Gas-Phase Chemistry and Thermochemistry of the Hydroxysulfide Anion, HOS-

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The chemistry and thermochemistry of the hydroxysulfide anion, HOS⁻, has been studied in a tandem flowing afterglow-selected ion flow tube (FA-SIFT). The reactions of HOS⁻ with O₂, CO, CO₂, CS₂, SO₂, H₂S, (CH₃)₃CSH, CH₃SH, CH₃Cl, and (CH₃)₂CHCl have been examined and compared to the corresponding reactions of HOO-. The gas-phase basicity of HOS- has been established via the bracketing technique $[\Delta G_{acid}^0(\text{HOS}H) = 347 \pm 3 \text{ kcal mol}^{-1}, \Delta H_{acid}^0(\text{HOS}H) = 354 \pm 3.5 \text{ kcal mol}^{-1}].$ Ab initio calculations have been carried out on HOS⁻, HSO⁻, HOSH, and H₂SO which demonstrate that HOS⁻ and HOSH are the more stable isomers. At the MP4SDTQ(FC)/6-311++G**//MP2(Full)/6-311++G** level of theory, these calculations predict $\Delta H_{acid}^0(HOSH) = 356.7$ kcal mol⁻¹, in agreement with the experimentally determined value. Measurement of the forward and reverse rate constants for the reaction generating HOS- yields ΔH_0^{f} $(HOS^{-}) = -38.7 \pm 2$ kcal mol⁻¹, which when combined with the experimental electron affinity of HOS, determines $\Delta H_{t}^{0}(HOS) = -0.5 \pm 2$ kcal mol⁻¹; this value is in good agreement with a recent *ab initio* determination. The gas-phase basicity of HSS-, the major product ion in the reaction of HOS- and CS₂, has also been determined via the bracketing technique $[\Delta G_{acid}^0(\text{HSSH}) = 339 \pm 3 \text{ kcal mol}^{-1}, \Delta H_{acid}^0(\text{HSSH}) =$ 346 ± 3.5 kcal mol⁻¹]. Combination of our gas-phase acidity values for HOSH and HSSH as well as for CH₃SSH reported in a previous paper, with known electron affinities for the corresponding radicals, allows determination of the S-H bond dissociation energies (D_{298}): HOSH (79 ± 3.5 kcal mol⁻¹), HSSH (76 ± 3.5 kcal mol⁻¹), and CH₃SSH (79 \pm 3.5 kcal mol⁻¹).

Introduction

Studies on the oxidation of sulfur compounds continue to play an important role in modeling the global atmospheric sulfur cycle.¹ Knowledge of the relative stabilities and heats of formation of various sulfur species is essential in assessing their importance in atmospheric processes.^{2,3} Such thermodynamic data remain scanty, however, especially for sulfur species in low oxidation states. For example, the heats of formation of H₂S=O, HOSH, and HOS[•] have not been determined experimentally, while that of HSO[•] remains uncertain;^{4,5} in fact the relative stability of the HOS[•] and HSO[•] radicals is an issue of continuing interest. Similarly, the heats of formation of many other sulfur-containing radicals remain unknown.

Gas-phase ion chemistry and spectroscopy provides a powerful tool for determining the thermochemistry of ions and neutrals via thermochemical cycles. For example, bond strengths can be determined via eqs 1-4.6

$$RH \rightarrow R^- + H^+ \qquad \Delta H^0_{acid}(RH)$$
 (1)

$$\mathbf{R}^- \to \mathbf{R}^\bullet + \mathbf{e}^- \qquad \mathbf{E}\mathbf{A}(\mathbf{R}^\bullet) \tag{2}$$

$$H^+ + e^- \rightarrow H^* - IP(H^*)$$
 (3)

$$\mathbf{RH} \rightarrow \mathbf{R}^{\bullet} + \mathbf{H}^{\bullet} \qquad D_{298}(\mathbf{R} - \mathbf{H}) \tag{4}$$

Thus, negative ion photoelectron spectroscopy⁷ is employed to measure the radical electron affinity, $EA(R^{\bullet})$, while protontransfer reactions are used to determine the gas-phase acidity, $\Delta H_{acid}^0(RH)$.⁸ These values can then be combined with the accurately known ionization potential of the hydrogen atom, IP-(H[•]),⁹ to yield the homolytic bond dissociation energy, $D_{298}(R-H)$, via eq 5.

$$D_{298}(R-H) = EA(R^{\circ}) + \Delta H_{acid}^{0}(RH) - IP(H^{\circ})$$
 (5)

These bond strengths can be combined with known heats of

formation of RH to determine the heats of formation of the radicals R^{\bullet} . This technique has recently been used to determine the C-H bond strengths of ethylene and acetylene¹⁰ as well as the S-H bond strength in simple thiols.¹¹ Similarly, rate coefficients for ion-molecule reactions can often be measured in both the forward and reverse direction to yield the reaction ergicity. Combination with known heats of formation of reactants and products can directly determine the previously unknown heat of formation of ionic or radical species.

One of the simplest oxidized sulfur anions is the hydroxysulfide anion, $HOS^{-,12,13}$ This ion can be generated as a minor product (eq 7) in the reaction between HO^- and COS (eqs 6 and 7).¹² Bowie and co-workers have also independently generated HOS⁻ via the collision-induced dissociation of deprotonated dimethyl sulfoxide (eq 8) and identified it as HOS⁻ rather than HSO⁻ via its collisional activation and charge reversal mass spectra.¹³

HO' + COS
$$-$$
 HOS' + CO₂ (6)

$$CH_3S(O)CH_2 \longrightarrow HOS' + CH_2=CH_2$$
 (8)

The gas-phase anion chemistry of sulfur compounds is also of general interest since comparisons can be made to (i) oxygen analogues and (ii) condensed phase reactivity. In particular, species which are highly reactive and difficult to study in solution are readily studied in the gas phase using various techniques. For example, we have recently studied the gas-phase ion-molecule chemistry of CH_3SO^- and $CH_3SS^{-.14}$ A recent review discusses the gas-phase anion chemistry of organosulfur compounds in more detail.¹⁵

This paper describes the gas-phase anion chemistry and thermochemistry of HOS⁻ and compares it with that of HOO^{-,16} We also determine S–H bond dissociation energies in HOSH, HSSH, and CH₃SSH by combining our experimental gas-phase acidity values with known electron affinities of the corresponding radicals.

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TABLE I:	Calculated	Geometries,	Vibrational .	Frequencies,	and Energ	es of HOS	S-, HSO-,	HOSH, a	nd H ₂ SO at t	he HF/
6-311++G*	* Level				-			-	_	

isomer	geometry ^a	frequencies ^b	energy ^c
<u></u> я—0 ^{-н}	SO 1.756 (1.807) OH 0.937 (0.959) SOH 105.4° (101.5°)	629, 1044, 3789	-472.979 196 (HF) -473.457 708 (MP2)
н <mark>`</mark> §=о	HS 1.354 (1.369) SO 1.584 (1.608) HSO 105.1° (105.8°)	748, 976, 2350	-472.949 215 (HF) -473.437 254 (MP2)
H_s-0 ^{-H}	HS 1.333 (1.338) SO 1.652 (1.690) OH 0.942 (0.962) HSO 98.3° (97.5°) SOH 109.8° (106.9°) HOSH 92.4° (93.8°)	436, 764, 1015, 1147, 2555, 3743 ⁴	-473.548 414 (HF) -474.031 132 (MP2)
H_S=0	HS 1.353 (1.370) SO 1.481 (1.502) HSO 108.1° (109.2°) HSH 96.2° (93.5°)	975, 976, 1048, 1222, 2412, 2418	-473.495 905 (HF) -473.988 134 (MP2)

^a Distances in Å and angles in deg. Values in parentheses represent optimized geometries at the MP2(Full)/6-311++G^{**} level of theory. ^b Frequencies in cm⁻¹ scaled by 0.9. ^c Energies are in hartrees. HF refers to the HF/6-311++G^{**}/HF/6-311++G^{**} energy. MP2 refers to the MP2(Full)/6-311++G^{**}/MP2(Full)/6-311++G^{**} energy. ^d The experimental frequencies of HOSH are 444.8, 763.0, 1177.0, and 3425.0 cm⁻¹, ref 3a.

Computational Methods

Structures were optimized at the Hartree-Fock level using the Gaussian 90^{17} program with the standard $6-311++G^{**}$ basis set.¹⁸ All structures were verified as minima on the potential energy surface by carrying out vibrational frequency analyses using the same basis set. The resulting frequencies and zero point vibrational energies were scaled by 0.9.19 To examine the effects of electron correlation on the optimized structures, the $HF/6-311++G^{**}$ geometries were reoptimized with the same basis set at the MP2 level where all electrons were correlated (this is designated as the MP2(Full)/6-311++G** level of theory). Single point energies were calculated to include electron correlation effects at the MP4SDTQ level using the frozen core approximation (this is designated as the MP4SDTQ(FC)/6- $311++G^{**}$ level of theory), using both the HF/6-311++G^{**} and the MP2(Full)/6-311++G** optimized geometries. Calculations at similar levels of theory have been shown to give relative stabilities, absolute gas-phase acidities, ^{20a} and proton affinities^{20b,c} which compare favorably to experimental values.

Experimental Section

All experiments were carried out at room temperature in a flowing afterglow-selected ion flow tube (FA-SIFT).²¹ This instrument has been described in detail previously²² and only a brief summary of its operation is given here. The FA-SIFT consists of four sections: a flow tube for ion preparation, an ion separation and purification region, a second flow tube for studying the chemical reactions of the mass-selected ions, and an ion detection region. In the first flow tube, HO- ions are prepared by electron impact on a mixture of N₂O and CH₄ and entrained in a rapidly flowing helium buffer gas. Carbonyl sulfide is added downstream through a moveable inlet to generate the products shown in eqs 6 and 7. At the end of the first flow tube the ions are sampled through a 2-mm orifice into the ion separation region, and the helium and other neutrals are removed by pumping, while the ions are focused into a quadrupole mass filter by a series of electrostatic lenses. This SIFT quadrupole is tuned to m/z 49 to inject HOS- into the second flow tube where these ions are again entrained in helium. The gas-phase chemistry of these mass-selected HOS⁻ ions can then be studied by introducing neutral gases into the second flow tube via radial inlets.

All reactions of HOS⁻ were studied at 298 K at a helium buffer gas pressure of 0.5 Torr and a flow of \sim 225 STP cm³s⁻¹. Product ions were monitored as a function of reaction distance, and product

branching ratios are reported as extrapolations to zero reaction distance to eliminate any effects of differential diffusion among the ions and of secondary reactions. Branching ratios were also corrected for mass discrimination in the detection region by directly measuring the detector response as a function of ion current at the sampling orifice. Rate coefficients were determined under pseudo-first-order conditions by monitoring the reactant ion density as a function of reaction distance (which is proportional to time) using a measured flow of the neutral reagent. Reported values of the rate coefficients are the average of at least three measurements using different reagent flows and are reproducible to within 10%; the absolute accuracy is $\pm 20\%$. Errors in the derived thermochemical quantities vary and are specifically indicated. These errors can be moderately large due to the nature of bracketing experiments as well as uncertainties introduced by other thermochemical values and the estimation of entropy contributions.

All reagents were obtained from commercial sources and were of the following purities: He (99.995%), N₂O (99.99%), CH₄ (99.99%), O₂ (99.95%), CO(>99%), CO₂ (99.5%), CS₂ (>99%), SO₂ (99.9%), H₂S (99.5%), (CH₃)₃CSH (99%), CH₃SH (99.5%), CH₃Cl (99.5%), and (CH₃)₂CHCl (>99%). The helium buffer gas was passed through a liquid-nitrogen cooled molecular sieve trap before entering the flow tubes.

Results and Discussion

(A) Computational Comparisons of HOS⁻ and HSO⁻ and Their Conjugate Acids HOSH and H₂S⁻O. A number of papers have been published on the *ab initio* structures of the radicals HOS^{*} and HSO^{*5,23} and the closed-shell neutrals HOSH and H₂S^{-0,24} At the MP4FC/6-31G^{*}//UHF/6-31G^{*} level of theory HOS^{*} is the more stable isomer by 4.5 kcal mol⁻¹ (at 0 K).²³ However, in a recent study using multireference configuration interaction calculations that systematically expand the orbital basis set, HSO^{*} is estimated to be more stable than HOS^{*} by 5.4 kcal mol⁻¹ (at both 0 and 298 K).⁵⁶ Calculations on HOSH and H₂S⁻O have shown that HOSH is the most stable form (at 0 K) by 27.9 kcal mol⁻¹ at the MP4/6-31G^{**}//HF/6-31G^{*} level of theory.^{24b}

To gain insights into the relative stabilities of the ions HOSand HSO-together with the absolute gas-phase acidities of HOSH, HOSH, and H_2 SO, we have carried out *ab initio* calculations on HOS⁻, HSO⁻, HOSH, and H₂SO at the same level of theory. The HF/6-311++G^{**} optimized geometries and vibrational frequencies and the MP2(Full)/6-311++G^{**} optimized geometries

TABLE II: Ab Initio Total Energies, Zero Point Energies, and Thermal Energies of HOS⁻, HSO⁻, HOSH, and H_2S =0

energy	E(HOS⁻)	E(HSO-)	E(HOSH)	$E(H_2S=0)$
MP4//HF ^a	-473.344 844	-473.326 056	-473.921 823	-473.879 662
MP4//MP2 ^b	-473.346 597	-473.326 902	-473.923 320	-473.881 340
ZPE	+7.8	+5.8	+13.8	+12.9
THERMAL ^d	+2.5	+2.4	+2.6	+2.4

^a Single point energies were calculated at the MP4SDTQ(FC)/6-311++G^{**} level using the geometries optimized at the HF/6-311++G^{**} level and are in hartrees. ^b Single point energies were calculated at the MP4SDTQ(FC)/6-311++G^{**} level using the geometries optimized at the MP2(Full)/6-311++G^{**} level and are in hartrees. ^c Zero point vibrational energies (scaled by 0.9) were calculated using the geometries optimized with the HF/6-311++G^{**} basis set and are in kcal mol⁻¹. ^d Thermal energy corrections are for 298 K and were calculated using the geometries optimized with the HF/6-311++G^{**} basis set and are in kcal mol⁻¹.

TABLE III: Calculated Gas-Phase Acidities of HOSH, HOSH, and H₂SO at 0 and 298 K

	0 1	K	298 Kª		
	MP4//MP2 ^b	MP4//HF ^c	MP4//MP2 ^b	MP4//HF ^c	
HOSH	355.9	356.1	356.7	356.8	
HOSH	366.3	365.9	367.0	366.5	
H ₂ SO	340.8	340.3	341.7	341.2	

^a Thermal corrections were carried out using the HF/6-311++G^{**} optimized geometries. ^b MP4//MP2 refers to MP4SDTQ(FC)/6-311++G^{**} //MP2(Full)/6-311++G^{**} acidity corrected for the HF/6-311++G^{**} zero point energy (scaled by 0.9). ^c MP4//HF refers to MP4SDTQ(FC)/6-311++G^{**} //HF/6-311++G^{**} acidity corrected for the HF/6-311++G^{**} zero point energy (scaled by 0.9).

of each of these species are listed in Table I. The MP4SDTQ-(FC)/6-311++G** single point energies, together with the HF/ 6-311++G** zero point energies and thermal energies (298 K) for HOS⁻, HSO⁻, HOSH, and H₂SO, are summarized in Table II. The optimized geometries for HOS⁻, HSO⁻, HOSH, and H₂SO are very similar at the HF/6-311++G** and the MP2-(Full)/6-311++G** levels. This is also true for the relative energies of HOS⁻ and HSO⁻ as well as HOSH and H₂SO.

At the highest level of theory, MP4SDTQ(FC)/6-311++G**/ /MP2(Full)/6-311++G** (including the HF/6-311++G** zero point energy corrections), our results indicate that HOS⁻ is more stable than HSO⁻ by 10.3 kcal mol⁻¹ (at 298 K). The HOS⁻ ion has a long O–S bond (1.807 Å) compared to that in HSO⁻ (1.608 Å), consistent with the fact that the latter ion has two resonance forms:

$$H \sim S = 0 \iff H \sim S = 0$$

The structures of HOSH and H₂S=O are similar to those previously calculated.²⁴ The calculated vibrational frequencies (corrected by 0.9) of HOSH are in reasonable agreement with values that have been experimentally observed.^{3a} We also find that HOSH is more stable than H₂S=O by 25.2 kcal mol⁻¹ (at 298 K) at the highest level studied (MP4SDTQ(FC)/6-311++G**//MP2(Full)/6-311++G**, with the HF/6-311 ++G** ZPE corrections included).

By calculating the absolute energies of HOS⁻, HSO⁻, HOSH, and H₂S=O at the same levels of theory, we are able to predict the gas-phase acidities (at 0 K) of HOSH, HOSH, and H₂SO via eq 9, where $E(A^-)$ is the total energy of the anion, corrected for zero point energy vibrations, and E(HA) is the total energy of the neutral, corrected for zero point energy vibrations. These acidities are listed in Table III.

$$\Delta H^0_{\text{acid }0K}(\text{HA}) = E(\text{A}^-) - E(\text{HA})$$
(9)

The acidities calculated via eq 9 must be corrected to room temperature (298 K) to make them comparable to experimental

TABLE IV: Gas-Phase Reactions of HOS- with Acids

reactant (AH)	$\Delta G^0_{\rm acid}(AH),^a$ kcal mol ⁻¹	A ⁻ observed?
HC(O)NHCH ₃	353.4 ± 2.0	no
CH ₃ SH	350.6 ± 2.0	no
CH ₃ NO ₂	349.7 ± 2.0	no
$(CH_3)_3CSH$	346.2 • 2.0	yes
H_2S	344.8 ± 2.0	yes
CH ₃ CO ₂ H	341.5 ± 2.0	yes
HCO ₂ H	338.3 ± 2.0	yes
4 D - 6		

^a Reference 26.

conditions.²⁰ We have calculated the room temperature thermal energy contributions due to translation, rotation, and vibration for the neutral (eq 10a) and deprotonated species (eq 10b) using the HF/6-311++G^{**} optimized geometries.^{20,25} The corresponding contribution for the proton is $3/_2RT$. This analysis assumes ideal gases and that all vibrations are harmonic, with force constants determined by calculating the analytical second derivatives of the electronic energy with respect to the nuclear coordinates at the optimized geometry. Results from systems with low-frequency vibrations that should be more appropriately treated as hindered rotations will exhibit slight errors in the thermal energy calculation as a result of these approximations.^{20b,c}

$$H_{\text{thermal}}(T, \text{HA}) = H_{\text{trans}}(T, \text{HA}) + H_{\text{rot}}(T, \text{HA}) + H_{\text{vib}}(T, \text{HA})$$
(10a)

$$H_{\text{thermal}}(T,A^{-}) = H_{\text{trans}}(T,A^{-}) + H_{\text{rot}}(T,A^{-}) + H_{\text{vib}}(T,A^{-})$$
 (10b)

The complete thermodynamic correction of the 0 K acidity is obtained by adding the difference in the thermal contributions of the deprotonated and neutral species and adding the translational energy contribution of the proton, via eq 11. The 298 K MP4SDTQ(FC)/6-311++G**//MP2(Full)/6-311++G** and MP4SDTQ(FC)/6-311++G**//HF/6-311++G** acidities of HOSH, HOSH, and H₂SO are listed in Table III.

$$\Delta H_{\text{acid 298K}} (\text{HA}) = \Delta H_{\text{acid 0K}} (\text{HA}) + (H_{\text{thermal}} (\text{T},\text{A}^{-}) - H_{\text{thermal}} (\text{T},\text{HA})) + \frac{3}{2} RT \quad T = 298 \text{ K} (11)$$

At the highest level of theory, MP4SDTQ(FC)/6-311++G**/ /MP2(Full)/6-311++G**, the predicted acidities (298 K) are ΔH^0_{acid} (HOSH) = 356.7 kcal mol⁻¹, ΔH^0_{acid} (HOSH) = 367.0 kcal mol⁻¹, and $\Delta H^0_{acid} H_2$ S=O = 341.7 kcal mol⁻¹.

(B) Experimental Gas-Phase Basicity of HOS⁻. The gas-phase basicity of HOS⁻ was experimentally determined via the bracketing technique, by allowing HOS⁻ to react with various acids. Although bracketing techniques are less accurate than measuring acidities via other methods,²⁶ they are necessitated here since HOSH is not available (and possibly not stable) as a neutral reagent. Our results are summarized in Table IV. By studying proton-transfer reactions with seven different reagents, we have been able to establish $\Delta G_{acid}^0(HOSH) = 347 \pm 3$ kcal mol⁻¹. Using the relationship $\Delta G = \Delta H - T\Delta S$, and by estimating the entropy change as $\Delta S_{acid}(HOSH) = 354 \oplus 3.5$ kcal mol⁻¹, which is in reasonable agreement with the value of 356.7 kcal mol⁻¹ calculated from *ab initio* methods.

(C) Experimental Gas-Phase Ion Chemistry of HOS⁻. Since the $[H,S,O]^-$ ion is formed via sulfur atom transfer from COS to HO⁻ (eq 7), the more reasonable structure is HOS⁻, rather than HSO⁻. This is corroborated by several observations: (i) Theoretical results discussed in section A clearly indicate that HOS⁻ is more stable than HSO⁻. (ii) The experimentally determined basicity of $[H,S,O]^-$ agrees with that calculated for an ion of structure HOS⁻ and not HSO⁻. (iii) Collision-induced dissociation (CID) of the injected $[H,S,O]^-$ ion supports the HOSstructure. We have previously shown that by raising the potential

TABLE V: Reactions of HOS⁻ with Various Neutrals: Products, Branching Ratios, Rate Constants, and Reaction Efficiencies

neutral	products ^a	branching ratios ^b	k _{expt} ^c	efficiencyd
<u>O</u> 2	HO ⁻ + SO ₂	0.80	0.11	0.02
	SO₂•- + HŌ•	0.20		
CO	$HO^- + COS$	0.40	0.33	0.04
	$HS^- + CO_2$	0.60		
CO ₂	HOS-CO2	1.00	<0.001*	
CS ₂	HSS- + COS	0.65	0.68	0.05
-	HOS→CS ₂	0.35		
SO ₂	$HS^- + SO_3$	0.65	0.91	0.05
-	SO ₃ ⊷ + HS•	0.25		
	HOS-SO2	0.10		
H ₂ S	HS- + HÖSH	0.95	12.1	0.74
-	HSS⁻ + H₂O	0.05		
(CH ₃) ₃ CSH	(CH ₃) ₃ CS ² +	0.40	10.4	0.46
	HOSH			
	(CH ₃) ₃ CSS ⁻ +	0.60		
	H ₂ O			
CH ₃ SH	$CH_3SS^- + H_2O$	1.00	6.2	0.30
CH ₃ Cl	Cl- + HOSCH ₃	1.00	0.64	0.03
(CH ₃) ₂ CHCl	CI-+HOSH+	1.00	<0.001*	
	CH ₂ CHCH ₃			

^a Neutral products are inferred. ^b Absolute accuracy $\pm 20\%$. ^c Experimental bimolecular rate coefficient in units of 10^{-10} cm³ molecule⁻¹ s⁻¹; standard deviation $\pm 10\%$, absolute accuracy $\pm 20\%$. ^d The reaction efficiency is the ratio of the experimental rate coefficient to the collision rate coefficient (k_{expt}/k_c), where $k_c = k_{Langevin}^{31}$ for neutral reactants with no dipole moment and $k_c = k_{var}^{32}$ for neutral reactants with dipole moments. ^e Product ion observed, immeasurably slow rate.

at which an ion is injected into the reaction flow tube, it is possible to induce dissociation.²² At high potentials the $[H,S,O]^-$ ion dissociates to S⁻. This fragment ion is identical to that observed in the high-energy CID spectrum of HOS⁻ reported by Bowie et al. (eq 12).¹³

$$HOS^{-} \xrightarrow{CID} S^{*-} + HO^{*}$$
 (12)

The branching ratios, rate coefficients, and efficiencies for the reactions between HOS- and various neutrals are shown in Table V. The gas-phase reactivity of HOS- is in line with its basicity, $\Delta H_{acid}^0(\text{HOS}H) = 354 \text{ kcal mol}^{-1}$. For example HOS⁻ is a weak sulfur nucleophile in the $S_N 2$ reaction with methyl chloride, which has a rate coefficient of $k = 0.64 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is in line with the observation that the S_N2 rate constants of nucleophiles decrease with decreasing basicity.27,28 Thus, HOSis intermediate in both basicity and nucleophilicity in comparison to two other sulfur nucleophiles: $H_2NS^- [\Delta H^0_{acid}(H_2NSH) =$ 362 kcal mol⁻¹, rate constant with CH₃Cl: $k = 1.5 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹] and HS⁻ [$\Delta H^0_{acid}(H_2S) = 351$ kcal mol⁻¹, rate constant with CH₃Cl: $k = 0.12 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$].²⁸ HOS- reacts with oxygen to form two product ions HO- and SO_2 as shown in eqs 13 and 14. The electron affinity of the hydroxyl radical (1.828 eV)²⁶ exceeds that of SO₂ (1.107 eV),²⁶ and the production of HO⁻ is favored over that of SO_2^{*-} by a factor of 4. A possible mechanism is shown in Scheme I. Thus initial attack forms a peroxy intermediate I, which subsequently undergoes proton transfer to form II. This latter species can undergo fragmentation to form the observed products. Alternatively, cyclization of intermediate I is possible through sulfur attack by the terminal oxygen. Cleavage of the HO-S bond would then yield the observed products.

HOS' +
$$O_2$$
 - HO' + SO₂ (13)

$$so_2^{\overline{i}} + HO'$$
 (14)

The reaction of HOS⁻ with CO forms two products, HO⁻ and HS⁻, shown in eqs 15 and 16. This reaction is analogous to that





between HOO⁻ and CO which forms HO^{-.16a} Thus initial attack on carbon forms [HOS-C \longrightarrow O]⁻, a formyl type anion intermediate, which can decompose to the ion-molecule complex [HO⁻(S \implies C \implies O)]. Both of the observed ions can be rationalized as proceeding from this complex. It is interesting to note that the reaction of HOS⁻ with CO (eq 15) is the reverse of reaction 7, by which HOS is synthesized.

HOS' + CO
$$-$$
 HO' + COS (15)
HS' + CO₂ (16)

The reaction of HOS⁻ with CO₂ is immeasurably slow and results solely in the formation of an adduct. This is in direct contrast to the rapid reaction of HOO⁻ and CO₂, which results in the formation of CO₃⁻ as the major product ion.^{16a}

HOS⁻ reacts with CS_2 to form the products shown in eqs 17 and 18. A possible mechanism is shown in Scheme II.

$$HOS' + CS_2 \longrightarrow HOS' + COS \qquad (17)$$

Three products are observed in the reaction between HOSand SO₂, as shown in eqs 19–21. The product ion of mass 33 was demonstrated to be HS⁻ and not HOO⁻ by injecting the HO³⁴S⁻ ion, which is present in 4.2% natural abundance; reaction of this anion with SO₂ generates H³⁴S⁻. A possible mechanism is shown in Scheme III.

$$HS + SO_3$$
(19)

$$HOS' + SO_2 \longrightarrow SO_3' + HS' \qquad (20)$$

$$HOS \cdot SO_2$$
 (21)

Finally we have also studied the reactions of HOS⁻ with three different thiols: H_2S , CH_3SH , and $(CH_3)_3CSH$. Apart from proton transfer from H_2S and $(CH_3)_3CSH$, which helped to bracket the acidity of HOSH, we also observed an interesting channel resulting in the formation of RSS⁻ ions (where R is either H or $(CH_3)_3C$). In the case of CH_3SH , proton transfer was not observed and the sole product is CH_3SS^- . We envisage this general class of reactions as proceeding via the mechanism outlined in Scheme IV. Thus the reactivities of HOO⁻ and HOS⁻ are quite different, due not only to their difference in basicity but also in their mode of reaction.

(D) Experimental Gas-Phase Basicity of HSS⁻. The HSS⁻ ion is the major product in the reaction of HOS⁻ and CS₂ (eq 17). By carrying out this reaction in the source flow tube, we are able to mass select the HSS⁻ ion and inject it cleanly into the second





flow tube. In analogy to HOS-, we have bracketed the basicity of HSS- by allowing it to react with various neutral acids. Our

SCHEME IV



TABLE VI: Gas-Phase Reactions of HSS- with Acids

reactant (AH)	$\Delta G^{0}_{acid}(AH),^{a}$ kcal mol ⁻¹	A ⁻ observed?
(CH ₃) ₃ CSH	346.2 ± 2.0	no
H ₂ S	344.8 ± 2.0	no
CH ₃ CO ₂ H	341.5 ± 2.0	no ^b
CH ₃ CH ₂ CO ₂ H	340.4 ± 2.0	no ^b
HCO ₂ H	338.3 ± 2.0	yes ^b
$CH_3C(O)CH_2C(O)CH_3$	336.6 ± 2.0	yes ^b
HC1	328.0 ± 0.3	yes

^a Reference 26. ^b The HSS-HA cluster was observed.

results are shown in Table VI, which establishes that ΔG^0_{acid} (HSSH) = 339 ± 3 kcal mol⁻¹ and ΔH^0_{acid} (HSSH) = 346 ± 3.5 kcal mol⁻¹.

(E) Thermochemistry of Sulfur Species. Our values for the gas-phase acidities of HOSH and HSSH reported in this paper as well as our value for CH₃SSH reported previously¹⁴ can be combined with known electron affinities of HOS,²⁹ HSS,¹¹ and CH₃SS¹¹ to determine the S-H bond dissociation energies in the parent compounds. These values together with the O-H bond dissociation energy of hydrogen peroxide are shown in Table VII. The S-H bond dissociation energies of HSS-H and RSS-H (where R = alkyl) compounds have previously been estimated to be 70 \pm 1.5 kcal mol^{-1.30} Our experimentally derived values for HSS-H and CH₃SS-H are 76 \pm 3.5 and 79 \pm 3.5 kcal mol⁻¹, respectively, indicating that these S-H bonds are substantially stronger than originally thought. Therefore the heat of formation of the HSS[•] radical must be revised. Using eq 22, together with the known heats of formation $\Delta H_f^0(\mathbf{H}^*) = 52.1 \text{ kcal mol}^{-1.9}$ and $\Delta H_f^0(\text{HSSH}) = 3.7 \text{ kcal mol}^{-1,26} \text{ yields } \Delta H_f^0(\text{HSS}^{\bullet}) = 28 \pm 3.5$ kcal mol⁻¹. This value is in contrast to the estimate of ΔH_{f}^{0} (HSS[•]) = 22.1 ± 1 kcal mol^{-1 30} but is in reasonable agreement with that derived from *ab initio* methods: $\Delta H_{\ell}^{0}(\text{HSS}^{\circ}) = 26.7$ kcal mol^{-1.5a} The heat of formation of the HSS- anion is derived to be -16 ± 3.5 kcal mol⁻¹ by combining the heat of formation of the radical with the electron affinity.¹¹

$$\Delta H_{\rm f}^0({\rm HSS}^{\bullet}) = {\rm BDE}({\rm HSS}_{\rm -}{\rm H}) + \Delta H_{\rm f}^0({\rm HSSH}) - \Delta H_{\rm f}^0({\rm H}^{\bullet})$$
(22)

As indicated in Table VII, the S-H bond dissociation energies in HOSH, HSSH, and CH₃SSH are very similar and between 8 and 11 kcal mol⁻¹ lower than the O-H bond energy in hydrogen peroxide. This behavior parallels that observed in the pairs H₂S [BDE(S-H) = 91.1 \pm 0.3 kcal mol⁻¹] and H₂O [BDE(O-H) = 119.2 \pm 0.1 kcal mol⁻¹] as well as in the pairs CH₃SH [BDE-(S-H) = 87.1 \pm 2.1 kcal mol⁻¹] and CH₃OH [BDE(O-H) =

TABLE VII: Gas-Phase Acidities of R-H, Electron Affinities of R[•], and Bond Dissociation Energies of R-H

R	$\Delta G_{\mathrm{acid}}^0$ (R-H), kcal mol ⁻¹	$\Delta H_{\rm acid}^0$ (R-H), kcal mol ⁻¹	EA (R•), eV	$\frac{D_{298} (R-H)^b}{\text{kcal mol}^{-1}}$	$\Delta H_{\rm f}({\rm R}),$ kcal mol ⁻¹	$\Delta H_{\rm f} ({\rm R}^{-}),$ kcal mol ⁻¹	$\Delta H_{\rm f} (\rm RH), \\ \rm kcal \ mol^{-1}$
HOO HOS HSS CH₃SS	368.6 ± 2.0^{a} 347 ± 3^{c} 339 ± 3^{c} 345 ± 3^{d}	375.9 ± 2.1^{a} 354 ± 3.5^{c} 346 ± 3.5^{c} 352 ± 3.5^{d}	$\begin{array}{c} 1.078 \pm 0.017^{a} \\ 1.655 \pm 0.04^{e} \\ 1.907 \pm 0.023^{f} \\ 1.757 \pm 0.022^{f} \end{array}$	87.2 ± 0.7^{a} 79 ± 3.5^{c} 76 ± 3.5^{c} 79 ± 3.5^{c}	2.5 ± 0.5^{a} -0.5 ± 2 ^c 28 ± 3.5 ^c	-22.4 ± 2.3^{a} -38.7 ± 2^{c} -16 ± 3.5^{c}	-32.6 ± 0.2^{a} -27 ± 3.5^{c} 3.7 ± 0.5^{a}

^a Values are taken from ref 26. ^b IP(H^{*}) = 313.587 kcal mol⁻¹ (ref 9). ^c This study. ^d Reference 14. ^e Reference 29. ^f Reference 11.

TABLE VIII: Hydride Affinities

R	$\Delta H_{\rm f}({ m R}),^a$ kcal mol ⁻¹	hydride affinity (R), ^b kcal mol ⁻¹
O ₂	0	57.1 ± 2.3
SÖ	1.5 ± 0.5	74.9 ± 2.0 (to form HOS ⁻)
SO		64.6 ^c (to form HSO ⁻)
S_2	30.7 ± 0.5	81.4 ± 3.5

^a Reference 26. ^b Employs data from Table VII and $\Delta H_{f}(H^{-}) = 34.7$ kcal mol⁻¹ (ref 26). ^c Employs our *ab initio* value of 10.3 kcal mol⁻¹ as the energy difference between HOS⁻ and HSO⁻.

 $104.4 \pm 1.0 \text{ kcal mol}^{-1}$. The magnitude of the difference in the S-H and O-H bond energies decreases, however, as the absolute energies decrease.

Our measurement of the rate coefficient for reaction 15 can be combined with our previous measurement for the rate coefficient of reaction 7 to determine that reaction 7 is excergic by 0.4 kcal mol⁻¹. Employing the entropy values for HO⁻ (41.22 eu),⁹ COS (55.35 eu),⁹ HOS⁻ (assumed equal to that of HOCI (56.53 eu),⁹ using the isoelectronic approximation⁶), and CO (47.24 eu)⁹ and employing the heats of formation of COS (-34.0 \pm 0.2 kcal mol⁻¹ ²⁶), HO⁻ (-32.8 \pm 0.1 kcal mol⁻¹ ²⁶), and CO (-26.4 \pm 0.1 kcal mol⁻¹ ²⁶), we find the heat of formation of HOS⁻ is -38.7 \pm 2 kcal mol⁻¹. Combining this value with the electron affinity of HOS[•] indicates that ΔH_{f}^{0} (HOS[•]) = -0.5 \pm 2 kcal mol⁻¹. This value is in excellent agreement with the upper limit of -0.7 \pm 1.3 kcal mol⁻¹ determined by *ab initio* methods^{5c} but is only in fair agreement with an earlier estimate of 5 \pm 4 kcal mol^{-1,30}

$$HO^- + COS \stackrel{k_7}{\underset{k_{15}}{\leftrightarrow}} HOS^- + CO$$

We note that our experimental heat of formation of HOS indicates that in the reaction between hydroxyl radical and carbonyl sulfide, formation of HOS (eq 23) is exothermic by 2 kcal mol⁻¹. Thus this process may represent the previously unidentified slow bimolecular channel for this reaction.^{1b} The corresponding process for the reaction of carbon disulfide (eq 24) is endothermic by 26 kcal mol⁻¹ and instead only a slow pressure dependent channel is observed.^{1b}

$$HO + COS \rightarrow HOS + CO$$
 (23)

$$HO + CS_2 \neq HOS + CS$$
 (24)

Our experimental value of $\Delta H_1^0(\text{HOS}^-)$ and our computed energy difference between HOS⁻ and HSO⁻ indicates that $\Delta H_1^0(\text{HSO}^-) = -28$ kcal mol⁻¹. Hydride affinities can be deduced from these values, as summarized in Table VIII. The hydride affinity of SO at the oxygen site is ≈ 18 kcal mol⁻¹ higher than that of O₂; similarly the hydride affinity of S₂ is ≈ 17 kcal mol⁻¹ greater than that of SO at the sulfur site.

Our experimental heat of formation of HOS can be combined with the known heats of formation of (a) SO⁻ $(-24 \text{ kcal mol}^{-1})^{26,33}$ and H⁺ (365.7 kcal mol}⁻¹)²⁶ to determine ΔH^{0}_{acid} (HOS) ≈ 342 kcal mol}⁻¹ and (b) SO (1.5 kcal mol}⁻¹)²⁶ and H (52.1 kcal mol}⁻¹)²⁶ to determine D_{298} (H–OS) ≈ 54 kcal mol}⁻¹. Employing the computed energy difference between HOS and HSO^{5b} gives the estimates ΔH^{0}_{acid} (HSO) ≈ 347 kcal mol}⁻¹ and D_{298} (H–SO) ≈ 59 kcal mol}⁻¹. An additional thermochemical quantity can be tentatively determined from the available data. The experimental EA(HOS[•]) and the computed energy differences between the radicals (5.4 kcal mol⁻¹)^{5b} and ions (10.3 kcal mol⁻¹) [this work] allows an estimation of the EA(HSO[•]) ≈ 1 eV; this value is very similar to the electron affinity of HO₂[•] which has been determined as 1.078 eV from photoelectron spectroscopy.²⁶

Conclusion

In summary, the tandem flowing afterglow-selected ion flow tube provides valuable insight into the chemistry and thermochemistry of the hydroxysulfide anion. Ab initio calculations indicate that HOS⁻ and HOSH are more stable than HSO⁻ and H₂SO, respectively; the computed gas-phase acidity of HOSH is in agreement with the experimentally determined value. Combination of our experimental gas-phase acidities determined with the FA-SIFT and electron affinities determined with laser photoelectron spectroscopy provide new experimental bond dissociation energies for three sulfur compounds, HOSH, HSSH, and CH₃SSH, that are ~8 kcal mol⁻¹ greater than previous estimates.

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References and Notes

(1) (a) Wayne, R. P. Chemistry of Atmospheres, 2nd ed.; Clarendon: Oxford, 1991. (b) Tyndall, G. S.; Ravishankara, A. R. Int. J. Chem. Kin. 1991, 23, 483-527.

(1) 23, 483-527.
(2) (a) Wang, N. S.; Howard, C. J. J. Phys. Chem. 1990, 94, 8787-8794.
(b) Lovejoy, E. R.; Wang, N. S.; Howard, C. J. J. Phys. Chem. 1987, 91, 5749-5755.
(c) Friedl, R. R.; Brune, W. H.; Anderson, J. G. J. Phys. Chem. 1985, 89, 5505-5510.
(d) Bulatov, V. P.; Vereshchuk, S. I.; Dzegilenko, F. N.; Sarkisov, O. M.; Khabarov, V. N. Khim. Fiz. 1990, 9, 1214-1223.
(a) (a) Smardzewski, R. R.; Lin, M. C. J. Chem. Phys. 1977, 66, 3197(b) Balvacci N. Bazvarti I. Casavarti N. J. Casavarti N. Valpi

 (3) (a) Smardzewski, R. R.; Lin, M. C. J. Chem. Phys. 1977, 66, 3197– 3204. (b) Balucani, N.; Beneventi, L.; Casavecchia, P.; Stranges, D.; Volpi, G. G. J. Chem. Phys. 1991, 94, 8611–8614.

(4) For experimentally derived estimates of the heat of formation of HSO^{*}, see: (a) Davidson, F. E.; Clemo, A. R.; Duncan, G. L.; Browett, R. J.; Hobson, J. H.; Grice, R. *Mol. Phys.* **1982**, *46*, 33-40. (b) Schurath, U.; Weber, M.; Becker, K. H. J. Chem. Phys. **1977**, *67*, 110-119. (c) White, J. N.; Gardiner, W. C., Jr. Chem. Phys. Lett. **1978**, *58*, 470-472.

(5) For an estimate of the heats of formation of HSO[•] and HOS[•] via *ab initio* techniques, see: (a) Luke, B. T.; McLean, A. D. J. Phys. Chem. 1985, 89, 4592–4596. (b) Xantheas, S. S.; Dunning, T. H., Jr. J. Phys. Chem. 1993, 97, 18–19. (c) Xantheas, S. S.; Dunning, T. H., Jr., personal communication, 1993.

(6) Bartmess, J. E.; McIver, R. T., Jr. In Gas Phase Ion Chemistry;
Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, pp 87-121.
(7) Mead, R. D.; Stevens, A. E.; Lineberger, W. C. In Gas Phase Ion

(7) Mead, R. D.; Stevens, A. E.; Lineberger, W. C. In Gas Phase Ion Chemistry; Bowers, M. T. Ed.; Academic: New York, 1984; Vol. 3, pp 213– 248. (8) Bartmess, J. E. Mass Spectrom. Rev. 1989, 8, 297-343.

 (9) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.;
 McDonald, R. A.; Syverud, A. N. J. Phys. Chem. Ref. Data 1985, 14, Suppl. No. 1.

(10) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. J. Am. Chem. Soc. 1990, 112, 5750-5759.

 (11) Moran, S.; Ellison, G. B. J. Phys. Chem. 1988, 92, 1794–1803.
 (12) Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. J. Phys. Chem. 1984, 88, 1389-1393.

(13) Bowie, J. H.; Stringer, M. B.; Hayes, R. N. Rapid Commun. Mass

Spectrom. 1990, 4, 129–130. (14) Downard, K. M.; Bowie, J. H.; O'Hair, R. A. J.; Krempp, M.; DePuy, C. H. Int. J. Mass Spectrom. Ion. Proc. 1992, 120, 217-229.

(15) O'Hair, R. A. J. Mass Spectrom. Rev. 1991, 10, 133-173.
(16) (a) Bowie, J. H.; DePuy, C. H.; Sullivan, S. A.; Bierbaum, V. M.; Can. J. Chem. 1986, 64, 1046-1050. (b) DePuy, C. H.; Bierbaum, V. M.; Schmitt, R. J.; Shapiro, R. H. J. Am. Chem. Soc. 1978, 100, 2920. (c) Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H. J. Am. Chem. Soc. 1981, 103, 6262-6263.

(17) Gaussian 90; Revision, J.; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol,

S.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1990.

(18) Hehre, W. J.; Radom, L.; Schleyer, P.v.R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, 1986.

(19) For a recent discussion on scaling factors for ab initio derived frequencies and zero point vibrational energies, see: Grev, R. S.; Janssen, C. L.; Schaefer, H. F. J. Chem. Phys. 1991, 95, 5128-5132.

(20) (a) Smith, B. J.; Radom, L. J. Phys. Chem. 1991, 95, 10549-10551. (b) Del Bene, J. E.; Mettee, H. D.; Frisch, M. J.; Luke, B. T.; Pople, J. A. J. Phys. Chem. 1983, 87, 3279–3282. (c) Ozment, J. L.; Schmiedekamp, A. M. Int. J. Quantum Chem. 1992, 43, 783–800.

(21) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. Int. J. Mass. Spectrom. Ion. Proc. 1987, 81, 85-100.

(22) Gronert, S.; O'Hair, R. A. J.; Prodnuk, S.; Sülzle, D.; Damrauer, R.; DePuy, C. H. J. Am. Chem. Soc. 1990, 112, 997-1003.

(23) Moore Plummer, P. L. J. Chem. Phys. 1990, 92, 6627-6634.

(24) For some recent ab initio calculations on HOSH and H₂S=O, see: (a) Solà, M.; Gonzalez, C.; Tonachini, G.; Schlegel, H. B. Theor. Chim. Acta.
 (a) Solà, M.; Gonzalez, C.; Tonachini, G.; Schlegel, H. B. Theor. Chim. Acta.
 (b) Wolfe, S.; Schlegel, H. B. Gazz. Chim. Ital. 1990, 120, 285–290.
 (c) Lee, T. J.; Handy, N. C.; Rice, J. E.; Scheiner, A. C.; Schaefer, H. F. J. Chem. Phys. 1986, 85, 3930–3938.

(25) This analysis was carried out using the program THERMO witten by Paul Rablen, Yale University, 1993.

(26) NIST Standard Reference Database 19B: NIST Negative Ion Energetics Database Version 2.07, program written/data compilation by John E. Bartmess, Department of Chemistry, University of Tennessee, Knoxville TN 37996-1600. This compilation is based on original data from Gas-Phase Ion and Neutral Thermochemistry. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. J. Phys. Chem. Ref. Data 1988, 17, Suppl. 1.

(27) Damrauer, R.; DePuy, C. H.; Bierbaum, V. M. Organometallics 1982, 1, 1553-1554.

(28) DePuy, C. H.; Gronert, S.; Mullin, A.; Bierbaum, V. M. J. Am. Chem. Soc. 1990, 112, 8650-8655.

(29) A preliminary value of the electron affinity of HOS^{*} has recently been determined: Gunion, R. F.; Polak, M. C.; Lineberger, W. C., personal communication, 1992.

(30) Benson, S. W. Chem. Rev. 1978, 78, 23-35.

(31) Gioumousis, G.; Stevenson, D. P. J. Chem. Phys. 1958, 29, 294-299. (32) Chesnavich, W. J.; Su, T.; Bowers, M. T. J. Chem. Phys. 1980, 72, 2641-2655.

(33) Polak, M. L.; Fiala, B. L.; Ervin, K. M.; Lineberger, W. C. J. Chem. Phys. 1991, 94, 6926-6927.