The Reaction of H_2S with SO_2: Molecular Structures, Energies, and Vibrational Data of Seven Isomeric Forms of H_2S_3O**

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Dedicated to Professor Shigeru Oae on the occasion of his 75th birthday

Abstract: High-level ab initio MO calculations (MP2/6-311G**//MP2/6-311G**) on 16 isomeric forms of H_2S_3O (including rotamers) have been performed. The nonhelical hydroxotrisulfane HOSSSH **1a** (motif $++-$) is the most stable isomer, while the chains with motifs $+++$ and $+-+$ are less stable by 1.7 and 3.7 kJ mol^{-1}, respectively. The other isomers of H_2S_3O increase in energy in the order HSS(O)SH < HOS(S)SH < HSOSSH < HS(O)SSH < HS(S)SOH < HS(S)OSH. The trisulfane-2-oxide HSS(O)SH **2a** (symmetry C_1) is less stable than **1a** by 67 kJ mol^{-1}. These molecules may be formed from H_2S and SO_2 via $H_2S_2O_2$ by condensation with H_2S. The calculated reaction energies support the view that H_2S_3O is a key intermediate in the room-temperature reaction of H_2S and SO_2 resulting in the formation of lower oxoacids of sulfur and finally in sulfane oxides.

Keywords
ab initio calculations · Claus process · elemental sulfur · sulfane oxides · sulfur oxoacids

Introduction

More than 25 million tons of elemental sulfur are produced annually by the Claus process,[1, 2] which is based on Equation (1). The technical process is carried out at elevated temperatures (ca. 250 °C) with alumina-based catalysts. However, the two gases also react without a catalyst both in the vapor and liquid phases as well as in organic solvents and in water.[3] The mechanism and possible intermediates of reaction (1) are only partly understood. Most likely, the primary product in the vapor phase is the van der Waals adduct $H_2S \cdot SO_2$, the structure of which has been elucidated by microwave spectroscopy: the two molecules are aligned on top of each other with their twofold rotation axes parallel, but their dipole vectors antiparallel.[4] We believe that this complex then rearranges by a proton shift from sulfur to oxygen to form dihydrogendioxothiosulfate(IV), HS-S(O)OH ("thiosulfurous acid"). Recent ab initio MO calculations have shown that this molecule is the most stable structure of all possible isomers of composition $H_2S_2O_2$.[5] Another isomer, the chainlike dihydroxodisulfane HO-S-S-OH, has been detected by neutralization–reionization mass spectrometry;[6] all other $H_2S_2O_2$ isomers are hypothetical.

$$2\,H_2S + SO_2 \longrightarrow 3\,S_{\text{liquid}} + 2\,H_2O \qquad (1)$$

In this work we show how $H_2S_2O_2$ may react further with H_2S to finally give the observed products, namely, elemental sulfur and water. It has repeatedly been observed[3, 7, 8] that the reaction between H_2S and SO_2, when carried out at ambient or lower temperatures, results in the formation of "polysulfane oxides" of composition $H_xS_yO_z$ ($y > z$). These compounds obviously consist of sulfur chains terminated by SH or OH groups, but, in addition, sulfoxide groups of the type -S-S(O)-S- are present as demonstrated by a strong infrared absorption near 1120 cm^{-1}.[7] This S_3O group is also present in the cyclic sulfur oxides S_nO ($n = 6-10$), which have been characterized by X-ray crystallography and/or vibrational spectroscopy.[9] In addition, a number of organic trisulfane oxides ("dithiosulfites") R-S-S(O)-S-R with R = ClC_6H_4, C_6H_5, and $(C_6H_5)_3C$ have been structurally characterized by X-ray crystallography.[10, 11, 12] All these compounds decompose on heating with formation of SO_2 and oxygen-free S_n chains. Application of this information to the H_2S/SO_2 reaction makes it likely that the primary product $H_2S_2O_2$ reacts with H_2S according to Equation (2). Depending on the isomeric structure of $H_2S_2O_2$, different isomers of H_2S_3O would be formed (Scheme 1). The three most stable isomers of $H_2S_2O_2$ are HS-S(O)OH, HO-S-S-OH, and $(HO)_2S{=}S$,[5] which would react with H_2S to form the H_2S_3O isomers HS-S(O)-SH, HO-S-S-S-H, and HO-S(S)-S-H, respectively. To elucidate the structures and relative energies of these species and of four related isomers of H_2S_3O, we have carried out extensive ab initio molecular orbital calculations. To support future work directed towards the identification of H_2S_3O by vibrational spectroscopy, we have also calculated the wavenumbers and infrared intensities of the twelve fundamental modes of the

$$H_2S_2O_2 + H_2S \longrightarrow H_2S_3O + H_2O \qquad (2)$$

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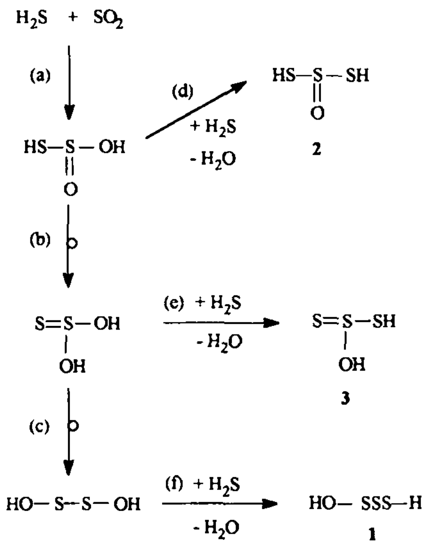


Scheme 1. Possible reactions of H_2S with SO_2 resulting in the formation of various isomers of $H_2S_2O_2$ and of H_2S_3O.

seven H_2S_3O isomers and their various rotamers (altogether 16 molecules). In addition, the reaction energies of several steps in Scheme 1 have been calculated.

Calculations

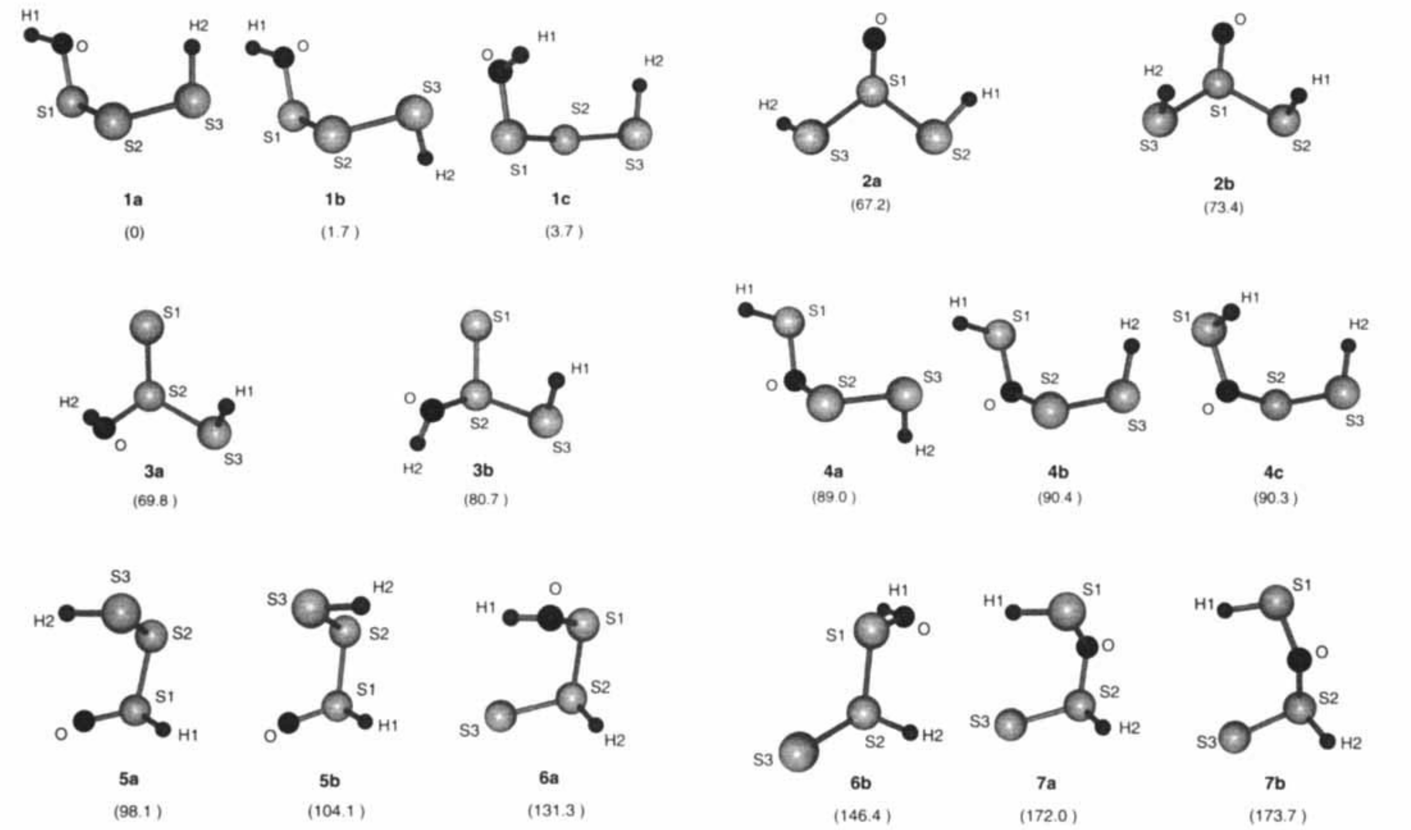
All calculations were performed with the GAUSSIAN 92 program package[13] for ab initio MO calculations on either an IBM/RISC 6000 workstation or a CRAY YMP-4E supercomputer. The molecular structures of the H_2S_3O isomers were fully optimized first at the Hartree–Fock level with the 6-311G** basis set. The optimization was done from different starting geometries with respect to the rotation around the SS and SO single bonds. Improved relative energies were obtained by single point calculations taking the electron correlation into account according to the second order of the Møller–Plesset perturbation theory (MP2).[14] Finally, the optimization was repeated at the MP2/6-311G** level of theory.

The harmonic vibrational wavenumbers were calculated analytically first at the HF/6-311G** level and finally at the MP2/6-311G** level of theory. Following the suggestion by Pople et al.[15] the wavenumbers were scaled by a factor of 0.8929 (HF) or 0.9427 (MP2), while the zero-point energies were scaled by a factor of 0.9135 (HF) or 0.9646 (MP2). For a general discussion of the basis sets and methods used see ref. [16].

Results and Discussion

Energies: In Figure 1 the seven H_2S_3O isomers considered in this work are shown. From a chemical point of view these structures seem to be the most reasonable ones, with the oxygen atom either one- or two-coordinate and the sulfur atoms one-, two-, or three-coordinate. These structures have been numbered **1**–**7** according to their decreasing stability at the MP2/6-311G** level. All of them correspond to energy minima with no imaginary vibrational wavenumbers.

The most stable structure is the six-atom chain **1**, which can exist as three rotamers (**1a**–**c**) depending on the signs of the torsional angles at the SO and SS bonds. The absolute and relative energies as well as the zero-point energies of all calculat-



1a (0) **1b** (1.7) **1c** (3.7) **2a** (67.2) **2b** (73.4)

3a (69.8) **3b** (80.7) **4a** (89.0) **4b** (90.4) **4c** (90.3)

5a (98.1) **5b** (104.1) **6a** (131.3) **6b** (146.4) **7a** (172.0) **7b** (173.7)

Fig. 1. Isomers and rotamers of H_2S_3O and numbering of atoms. The relative energies with respect to the most stable isomer **1a** are given in brackets.

Table 1. Total energies (h = 2625.5 kJ mol^{-1}) of various isomers of H_2S_3O, the corresponding zero-point vibrational energies (ZPE) scaled by 0.9135 in kJ mol^{-1}, and the energies (kJ mol^{-1}) in relation to the energy of **1** taking the zero-point energies into account.

	HF/6-311G**	ZPE [a]	E_{rel}	MP2//6-311G** [b]	E'_{rel} [c]	MP2/6-311G** [d]	ZPE [e]	E''_{rel}
1a	−1268.615391	68.9	0	−1269.204039	0	−1269.205280	68.0	0
1b	−1268.614695	68.8	1.7	−1269.203352	1.7	−1269.204611	67.9	1.7
1c	−1268.613763	68.8	4.2	−1269.202552	3.8	−1269.203838	67.9	3.7
2a	−1268.565869	60.9	122.1	−1269.174038	70.8	−1269.176734	60.8	67.2
2b	−1268.566835	60.2	118.8	−1269.171988	75.5	−1269.173894	59.0	73.4
3a	−1268.580445	68.6	91.5	−1269.175142	75.6	−1269.178220	66.7	69.8
3b	−1268.573820	67.7	108.0	−1269.169880	88.5	−1269.173695	65.8	80.7
4a	−1268.577012	61.9	93.8	−1269.167261	89.6	−1269.168909	61.5	89.0
4b	−1268.576408	61.9	95.4	−1269.166724	90.9	−1269.168411	61.6	90.4
4c	−1268.576233	62.0	95.9	−1269.166763	90.9	−1269.168457	61.6	90.3
5a	−1268.564546	64.8	129.4	−1269.164482	99.8	−1269.166320	63.8	98.1
5b	−1268.561306	64.6	137.7	−1269.161984	106.1	−1269.163957	63.6	104.1
6a	−1268.563825	70.9	137.4	−1269.152913	136.2	−1269.155715	69.2	131.3
6b	−1268.559124	70.6	149.4	−1269.146905	151.7	−1269.149970	69.2	146.4
7a	−1268.538261	65.4	199.0	−1269.133707	181.2	−1269.138002	63.4	172.0
7b	−1268.535548	65.5	206.3	−1269.131365	187.4	−1269.136810	63.9	173.7

[a] ZPE taken from HF/6-311G** calculations. [b] Geometries optimized at HF/6-311G**. [c] Geometries optimized at HF/6-311G**, ZPE taken from HF/6-311G** calculations. [d] Geometries optimized at MP2/6-311G**. [e] ZPE taken from MP2/6-311G** calculations.

ed species are given in Table 1. The most stable rotamer of **1** is not the helical all-*trans* form **1b** (motif + + +), but the *cis-trans* form **1a** (motif + + −) while the all-*cis* form **1c** is least stable. The same order has been found in ab initio MO calculations in the case of the isoelectronic chains HOSSOH[5] and HSSSSH.[17] However, the energy differences between the three rotamers are quite small in all cases.

The isomer **2a**, discussed above as possibly resulting from a condensation reaction between HS-S(O)OH and H_2S, is less stable than **1a** by 67.2 kJ mol^{-1} (only the energies obtained at the highest level will be discussed). Surprisingly, **2** exists as two rotamers of C_1 (**2a**) and C_S (**2b**) symmetry, which differ in energy by 6.2 kJ mol^{-1}. The geometry of these rotamers will be discussed in detail below.

Most surprisingly the thiosulfoxide **3a** is only 2.6 kJ mol^{-1} less stable than the sulfoxide **2a**. This will partly be due to the high bond energy of the OH bond present in **3a** but not in **2a**. Isomer **3** also exists as two rotamers, which differ in energy by a remarkable 9.9 kJ mol^{-1}. The chainlike structure **4** exists as three rotamers, which differ in energy by only 1.4 kJ mol^{-1} or less. In this case the helical form **4a** (motif + + +) is most stable followed by **4c** (+ − +) and **4b** (+ + −); the latter two are practically of identical energy (within 0.1 kJ mol^{-1}). Comparison of **4a** with **1a** indicates that the connectivity H-S-O is much less favorable than the alternative H-O-S. The same result has been obtained by MO calculations for H_2SO,[18] H_2SO_2,[19] H_2S_2O,[20] and $H_2S_2O_2$.[5]

Of the remaining isomers the trisulfane-1-oxide **5a** is remarkably less stable than the trisulfane-2-oxide **2a** (the numbers indicate the position of the oxygen atom). These two isomers are isodesmic (same numbers of SH, SS and SO bonds) but differ in energy by 21.9 kJ mol^{-1}. Isomer **5** also exists as two rotamers of considerably different energy (ΔE = 15.0 kJ mol^{-1}). Of the two thiosulfoxides **6** and **7** the one with the OH bond is more stable. These two species are so much higher in energy than **1** (by more than 130 and 170 kJ mol^{-1}, respectively) that they will be excluded from a detailed discussion of their properties. Again, these molecules each exist as two rotamers.

Geometries: The bond lengths, valence angles, and torsional angles of **1**–**7** are given in Tables 2–4. The parameters of the hydroxotrisulfane **1** show that the bond lengths and angles in the three rotamers are very similar. The two SS bonds show the expected differences: the electronegative OH group causes a shortening of the neighboring SS bond (203.5 pm), as has been observed in many disulfanes X-SS-X.[21,22] As a result of this shortening the other SS bond is longer (209 pm) than the SS single-bond length calculated, for example, as 207.5 pm in the

Table 2. Bond lengths d (pm) of the various isomers of H_2S_3O (MP2/6-311G**).

	d(H1S1)	d(H2S3)	d(HO)	d(S1O)	d(S2O)	d(S1S2)	d(S2S3)
1a	133.6	–	96.4	167.8	–	203.5	208.8
1b	133.7	–	96.4	167.5	–	203.7	208.9
1c	133.7	–	96.4	167.9	–	203.5	209.4
2a	133.6	133.7	–	146.9	–	217.2	217.8
2b	133.8	133.8	–	147.4	–	216.9	216.9
3a	–	133.9	97.1	–	165.8	193.1	214.9
3b	–	133.8	96.8	–	168.6	190.9	216.5
4a	134.0	133.9	–	170.0	169.6	204.0	–
4b	134.0	133.9	–	169.8	169.7	204.0	–
4c	134.0	133.9	–	169.8	169.6	204.3	–
5a	136.8	133.7	–	148.4	–	218.8	206.4
5b	136.9	133.8	–	148.1	–	219.5	206.5
6a	134.8	–	96.8	165.5	–	217.3	197.9
6b	134.9	–	96.4	166.7	–	219.3	197.5
7a	134.1	135.5	–	168.6	175.4	–	192.6
7b	134.1	135.0	–	167.8	179.8	–	192.3

Table 3. Bond angles α (°) of the various isomers of H_2S_3O (MP2/6-311G**).

	α(SOH)	α(SSO)	α(SSS)	α(SSH)	α(SOS)	α(HSO)
1a	106.4	104.7	107.7	97.0	–	–
1b	106.4	105.5	108.1	97.2	–	–
1c	105.9	105.2	107.6	97.0	–	–
2a	–	111.9 110.2	88.1	91.3 90.2	–	–
2b	–	107.0	102.2	91.7	–	–
3a	107.3	100.7	108.7	92.9	–	–
3b	106.2	98.1	111.4	92.5	–	–
4a	–	104.8	–	98.8	117.8	97.3
4b	–	105.0	–	98.9	117.6	97.6
4c	–	104.6	–	98.9	117.5	96.7
5a	–	111.7	102.1	97.7	–	107.2
5b	–	113.5	104.2	98.0	–	107.4
6a	107.2	101.4	109.1	97.1	–	–
6b	107.0	99.4	110.3	93.8	–	–
7a	–	113.5	–	104.9	117.9	98.2 (S^{II}) 91.8 (S^{IV})
7b	–	113.1	–	106.6	114.3	98.3 (S^{II}) 83.9 (S^{IV})

Table 4. Torsional angles τ (°) of the various isomers of H_2S_3O (MP2/6-311G**).

	τ(HOSS)	τ(OSSS)	τ(HSSS)	τ(HSOS)	τ(SOSS)	τ(OSSH)
1a	84.1	83.6	−85.1	–	–	–
1b	82.8	82.5	87.9	–	–	–
1c	93.0	−84.2	93.9	–	–	–
2a	–	–	159.3 167.1	–	–	−89.7 54.5
2b	–	–	±78.7	–	–	±33.5
3a	−81.8	–	−21.4	–	–	92.0
3b	79.7	–	−43.0	–	–	65.9
4a	–	–	–	80.2	77.9	82.8
4b	–	–	–	78.2	77.8	−90.1
4c	–	–	–	94.0	−78.6	92.9
5a	–	−51.5	56.5 80.2	–	–	–
5b	–	−51.9	56.4 −93.4	–	–	–
6a	77.5	−43.6	–	–	–	64.4
6b	−90.2	161.6	–	–	–	−89.6
7a	–	–	–	79.1 56.4	−50.8	–
7b	–	–	–	−87.0 177.1	71.6	–

case of H_2S_4.[17] Of the other parameters of **1** only the torsional angles deserve a comment. The OSSS angles are all close to 83°, which seems to be the optimum for chains of chalcogen atoms. In the case of H_2S_4 the SSSS angles were calculated as 80°,[17] while the experimental OSSO angle of the related dimethoxydisulfane ($CH_3OSSOCH_3$) is 91° in the vapor phase and 81.5° in the solid.[22, 23] Organic derivatives of **1** of type ROSSSR are known,[24] but no structure determinations have been reported.

As outlined in the Introduction, the trisulfane-2-oxide **2** is the most interesting isomer of H_2S_3O as far as the reaction of H_2S with SO_2 is concerned. There are a large number of symmetrical and unsymmetrical organic derivatives of type RSS(O)SR and RSS(O)SR′, both chainlike[10, 11, 12, 25] and cyclic.[26] Structure determinations of the chainlike derivatives[10, 11, 12] show that the S_3O group has the geometry of the related thionyl chloride molecule (symmetry C_S); this is confirmed by the present work. The more stable rotamer **2a** has no symmetry; however, its HSSSH backbone is of approximate C_2 symmetry. The hydrogen atoms are located on different sides of the plane defined by the three sulfur atoms (torsional angles HSSS both positive; values ca. 165°). As a consequence, the two HSSO torsional angles are very different (− 89.7° and + 54.5°). There is no intramolecular $H\cdots O$ hydrogen bond. The two SS bonds are much longer (217.2/217.8 pm) than single bonds (H_2S_2:205 pm). In rotamer **2b** the hydrogen atoms are both on the same side of the SSS plane as the oxygen atom with HSSS torsional angles of ±78.7°. Again the SS bonds (216.9 pm) are much longer than single bonds. There is no obvious reason why **2a** is more stable than **2b**.

The known organic derivatives R_2S_3O more or less resemble the parent compound **2a**. When R is 4-chlorophenyl, the two torsional angles τCSSS are −176.8°, and the SS bond lengths 212.5 pm.[10] When R is C_6H_5, the angles τ(CSSS) are +158.5 and +162.9°, and the bond lengths d(SS) are 212.4 and 214.1 pm,[11] while the corresponding values for R = Ph_3C are $\tau(CSSS) = -172.3°$ and +160.7° and $d(SS) = 188.2$ and 188.0 pm.[12] The latter compound shows an unusually small SSS bond angle of 83.8° compared to the 88.1° calculated for **2a**; the corresponding angle of **2b** (102.2°) is much larger.

The remarkable stability of the thiosulfoxide **3a** indicates that it might be possible to prepare an organic derivative RO-S(S)-SR such as, for example, a cyclic species similar to the stable compound RO-S(S)-OR (R = cyclohexyl), which forms colorless crystals.[27] The two SS bonds of **3a** are 193.1 and 214.9 pm in length at the MP2 level but 198.7 and 209.5 pm at the HF level. This result shows clearly the importance of the electron correlation for the geometry optimization. The value of 193.1 pm may be compared to the 190.1 pm observed for the above-mentioned cyclic thionosulfite.[27] It should, however, be pointed out that the two hydrogen atoms of **3a** seem to be involved in hydrogen bonds to the terminal sulfur atom, since the corresponding distances ($d(OH\cdots S) = 279.7$ and $d(SH\cdots S) = 293.7$ pm) are smaller than the van der Waals distance of 300 pm. There are no such short $H\cdots S$ contacts in rotamer **3b**; this explains its considerably higher energy.

The isomers **4** and **7** contain an SOS bridge with two-coordinate sulfur atoms, which is labile and structurally characterized only in compounds like the disulfate ion $^-O_3S\text{-}O\text{-}SO_3^-$ and the bis(pentafluorosulfur)oxide $F_5S\text{-}O\text{-}SF_5$. Attempts to prepare organic compounds of the type RS-O-SR resulted in formation of thiosulfinates RS(O)-SR (disulfane oxides).

Organic derivatives of the trisulfane-1-oxide **5** are known (both cyclic and chainlike),[28] but no structures have been determined. This molecule does not contain an intramolecular hydrogen bond, since the distance of the H atom at one chain end to the terminal (negatively charged) oxygen atom at the other end is larger than the van der Waals distance. The same holds for all other isomers and rotamers except **3a**.

The dipole moments of the H_2S_3O isomers are given in Table 5. The values range from 0.76 to 4.25.

Table 5. The dipole moments μ ($D \approx 3.33 \times 10^{-30}$ C m) of the various isomers of H_2S_3O (MP2/6-311G**).

Molecule	μ	Molecule	μ
1a	1.69	**4b**	2.79
1b	1.37	**4c**	2.77
1c	2.21	**5a**	2.21
2a	2.66	**5b**	4.25
2b	2.18	**6a**	3.31
3a	2.51	**6b**	4.00
3b	4.06	**7a**	2.33
4a	0.76	**7b**	1.74

Vibrational Spectra: Table 6 shows the harmonic wavenumbers of the twelve fundamental modes of H_2S_3O in its various connectivities and some of their rotamers. All species are of C_1 symmetry except **2b**, which is of C_S symmetry. In addition, the calculated infrared intensities are given. The spectra of the less stable rotamers are given only in those cases where there are substantial wavenumber or intensity differences compared to the data of the most stable rotamer. The following assignments are based on the Cartesian displacements of the atoms.

The assignment of the OH stretching modes at 3529–3626 cm^{-1} is straightforward. The SH stretching modes occur at 2354–2634 cm^{-1}. It can clearly be recognized that the SH groups with two-coordinate sulfur have their stretching modes at higher wavenumbers (2595–2634 cm^{-1}) than those with three-coordinate sulfur atoms (2354–2495 cm^{-1}). This result is in agreement with the different bond lengths of the corresponding SH bonds: those originating from three-coordinate sulfur atoms are longer by up to 3 pm. Remarkably, the IR intensities of the SH stretching modes are low when the sulfur is two-coordinate, but much higher for three-coordinate sulfur atoms.

Table 6. Harmonic wavenumbers (cm^{-1}) of the twelve fundamental vibrations of seven isomers of H_2S_3O (MP2/6-311G**). Relative IR intensities are given in parentheses. Wavenumbers have been scaled by a factor of 0.9427.

	1a	**2a**	**2b**	**3a**	**3b**	**4a**	**5a**	**5b**	**6a**	**6b**	**7a**	**7b**
1	3626 (77)	2634 (0.1)	2623 (A) (0.2)	3529 (30)	3580 (39)	2608 (4)	2626 (0.01)	2612 (1)	3570 (47)	3616 (97)	2598 (3)	2595 (5)
2	2629 (1)	2632 (1)	2622 (B) (0.4)	2611 (1)	2620 (1)	2604 (15)	2368 (45)	2354 (54)	2493 (12)	2493 (16)	2445 (21)	2495 (12)
3	1103 (36)	1165 (100)	1143 (A) (100)	1075 (44)	1058 (28)	963 (11)	1118 (100)	1127 (100)	1143 (34)	1116 (40)	972 (15)	988 (22)
4	835 (7)	821 (0.4)	770 (A) (14)	772 (5)	751 (5)	856 (8)	1054 (3)	1056 (4)	904 (26)	877 (25)	958 (19)	968 (14)
5	699 (90)	727 (7)	718 (B) (1)	666 (94)	618 (100)	680 (100)	859 (4)	854 (4)	749 (45)	731 (65)	834 (5)	852 (2)
6	465 (1)	428 (29)	412 (B) (97)	583 (90)	616 (31)	580 (32)	770 (14)	765 (13)	693 (6)	729 (34)	667 (16)	665 (12)
7	458 (16)	406 (45)	378 (A) (40)	419 (100)	366 (83)	487 (32)	483 (1)	481 (1)	523 (100)	532 (100)	617 (72)	630 (75)
8	438 (100)	309 (8)	288 (A) (10)	367 (8)	307 (10)	412 (26)	360 (25)	357 (35)	417 (81)	490 (70)	394 (100)	404 (100)
9	315 (8)	266 (1)	269 (B) (1)	284 (10)	271 (6)	323 (1)	307 (14)	308 (1)	318 (14)	377 (29)	333 (2)	330 (6)
10	250 (7)	227 (14)	237 (A) (12)	238 (8)	225 (7)	258 (19)	265 (7)	271 (7)	276 (3)	201 (4)	288 (4)	275 (5)
11	197 (7)	182 (1)	157 (A) (2)	198 (3)	206 (12)	199 (21)	145 (4)	141 (2)	140 (4)	118 (4)	159 (7)	166 (12)
12	100 (1)	160 (0.2)	29 (B) (2)	163 (2)	130 (2)	84 (6)	68 (6)	58 (4)	75 (8)	29 (7)	90 (7)	64 (5)

The SOH bending modes occur in the narrow range of 1058–1143 cm^{-1}, while the SH bending vibrations are calculated to fall within the much wider range of 693–1056 cm^{-1}. This can again be explained by the fact that these modes are either OSH or SSH bending and that the central sulfur atom is either two- or three-coordinate. For example, the highest value (1056 cm^{-1}) represents δ(OSH) of species **5b**, while the lowest value (693 cm^{-1}) is δ(SSH) of **6a**. The stretching modes of the sulfoxide groups of **2** and **5** occur at 1118–1165 cm^{-1}, which is in agreement with the value of around 1120 cm^{-1} observed for various organic trisulfane-2-oxides[29] and for S_8O.[9]

The fundamental modes in the region below 800 cm^{-1} are more difficult to assign, since, owing to the low symmetry of the molecules, vibrational coupling is extensive. However, wavenumbers at 394–731 cm^{-1} can be assigned to the stretching modes of the formal SO single bonds of **1**, **3**, **4**, **6**, and **7**; these vibrations are expected to result in strong or very strong IR absorptions. The stretching modes of the formal SS double bonds to the terminal sulfur atoms of **3**, **6**, and **7** occur at 523–630 cm^{-1}; these modes also give rise to bands of high intensities. The remaining vibrations are SS stretching as well as bending and torsion vibrations.

The H_2S/SO_2 Reaction: In Scheme 1 it is shown how the H_2S_3O isomers **1**–**3** may be formed from H_2S and SO_2 via $H_2S_2O_2$. In step (a) the most stable isomer of $H_2S_2O_2$ is obtained, which, at elevated temperatures or under the influence of polar solvents, may isomerize to give the slightly less stable isomers $S{=}S(OH)_2$ and HOSSOH [steps (b) and (c)]. The following condensation of OH groups of $H_2S_2O_2$ with H_2S results in the isomers **1**–**3**. By a series of analogous reactions with either SO_2 or H_2S, it is possible to obtain the polysulfane oxide type products observed experimentally and characterized by groups like -SH, -OH, -S-S-, -S-S(O)-S-, and -S-S(O)-O-. For example, **2** may react with SO_2 to give HS-S(O)-S-SO_2H, and condensation of **2** with HS-S(O)OH would result in HS-S(O)-S-S(O)-SH. These subsequent reactions of H_2S_3O will be dealt with in a separate publication.

The calculated total energies allow the estimation of the reaction energies ΔU of all steps in Scheme 1. This requires, however, that all species are calculated at the same level of theory. We have therefore repeated our previous MO treatment[5] of $H_2S_2O_2$, SO_2, S_2O, and H_2S by calculating these species at the MP2/6-311G**//MP2/6-311G** level of theory. The results are shown in Table 7. As can be seen, the most stable rotamer of HOSSOH is of motif+ + −. Its formation from H_2S and SO_2 is endothermic by 80.2 kJ mol^{-1} (at 298.2 K) when the scaled zero-point energies and the (unscaled) thermal energies of all reactants are taken into account [Eq. (3)]. The more probable formation of HOS(O)SH is also endothermic [Eq. (4)]. The

Table 7. Total energies (hartrees) of several isomers/rotamers of $H_2S_2O_2$ and of H_2O, H_2S, SO_2, and S_2O, their zero-point energies (kJ mol^{-1}; scaled by 0.9646), and the temperature corrections for the internal energy U (kJ mol^{-1}).

	MP2/6-311G**	ZPE	$U_{298}-U_0$
HOSSOH (motif + + −)	−946.599001	78.5	14.0
HOSSOH (motif + − +)	−946.597457	78.3	14.1
HOSSOH (motif + + +)	−946.598348	78.4	14.1
HOS(O)SH	−946.596686	72.0	14.2
H_2O	−76.263972	55.3	7.4
H_2S	−398.846478	39.7	7.5
SO_2	−547.775263	16.7	8.1
S_2O	−870.347612	12.5	8.7

$$H_2S + SO_2 \longrightarrow \text{HOSSOH } (+\,+\,-) \qquad (3)$$

$$\Delta U_{298} = 80.2\ \text{kJ mol}^{-1}$$

$$H_2S + SO_2 \longrightarrow \text{HOS(O)SH} \qquad (4)$$

$$\Delta U_{298} = 80.0\ \text{kJ mol}^{-1}$$

higher zero-point energy of HOSSOH ($78.5\,\mathrm{kJ\,mol^{1-}}$) compared to that of HOS(O)SH ($72.0\,\mathrm{kJ\,mol^{-1}}$) makes reaction (4) slightly more energetically favorable than reaction (3). The condensation reaction of HOSSOH with H_2S resulting in **1a** is exothermic [Eq. (5)], but the formation of H_2S_3O (**2a**) is slightly endothermic [Eq. (6)]. Sulfane oxides HSS(O)S···SH decompose on gentle heating in a vacuum with formation of S_2O and elemental sulfur;[3] the model reaction for this process is the decomposition of $(HS)_2SO$, which is in fact exothermic [Eq. (7)].

$$H_2S + HOSSOH \longrightarrow HOSSSH + H_2O \qquad (5)$$
$$\Delta U_{298} = -58.4\,\mathrm{kJ\,mol^{-1}}$$

$$H_2S + HOS(O)SH \longrightarrow (HS)_2SO + H_2O \qquad (6)$$
$$\Delta U_{298} = 12.6\,\mathrm{kJ\,mol^{-1}}$$

$$(HS)_2SO \longrightarrow S_2O + H_2S \qquad (7)$$
$$\Delta U_{298} = -54.0\,\mathrm{kJ\,mol^{-1}}$$

These thermodynamic data show that the overall reactions of H_2S with SO_2 to give H_2S_3O are slightly endothermic. It is known that the dry gases react only on heating, but in the presence of traces of water spontaneous reaction occurs. Two reasons may be given for this influence of water. First, in the presence of H_2O the oxoacids $H_2S_2O_2$ and H_2S_3O will form either hydrogen-bonded adducts or ion pairs $H_3O^+X^-$, which are more stable, and this may change the reaction energies in such a way that reactions (3) and (4) become exothermic. Second, the presence of H_2O may facilitate the proton transfer from H_2S to SO_2 in reaction (2) by allowing a concerted reaction via a cyclic transition state (Fig. 2). Such a mechanism has been shown to operate in the analogous reaction of SO_3 with H_2O to give H_2SO_4.[30]

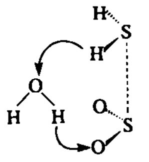


Fig. 2.

Conclusion

Our data show that H_2S and SO_2 may react in a slightly endothermic reaction to give first $H_2S_2O_2$. Depending on the isomeric structure of $H_2S_2O_2$, the further reaction with H_2S will be exothermic to give HOSSSH or slightly endothermic to give HSS(O)SH. A series of similar addition or condensation reactions with either SO_2 or H_2S result in the formation of the observed polysulfane oxides $H_xS_yO_z$ ($y > z$). On heating these will decompose exothermically to give SO_2, H_2O, and elemental sulfur. The presence of water facilitates the formation of $H_2S_2O_2$ and probably H_2S_3O by stabilizing these oxoacids through formation of strong hydrogen bonds. Obviously, these findings are also of relevance to those natural systems in which H_2S and SO_2 occur simultaneously, for example, in cultures of bacteria that reduce sulfite to sulfide[31] or oxidize sulfide to sulfite.[32]

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[1] H. Fischer in *Ullmanns Enzyklopädie der technischen Chemie*, VCH, Weinheim **1982**, *Vol. 21*, pp. 8–25; J. R. West in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York **1983**, *Vol. 22*, pp. 267–297.
[2] B. G. Goar, J. A. Lagas, J. Borsboom, G. Hejkoop, *Sulphur* **1992**, *222*, 44; Anonymous, *Sulphur*, **1991**, *211*, 27; **1993**, *229*, 25 (Statistical Supplement).
[3] P. W. Schenk, R. Steudel, *Angew. Chem.* **1965**, *77*, 437; *Angew. Chem. Int. Ed. Engl.* **1965**, *5*, 402.
[4] S. G. Kukolich, D. J. Pauley, *J. Chem. Phys.* **1990**, *93*, 871; R. E. Bumgarner, D. J. Pauley, S. G. Kukolich, *J. Chem. Phys.* **1987**, *87*, 3749.
[5] K. Miaskiewicz, R. Steudel, *J. Chem. Soc. Dalton Trans.* **1991**, 2395.
[6] H. Schmidt, R. Steudel, D. Sülzle, H. Schwarz, *Inorg. Chem.* **1992**, *31*, 941.
[7] R. Ludwig, Doctoral Dissertation, Techn. Univ. Berlin **1969**.
[8] P. W. Schenk, W. Kretschmer, *Angew. Chem.* **1962**, *74*, 695; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 550.
[9] R. Steudel, *Comments Inorg. Chem.* **1982**, *1*, 313; R. Steudel in *Sulfur: Its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology*, (Eds.: A. Müller, B. Krebs), Elsevier, Amsterdam, **1984**, Chapt. 1, p. 1; *Gmelin Handbuch der Anorganischen Chemie, Schwefel, Erg. bd. 3*, 8th ed., Springer, Berlin **1980**, p. 1.
[10] R. Steudel, P. Luger, H. Bradaczek, *Chem. Ber.* **1977**, *110*, 3553.
[11] C. Th. Kiers, A. Vos, *Rel. Trav. Chim. Pays-Bas* **1978**, *97*, 166.
[12] R. Steudel, M. Pridöhl, J. Buschmann, P. Luger in preparation; M. Pridöhl, Doctoral Dissertation, Techn. Univ. Berlin **1994**.
[13] GAUSSIAN 92/DFT, Revision F.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian Inc., Pittsburgh, PA **1992**.
[14] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.
[15] J. A. Pople, A. P. Scott, M. W. Wong, L. Radom, *Isr. J. Chem.* **1993**, *33*, 345.
[16] W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York **1986**.
[17] Y. Drozdova, K. Miaskiewicz, R. Steudel, *Z. Naturforsch. Part B*, submitted.
[18] S. Besnainou, J. L. Whitten, *J. Am. Chem. Soc.* **1980**, *102*, 744.
[19] T. Steiger, R. Steudel, *J. Mol. Struct. (THEOCHEM)* **1992**, *257*, 313.; D. Laakso, P. Marshall, *J. Phys. Chem.* **1992**, *96*, 2471.
[20] R. Steudel, Y. Drozdova, R. Hertwig, W. Koch, *J. Phys. Chem.*, in press.
[21] R. Steudel, *Angew. Chem.* **1975**, *87*, 683; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 655.
[22] T. Koritsanszky, J. Buschmann, P. Luger, H. Schmidt, R. Steudel, *J. Phys. Chem.* **1994**, *98*, 5416.
[23] R. Steudel, H. Schmidt, E. Baumeister, H. Oberhammer, T. Koritsanszky, *J. Phys. Chem.*, submitted.
[24] H. Kagami, S. Motoki, *J. Org. Chem.* **1977**, *42*, 4139.
[25] L. Field, W. B. Lacefield, *J. Org. Chem.* **1966**, *31*, 3555; R. Steudel, P. W. Schenk, J. Bilal, *Z. Anorg. Allg. Chem.* **1967**, *353*, 250; R. Steudel, G. Scheller, *Z. Naturforsch. Part B* **1969**, *24*, 351; S. Motoki, H. Satsumabayashi, *J. Org. Chem.* **1973**, *38*, 3654.
[26] H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, T. L. Cairns, *J. Am. Chem. Soc.* **1962**, *84*, 4746, 4772.
[27] D. N. Harpp, K. Steliou, C. J. Cheer, *J. Chem. Soc. Chem. Commun.* **1980**, 825.
[28] R. Steudel, J. Latte, *Chem. Ber.* **1977**, *110*, 423.; F. Freeman, C. Lee, *J. Org. Chem.* **1988**, *53*, 1263; B. Milligan, J. M. Swan, *J. Chem. Soc.* **1965**, 2901.
[29] R. Steudel, *Z. Naturforsch. Part B* **1970**, *25*, 156.
[30] K. Morokuma, C. Muguruma, *J. Am. Chem. Soc.* **1994**, *116*, 10316.
[31] L. M. Siegel in *Metabolism of Sulfur Compounds, Vol. VII*, (Ed.: D. M. Greenberg), Academic Press, New York, **1975**, Chapt. 7, p. 217.
[32] H. G. Trüper in *Biology of Inorganic Nitrogen and Sulfur*, (Eds.: H. Bothe, A. Trebst), Springer, Berlin, **1981**, p. 199.

0570-0833/95/0303-0198 $ 30.00+.25/0