Microsolvation of Thiosulfuric Acid and Its Tautomeric Anions $[HSSO_3]^-$ and $[SSO_2(OH)]^-$ Studied by B3LYP-PCM and G3X(MP2) Calculations

Ralf Steudel* and Yana Steudel

Institut für Chemie, Sekretariat C2, Technische Universität Berlin, D-10623 Berlin, Germany

Received: June 04, 2009; Revised Manuscript Received: July 23, 2009

The interaction of thiosulfuric acid and its monoanion with up to three water molecules has been studied by density functional and high-level ab initio calculations. More than 40 molecules and anions both as OH and SH tautomers were investigated. The structures in the gas phase as well as in a polarizable continuum were optimized at the B3LYP/6-31G(2df,p) level of theory, whereas G3X(MP2) single-point calculations were applied to obtain enthalpies and Gibbs energies of the gaseous species. In the gas phase, all monoanions of composition $[H,S_2,O_3]^- \cdot nH_2O$ ($n = 0-3$) are predicted to be most stable as SH tautomers $[HSSO_3]^-$. The enthalpies of hydration are -51 ± 5 kJ mol^{-1} per water molecule. In a polarizable phase simulating the dielectric properties of water the OH forms $[SSO_2(OH)]^-$ of the hydrated and unhydrated monoanions are always most stable. Thiosulfuric acid and its mono- and dihydrates are most stable in the SH/OH form, both in the gas phase and in the polarizable continuum. However, the trihydrate $H_2S_2O_3 \cdot 3H_2O$ prefers the OH/OH form in the polarizable phase, whereas in the gas phase the SH/OH tautomer represents the lowest minimum structure. The hydration enthalpy of the acid is slightly smaller than predicted for the monoanions. We predict that both thiosulfuric acid and its monoanion exist as equilibrium mixtures of the corresponding tautomers in aqueous solution. The acid decomposition of thiosulfate involves sulfur transfer reactions, but the formerly accepted reaction between two monoanions producing sulfite and $[HSSSO_3]^-$ ions is endothermic and endergonic both for the naked anions and their trihydrates. Therefore, we propose that the sulfur transfer takes place between $[HSSO_3]^-$ and $H_2S_2O_3$ producing $[HSSSO_3]^-$, SO_2, and H_2O. This reaction is exothermic and exergonic both in the gas phase and in the polarizable phase. From $[HSSSO_3]^-$ the longer chain sulfane monosulfonate ions $[HS_nSO_3]^-$ are formed by a series of sulfur transfer reactions, and these ions eventually split off homocyclic sulfur molecules S_n. The initial decomposition reaction is hindered by SO_2 which reacts with thiosulfate ions to the novel adduct $[O_2SSSO_3]^{2-}$ which seems to be also a key intermediate in the synthesis of trithionate from thiosulfate and SO_2. The implications of these results for the enzymatic thiosulfate metabolism by sulfur bacteria are discussed. The adduct $H_2S \cdot SO_3$, an isomer of thiosulfuric acid, has been studied in addition. Its conversion into $H_2S_2O_3$ is predicted to be exothermic, by -39.5 kJ mol^{-1}.

I. Introduction

Textbooks of inorganic chemistry mention at least 10 ternary oxoacids of sulfur of composition $H_2S_xO_y$, but only very few of these compounds have been prepared as pure materials. These are sulfuric acid H_2SO_4 and its peroxo derivatives H_2SO_5 and $H_2S_2O_7$.[1] Other species such as H_2SO,[2] H_2SO_2,[3] H_2SO_3,[4] H_2S_2O,[5] and $H_2S_2O_2$[6] have been prepared in dilute gas phases or by low-temperature matrix experiments and have been studied spectroscopically only. Still other S−O acids have never been observed, and their possible existence has just been concluded from well-known derivatives such as salts and esters. However, practically all of these acids and their anions have been studied by modern quantum-chemical calculations. Needless to say, many of these compounds are of central importance in atmospheric chemistry[7] and in the environment[8] as well as in many industrial processes.[9] They also are key components of the global biogeochemical sulfur cycle,[10] and sulfur bacteria play a significant role in this process.[10,11]

Thiosulfuric acid $H_2S_2O_3$ is one of those molecules which has never been observed directly although thiosulfates such as $Na_2S_2O_3$ and $[NH_4]_2S_2O_3$ have been known for a long time and are produced industrially on a fairly large scale.[9] In both salts the dianion $[S_2O_3]^{2-}$ is of C_{3v} symmetry.[12] The first and so far only example of a hydrogen thiosulfate has been prepared in 1989.[13] By reaction of $[NH_4]_2[S_2O_3]$ with concentrated H_2SO_4 in methanol or methanol-d_1 at low temperatures the colorless salt $[NH_4][HS_2O_3]$ and its deuterium derivative $[ND_4][DS_2O_3]$ were obtained and characterized by Raman spectroscopy. These salts as well as the free acid are unstable at 25 °C decomposing to give elemental sulfur, sulfur dioxide, and polythionates as major products:

$$H_2S_2O_3 \rightarrow \tfrac{1}{8}S_8 + SO_2 + H_2O \qquad (1)$$

$$2[NH_4][HS_2O_3] \rightarrow [NH_4]_2S_2O_3 + \tfrac{1}{8}S_8 + SO_2 + H_2O \qquad (2)$$

The decomposition of thiosulfates in acidic aqueous solution, i.e., formally the decomposition of $H_2S_2O_3$(aq), has been studied several times. Although aqueous thiosulfates are stable at pH > 5, more acidic solutions rapidly decompose at 25 °C. It has been suggested[13−15] that the simultaneous presence of $[HS_2O_3]^-$ and $[S_2O_3]^{2-}$ anions results in a series of sulfur transfer reactions

---

* To whom correspondence should be addressed. E-mail: steudel@sulfur-research.de.

10.1021/jp905264c CCC: $40.75

to give hydrogen sulfite and polysulfane monosulfonate ions according to eqs 3 and 4.

$$[HS_2O_3]^- + [S_2O_3]^{2-} + H^+ \rightarrow [HS_3O_3]^- + [SO_3H]^- \quad (3)$$

$$[HS_3O_3]^- + [S_2O_3]^{2-} + H^+ \rightarrow [HS_4O_3]^- + [SO_3H]^- \quad \text{etc.} \quad (4)$$

In these reactions, the strong nucleophile $[S_2O_3]^{2-}$ is assumed to attack the sulfane sulfur atom of the hydrogen thiosulfate ion with replacement of the sulfonate unit. This chain-growth mechanism is said to produce a complex mixture of sulfane monosulfonate ions $[HS_nSO_3]^-$. As soon as the sulfur chain of these ions has reached a certain length homocyclic sulfur molecules can be split off:

$$[HS_nSO_3]^- \rightarrow \textit{cyclo}\text{-}S_n + [SO_3H]^- \qquad (n > 5) \quad (5)$$

By HPLC analysis, the homocycles S_6, S_7, and S_8 have been detected in these reaction mixtures, and pure crystalline S_6 has been prepared in this way.[15,16] All the reactions shown above are reversible, and the position of the equilibrium strongly depends on the pH value of the solution. In additional side reactions polythionate ions $[O_3S{-}S_x{-}SO_3]^{2-}$ with up to 19 sulfur atoms are formed proving the presence of long-chain sulfane monosulfonates in the reaction mixture:

$$2[HS_nSO_3]^- \rightarrow H_2S + [S_{2n+1}O_6]^{2-} \quad (6)$$

These polythionates have been separated by ion-pair chromatography and detected by their UV absorption.[17]

According to the above equations, the decomposition of acidic thiosulfate solutions depends on the simultaneous presence of thiosulfate and hydrogen thiosulfate ions and probably undissociated thiosulfuric acid. This claim is in line with the observation that highly acidic solutions of thiosulfates which will contain the free acid but not the dianion decompose much more slowly and can be stored at 0 °C for several hours without any sign of decomposition.[18] On the other hand, a reaction between two anions as in eqs 3 and 4 seems rather unlikely for electrostatic reasons.

Schmidt and co-workers reported the preparation of free thiosulfuric acid under nonaqueous conditions at low temperatures.[19] For this purpose $Na_2S_2O_3$ was reacted with anhydrous HCl in an organic solvent:

$$NaS_2O_3 + 2HCl \rightarrow H_2S_2O_3 + 2NaCl \quad (7)$$

Alternatively, H_2S was condensed with chlorosulfuric acid $ClSO_3H$:

$$H_2S + ClSO_3H \rightarrow H_2S_2O_3 + HCl \quad (8)$$

Oily products were obtained in these reactions, which showed a reactivity toward iodine and bases such as NH_3 as would be expected for $H_2S_2O_3$. At ambient temperature the oily products decomposed according to eq 1. Neither elemental analyses nor spectra or experimental structure determinations of $H_2S_2O_3$ have been reported. Schmidt and co-workers also investigated the reaction between SO_3 and H_2S and observed that a colorless solid adduct was formed at low temperatures, which on warming reversibly dissociated into the components rather than isomerizing to $H_2S_2O_3$:

$$H_2S + SO_3 \rightarrow H_2S\cdot SO_3 \quad (9)$$

The structure of this adduct is also unknown.

However, the structures of the free thiosulfuric acid molecule and of its monoanions have been studied by high-level ab initio calculations.[20] According to these results, the SH tautomers of both species are more stable than the OH forms and the anti conformation of the acid is preferred over the syn isomer. The relative enthalpies at 25 °C (kJ mol^{-1}) calculated at the G2 level of theory[20b] are shown in Figure 1.

The existence of the SH form of the hydrogen thiosulfate anion was confirmed by the Raman spectra of the above-mentioned ammonium salts $[NH_4][HS_2O_3]$ and $[ND_4][DS_2O_3]$, which exhibit lines both for the SH/SD stretching and SSH/SSD bending vibrations.[13] However, in aqueous solution the connectivities of these anions and of the free acid may be different due to strong hydrogen bonding with the surrounding water molecules. For example, the well-known "hydrogen sulfite anion" of composition $[H,S,O_3]^-$ was predicted by quantum-chemical calculations to be most stable as sulfonate ion $[HSO_3]^-$ containing an SH bond rather than as hydrogen sulfite ion $[SO_2(OH)]^-$ in the gas phase. However, several spectroscopic investigations of acidic sulfite solutions have convincingly demonstrated that the concentration ratio of these two anions in water at 25 °C is close to 1:5 in favor of the OH tautomer.[21] This result has recently been confirmed by ab initio calculations of the hydrates of these anions with up to eight water molecules.[22] Therefore, we have studied for the first time the structures and energies of several hydrates of thiosulfuric acid and of its tautomeric monoanions of composition $[H,S_2,O_3]^-$ by ab initio calculations both in the gas phase and in a polarizable continuum using the PCM method developed by Tomasi et al.[23] It turned out that the most stable solution species differ considerably from the energetically preferred gas phase structures. Our procedures are analogous to the recent microsolvation studies of other small sulfur-containing species such as SO_2,[22] H_2S,[24a] $[SO_4]^{2-}$,[24b] HSO_3F,[24c] HSO_3Cl,[24d] and cysteine.[24e]

II. Computational Methods

The structures and energies of the various molecules and ions were examined according to the G3X(MP2) theory[25] using the Gaussian 03[26] program package. This composite method corresponds effectively to QCISD(T)/G3XL//B3LYP/6-31G(2df,p) energy calculations together with zero-point vibrational and isogyric corrections. The G3X(MP2) theory represents a modification of the G3(MP2)[27] theory with three important changes: (1) B3LYP/6-31G(2df,p) geometry, (2) B3LYP/6-31G(2df,p) zero-point energy, and (3) addition of a *g* polarization function to the G3Large basis set for the second-row atoms at the Hartree−Fock level. All three features are particularly important for the proper description of sulfur-containing species as examined in this work. In the light of the rather large basis set no basis set superposition corrections were carried out. Harmonic fundamental vibrations were calculated at the B3LYP/6-31G(2df,p) level to characterize stationary points as equilibrium structures, with all frequencies real. The wavenumbers given

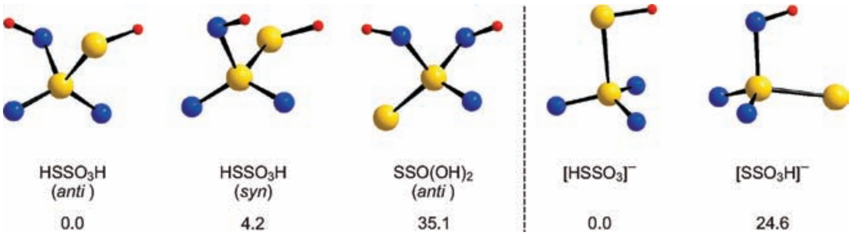


Figure 1. Tautomers of thiosulfuric acid and its monoanion with relative enthalpies calculated at the G2 level of theory (kJ mol^{-1}, according to ref 20b).

are unscaled, but for the calculation of the zero-point energy and the entropy a scaling factor of 0.8929 was used. For all investigated species, a charge density analysis was performed by a natural population analysis (NPA) based on the B3LYP/6-31G(2df,p) wave function.[28] As far as gas phase species are concerned, all relative energies and enthalpies reported in the text correspond to the G3X(MP2) level, whereas all reported structural parameters correspond to the B3LYP/6-31G(2df,p) level. The lowest minimum structures were obtained from a variety of starting geometries using the experience from related calculations[22,24] and designed to obtain a maximum of hydrogen bonds with bond angles at the bridging H atoms as large as possible. Thus, we are confident that we obtained the global minimum structures. Absolute energies and enthalpies are listed in Table S1a in the Supporting Information.

Some of the investigated complexes are characterized by large dipole moments. Therefore, it was to be expected that the thermodynamics of such species in the solid state and in polar solvents will be different from that in the gas phase. To study the influence of a polar environment, calculations according to Tomasi's polar continuum model (IEF-PCM)[29] as implemented in Gaussian 03 were carried out at the B3LYP/6-31G(2df,p) level. In this model, the solvent is represented by a continuous dielectric, characterized by a given dielectric constant (ε). The solute is assumed to be embedded in a cavity in the medium. The size of the cavity is calculated from atomic radii of the UFF force field for non-hydrogen atoms while the latter are enclosed in the sphere of the heavy atom to which they are linked (by default). The permanent dipole of the solute induces a dipole moment in the medium, which in turn interacts with the molecular dipole leading to stabilization. A dielectric constant of 78.0 was used for the PCM calculations to represent the aqueous phase. Except for the acid hydrates **9**−**12** a geometry optimization was performed. Since this resulted in structural changes the novel structures are indicated by a prime (e.g., **5a** and **5a′**). However, if the PCM structure differs totally from the gas phase geometries it will get its own label (e.g., **6f**). The thermodynamic functions H(PCM) and G(PCM) were calculated for $T = 298$ K and $p = 1.013$ bar; these data are given in Table S1b in the Supporting Information.

III. Results and Discussion

III.A. Reference Calculations. The hydrates of sulfuric acid $H_2SO_4 \cdot nH_2O$ are related to the present work. These molecules have been studied many times theoretically,[30] and for the monohydrate there is also an experimental structure determination by microwave spectroscopy[31] as well as a crude estimation of the Gibbs energy of formation from the two components.[32] Therefore, we have used $H_2SO_4 \cdot H_2O$ as a reference molecule to check whether the B3LYP/6-31G(2df,p) method yields reliable structural information and whether the G3X(MP2) single-point calculations give satisfying thermodynamic results.

Two conformational isomers of $H_2SO_4 \cdot H_2O$ have been located on the potential energy surface (PES). These isomers are of almost identical enthalpy and Gibbs energy and should exist next to each other under equilibrium conditions. The more stable isomer **1a** is structurally identical to the species discovered by microwave spectroscopy[31] if the small differences are taken into account which usually exist between equilibrium structures obtained by quantum-chemical calculations and experimental structures corresponding to the vibrational conditions at the temperature of the experiment. In Figure 2 the structure of **1a** is shown together with some geometrical parameters obtained by our calculation and by microwave spectroscopy. In addition, the structure of the less stable isomer **1b** is given which differs thermodynamically from **1a** by the very small relative energies $\Delta H°_{298} = \Delta G°_{298} = 0.4$ kJ mol^{-1}.[33] The main structural difference between **1a** and **1b** is the location of the water hydrogen atom not taking part in hydrogen bonding. In fact, the structure of **1b** can be generated from **1a** by rotating the water molecule around the axis of that O−H bond which takes part in hydrogen bonding within the heterocycle S−O−H···O−H···O.[34] In both isomers this heterocycle is rather flat with all torsion angles smaller than 18°. The atomic coordinates of all species calculated in this work are given in the Supporting Information.

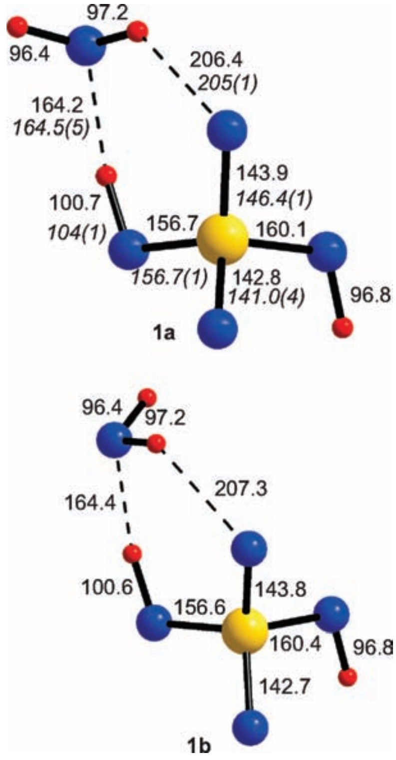


Figure 2. Structures of two conformational isomers of the gaseous acid hydrate $H_2SO_4 \cdot H_2O$ (**1a**,**b**), calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm); experimental microwave data are given in italics with standard deviation in parentheses.

The formation of **1a** from the gaseous components is predicted to be exothermic as well as exergonic:

$$H_2O + H_2SO_4 \rightarrow H_2SO_4 \cdot H_2O\ (\mathbf{1a}) \qquad (10)$$

$$\Delta H^\circ_{298} = -44.2\ \text{kJ mol}^{-1}, \quad \Delta G^\circ_{298} = -4.5\ \text{kJ mol}^{-1}$$

Although these data are in good agreement with the most sophisticated previous calculations,[30c,d] the only experimental value we are aware of for the reaction given in eq 10 is the Gibbs energy of formation for **1a** of -3.6 ± 1 kcal mol^{-1} (-15 ± 4 kJ mol^{-1}), derived from diffusion experiments of H_2SO_4 in an atmosphere of humidified nitrogen.[32] Since the latter number is a somewhat crude estimate and taking our previous reference calculations on the water trimer[22] into account, we conclude that the G3X(MP2) method provides reliable data of the molecules treated in this work. Nevertheless, we studied the species of eq 10 also with an additional diffuse function, i.e., the structures were obtained at the B3LYP/6-31+G(2df,p) level of theory and the energies then calculated at the G3X(MP2) level. The thermodynamic results $\Delta H^\circ_{298} = -45.9$ kJ mol^{-1} and $\Delta G^\circ_{298} = -6.0$ kJ mol^{-1} do not differ significantly from the data obtained without the diffuse function, but the two hydrogen-bond lengths of **1a** were now predicted as 167.2 and 222.1 pm. These bond lengths deviate from the experimental values (164.5 and 205 pm) much more than the distances calculated without the diffuse function (164.2 and 206.4 pm). Thus, our decision is justified to use the unmodified G3X(MP2) method, based on B3LYP/6-31G(2df,p) geometry calculations, for all data reported below.

More than 40 molecules of composition $[H,S_2,O_3]^- \cdot nH_2O$ and $H_2S_2O_3 \cdot nH_2O$ with $n = 0-3$ have been calculated, both as SH and OH tautomers. For reasons outlined in the Introduction, we have also studied several tautomers of the related more sulfur-rich anions $[HSSSO_3]^-$ and $[SSSO_2(OH)]^-$. For each group of species, we will first discuss the structures and relative stabilities in the gas phase followed by the situation in the polarizable phase simulating an aqueous solution. Enthalpies and Gibbs energies both for the gas phase and the polarizable continuum apply to 298 K and 1.013 bar, whereas the B3LYP-PCM energy calculations (E_e) refer to the potential energy minimum. A complete listing of the absolute energies, enthalpies, Gibbs energies, and dipole moments of all investigated molecules and ions is given in Tables S1a and S1b in the Supporting Information, which also contains the atomic coordinates of all calculated species. Throughout this work, we consider O···H hydrogen bonds as normal only if the OH distance is smaller than 230 pm and S···H bonds only if the SH distance is smaller than 260 pm. Recently, the sulfur atom of Me_2S has been shown to be nearly equivalent thermodynamically to the oxygen atom of Me_2O as a hydrogen-bond acceptor toward methanol,[35] whereas *p*-cresol interacts about twice as strongly with H_2O compared to H_2S.[36] Therefore, we expect OH···S but also SH···O bonding to occur in some of the investigated species.

III.B. Anions of Composition $[H,S_n,O_3]^-$ and $[H,S_n,O_5]^-$ ($n = 1-3$). As outlined in the Introduction, the acid decomposition of thiosulfate ions is assumed to involve a series of sulfur atom transfer reactions starting with the hydrogen thiosulfate anion $[HSSO_3]^-$ from which the sulfur-rich derivative $[HSSSO_3]^-$ is formed together with hydrogen sulfite ions $[HSO_3]^-$. However, in aqueous solution all these ions may also exist as the tautomers $[SSO_3H]^-$, $[SSSO_3H]^-$, and $[SO_3H]^-$. Furthermore, the decomposition of thiosulfate in acidic solution has been reported to be slowed down by the presence of sulfur dioxide. Most likely the nucleophiles $[S_2O_3]^{2-}$ and $[SSO_3H]^-$ react with the Lewis acid SO_2 to give complex anions which may be of connectivity $[O_2SSSO_3]^{2-}$, $[O_2SSSO_3H]^-$, or $[HO_2SSSO_3]^-$. These hypothetical species have not been studied previously. Therefore, we have investigated all the above-mentioned anions both in the gas phase and in a polarizable continuum using the dielectric constant of water at 25 °C and optimizing the geometry in both phases.

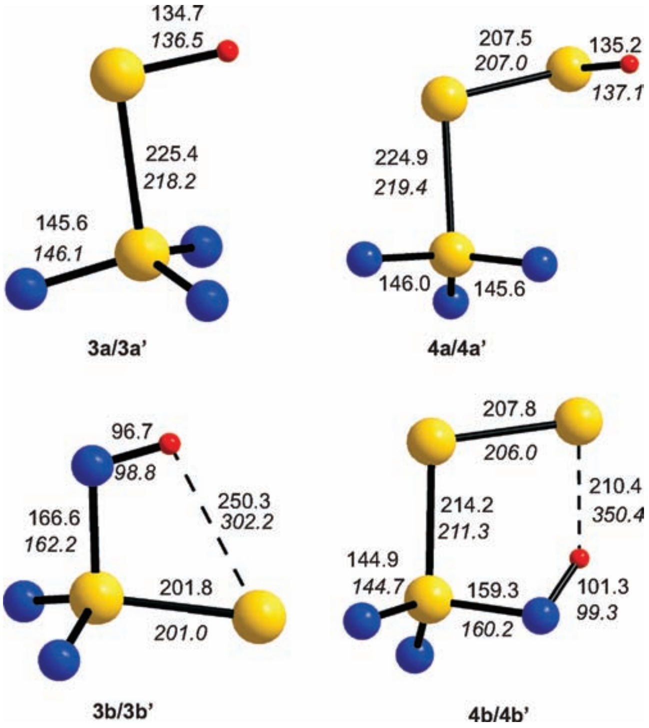


Figure 3. Structures of two tautomers of the gaseous monoanions of thiosulfuric acid $[H,S_2,O_3]^-$ (**3a**,**b**) and of disulfane monosulfonic acid $[H,S_3,O_3]^-$ (**4a**,**b**), calculated at the B3LYP/6-31G(2df,p) level of theory. The bond lengths given in italics apply to the polarizable phase calculated by the PCM method resulting in a slightly differing geometry (species **3a′**,**b′** and **4a′**,**b′**; all values in pm).

Structures and thermodynamic properties of the sulfonate ion (**2a**) and the tautomeric hydrogen sulfite anion (**2b**) have been published before;[22] here, we just redetermined the PCM energy with geometry optimization.

III.B.1. Structures and Relative Stabilities in the Gas Phase. The most stable structures of $[HSSO_3]^-$ (**3a**), $[SSO_3H]^-$ (**3b**), $[HSSSO_3]^-$ (**4a**), and $[SSSO_3H]^-$ (**4b**) are shown in Figure 3. As in the case of **2a** and **2b**, the SH isomer is always more stable than its OH tautomer. The structure of **4a** is analogous to that of the isoelectronic peroxomonosulfate ion $[HOOSO_3]^-$,[37] which is also more stable than its tautomer $[OOSO_3H]^-$.[20b]

The absolute enthalpy differences ΔH°_{298} between these pairs of tautomers are 21.9 kJ mol^{-1} for **2a**/**2b**, 21.3 kJ mol^{-1} for **3a**/**3b**, and 40.0 kJ mol^{-1} for **4a**/**4b** (see Table 1).

As reported previously,[20b] the gas phase structures of **3a** and **3b** are both of C_s symmetry. Only **3b** shows signs of an intramolecular hydrogen bond (OH···S). Inserting another sulfur atom into the SS bond of **3a** to produce the disulfane monosulfonate ion $[HSSSO_3]^-$ (**4a**) results in the loss of symmetry. The distance between the hydrogen atom and the oxygen atoms is now too large for any intramolecular O···H hydrogen bonding. However, in the tautomer $[SSSO_3H]^-$ (**4b**) the S_{term}···H distance of 210.4 pm indicates a normal hydrogen bond with a bond angle at the H atom of 148.7° (Figure 3).

TABLE 1: Negative Absolute Energies *E*, Enthalpies *H*, and Gibbs Energies *G* (all in hartree) of Various Tautomeric Anions of Composition $[S_n,H,O_3]^-$ and $[S_n,H,O_5]^-$ ($n = 1-3$) Both in the Gas Phase and in a Polarizable Continuum (PCM, with Geometry Optimization)[a]

species	E_e (B3LYP/6-31G(2df,p))	$H°_{298}$ (G3X/MP2)	$G°_{298}$ (G3X/MP2)	μ (D)
$[HSO_3]^-$ (**2a**)	**624.50447**	**623.87214**	**623.90308**	2.16
(**2a′**)	**624.60975** (PCM)			2.71
$[SO_3H]^-$ (**2b**)	624.49972	623.86378	623.89628	1.24
(**2b′**)	624.60712 (PCM)			2.33
$[HSSO_3]^-$ (**3a**)	**1022.72614**	**1021.64757**	**1021.68363**	1.55
(**3a′**)	1022.82225 (PCM)			3.66
$[SSO_3H]^-$ (**3b**)	1022.72118	1021.63944	1021.67577	2.13
(**3b′**)	**1022.82324** (PCM)			4.30
$[HSSSO_3]^-$ (**4a**)	**1420.93150**	**1419.41342**	**1419.45474**	3.21
(**4a′**)	**1421.02467** (PCM)			6.02
$[SSSO_3H]^-$ (**4b**)	1420.92269	1419.39971	1419.43919	1.32
(**4b′**)	1421.01032 (PCM)			4.85
$[O_2SSSO_3H]^-$ (**5a**)	**1571.38134**	**1569.71599**	**1569.76209**	2.79
(**5a′**)	**1571.46288** (PCM)			5.03
$[HO_2SSSO_3]^-$ (**5b**)	1571.37741	1569.71318	1569.75791	2.90
(**5b′**)	1571.46033 (PCM)			5.24
$[O_2S(H)SSO_3]^-$ (**5c**)	1571.34913	1569.69404	1569.73931	1.70
(**5c′**)	1571.43521 (PCM)			4.55

[a] Data of the lowest minimum structures are given in bold numbers. The dipole moments μ calculated at the B3LYP/6-31G(2df,p) level both for the gas phase and the polarizable continuum are given in Debye. The first dipole moment applies to the gas phase, the second to the polarizable phase.

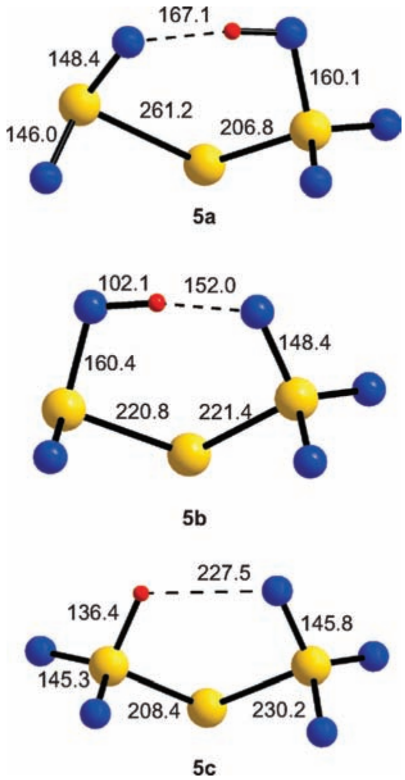


Figure 4. Structures of three isomers of the gaseous anion $[HS_3O_5]^-$ (**5a**,**b**,**c**), calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm). The relative stabilities decrease in the order **a** > **b** > **c**.

The NPA atomic charges of the two involved atoms are +0.50 for hydrogen and −0.64 for the terminal sulfur atom. This anion (**4b**) formally contains a relatively flat heterocycle of connectivity SSSOH (torsion angles $\tau_{SSSO} = 33.1°$, $\tau_{SSOH} = -25.8°$, $\tau_{SOH\cdots S} = 11.0°$).

For the hypothetical anions of composition $[S_3O_5H]^-$ obtained by addition of SO_2 to the terminal S atom of **3b** three isomers were located as minima on the PES. Their structures are given in Figure 4. In this species, the most favorable location of the proton is at the sulfonic acid part of the ion (**5a**), followed by one of the sulfinic oxygen atoms (**5b**, relative enthalpy $\Delta H°_{298} = +7.4$ kJ mol^{-1}), whereas locating the proton at the three-coordinate sulfur atom results in a much less stable tautomer of relative enthalpy +57.6 kJ mol^{-1} (**5c**).

The structure of **5a** may be interpreted as an adduct between the Lewis acid SO_2 and the anion $[SSO_3H]^-$ (**3b**) held together by a long SS bond of 261.2 pm and a rather short O···HO hydrogen bond of length 167.1 pm. The terminal sulfur atom of **3b** bears an atomic charge of −0.75 units (see below) making this ion a strong nucleophile which attracts the positively charged sulfur atom of SO_2 with formation of a dative but partly ionic SS bond. The NPA atomic charge transfer to the SO_2 part of the ion is −0.34 electrostatic units.

If the proton in the O···HO bridge of **5a** switches its position to OH···O, the isomer **5b** is formed, which is characterized by two SS bonds of more normal length (220.8 and 221.4 pm) and a very short hydrogen bond of length 152.0 pm. This ion is clearly a structural relative of the well-known trithionate ion $[O_3S{-}S{-}SO_3]^{2-}$. On the other hand, if the hydrogen atom is attached to the three-coordinate sulfur atom as in isomer **5c** the resulting SH···O hydrogen bond is very weak as can be concluded from its O···H distance of 227.5 pm.

Trithionate is usually prepared from thiosulfate by reaction with SO_2 in aqueous solution.[38] First, a yellow color is observed which is typical for certain species with more than one SS bond and which may be due to ion **5a** or its related dianion, which then seems to undergo an intermolecular redox reaction forming trithionate and elemental sulfur:

$$[SSO_3]^{2-} + SO_2 \rightarrow [O_2SSSO_3]^{2-} \tag{11}$$

$$2[O_3SSSO_3]^{2-} + SO_2 \rightarrow 2[O_3SSSO_3]^{2-} + \tfrac{1}{8}S_8 \tag{12}$$

In other words, our calculations now indicate the possible nature of the intermediate in this process.

III.B.2. Structures and Thermodynamics in the Polarizable Phase. The reoptimization of the above gas phase structures in the polarizable phase resulted in changes of some geometrical parameters, especially in the case of **3b/3b′** and **4b/4b′**, and the absolute and relative energies as well as of the dipole moments changed accordingly (Table 1). In Figure 3, the geometrical parameters of the ions predicted for the polarizable phase are given in italics. These data demonstrate that the intramolecular OH···S hydrogen bonds of **3b** and **4b** are dissolved in the polarizable continuum. The torsion angle $\tau_{SSOH} = -0.9°$ of **3b** changed to −61.8° in **3b′** since the hydrogen atom prefers to be in one plane with one of the terminal oxygen atoms in the polarizable phase. Similarly, the torsion angles $\tau_{SSSO(H)} = 33.1°$ and $\tau_{SSOH} = -25.8°$ of **4b** changed to 68.4° and −85.8°, respectively, in **4b′** resulting in a relatively close O···H contact of 251.0 pm.

Since the PCM calculations have been performed at the B3LYP/6-31G(2df,p) level of theory, the relative energies can only cautiously be compared to the gas phase data obtained at the much higher G3X(MP2) level. Generally, the intramolecular hydrogen bonds observed in the gas phase structures are often missing in the polarizable phase and dipole moments are almost always much higher than in the gas phase. Also, OH tautomers are somewhat more stabilized than SH isomers compared to the gas phase.

In the case of the tautomeric pairs of ions **2a/2b** and **4a/4b** the PCM calculations predict the SH form (**a**) still to be more stable than the OH isomer (**b**), by 6.9 kJ mol^{-1} (**2a′/2b′**) and by 37.7 kJ mol^{-1} (**4a′/4b′**), respectively. However, in the case of **3a′** and **3b′**, the latter is now more stable at the potential energy minimum ($\Delta E_e = 2.6$ kJ mol^{-1}; Table 1), but at 298 K **3a′** is more stable than **3b′**, by $\Delta H_{298} = 3.3$ kJ mol^{-1} (Supporting Information Table S1b). We therefore conclude that at least the tautomers **3a′/3b′** exist next to each other in aqueous solution as has been observed spectroscopically for the related sulfonate and hydrogen sulfite ions $[HSO_3]^-$ (**2a**) and $[SO_3H]^-$ (**2b**).[21]

Similar predictions can be made for the two isomers **5a** and **5b** of composition $[S_3O_5H]^-$. The species **5a** is most stable both in the gas phase and in the polarizable continuum (**5a′**), but the tautomer **5b′** has a relative enthalpy ΔH_{298} of only +5.5 kJ mol^{-1} in the polarizable phase. Once more we predict that both ions exist in comparable concentrations in aqueous solutions at ambient conditions. In contrast, isomer **5c′** is much less stable than **5a′**, by $\Delta H_{298} = +70.6$ kJ mol^{-1}, and thus has no chance to exist under equilibrium conditions.

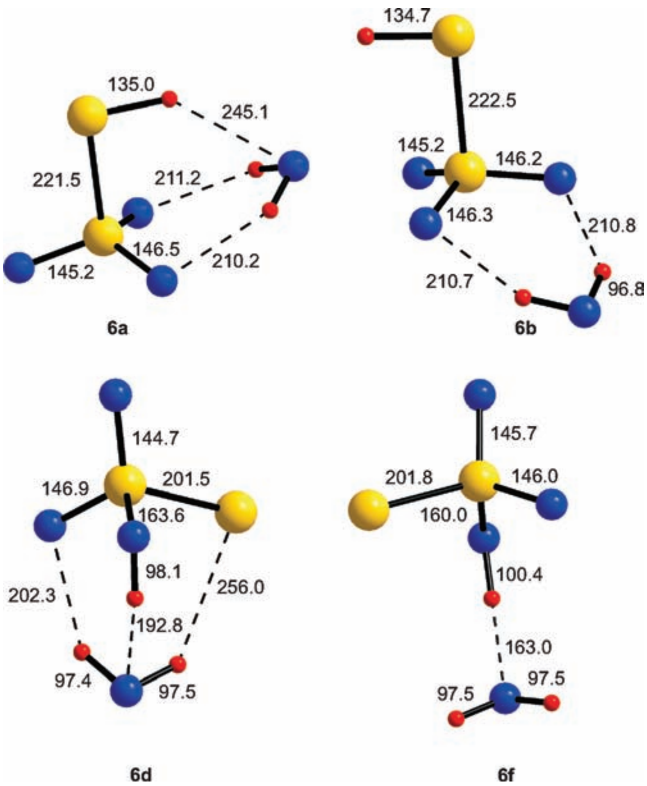
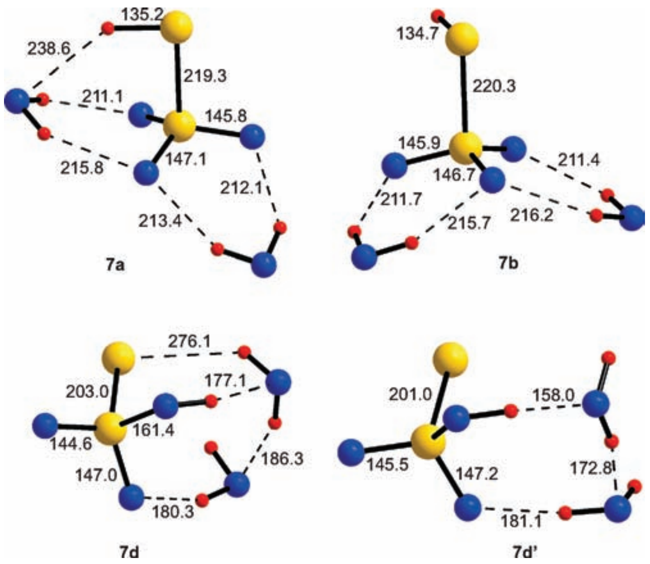


Figure 5. Structures of various isomers of the anionic hydrate $[H,S_2,O_3]^- \cdot H_2O$ both in the gas phase (**6a**,**b**,**d**) and in the polarizable phase (**6f**), calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm).

III.C. Monohydrates of the Tautomeric Anions $[HSSO_3]^-$ and $[SSO_2(OH)]^-$. ***III.C.1. Structures and Thermodynamics in the Gas Phase.*** For the monohydrates of composition $[H,S_2,O_3]^- \cdot H_2O$ five minimum energy structures have been identified on the PES (**6a**−**e**). The global minimum structure **6a** is the monohydrate of $[HSSO_3]^-$ (**3a**) with two normal and one rather long hydrogen bond and an approximate C_s symmetry; see Figure 5. This gas phase structure represents also the global minimum at the B3LYP level but not in the polarizable continuum (see below). There are two more structures of connectivity $[HSSO_3]^- \cdot H_2O$ with relative enthalpies of 0.7 kJ mol^{-1} (**6b**) and 8.5 kJ mol^{-1} (**6c**; not shown) containing also two hydrogen bonds each. The two most stable monohydrates of the tautomer $[SSO_2(OH)]^-$ are by 17.9 kJ mol^{-1} (**6d**) and 25.1 kJ mol^{-1} (**6e**) less stable than **6a**. The latter two hydrates are characterized by two O···H and one S···H hydrogen bond, but the S···H distances are slightly larger than 250 pm. In other words, the terminal sulfur atoms are poor hydrogen-bond acceptors in these ions; see Figure 5 for the structure of **6d** which is of C_1 symmetry.

III.C.2. Structures and Thermodynamics in the Polarizable Phase. Interestingly, the most stable monohydrate in the polarizable phase has a structure different from all the above-mentioned gas phase structures **6a**−**e**. This species of C_1 symmetry is therefore labeled as **6f** and is shown in Figure 5; it is a derivative of the OH tautomer of the hydrogen thiosulfate anion and has just one but very short O···H bond of length 163 pm. Interestingly, this structure resulted from the geometry optimization of both **6b** and **6d** in the polarizable phase. The most stable monohydrate of the SH tautomer obtained from the gas phase geometry **6a** is by $\Delta E_e = 15.4$ kJ mol^{-1} and $\Delta H_{298} = 10.2$ kJ mol^{-1} less stable than **6f** at the B3LYP-PCM level. This structure (**6a′**) has two hydrogen bonds of length 190.3 and 213.7 pm (not shown).

III.D. Dihydrates of the Tautomeric Anions $[HSSO_3]^-$ and $[SSO_2(OH)]^-$. ***III.D.1. Structures and Thermodynamics in the Gas Phase.*** Eight isomers of composition $[H,S_2,O_3]^- \cdot 2H_2O$ (**7a**−**h**) have been studied. In these ions the two water molecules can either be separate from each other or form a dimer which is connected to the thiosulfate ion by H bonds. The most stable structures **7a** and **7b** differ in enthalpy by just 0.6 kJ mol^{-1}; both are shown in Figure 6. These species are derivatives of the SH tautomer of the anion with five (**7a**) and four (**7b**) hydrogen bonds, respectively. In both cases the water molecules are separate. A third isomer (**7c**; not shown) with an SH bond and with the water molecules linked to each other is by 2.6 kJ mol^{-1} less stable than **7a** followed by the most stable dihydrate of the OH tautomer (**7d**), which also contains a water dimer (Figure 6). At the B3LYP and B3LYP-PCM levels of theory **7d** is the lowest minimum structure. In the gas phase this hydrate is characterized by three short O···H hydrogen bonds, one rather



7a **7b** **7d** **7d'**

Figure 6. Structures of various isomers of the anionic dihydrate $[H,S_2,O_3]^- \cdot 2H_2O$ both in the gas phase (**7a**,**b**,**d**) and in the polarizable phase (**7d′**), calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm).

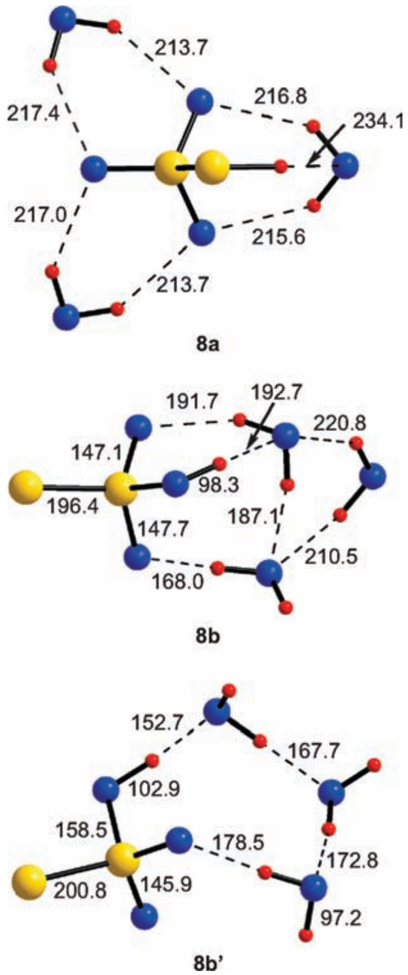
long S···H bond, and one dangling H atom not involved in any hydrogen bonding. The relative enthalpy of **7d** compared to **7a** is 12.1 kJ mol^{-1}.

The less stable dihydrates **7e**−**h** can also be derived from the OH tautomer of the anion. Their atomic coordinates are given in the Supporting Information.

III.D.2. Structures and Thermodynamics in the Polarizable Phase. On geometry optimization using the PCM method the dihydrate structure **7d** was modified to **7d′** the geometry of which is shown in Figure 6. These two species differ mainly in the number of hydrogen bonds, which is lower in the polarizable phase where two H atoms do not take part in hydrogen bonding. The second most stable dihydrate under PCM conditions (**7g**) is also an OH tautomer and is of relative energy $\Delta E_e = 2.2$ kJ mol^{-1}. The most stable SH tautomer (**7c′**) is by $\Delta H_{298} = 16.9$ kJ mol^{-1} less stable than **7d′**.

III.E. Trihydrates of the Tautomeric Anions $[HSSO_3]^-$ and $[SSO_2(OH)]^-$. ***III.E.1. Structures and Thermodynamics in the Gas Phase.*** Four trihydrates of the two tautomeric hydrogen thiosulfate anions were studied, and once again the SH form, $[HSSO_3]^- \cdot 3H_2O$ (**8a**), represents the lowest minimum structure; see Figure 7. This hydrated anion is of approximate C_s symmetry with six OH···O hydrogen bonds shorter than 220 pm and just one dangling H atom (SH) which is, however, directed toward one of the water oxygen atoms (SH···O distance 234.1 pm). The most stable OH tautomer (**8b**) has also six hydrogen bonds and is by 19.5 kJ mol^{-1} less stable than **8a**. However, at the B3LYP level **8b** corresponds to the global minimum structure. Whereas the water molecules are separate in **8a**, they form a trimer in **8b**. It has repeatedly been reported before that the water molecules tend to stick together in the higher hydrates of sulfur-containing molecules.[22,24] The other two trihydrate ions **8c** and **8d** (not shown) are also derivatives of the OH tautomer of the anion and are by 19.8 and 22.8 kJ mol^{-1}, respectively, less stable than **8a**.

III.E.2. Structures and Thermodynamics in the Polarizable Phase. On geometry optimization of **8b** in the polarizable continuum structure **8b′** was obtained which is the most stable trihydrate under these conditions. As in the structure of **8b**, the water molecules form a cluster which is connected to the sulfur oxoanion by four hydrogen bonds, but there are three dangling H atoms compared to six hydrogen bonds and only one dangling H in the gas phase structure **8b**; see Figure 7. The most stable SH tautomer of $[H,S_2,O_3]^- \cdot 3H_2O$ (**8d′**; not shown) is by $\Delta H_{298} = 29.9$ kJ mol^{-1} less stable than **8b′**.



8a **8b** **8b'**

Figure 7. Structures of two isomers of the anionic trihydrate $[H,S_2,O_3]^- \cdot 3H_2O$ both in the gas phase (**8a**,**b**) and in the polarizable phase (**8b′**), calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm).

III.F. Hydrates of the Isomeric Acids HS−SO$_2$−OH and HO−SO(S)−OH. ***III.F.1. Structures and Thermodynamics in the Gas Phase.*** As outlined above, the molecules of thiosulfuric acid $H_2S_2O_3$ may exist as either SH/OH or OH/OH tautomers; in addition, syn and anti conformers are possible (Figure 1). Previous studies have shown that the anti conformation of HS−SO$_2$−OH (**9a**) represents the global minimum structure.[20b] According to the present results, the syn isomer **9b** is by $\Delta H°_{298} = 2.9$ kJ mol^{-1} less stable, whereas the anti form of HO−SO(S)−OH (**9c**) is by 33.6 kJ mol^{-1} less stable than **9a**. Attempts to optimize the syn form of the OH/OH tautomer failed, and the anti isomer was obtained instead. The question was then whether the hydration of these acids by up to three water molecules would change the order of relative stabilities. The data in Table 2 demonstrate that all gaseous hydrates $(H_2,S_2,O_3) \cdot nH_2O$ ($n = 1-3$) are most stable as SH tautomers. Thirteen isomers of these hydrates have been located as minimum structures on the corresponding potential energy surfaces, but here we will discuss only the structures of those species which represent the lowest minima for $n = 1-3$. For all other species the atomic coordinates and thermodynamic data are given in the Supporting Information.

TABLE 2: Negative Absolute Energies *E*, Enthalpies *H*, and Gibbs Energies *G* (all in hartree) of the Hydrates of Composition $(H_2,S_2,O_3)\cdot nH_2O$ (*n* = 1−3), Both in the Gas Phase and in a Polarizable Continuum without Geometry Optimization (PCM*)[a]

species	E_e (B3LYP/6-31G(2df,p))	$E°_{298}$ (G3X/MP2)	$H°_{298}$ (G3X/MP2)	$G°_{298}$ (G3X/MP2)	μ
$H_2S_2O_3\cdot H_2O$	**1099.69252**	**1098.50160**	**1098.49167**	**1098.53453**	3.88
(anti) (**10a**)	**1099.71248** PCM*				4.94
$H_2S_2O_3\cdot H_2O$	1099.69144	1098.50085	1098.49089	1098.53396	3.64
(**10b**) (syn)	1099.71176 PCM*				4.75
$H_2S_2O_3\cdot H_2O$	1099.68348	1098.48867	1098.47886	1098.52143	2.25
(**10c**) (anti)	1099.70716 PCM*				2.77
$H_2S_2O_3\cdot 2H_2O$	**1176.14162**	**1174.85921**	**1174.84676**	**1174.89476**	5.56
(syn) (**11a**)	**1176.16224** PCM*				6.87
$H_2S_2O_3\cdot 2H_2O$	1176.13449	1174.85287	1174.83997	1174.88953	1.46
(anti) (**11b**)	1176.15414 PCM*				1.58
$H_2S_2O_3\cdot 2H_2O$	1176.13399	1174.84680	1174.83432	1174.88323	2.94
(anti) (**11c**)	1176.15674 PCM*				3.67
$H_2S_2O_3\cdot 3H_2O$	**1252.58858**	**1251.21187**	**1251.19687**	1251.25018	6.60
(syn) (**12a**)	1252.61070 PCM*				8.10
$H_2S_2O_3\cdot 3H_2O$	1252.58559	1251.21105	1251.19558	**1251.25137**	2.00
(anti) (**12b**)	1252.60860 PCM*				2.54
$H_2S_2O_3\cdot 3H_2O$	1252.58717	1251.20539	1251.19087	1251.24289	7.67
(**12c**) (syn)	**1252.61193** PCM*				9.44

[a] Global minimum data are given in bold. The dipole moments μ calculated at the B3LYP/6-31G(2df,p) level are given in Debye. The first dipole moment applies to the gas phase, the second to the polarizable phase.

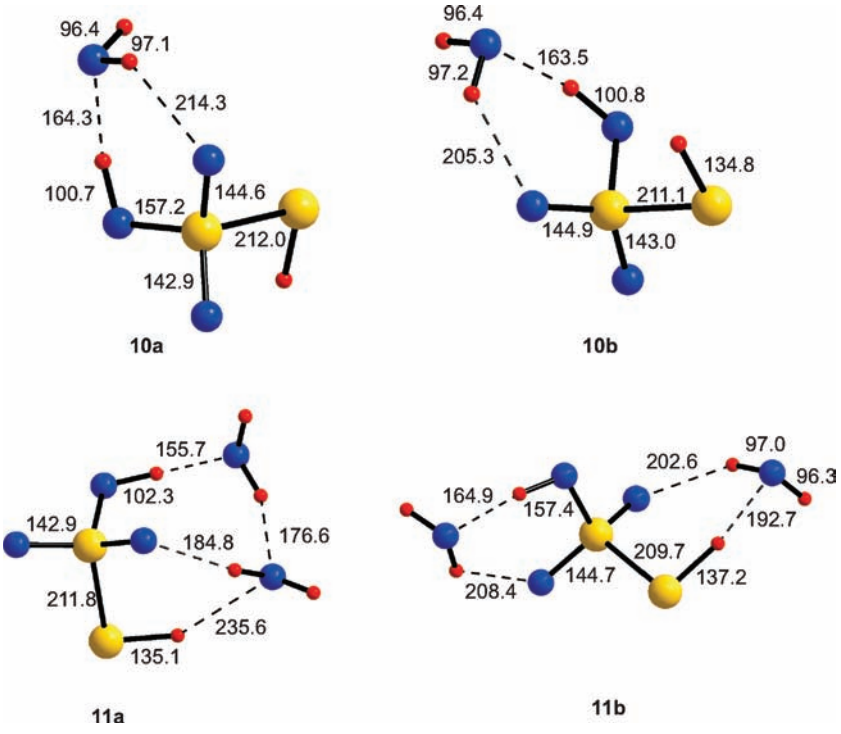


Figure 8. Structures of two isomers each of the gaseous acid hydrates $H_2S_2O_3\cdot H_2O$ (**10a**,**b**) and $H_2S_2O_3\cdot 2H_2O$ (**11a**,**b**), calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm).

The most stable monohydrate $(H_2,S_2,O_3)\cdot H_2O$ is the anti conformer **10a** shown in Figure 8. However, the enthalpy of the corresponding syn derivative **10b** is only 2.0 kJ mol^{-1} larger. Two other isomers (not shown) follow with relative enthalpies of 33.6 and 40.5 kJ mol^{-1} (**10c**,**d**). Isomer **10c** is the most stable monohydrate of the OH/OH form of the acid.

The heterocyclic structure of **10a** is analogous to that of $H_2SO_4\cdot H_2O$ (**1b**) shown in Figure 2. In **10a**, there are two OH···O hydrogen bonds of lengths 164.3 and 214.3 pm, similar to those of **1b**. The SH group is not involved in any hydrogen bonding. This statement also holds for the syn conformer **10b** which is also shown in Figure 8.

Of the four investigated dihydrates $H_2S_2O_3\cdot 2H_2O$ (**11a**−**d**) the syn form **11a** represents the lowest minimum followed by the anti isomer **11b** with a relative enthalpy of 17.8 kJ mol^{-1}. Both molecules are SH tautomers and are characterized by four hydrogen bonds; see Figure 8. The two most stable OH/OH isomers **11c** and **11d** (not shown) are by 32.6 and 35.2 kJ mol^{-1}, respectively, less stable.

Five structures have been found for the composition $(H_2,S_2,O_3)\cdot 3H_2O$ (**12a**−**e**), and the two most stable structures (**12a**,**b**) are again SH tautomers (Figure 9). The enthalpy difference between the structure **12a** (syn conformer) with six hydrogen bonds and the anti isomer **12b** with four H bonds is only 3.4 kJ mol^{-1}. The most stable trihydrate of the OH/OH

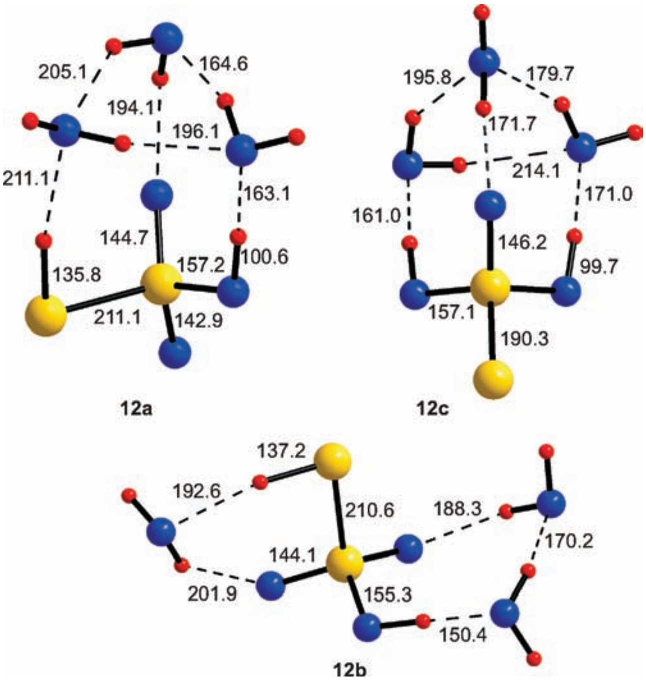


Figure 9. Structures of three isomers of the gaseous acid trihydrate $(H_2S_2O_3)\cdot 3H_2O$ (**12a**,**b**,**c**), calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm).

tautomer of thiosulfuric acid has a relative enthalpy of 15.8 kJ mol^{-1} (**12c**; Figure 9), whereas two other isomers (**12d**,**e**; not shown) are by more than 19 kJ mol^{-1} less stable (Table 2 and Supporting Information Table S1a).

III.F.2. Thermodynamics in the Polarizable Phase. The various isomers of $H_2S_2O_3$ (**9**) and its hydrates (**10**−**12**) have been calculated by the PCM method starting from the gas phase geometries. Although the free acid was treated as its anions (with geometry optimization), the acid hydrates were calculated without geometry reoptimization (symbolized in the tables by PCM*). The interaction with the polarizable continuum results in different energies and dipole moments. The relative energies changed as follows: The *anti*-SH tautomer of the free acid (**9a′**) still represents the global minimum with the *syn*-SH conformer **9b′** by just 1.3 kJ mol^{-1} less stable. For the mono- and dihydrates the global minimum structures of the gas phase are also the most stable isomers in the polarizable phase (**10a′**, **11a′**). However, in the case of the trihydrate the syn conformer of the OH/OH tautomer (**12c′**) is now the most stable structure with the SH form **12a′** just 3.2 kJ mol^{-1} less stable (ΔE_e). From all this it follows that thiosulfuric acid is expected to exist in aqueous solution as a mixture of SH/OH (syn and anti conformation) and OH/OH tautomers, whereas in the gas phase the SH/OH isomer is definitely favored.

III.G. Atomic Charges. For a mechanistic interpretation of the reactions discussed in the Introduction it is useful to know the atomic charges of the key species $[HSSO_3]^-$ (**3a**), $[SSO_3H]^-$ (**3b**), $[HSSO_3]^-\cdot 3H_2O$ (**8a**), $[SSO_3H]^-\cdot 3H_2O$ (**8b**), $H_2S_2O_3$ (**9a**), and $(H_2,S_2,O_3)\cdot 3H_2O$ (**12a**−**c**) both in the gas phase and in the polarizable phase. In particular, the charges on the various sulfur atoms are important since the sulfur transfer reactions are assumed to take place at these positions although it is unclear which species are most likely to react with each other: anions with anions or anions with neutral molecules such as undissociated thiosulfuric acid. The data in Table 3 show that a reaction between two ions $[HSSO_3]^-$ (**3a**) or between the tautomers $[HSSO_3]^-$ (**3a**) and $[SSO_3H]^-$ (**3b**) is unlikely since the sulfane sulfur atom of **3a** bears a considerable negative charge, which in addition to the anionic charge produces a strong repulsion for any incoming nucleophilic anion such as **3b**. This also holds for the hydrated anion $[HSSO_3]^-\cdot 3H_2O$ (**8a**), although to a lesser degree. On the other hand, the terminal sulfur atoms of $[SSO_3H]^-$ (**3b**) and $[SSO_3H]^-\cdot 3H_2O$ (**8b**) are highly charged making these species strong nucleophiles. Therefore, the most reasonable reaction seems to be the attack of $H_2S_2O_3$ (**12a**,**b**) by one of the anions just mentioned (**3b** or **8b**) since the sulfane sulfur atoms of **12a** and **12b** are only moderately charged (−0.24 to −0.29 electrostatic units).

The hydrogen bonds between the monoanions and the surrounding water molecules result in a small transfer of electron density from the anions to the water shell, and the remaining anion charge in the gas phase structures of the tautomeric species $[HSSO_3]^-\cdot 3H_2O$ (**8a**) and $[SSO_3H]^-\cdot 3H_2O$ (**8b**) is only −0.94 electrostatic units in both cases.

III.H. Thermodynamics of Hydration and of Sulfur Transfer Reactions. ***III.H.1. Energetics of Hydration.*** The enthalpies of hydration of the tautomeric hydrogen thiosulfate anions are of the order of -50 ± 5 kJ mol^{-1} per water molecule; they decrease with increasing number of H_2O molecules. Details are given in Table 4 from which it can be seen that the OH tautomer interacts more strongly with water molecules compared to the SH isomer.

In the case of thiosulfuric acid the absolute enthalpies of hydration are considerably smaller than those of the monoanions, by ca. 10 kJ mol^{-1} or 20%, and they are about the same for the syn and anti forms of the acids; see Table 5.

One of the purposes of this work was to determine the *energetic differences between the tautomers* of hydrogen thiosulfate and of thiosulfuric acid in the gas phase, in a polarizable phase, and in a hydrated state. For the anions the results are shown in Table 6. In the polarizable phase the OH tautomers are as more preferred as higher the degree of hydration, whereas the SH forms clearly dominate in the gas phase.

For the tautomeric hydrates of thiosulfuric acid the energy differences are given in Table 7. These data demonstrate that the OH/OH isomer should be the preferred species in aqueous solution since the Gibbs energy difference to the SH/OH tautomer is getting smaller with increasing degree of hydration, and in the polarizable phase the trihydrate **12c′** is already more favorable than the SH/OH form (**12a′**).

III.H.2. Sulfur Transfer Reactions. Now we come back to the question whether the initial reaction of the thiosulfate decomposition in acidic media is a sulfur transfer between two anions or between an anion and a neutral molecule. In the following equations the thermodynamic data $\Delta H°_{298}$ and $\Delta G°_{298}$ apply to the gas phase and ΔH_{298} and ΔG_{298} to the polarizable continuum (PCM).

The mutual attack of two hydrogen thiosulfate anions **3a** with sulfur transfer is endothermic and endergonic and therefore unlikely in the gas phase:

$$2[HSSO_3]^-\ (\mathbf{3a}) \rightarrow [HSO_3]^-\ (\mathbf{2a}) + [HSSSO_3]^-\ (\mathbf{4a}) \tag{13}$$

$$\Delta H°_{298} = +25.2\ \mathrm{kJ\ mol^{-1}};\quad \Delta G°_{298} = +24.8\ \mathrm{kJ\ mol^{-1}}$$

In the polarizable phase, starting with the then more stable tautomer **3b′**, the reaction is also endothermic and endergonic [ΔH_{298}(PCM) = +25.6 kJ mol^{-1}; ΔG_{298}(PCM) = +22.7 kJ

TABLE 3: Atomic Charges of Anions and Molecules from a Natural Population Analysis (NPA) in Electrostatic Units, Calculated at the B3LYP/6-31G(2df,p) Level of Theory

species	H(S)	H(O)	S(H)	S_{term}	S_{sulfon}	O(H)	O_{term}
$[HSSO_3]^-$ (**3a**)	0.13		−0.50		2.36		−1.00
$[SSO_3H]^-$ (**3b**)		0.50		−0.75	2.17	−0.96	−0.99
$[HSSSO_3]^-$ (**4a**)[a]	0.13		−0.21		2.34		−0.98
$[HSSO_3]^-\cdot 3H_2O$ (**8a**)	0.16		−0.39		2.34		−1.01
$[SSO_3H]^-\cdot 3H_2O$ (**8b**)		0.51		−0.60	2.15	−0.96	−1.02
$HSSO_3H$ (**9a**)	0.17	0.53	−0.24		2.27	−0.90	−0.91
$HSSO_3H\cdot 3H_2O$ (**12a**)	0.17	0.54	−0.25		2.30	−0.94	−950.03
$HSSO_3H\cdot 3H_2O$ (**12b**)	0.20	0.54	−0.29		2.31	−0.95	−960.01
$SSO_2(OH)_2\cdot 3H_2O$ (**12c**)		0.53		−0.38	2.10	−0.94	−0.99

[a] Charge on central sulfur atom: −0.29.

TABLE 4: Enthalpies of Hydration of the Gaseous Hydrogen Thiosulfate Anions (in kJ mol^{-1}), Calculated at the G3X(MP2) Level of Theory Based on B3LYP/6-31G(2df,p) Geometries

anion	$\Delta H°_{298}$ (total)	$\Delta H°_{298}$ (per H_2O)
$[HSSO_3]^-\cdot H_2O$ (**6a**)	−51.4	−51.4
$[SSO_3H]^-\cdot H_2O$ (**6d**)	−56.9[a]	−56.9[a]
$[HSSO_3]^-\cdot 2H_2O$ (**7a**)	−97.6	−48.8
$[SSO_3H]^-\cdot 2H_2O$ (**7d**)	−106.6	−53.3
$[HSSO_3]^-\cdot 3H_2O$ (**8a**)	−139.9	−46.6
$[SSO_3H]^-\cdot 3H_2O$ (**8b**)	−141.7	−47.2

[a] With the larger basis set 6-31+G(2df,p) the reaction enthalpy was calculated as −56.6 kJ mol^{-1}.

TABLE 5: Enthalpies of Hydration of the Gaseous Thiosulfuric Acid Tautomers (in kJ mol^{-1}), Calculated at the G3X(MP2) Level of Theory

molecule	$\Delta H°_{298}$ (total)	$\Delta H°_{298}$ (per H_2O)
$HS{-}SO_2{-}OH\cdot H_2O$ (**10a**)	−43.3	−43.3
$SSO_2(OH)_2\cdot H_2O$ (**10c**)	−43.2	−43.2
$HS{-}SO_2{-}OH\cdot 2H_2O$ (**11a**)	−83.5	−41.7
$SSO_2(OH)_2\cdot 2H_2O$ (**11c**)	−84.5	−42.2
$HS{-}SO_2{-}OH\cdot 3H_2O$ (**12a**)	−110.6	−36.9
$SSO_2(OH)_2\cdot 3H_2O$ (**12c**)	−128.4	−42.8

mol^{-1}]. When the trihydrates of the reagents are used the thermodynamics is unfavorable as well:

$$2[HSSO_3]^-\cdot 3H_2O\ (\mathbf{8a}) \rightarrow [HSO_3]^-\cdot 3H_2O\ (\mathbf{14a}) + [HSSSO_3]^-\cdot 3H_2O\ (\mathbf{13a}) \quad (14)$$

$$\Delta H°_{298} = +23.6\ \text{kJ mol}^{-1};\quad \Delta G°_{298} = +16.0\ \text{kJ mol}^{-1}$$

In the polarizable continuum, the analogous reaction of **8b′** to **14b′** plus **13a′** is calculated as strongly endothermic ($\Delta E_e = +88.3$ kJ mol^{-1}). The structure of **13a** is characterized by six or seven hydrogen bonds (the seemingly dangling H is 251.9 pm apart from the nearest oxygen atom) and a torsion angle SSSH of 62.9°; see Figure 10. This structure was derived from that of **8a** by adding one sulfur atom and keeping the number of hydrogen bonds at maximum. The rather long and highly polar $S{-}SO_3$ bond of length 220.6 pm makes this ion a suitable candidate for transfer of the HSS group to an incoming nucleophilic thiosulfate ion with formation of $[HSSSSO_3]^-$ as another intermediate on the route to S_6, S_7, and S_8. In the polarizable continuum the anion structure **13a′** is basically the same, but the number of H bonds is reduced to four (three OH···O and one SH···O; $\tau_{HSSS} = 77.5°$, $d_{SS} = 207.0$ and 217.0 pm).

If the trihydrates of the two tautomeric hydrogen thiosulfate anions attack each other the gas phase equilibrium is predicted to be on the right side ($\Delta G°_{298} < 0$), but the reaction is endothermic both in the gas phase and in the polar phase:

$$[HSSO_3]^-\cdot 3H_2O\ (\mathbf{8a}) + [SSO_3H]^-\cdot 3H_2O\ (\mathbf{8b}) \rightarrow [HSO_3]^-\cdot 3H_2O\ (\mathbf{14a}) + [HSSSO_3]^-\cdot 3H_2O\ (\mathbf{13a}) \quad (15)$$

$$\Delta H°_{298} = +4.1\ \text{kJ mol}^{-1};\quad \Delta G°_{298} = -17.0\ \text{kJ mol}^{-1};\quad \Delta E_e = +52.2\ \text{kJ mol}^{-1}$$

In addition, taking the negative charge of the sulfane sulfur atom of **8a** into account (Table 3) this atom is not likely to be attacked by the terminal sulfur atom of **8b** (see the discussion above).

In contrast, the sulfur transfer between hydrogen thiosulfate and thiosulfuric acid is thermodynamically strongly favored ($\Delta G°_{298} < 0$) both for the unhydrated anions as well as for the trihydrates, also if the less stable tautomers of the hydrogen thiosulfate ion (**3b** or **8b**) are used as starting materials:

$$[HSSO_3]^-\ (\mathbf{3a}) + H_2S_2O_3\ (\mathbf{9a}) \rightarrow [HSSSO_3]^-\ (\mathbf{4a}) + SO_2{+}H_2O \quad (16)$$

$$\Delta H°_{298} = -48.5\ \text{kJ mol}^{-1};\quad \Delta G°_{298} = -97.1\ \text{kJ mol}^{-1}$$

$$[SSO_3H]^-\ (\mathbf{3b}) + H_2S_2O_3\ (\mathbf{9a}) \rightarrow [HSSSO_3]^-\ (\mathbf{4a}) + SO_2{+}H_2O \quad (17)$$

$$\Delta H°_{298} = -69.8\ \text{kJ mol}^{-1};\quad \Delta G°_{298} = -117.7\ \text{kJ mol}^{-1}$$

$$\Delta H_{298}(\text{PCM}) = -20.0\ \text{kJ mol}^{-1};\quad \Delta G_{298}(\text{PCM}) = -72.7\ \text{kJ mol}^{-1}$$

$$[HSSO_3]^-\cdot 3H_2O\ (\mathbf{8a}) + H_2S_2O_3\cdot 3H_2O\ (\mathbf{12a}) \rightarrow [HSSSO_3]^-\cdot 3H_2O\ (\mathbf{13a}) + SO_2{+}4H_2O \quad (18)$$

$$\Delta H°_{298} = +73.8\ \text{kJ mol}^{-1};\quad \Delta G°_{298} = -100.2\ \text{kJ mol}^{-1}$$

If the interaction between SO_2 and the four water molecules on the right sides of eqs 18 and 19 is taken into account to give the hydrate $SO_2\cdot 4H_2O$[22] these reactions are both predicted to be exothermic, by $\Delta H°_{298} = -2.7$ and −22.2 kJ mol^{-1}, respectively, and to be still exergonic, by $\Delta G°_{298} = -26.0$ and −59.0 kJ mol^{-1}, respectively.

TABLE 6: Thermodynamic Differences between the Most Stable Tautomeric Anions $[HSSO_3]^-\cdot nH_2O$ and $[SSO_3H]^-\cdot nH_2O$ in the Gas Phase at the G3X(MP2) Level of Theory ($\Delta H°_{298}$ and $\Delta G°_{298}$) and in the Polarizable Continuum at the B3LYP/6-31G(2df,p) Level (PCM)[a]

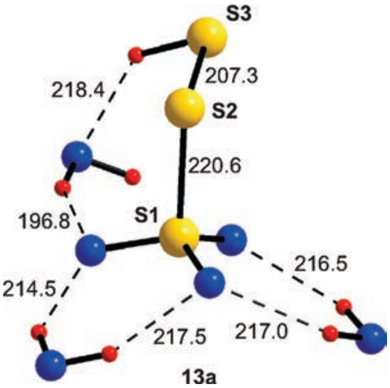
n:	0	1	2	3
$\Delta H°_{298}$	−21.3 (**3a/b**)	−17.9 (**6a/d**)	−12.1 (**7a/d**)	−19.5 (**8a/b**)
$\Delta G°_{298}$	−20.6 (**3a/b**)	−17.1 (**6a/e**)	−27.1 (**7b/e**)	−22.1 (**8a/c**)
ΔE_e(PCM)	−2.6 (**3a′/b′**)	+15.4 (**6a′/f**)	+21.3 (**7c′/d′**)	+35.8 (**8d′/b′**)
ΔH_{298}(PCM)	−3.3 (**3a′/b′**)	+10.2 (**6a′/f**)	+16.9 (**7c′/d′**)	+29.9 (**8d′/b′**)
ΔG_{298}(PCM)	−4.6 (**3a′/b′**)	+15.3 (**6a′/f**)	+15.4 (**7c′/d′**)	+14.7 (**8d′/b′**)

[a] Given is the energy difference between the most stable SH tautomer minus the most stable OH form (in kJ mol^{-1}; negative values mean that the SH isomer is more stable.

TABLE 7: Energy Differences between the Most Stable Tautomers of the Acids $HSSO_3H^-\cdot nH_2O$ and $SSO(OH)_2{}^-\cdot nH_2O$ in the Gas Phase at 298 K ($\Delta H°_{298}$ and $\Delta G°_{298}$) and in the Polarizable Continuum (PCM)[a]

n:	0	1	2	3
$\Delta H°_{298}$	−33.6 (**9a/c**)	−33.6(**10a/c**)	−32.6 (**11a/c**)	−15.8 (**12a/c**)
$\Delta G°_{298}$	−34.0 (**9a/c**)	−34.4 (**10a/c**)	−30.3 (**11a/c**)	−22.3 (**12b/c**)
ΔE_e(PCM/PCM*)	−10.6 (**9a′/c′**)	−14.0 (**10a′/c′**)	−13.6 (**11a′/d′**)	+3.2 (**12a′/c′**)
ΔH_{298}(PCM)	−15.1 (**9a′/c′**)			
ΔG_{298}(PCM)	−16.2 (**9a′/c′**)			

[a] Given is the energy difference between the most stable SH tautomer minus the most stable OH form (in kJ mol^{-1}; negative values mean that the SH isomer is more stable).



13a

Figure 10. Structure of the gaseous trihydrate $[HS_3O_3]^-\cdot 3H_2O$ (**13a**), calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm). The NPA atomic charges of the sulfur atoms are as follows: S1, +2.32; S2, −0.22; S3, −0.20.

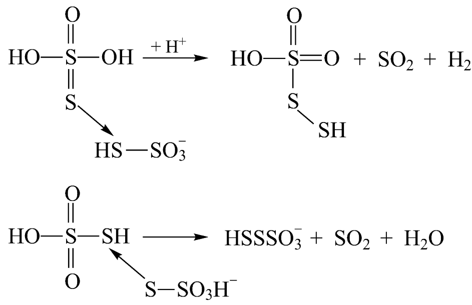
$$[SSO_3H]^-\cdot 3H_2O\ (\mathbf{8b}) + H_2S_2O_3\cdot 3H_2O\ (\mathbf{12a}) \rightarrow [HSSSO_3]^-\cdot 3H_2O\ (\mathbf{13a}) + SO_2 + 4H_2O \quad (19)$$

$$\Delta H°_{298} = +54.3\ \text{kJ mol}^{-1};\quad \Delta G°_{298} = -133.2\ \text{kJ mol}^{-1}$$

From the data given in the above equations we conclude that the sulfur transfer reactions during the acid decomposition of thiosulfate most likely take place between the two tautomeric hydrogen thiosulfate anions on the one hand and neutral thiosulfuric acid molecules on the other hand and not between two anions; see Scheme 1. The principle of these reactions is that the negatively charged terminal sulfur atoms attack the sulfane sulfur atoms with nucleophilic displacement resulting in the stepwise growth of a sulfur chain from which homocyclic sulfur molecules (S_6, S_7, and S_8) can eventually be split off.

This reaction mechanism can explain why the reaction is fastest at pH values of between 1 and 4 when the two types of species coexist in aqueous solution. This conclusion is also in line with the discussion of the atomic charges above. The first dissociation constant of thiosulfuric acid in water has been reported as $K_1 = 0.25$ at 298 K[39] corresponding to a molar ratio $[SSO_3H]^-/H_2S_2O_3$ of 25 at pH = 2 and of 2.5 at pH = 1 in dilute solution.

SCHEME 1



As a side reaction we postulate the formation of adducts between SO_2 and the various sulfane monosulfonate anions $[HS_nSO_3]^-$ ($n > 0$) by which the formation of elemental sulfur is suppressed in favor of polythionate formation. The addition of SO_2 to the gaseous tautomeric hydrogen thiosulfate ions **3a** and **3b** with formation of the monoanion of sulfane sulfinic sulfonic acid **5a** is predicted as strongly exothermic as well as exergonic:

$$[HSSO_3]^-\ (\mathbf{3a}) + SO_2 \rightarrow [O_2SSSO_3H]^-\ (\mathbf{5a}) \quad (20)$$

for **3a**:

$$\Delta H°_{298} = -53.0\ \text{kJ mol}^{-1};\quad \Delta G°_{298} = -5.3\ \text{kJ mol}^{-1}$$

for **3b**:

$$\Delta H°_{298} = -74.3\ \text{kJ mol}^{-1};\quad \Delta G°_{298} = -25.9\ \text{kJ mol}^{-1}$$

In the polarizable phase the most stable isomers of **3** and **5** are **3b′** and **5a′**. Their reaction according to eq 20 is calculated as exothermic, by ΔH_{298}(PCM) = −11.8 kJ mol^{-1}, but as endergonic, by ΔG_{298}(PCM) = +33.7 kJ mol^{-1}. However, if the dianions $[S_2O_3]^{2-}$ and $[S_3O_5]^{2-}$ are used in eq 20 the thermodynamics is more favorable: ΔH_{298}(PCM) = −41.8 kJ mol^{-1} and ΔG_{298}(PCM) = +2.6 kJ mol^{-1}. Thus, the equilibrium is expected to lie on the right side at temperatures below 0 °C or in the presence of a large excess of SO_2.

The reaction shown in eq 20 or a similar process between SO_2 and a thiol or thiolate anion may also be responsible for the repeatedly observed inhibition of the thiosulfate oxidation

TABLE 8: Comparison between the Raman Frequencies of the Anion in the Salt $[NH_4][HS_2O_3]$ and the Two Hydrates $[HSSO_3]^- \cdot nH_2O$ (n = 2, 3; Values in cm^{-1}) Calculated in the Polarizable Phase with Geometry Optimization (B3LYP-PCM)[a,b]

mode	$[NH_4][HS_2O_3]$[a]	$[HSSO_3]^- \cdot 2H_2O$ (**7a′**)	$[HSSO_3]^- \cdot 3H_2O$ (**8a′**)
ν_{SH}	2486	2533 (+47)	2529 (+43)
δ_{SSH}	873	886 (+13)	897 (+25)
ν_{SO}	1219	1248 (+29)	1256 (+37)
ν_{SO}	1183	1216 (+33)	1192 (+9)
ν_{SO}	1027	1023 (−4)	1017 (−10)
ν_{SS}	403	356 (−47)	358 (−45)

[a] See ref 13. [b] The deviations of the calculated wavenumbers (unscaled) from the experimental values are given in parentheses (ν, stretching; δ, bending mode).

catalyzed by the enzyme thiosulfate dehydrogenase by sulfite ions, which at acidic pH values are in equilibrium with molecular SO_2[22] and which had already been suspected to interact with the enzyme in some unspecified manner;[40] see the discussion below.

III.I. Vibrational Spectra. Vibrational spectroscopy is a powerful method to investigate sulfur oxoanions and the corresponding acids in solution and in the solid state. The published spectra may be compared to the calculated frequencies to check the reliability of the calculations. Of all the species investigated in this work only $[SSO_3]^{2-}$ and $[HSSO_3]^-$ have been studied experimentally. The Raman spectrum of solid $[NH_4][HS_2O_3]$ and its deuterated derivative provided evidence for the SH form of the anions.[13] The exact structures of these two salts are not known, but it can be expected that anions and cations are strongly interconnected by hydrogen bonds as has been reported for the related salt $[NH_4]_2[S_2O_3]$.[12b] Since the stretching modes of polar bonds are strongly affected by hydrogen bonds a perfect agreement of the frequencies calculated for $[HSSO_3]^-$ with the Raman spectrum of $[NH_4][HS_2O_3]$ cannot be expected. In Table 8, the most important modes of this anion are compared to the frequencies calculated for the di- and the trihydrate in the polarizable continuum for which the best agreement was obtained. This agreement is fair with the exception of the SS stretching mode which is strongly coupled in the hydrates **7a′** and **8a′**.

III.J. The Adduct of H_2S with SO_3 as an Isomer of $H_2S_2O_3$. It has been reported that H_2S and SO_3 at low temperatures form a colorless adduct which does not isomerize to thiosulfuric acid but decomposes to the components on warming in a vacuum.[19b] The direct evidence for this adduct formation and its composition, however, is rather scarce. The only additional information is the infrared spectrum of a matrix-isolated mixture of SO_3 and H_2S with absorption bands at 1377 and 1380 cm^{-1} which have been assigned to the asymmetric SO stretching vibration of the adduct.[41] This mode evidently is split into two components by the reduced symmetry of the complex (C_s) compared to free SO_3 (D_{3h}). Therefore, we have studied the reaction between the two components theoretically, and we predict the following thermodynamic gas phase data:

$$H_2S + SO_3 \rightarrow H_2S \rightarrow SO_3 \quad (21)$$

$$\Delta H^{\circ}_{298} = -27.1 \text{ kJ mol}^{-1}; \quad \Delta G^{\circ}_{298} = +9.2 \text{ kJ mol}^{-1}$$

These results are in agreement with the observation that the adduct is not stable at ambient temperatures. The structure shown in Figure 11 is of C_s symmetry. The extremely long dative SS bond of length 286.5 pm is in line with the small binding enthalpy. The SO_3 unit is slightly pyramidal. All O···H distances are larger than 326 pm and do not indicate any attractive interaction. The calculated NPA atomic charges of the two sulfur atoms in the adduct are +2.46 (SO_3) and −0.27 (H_2S), and the charge transfer from H_2S to the SO_3 unit is −0.10 electrostatic units. The oxygen atoms are negatively (−0.85) and the hydrogen atoms positively charged (+0.18). The weak bond between the two molecules may therefore be considered as mainly electrostatic. The SO stretching vibrations are predicted at 1060 (sym), 1389, and 1393 cm^{-1}. The latter two wavenumbers arising from the formerly degenerate asymmetric SO stretching vibration of SO_3 are in very good agreement with the observed infrared bands at 1377 and 1380 cm^{-1} reported by Sass and Ault.[41] The harmonic wavenumbers of the normal modes of the H_2S unit are calculated as 1210 (bending), 2677 (sym stretch), and 2694 cm^{-1} (asym stretch), whereas the SS stretching vibration is predicted at 110 cm^{-1} (all unscaled). The conversion of $H_2S \cdot SO_3$ into thiosulfuric acid **9a** at 298 K is exothermic by −39.4 kJ mol^{-1} and exergonic by −27.1 kJ mol^{-1} in the gas phase.

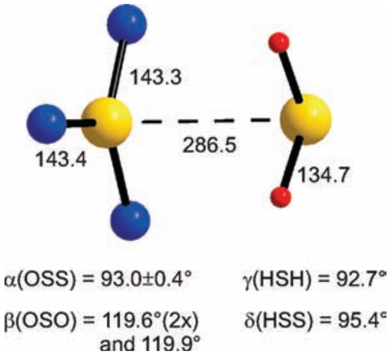


Figure 11. Structure of the gaseous adduct $H_2S \rightarrow SO_3$, calculated at the B3LYP/6-31G(2df,p) level of theory (bond lengths in pm).

IV. Biochemical Implications

Thiosulfate ions are part of the biogeochemical sulfur cycle since $[S_2O_3]^{2-}$ ions are formed by enzymatic oxidation of sulfide and elemental sulfur, by reaction of sulfite with either elemental sulfur, polysulfanes, or polysulfides, and by hydrolysis of trithionate anions. Therefore, thiosulfate together with sulfide ions (SH^-) are the most abundant reduced inorganic sulfur species in the environment. Certain sulfur bacteria utilize thiosulfate ions to gain energy by oxidation[42] to either tetrathionate (with the enzymes *thiosulfate dehydrogenase*,[43] *tetrathionate synthase*, or *thiosulfate:quinone oxidoreductase*[40b]) according to eq 22

$$2[S_2O_3]^{2-} \rightarrow [S_4O_6]^{2-} + 2e^- \quad (22)$$

or to sulfate using a multienzyme complex termed "Sox"[44] according to eq 23:

$$[S_2O_3]^{2-} + 5H_2O \rightarrow 2[SO_4]^{2-} + 10H^+ + 8e^- \quad (23)$$

Another metabolic pathway is the reduction of thiosulfate (with the help of a *thiosulfate reductase*), e.g., by glutathione (GSH), which is turned into its persulfide[45] or, more accurately, the disulfane GSSH; eq 24.

$$[S_2O_3]^{2-} + GSH \rightarrow [SO_3]^{2-} + GSSH \quad (24)$$

With the help of a *thiosulfate sulfurtransferase* the sulfane sulfur atom of the anion may also be transferred to a thiophilic acceptor molecule such as cyanide ions:

$$[S_2O_3]^{2-} + [CN]^- \rightarrow [SO_3]^{2-} + [SCN]^- \qquad (25)$$

Finally, the enzyme *thiosulfate hydrolase* catalyzes the cleavage of the SS bond:[46]

$$[S_2O_3]^{2-} + H_2O \rightarrow [SO_4]^{2-} + H_2S \qquad (26)$$

All the mentioned enzymes may have a differing composition, molecular size, and other properties in different organisms.

Equations 22−26 have been written in a form as is common in the microbiological literature. The optimum pH values for the enzymes mentioned are usually between 3.0 and 5.5, more seldomly up to 7.8. However, in acidic solutions sulfite[22] and thiosulfate ions are expected to be present mainly as a monoanions, and these are hydrated by water molecules as shown above. For the interaction with the reaction center of the particular enzymes the water of hydration must be stripped off, at least partly. Within the pockets or channels of the enzyme which connect the reaction center with the outside world the anions are likely to interact with the polar parts of the amino acids of the protein such as NH and CO groups. However, since the hydrogen bonds between the S=O groups of the sulfur oxoanions and the surrounding water molecules are stronger than those between S=O and the NH bonds of the protein the dehydration of the anions is predicted to be endothermic, even inside a protein environment.

Here we want to discuss in more detail the interaction of thiosulfate and sulfite with the sulfur-oxidizing multienzyme complex “Sox” since the structure of this heme-containing complex[44] and the mechanism of thiosulfate oxidation to sulfate[42] are known. “Sox” consists of four independent enzymes responsible for the series of reactions described in eqs 27−30. The reactive site of the oxidizing enzyme “SoxXA” is believed to be a thiolate group of a cysteine residue to which the thiosulfate anion is oxidatively coupled (R = alanyl):

$$[R - S]^- + [SSO_3H]^- \rightarrow [R - S - S - SO_3]^- + H^+ + 2e^- \qquad (27)$$

The electrons are taken up by the neighboring heme groups to reduce Fe^{3+} to Fe^{2+}. For reaction 27 a protonated thiosulfate anion is more suitable than the dianion since the latter would suffer a strong Coulomb repulsion by the thiolate anion. The disulfane sulfonate resulting from eq 27 is then hydrolyzed by another Sox enzyme at the weak and polar $S-SO_3$ bond:

$$[R - S - S - SO_3]^- + H_2O \rightarrow [R - S - S]^- + [SO_4]^{2-} + 2H^+ \qquad (28)$$

The formed disulfide $[RSS]^-$, also termed as persulfide, is known[47] to react with dioxygen to a Bunte salt or S-sulfonate the hydrolysis of which regenerates the starting thiolate as shown in eqs 29 and 30:

$$[R - S - S]^- + \tfrac{3}{2}O_2 \rightarrow [R - S - SO_3]^- \qquad (29)$$

$$[R - S - SO_3]^- + H_2O \rightarrow [R - S]^- + [SO_4]^{2-} + 2H^+ \qquad (30)$$

As mentioned above by eq 22, some sulfur bacteria produce tetrathionate either exclusively or besides sulfate by oxidation of thiosulfate. In this case, we assume that the initial reaction is as shown in eq 27, but lacking an enzyme for hydrolysis of the $[RSSSO_3]^-$ ion this species may eventually be attacked at the central sulfur atom by another thiosulfate ion as shown in eq 31 which describes another nucleophilic displacement reaction which are quite common in sulfur chemistry:

$$[R - S - S - SO_3]^- + [SSO_3H]^{2-} \rightarrow [S_4O_6]^{2-} + [R - S]^- \qquad (31)$$

Since many *thiosulfate dehydrogenases* are most active at pH values of between 3.0 and 4.0 the protonated thiosulfate ion is expected to be the dominating reagent in this case also. The attacked central sulfur atom of the $[RSSSO_3]^-$ ion bears only a small negative charge of −0.25 units in water (Table 3).

The key role of thiolate docking sites for the thiosulfate substrate may be the reason why some of these enzymes are inhibited by sulfite, disulfite, and dithionite ions.[40a] In acidic solution these oxoanions are in equilibrium with SO_2, and this molecule has been shown above to react exothermically with hydrogen thiosulfate ions forming an adduct $[O_2SSSO_3]^{2-}$ or $[O_2SSSO_3H]^-$; see Figure 4 and eq 20. A detailed investigation of the corresponding reaction of SO_2 with cysteine and the related thiolate and persulfide anions is now underway in this laboratory.

V. Conclusions

We have shown that thiosulfate exists in acidic aqueous solution most probably as equilibrium mixtures of the tautomeric species $[HSSO_3]^-$ and $[SSO_3H]^-$ on the one hand and as the acids $HSSO_3H$ and $HOS(S)O_2H$ on the other hand. Their relative stabilities are strongly influenced by the degree of hydration and by a polarizable environment as simulated by Tomasi’s PCM method. In the gas phase all species are most stable as SH tautomers, whereas the relative stabilities in water are more complex and dominated by hydrogen bonding. The well-known decomposition reaction of aqueous thiosulfate on acidification to give SO_2 and elemental sulfur is predicted to start with a nucleophilic attack of the terminal S atom of either (a) the monoanion $[SSO_3H]^-$ on the sulfane sulfur atom of $HSSO_3H$ or (b) of $SSO_2(OH)_2$ on the sulfane sulfur atom of $[HSSO_3]^-$ producing sulfane monosulfonic acid $[HS_nSO_3H]$ which is expected to undergo a chain-growth reaction by a series of similar S transfer reactions. These reactions are predicted to be exothermic and exergonic in water. As soon as the chain length n exceeds five sulfane sulfur atoms homocyclic sulfur molecules such as S_6 can be split off while the remaining sulfite anion decomposes to SO_2 and hydroxide ions. If the SO_2 is not allowed to escape it inhibits the further decomposition by reaction with the sulfane monosulfonate ions forming the novel species $[O_2SSSO_3H]^-$ which is most likely the primary intermediate in the customary synthesis of trithionate from thiosulfate and SO_2. In this way it is now possible to explain the well-known inhibition of thiolate-based enzymes by sulfite ions in the biological metabolism of thiosulfate ions by sulfur bacteria.

Acknowledgment. We are grateful to the Technische Universität Berlin and to the Hoch- und Höchstleistungsrechenzentrum Nord (HLRN) for continuing support.

Supporting Information Available: Absolute energies, enthalpies, Gibbs energies, and dipole moments for all calculated species (Table S1) as well as atomic coordinates of all species. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Steudel, R. *Chemie der Nichtmetalle*, 3rd ed.; de Gruyter: Berlin, 2008. (b) Holleman-Wiberg. *Lehrbuch der Anorganischen Chemie*, 102nd ed.; de Gruyter: Berlin, 2007. (c) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, U.K., 1997.

(2) Winnewisser, G.; Lewen, F.; Thorwirth, S.; Behnke, M.; Hahn, J.; Gauss, J.; Herbst, E. *Chem.—Eur. J.* **2003**, *9*, 5501.

(3) (a) Fender, M. A.; Sayed, Y. M.; Prochaska, F. T. *J. Phys. Chem.* **1991**, *95*, 2811. See also the criticism of this work by (b) Steiger, T.; Steudel, R. *J. Mol. Struct. (THEOCHEM)* **1992**, *257*, 313 and by(c) Napolion, B.; Huang, M.-J.; Watts, J. D. *J. Phys. Chem. A* **2008**, *112*, 4158.

(4) Sülzle, D.; Verhoeven, M.; Terlouw, J. K.; Schwarz, H. *Angew. Chem.* **1988**, *100*, 1591; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1533.

(5) (a) Königshofen, A.; Behnke, M.; Hoverath, M.; Hahn, J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1779. (b) Koerber, M.; Baum, O.; Giesen, T. F.; Schlemmer, S.; Hahn, J.; Gauss, J. *Inorg. Chem.* **2009**, *48*, 2269.

(6) Schmidt, H.; Steudel, R.; Sülzle, D.; Schwarz, H. *Inorg. Chem.* **1992**, *31*, 941.

(7) (a) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; Wiley: New York, 1998. (b) Möller, D. *Luft—Chemie, Physik, Biologie, Reinhaltung, Recht*; de Gruyter: Berlin, 2003.

(8) Lens, P., Pol, L. H., Eds. *Environmental Technologies to Treat Sulfur Pollution*; IWA Publishing: London, 2000.

(9) *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; Elvers, B., Hawkins, S., Russey, W., Eds.; VCH: Weinheim, Germany, 1994; Vol. 25A, p 447.

(10) Cole, J. A., Ferguson, S. J., Eds. *The Nitrogen and Sulfur Cycles*; Cambridge University Press: Cambridge, U.K., 1988.

(11) (a) Schlegel, H. G., Bowien, B., Eds. *Autotrophic Bacteria*; Springer: Berlin, 1989. (b) Takakuwa, S. In *Organic Sulfur Chemistry: Biochemical Aspects*; Oae, S., Okuyama, T., Eds.; CRC Press: Tokyo, 1992; p 1. (c) Barton, L. *Sulfate-Reducing Bacteria*; Plenum: New York, 1995.

(12) (a) Teng, S. T.; Fuess, H.; Bats, J. W. *Acta Crystallogr.* **1984**, *C40*, 1785. (b) Teng, S. T.; Fuess, H.; Bats, J. W. *Acta Crystallogr.* **1979**, *B35*, 1682.

(13) Steudel, R.; Prenzel, A. *Z. Naturforsch., B: Chem. Sci.* **1989**, *44*, 1499.

(14) Davis, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 3565.

(15) Steudel, R.; Mäusle, H.-J. *Z. Anorg. Allg. Chem.* **1979**, *457*, 165.

(16) Engel, M. *C. R. Hebd. Seances Acad. Sci.* **1891**, *112*, 866.

(17) Steudel, R.; Göbel, T.; Holdt, G. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 203.

(18) (a) Gil, J. C.; Beato, J. *Ber. Deutsch. Chem. Ges.* **1923**, *56*, 2451. (b) Janickis, J. *Z. Anorg. Allg. Chem.* **1937**, *234*, 193.

(19) (a) Schmidt, M. *Z. Anorg. Allg. Chem.* **1957**, *289*, 141. (b) Schmidt, M.; Talsky, G. *Chem. Ber.* **1959**, *92*, 1526, 1539.

(20) (a) Miaskiewicz, K.; Steudel, R. *Angew. Chem.* **1992**, *104*, 87; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 58. (b) Steudel, R.; Otto, A. H. *Eur. J. Inorg. Chem.* **2000**, 2379.

(21) (a) Horner, D. A.; Connick, R. E. *Inorg. Chem.* **1986**, *25*, 2414. (b) Littlejohn, D.; Walton, S. A.; Chang, S.-G. *Appl. Spectrosc.* **1992**, *46*, 848. (c) Risberg, E. D.; Eriksson, L.; Mink, J.; Petterson, L. G. M.; Skripin, M. Yu.; Sandström, M. *Inorg. Chem.* **2007**, *46*, 8332.

(22) Steudel, R.; Steudel, Y. *Eur. J. Inorg. Chem.* **2009**, 1393.

(23) Tomasi, J.; Cammi, R.; Mennucci, B.; Cappelli, C.; Corni, S. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5697.

(24) (a) Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2008**, *112*, 2962. (b) Wang, X.-B.; Sergeeva, A. P.; Yang, J.; Xing, X.-P.; Boldyrev, A. I.; Wang, L.-S. *J. Phys. Chem. A* **2009**, *113*, 5567. (c) Li, S.; Tao, F.; Gu, R. *Chem. Phys.* **2006**, *323*, 397. (d) Li, S.; Tao, F.; Gu, R. *Sci. China, Ser. B* **2008**, *51*, 305. (e) Bachrach, S. M.; Nguyen, T. T.; Demoin, D. W. *J. Phys. Chem. A* **2009**, *113*, 6172.

(25) Curtis, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J. J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(27) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.

(28) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(29) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (b) Miertus, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239. (c) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327.

(30) See, for example: (a) Kurtén, T.; Sundberg, M. R.; Vehkamäki, H.; Noppel, M.; Blomquist, J.; Kulmala, M. *J. Phys. Chem. A* **2006**, *110*, 7178. (b) Al Natsheh, A.; Nadykto, A. B.; Mikkelsen, K. V.; Yu, F.; Ruuskanen, J. *J. Phys. Chem. A* **2004**, *108*, 8914. (c) Al Natsheh, A.; Nadykto, A. B.; Mikkelsen, K. V.; Yu, F.; Ruuskanen, J. *J. Phys. Chem. A* **2006**, *110*, 7982. (d) Re, S.; Osamura, Y.; Morokuma, K. *J. Phys. Chem. A* **1999**, *103*, 3535. (e) Bandy, A. R.; Ianni, J. C. *J. Phys. Chem. A* **1998**, *102*, 6533.

(31) Fiacco, D. L.; Hunt, S. W.; Leopold, K. R. *J. Am. Chem. Soc.* **2002**, *124*, 4504.

(32) Hanson, D. R.; Eisele, F. *J. Phys. Chem. A* **2000**, *104*, 1715.

(33) At the B3LYP/6-31G(2df,p) level of theory **1b** is more stable than **1a**, by 0.1 kJ mol^{-1}, but with the basis set 6-31+G(2df,p) **1a** becomes the global minimum structure as in the gas phase.

(34) Still another low-lying rotational isomer of $H_2SO_4 \cdot H_2O$ has been calculated by Nielsen, but neither the method nor structural details were given; cited in Rozenberg, M.; Loewenschuss, A. *J. Phys. Chem. A* **2009**, *113*, 4963 as a personal communication.

(35) Howard, D. L.; Kjaergaard, H. G. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4113.

(36) Biswal, H. S.; Shirhatti, P. R.; Wategaonkar, S. *J. Phys. Chem. A* **2009**, *113*, 5633.

(37) X-ray structural analysis of $K[HSO_5] \cdot H_2O$: (a) Flanagan, J.; Griffith, W. P.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1574. (b) Schlemper, E. O.; Thompson, R. C.; Fair, C. K.; Ross, F. K. *Acta Crystallogr.* **1984**, *C40*, 1781.

(38) Fehér, F. In *Handbuch der Präparativen Anorganischen Chemie*; Brauer, G., Ed.; Enke: Stuttgart, Germany, 1975; Vol. 1, p 398.

(39) (a) Page, F. M. *J. Chem. Soc.* **1953**, 1719. (b) Housecroft, C. E.; Sharpe, A. G. *Anorganische Chemie*, 2nd ed.; Pearson Studium: München, Germany, 2006; p 504.

(40) (a) Visser, J. M.; de Jong, G. A. H.; Robertson, L. A.; Kuenen, J. G. *Arch. Microbiol.* **1997**, *166*, 372. (b) Müller, F. H.; Bandeiras, T. M.; Urich, T.; Teixeira, M.; Gomes, C. M.; Kletzin, A. *Mol. Microbiol.* **2004**, *53*, 1147.

(41) Sass, C. S.; Ault, B. S. *J. Phys. Chem.* **1987**, *91*, 551.

(42) Frigaard, N.-U.; Dahl, C. *Adv. Microbiol.* **2009**, *54*, 103.

(43) Nakamura, K.; Nakamura, M.; Yoshikawa, H.; Amano, Y. *Biosci., Biotechnol., Biochem.* **2001**, *65*, 102 and references therein.

(44) Bamford, V. A.; Bruno, S.; Rasmussen, T.; Appia-Ayme, C.; Cheesman, M. R.; Berks, B. C.; Hemmings, A. M. *EMBO J.* **2002**, *21*, 5599.

(45) Chauncey, T. R.; Uhteg, L. C.; Westley, J. In *Methods in Enzymology*; Jakoby, W. B., Griffith, O. W., Eds.; Academic Press: Orlando, FL, 1987; Vol. 143, p 350.

(46) Finster, K.; Liesack, W.; Thamdrup, B. *Appl. Environ. Microbiol.* **1998**, *64*, 119.

(47) (a) Steudel, R.; Albertsen, A. *J. Chromatogr.* **1992**, *606*, 260. (b) Steudel, R.; Albertsen, A.; Kustos, M.; Pickardt, J. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 555.

JP905264C