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Geometries, Acidities, and Dissociation Reactions of the Gaseous Superacids $H_2S_2O_3$, H_2SO_5, HSO_3F, and HSO_3Cl

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Dedicated to Professor J. Gijs Kuenen, Delft, on the occasion of his 60th birthday

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The gas-phase geometries, dipole moments, enthalpies, and Gibbs free energies of thiosulfuric acid $H_2S_2O_3$, peroxosulfuric acid H_2SO_5, fluorosulfuric acid HSO_3F, and chlorosulfuric acid HSO_3Cl as well as of their monoanions have been determined by ab initio MO calculations at various levels of theory. The most stable conformations of the four acid molecules are all of C_1 symmetry. The acidities, defined as $\Delta G°_{298}$ of the deprotonation reaction, obtained by the G2 method are as follows [kJ mol^{-1}]: *H*O–SO$_2$–SH 1251 and HO–SO$_2$–S*H* 1276, *H*O–SO(=S)–OH 1241, *H*O–SO$_2$–OOH 1239, *H*O–SO$_2$–F 1229, *H*O–SO$_2$–Cl 1219. Good agreement of the calculated acidities of HSO_3F and HSO_3Cl is observed with the experimental gas-phase acidities, which are the only experimental values available. The OH acidities of all five species are higher than that of sulfuric acid (1268 kJ mol^{-1}). Therefore, these compounds may be termed as superacids. In contrast to the liquid state, chlorosulfuric acid is a stronger proton donor than fluorosulfuric acid in the gas phase. The dissociation of the acid molecules HSO_3X (X = SH, OOH, F, Cl) into SO_3 and HX is endothermic and endergonic in all cases. The same holds for the dissociation of the anions SO_3X^- into SO_3 and X^-. From these dissociation enthalpies and literature data the enthalpies of formation of the mentioned sulfonic acids and their anions are calculated.

Introduction

According to a suggestion by R. J. Gillespie[1] superacids are those nonaqueous systems which are of higher acidity than pure sulfuric acid as far as Brønsted acids are concerned. Using the Hammett acidity scale[2] 100% H_2SO_4 has the acidity $H_o = -12$. Well-known examples of superacids (H_o in parentheses) are disulfuric acid $H_2S_2O_7$ (−14.8), chlorosulfuric acid HSO_3Cl (−13.8), and fluorosulfuric acid HSO_3F (−15.1). A 1:9 mixture of HSO_3F and SbF_5 exhibits the highest known acidity ($H_o = -27$).[3,4] This mixture is called *magic acid* since it protonates and consequently dissolves even saturated hydrocarbons.

The concept of superacids can also be applied to gaseous Brønsted acids again using the acidity of sulfuric acid as a reference value. The acidity of gaseous H_2SO_4 may be defined as the Gibbs free energy change for the deprotonation reaction [Equation (1)].

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \qquad (1)$$

It is obvious that this enthalpy change will always be strongly endothermic (> 1200 kJ mol^{-1}). For example, $\Delta G°_{298}$ [Equation (1)] was determined experimentally[5] as 1265±10 kJ mol^{-1} while 1268 kJ mol^{-1} was calculated by high-level ab initio MO methods.[6] As part of a systematic study of the acidities of the sulfur oxo acids we report here a detailed study of the geometries and acidities of the gaseous compounds $H_2S_2O_3$, H_2SO_5, HSO_3F, and HSO_3Cl which are of general formula HO−SO$_2$−X (X = SH, OOH, F, Cl).

To obtain accurate gas-phase acidities for the above-mentioned species *at identical levels of theory* we have calculated the energies of these acids HA and their corresponding anions A^- at the G2 level of theory, which has been shown to provide reliable acidity data for sulfur compounds, agreeing with the best experimental values within ca. 8 kJ mol^{-1}.[7] In addition, the CBS-Q and G2(MP2) methods were applied to all species since these more economical levels of theory will be used in an upcoming publication on several larger sulfur oxo acid molecules like polythionic acids, $H_2S_nO_6$, and polysulfuric acids, $H_2S_nO_{3n+1}$ ($n > 1$). In this way a comparison of data for different acids as well as a discussion of trends in acidities as a function of molecular structure will be possible. Since the gas-phase acidity has been defined in the literature as either $\Delta G°_{298}$ or $\Delta H°_{298}$ of the deprotonation reaction we also calculated both values for the systems investigated.

Calculations

Ab initio molecular orbital calculations were performed at the CBS-Q,[8] G2(MP2),[9] and G2[10] levels of theory us-

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ing the GAUSSIAN program system.[11] The G2 method essentially implies an energy calculation at the QCISD(T)/6-311+G(3df,2p) level using geometries optimized at the MP2(fu)/6-31G(d) level. Harmonic vibrational wavenumbers were obtained at the HF/6-31G(d) level and were scaled by a factor of 0.893. 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 rather than the fourth order (MP4). G2(MP2) is almost as accurate as the G2 method but at a substantially reduced computational expense.

Complete Basis Set (CBS) model chemistries utilize the "dagger" 6-31G† basis set[12] in trying to overcome some deficiencies in the standard 6-31G(d) basis set. While the latter arbitrarily assigns an exponent of 0.8 to all four elements, the former uses the exponents from the d functions in the 6-311G basis set. The CBS models[10] use the asymptotic convergence of pair natural orbital expansion to extrapolate from calculations using a finite basis set to the estimated CBS limit. The CBS method consists 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 all of these methods in predicting gas-phase acidities of small molecules is well established.[13]

To obtain reliable geometries of the most stable isomers complete optimizations as well as wavenumber calculations were performed at the MP2/6-311++G(d,p) level.

For details of the quantum chemical methods see ref.[14] All calculations were carried out with a Cray J90 or a Linux workstation. A list of the absolute enthalpies H°_{298} and Gibbs free energies G°_{298} of all species used in this work at the levels CBS-Q, G2(MP2) and G2 is given in the Appendix (Table 12). 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

Molecular Structures

Thiosulfuric Acid $H_2S_2O_3$

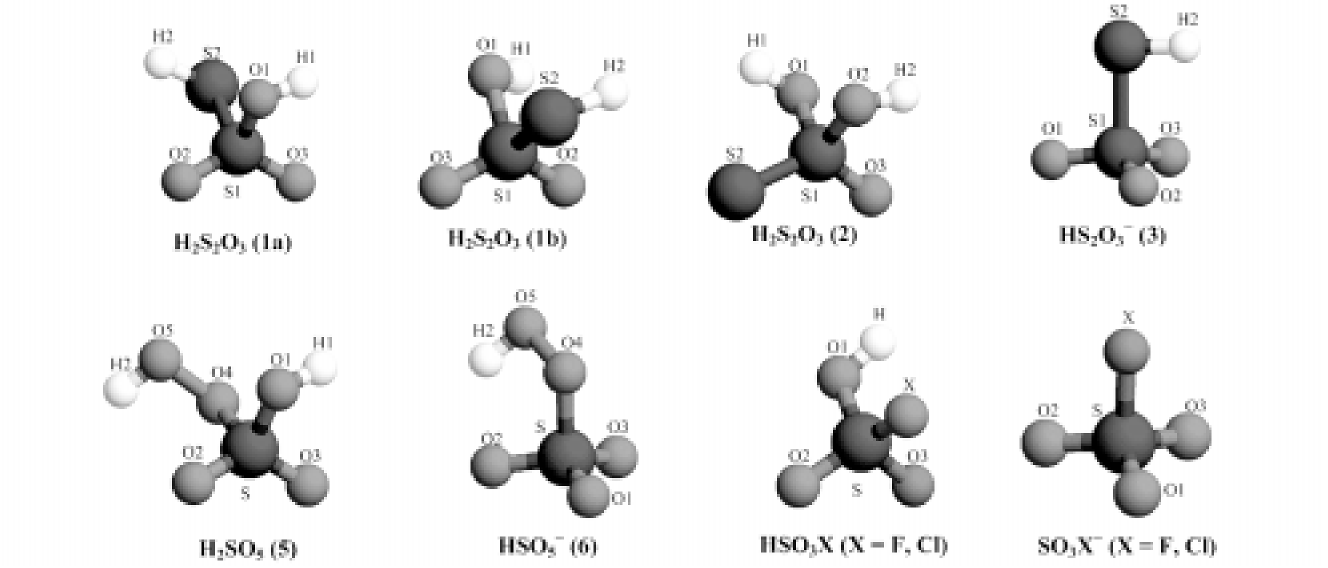
No experimental structures of $H_2S_2O_3$ or its monoanion are known since these species are thermally unstable at temperatures above −20 °C. In fact, the molecule $H_2S_2O_3$ has never been observed although this compound is mentioned in practically all inorganic chemistry textbooks. The anion $HS_2O_3^-$ is contained in the ammonium salt $NH_4[HS_2O_3]$ which is the only hydrogen thiosulfate which has ever been prepared.[15] The low-temperature Raman spectra of this salt and its deuterated derivative demonstrated that the connectivity of the anion is $HS-SO_3^-$ rather than $HO-SO_2(=S)^-$. By ab initio MO calculations at the MP4/6-311G(d,p)//HF/6-311G(d,p) + ZPE level of theory it was shown that the most stable connectivity of thiosulfuric acid is $HO-SO_2-SH$ (**1**) which is 41 kJ mol^{-1} more stable than the alternative $HO-SO(=S)-OH$ (**2**) and that the connectivity $HS-SO_3^-$ (**3**) is 20 kJ mol^{-1} more stable than the tautomer $HO-SO_2(=S)^-$ (**4**).[16] Calculations at the MP2/6-31+G(d)//HF/6-31G(d) level revealed that **1** exists as two conformers **1a** and **1b** (Figure 1).[17] The energy difference between these species was calculated as 4 kJ mol^{-1} (at 0 K) with **1a** as the global minimum.

The geometries of $H_2S_2O_3$ and its monoanion obtained at the MP2/6-311++G(d,p) level are given in Table 1; the numbering of atoms is shown in Figure 1. In accordance with the previous results the thiosulfuric acid molecule is of C_1 symmetry and two conformations **1a** and **1b** exist which differ only by the orientation of the SH and OH groups with respect to the terminal oxygen atoms. The global minimum is the conformer **1a** which has an analogous conformation to the sulfuric acid molecule. The bonds O−H and S−H point in almost opposite directions. The second conformer **1b** and the isomer **2** with two O−H bonds are less stable by 2.9 and 34.7 kJ mol^{-1}, respectively, if ΔG°_{298} at the G2 level is taken as a measure (Table 2). The anions **3** (SH) and **4** (OH) are of C_s and C_1 symmetry, respectively. The OH species **4** is by 24.7 kJ mol^{-1} less stable than the SH tautomer **3** and therefore has not been considered any further. Very similar thermodynamic data were obtained at the levels CBS-Q and G2(MP2) (see Table 2).

Compared to our previous calculations there are some significant changes in the geometrical parameters. In particular, the S−S bond lengths are now considerably longer and calculated as 210.1 and 222.6 pm for the acid and the anion while 205.7 and 215.5 pm had been obtained at the HF/6-311G(d,p) level.[16]

Peroxosulfuric Acid H_2SO_5

The molecular structure of crystalline peroxosulfuric acid is known from an X-ray diffraction study of single crystals.[18] However, the gas-phase structure seems to be unknown. The crystal structure is characterized by extensive intermolecular hydrogen bonding but there are no intramolecular hydrogen bonds (Table 3). The O−O bond length (146.4 pm) and the S−O−O−H torsion angle (104°) have values typical for covalent peroxides. The molecular symmetry is C_1 (Figure 1). The structure of the monoanion HSO_5^- is known from two independent X-ray crystal structure determinations of the potassium salt $KHSO_5 \cdot H_2O$ (Table 4).[19,20] The anion is of C_1 symmetry with the connectivity $HO-O-SO_3^-$. The O−O distance was determined as 146 pm while the S−O−O−H torsion angle was given as "ca. 90°"[19] and 87°.[20] Again, intermolecular hydrogen bonding is a characteristic feature of the structure. The structure of this anion has also been investigated by ab



$H_2S_2O_3$ (1a) $H_2S_2O_3$ (1b) $H_2S_2O_3$ (2) $HS_2O_3^-$ (3)

H_2SO_5 (5) HSO_5^- (6) HSO_3X (X = F, Cl) SO_3X^- (X = F, Cl)

Figure 1. Structures of the acids $H_2S_2O_3$, H_2SO_5, HSO_3F, HSO_3Cl, and of their anions

Table 1. Geometrical parameters of $H_2S_2O_3$ (**1a**, C_1) and $HS_2O_3^-$ (**3**, C_s) calculated at the MP2/6-311++G(d,p) level (internuclear distances in pm, bond angles and torsion angles in °); for numbering of atoms see Figure 1

Parameter	$HO-SO_2-SH$	$HS-SO_3^-$
H1−O1	96.9	−
S1−O1	162.4	146.9
S1−O2	143.6	146.9
S1−O3	144.2	146.7
S1−S2	210.1	222.6
S2−H2	133.9	133.7
H1−O1−S1	108.6	−
O1−S1−O2	104.4	114.4
O1−S1−O3	108.2	115.5
O2−S1−O3	124.0	115.5
O2−S1−S2	110.1	104.0
O3−S1−S2	105.3	100.9
O1−S1−S2	102.9	104.0
S1−S2−H2	92.7	92.8
H1−O1−S1−S2	−78.6	−
O1−S1−S2−H2	−66.0	−60.0
O2−S1−S2−H2	44.7	60.0
O3−S1−S2−H2	−179.3	180.0
O3−S1−O1−H1	32.6	−

Table 2. Relative enthalpies and Gibbs free energies [kJ mol^{-1}] of the isomers of thiosulfuric acid $H_2S_2O_3$ and of their anions $HS_2O_3^-$ at 298 K

Species	CBS-Q		G2(MP2)		G2	
	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
1a, (HS)(HO)SO_2	0	0	0	0	0	0
1b, (HS)(HO)SO_2	4.5	2.8	3.8	2.6	4.2	2.9
2, $(HO)_2S(=S)O$	34.7	34.4	33.8	33.4	35.1	34.7
3, $(HS)SO_3^-$	0	0	0	0	0	0
4, $(HO)S(=S)O_2^-$	23.3	23.4	24.6	24.7	24.6	24.7

initio MO calculations at the MP2/3-21+G$^{(*)}$ level.[21] These data will be discussed below.

Table 3. Structural parameters of H_2SO_5 (C_1) in the gas phase and in the crystal (internuclear distances in pm, bond angles and torsion angles in °); for numbering of atoms see Figure 1

Parameter	MP2/6-311++G(d,p)	X-ray diffraction[a]
H1−O1	96.9	94 (4)
H2−O5	96.9	95.4
O4−O5	144.0	146.4 (3)
S−O1	160.2	152.4 (2)
S−O2	143.0	141.8 (2)
S−O3	144.2	143.2 (2)
S−O4	166.1	160.2
H1−O1−S	109.0	112 (2)
O1−S−O2	105.9	106.8 (1)
O1−S−O3	110.2	112.9 (1)
O1−S−O4	101.7	104.0 (1)
O2−S−O3	125.2	121.4 (2)
O3−S−O4	101.9	101.0 (1)
S−O4−O5	109.5	108.7 (2)
O4−O5−H2	100.6	98 (3)
H1−O1−S−O4	−74.9	−68
O1−S−O4−O5	−63.6	−59.4
S−O4−O5−H2	−95.2	−104

[a] See ref.[18]

As part of the acidity calculation we have optimized the structures of H_2SO_5 (**5**) and HSO_5^- (**6**) with no symmetry restrictions first at the MP2/6-31G(d) level. The vibrational eigenvalues of the structures found were all positive. After the most stable conformations of H_2SO_5 and HSO_5^- had been located on the energy hypersurface these structures were optimized at the MP2/6-311++G(d,p) level. In Table 3 and Table 4 we compare the calculated geometries with the solid-state structures.

There is a remarkably good agreement between the two conformations of H_2SO_5 calculated for the free molecule and found in the crystal. This can be seen from the close agreement of the three torsion angles given in Table 3. The two O−H bonds point into practically opposite directions and the four atoms O3−S−O4−O5 (torsion angle −177.4°) are almost located in a plane. Most of the bond lengths and bond angles agree rather closely with the solid-state

Table 4. Comparison of calculated and crystallographic structure data for the peroxymonosulfate ion HSO_5^- (C_1) (internuclear distances in pm, bond angles and the torsion angle in °); for numbering of atoms see Figure 1

Parameter	Calculated MP2/6-311++G(d,p)	Experimental	
Schlemper et al.[a]	Flanagan et al.[b]		
H2−O5	97.6	87 (2)	−
O4−O5	145.4	146.3 (1)	146.0 (3)
S−O4	173.2	163.4 (1)	163.2 (2)
S−O2	147.9	145.0 (1)	144.4 (2)
S−O3	146.3	144.6 (1)	143.7 (2)
S−O1	146.0	144.0 (1)	143.5 (2)
H2−O5−O4	99.1	101	−
S−O4−O5	108.2	109.2	109.4
O2−S−O4	100.7	105.7	105.9
O3−S−O4	106.9	106.9	106.8
O1−S−O4	99.2	99.1	99.0
O2−S−O3	114.3	113.1	113.1
O1−S−O2	116.3	115.2	115.2
O1−S−O3	116.2	115.0	115.0
H2−O5−O4−S	43.2	87	ca. 90

[a] $KHSO_5H_2O$: ref.[19] – [b] $KHSO_5H_2O$: ref.[20]

structure. Exceptions are the two S−O single bonds involving O1 and O4 which are calculated to be 6−8 pm longer than observed in the crystal. Since these oxygen atoms do not take part in the hydrogen bonding network we have no explanation for the differing bond lengths. There are no intramolecular hydrogen bonds in **5** since the shortest nonbonded contact distance (O3···H1: 254.1 pm) is about equal to the sum of the van der Waals radii.

The calculated anion structure (Table 4) also agrees quite well with the crystallographically determined structure of $KHSO_5 \cdot H_2O$ despite the fact that the anion is coordinated by six cations and three water molecules. The differing H−O−O−S torsion angles (calcd. 43.2° versus 87°) may be caused by the intermolecular hydrogen bonding in the crystal on one hand and by the intramolecular hydrogen bond in the free ion. The strongest hydrogen bond in the crystal originates from the peroxide hydrogen and ends at the oxygen atom of a neighboring water molecule.[20] In the free ion the same hydrogen atom is linked to the oxygen atom O2 by a weak hydrogen bond of length 200.9 pm. The S−O single bond to the peroxide oxygen atom is calculated much longer (173.2 pm) than observed in the crystal (163.3 pm) which may be caused by the coordination of the peroxomonosulfate ion to the surrounding potassium ions. All other calculated S−O bond lengths agree within 2.6 pm with the solid-state data but the deviations always follow the same trend: The calculated distances are larger than the observed ones. The same type of deviations have been observed when the structure of HSO_5^- was calculated at the MP2/3-21+G$^{(*)}$ level.[21]

Attempts to optimize the structure of the isomeric anion $HO_3S{-}O{-}O^-$ failed since its structure always rearranged to the more stable isomer $HO{-}O{-}SO_3^-$. Therefore, the acidity of the peroxide proton of H_2SO_5 could not be calculated.

Fluorosulfuric Acid HSO_3F

The molecular structure of gaseous HSO_3F seems to be unknown but the crystalline acid has been studied by X-ray diffraction at 123 K.[22] The $HO{-}SO_2{-}F$ molecules form infinite chains via OH···O hydrogen bonds. The site symmetry is C_1. The structural parameters are given in Table 5 together with the results of our calculations at the MP2/6-311++G(d,p) level. Previous geometry calculations had been performed at the HF/6-31+G(d)[23,24] and HF/6-31G(d) levels.[17] The gas-phase symmetry is also C_1. The hydrogen atom shows no tendency to move close to the fluorine atom and there is no intramolecular O···H bond either: The closest O···H distance is 252.3 pm (with O3), which is about identical to the van der Waals distance. There is a fairly good agreement between calculated and observed bond lengths and angles taking the two different phases into account. Besides the OH bond length, which cannot be determined accurately by X-ray diffraction, the largest difference between the calculated and the solid-state structures is found for the S−OH single bond which is calculated to be too long by 8 pm. Next is the S−F bond, which is calculated to be too long by 6.6 pm. However, by comparison with a gaseous derivative of HSO_3F it can been demonstrated that the calculated structure is basically correct. The structure of the methyl ester $Me{-}O{-}SO_2{-}F$ has been determined by microwave spectroscopy and electron diffraction.[25] Assuming identical lengths for the two S=O bonds of the sulfone group the following internuclear distances [pm] and bond angles [°] were obtained: S=O 141.0(2), S−O 155.8(7), S−F 154.5(6), O−S=O 109.5(6), O=S=O 124.4(7), F−S=O 106.8(5). The S−O bond length agrees within 4 pm with our data for HSO_3F while the S−F bond deviates by 6.1 pm. The three bond angles agree within 1.5°. Taking into account the fact that two different, although related molecules are being compared and that ab initio MO methods reproduce S−F and S−O single bond lengths only poorly, the agreement of the data may be considered fairly good.

Table 5. Molecular structure of HSO_3F (C_1) in the gas phase and in the crystal (internuclear distances in pm, bond angles and the torsion angle in °); for numbering of atoms see Figure 1

Parameter	MP2/6-311++G(d,p)	X-ray diffraction[a]
H−O1	96.9	63 (3)
S−O1	59.6	151.4 (2)
S−O2	143.1	142.0 (1)
S−O3	142.3	141.2 (1)
S−F	160.6	154.0 (1)
O1−S−O2	110.2	107.2 (1)
O1−S−O3	107.0	113.1 (1)
O2−S−O3	125.4	120.9 (1)
O1−S−F	98.1	100.7 (1)
O2−S−F	105.7	106.2 (1)
O3−S−F	106.9	106.6 (1)
H−O−S	109.5	−
H−O−S−F	−78.6	−
H−O1−S−O3	31.5	−
H−O1−S−O2	170.8	−

[a] See ref.[22]

The structure of the fluorosulfate anion has been determined, for example, by X-ray crystallography of the lithium salt.[26] The gas-phase symmetry of the anion is C_{3v} but owing to its unsymmetrical coordination by lithium cations in $LiSO_3F$ the site symmetry is C_s. The structural parameters are compared to our calculated data in Table 6. Previous geometry calculations had been performed at the HF/6-31G(d)[17] and HF/6-31+G(d)[23,24] levels.

Table 6. Molecular structure of the anion SO_3F^- in the gas phase (C_{3v}) and in the crystal of $LiSO_3F$ (internuclear distances in pm, bond angles in °); for numbering of atoms see Figure 1

Parameter	MP2/6-311++ G(d, p)	X-ray diffraction[a]
S−O1	146.1	145.5 (6)
S−O2,3	146.1	142.4 (4)
S−F	169.8	155.5 (7)
O1−S−O2	116.0	113.5 (2)
O2−S−O3	116.0	117.4 (4)
O1−S−F	101.7	104.5 (5)
O2−S−F	101.7	102.8 (3)

[a] See ref.[26]

The anion of $LiSO_3F$ is coordinated to eight cations through Li−O contacts. There is no Li−F contact shorter than the sum of the van der Waals radii. Therefore, the S−F bond length should not be influenced too much and should approximately agree with the value calculated for the free molecule. However, at the level MP2/6-311++G(d,p) the agreement is rather poor: the calculated S−F distance is 14.3 pm or 9% too large! The previous uncorrelated calculations with smaller basis sets reproduced the S−F bond length much better although in all cases too long (by 3.5% or more). The larger deviation between calculated and observed solid-state bond lengths, especially in anions, may be partly caused by the coordination of the lithium cations which withdraw electron density and therefore strengthen the S−O and S−F bonds in a manner similar to that what protonation of anions does: The S−F bond of HSO_3F is 9.2 pm or 6% shorter than that of SO_3F^-. Similar effects are observed with the S−Cl bonds in HSO_3Cl and SO_3Cl^-.

Chlorosulfuric Acid HSO_3Cl

The structure of chlorosulfuric acid has never been determined experimentally but a number of theoretical studies have been published. Basch and Hoz[17] as well as Otto et al.[23] and Bencivenni et al.[24] found a structure of C_1 symmetry at the HF/6-31G(d) and HF/6-31+G(d) levels. The conformation is analogous to that of fluorosulfuric acid (see above). Our results obtained for the most stable conformation of this acid and for its anion at the MP2/6-311++G(d,p) level are shown in Table 7. A comparison of these data with the previous results shows once more that the uncorrelated calculations with the smaller basis sets yield shorter internuclear distances for all three types of bonds. The only experimental data available for comparison are the geometrical parameters of the methyl ester of chlorosulfuric acid, the structure of which has been determined by electron diffraction assuming identical S=O bond lengths in the sulfonyl group.[27] The following internuclear distances [pm] and bond angles [°] were obtained: S−O 156.2(4), S=O 141.9(3), S−Cl 202.3(4), O−S=O 108.7(8), O=S=O 122.2(15), Cl−S−O 102.8(14), Cl−S=O 106.4(6). The maximum deviation of the bond lengths from our data for HSO_3Cl amounts to 4.4 pm while the bond angles agree within 2.7°.

Table 7. Molecular structures of chlorosulfuric acid HSO_3Cl and of its anion calculated at the MP2/6-311++G(d,p) level (internuclear distances in pm, bond angles and torsion angles in °); for numbering of atoms see Figure 1

Parameter	HSO_3Cl (C_1)	SO_3Cl^- (C_{3v})
H−O1	97.0	−
S−O1	160.6	146.1
S−O2	142.9	146.1
S−O3	143.7	146.1
S−Cl	206.2	224.2
O1−S−O2	106.0	116.1
O1−S−O3	109.0	116.1
O2−S−O3	124.6	116.1
O1−S−Cl	100.1	101.5
O2−S−Cl	107.7	101.5
O3−S−Cl	106.8	101.5
H−O1−S−Cl	−80.4	−
H−O1−S−O2	167.8	−
H−O1−S−O3	31.5	−

An interesting feature of the two structures shown in Table 7 are the quite different S−Cl bond lengths in HSO_3Cl (206.2 pm) and in its anion (224.2 pm). Obviously, the strengthening of the bond S−O1 on deprotonation is partly due to a simultaneous weakening of the S−Cl bond. The anion may therefore be viewed as an adduct between SO_3 and a chloride anion. Below it will be shown that the thermodynamics of this adduct formation (or of the reverse dissociation) supports this view.

The shortest intramolecular nonbonded O···H contact distance of 250.8 pm (O3···H) corresponds to the sum of the van der Waals radii.

Acidities

The gas-phase acidity data calculated for various sulfonic acids of the type $HO-SO_2-X$ like H_2SO_3,[6] H_2SO_4,[6] $H_2S_2O_3$, H_2SO_5, HSO_3F, and HSO_3Cl are given in Table 8. The acidity is defined here as either $\Delta H°_{298}$ or $\Delta G°_{298}$ of the deprotonation reaction. The Gibbs free energies obtained at the CBS-Q and G2(MP2) levels differ by only 6 kJ mol^{-1} (0.5%) or less from the G2 data.

Table 8. Gas phase acidities [kJ mol^{-1}] of the sulfonic acids $HO-SO_2-X$ (X = H, OH, SH, OOH, F, Cl)

	CBS-Q		G2(MP2)		G2	
	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$	$\Delta H°_{298}$	$\Delta G°_{298}$
*H*O−SO$_2$−H	1303	1275	1310	1282	1307	1279
*H*O−SO$_2$−OH	1299	1264	1307	1271	1305	1268
*H*O−SO$_2$−SH	1280	1247	1286	1254	1284	1251
HO−SO$_2$−S*H*	1303	1271	1311	1278	1308	1276
*H*O−SO$_2$−OOH	1264	1233	1272	1241	1270	1239
*H*O−SO$_2$−F	1256	1223	1263	1232	1260	1229
*H*O−SO$_2$−Cl	1243	1213	1252	1222	1249	1219

The OH acidities presented in Table 8 obviously depend on the electronegativity and the charge capacity of the substituent X. Therefore, sulfonic acid $HO-SO_2-H$ (X = H) is the weakest of the mentioned sulfonic acids, followed by sulfuric acid $HO-SO_2-OH$. Surprisingly, thiosulfuric acid and peroxosulfuric acid are considerably stronger than sulfuric acid and therefore may be termed as *superacids*. Obviously, the charge capacity of the substituents SH and OOH, i.e., the ability to accommodate an additional negative charge in the anion, is larger than that of the OH group in sulfuric acid. For the same reason, gaseous chlorosulfuric acid is stronger than fluorosulfuric acid, in contrast to the pure liquids. The experimental deprotonation enthalpy of HSO_3F at 368 K was reported as $\Delta H°_{368} = 1285$ kJ mol^{-1} with $\Delta G°_{368} = 1255 \pm 10$ kJ mol^{-1}.[5] Both values deviate by 26 kJ mol^{-1} from our G2 data. This deviation is much smaller than from the previously reported theoretical data[23] obtained using geometries calculated at a much lower level than in this work. It should be pointed out that the experimental acidity of sulfuric acid[5] perfectly agrees with the G2 results cited in Table 8. No experimental acidity data are known for $H_2S_2O_3$ and H_2SO_5. In the case of thiosulfuric acid we also computed the SH acidity ($\Delta G°_{298} = 1276$ kJ mol^{-1}) which is of course much smaller than the OH acidity (1251 kJ mol^{-1}) of this compound but still comparable to the OH acidity of sulfonic acid (1279 kJ mol^{-1}) which is a tautomer of sulfurous acid. The OH acidity of the metastable tautomer of thiosulfuric acid, $HO-SO(=S)-OH$ **2**, was calculated as $\Delta G°_{298} = 1241$ kJ mol^{-1} at the G2 level.

The *dipole moments* of the acids calculated at the MP2/6-311++G(d,p) level are as follows (in D): H_2SO_3 3.77, H_2SO_4 3.63, $H_2S_2O_3$ (**1a**) 4.18, H_2SO_5 2.26, HSO_3F 3.15, HSO_3Cl 3.28.

Dissociation Reactions

Sulfonic acid $HO-SO_2-H$ is unstable with respect to dissociation to H_2O and SO_2[6] and a number of the acids investigated in this work also decompose easily either at room temperature ($H_2S_2O_3$) or on heating (H_2SO_5, HSO_3Cl). Even sulfuric acid partly decomposes into H_2O and SO_3 on distillation at ambient pressure. Therefore, we have calculated the reaction enthalpies and Gibbs free reaction energies of the dissociation reactions of the most stable conformers of $HO-SO_2-X$ into SO_3 and HX (X = H, OH, SH, OOH, F, Cl). The results are shown in Table 9.

In contrast to the instability of H_2SO_3 all other decomposition reactions are endothermic and endergonic at 298 K. However, the dissociation of HSO_3Cl requires a Gibbs free energy of only 9.8 kJ mol^{-1}. It is therefore understandable that this compound cannot be purified by distillation. In fact, chlorosulfuric acid is difficult to prepare in a pure state except by fractional crystallization.[28]

We have also studied the dissociation of the related gaseous anions SO_3X^- into X^- and SO_3 (SO_2 in the case of the sulfonate ion). Only the most stable tautomers and conformations were used. As the data in Table 10 demonstrate

Table 11. Enthalpies of formation of the gaseous acids $HO-SO_2-X$ (X = H, OH, SH, OOH, F, Cl) and of their anions [kJ mol^{-1}]. Experimental values in parentheses

Acid	$\Delta_f H°_{298}$	Anion	$\Delta_f H°_{298}$
$HO-SO_2-H$	−520	$H-SO_3^-$	−711 (−693±12)
$HO-SO_2-OH$	−722 (−735)	$HO-SO_3^-$	−951 (−967±11)
$HO-SO_2-SH$	−485	$HS-SO_3^-$	−735/−722
$HO-SO_2-OOH$	−623	$HOO-SO_3^-$	−885
$HO-SO_2-F$	−739 (−753)	SO_3F^-	−1006 (ca. −986)
$HO-SO_2-Cl$	−538 (−543)	SO_3Cl^-	−822

Table 9. Stabilities of some sulfonic acids $HO-SO_2-X$ with respect to dissociation into HX and SO_3 or SO_2 [kJ mol^{-1}]

	CBS-Q $\Delta H°_{298}$	$\Delta G°_{298}$	G2(MP2) $\Delta H°_{298}$	$\Delta G°_{298}$	G2 $\Delta H°_{298}$	$\Delta G°_{298}$
$H_2SO_3 \rightarrow H_2O + SO_2$	−18	−61	−20	−63	−19	−62
$H_2SO_4 \rightarrow H_2O + SO_3$	88	44	81	37	84	40
$H_2S_2O_3 \rightarrow H_2S + SO_3$	73	30	67	25	69	26
$H_2SO_5 \rightarrow H_2O_2 + SO_3$	94	48	89	43	91	45
$HSO_3F \rightarrow HF + SO_3$	74	34	68	28	71	31
$HSO_3Cl \rightarrow HCl + SO_3$	55	15	48	8.5	50	9.8

Table 10. Stabilities of the anions SO_3X^- with respect to dissociation into HX and SO_3 or SO_2 [kJ mol^{-1}]

	CBS-Q $\Delta H°_{298}$	$\Delta G°_{298}$	G2(MP2) $\Delta H°_{298}$	$\Delta G°_{298}$	G2 $\Delta H°_{298}$	$\Delta G°_{298}$
$HSO_3^- \rightarrow HO^- + SO_2$	287	240	261	214	277	231
$HSO_4^- \rightarrow HO^- + SO_3$	428	390	400	362	418	381
$HS_2O_3^- \rightarrow HS^- + SO_3$	259	220	255	217	258	220
$HSO_5^- \rightarrow HO_2^- + SO_3$	405	355	394	345	395	346
$SO_3F^- \rightarrow F^- + SO_3$	377	343	361	327	362	328
$SO_3Cl^- \rightarrow Cl^- + SO_3$	202	168	196	163	199	165

all reactions are strongly endothermic and endergonic. The reverse reactions are the nucleophilic additions of the Lewis bases X^- to the strong Lewis acid SO_3. By far the lowest reaction energy is that calculated for the addition of chloride anions to SO_3, which is in agreement with the structure of the chlorosulfate anion and its rather weak S−Cl bond as discussed above.

From the G2 enthalpies in Table 9 and 10 and the published enthalpies of formation[29] of SO_2, SO_3, H_2O, H_2S, H_2O_2, HF, HCl, OH^-, OOH^-, SH^-, F^-, and Cl^- we have calculated the enthalpies of formation of the gaseous acids and their monoanions as given in Table 11. Only few experimental data[28] are available for comparison and these are often not very accurate. Nevertheless, the agreement is reasonable. In the case of the hydrogen sulfide anion two slightly different values for the enthalpy of formation have been published.[28] Therefore, two enthalpies are given for $HSSO_3^-$ in Table 11 with the second value probably being more reliable. In the case of HSO_3Cl the enthalpy of formation was calculated from $\Delta_f H°_{298}$ of the liquid substance (-597.5 kJ mol^{-1})[28] and the enthalpy of evaporation at the boiling point (53.6 kJ mol^{-1} at 150°C).[28] The result (-543 kJ mol^{-1}) perfectly agrees with the value found in the present study (-538 kJ mol^{-1}).

Conclusion

The five sulfur oxo acids $HO-SO_2-SH$, $HO-SO(=S)-OH$, $HO-SO_2-OOH$, $HO-SO_2-F$, and $HO-SO_2-Cl$, as well as their monoanions, were investigated by ab initio MO calculations at the CBS-Q, G2(MP2), and G2 levels of theory to obtain their structures as well as their enthalpies and Gibbs free energies, from which the thermodynamics of the deprotonation reactions at 298 K were calculated. Unexpectedly, the OH acidities of all spe-

Table 12. Enthalpies $H°$ and Gibbs free energies $G°$ (negative a.u.) of the acids $HO-SO_2-X$ (X = H, OH, SH, OOH, F, Cl), their anions, and the products of decomposition at 298 K

	Species	Symmetry	CBS-Q	G2(MP2)	G2
$H°$	**1a**, $(HS)(HO)SO_2$	C_1	1022.104627	1022.056003	1022.073874
	1b, $(HS)(HO)SO_2$	C_1	1022.102887	1022.054539	1022.072275
	2, $(HO)_2S(=S)O$	C_1	1022.091394	1022.043125	1022.060501
	3, $(HS)SO_3^-$	C_s	1021.619545	1021.568491	1021.587345
	4, $(HO)S(=S)O_2^-$	C_1	1021.610670	1021.559117	1021.577958
	5, H_2SO_5	C_1	774.555147	774.501182	774.517270
	6, HSO_5^-	C_1	774.076138	774.018928	774.036091
	FSO_3H	C_1	723.531263	723.479661	723.494518
	FSO_3^-	C_{3v}	723.055130	723.000806	723.016835
	$ClSO_3H$	C_1	1083.512145	1083.456827	1083.476593
	$ClSO_3^-$	C_{3v}	1083.041134	1082.982326	1083.003139
	SO_2	$D_{\infty v}$	548.031089	548.003069	548.011734
	SO_3	D_{3h}	623.147303	623.110157	623.120863
	H_2O	C_{2v}	76.332707	76.326223	76.328266
	H_2O_2	C_2	151.371965	151.357146	151.361601
	HO_2^-	C_s	150.774768	150.758876	150.764873
	OH^-	$C_{\infty v}$	75.710924	75.709473	75.706670
	H_2S	C_{2v}	398.929676	398.920280	398.926912
	HS^-	$C_{\infty v}$	398.373711	398.361053	398.368281
	HF	$C_{\infty v}$	100.355756	100.343723	100.346696
	F^-	K_h	99.764381	99.753329	99.758238
	HCl	$C_{\infty v}$	460.343766	460.328319	460.336872
	Cl^-	K_h	459.817037	459.797359	459.806635
$G°$	**1a**, $(HS)(HO)SO_2$	C_1	1022.140619	1022.092206	1022.110076
	1b, $(HS)(HO)SO_2$	C_1	1022.139574	1022.091241	1022.108977
	2, $(HO)_2S(=S)O$	C_1	1022.127526	1022.079485	1022.096861
	3, $(HS)SO_3^-$	C_s	1021.654964	1021.604105	1021.622960
	4, $(HO)S(=S)O_2^-$	C_1	1021.646045	1021.594713	1021.613555
	5, H_2SO_5	C_1	774.592206	774.538476	774.554564
	6, HSO_5^-	C_1	774.112025	774.054995	774.072158
	FSO_3H	C_1	723.564782	723.513358	723.528215
	FSO_3^-	C_{3v}	723.087758	723.033560	723.049589
	$ClSO_3H$	C_1	1083.547130	1083.491983	1083.511749
	$ClSO_3^-$	C_{3v}	1083.074585	1083.015955	1083.036769
	SO_2	$D_{\infty v}$	548.059176	548.031188	548.039853
	SO_3	D_{3h}	623.176331	623.139258	623.149965
	H_2O	C_{2v}	76.354061	76.347599	76.349642
	H_2O_2	C_2	151.397722	151.382895	151.387350
	HO_2^-	C_s	150.800350	150.784475	150.790471
	OH^-	$C_{\infty v}$	75.730474	75.729025	75.726222
	H_2S	C_{2v}	398.952984	398.943590	398.950222
	HS^-	$C_{\infty v}$	398.394858	398.382201	398.389429
	HF	$C_{\infty v}$	100.375430	100.363410	100.366383
	F^-	K_h	99.780901	99.769848	99.774758
	HCl	$C_{\infty v}$	460.364929	460.349482	460.358035
	Cl^-	K_h	459.834421	459.814742	459.824019

cies are higher than that of sulfuric acid. Therefore, these species may be termed superacids. The OH acidity of acids of type $\mathrm{HO{-}SO_2{-}X}$ obviously depends on the electronegativity as well as on the charge capacity of the substituent X (X = H, OH, SH, OOH, F, Cl). In addition, the enthalpies and Gibbs free energies of the products of the two dissociation reactions $\mathrm{HO{-}SO_2{-}X \rightarrow SO_3 + H{-}X}$ and $\mathrm{SO_3X^- \rightarrow SO_3 + X^-}$ were calculated to obtain the reaction enthalpies. All these reactions are endothermic and endergonic. In other words, both the acids and their monoanions are thermodynamically stable species in the gas phase at 298 K. From these dissociation enthalpies and literature data of the dissociation products we have calculated the enthalpies of formation of the gaseous acids $\mathrm{H_2SO_3}$, $\mathrm{H_2S_2O_3}$, $\mathrm{H_2SO_5}$, $\mathrm{HSO_3F}$, and $\mathrm{HSO_3Cl}$.

Appendix

Enthalpies $H°$ and Gibbs free energies $G°$ of the acids $\mathrm{HO{-}SO_2{-}X}$ (X = H, OH, SH, OOH, F, Cl), their anions, and the products of decomposition at 298 K are given in Table 12.

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