Sulfur Compounds, 209[+]
The Gas Phase Acidities of the Sulfanes H_2S_n ($n = 1–4$)

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The gas-phase acidities ΔG_{acid}(298 K) of the sulfanes H_2S_n (n = 1–4) have been calculated by ab initio molecular orbital theory using the G2 and G2(MP2) methods, which were applied to the geometries of lowest energy. The results show that the higher sulfanes are surprisingly strong proton donors. The acidities (in kJ mol^{-1}) are as follows: H_2S (1444), H_2S_2 (1406), H_2S_3 (1370), H_2S_4 (1347). The latter three values may be compared to those of other strong Brønsted acids like gaseous HNO_2 (1396), HCl (1371), and HBr (1332). The monoanions HS_n^- exhibit an interesting bond length distribution as a consequence of the charge delocalization by hyperconjugation, which in turn may be responsible for the high acidities of the sulfanes.

Introduction

The hydrogen polysulfides or sulfanes H_2S_n ($n > 1$) form a long series of homologous chain-like molecules since the number of sulfur atoms can practically assume any value. Only the lower members with $n = 2-6$ have been prepared as pure compounds.[1] Under standard conditions they form colorless to light yellow liquids. H_2S_2, H_2S_3, and H_2S_4 can be distilled in vacuo. However, all members with n values up to 35 have been detected by ^{1}H-NMR spectroscopy in so-called crude sulfane.[2] These higher members of the series are often called polysulfanes.

For a long time these species were considered to be of academic interest only until it was suspected that H_2S_2 is present in certain "sour gases"[3] while the higher members were detected in the elemental sulfur produced from sour gas. Sour gas is a natural gas that contains substantial concentrations of H_2S (up to 50%). It is produced in large quantities, for instance, in Northern Germany, in Alberta (Canada), and in The United States. If the underground reservoir of the gas also contains elemental sulfur, the following equilibrium will be established (Equation 1).

$$H_2S\,(g.) + 1/8\,S_8\,(s.) \rightleftharpoons H_2S_2\,(l.) \qquad (1)$$

The very high pressure in the underground gas bearing deposits shifts this equilibrium to the right. Since H_2S_2 is a volatile compound, the gas seems to transport elemental sulfur when it is produced.[4] However, during production the gas is partly decompressed and cools down resulting in decomposition of any sulfanes H_2S_n with precipitation of elemental sulfur. This process sometimes causes severe plugging of pipes and valves by solid sulfur. Before such a natural gas can be used as a fuel or as a reagent in the chemical industry the H_2S must be extracted by treatment with ethanolamine or similar solvents, which on heating liberate the H_2S again. This almost pure H_2S is then oxidized by the Claus process to elemental sulfur (Equation 2).

$$H_2S + 1/2\ O_2 \rightarrow 1/n\ S_m + H_2O \qquad (2)$$

The sulfur (S_m) produced by this method is obtained in the liquid form. It consists mainly of S_8 molecules but other homocycles, like S_7, S_6, and larger rings, are also present.[5] However, since reaction (2) will never be complete the liquid sulfur produced also contains some H_2S, which is present mainly as a mixture of long-chain polysulfanes H_2S_n.[6]

$$H_2S\,(g.) + x\,S_m\,(l.) \rightleftharpoons H_2S_n\,(l.) \qquad (3)$$

Due to the high toxicity of H_2S and to the danger of explosions, both the polysulfanes and the H_2S must be removed almost quantitatively from the liquid sulfur, a goal that is achieved by purging with air.[7]

The gas phase structures of the first three members of the sulfane series are well-known from either microwave spectra (H_2S_2,[8] H_2S_3[9]) or high-level ab initio MO calculations (H_2S_4[10]). While H_2S_2 adopts a conformation of C_2 symmetry similar to that of H_2O_2, the higher members H_2S_3 and H_2S_4 exist as equilibrium mixtures of several conformational isomers of almost identical energy. All sulfane molecules are characterized by torsional angles at the S−S bonds of 90°(±10°), but these angles may be positive or negative resulting in the aforementioned conformational variety. The signs of the torsional angles define the so-called motif, which characterizes each conformational isomer. For H_2S_2 the two isomers with $\tau = \pm 90°$ are enantiomers. In the case of H_2S_3 the motif may be either + + (symmetry C_2; the enantiomer has the motif − −) or + − (identical to motif − +; both are of C_s symmetry). In the case of H_2S_4 the motif may be + + + (or − − −; these are enantiomers and of C_2 symmetry), + + − (or − − +; C_1) or +

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− + (identical to − + −; C_s); these conformational isomers are shown in Figure 1.

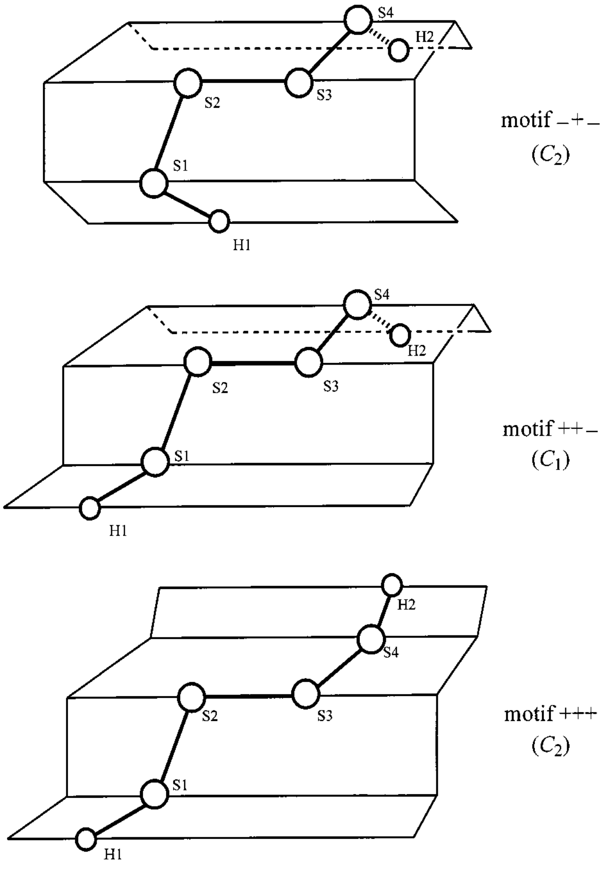

Figure 1. Conformational isomers of H_2S_4 according to a high-level ab initio MO calculation (ref.[10]); the isomer of C_1 symmetry is of lowest energy at 0 K

Hydrogen sulfide, H_2S, is a weak acid in water with pK_a values of 7 and 17 for the first and second dissociation steps (Equations 4, 5).[11]

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad pK_a = 7 \qquad (4)$$

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-} \qquad pK_a = 17 \qquad (5)$$

The corresponding pK_a values of the higher sulfanes are not known with certainty. The only related information available comes from the investigation of aqueous polysulfide solutions, which formally contain the dianions of the polysulfanes. In 1960 Schwarzenbach and Fischer[12] titrated aqueous solutions of pure alkali polysulfides (Na_2S_n and K_2S_n with n = 2−5) with hydrochloric acid in a flow system and measured the pH value of the mixtures obtained. From these data they derived the following pK_a values for the first and second deprotonation reactions of H_2S_4 and H_2S_5.

$$\begin{array}{lcc}
 & pK_a(1) & pK_a(2) \\
H_2S_4 + H_2O \rightleftharpoons H_3O^+ + HS_4^- & 3.8 & \\
HS_4^- + H_2O \rightleftharpoons H_3O^+ + S_4^{2-} & & 6.3 \\
H_2S_5 + H_2O \rightleftharpoons H_3O^+ + HS_5^- & 3.5 & \\
HS_5^- + H_2O \rightleftharpoons H_3O^+ + S_5^{2-} & & 5.7
\end{array}$$

These authors assumed that their starting solutions did not contain any other anions besides HS^-, S_4^{2-}, and S_5^{2-}. Today it is known that this assumption is a crude approximation.[13][14] Therefore, the results obtained by these authors must be considered as approximate. Nevertheless, it became clear that the acidity of the H_2S_n species increases markedly with increasing number of sulfur atoms.

The gas phase acidity of sulfanes is defined as the Gibbs free energy of the dissociation reaction (Equation 6).

$$H_2S_n \rightarrow HS_n^- + H^+ \qquad (6)$$

In the vapor phase the acidity of H_2S has been determined experimentally as ΔG_{acid}(298 K) = 1443±8 kJ mol^{-1}.[15] Similar values[16] have been obtained by ab initio MO calculations.[17,18,19]

In the case of H_2S_2 the mass spectrometric investigation of the reaction of the anion HS_2^- with a number of proton donors of known acidity has resulted in a value of ΔG_{acid} of 1418±13 kJ mol^{-1} at 298 K.[20] No experimental or theoretical data are available for the gas phase acidities of H_2S_3 and H_2S_4.

We have studied the gas phase acidities of H_2S, H_2S_2, H_2S_3, and H_2S_4 by theoretical methods. Such data are of significance for studying the problem of corrosion of steel by sour gas containing these species.

Computational Methods

Ab initio molecular orbital calculations were performed at the G2[21] and G2(MP2)[22] levels of theory using the GAUSSIAN program system.[23] The G2 method essentially implies an energy calculation at the QCISD(T)/6-311+G(3df,2p) level of geometries optimized at the

Table 1. Gibbs free energies (hartrees) at 298 K of the species H_2S_n and HS_n^- (n = 1−4)

System	Symmetry	G2(MP2)	G2
H_2S	C_{2v}	−398.943608	−398.950239
HS^-	$C_{\infty v}$	−398.382201	−398.389429
H_2S_2	C_2	−796.684079	−796.696107
HS_2^-	C_s	−796.137611	−796.150449
H_2S_3	C_2	−1194.434343	−1194.451534
HS_3^-	C_1	−1193.901631	−1193.919657
H_2S_4 (+ − +)	C_2	−1592.186658	−1592.208909
H_2S_4 (+ − −)	C_1	−1592.186948	−1592.209235
HS_4^- (+ −)	C_1	−1591.662292	−1591.685518

Table 2. Bond distances [pm], bond angles [°] and torsion angles [°] of the species H_2S_n and HS_n^- (n = 2−4)

Parameter	H_2S_2 (C_2)	HS_2^- (C_s)	H_2S_3 (C_2)	HS_3^- (C_1)	H_2S_4 (C_2)	H_2S_4 (C_1)	HS_4^- (C_1)
S(1)−S(2)	206.9	210.9	206.8	213.6	206.7	206.5	210.8
S(2)−S(3)			206.8	204.1	206.5	206.7	207.6
S(3)−S(4)					206.7	206.8	204.0
S−H	134.4	135.1	134.5	134.9	134.5	134.5	134.6
S(1)−S(2)−S(3)			107.5	111.1	107.0	107.2	108.2
S(2)−S(3)−S(4)					107.0	106.9	109.9
H(1)−S(1)−S(2)	99.0	102.9	99.0	100.1	98.4	98.4	97.7
H(2)−S(4)−S(3)					98.4	99.0	
H(1)−S(1)−S(2)−H(2)	99.4						
H(1)−S(1)−S(2)−S(3)			85.4	76.1	93.3	89.7	73.4
H(2)−S(4)−S(3)−S(2)			85.4		93.2	−83.6	
S−S−S−S					−82.1	−81.4	−75.7

MP2(full)/6-31G(d) level. Harmonic vibrational wavenumbers were obtained at the HF/6-31G(d) level and were scaled by a factor of 0.8929. The G2(MP2) method is a modified version of G2 but uses the second order Møller−Plesset perturbation theory (MP2) for the basis set extension correction instead of the fourth order (MP4). G2(MP2) is nearly as accurate as the full G2 method at a substantially reduced computational expense. The excellent performance of these methods in predicting gas phase acidities of small molecules is well established.[24]

In order to calculate the atomic charges in the anions HS_n^- (n = 1−4) a natural bond orbital (NBO) analysis was carried out at the MP2(fu)/6-31G(d) level of theory.

For details of the quantum chemical methods see ref.[25] All calculations were carried out on a Cray J90 or on a Linux workstation.

In order to allow for the thermal corrections to the Gibbs free energy of the proton a value of −0.010654 Hartree (−28 kJ mol^{-1}) was used.

Results and Discussion

The Gibbs free energies at 298 K of the species H_2S_n and HS_n^- for n = 1−4 are given in Table 1. In the case of H_2S_3 the most stable conformation with the motif + + (helical chain) was calculated. For H_2S_4 there are two entries: one for the most stable conformer (motif + + −) and one for the helical isomer of C_2 symmetry, which is slightly less stable.

The geometrical parameters of the sulfanes and of their monoanions are presented in Table 2.

The structures of the neutral sulfanes have been discussed several times by previous authors. However, the monoanions HS_n^- with more than one sulfur atom have neither been calculated nor observed before (excepting HS_2^- by mass spectrometry[20]). These species show an interesting bond length pattern in so far as the S−S bond adjacent to the S−H bond is the longest in the anion (210.8−213.6 pm) and much longer than the single bond length as calculated, for example, for H_2S_2 (206.9 pm). On the other hand, the terminal S−S bonds in HS_3^- and HS_4^- are shorter (204 pm) than the single bond while the central S−S bond in HS_4^- is of intermediate length (207.6 pm). Since the torsion angles at all S−S bonds are in the normal range of 73−100° the differing S−S bond lengths must be caused by the delocalization of the additional negative charge within the anion. An explanation is provided by the concept of hyperconjugation between the lone pair in the 3p orbital at an atom S(x) and the antibonding σ* molecular orbital of the bond between atoms S(x + 1) and S(x + 2) (Figure 2).

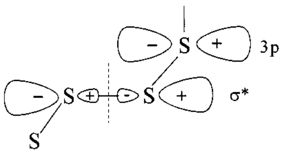

Figure 2. Interaction of the lone pair orbital of sulfur atom S(x) with the empty antibonding σ* molecular orbital of the bond between atoms S(x + 1) and S(x + 2) (hyperconjugation); as a consequence the bond S(x)−S(x + 1) is strengthened while bond S(x + 1)−S(x + 2) is weakened

This type of interaction is well-known in sulfur chemistry.[26] It results in a π bond between atoms S(x) and S(x + 1) (shortened bond) but in a weakening of the bond between atoms S(x + 1) and S(x + 2). In HS_4^- two such interactions have to be assumed since the lone pair at S(4) will be delocalized into the σ* MO between S(3) and S(2) and the lone pair at S(3) will be delocalized into the σ* MO at bond S(2)−S(1). In this way the steady increase in the S−S bond lengths from the terminal S atom towards the SH group can be understood.

Table 3. Natural charges (NBO analysis) of the atoms in the anions HS_n^- (n = 1−4)

n	H	S(1)	S(2)	S(3)	S(ω)
1	0.05322				−1.05322
2	0.07353	−0.30214			−0.77139
3	0.09949	−0.27652	−0.09775		−0.72522
4	0.13539	−0.23008	−0.09715	−0.07954	−0.72863

The calculated NBO atomic charges of the four anions are presented in Table 3. All sulfur atoms are negatively charged and the hydrogen atoms are always positively charged. This positive charge slightly increases with increasing number of sulfur atoms from +0.05 for HS^- through 0.07 in HS_2^- to 0.10 in HS_3^- and 0.14 in HS_4^-. The terminal sulfur atom is always the most negatively charged atom but its charge decreases from −1.05 in HS^- through −0.77 in HS_2^- to −0.73 in HS_3^- and HS_4^-. The second most negatively charged atom is always the one linked to the hydrogen atom; its charge decreases from −0.30 in HS_2^- through −0.28 in HS_3^- to −0.23 in HS_4^-. The other atoms carry a charge of less than −0.1.

In the case of HS_2^- the geometry and the NBO charges were also calculated at the MP2/6-311++G(d,p) level. While the S−S bond length was calculated as 212.6 pm (0.8% longer than above) the charge of the terminal atom was practically identical (−0.766) as that calculated with the smaller basis set (−0.771).

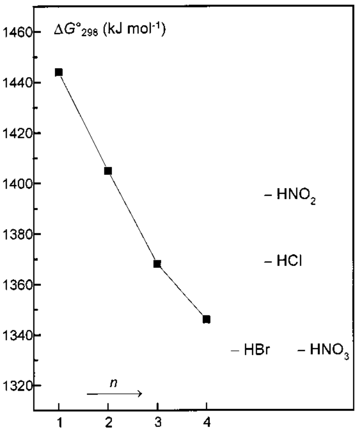

Figure 3. Dependence of the gas phase acidities of the sulfanes H_2S_n (n = 1−4) on the number of sulfur atoms (n) and comparison with the gas phase acidities of HNO_2, HCl, HBr, and HNO_3

The gas phase acidities derived from the data in Table 1 are given in Table 4 and are depicted in Figure 3.

Table 4. Gas phase acidities ΔG°_{298} [kJ mol^{-1}] of the species H_2S_n (n = 1−4) calculated by the G2(MP2) and G2 methods

System	Symmetry	G2(MP2)	G2
H_2S	C_{2v}	1446	1444
H_2S_2	C_2	1407	1405
H_2S_3	C_2	1371	1368
H_2S_4 (+ − +)	C_2	1349	1346
H_2S_4 (+ − −)	C_1	1350	1347

The acidities calculated for H_2S by the G2 and G2(MP2) methods of 1446 and 1444 kJ mol^{-1}, respectively, are in excellent agreement with the experimental value of 1443 kJ mol^{-1} quoted above. This demonstrates once more that these methods yield reliable data for sulfur compounds.

The dissociation of di-, tri-, and tetrasulfane requires much less Gibbs free energy (free enthalpy) than that of H_2S. There is a drop in ΔG_{acid}(298 K) by 40 kJ mol^{-1} from H_2S to H_2S_2 and of 37 kJ mol^{-1} from H_2S_2 to H_2S_3. Even the addition of another sulfur atom, as in H_2S_4, reduces ΔG_{acid}(298 K) by another 22 kJ mol^{-1}. In other words, the gas phase acidities of di-, tri-, and tetrasulfane are much higher than that of H_2S. The value obtained for disulfane (1406 kJ mol^{-1}) is in excellent agreement with the experimental value of 1418 ± 13 kJ mol^{-1}[20] and comparable to the gas phase acidity[27] of nitrous acid HNO_2 (1396 kJ mol^{-1}). Trisulfane (1370 kJ mol^{-1}) is as strong a proton donor as hydrogen chloride HCl (1371 kJ mol^{-1}), while the acidity of tetrasulfane (1347 kJ mol^{-1}) comes close to that of hydrogen bromide HBr (1332 kJ mol^{-1}) and of nitric acid HNO_3 (1330 kJ mol^{-1})! Since the increase in acidity from H_2S_3 to H_2S_4 is still considerable it can be assumed that H_2S_5 and H_2S_6 will be even stronger acids. A rational explanation for the increase of the acidities with increasing number of sulfur atoms can be given on the basis of the charge capacity of the HS_n fragments, which can obviously accommodate an additional electron more easily the more sulfur atoms they contain since the charge is delocalized onto all sulfur atoms, as discussed above. Therefore, the dissociation of H_2S_2 requires much less Gibbs free energy than that of H_2S and the dissociation of H_2S_3 requires less than that of H_2S_2 and so forth. Since the charge delocalization in the monoanions will also occur in aqueous solution, one would expect the acidity of the aqueous sulfanes to be much higher than that of aqueous H_2S, which is in agreement with the measurements by Schwarzenbach and Fischer.

Derivatives of the sulfanes like the sulfane oxides H−S−S−OH[28] and H−S−S(O)−S−H[29] will probably be similarly strong acids in the vapor phase. These molecules have been proposed as intermediates in the aforementioned Claus process.[29]

In the presence of water vapor the high acidity of gaseous H_2S_2, for example, will result in the formation of hydrated ion pairs like $H_3O^+(H_2O)_x \cdot HS_2^-$ as has been demonstrated in the case of other acids.[30] Since the sour gas always contains water vapor, such ion pairs will be formed and these may be the species responsible for the severe corrosion of steel pipes that has been observed in cases where the sour gas deposit contains both elemental sulfur and H_2S resulting in the formation of H_2S_2.

Acknowledgments

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