Electron Photodetachment from Mercaptyl Anions (RS^-). Electron Affinities of Mercaptyl Radicals and the S–H Bond Strength in Mercaptans

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Abstract: Cross sections for electron photodetachment have been measured for hydrosulfide, methyl mercaptyl, ethyl mercaptyl, *n*-propyl mercaptyl, isopropyl mercaptyl, *n*-butyl mercaptyl, *tert*-butyl mercaptyl, and *n*-pentyl mercaptyl anions using an ion cyclotron resonance spectrometer in conjunction with either a xenon arc lamp or tunable dye laser. The gas-phase electron affinities (eV) are determined to be EA(HS) = 2.31 ± 0.01, EA(CH_3S) = 1.861 ± 0.004, EA(CD_3S) = 1.858 ± 0.006, EA(C_2H_5S) = 1.953 ± 0.006, EA(n-C_3H_7S) = 2.00 ± 0.02, EA(i-C_3H_7S) = 2.02 ± 0.02, EA(n-C_4H_9S) = 2.03 ± 0.02, EA(t-C_4H_9S) = 2.07 ± 0.02, and EA(n-$C_5H_{11}S$) = 2.09 ± 0.02. These electron affinities, when used with gas-phase acidity data, give the following bond strengths (kcal/mol): DH°(HS–H) = 92.9 ± 2, DH°(CH_3S–H) = 88.1 ± 2, DH°(CD_3S–H) = 88.3 ± 2, DH°(C_2H_5S–H) = 88.6 ± 2, DH°(n-C_3H_7S–H) = 88.7 ± 2, DH°(i-C_3H_7S–H) = 88.4 ± 2, and DH°(t-C_4H_9S–H) = 88.6 ± 2. A perturbation molecular orbital model is employed to explain the mercaptyl radical electron affinity trend, and the gas-phase acidity order $H_2S > CH_3SH$ is discussed.

Introduction

Electron photodetachment spectroscopy is one of the most useful methods available for studying the spectroscopic properties and thermochemistry of negative ions and highly reactive neutrals.[1-5] Experiments of this type provide a means of acquiring molecular electron affinities by determining the minimum energy required to remove an electron from a molecular anion.[6] For large molecules the determination of this threshold energy can, in principle, be complicated by hot-band transitions, rotational broadening, and weak Franck-Condon intensity in the $v'' = 0 \rightarrow v' = 0$ transition. However, recent photodetachment studies on alkoxyl anions[7] and the methyl mercaptyl anion[8] (CH_3S^-) have addressed these problems and led to accurate molecular electron affinities.

In this paper we report the measured photodetachment cross sections for a series of mercaptyl anions (RS^-) where R = H (hydrosulfide), CH_3 (methyl mercaptyl), CD_3 (methyl mercaptyl-d_3), C_2H_5 (ethyl mercaptyl), n-C_3H_7 (*n*-propyl mercaptyl), i-C_3H_7 (isopropyl mercaptyl), n-C_4H_9 (*n*-butyl mercaptyl), t-C_4H_9 (*tert*-butyl mercaptyl), and n-C_5H_{11} (*n*-pentyl mercaptyl). The use of a tunable dye laser as a light source enables us to resolve individual vibronic transitions in the small members of this series[8] and to draw general conclusions concerning the threshold wavelengths associated with the large members of the series. This analysis leads to accurate electron affinities (±0.02 eV) for the mercaptyl radicals and allows us to determine the S–H bond strengths in the parent mercaptans by utilizing gas-phase acidity data. Finally, we compare the electron-affinity trend observed in the mercaptyl radicals with that previously observed in the alkoxyl radicals to determine if the perturbation molecular orbital model used to explain the trend in alkoxyl anion stabilities can be generalized to the sulfur analogues.

Experimental Section

Instrumental. A Varian V-5900 ion cyclotron resonance spectrometer with a modified square cell design[9,10] was used to generate, trap, and detect the mercaptyl anions. Typical cell conditions employed high trapping (1.3–2.5 eV), moderate source drift (0.0–1.5 eV), and low analyzer (<0.3 eV) potentials. Low neutral gas pressures (3–9×10^{-7} Torr) were employed to reduce ion losses.

A 1000-W xenon arc lamp, in conjunction with a grating monochromator, was employed as a light source. A grating blazed at 300 nm was used in the first order (resolution of 14.1 nm, fwhm) for HS^- photodetachment. A visible grating blazed at 600 nm (resolution of 23.8 nm, fwhm) was used for CH_3S^-. The remaining anions were photodetached at a resolution of 13.2 nm (fwhm) using the visible grating. The monochromator was calibrated against a He-Ne laser and Hg arc lamp; an uncertainty of ±0.25 nm was noted at 625 nm. However, a liberal 4-nm uncertainty in the zero grating position was assigned to the wavelength calibration.

The light source used in the high-resolution experiments consisted of a Coherent Radiation Model 590 dye laser pumped with a Coherent Radiation Model CR-12 argon ion laser. The dyes employed in these studies were (Exciton) rhodamine 6G (575–635 nm) and rhodamine 640 (620–685 nm). A typical experiment employed output powers of 50–400 mW and a line width of <0.1 nm. At each wavelength, approximately 4% of the beam was split off and directed into an Eppley thermopile, from which the relative output power was recorded. After each run, the wavelength of the dye laser output was calibrated to ±0.3 nm against a Beck wavelength reversion spectroscope.

Anion Generation. All samples, except H_2S (Matheson) and NF_3, were outgassed by multiple freeze-pump-thaw cycles. The following compounds were used without further purification: CH_3SSCH_3, t-C_4H_9SH, n-$C_5H_{11}SH$ (Eastman Organic), C_2H_5SH, i-C_3H_7SH, n-C_4H_9SH (Aldrich), n-C_3H_7SH (Matheson), and CD_3SSCD_3 (Merck). Methyl mercaptan (J. T. Baker) was fractionally distilled at −94.5 °C before use.

The following reactions, confirmed by double resonance, were used to generate the anions of interest:

$$H_2S + e^- \text{ (1.9 eV)} \rightarrow H + HS^- \tag{1}$$

$$CH_3SSCH_3 + e^- \text{ (0.3 eV)} \rightarrow CH_3S + CH_3S^- \tag{2}$$

$$CD_3SSCD_3 + e^- \text{ (0.3 eV)} \rightarrow CD_3S + CD_3S^- \tag{2a}$$

$$RSH + e^- \text{ (1.9 eV)} \rightarrow H + RS^- \tag{3}$$

$$CH_3SH + F^- \rightarrow HF + CH_3S^- \tag{4}$$

$$RSH + CN^- \rightarrow HCN + RS^- \tag{5}$$

$$RSH + HS^- \rightarrow H_2S + RS^- \tag{6}$$

Fluoride anion was generated from NF_3 by dissociative electron capture (1.7 eV). Cyanide anion was present in the cell from unknown sources. The HS^- in eq 6 is produced from H_2S which is present in the mercaptans as an impurity.

Data Analysis. Techniques for data acquisition and analysis have been previously described.[8]

Results

The relative photodetachment cross sections for the series of mercaptyl anions, RS^-, were measured where R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9, and n-C_5H_{11}. The photodetachment cross sections for HS^- and CH_3S^- are

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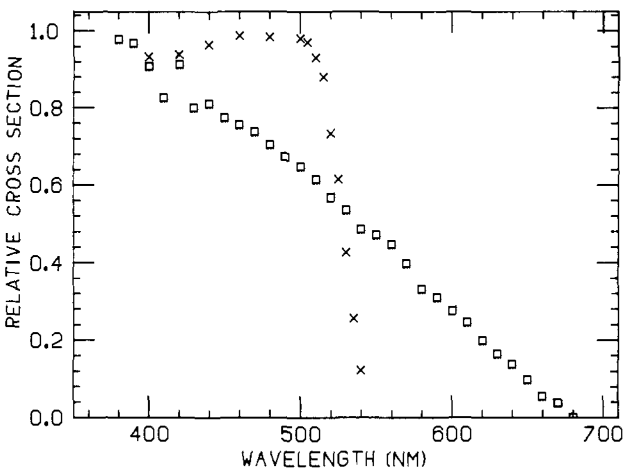

Figure 1. Photodetachment cross sections of HS^- (×) and CH_3S^- (□). The HS^- data represent the average of six runs. Owing to eq 6, the cross section for CH_3S^- photodetachment shows a sharp rise at 540 nm from HS^- photodetachment. This contribution has been subtracted from the CH_3S^- cross section.

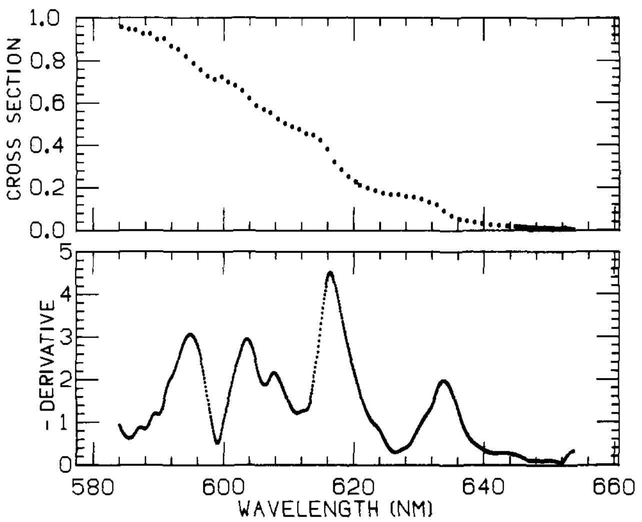

Figure 2. Photodetachment cross section for $C_2H_5S^-$ (top) and differentiated spline of cross section (bottom).

shown in Figure 1. The remainder of the mercaptyl anions showed qualitatively the same behavior as that observed for CH_3S^-, i.e., a linear rise in the cross section with increasing photon energy. Cross sections for the mercaptyl anions represent an average of three to four spectra with maximum ion destruction of approximately 12%. In the threshold region, the minimum observable ion destruction was approximately 0.5%.

As a first approximation to the photodetachment threshold wavelength for the mercaptyl anions, the cross sections have been extrapolated to zero by a linear least-squares analysis. The threshold wavelengths obtained by this procedure (nm) follow: HS^-, 543.1 ± 3.5; CH_3S^-, 677.9 ± 3.0; $C_2H_5S^-$, 647.1 ± 3.0; *n*-$C_3H_7S^-$, 631.4 ± 2.0; *i*-$C_3H_7S^-$, 626.5 ± 2.0; *n*-$C_4H_9S^-$, 624.6 ± 2.0; *t*-$C_4H_9S^-$, 610.8 ± 6.0; *n*-$C_5H_{11}S^-$, 606.5 ± 6.0.

Previous work on alkoxyl anions[7] has shown that we can resolve fine structure in photodetachment spectra corresponding to transitions to excited vibrational states of the product radicals. We have extended this high-resolution work to the mercaptyl anions in order to obtain accurate electron affinities and spectroscopic information on the mercaptyl radicals. Recent results[8] on CH_3S^- and CD_3S^- led to the determination of the spin-orbit splitting in the methyl mercaptyl (thiomethoxyl) radical in addition to electron affinities accurate to ±0.004 and ±0.006 eV, respectively. Also, we have observed rotational fine structure in HS^- photodetachment.[11] The tunable dye laser photodetachment spectrum of $C_2H_5S^-$ is shown in Figure 2. To make any fine structure in the cross section more obvious, we have included the derivative of the cross section which had been fit to a cubic spline function which was chosen such that random noise was removed. Results obtained with the dye laser on the larger homologues of the mercaptyl series did not show any fine structure when points were taken at 1-nm intervals (resolution = 25 cm^{-1}).

Discussion

Threshold Laws. In order to obtain accurate electron affinities from the threshold wavelength data presented above, it is useful to have some theoretical description of the behavior of the photodetachment cross section near threshold. A simple model for the prediction of photodetachment threshold behavior has been previously described[12] and used to analyze photodetachment data.[13] This model treats photodetachment as a one-electron transition from a bound orbital of the anion to a free-electron continuum state. For a given symmetry of the anion bound state, dipole selection rules may be used to determine the lowest order partial wave for the detached electron. For HS^-, the highest occupied molecular orbital (HOMO) is a π orbital which transforms as x or y in the point group of the molecule; this predicts a cross-section behavior of

$$\sigma \propto E_k^{1/2} \qquad (7)$$

where E_k is the energy of the ejected electron. For methyl mercaptyl anion and *tert*-butyl mercaptyl anion (C_{3v} symmetry) the HOMOs have E symmetry which again transforms as x or y leading to the cross-section behavior predicted by eq 7. Likewise, the remainder of the mercaptyl anions should obey eq 7 as should any anion with C_s or lower symmetry.[13b]

The above group theoretical model can be extended to determine the energy dependence of the cross section above threshold. Previously, we have used HOMO initial states found by CNDO/2 to calculate alkoxyl anion photodetachment cross sections and show the relationship between electron density delocalization in the HOMO and threshold shape.[7] In mercaptyl anions, both semiempirical and ab initio calculations show very little delocalization of the HOMO onto the alkyl group. For example, the results of a minimal basis set (STO-3G) ab initio calculation on CH_3S^- give an HOMO with 95% of the electron density on the sulfur atom; similar results were obtained with the larger members of the series. Therefore, the calculated cross sections for HS^-, CH_3S^-, and $C_2H_5S^-$ show almost identical behavior: a steep rise ($\sigma \propto E_k^{1/2}$) which levels off approximately 0.10 eV above threshold. From these results, we conclude that the effect of HOMO delocalization on the calculated cross sections of these anions is very slight. The experimental high-resolution spectra (Figure 2) show that the individual vibronic transitions are in good agreement with these predictions.[8]

Electron Affinities. HS. The photodetachment transition

$$HS^-(^1\Sigma^+) \rightarrow HS(^2\Pi_i) + e^- \qquad (8)$$

will not be complicated by off-diagonal Franck-Condon factors[14] since $R_e(HS^-) \approx R_e(HS)$. However, it is possible to access both the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states of the product neutral so we would expect to observe two transitions separated by[14a] 379.6 cm^{-1}. Recent high-resolution results[11,15] and theoretical considerations[16] indicate that this splitting will be obscured by rotational effects. Even in the absence of rotational broadening, we do not expect to resolve the two transitions at the resolution of the data in Figure 1 (~500 cm^{-1} fwhm).

Table I. Vibrational Frequencies in C_2H_5S

	C_2H_5S,[a] cm^{-1}	C_2H_5Cl,[b] cm^{-1}
C-C-S bend	435	336
C-S stretch	675	676
CH_2 rock	784	785
CH_3 rock	1035	1071, 1080

[a] Error estimated as $\pm 50\ cm^{-1}$. [b] Frequencies taken from ref 18.

Table II. Electron Affinities of the Mercaptyl Radicals

	eV	kcal/mol
HS	2.31 ± 0.01	53.3 ± 0.2
CH_3S	1.861 ± 0.004	42.91 ± 0.09
CD_3S	1.856 ± 0.006	42.80 ± 0.14
C_2H_5S	1.953 ± 0.006	45.04 ± 0.14
n-C_3H_7S	2.00 ± 0.02	46.1 ± 0.5
i-C_3H_7S	2.02 ± 0.02	46.6 ± 0.5
n-C_4H_9S	2.03 ± 0.02	46.8 ± 0.5
t-C_4H_9S	2.07 ± 0.02	47.7 ± 0.5
n-$C_5H_{11}S$	2.09 ± 0.02	48.2 ± 0.5

To extract an accurate electron affinity for HS from the data in Figure 1 we assume that the experimental cross section is due to only the two transitions to the spin-orbit states of the radical. We then construct a spectrum consisting of two theoretical HS^- cross sections separated by 379.6 cm^{-1} and broadened by the appropriate monochromator bandwidth. The threshold energy of this synthetic spectrum is then varied to find the energy which best describes the experimental data.[17] The result of this procedure gives EA(HS) = 2.31 ± 0.01 eV. This electron affinity is in agreement with the photodetachment results of Steiner[14c] (EA = 2.319 ± 0.010 eV) and a recent high-resolution determination[11] (EA = 2.314 ± 0.003 eV). The high-resolution value of Eyler and Atkinson[15] (EA = 2.301 ± 0.001 eV) is slightly lower but is probably in error owing to the neglect of rotational effects[11,16] in the analysis of the data.

CH_3S. Recent high-resolution work[8] has shown that the linear rise of the CH_3S^- photodetachment cross section (Figure 1) is due to the superposition of several vibronic transitions in the threshold region. After making assignments to these transitions and accounting for rotational broadening, this work[8] gave $EA(CH_3S) = 1.861 \pm 0.004$ eV. A similar analysis of high-resolution CD_3S^- photodetachment data gave $EA(CD_3S) = 1.858 \pm 0.006$ eV.

C_2H_5S. As seen in Figure 2, tunable dye laser photodetachment of $C_2H_5S^-$ allows the resolution of individual vibronic transitions in the threshold region. A CNDO/2 optimization of the geometries of $C_2H_5S^-$ and C_2H_5S indicates a minimal geometry difference and suggests that the first strong transition (at 634 nm) corresponds to the adiabatic electron affinity. Therefore, $EA(C_2H_5S) = 1.953 \pm 0.006$ eV. The remainder of the transitions can be associated with vibrational excitation of the ethyl mercaptyl radical. These vibrational assignments are summarized in Table I.

***n*-C_3H_7S, *i*-C_3H_7S, *n*-C_4H_9S, *t*-C_4H_9, and *n*-$C_5H_{11}S$.** The high-resolution results for CH_3S^- and $C_2H_5S^-$ indicate that the linear rise in the low-resolution spectra of the mercaptyl ions is due to the unresolved superposition of several vibronic transitions. Since these transitions cannot be resolved in the homologues larger than $C_2H_5S^-$, the accuracy of the electron affinities which can be obtained from the photodetachment data will be limited.

To analyze this problem, we consider the threshold behavior of a linearly rising cross section which is broadened by a triangular slit function of[19] δ (fwhm). Extrapolation of the linear portion of the cross section to zero will result in the true threshold wavelength, λ_0, while the broadened cross section will reach zero at $\lambda_0 + \delta$. If we employ a least-squares fit to this broadened threshold, the least-squares line will intercept zero cross section between λ_0 and $\lambda_0 + \delta$. Therefore, to a first approximation, we consider the threshold wavelengths determined by linear least squares (see Results section) to be at wavelengths longer than the respective λ_0's, but not longer than $\lambda_0 + \delta$. However, aside from this instrumental broadening, the least-squares thresholds may be pushed to longer wavelengths by hot band transitions. Even if the ions have a vibrational temperature of 300 K, a long-wavelength tail of 15-20 nm can be expected (cf. Figure 2) depending on Franck-Condon factors. This effect could, in principle, push the least-squares threshold to wavelengths greater than $\lambda_0 + \delta$.

Table III. Bond Strengths of Aliphatic Mercaptans

	gas-phase acidity,[a] kcal/mol	RS-H bond strength, kcal/mol
HSH	353.4 ± 2	92.9 ± 2
CH_3SH	359.0 ± 2	88.1 ± 2
CD_3SH	359.3 ± 2[b]	88.3 ± 2
C_2H_5SH	357.4 ± 2	88.6 ± 2
n-C_3H_7SH	356.4 ± 2	88.7 ± 2
i-C_3H_7SH	355.6 ± 2	88.4 ± 2
t-C_4H_9SH	354.7 ± 2	88.6 ± 2

[a] Acidities taken from ref 20. [b] Reference 25b.

To determine the relationship between λ_0 and the least-squares thresholds, we compare the high- and low-resolution data obtained for the ethyl mercaptyl anion. The least-squares threshold (647.1 nm) is at a wavelength 12.3 nm greater than λ_0 (634.8 nm). However, the monochromator bandwidth (δ) for the low-resolution data was 13.2 nm (fwhm). Therefore, subtracting δ from the least-squares threshold gives a threshold wavelength in excellent agreement with the "true" threshold wavelength. If hot bands do not play an important role in the larger homologues of the mercaptyl anion series, we conclude that subtracting δ from the least-squares thresholds will account for the broadening in a systematic way. This conclusion is reasonable in view of previous work on the *tert*-butoxyl anion[7] which suggested that only thermal hot bands were making a contribution to the photodetachment spectrum. A summary of the mercaptyl radical electron affinities produced by this analysis is given in Table II. The estimated error (±0.02 eV) for the larger members of the series reflects the size of the monochromator bandwidth (δ = 0.04 eV fwhm).

Bond Strengths. Electron affinities, when used with gas-phase acidity data, can lead to accurate bond strengths. The utility of this method has been recently demonstrated for acetylene,[17] where traditional bond-strength determinations are difficult owing to the magnitude of the HC_2-H bond dissociation energy. To find a bond strength by this method, we make use of a thermochemical cycle which includes the gas-phase acidity of RS-H, the electron affinity of RS, and the RS-H bond strength, which leads to the relation

$$DH^\circ(RS\text{-}H) = EA(RS) + \Delta H^\circ_{298}(RSH \rightarrow RS^- + H^+) - IP(H) \quad (9)$$

In Table III we present the RS-H bond strengths calculated by this method for those mercaptans with known gas-phase acidities.[20] As was the case for the O-H bond strengths in the aliphatic alcohols,[7] we expect to observe a constant RS-H bond strength in the mercaptans. The bond strengths in Table III are in good agreement with those reported by Shaw[21] but are in disagreement with the bond strengths published by Benson[22,23] [$DH^\circ(CH_3S\text{-}H) = 91.8 \pm 2.0$ kcal/mol and $DH^\circ(RS\text{-}H) = 92 \pm 2$ kcal/mol]. However, the methyl mercaptan bond strength reported by Benson depends upon the heat of formation of the benzyl radical, which recently

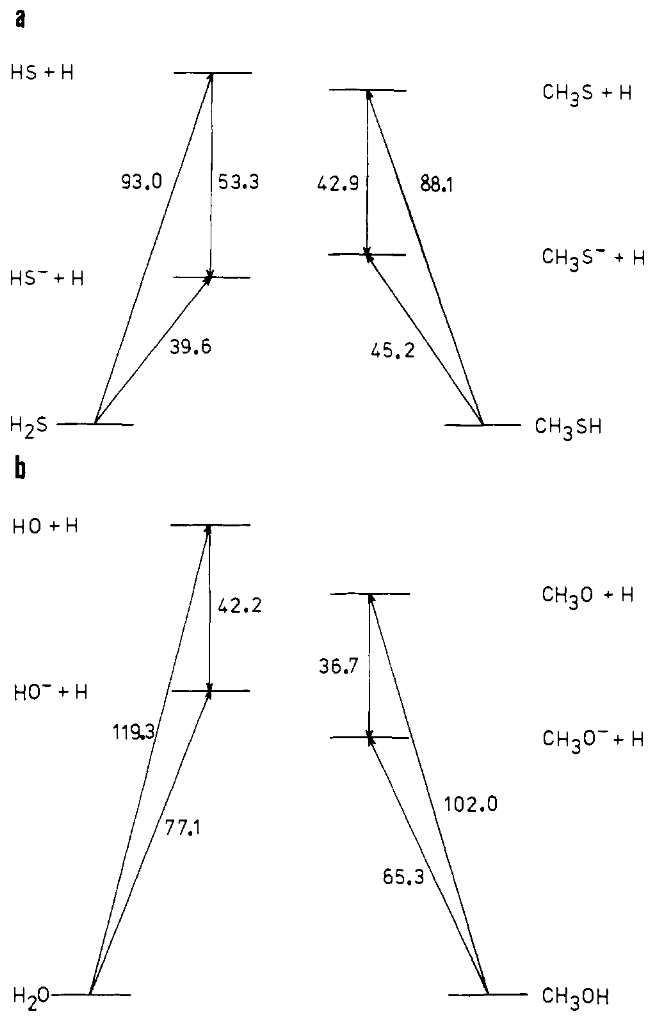

Figure 3. Schematic representation of the relative acidities of (a) CH_3SH/H_2S and (b) CH_3OH/H_2O. All quantities are in kcal/mol.

was determined[24] to be ~3 kcal/mol higher than the previously accepted value. Incorporating this new value [$\Delta H_f°_{298}$(benzyl) = 47.0 ± 1.0 kcal/mol] into Benson's results gives DH°(CH_3S-H) = 89.0 ± 2.0 kcal/mol, which agrees with the value reported here within experimental error. The initial discrepancy points out the potential problems in deriving bond strengths from heats of formation of radicals. Indeed, in cases where electron affinity and gas-phase acidity data are available, we believe that the determination of bond strengths via eq 9 can often provide more accurate values than "direct" determinations.

The measurement[8] of EA(CD_3S) and the known relative acidities[25b] of CH_3SH/CD_3SH

$$CD_3S^- + CH_3SH \rightleftharpoons CD_3SH + CH_3S^- \qquad (10)$$
$$\Delta G° = -0.30 \pm 0.08 \text{ kcal/mol}$$

allow us to calculate the relative S-H bond dissociation energies in CH_3SH and CD_3SH. Using eq 9 with the data in Tables II and III and eq 10 we find that the S-H bond in CH_3SH is 0.19 kcal/mol weaker than that in CD_3SH. We believe that this difference is real since the relative acidities of CH_3SH/CD_3SH were determined by the equilibrium constant in eq 10 ($\Delta G°$ accurate to ±0.08 kcal/mol) and because the electron affinities of CH_3S and CD_3S are accurate to ~0.1 kcal/mol.

The bond-strength ordering DH°(CH_3S-H) < DH°(CD_3S-H) is direct experimental evidence for a β secondary deuterium isotope effect for a system with a free-radical center.[26-28] The mechanism for such an effect, in terms of perturbation molecular orbital theory, is twofold:[29] the half-filled p orbital on sulfur can accept electron density from the filled methyl-group π orbital and donate electron density to the empty methyl-group π^* orbital. The consequence of these interactions is the weakening of the C-H bonds and a predominance of the lighter radical in a hypothetical equilibrium of the type

$$CD_3S\cdot + CH_3SH \rightleftharpoons CD_3SH + CH_3S\cdot \qquad (11)$$

Substituent Effects. As observed for the alkoxyl radicals[7] the electron affinities of the mercaptyl radicals follow the trend EA(R′S) > EA(RS) where R′ is a larger alkyl group than R. Since the simplest picture of the mercaptyl anion is analogous to the alkoxyl anion, i.e., an alkyl group attached to a charge-bearing atom, we expect that we could generalize the perturbation model used to describe alkoxyl anion stability to the mercaptyl anions.

In this model,[7,25] we considered the mechanism for anion stabilization to be due to the interaction of vacant π^* orbitals on the alkyl group and filled 2p orbitals on oxygen.[30] One result of such an interaction was the decrease in the C-H overlap populations in CH_3O^- compared to $CH_3O\cdot$ due to the partial occupation of the alkyl π^* orbital. Thus, we would consider the presence of such an effect in $CH_3S^-/CH_3S\cdot$ to be evidence for an alkyl π^*-sulfur 3p interaction in the mercaptyl system. Ab initio molecular orbital calculations[31] at the 4-31G level show this effect: the C-H bond order in CH_3S^- is 0.350 while that in $CH_3S\cdot$ is 0.360. This theoretical result is consistent with the observation of a secondary isotope effect[25b] which favors the lighter anion in reaction 10 (see above). Therefore, the alkyl π^*-sulfur 3p interaction appears to be occurring in the mercaptyl anions, and we would predict that as the size of the alkyl group is increased there will be more π^* orbitals available for mixing and the interaction will be stronger giving rise to the observed electron-affinity trend.

As in the oxygen compounds, the π^*-p orbital mixing does not appear to be the dominant factor in determining the ionization-potential trend in the neutral mercaptans. The experimental result[32] IP(CH_3SH) > IP(C_2H_5SH) > IP(C_3H_7SH) indicates that the π-p closed-shell repulsive interaction dominates in this case.

There is evidence that the π^*-p orbital interaction in the mercaptyl anions is weaker than that in the alkoxyl anions. For example, in CH_3O^-, the partial occupation of the methyl π^* orbital results in a C-H bond which is calculated[33] to be 0.04 Å longer than the C-H bond in CH_3O. By comparison, calculations on CH_3S^- and CH_3S indicate that, while the C-H overlap population is smaller in the anion, the equilibrium C-H bond lengths in the two species are essentially identical.[8] Also, the analogous reaction to that in eq 10 has $\Delta G°$ = −0.50 ± 0.10 kcal/mol for the oxygen compounds.[28b]

In addition to the stabilizing π^*-p interaction, there is evidence for a competing alkyl-group *destabilizing* effect in the mercaptyl anions. We note in Table III that H_2S has a greater gas-phase acidity than any of the mercaptans studied in this work. By comparison, in the analogous oxygen compounds, even CH_3OH has a greater acidity[20] than H_2O.

To consider what is responsible for this trend, we rewrite eq 9 to give

$$\Delta H°_{298}(RSH \rightarrow RS^- + H^+) = DH°(RS\text{-}H) - EA(RS) + IP(H) \qquad (12)$$

In Figure 3a we arbitrarily set CH_3SH and H_2S at the same energy and decompose the acidity according to eq 12. The same procedure is employed to compare CH_3OH and H_2O in Figure 3b. In the sulfur compounds, the methyl group has a weak stabilizing effect on the CH_3S radical which produces a lower S-H bond strength in CH_3SH than in H_2S (88 vs. 93 kcal/

mol). However, the electron-affinity difference [EA(HS) − EA(CH_3S) = 10.4 kcal/mol] more than compensates for the bond-strength difference and results in H_2S being a stronger acid than CH_3SH. Since the stabilizing effect of the methyl group in CH_3S cannot, by itself, account for the relative acidities of H_2S and CH_3SH, we conclude that there must be a destabilizing effect in CH_3S^- due to the methyl group. The mechanism for such an effect has been previously described[7] and is, most likely, a closed-shell methyl π-sulfur 3p repulsive interaction (inductive effect). By an analogous argument, it appears that this destabilizing interaction is also present in the larger mercaptyl systems since all RSH are weaker acids than H_2S. For the oxygen compounds, on the other hand, the bond-strength difference [DH°(HO-H) = 119.3 kcal/mol[34] vs. DH°(CH_3O-H) = 102.0 kcal/mol[35]] indicates a substantial stabilizing effect of the methyl group in CH_3O. Although we expect a π-p destabilizing interaction in CH_3O^-, it appears not to be strong enough to make CH_3OH a weaker acid than H_2O.

We conclude that, since DH°(RS-H) is independent of R, any stabilizing effect of the alkyl group on the mercaptyl *radicals* is not a function of the size of the alkyl group. Therefore, the electron-affinity trend in the mercaptyls is due to the relative strengths of the π^*-3p stabilizing interaction and π-3p destabilizing interaction in the mercaptyl *anions*.

Summary

Photodetachment spectroscopy has been applied to a series of mercaptyl anions, and electron affinities of the corresponding radicals have been determined from the threshold wavelengths. These electron affinities are used with gas-phase acidity data on mercaptans to derive RS-H bond strengths. The electron-affinity trend in the mercaptyl radicals is explained by a simple perturbation molecular orbital model.

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