Structures, Energies and Vibrational Spectra of Four Isomers of Hydrogendioxothiosulfate(IV) Anion ($HS_2O_2^-$) and of the Related Anion $ClSO_2^-$: an *ab-initio* Molecular-orbital Study

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The ground-state geometries, energies, atomic charges and vibrational wavenumbers of four isomeric forms of the $HS_2O_2^-$ anion as well as of the related $ClSO_2^-$ anion have been calculated at the HF/6-311G** and HF/6-311++G** levels. Electron correlation has been taken into account according to second order Møller–Plesset perturbation theory (MP2). The most stable isomer of $HS_2O_2^-$ is $HSSO_2^-$ **1** the formation of which from SO_2 and HS^- is exothermic by *ca.* 108 kJ mol^{-1} (calculated reaction energy). The analogous formation of $ClSO_2^-$ from SO_2 and Cl^- is exothermic by 79 kJ mol^{-1}. Slightly less stable than **1** are $HOS(S)O^-$ **2** and $HS(S)O_2^-$ **4** and least stable is the isomer $HOSSO^-$ **3**. Anions **1**–**3** are of C_1 symmetry and **4** as well as $ClSO_2^-$ are of C_s symmetry. The likely intermediates of the reaction between H_2S and SO_2 in its early stage are discussed. The calculated wavenumbers of the fundamental modes of $ClSO_2^-$ agree well with experimental data.

The reaction of sulfur dioxide with hydrogen sulfide according to equation (1) is one of the most important industrial processes

$$2H_2S + SO_2 \longrightarrow 3S(l) + 2H_2O \qquad (1)$$

since more than 25 million tons of elemental sulfur annually are produced in this way.[1,2] The technical process is carried out at elevated temperatures using alumina- or titanium dioxide-based catalysts. However, the two gases react also without catalysts both in the vapour and liquid phases as well as in organic solvents, but it seems that traces of moisture are needed in these cases.[3]

The mechanism and possible intermediates of reaction (1) are not known with certainty. Most likely the primary product in the vapour phase is the van der Waals complex $H_2S{\cdot}SO_2$ which has been structurally characterized by microwave spectroscopy:[4] the two molecules are aligned on top of each other with their two-fold rotation axes almost parallel but their dipole vectors antiparallel. The $S\cdots S$ distance of 345 pm corresponds to the van der Waals distance. This adduct may then rearrange by a proton shift from sulfur to oxygen to form dihydrogen dioxothiosulfate(IV), $HS{-}SO_2H$. This molecule has never been observed but *ab-initio* molecular-orbital (MO) calculations[5] have shown that it is the most stable structure of all possible isomers of composition $H_2S_2O_2$. According to a mass spectroscopic study the chain-like isomer HO–S–S–OH can be produced by electron-impact-induced decomposition of its diisopropyl ester followed by collision-induced neutralization of the cation to give the neutral molecule.[6]

While the various isomers of $H_2S_2O_2$ are well characterized their anions are not. Owing to the formation of water in reaction (1) and since water seems to be required to initiate it under non-catalytic conditions, the formation of $HS_2O_2^-$ according to equation (2) has to be taken into account. Compounds

$$H_2S_2O_2 + H_2O \longrightarrow H_3O^+ + HS_2O_2^- \qquad (2)$$

containing the hydrogendioxothiosulfate(IV) anion $HS_2O_2^-$ are unknown and no information whatsoever is available about this species. Therefore, we have carried out a detailed *ab-initio* MO study on four isomers of $HS_2O_2^-$ to determine their structures, energies and vibrational spectra. The $HS_2O_2^-$ anion is isoelectronic with the well known hydrogensulfite anion HSO_3^- and with the less well studied chlorosulfite anion $ClSO_2^-$ (also known as chlorosulfinate anion). Salt-like compounds apparently containing the $ClSO_2^-$ ion have been prepared,[7] but besides their optical and vibrational spectra little is known about their properties. For this reason the $ClSO_2^-$ ion was included in the present MO calculation to elucidate its structure and to compare the calculated and experimental vibrational spectra.

Calculations

All quantum-chemical calculations were performed with the GAUSSIAN 92 program package[8] for *ab-initio* MO calculations. Molecular structures were fully optimized at the Hartree–Fock level with the 6-311G** and 6-311++G** basis sets. Single-point calculations at the MP2 levels were done on the optimized structures. Zero-point vibrational energies were calculated from the wavenumbers (scaled by 0.89) obtained from the optimized structures.

The vibrational wavenumbers given in the Tables have been scaled by a factor of 0.89 according to the suggestion by Pople *et al.*[9] For each of the isomers of $HS_2O_2^-$ the optimizations were performed with different starting geometries towards rotation around S–SH and S–OH bonds. The most stable rotamers were taken into consideration and are presented here. The thermochemical properties were calculated by standard methods.[10]

Results and Discussion

The Hydrogendioxosulfate(IV) *Anion*.—Since $H_2S_2O_2$ may exist as different isomers[5] the same is to be expected for its monoanion $HS_2O_2^-$. Therefore, four different connectivities have been considered; these correspond to the five most stable structures of the parent compound $H_2S_2O_2$. Regardless of the

Table 1 Total energies (in E_h = 4.36 × 10^{-18} J) of four $HS_2O_2^-$ isomers, of $ClSO_2^-$, Cl^-, HS^- and SO_2 obtained with different basis sets, and corresponding zero-point vibrational energies scaled by 0.89 (in kJ mol^{-1})

Ion/Molecule	HF/6-311G**	Zero-point energy	MP2//6-311G**	HF/6-311++G**	Zero-point energy	MP2//6-311++G**
1 $HSSO_2^-$	−945.388 305 45	39.5	−946.070 742 42	−945.402 366 41	40.4	−946.096 463 65
2 $HOS(S)O^-$	−945.396 576 13	50.0	−946.062 672 37	−945.410 413 56	49.8	−946.089 526 83
3 $HOSSO^-$	−945.347 686 69	46.3	−946.013 853 36	−945.374 169 38	46.3	−946.056 137 86
4 $HS(S)O_2^-$	−945.383 151 07	52.0	−946.050 809 38	−945.392 284 76	51.4	−946.072 085 65
$ClSO_2^-$	−1006.814 234 3	21.0	−1007.493 629 2	−1006.823 398 4	21.0	−1007.514 446 5
Cl^-	−459.564 047 0	—	−459.700 263 8	−459.565 425 1	—	−459.703 570 2
HS^-	−398.134 262 9	14.7	−398.270 955 0	−398.135 594 6	14.8	−398.273 506 6
SO_2	−547.225 081 9	18.8	−547.767 141 2	−547.231 447 7	18.6	−547.779 818 8

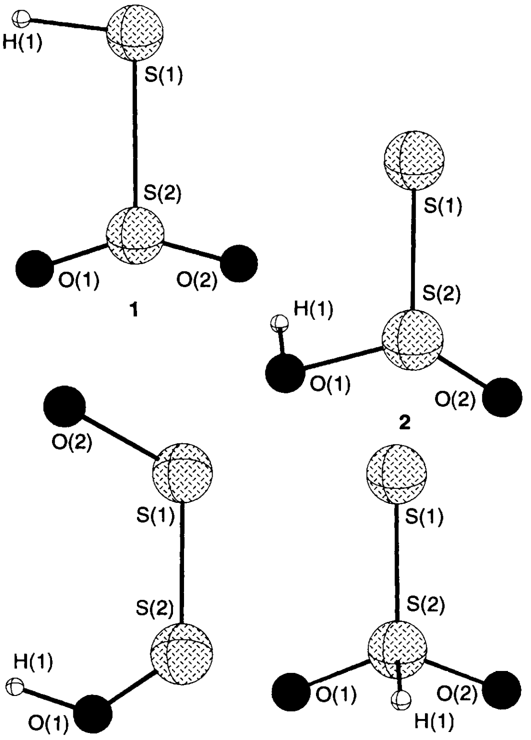
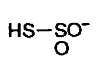
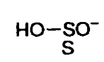


Fig. 1 Structures of four isomers of the $HS_2O_2^-$ anion and numbering of atoms



$HS{-}\underset{O}{SO^-}$

1

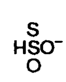


$HO{-}\underset{S}{SO^-}$

2

$HO{-}SS{-}O^-$

3



$\overset{S}{\underset{O}{HSO^-}}$

4

starting geometry only one conformation each was found for the anions **1**–**4**; in other words, no rotational isomers were stable enough to have their geometries optimized. The stable structures are shown in Fig. 1, the total energies in Table 1, the relative stabilities in Table 2, the geometrical parameters in Table 3 and the atomic charges in Table 4. At the HF/6-311G** and HF/6-311++G** levels of theory isomer **2** is the most stable, but the energy difference between it and **1** is only *ca.* 11 kJ mol^{-1}. When electron correlation according to the second-order Møller–Plessert perturbation theory is taken into account isomer **1** becomes most stable both with and without diffuse functions included. It should be noted that this isomer is also favoured by its low zero-point energy (see Table 1). At the MP2 level isomer **4** is less stable than **1** by *ca.* 76 kJ mol^{-1} and isomer **3** by more than 110 kJ mol^{-1}.

The geometrical parameters of the $HS_2O_2^-$ anions are most interesting (Table 3). While isomers **1**–**3** are of C_1 symmetry, **4** is of C_s symmetry. The $HSSO_2^-$ ion is related to the hydrogenthiosulfate ion $HSSO_3^-$ which has been isolated as $NH_4HS_2O_3$[11] and treated by *ab-initio* MO methods.[12] The most striking feature of $HSSO_2^-$ **1** is the extremely long S–S bond of 241.4 pm. This value may be compared to that calculated for the related dithionite anion $S_2O_4^{2-}$ (216.9 pm),[13] while d(S–S) = 215.5 pm has been obtained for $HS_2O_3^-$.[12] The S–S bond length of **1** is quite sensitive to the kind of basis set applied: at the HF/6-311G** level it was optimized at 259.7 pm. Another unusual feature of **1** is the fact that the molecule is not of C_s symmetry. The two non-bonding distances H ··· O are 301 and 389 pm (HF/6-311++G**). In other words, the hydrogen atom is leaning towards one of the terminal oxygens [O(1)] rather than towards the centre of charge of the two oxygen atoms; as a consequence the bond length d[S–O(1)] = 144.8 pm is slightly larger than d[S–O(2)] = 144.7 pm and the two angles S–S–O are different: α[S–SO(1)] = 100.5 and α[S–S–O(2)] = 102.3°. The calculated structure of $HSSO_2^-$ is rather similar to the structure of the most stable isomer of hydrogensulfite $HOSO_2^-$. This anion is also not of C_s symmetry but the hydrogen atom is closer to one of the terminal oxygen atoms than to the other.[14] The structure of isomer **1** may be considered as an adduct between the Lewis base HS^- and the Lewis acid SO_2 [equation (3)].

$$HS^- + SO_2 \longrightarrow HSSO_2^- \qquad (3)$$

The thermodynamics of this adduct formation will be discussed below. However, it is interesting that in other SO_2 adducts with Lewis bases D similar long bonds D–S have been reported. For example, for $H_2O \cdots SO_2$ $d(S \cdots O)$ = 282 pm[15] and for $C_5H_5N \cdots SO_2$ $d(S \cdots N)$ = 261 pm[16] have been observed by microwave spectroscopy of the gaseous compounds. The ion $HSSO_2^-$ is isoelectronic with $ClSO_2^-$ for which d(S–Cl) = 274.7 pm has been calculated (see below). It may also be compared with the SO_2 adduct of thiocyanate ion $[NCS \cdots SO_2]^-$, which has been isolated with the cation $[K(18\text{-crown-}6)]^+$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane). An X-ray diffraction analysis of the yellow crystals showed the anion to be of C_1 symmetry with an S–S bond distance of 273.6 pm.[17]

The $HOS(S)O^-$ anion **2** has a similar conformation to that of isomer **1**; in this case the hydrogen atom is closer to the terminal sulfur (268 pm) than to the terminal oxygen atom (280 pm) but the difference between these two non-bonded contacts is small. The terminal sulfur has in fact a slightly larger atomic charge (−0.64) than that of the terminal oxygen (−0.55); see Table 4. All geometrical parameters of **2** have normal values, and its structure corresponds to the most stable conformer of the hydrogensulfite isomer $HOSO_2^-$.[14]

The five-atomic chain $HOSSO^-$ **3** should form on deprotonation of the experimentally observed uncharged dihydroxydisulfane molecule, HOSSOH.[6] However, **3** is the least stable of the various $HS_2O_2^-$ isomers. Obviously those isomers are favoured which have both oxygen atoms linked to

Table 2 Energies (kJ mol^{-1}) of the four isomeric structures of $HS_2O_2^-$ in relation to the energy of isomer **1**. The zero-point energies obtained by the HF calculations have been taken into account

Isomer	HF/6-311G**	MP2//6-311G**	HF/6-311++G**	MP2//6-311++G**
1	0	0	0	0
2	−11.2	31.8	−11.6	27.7
3	113.5	156.3	80.0	111.8
4	25.4	64.2	38.3	75.8

Table 3 Bond distances *d*/pm, valence angles α/° and torsion angles τ/° of four isomers of $HS_2O_2^-$ (HF/6-311++G** level). Species **1**–**3** are of C_1 and **4** is of C_s symmetry

	1	**2**	**3**	**4**
d(S–S)	241.4	203.5	205.0	199.4
d(S=O)	144.7/144.8	147.1	154.2	144.6
d(S–OH)	—	165.0	169.0	—
d(S–H)	133.4	—	—	134.4
d(O–H)	—	94.7	94.2	—
α(S–S–O)	100.5/102.3	111.0	110.0	113.7
α(S–S–O_H)	—	99.8	106.7	—
α(O–S–O)	114.0	105.4	—	115.6
α(S–S–H)	94.8	—	—	103.0
α(O–S–H)	—	—	—	104.5
α(S–O–H)	—	108.6	107.4	—
τ(SS)	161.1	—	−80.7	—
τ(SO)	—	35.2	65.8	—

the same sulfur atom. This then results in stronger S–O bonds as can be seen from the corresponding bond distances (Table 3). The interesting features of isomer **3** are the two torsional angles τ(O–S–S–O) = −80.7 and τ(H–O–S–S) = 65.8°. Normally these angles adopt values close to ±80°;[6,18] the somewhat smaller angle at the S–O bond may be a result of the attraction between the hydrogen atom and the terminal oxygen atom (H···O 338 pm). The Mulliken charges of these atoms are listed in Table 4.

The structure of isomer **4**, $HS(S)O_2^-$, corresponds to the alternative structure (C_{3v} symmetry) of the hydrogensulfite ion, HSO_3^-, as observed in solid $CsHSO_3$.[19] It is interesting that the S–O and S–S bonds of **4** are shorter (stronger) than in the other three isomers and nevertheless it is not the most stable $HS_2O_2^-$ anion. All the geometrical parameters of **4** have normal values. These may be compared to the results of an X-ray diffraction analysis of $MeS(S)O_2Na{\cdot}H_2O$.[20] The $MeS(S)O_2^-$ anion **5** is the simplest possible organic derivative of anion **4**. In **5** the bond lengths and valence angles are as follows: *d*(S–S) = 198, *d*(S–O) = 145, *d*(S–C) = 177 pm; α(S–S–O) = 110.8, α(O–S–O) = 115.4, and α(S–S–C) = 108.4°. There is very close agreement between these results and those for the structure calculated for $HS(S)O_2^-$ (Table 3).

To support further work directed towards the identification of $HS_2O_2^-$ in reaction mixtures or the preparation of salts with this anion, we have calculated the wavenumbers of the normal modes of isomers **1**–**4** as well as their infrared and Raman intensities (Table 5). The assignments given are based on the atomic displacements but should be considered as tentative since the low molecular symmetries result in strong vibrational couplings between various types of motions.

The Chlorosulfite Anion.—Salts with the anion $ClSO_2^-$ have been prepared and characterized by optical and vibrational spectroscopy[7,21,22] but no experimental structure determinations have been published. An *ab-initio* MO study apparently assuming C_{2v} symmetry for $ClSO_2^-$ and applying a 6-21G basis set has resulted in the structural parameters[23] *d*(S–Cl) = 329 pm, *d*(S–O) = 154 pm, and α(O–S–Cl) = 124.9°; no further details were given. The $ClSO_2^-$ ion forms on addition of SO_2 to chloride ions [equation (4)], a process believed to occur even

$$Cl^- + SO_2 \longrightarrow ClSO_2^- \qquad (4)$$

in the earth's atmosphere.[24] Solid chlorosulfites easily loose SO_2 indicating the weakness of the S–Cl bond. According to several experimental studies reaction (4) is exothermic in the vapour phase. The reaction enthalpy has been estimated from high-pressure mass spectrometric measurements as −91.2 kJ mol^{-1}.[25] On the other hand a value of −79.9 kJ mol^{-1} has been derived from the dissociation energy of $Cl(H_2O)^-$ and the free enthalpy of the displacement reaction (5) in the vapour phase at 23 °C.[24]

$$SO_2 + Cl(H_2O)^- \longrightarrow ClSO_2^- + H_2O \qquad (5)$$

In solution the equilibrium between the solvated species depends on the solvent (solv), equation (6). The equilibrium

$$Cl^-(solv)_x + SO_2(solv)_y \rightleftharpoons ClSO_2^-(solv)_z + n\,solv \qquad (6)$$

constant *K* was determined as 2000 ± 600 in 1,2-dichloroethane,[7] 365 ± 6 in acetonitrile[21,26,27] and 26 in dimethyl sulfoxide at 25 °C.[21] Calorimetric measurements have resulted in a reaction enthalpy of −17.2 kJ mol^{-1} in acetonitrile and of −2.9 kJ mol^{-1} in dimethyl sulfoxide at 25 °C.[22]

In this study the structure of $ClSO_2^-$ was optimized with the 6-311G** and 6-311++G** basis sets; the results are shown in Table 6. The absolute energies of $ClSO_2^-$ and of species related to $HS_2O_2^-$ and $ClSO_2^-$ are given in Table 1. The $ClSO_2^-$ ion is of C_s symmetry and similar in geometry to the $HSSO_2^-$ ion **1**; see Table 3. Comparison of the parameters of $ClSO_2^-$ with those calculated for SO_2 using the same basis set (HF/6-311++G**) shows that the S–O bond lengths of SO_2 (140.8 pm) increase on chloride ion addition (to 142.2 pm in $ClSO_2^-$). The O–S–O angle expectedly decreases from 118.7° in SO_2 to 115.1° in $ClSO_2^-$.

The calculated vibrational spectrum of $ClSO_2^-$ (Table 7) may be compared to the Raman spectrum of tetraalkylammonium chlorosulfites which have been recorded both for solid and dissolved samples.[7] As the data in Table 7 demonstrate there is a very satisfactory agreement between calculated (scaled by 0.89) and observed wavenumbers for four of the six fundamental modes of $ClSO_2^-$. The two lowest-energy modes also fit two weak Raman lines if the published assignment of these two lines is reversed. The close agreement then reached demonstrates the reliability of the calculation procedure applied.

Comparison of the $ClSO_2^-$ and $HSSO_2^-$ spectra with the vibrational modes of SO_2 demonstrates the impact of the donor (Cl^-, HS^-) on the bonding in the SO_2 unit. For SO_2 the scaled wavenumbers are ν_1 1203, ν_2 531 and ν_3 1378 cm^{-1} (HF/6-311++G** level). The data in Tables 5 and 7 show that the symmetric and asymmetric SO stretching modes are shifted to considerably lower wavenumbers on adduct formation. In contrast, the SO_2 bending mode is practically not affected and is calculated to occur at 522–540 cm^{-1} for all three species ($ClSO_2^-$, $HSSO_2^-$, SO_2).

Thermodynamic Considerations.—To determine the energy change of the gas-phase reactions (3) and (4) the total energies of the anions HS^-, Cl^- and of SO_2 were calculated applying the

Table 4 Mulliken charges of four isomers of $HS_2O_2^-$ and of $ClSO_2^-$ calculated with the 6-311++G** basis set. For atom numbering see Fig. 1

Atom	$HSSO_2^-$	$HOS(S)O^-$	$HOSSO^-$	$HS(S)O_2^-$	$ClSO_2^-$
S(1)	−0.39	−0.64	−0.12	−0.51	+0.68
S(2)	+0.50	+0.36	−0.10	+0.51	—
O(1)	−0.54	−0.45	−0.37	−0.48	−0.46
O(2)	−0.54	−0.55	−0.67	−0.48	−0.46
H/Cl	−0.03	+0.28	+0.27	−0.03	−0.77

Table 5 Wavenumbers (cm^{-1}) of the nine fundamental vibrations of the four $HS_2O_2^-$ isomers calculated with the HF/6-311++G** basis set. Relative (infrared, Raman) intensities are given in parentheses. Wavenumbers have been scaled by a factor of 0.89 (ν = stretching, δ = bending, τ = torsional mode)

	$HSSO_2^-$	$HOS(S)O^-$	$HOSSO^-$	$HS(S)O_2^-$
ν(OH)	—	3635 (17, 100)	3698 (30, 100)	—
ν(SH)	2525 (7, 100)	—	—	2416 (36, 100)
δ(SOH)	—	1117 (31, 5)	1108 (30, 11)	—
δ(SH)	587 (93, 5)	—	—	1114 (5, 6)
δ(SH)	—	—	—	1071 (57, 7)
$\nu_{asym}(SO_2)$	1181 (100, 21)	—	—	1181 (100, 4)
$\nu_{sym}(SO_2)$	1051 (6, 5)	—	—	1043 (86, 4)
ν(SO)	—	1031 (100, 16)	840 (100, 42)	—
ν(S–OH)	—	691 (64, 10)	666 (78, 50)	—
ν(SS)	150 (10, 3)	507 (35, 29)	426 (1, 24)	557 (36, 7)
δ(OSO)	522 (44, 1)	446 (17, 4)	—	516 (14, 1)
δ(SSO)	383 (1, 1)	367 (11, 10)	339 (64, 3)	381 (2, 5)
δ(SSO)	215 (26, 20)	321 (4, 10)	316 (1, 18)	311 (1, 2)
τ(S–O)	—	209 (12, 6)	228 (10, 8)	—
τ(S–S)	133 (8, 4)	—	118 (7, 5)	—

Table 6 Bond distances *d*/pm and valence angles α/° of the $ClSO_2^-$ anion calculated with and without diffuse functions in the basis set

	HF/6-311G**	HF/6-311++G**
d(S–Cl)	288.0	247.7
d(S–O)	141.8	142.2
α(Cl–S–O)	103.4	102.7
α(O–S–O)	115.6	115.1

Table 7 Wavenumbers (cm^{-1}) of the six fundamental vibrations of the $ClSO_2^-$ anion calculated with the HF/6-311++G** basis set and scaled by a factor of 0.89. Relative (infrared, Raman) intensities are given in parentheses. The vibrational wavenumbers[7] observed for solid and dissolved (liquid SO_2) $[NR_4][ClSO_2]$ (R = Me or Et) are also given

			$[NR_4][ClSO_2]$	
Mode	Symmetry	Calculated	solid	solution
ν(SO)	A″	1293 (100, 9)	1290	1314
ν(SO)	A′	1155 (50, 100)	1120	1123
$\delta(SO_2)$	A′	540 (17, 2)	535	527
ν(SCl)	A′	282 (25, 6)	215	214
δ(OSCl)	A″	147 (1, 2)	—	172*
δ(OSCl)	A′	93 (16, 1)	—	103*

* In ref. 7 the assignment of these weak Raman lines is reversed.

HF/6-311G** and HF/6-311++G** approximations and taking electron correlation into account. The results are given in Table 1. The molecular parameters of HS^- are as follows: *d*(SH) = 133.9 pm; ν(SH) 2774 cm^{-1} (unscaled); atomic charges S −0.925, H −0.075 (all calculated by HF/6-311++G**).

From the data in Table 1 the energy change for reaction (3) is calculated as −113.2 kJ mol^{-1}, and for reaction (4) −81.5 kJ mol^{-1} is obtained (MP2/6-311++G** basis). If the zero-point energies of the species involved are taken into account the reaction energies are −105.3 kJ mol^{-1} [(3)] and −78.8 kJ mol^{-1} [(4)]. Using the heat capacities the reaction energies at 298.15 K were obtained as −108.2 kJ mol^{-1} for (3) and −79.2 kJ mol^{-1} for (4). The latter value is in excellent agreement with the experimental enthalpy data mentioned above. Finally, it should be mentioned that the electron affinities of Cl, SH and SO_2 are all positive.[28] In other words, the anions Cl^-, SH^- and SO_2^- are stable with regard to electron loss. We therefore expect the same for the more complex anions $HS_2O_2^-$ and $ClSO_2^-$.

Summarizing it may be stated that the most stable isomer of the still hypothetical hydrogendioxothiosulfate(IV) anion is similar in geometry and in its energy of formation from SO_2 to the experimentally proven chlorosulfite ion. It therefore can be expected that $HS_2O_2^-$ isomers play a role in the reaction between H_2S and SO_2 and in other redox reactions of sulfur compounds.[29] Furthermore it seems likely that salts with the $HS_2O_2^-$ anion will be prepared in the future. The reaction of SO_2 with ionic hydrogensulfides M^+HS^- under mild conditions (to avoid redox reactions) may be a suitable route to such species. The further reactions of $H_2S_2O_2$ and $HS_2O_2^-$ with either SO_2 or H_2S will be dealt with in a separate publication.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft.

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Received 30*th March* 1994; *Paper* 4/01936I