The $RS^-{\cdot}HSR$ Hydrogen Bond: Acidities of α,ω-Dithiols and Electron Affinities of Their Monoradicals

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Abstract: Gas-phase acidities (ΔG°_{acid}) have been measured for 1,2-ethanedithiol, 1,3-propanedithiol, and 1,4-butanedithiol, using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Adiabatic electron affinities (EAs) of the thiolate monoradicals of these compounds were assigned from electron photodetachment spectra of their corresponding thiolate monoanions, acquired using a cw-ICR. The dithiols exhibit enhanced acidities (up to 8.7 kcal/mol in ΔG°_{acid}) and greater EAs (up to 6.7 kcal/mol) than analogous monothiol species. These differences are attributed to an intramolecular $RS^-{\cdot}HSR$ hydrogen bond in the thiolate anion. Considerations of the $RO^-{\cdot}HOR$ hydrogen bond in monoanions of α,ω-diols and in the $[CH_3O^-{\cdot}HOCH_3]$ complex anion suggest that the $RS^-{\cdot}HSR$ hydrogen bond provides up to 9 kcal/mol extra stabilization.

Introduction

The purpose of this study is to examine the nature of the $RS^-{\cdot}HSR$ hydrogen bond. Very little is understood about this interaction, despite the prevalence of the thiol group in proteins—namely, in cysteine residues. The potential importance of this type of hydrogen bond can be seen in the thioredoxin family of disulfide oxidoreductases. The primary structure at the active site contains the -Cys-X-Y-Cys- sequence, where X and Y are individual residues. In all proteins of the thioredoxin family, only one cysteine residue is accessible and reactive. In some of these proteins, the acidity of the accessible cysteine is enhanced considerably, representing a stabilization of the thiolate anion. In glutaredoxin, for example, that pK_a is[1,2] 3.5, some 5 pK_a units lower (about 7 kcal/mol stabilization of the anion) than the normal thiol value of about 8.8. Recent NMR[3] and X-ray crystallography[4,5] studies suggest that the thiolate stabilization is the result of an $RS^-{\cdot}HSR$ hydrogen bond between the Cys-14 thiol and the Cys-11 thiolate.

Other studies that have been carried out on the $RS^-{\cdot}HSR$ interaction are scarce.[6] Boorman and co-workers[7] have presented structural evidence of an $RS^-{\cdot}HSR$ hydrogen bond in the crystal structure of $(PPh_4)(HSCH_2CH_2SCH_2CH_2S)$. They noted that pairs of the $HSCH_2CH_2SCH_2CH_2S^-$ anions were coupled in a head-to-tail fashion by very strong $RS^-{\cdot}HSR$ hydrogen bonds, with nearly linear SHS angles. The interatomic SS distance they measured, 3.45 Å, is smaller than the sum of their van der Waals radii of 3.7 Å. McDaniel and Evans[8] have provided insight into the strength of the $RS^-{\cdot}HSR$ interaction. From their studies of tetraalkylammonium hydrosulfide adducts with H_2S, they concluded that the complexation enthalpy of H_2S with SH^- is between 7 and 14 kcal/mol. Early theoretical work by Sabin suggests that this complexation results in a linear $RS^-{\cdot}HSR$ hydrogen bond.[9]

To study the $RS^-{\cdot}HSR$ interaction, we have measured the acidities of a series of dithiols, $HS(CH_2)_nSH$, where $n = 2-4$. We have also acquired the electron photodetachment spectra of their corresponding thiolate monoanions, $HS(CH_2)_nS^-$ from which we derive the adiabatic electron affinities (EAs) of the monoradicals, $HS(CH_2)_nS^\bullet$. Experimental results are supplemented by ab initio calculations, and comparisons are made between the $RS^-{\cdot}HSR$ and $RO^-{\cdot}HOR$ systems.

We find that the acidities of each of the dithiols and the EAs of the dithiol monoradicals are significantly enhanced over their monothiol counterparts. These differences are evidence of a hydrogen bond in the monoanions of the dithiols, worth up to 9 kcal/mol of stabilization.

Experimental Section

Chemicals. All dithiols were purchased from Aldrich (>90% purity) and were used without further purification. Nitrogen trifluoride was purchased from Ozark-Mahoning. Multiple freeze−pump−thaw cycles were performed on each compound to degas the samples and remove any possible volatile impurities. The negative ion mass spectrum of each dithiol, produced upon reaction with F^-, showed only an (M-1) peak at short times. Impurities are therefore believed not to interfere significantly with the equilibrium measurements.

Acidities. Equilibrium acidities were measured in an IonSpec Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, described in detail elsewhere.[10] Reactions took place in a 2-in. cubic cell, placed between the poles of an electromagnet. The operating magnetic field was 0.60 T.

Pressures of the neutral gases were measured with a vacuum ionization gauge (Granville Phillips 330), and these uncorrected pressures were calibrated against a capacitance manometer (MKS 170 Baratron with a 315BH-1 sensor). Typical operating pressures were 0.5 to 5×10^{-7} Torr, at which ions could be trapped for longer than

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10 s. Ion ejection was achieved using single-frequency excitation.

The primary ion was F^- and was formed via dissociative electron attachment to nitrogen trifluoride (eq 1). Subsequent formation of thiolate anions was achieved by deprotonating the thiol acids with F^- (eq 2).

$$NF_3 + e^- \rightarrow NF_2 + F^- \tag{1}$$

$$F^- + HSR \rightarrow FH + {}^-RS \tag{2}$$

$$RS^- + HSR' \rightleftharpoons RSH + {}^-SR' \tag{3}$$

Proton-transfer equilibrium ion ratios were measured by first isolating a single thiolate anion, and then allowing it to react with a different thiol (eq 3). After the ion ratio reached steady state (about 3 s), the first thiolate ion was ejected, and reaction was observed until steady state was reestablished. The same steady-state ion ratio before and after ejection of the thiolate ion ensured that equilibrium had been reached. Equilibrium constants were computed using both this ion ratio and the ratio of the neutral pressures (eq 4). Each experiment was repeated on a different day, and the equilibrium constants were reproducible within 10%.

$$K_{eq} = \frac{I_{R'S^-}}{I_{RS^-}} \times \frac{P_{RSH}}{P_{R'SH}} \tag{4}$$

$$\Delta G^\circ_{acid} = -RT \ln K_{eq} \tag{5}$$

The relative ΔG°_{acid} was determined from the equilibrium constant (eq 5), where the temperature, T, has previously been measured to be about 350 K.[11] Absolute acidities were assigned by measuring the relative acidity of $HS(CH_2)_4SH$ with respect to hydrogen sulfide ($\Delta G^\circ_{acid}(H_2S) = 344.8 \pm 2.0$ kcal/mol).[12]

Uncertainties in the relative acidities arise from two main sources of error. The first is due to volatile impurities. Reproducibility of the equilibrium constant ensured that there was minimal contribution from volatile impurities to overall pressure measurements. We nevertheless assign an uncertainty of ±20% to the uncorrected pressure readings. We also estimate the uncertainty in pressure calibration to be ±20%.[13] In free energy, the total error in relative acidities is about 0.4 kcal/mol. The uncertainly in the absolute acidities is ±2.1 kcal/mol, due to the ±2.0 kcal/mol uncertainty in the acidity of the reference acid.

Electron Affinities. All electron affinity (EA) experiments were performed in a continuous-wave ion cyclotron resonance (cw-ICR) mass spectrometer, described in detail elsewhere.[14] Experiments took place in a cell with a 1-square-inch cross section, placed between the poles of an electromagnet. Experiments were run using a constant magnetic field strength, between 0.2 and 1.0 T.

Pressures were measured with a Varian 844 vacuum ionization gauge. Accurate pressures were not necessary for these experiments, and therefore no calibration was performed. Typical uncorrected pressures were about 2×10^{-7} Torr, at which trapping times of about 1 s were achieved.

Coherent ion motion was effected by a continuous driving signal, typically around 150 kHz. The small ion signals were amplified using a digital lock-in amplifier (EG&G). By employing both capacitance bridge detection and a frequency lock,[15] changes of less than 0.5% in steady-state ion signal were detectable.

The light source was a 1000 W xenon−mercury arc lamp (Schoeffel). Wavelength selection was accomplished using a 0.25 m high throughput monochromator (Spectral Energy), employing a visible grating (350−850 nm). The monochromator was calibrated using a Beck reversion spectroscope, accurate to ±1 nm. With 7.7 mm slits, the bandwidth was 25 nm (fwhm). The relative output power was measured by directing the exit light into a thermopile (Eppley Laboratory, Inc.) and recording the output voltage.

As with the acidity experiments, the primary ion was F^- (eq 1). The thiolate anions were formed via deprotonation of the corresponding thiol acid (eq 2).

Electron photodetachment spectra of the thiolate anions were measured to assign the EAs of their radicals. Fractional decrease (FD) of the ion signal with light (eq 6) was measured at each wavelength (λ), where I_{on} and I_{off} are the ion signal intensities with and without light, respectively. Relative cross sections (σ_{rel}) for electron detachment[16] were then computed (eq 7), where P is the relative power of incident light. Each spectrum shows σ_{rel} plotted as a function of λ. Maximum fractional decreases were typically around 10%. Minimum measurable fractional decreases were about 0.5%. Each data point represents the average of at least five scans.

$$FD = 1 - \left(\frac{I_{on}}{I_{off}}\right) \tag{6}$$

$$\sigma_{rel} = \frac{FD}{\lambda \cdot P \cdot (1 - FD)} \tag{7}$$

The anions in the detection region of the cell are expected to be collisionally thermalized, thereby minimizing electron photodetachment from vibrationally excited anions. Additionally, we expect favorable Franck−Condon factors for photodetachment due to the relatively small changes in geometry between the thiol anions and radicals (see Discussion). The adiabatic EA is therefore taken to be the minimum energy observed to effect electron loss from the anion—that is, the energy at which the cross section first becomes nonzero. Because of signal-to-noise problems in regions of small fractional decrease, the EA was determined via a linear extrapolation of the nonzero cross-section values.[16]

The uncertainty in the absolute EA assignment stems largely from the bandwidth of light from the monochromator. This 25 nm bandwidth translates into an uncertainty in energy of about ±0.6 kcal/mol. Uncertainty in the EA difference between any two thiolate radicals is much smaller, because the slope of absolute cross section versus wavelength near threshold is expected to be similar for each of the dithiol anions. Instead, the major contribution to the uncertainty is the extrapolation procedure. The near-unity R value (>0.99) of the data points in the linear region of each spectrum suggests a ±2 nm uncertainty, which translates into ±0.1 kcal/mol.

Quantum Calculations. Ab initio calculations (Gaussian 98) were performed on the acid, the anion, and the radical of each thiol and alcohol under study. Geometries were optimized at the MP2/6-31+G* level of theory. Zero-point energies and thermal corrections were obtained from frequency calculations on the resultant geometries.

Relative thermochemical values were obtained from isodesmic reactions of each thiol with ethanethiol—proton transfers for the acidity, electron transfers for the EA, and hydrogen-atom transfer for the bond dissociation energy. Absolute values were obtained by adding each of the calculated relative values to the experimental value of ethanethiol.[17]

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[12] Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6047 measured the acidity of H_2S to be 344.8 ± 2.0 kcal/mol. Although the acidity is known more accurately, we choose to anchor our dithiol acidity measurements to this number because later we make comparisons between monothiols and dithiols. In these comparisons, the values we use for the monothiols are either those in this reference or are dependent on values of other species whose acidities Bartmess has measured.

[13] The estimate for the error in pressure calibration using the capacitance manometer is based on experience with reaction rate constant measurements of well-studied reactions, such as the $CH_4^+ + CH_4 = CH_5^+ + CH_3$ reaction. Agreement between literature values and values measured in our laboratory is typically within ±15%. A modest estimate of ±20% is therefore assigned as the uncertainty in the absolute pressure measurements.

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Table 1. Experimental Acidity of Mono- and Dithiols

n	$\Delta G^\circ_{acid}(CH_3(CH_2)_nSH)$[a] (kcal/mol)	$\Delta G^\circ_{acid}(HS(CH_2)_nSH)$[b] (kcal/mol)	$\Delta\Delta G^\circ_{acid}$[c] (kcal/mol)
2	347.9 ± 2.0	339.2 ± 2.1	−8.7 ± 2.9
3	347.4 ± 2.0	341.6 ± 2.1	−5.8 ± 2.9
4	346.2 ± 2.0	341.6 ± 2.1	−4.6 ± 2.9

[a] Obtained from ref 19. [b] Equilibrium measurements, this study. [c] Acidity difference between mono- and dithiols.

Table 2. Experimental Acidity of Mono- and Di-alcohols

n	$\Delta G^\circ_{acid}(CH_3(CH_2)_nOH)$[a] (kcal/mol)	$\Delta G^\circ_{acid}(HO(CH_2)_nOH)$[b] (kcal/mol)	$\Delta\Delta G^\circ_{acid}$[c] (kcal/mol)
2	369.4 ± 2.0	360.9 ± 2.0	−8.5
3	368.8 ± 2.0	355.8 ± 2.0	−13.0
4	367.5 ± 2.0	354.6 ± 2.0	−12.9

[a] Obtained from ref 19. [b] Obtained from ref 18. [c] Acidity difference between mono- and di-alcohols.

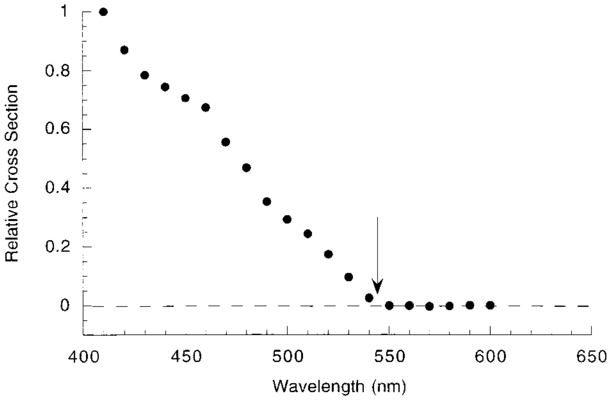

Figure 1. Electron photodetachment spectrum of $HS(CH_2)_2S^-$. The electron affinity assignment is indicated by the arrow.

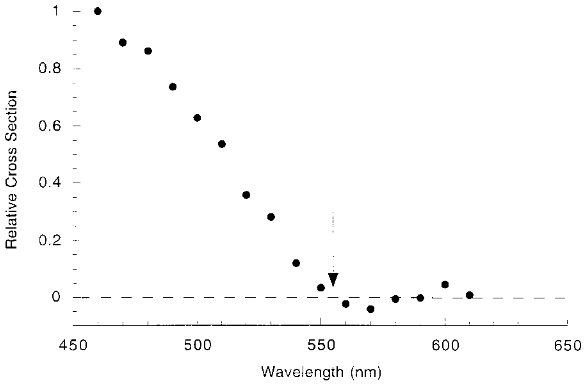

Figure 2. Electron photodetachment spectrum of $HS(CH_2)_3S^-$. The electron affinity assignment is indicated by the arrow.

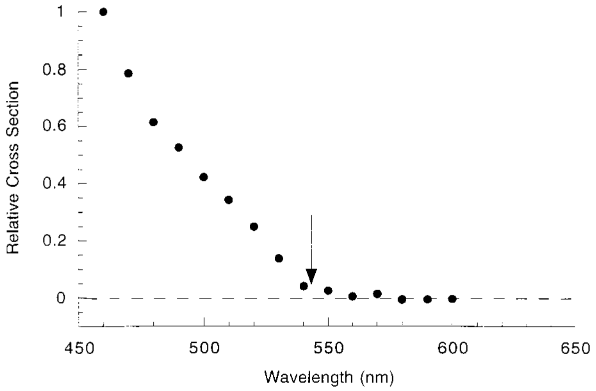

Figure 3. Electron photodetachment spectrum of $HS(CH_2)_4S^-$. The electron affinity assignment is indicated by the arrow.

Table 3. Experimental EAs of Mono- and Dithiol Monoradicals

n	$EA(CH_3(CH_2)_nS^\bullet)$[a] (kcal/mol)	$EA(HS(CH_2)_nS^\bullet)$[b] (kcal/mol)	ΔEA[c] (kcal/mol)
2	46.1 ± 0.5	52.8 ± 0.6	+ 6.7 ± 0.8
3	46.8 ± 0.5	51.6 ± 0.6	+ 4.8 ± 0.8
4	48.2 ± 0.5	53.0 ± 0.6	+ 4.8 ± 0.8

[a] Obtained from ref 17. [b] Photodetachment experiments, this study. [c] Electron affinity difference between mono- and dithiols.

Table 4. Derived Bond Dissociation Energies of Monothiols

n	$\Delta H^\circ_{acid}(CH_3(CH_2)_nSH)$[a] (kcal/mol)	$BDE(CH_3(CH_2)_nSH)$[b] (kcal/mol)
2	354.2 ± 2.2	86.1 ± 2.3
3	353.7 ± 2.2	86.1 ± 2.3
4	352.5 ± 2.2	86.2 ± 2.3

[a] Obtained from ref 19. [b] Calculated from eq 8.

Table 5. Calculated Cyclization Energies and Geometries of $HS(CH_2)_nS^-$ (MP2/6-31+G*)

n	ΔE_{cyc}[a] (kcal/mol)	HSCS[b] dihedral angle (deg)	SHS bond angle (deg)	HS distance (Å)	SS distance (Å)
2	−3.4	7.3	127.1	1.366	3.39
3	−3.9	3.8	148.5	1.377	3.50
4	−5.0	2.9	163.7	1.396	3.53

[a] Energy difference between the cyclic and the fully anti conformations. [b] See Figure 4.

Results

The dithiol acidities are shown in Table 1. For comparison, the diol acidities, measured by Bartmess and co-workers,[18] are shown in Table 2. Electron photodetachment spectra of the dithiol radicals are shown in Figures1−3, and their assigned EAs are listed in Table 3. Values for the acidities[19] and EAs[17] of relevant monothiols and monoalcohols are included in these tables as points of reference.

Table 4 lists the values of ΔH°_{acid} and bond dissociation energy (BDE) for the monothiols. The bond dissociation energies have been calculated using eq 8, which was derived through a thermochemical cycle. $IP(H^\bullet)$ is the ionization potential of the hydrogen atom.

$$BDE = \Delta H^\circ_{acid} + EA - IP(H^\bullet) \tag{8}$$

Theory. Ab initio calculations suggest that the lowest-energy conformation for each of the monothiols is the acyclic, fully anti conformation. The same is true for the neutral acids of the dithiols. The lowest-energy conformations of the dithiol anions and radicals, however, are all cyclic. Cyclization energies (i.e., the energy difference between the cyclic and the fully anti conformation) and relevant specific geometric parameters of the anions and radicals are shown in Tables5 and 6, respectively.

Calculated acidities of mono- and dithiols are listed in Table 7. Calculated EAs of mono- and dithiols are listed in Table 8.

Discussion

Acidity. The acidity of each dithiol is significantly enhanced relative to that of the monothiol containing the same number of methylene units (Table 1). A similar enhancement of the

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Table 6. Calculated Cyclization Energies and Geometries of $HS(CH_2)_nS^•$ (MP2/6-31+G*)

n	ΔE_{cyc}[a] (kcal/mol)	HSCS[b] dihedral angle (deg)	HS distance (Å)	SS distance (Å)
2	−2.0	97.8	1.343	3.44
3	−1.8	82.3	1.342	3.20
4	−0.1	85.7	1.342	3.61

[a] Energy difference between the cyclic and the fully anti conformations. [b] See Figure 5.

Table 7. Calculated Acidity of Mono- and Dithiols

n	$\Delta H^\circ_{\text{acid}}(CH_3(CH_2)_nSH)$ (kcal/mol)	$\Delta H^\circ_{\text{acid}}(HS(CH_2)_nSH)$ (kcal/mol)	$\Delta\Delta H^\circ_{\text{acid}}$[a] (kcal/mol)
2	354.6	343.3	−11.3
3	354.3	345.5	−8.8
4	354.0	345.2	−8.8

[a] Acidity difference between mono-and dithiols.

Table 8. Calculated EAs of Mono- and Dithiol Monoradicals

n	$EA(CH_3(CH_2)_nS^•)$ (kcal/mol)	$EA(HS(CH_2)_nS^•)$ (kcal/mol)	ΔEA[a] (kcal/mol)
2	44.7	54.3	+9.6
3	45.0	51.5	+6.5
4	45.1	53.6	+8.5

[a] Electron Affinity difference between mono-and dithiols.

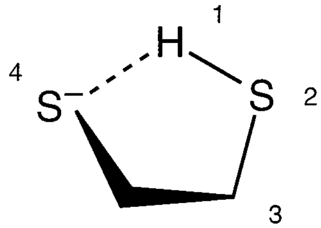

Figure 4. Cyclic conformation of the thiolate monoanion of ethanedithiol, depicting the thiol hydrogen roughly in the plane of the ring. The HSCS dihedral angle to which the text refers is the 1,2,3,4 dihedral angle.

dithiol radical EAs (Table 3) suggests that this is due to stabilization of the dithiol anion. The polar and polarizable nature of the neutral sulfur-containing group is partly responsible for this extra stability. The $\Delta G^\circ_{\text{acid}}$ of CH_3SCH_2SH is 343.0 ± 4.0 kcal/mol,[20] some 5 kcal/mol more acidic than $CH_3(CH_2)_2SH$. This polar effect, however, would be diminished considerably with each additional methylene unit and therefore fails to account for much of the acidity enhancement in the dithiols we have studied. We therefore believe that there is an intramolecular RS$^-$•HSR hydrogen bond formed in the dithiol anions.

For an RS$^-$•HSR hydrogen bond to exist in these compounds, the conformation of the anion must be cyclic. The experimental results provide insight into the anion's conformation. One can see that the values of $\Delta G^\circ_{\text{acid}}$ are dependent upon the dithiol chain length (Table 1). The same is true of the EAs (Table 3), but the dependence on chain length is slightly different. If the neutral dithiols all have the same S−H bond dissociation energies, then, since $\Delta G^\circ_{\text{acid}} = \Delta H^\circ_{\text{acid}} - T\Delta S^\circ_{\text{acid}}$, it immediately follows from eq 8 that $\Delta S^\circ_{\text{acid}}$ is dependent on chain length and is more negative in the larger compounds. If the conformations of the neutral acids and the anions were both acyclic, then we would not expect such a dependence of entropy on chain length. This suggests that the conformations of the anions are cyclic.

Although it is difficult to estimate the absolute entropies,[21] a quantitative treatment[22] suggests that the relative values for $\Delta S^\circ_{\text{acid}}$ decrease by about 3.5 eu (about 1.2 kcal/mol in $T\Delta S^\circ_{\text{acid}}$) with each additional methylene unit. This observation is consistent with the formation of a cyclic, hydrogen-bonded anion from an acyclic acid, where each additional methylene unit represents additional loss of entropy from the conversion of a rotation to a vibration.

Ab initio calculations give geometries of the dithiol anions. For each dithiol anion, the cyclic conformation is the lowest in energy—lower than the fully anti conformation by 3.4−5.0 kcal/mol (Table 5). Additionally, the calculated acidities ($\Delta H^\circ_{\text{acid}}$) are in good qualitative agreement with experiment ($\Delta G^\circ_{\text{acid}}$) when the anion conformations are taken to be cyclic. Theory is therefore consistent with a cyclic nature of the dithiol anions, proposed above.

An examination of the ab initio geometric parameters surrounding the RS$^-$•HSR interaction, Table 5, provides further insight, as to its nature. For each of these cyclic anions, the thiol hydrogen is between the two sulfur atoms and is roughly in the plane of the ring, illustrated in Figure 4. A measure of this planarity is given by the HSCS dihedral angle (Figure 4), which approaches 0° for $HS(CH_2)_4S^-$. Additionally, the SHS angle is markedly large for each of these species and is nearly linear for $HS(CH_2)_4S^-$. The thiol SH bond lengths are significantly longer than the 1.342 Å calculated for closed-shell, neutral thiols. Furthermore, the lengthening is more pronounced as the ring-size increases. Finally, the SS distance in each anion is smaller than the sum of their van der Waals radii (3.7 Å) by about 0.25 Å. Each of these observations is consistent with a hydrogen bond that approaches its ideal geometry as the system becomes less strained.

A comparison of the acidities of the α,ω-dithiols, $HS(CH_2)_nSH$ (Table 1), against those of the α,ω-diols, $HO(CH_2)_nOH$ (Table 2), sheds light on some properties of the RS$^-$•HSR hydrogen bond. In the relatively strain-free $HO(CH_2)_4OH$, where the anion can attain a linear OHO geometry, the acidity is enhanced by about 18 kcal/mol in $\Delta H^\circ_{\text{acid}}$.[18] The acidity of the corresponding dithiol, on the other hand, is enhanced by about 9.2 kcal/mol in $\Delta H^\circ_{\text{acid}}$.[23] Clearly the RO$^-$•HOR hydrogen bond is much stronger than the RS$^-$•HSR hydrogen bond.

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(21) Because $\Delta S^\circ_{\text{acid}}$ was not measured experimentally, an estimate must be made to extract $\Delta H^\circ_{\text{acid}}$ from $\Delta G^\circ_{\text{acid}}$. The entropy for proton loss in dithiols can be expressed as: $\Delta S^\circ_{\text{acid}}(HS(CH_2)_nSH) = \Delta S^\circ_{\text{acid}}(CH_3(CH_2)_nSH) + \Delta S^\circ_{\text{cyc}}(HS(CH_2)_nS^-) + \Delta S_\sigma$, where the first term is the entropy change for proton loss in the corresponding monothiol, the second term is the entropy associated with cyclizing, and the third term accounts for symmetry. The cyclization term is difficult to estimate. Ab initio frequency calculations can provide accurate estimates of vibrational entropies for a single conformation, but it is not clear how to account for the many conformations of the acyclic anion that are lost during cyclization. A reasonable empirical method would be to use the experimentally derived entropy loss in the formation of cyclic alkanes from *n*-alkanes. These entropies would be assigned to the dithiol system, matching the number of rotations lost during cyclization. However, this method does not account for low-frequency vibrations associated with a hydrogen bond. Yamdagni and Kebarle (Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504−3510) experimentally derived the cyclization entropies of protonated diamines, but this method may not be precisely applicable here. First, the formation of a hydrogen bond in $H_2N(CH_2)_nNH_3^+$ involves the loss of an additional internal rotation compared with the formation of an internal hydrogen bond in $HS(CH_2)_nS^-$. Second, the RS$^-$•HSR hydrogen bond is weaker than the R_3NH^+•HNR_2 hydrogen bond, and the vibrational entropy contributions will be different.

(22) Here we assume that the bond dissociation energies of the dithiol monoradicals are the same, for which it follows that $\Delta H^\circ_{\text{acid}}$ tracks the EAs. From the relative $\Delta H^\circ_{\text{acid}}$ and $\Delta G^\circ_{\text{acid}}$, we compute the relative $\Delta S^\circ_{\text{acid}}$ using a cell temperature of 350° (see text).

(23) Although it is difficult to estimate the entropy of cyclization of the monoanion, there is reasonable agreement in this value for $HS(CH_2)_4S^-$, among three different methods. The experimental entropy of cyclization of the diamine is taken to be −14 eu. The entropy loss for the conversion of

Another difference between the diols and the dithiols is the function of acidity with chain length. The larger diol species are the stronger acids, while among the thiols, $HS(CH_2)_2SH$ is the strongest acid in $\Delta G^\circ_{\text{acid}}$. The function of diol acidity on ring size is attributed largely to the product anion's ability to form a linear hydrogen bond.[18] That is, a small ring is less acidic because of the resultant ring strain in the anion. The different ring-size dependence in the set of dithiols, on the other hand, results from two sources. The first is that the $RS^-{\cdot}HSR$ hydrogen bond is significantly weaker than the $RO^-{\cdot}HOR$ hydrogen bond. Therefore, as a function of ring size, the $T\Delta S^\circ_{\text{acid}}$ term of the free energy is expected to be more important in the sulfur system, than in the oxygen. The second source is that ring strain is less important in the small dithiol anions than in the diol anions. This is possible, given the small natural RSH bond angle of around 92°.[24]

Ab initio calculations (MP2/6-31+G*) of the $HO(CH_2)_2O^-$ and $HS(CH_2)_2S^-$ provide insight into the differential strain between the two types of hydrogen bonds. The OHO angle and the SHS angles are similar, at about 132° and 127°, respectively. Because the $RO^-{\cdot}HOR$ bond is considerably stronger, this represents a greater strain in $HO(CH_2)_2O^-$ than in $HS(CH_2)_2S^-$. Additionally, angle strain is apparent at the alcohol and thiol carbons. The COH angle is calculated to be 96.7°, about 8° from ideal, whereas the CSH angle is calculated to be 89.5°, only about 2.5° from ideal.

To better understand the nature of the hydrogen-bonded interaction in the diol and dithiol anions, we compare the stabilization in the bifunctional anions with that seen in their respective bimolecular complex anions. The complexation energy of $[CH_3O^-{\cdot}HOCH_3]$, for example, is about 29 kcal/mol,[25-27] whereas the acidity enhancement in the relatively strain-free $HO(CH_2)_4OH$ system is only 18 kcal/mol.[18] It appears that there is more stabilization in the bimolecular complex anion than in the bifunctional anion.

The origin of this additional stabilization can be seen by identifying the two main interactions that contribute to the overall binding energy. The first is the charge-dipole interaction, $\Delta H^\circ_{\text{charge-dipole}}$, between the methoxide anion and methanol. The second is the $RO^-{\cdot}HOR$ hydrogen bond, $\Delta H^\circ_{\text{H-bond}}$. The total binding energy of the complex anion, $\Delta H^\circ_{\text{complex}}$, can therefore be defined as the sum of these interactions (eq 9). If $\Delta H^\circ_{\text{charge-dipole}}$ is taken to be the same as that of the $[Cl^-{\cdot}CH_3Cl]$ complex, that is about 13 kcal/mol,[28] the $RO^-{\cdot}HOR$ hydrogen bond provides about 16 kcal/mol extra stabilization in the $[CH_3O^-{\cdot}HOCH_3]$ complex. Ab initio calculations (MP2/6-31+G*) suggest that the difference in binding energy between the hydrogen-bonded and the non-hydrogen-bonded complexes of methanol-methoxide, i.e., $[CH_3O^-{\cdot}HOCH_3]$ and $[CH_3O^-{\cdot}CH_3OH]$, is about 19 kcal/mol.

$$\Delta H^\circ_{\text{complex}} = \Delta H^\circ_{\text{H-bond}} + \Delta H^\circ_{\text{charge-dipole}} \qquad (9)$$

The 11 kcal/mol of stabilization present in $[CH_3O^-{\cdot}HOCH_3]$, but absent in $HO(CH_2)_4O^-$, is on the order of the binding energy in a typical ion-dipole complex. This can be rationalized, at least in part, by the internal solvation of the negative charge in $HO(CH_2)_4O^-$. A more diffuse negative charge would lead to a decrease in the value of the $\Delta H^\circ_{\text{charge-dipole}}$ term in eq 9. The negative charge of the methoxide anion, on the other hand, cannot be internally solvated to the same degree.

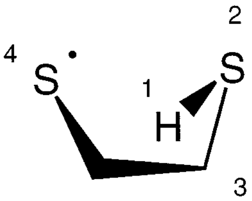

Figure 5. Cyclic conformation of the thiolate monoradical of ethanedithiol, depicting the thiol hydrogen roughly perpendicular to the plane of the ring. The HSCS dihedral angle to which the text refers is the 1,2,3,4 dihedral angle.

A treatment of the $RS^-{\cdot}HSR$ bond in the same fashion as the $RO^-{\cdot}HOR$ cannot be done, because the binding energy of $[CH_3S^-{\cdot}HSCH_3]$ has not been measured. However, by analogy with the oxygen-containing system, we take the "extra" stabilization provided by the $RS^-{\cdot}HSR$ hydrogen bond to be the acidity enhancement (in $\Delta H^\circ_{\text{acid}}$) of $HS(CH_2)_4SH$ over $CH_3(CH_2)_4SH$. That is, the $RO^-{\cdot}HOR$ hydrogen bond is worth about 9 kcal/mol. Indeed, ab initio calculations are consistent with this number, suggesting that the binding energy of $[CH_3S^-{\cdot}HSCH_3]$ is about 7.5 kcal/mol stronger than the non-hydrogen-bonded $[CH_3S^-{\cdot}CH_3SH]$ complex.

Electron Affinities. As in all optical transitions, there is a question as to whether the first observed onset for photodetachment is the energy of the 0-0 transition. That is, are the EAs derived from the dithiol photodetachment spectra the adiabatic EAs? For this to be the case, there must be a reasonably large Franck-Condon factor (FCF) for the 0-0 transition; the geometry change between the ground-state anion and the ground-state radical must be small. We have argued that the ground-state anions are cyclic. Adiabatic electron detachment can therefore only occur if the ground-state radicals are also cyclic.

It is difficult to derive conformational information of the radical's ground-state geometry directly from EAs. However, the bond dissociation energies (BDEs), derived from eq 8, provide some insight into the conformation of the dithiol radicals. If the ground-state conformation of the dithiol radicals were acyclic, we would expect their BDEs to be the same as those of the monothiols (Table 4). We would also expect the BDEs derived from eq 8 to be larger than the monothiol BDEs, due to the introduced strain in the cyclic radicals. Instead, the dithiol BDEs are all between 2.5 and 6.3 kcal/mol weaker than their monothiol counterparts.[29] We therefore believe that the ground-state conformation of the dithiols radicals are cyclic and that our photodetachment spectra give the adiabatic EAs.

Results from ab initio calculations (MP2/6-31+G*) suggest that the radicals have a cyclic ground-state conformation in which the SH bond is roughly perpendicular to the plane of the ring (Figure 5). These calculations are in agreement with higher-level calculations (B3LYP/6-31++G(2d,p) and MP2(FULL)/6-31++G(2d,p)) performed by Tureček, et al.,[30] The cyclic nature of the radicals would therefore tend toward favorable FCFs for the 0-0 transition, but the large difference in the position of the hydrogen between the anion and the radical is a

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n-pentane to cyclopentane is −13.5 eu, and that derived from the experimentally measured $\Delta G^\circ_{\text{acid}}$ and the calculated $\Delta H^\circ_{\text{acid}}$ of $HS(CH_2)_4SH$ is −11 eu. We therefore take the entropy of cyclization of this dithiol anion to be about −13 eu, with an uncertainty of ±2 eu.

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concern. Clary, however, has noted extraordinarily large amplitude motions of non-hydrogen-bonded hydrogen atoms in some hydrogen-bonded systems such as water clusters.[31] Similar large amplitude motions of the hydrogen in the thiol radical could enable the ground-state radical geometry to be accessed by the ground-state anion. It is therefore reasonable that the geometries from quantum calculations are accurate and that our electron photodetachment experiments give adiabatic EAs.

The cyclic conformation of the radicals suggests that there is a stabilizing interaction between the sulfur radical and the thiol group—enough to overcome the added gauche interactions. Calculations show that this is not a hydrogen-bonded interaction. Instead, it appears that there is a stabilizing interaction between the thiol sulfur and the sulfur radical. The thiol hydrogen has been pushed out from between the two sulfurs, and the SS distance is significantly smaller than the sum of their van der Waals radii of 3.7 Å (Table 6). In Tureček's treatment of these species, this interaction is in fact viewed as a disulfide bond in which one of the sulfur atoms is hypervalent.

To model this interaction, ab initio calculations were performed on the $[CH_3S^{\bullet}\cdot S(H)CH_3]$ radical complex. Geometry optimization (MP2/6-31+G*) produced a complex with a binding energy of more than 3 kcal/mol, in relatively good agreement with Tureček's higher-level calculations (8.0 kcal/mol using G2++(MP2)).[30] The $HSCS^{\bullet}$ dihedral for this complex is about 81° (MP2/6-31+G*), which is very similar to that found in the cyclic dithiol radicals (Table 6). Because this orientation is necessary for favorable orbital overlap between the two sulfur atoms, we suggest that there is a modest bonding interaction between the radical sulfur and the thiol sulfur. Confirming this bonding interaction, however, is not trivial. A natural bond order (NBO) analysis (MP2/6-31+G*) failed to show significant bonding character between the sulfur atoms. If this were a hyperconjugative effect, involving a resonance structure with a full S−S bond, then additional spin density would be expected on the thiol hydrogen or the thiol carbon (Figure 6). A lengthening of the thiol SH or SC bond would also be expected. However, no such effects are observed.

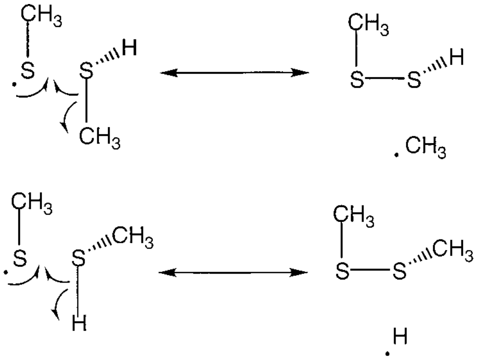

Figure 6. Resonance structures of the $CH_3S^{\bullet}\cdot S(H)CH_3$ radical complex. Possible hyperconjugative effects include lengthening of SC bond and significant spin density on the thiol carbon (top), or lengthening of the SH bond and significant spin density on the thiol hydrogen (bottom).

Conclusions

We have shown that the acidities of dithiols are significantly enhanced relative to those of their monothiol analogues. We have also shown that the EAs of the dithiol radicals are considerably greater than those of the monothiols. We attribute these effects largely to an enhanced stabilization of the dithiol anion, resulting from an intramolecular $RS^{-}\cdot HSR$ hydrogen bond. From comparison with oxygen-containing systems, we estimate that the $RS^{-}\cdot HSR$ hydrogen bond provides up to 9 kcal/mol in "extra" stabilization relative to the non-hydrogen-bonded $[RS^{-}\cdot RSH]$ complex ion.

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