Gas-Phase Structures and Acidities of the Sulfur Oxoacids $H_2S_nO_6$ ($n = 2-4$) and $H_2S_2O_7$[‡]

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The gas-phase geometries, dipole moments, enthalpies, and Gibbs free energies of dithionic acid $H_2S_2O_6$, trithionic acid $H_2S_3O_6$, tetrathionic acid $H_2S_4O_6$, and disulfuric acid $H_2S_2O_7$ have been determined by ab initio MO calculations at various levels of theory. The most stable conformations of $H_2S_2O_6$ and $H_2S_2O_7$ are of C_2 symmetry, the other two acids are of C_1 symmetry. The gas-phase acidities defined as $\Delta G°_{298}$ of the deprotonation reaction obtained at the {MP2/6-311++ G(3df, 3pd)//MP2/6-31+ G(d) + ZPVE[HF/6-31+ G(d)]} level are as follows [$kJ\cdot mol^{-1}$]: $H_2S_2O_6$ 1180, $H_2S_3O_6$ 1162, $H_2S_4O_6$ 1156, $H_2S_2O_7$ 1171. All four acids are much stronger than fluorosulfuric acid and chlorosulfuric acid in the gas phase. The decomposition of $H_2S_2O_7$ into SO_3 and H_2SO_4 is slightly endothermic and the same holds for the decomposition of $H_2S_3O_6$ into SO_3 and $H_2S_2O_3$, but the reaction of $H_2S_2O_6$ to SO_2 and H_2SO_4 is strongly exothermic. The structures of the monoanions $HS_2O_6^-$, $HS_3O_6^-$, $HS_4O_6^-$, and $HS_2O_7^-$ are characterized by intramolecular hydrogen bonds.

Introduction

Sulfur forms numerous ternary oxoacids $H_2S_mO_n$ where the oxidation numbers of the sulfur atom(s) are between -1 and $+6$.[1] Most of these compounds are unstable at ambient temperatures and have been detected only in aqueous solution (as anions) or in the vapour phase by mass spectrometry. Consequently, the structures and physical properties of almost all sulfur oxoacids have remained unknown for a long time.[2] More recently high-level ab initio MO calculations of a number of these compounds provided, for the first time, the gas-phase structures and, in some cases, the gas-phase acidities of H_2SO,[3] H_2SO_2,[3] H_2SO_3,[3] H_2SO_4,[3,4] H_2SO_5,[5] H_2S_2O,[6] $H_2S_2O_2$,[7] $H_2S_2O_3$,[5] $H_2S_2O_4$,[8] and H_2S_3O.[9] In this work we report on the gas-phase structures and acidities of three disulfonic acids $H_2S_nO_6$ ($n = 2-4$) and of disulfuric acid $H_2S_2O_7$.

Disulfuric acid is an industrial chemical prepared in huge amounts as an intermediate in the production of sulfuric acid from SO_3 and water. The sulfur trioxide from the contact process is absorbed into concentrated sulfuric acid with the formation of polysulfuric acids that are subsequently hydrolysed to give H_2SO_4:[10]

$$x\,SO_3 + H_2SO_4 \rightarrow H_2S_{x+1}O_{3x+4} \quad (1)$$

$$H_2S_{x+1}O_{3x+4} + x\,H_2O \rightarrow (x+1)\,H_2SO_4 \quad (2)$$

If $x = 1$, disulfuric acid is formed. Its structure is unknown but its gas-phase acidity has recently been determined by density functional calculations, at the B3LYP/6-311+ G(d, p) level of theory[11], as $\Delta G°_{298} = 1147\ kJ\cdot mol^{-1}$. This enthalpy applies to the deprotonation reaction resulting in the gaseous monoanion $HS_2O_7^-$. The structure of this anion is known from X-ray crystallography of a number of salts, e.g. $[NO_2][HS_2O_7]$[12] and $[Se_4][HS_2O_7]_2$.[13] The connectivity of the anion is $HO-SO_2-O-SO_2^-$ but the structures of the two salts are characterized by strong intermolecular O−H···O hydrogen bonds.

The disulfonic acids $H_2S_nO_6$ with $n = 2, 3, 4, ...$ occur in various natural habitats[14] as well as in industrial processes.[15] Consequently, they play a role in the global sulfur cycle. However, neither their structures nor their gas-phase acidities are known. The acidity of aqueous dithionic acid $H_2S_2O_6$ has recently been determined as $pK_a = 1.9$,[16] but no data for the other acids are available. The structures of the monoanions $HS_nO_6^-$ are also unknown since no corresponding salts have ever been isolated. However, a number of salts containing the dianions $S_nO_6^{2-}$ have been analyzed by X-ray crystallography.[17] From these studies it follows that the acids should have the connectivities $HO-SO_2-S_{n-2}-SO_2-OH$ ($n = 2-4$). In other words, all these molecules contain at least one sulfur−sulfur bond.

Calculations

Ab initio molecular orbital calculations were performed with CBS-Q,[18] G2(MP2),[19] and an MP2 treatment[20] elaborated in our group. The G2(MP2) method is a modified version of G2[21] and is almost as accurate as the G2 method, but at a substantially reduced computational expense.

The Complete Basis Set (CBS) model CBS-Q utilizes the "dagger" 6-31G† basis set[22] trying to overcome some deficiencies in the standard 6-31G(d) basis set. CBS-Q consists

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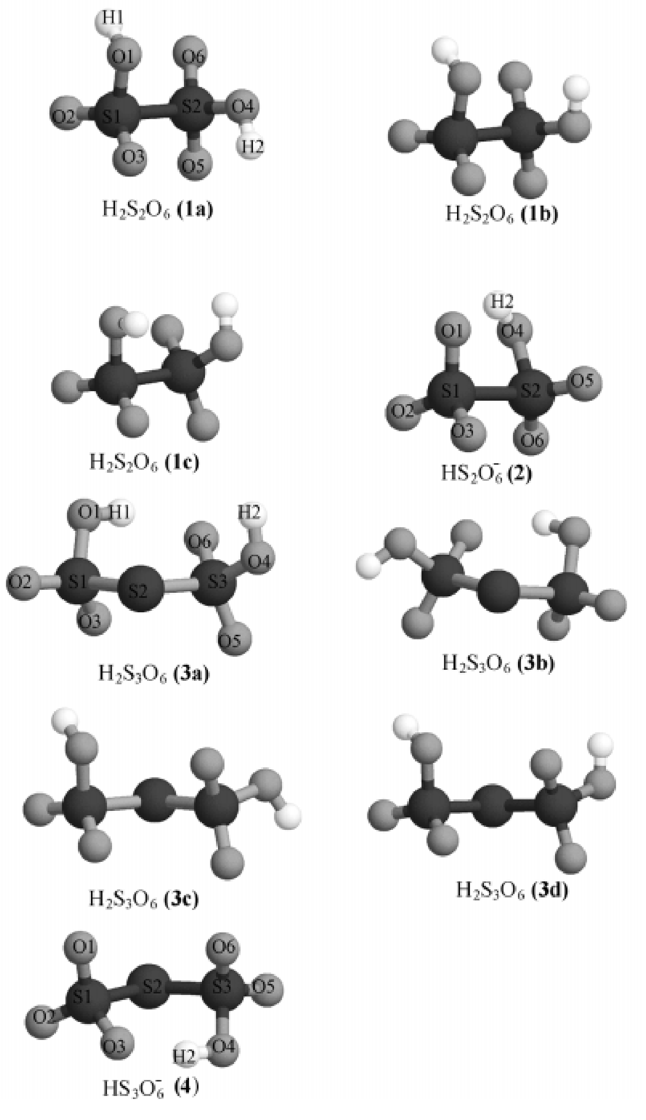
of the following steps: Geometry optimization at the HF/6-31G† level, thermal corrections using wavenumbers obtained at the same level and scaled by a factor of 0.918, reoptimization at the MP2/6-31G† level followed by energy calculations using a large basis set in combination with HF and MP2. The next steps are MP4(sdq) and QCISD(T) calculations applying medium size basis sets. Then the CBS extrapolation is made and empirical corrections are added to obtain the final thermodynamic data.

The excellent performance of both CBS-Q and G2(MP2) in predicting gas-phase acidities of small molecules is well established.[23]

For an effective estimation of Brønsted acidities, a special MP2 treatment is elaborated. This approach consists of MP2/6-31+ G(d) geometry optimizations followed by MP2/6-311++ G(3df, 3pd) energy calculations while the thermal corrections were obtained from HF/6-31+ G(d) wavenumbers scaled by 0.9.



$H_2S_2O_6$ (**1a**) $H_2S_2O_6$ (**1b**)

$H_2S_2O_6$ (**1c**) $HS_2O_6^-$ (**2**)

$H_2S_3O_6$ (**3a**) $H_2S_3O_6$ (**3b**)

$H_2S_3O_6$ (**3c**) $H_2S_3O_6$ (**3d**)

$HS_3O_6^-$ (**4**)

Figure 1. Conformations of the sulfur oxoacids $H_2S_nO_6$ (n = 2, 3) and of their anions as well as numbering of atoms in the most stable conformers

For details of the quantum chemical methods see ref.[24] To allow for the thermal corrections to the Gibbs free energy of the proton a value of −0.010654 hartree (−28 $kJ\cdot mol^{-1}$) was used.

All calculations were carried out on a Cray J90 or on a Linux workstation using the GAUSSIAN program system.[25]

Results and Discussion

Molecular Structures

Dithionic Acid $H_2S_2O_6$

Three conformations of $H_2S_2O_6$ (**1a−1c**) were found to be minima on the potential energy surface (PES) of $(SO_3H)_2$. These structures are shown in Figure 1. Basically, they are rotational isomers which differ mainly by the signs and values of the torsion angles at the three axes H−O−S−S, (H)O−S−S−O(H), and S−S−O−H. The signs of these torsion angles, if one goes from one hydrogen atom to the other, are termed *motifs* which are used in the following tables to identify the different rotamers. In all three $H_2S_2O_6$ molecules the trigonal-pyramidal SO_3 groups are staggered. The conformers **1a** and **1b** are of C_2 symmetry while **1c** is of C_1 symmetry.

The geometrical parameters of the most stable isomer **1a** are listed in Table 1. The enthalpy and Gibbs energy differ-

Table 1. Geometrical parameters of $H_2S_2O_6$ (**1a**, C_2, motif + + +) and $HS_2O_6^-$ (**2**, C_1) calculated at the MP2/6-31+ G(d) level (internuclear distances in pm, bond angles and torsion angles in °). For numbering of atoms see Figure 1

Parameter	**1a** $HO-SO_2-SO_2-OH$	**2** $HO-SO_2-SO_2-O^-$
H1−O1	98.5	−
S1−O1	162.3	149.2
S1−O2	145.6	147.5
S1−O3	145.3	147.4
S1−S2	219.2	226.6
S2−O4	162.3	166.5
H2−O4	98.5	98.9
S2−O5	145.6	147.3
S2−O6	145.3	146.9
O1−H2	296.1	209.6
H1−O1−S1	109.4	−
O1−S1−O2	109.9	115.6
O1−S1−O3	106.1	116.4
O2−S1−O3	125.0	117.3
O1−S1−S2	99.2	96.0
O2−S1−S2	106.9	103.2
O3−S1−S2	106.7	103.9
S1−S2−O4	99.2	96.2
S1−S2−O5	106.9	109.2
S1−S2−O6	106.7	116.0
O4−S2−O5	109.9	108.1
O4−S2−O6	106.1	104.6
O5−S2−O6	125.0	119.7
S2−O4−H2	109.4	104.7
H1−O1−S1−S2	80.8	−
O1−S1−S2−O4	61.7	−40.8
S1−S2−O4−H2	80.8	37.1

Table 2. Relative enthalpies and Gibbs free energies [kJ·mol^{-1}] of the isomers of dithionic acid $H_2S_2O_6$ (**1**)

Species	Motif	Symmetry	MP2/6-31+ G(d)[a]		MP2/6-311++ G(3df, 3pd)[b]		CBS-Q		G2(MP2)	
			$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
1a	+++	C_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1b	−++	C_1	3.5	1.4	6.1	4.1	7.2	5.1	6.4	4.4
1c	−+−	C_2	10.2	9.4	13.2	12.4	14.0	14.0	14.3	13.6

[a] MP2/6-31+ G(d) +ZPVE[HF/6-31+ G(d)]. − [b] MP2/6-311++ G(3df, 3pd)//MP2/6-31+ G(d) +ZPVE[HF/6-31+ G(d)].

ences between the three conformers calculated at various levels of theory are shown in Table 2.

At the highest level, conformer **1b** is 4 kJ·mol^{-1} less stable than **1a**, and **1c** is 13 kJ·mol^{-1} less stable. None of these molecules seem to contain intramolecular hydrogen bonds, since the shortest O···H contacts are 256 pm in **1a**, 252 pm in **1b**, and 246 pm in **1c**. These distances are roughly equivalent to the van der Waals distance between oxygen and hydrogen atoms. For comparison, the length of the weak hydrogen bond in the gaseous water dimer $(H_2O)_2$ is 200 pm.[1a] The calculated bond lengths O−H and S−O as well as the bond angles show the expected values. Interestingly, the S−S bond (219.2 pm) is considerably longer than the single bond length of 205 pm observed in H_2S_2 and in S_8. This fact is in line with the evidence that S−S distances depend on the coordination numbers (CNs) of the two atoms and increase with higher CNs. An even longer S−S bond of 226.6 pm is calculated for the monoanion $HS_2O_6^-$ (**2**) the structural parameters of which are also listed in Table 1. This anion is of C_1 symmetry and, in contrast to **1a**−**1c**, contains an O···H hydrogen bond of length 209.6 pm (O1···H2). For the anion of potassium dithionate ($K_2S_2O_6$) the S−S bond length has been determined by X-ray crystallography as 214 pm (S−O 145 pm, S−S−O 105°, O−S−O 114°).[17]

Trithionic Acid $H_2S_3O_6$

Trithionic acid is also termed as sulfane disulfonic acid since it is formally a derivative of sulfane H_2S as the following formula shows: $S(SO_3H)_2$. Four conformational isomers (rotamers) were located as minima on the PES. The structures of these isomers (**3a**−**3d**) are shown in Figure 1; they are all of symmetry C_1 and differ mainly by the values and signs of the four torsion angles H1−O−S−S, (H1)O−S−S−S, S−S−S−O(H2), and S−S−O−H2. The signs of these angles (*motifs*) are given in Table 3. The most stable species **3a** is characterized by a weak intramolecular hydrogen bond between O6 and H1 (length 201.0 pm). Isomer **3b** is 5 kJ·mol^{-1} less stable than **3a** and also contains a hydrogen bond (O3···H2) with a length of 200.6 pm. In contrast, the shortest intramolecular O···H contacts in **3c** and **3d** are 243 and 248 pm, respectively. These rotamers are 19 and 20 kJ·mol^{-1}, respectively, less stable than **3a** (Gibbs energies; see Table 3).

The geometrical parameters of the stable isomer **3a**, together with those of the monoanion $HS_3O_6^-$ (**4**), are given in Table 4.

While the O−H and S−O bond lengths as well as the bond angles show the normal values, the two S−S bonds of **3a** (212.2 and 214.4 pm) are not equivalent, probably as a result of the hydrogen bond which makes the two SO_3H groups inequivalent. An even larger difference between the two S−S bonds is calculated for the anion **4** (208.3 and 226.3 pm) which is characterized by a strong hydrogen bond that is 172.8 pm (O3···H2; see Figure 1) in length; this is about the same length as observed for the hydrogen bonds in ice I (176 pm).[1a] For the anion of potassium trithionate ($K_2S_3O_6$) the two S−S distances have been determined by X-ray crystallography as 215 pm.[17]

Attempts to optimize the geometry of the zwitterion $HO_3S{-}S^+(H){-}SO_3^-$ at the MP2/6-31+G(d) level of theory led to the dissociation of this tautomer of trithionic acid into thiosulfuric acid, $H_2S_2O_3$, and sulfur trioxide.

Tetrathionic Acid $H_2S_4O_6$

Ten rotational isomers were located as minima on the PES of $H_2S_4O_6$. Seven of these species are of C_1 symmetry and three are of C_2 symmetry; their structures are shown in Figure 2. To characterize these rotamers we once again use the motif which in this case represents the signs of the five torsional angles H1−O−S−S, (H1)O−S−S−S, S−S−S−S, S−S−S−O(H2), and S−S−O−H2. The structures **5a**−**5d** as well as **5f** contain one intramolecular hydrogen bond each which are of the lengths 190.5 pm (**5a**), 187.8

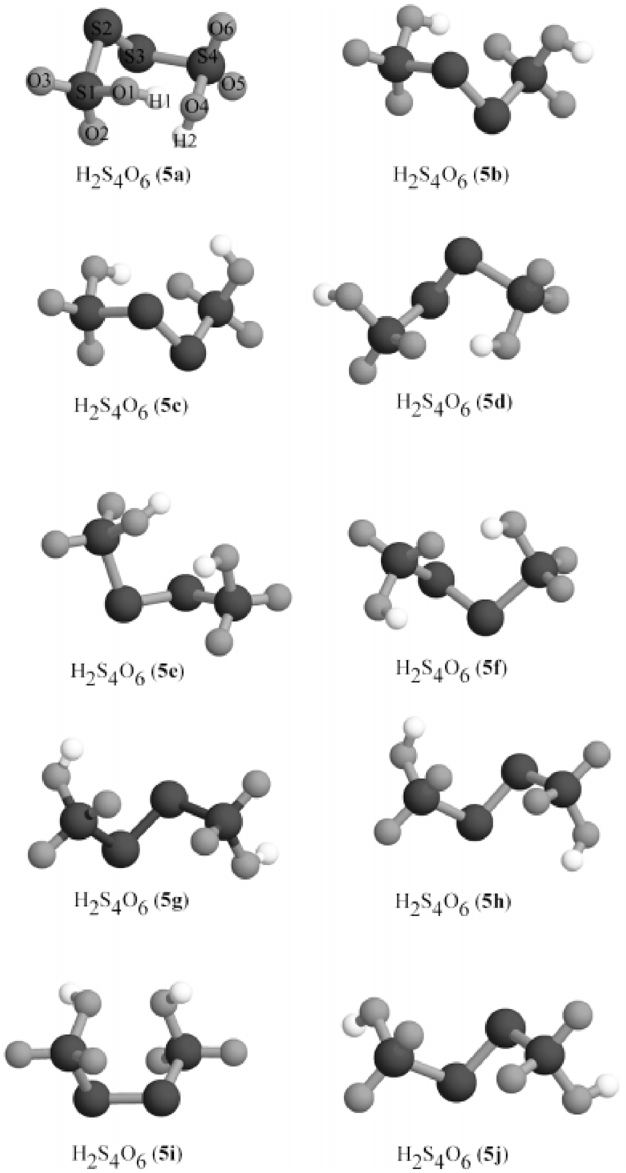
Table 3. Relative enthalpies and Gibbs free energies [kJ·mol^{-1}] of the isomers of trithionic acid $H_2S_3O_6$ (**3**)

Species	Motif	Symmetry	MP2/6-31+ G(d)[a]		MP2/6-311++ G(3df, 3pd)[b]	
			$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
3a	− + − +	C_1	0.0	0.0	0.0	0.0
3b	− + − −	C_1	1.5	5.2	1.7	5.4
3c	− − + +	C_1	20.2	20.4	19.0	19.2
3d	+ − + +	C_1	20.6	21.1	19.2	19.8

[a] MP2/6-31+ G(d) +ZPVE[HF/6-31+ G(d)]. − [b] MP2/6-311++ G(3df, 3pd)//MP2/6-31+ G(d) +ZPVE[HF/6-31+ G(d)].

Table 4. Geometrical parameters of $H_2S_3O_6$ (**3a**, C_1, motif $- + - +$) and $HS_3O_6^-$ (**4**, C_1) calculated at the MP2/6-31+ G(d) level (internuclear distances in pm, bond angles and torsion angles in °). For numbering of atoms see Figure 1

Parameter	**3a** HO−SO₂−S−SO₂−OH	**4** HO−SO₂−S−SO₂−O⁻
H1−O1	99.1	−
S1−O1	161.2	147.0
S1−O2	144.8	147.4
S1−O3	145.4	149.6
S1−S2	214.4	226.3
S2−S3	212.2	208.3
S3−O4	162.4	162.0
H2−O4	98.4	100.6
S3−O5	144.5	146.3
S3−O6	146.9	146.3
O6···H1	201.0	
O3···H2		172.8
H1−O1−S1	108.0	−
O1−S1−O2	106.0	117.2
O1−S1−O3	109.1	114.8
O2−S1−O3	125.0	114.9
O1−S1−S2	103.0	106.1
O2−S1−S2	103.9	98.7
O3−S1−S2	107.6	101.9
S1−S2−S3	96.9	100.5
S2−S3−O4	98.1	103.2
S2−S3−O5	111.6	107.2
S2−S3−O6	107.4	110.5
O4−S3−O5	105.9	105.3
O4−S3−O6	107.9	108.5
O5−S3−O6	123.0	120.6
S3−O4−H2	109.4	106.3
H1−O1−S1−S2	−72.0	−
O1−S1−S2−S3	69.1	−81.8
S1−S2−S3−O4	−153.1	−59.5
S2−S3−O4−H2	83.2	53.2



$H_2S_4O_6$ (**5a**) $H_2S_4O_6$ (**5b**) $H_2S_4O_6$ (**5c**) $H_2S_4O_6$ (**5d**) $H_2S_4O_6$ (**5e**) $H_2S_4O_6$ (**5f**) $H_2S_4O_6$ (**5g**) $H_2S_4O_6$ (**5h**) $H_2S_4O_6$ (**5i**) $H_2S_4O_6$ (**5j**)

Figure 2. Conformations of the sulfur oxoacid $H_2S_4O_6$ as well as numbering of atoms in the most stable conformers

pm (**5b**), 188.6 pm (**5c**), 201.2 pm (**5d**), and 191.5 pm (**5f**). For the other five species the shortest O···H contacts were calculated as 241 pm or longer.

At the highest level of theory employed, the three species **5a**−**5c** practically have identical Gibbs energies (see Table 5) while the other molecules are 8−22 $kJ \cdot mol^{-1}$ less stable.

The geometrical parameters of the most stable species **5a** are given in Table 6. The most interesting data are those of the S−S bonds. As expected, the central S−S bond (202.7 pm) is considerably shorter than the other two (212.9 and 216.5 pm) as a result of the higher CNs within the sulfonic groups. The S−S−S−S torsion angle of 80.9° is quite normal for sulfur chains.[26]

For the monoanion $HS_4O_6^-$, three rotational isomers of C_1 symmetry (**6a**−**6c**) were found as local minima on the PES. Their structures are shown in Figure 3 and their relative enthalpies are given in Table 7.

The more stable structures **6a** and **6b** contain hydrogen bonds of length 162.0 and 159.8 pm, respectively, while no such bond is present in isomer **6c**. The geometrical parameters of **6a** are given in Table 6. The lengths of the S−S bonds show an interesting pattern: while the central bond (203.6 pm) has changed little compared to the free acid **5a** (202.7 pm), the bond in the $S-SO_3H$ group (213.8 pm) has shortened by 2.7 pm and the bond $S-SO_3^-$ (220.8 pm) has increased in length by 8 pm on deprotonation. For the anion of potassium tetrathionate the S−S bond lengths have been determined by X-ray crystallography as 202 pm (central bond) and 212 pm (terminal bonds); the S−S−S bond angles were found as 102° and 104°.[17]

Disulfuric Acid $H_2S_2O_7$

The structure of the disulfuric acid molecule **7** is of C_2 symmetry as shown in Figure 3. Only one minimum was located on the PES. This structure is stabilized by two hydrogen bonds of length 204.3 pm. The geometrical parameters of $H_2S_2O_7$ **7** as well as of its monoanion **8** are given in Table 8. The anion is characterized by a strong but asymmetric hydrogen bond of length 178.6 pm (symmetry C_1;

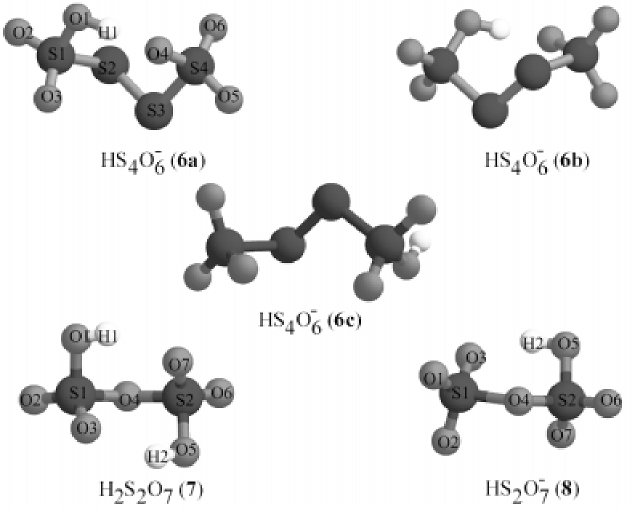
Table 5. Relative enthalpies and Gibbs free energies [kJ·mol^{-1}] of the isomers of tetrathionic acid $H_2S_4O_6$ (**5**)

Species	Motif	Symmetry	MP2/6-31+ G(d)[a]		MP2/6-311++ G(3df, 3pd)[b]	
			$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
5a	− + − + +	C_1	0	0	5	0
5b	+ − + + +	C_1	5	10	0	1
5c	− + + − +	C_1	5	11	1	2
5d	− − + + +	C_1	15	17	11	8
5e	+ − + − +	C_2	17	15	16	9
5f	+ − − + +	C_1	12	20	8	11
5g	− + + + +	C_1	28	22	24	13
5h	− + + + −	C_2	28	22	24	13
5i	+ + − + +	C_2	19	19	18	14
5j	+ + + + +	C_1	30	31	26	22

[a] MP2/6-31+ G(d) +ZPVE[HF/6-31+ G(d)]. − [b] MP2/6-311++ G(3df, 3pd)//MP2/6-31+ G(d) +ZPVE[HF/6-31+ G(d)].

Table 6. Geometrical parameters of the $H_2S_4O_6$ (**5a**, C_1, motif − + − + +) and $HS_4O_6^-$ (**6a**, C_1, motif − + − +) calculated at the MP2/6-31+G(d) level (internuclear distances in pm, bond angles and torsion angles in °). For numbering of atoms see Figure 2

Parameter	**5a** HO−SO$_2$−S−S−SO$_2$−OH	**6a** HO−SO$_2$−S−S−SO$_2$−O$^-$
H1−O1	99.2	102.3
S1−O1	161.4	160.0
S1−O2	146.2	146.4
S1−O3	145.0	146.2
S1−S2	216.5	213.8
S2−S3	202.7	203.6
S3−S4	212.9	220.8
S4−O4	166.0	150.4
H2−O4	98.7	−
S4−O5	145.6	147.5
S4−O6	145.0	147.4
O4···H1	190.5	162.0
H1−O1−S1	108.0	109.7
O1−S1−O2	108.9	105.8
O1−S1−O3	105.7	109.9
O2−S1−O3	124.3	121.5
O1−S1−S2	101.4	103.4
O2−S1−S2	108.3	104.9
O3−S1−S2	105.9	109.8
S1−S2−S3	102.4	103.9
S2−S3−S4	101.6	101.8
S3−S4−O4	100.6	102.3
S3−S4−O5	104.7	100.2
S3−S4−O6	112.1	106.2
O4−S4−O5	108.5	114.0
O4−S4−O6	102.8	113.6
O5−S4−O6	125.4	117.9
S4−O4−H2	109.4	−
H1−O1−S1−S2	−69.5	−56.6
O1−S1−S2−S3	101.7	83.3
S1−S2−S3−S4	−80.9	−80.6
S2−S3−S4−O4	64.8	66.4
S3−S4−O4−H2	66.0	−



$HS_4O_6^-$ (**6a**) $HS_4O_6^-$ (**6b**) $HS_4O_6^-$ (**6c**) $H_2S_2O_7$ (**7**) $HS_2O_7^-$ (**8**)

Figure 3. Conformations of the anion $HS_4O_6^-$, the acid $H_2S_2O_7$ and its anion $HS_2O_7^-$, as well as numbering of atoms in the most stable conformers

Figure 3). The calculated anion structure is in reasonable agreement with the X-ray structure of [Se$_4$][HS$_2$O$_7$]$_2$ if one takes into account the fact that there are interanionic hydrogen bonds in the solid-state structure which are absent in the free ion. The S−O−S bridge is asymmetric with bond lengths of 160.2 pm and 184.1 pm and a bond angle of 120.5°; the experimental values are: 160(2) pm, 167(2) pm, 123(1)°.[13]

Acidities

The gas-phase acidities of the four acids investigated in this work are listed in Table 9. Only the most stable conformers were used. The acidities are defined as the enthalpies or Gibbs energies of the deprotonation reaction at 298 K. As a reference the acidity of gaseous sulfuric acid is used which has been calculated at the G2 level of theory[3] as $\Delta H°_{298} = 1305$ and $\Delta G°_{298} = 1268$ kJ·mol^{-1} in excellent agreement with experimental studies. Acids that have a higher acidity than sulfuric acid are termed superacids. The results in Table 9 demonstrate that both disulfuric acid and all the polythionic acids, including dithionic acid, are superacids that are stronger proton donors than HSO_3F, HSO_3Cl and $HClO_4$. They are surpassed only by a few extremely superacidic molecules like $HSO_3F·SO_3$, $H_2S_3O_{10}$, and $HSO_3F·SbF_5$.[11] Figure 4 shows a comparison of the acidities of sulfur-containing superacids.

Table 7. Relative enthalpies and Gibbs free energies [kJ·mol^{-1}] of the isomers of the anions $HS_4O_6^-$ (**6**)

Species	Motif	Symmetry	MP2/6-31+ G(d)[a]		MP2/6-311++ G(3df, 3pd)[b]	
			ΔH°_{298}	ΔG°_{298}	ΔH°_{298}	ΔG°_{298}
6a	− + − +	C_1	0.0	0.0	0.0	0.0
6b	+ + − +	C_1	10.5	10.6	8.4	8.4
6c	+ + + +	C_1	71.7	63.5	74.4	66.3

[a] MP2/6-31+ G(d) +ZPVE[HF/6-31+ G(d)]. − [b] MP2/6-311++ G(3df, 3pd)//MP2/6-31+ G(d) +ZPVE[HF/6-31+ G(d)].

Table 8. Geometrical parameters of $H_2S_2O_7$ (**7**, C_2) and $HS_2O_7^-$ (**8**, C_1) calculated at the MP2/6-31+ G(d) level (internuclear distances in pm, bond angles and torsion angles in °). For numbering of atoms see Figure 3

Parameter	**7** HO−SO_2−O−SO_2−OH	**8** HO−SO_2−O−SO_2−O$^-$
H1−O1	99.2	−
S1−O1	159.7	146.5
S1−O2	143.7	146.4
S1−O3	146.1	149.0
S1−O4	168.5	184.1
S2−O4	168.5	160.2
S2−O5	159.7	162.4
H2−O5	99.2	100.0
S2−O6	143.7	145.6
S2−O7	146.1	146.0
O3···H2	204.3	178.6
H1−O1−S1	108.4	−
O1−S1−O2	107.6	117.9
O1−S1−O3	110.1	115.9
O2−S1−O3	124.1	115.8
O1−S1−O4	101.5	98.1
O2−S1−O4	105.5	103.8
O3−S1−O4	105.6	100.6
S1−O4−S2	117.0	120.5
O4−S2−O5	101.5	102.0
S2−O5−H2	108.4	105.0
O4−S2−O6	105.5	107.3
O4−S2−O7	105.6	110.7
H1−O1−S1−O4	−63.1	−
O1−S1−O4−S2	73.7	−155.5
S1−O4−S2−O5	73.7	63.8
O4−S2−O5−H2	−63.1	−49.4

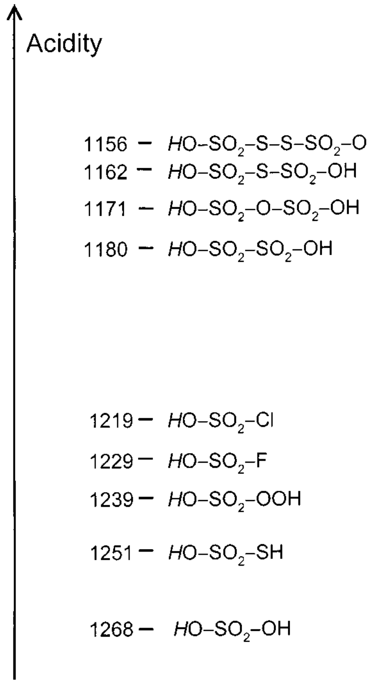


Figure 4. Gas phase acidities of the sulfur oxoacids $H_2S_nO_6$ (n = 2, 3, 4) and $H_2S_2O_7$ compared to the acidities of other superacidic proton donors. The values of ΔG°_{298} [kJ·mol^{-1}] for the deprotonation reaction are given

It is obvious from this data that the acidity increases with increasing anion size. This may be rationalized by the better stabilization of the excess negative charge and this stabilization should be easier the larger the anion becomes with regard to the total number of electrons.[27] Similar observations have been made before with peroxosulfuric acid and chlorosulfuric acid.[5]

According to our previous experience[5] the acidities calculated at the CBS-Q level agree with those from the G2(MP2) level within 10 kJ·mol^{-1}. Therefore, we consider our acidity of disulfuric acid of 1169 kJ·mol^{-1} (ΔG°_{298}) as

Table 9. Gas phase acidities [kJ·mol^{-1}] and dipole moments [Debye] of the polythionic acids HO−SO_2−S_n−SO_2−OH (n = 0, 1, 2) (**1**, **3**, **5**) and disulfuric acid HO−SO_2−O−SO_2−OH (**7**)

Species	MP2		CBS-Q		G2(MP2)		MP2[a]
	ΔH°_{298}	ΔG°_{298}	ΔH°_{298}	ΔG°_{298}	ΔH°_{298}	ΔG°_{298}	μ
HO−SO_2−SO_2−OH (**1a**)	1214	1180	1204	1171	1215	1182	2.66
HO−SO_2−S−SO_2−OH (**3a**)	1188	1162					5.04
HO−SO_2−S−S−SO_2−OH (**5a**)	1182	1156					1.48
HO−SO_2−O−SO_2−OH (**7**)	1205	1171	1203	1169			2.28

[a] MP2/6-311++ G(3df, 3pd)//MP2/6-31+ G(d).

more reliable than the literature value[11] of 1147 kJ·mol^{-1} obtained by B3LYP calculations. It has been shown[28] that B3LYP provides accurate Brønsted acidities only in combination with large basis sets.

Stabilities

Since heating can easily decompose all the acids investigated in this work, we have calculated the Gibbs energies ($\Delta G°_{298}$) of some typical dissociation reactions. The data in Table 10 show that the decomposition of dithionic acid to sulfuric acid and sulfur dioxide is exothermic. This reaction has in fact been observed in aqueous solution.[29] The decomposition of trithionic acid into sulfur trioxide and thiosulfuric acid is slightly endothermic. This also holds for the decomposition of disulfuric acid into sulfuric acid and SO_3. However, in the case of $H_2S_3O_6$ other redox reactions are also possible.

Table 10. Stabilities ($\Delta G°_{298}$) of the polythionic acids $HO-SO_2-S_n-SO_2-OH$ (n = 0, 1) (**1**, **3**) and disulfuric acid (**7**) $HO-SO_2-O-SO_2-OH$ with respect to the decomposition into lower acids and SO_2 or SO_3

Decomposition	MP2[a]	CBS-Q	G2(MP2)
$H_2S_2O_6$ (**1a**) → H_2SO_4 + SO_2	−121	−116	−122
$H_2S_3O_6$ (**3a**) → $H_2S_2O_3$ + SO_3	21		
$H_2S_2O_7$ (**7**) → H_2SO_4 + SO_3	15	32	

[a] MP2/6-311++ G(3df, 3pd)//MP2/6-31+ G(d) + ZPVE[HF/6-31+ G(d)].

The calculated enthalpies $H°$ and Gibbs energies $G°$ of the 24 conformers corresponding to the four sulfur oxoacids and their anions are given in Table 11S while Table 12S contains the data from which the stabilities have been determined. These Tables are available as Supplementary Information (see also first page of this article).

Conclusions

The four sulfur oxo acids $HO-SO_2-SO_2-OH$ (**1**), $HO-SO_2-S-SO_2-OH$ (**3**), $HO-SO_2-S-S-SO_2-OH$ (**5**), and $HO-SO_2-O-SO_2-OH$ (**7**), as well as their monoanions, were investigated by ab initio MO calculations at various levels to obtain their structures as well as their enthalpies and Gibbs energies from which the thermodynamics of the deprotonation reactions, at 298 K, were calculated. In most cases several different conformations were located as minima on the PES. The monoanions and some of the acid molecules are stabilized by intramolecular hydrogen bonds. The sulfonic acid groups are always staggered to each other. The S−S bonds are scattered over the range 202.7−226.6 pm with long distances occurring between sulfur atoms of CN = 4 and short distances with sulfur of CN = 2. All other structural parameters show normal values. Unexpectedly, the gas-phase acidities of these acids are much higher than that of sulfuric acid. Therefore, these species may be termed as superacids. The decomposition of dithionic acid **1** to sulfur dioxide and sulfuric acid is strongly exothermic. Tetrathionic acid is even stronger than disulfuric acid.

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