at the CCSD(T)/aV(Q+d)Z level. CCSD(T)/aVnZ atomization energies in kcal/mol. Calculated heats of formation (kcal/mol) from DTQ extrapolations (eq 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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JP905847E