The Thermal Decomposition of S_2O Forming SO_2, S_3, S_4 and S_5O − An ab initio MO Study

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All chemically reasonable [2+2] and [2+3] dipolar addition reactions between two S_2O molecules forming heterocyclic intermediates of composition S_4O_2, as well as the decomposition of these species to generate the observed products S_3 and SO_2, have been studied by gas-phase ab initio MO calculations at the G3X(MP2) level of theory. The reaction enthalpies, Gibbs energies and, partly, activation enthalpies of 17 reactions have been calculated. The [2+2] cycloadditions of S_2O are all endothermic and are characterized by high barriers. The reaction of lowest activation enthalpy ($\Delta H^{\#}_{298}$ = 11 kJ·mol^{-1}) is the exothermic [2+3] cycloaddition of two S_2O molecules resulting in the five-membered heterocycle oxatetrathiolane 2-oxide S_4O_2 (**7**), which is predicted to decompose at 298 K exothermally and without any activation enthalpy to SO_2 plus S_3. The S_3 molecule is predicted to add exothermally to S_2O to give the five-membered homocycle S_5O which has, in fact, been prepared in this way before. The bimolecular decomposition of S_5O to SO_2, S_4 and S_5 is also exothermic and may explain the formation of the red S_4 molecule on condensation of S_2O at temperatures below −130 °C. The implications of these results for the understanding of the chemistry on Jupiter's moon Io are discussed.

Introduction

Disulfur monoxide is a combustion product of elemental sulfur under special reaction conditions, along with SO_2 and SO_3. S_2O is also formed in numerous redox reactions between reduced sulfur compounds and oxidizing agents as well as in thermal decomposition reactions of sulfur-rich sulfane oxides and sulfur oxides.[1] S_2O can be obtained in a practically pure form by the heterogeneous reaction of thionyl chloride vapor with solid silver sulfide at 160 °C and low pressures, see Equation (1).[2]

$$SOCl_2 + Ag_2S \rightarrow S_2O + 2AgCl \qquad (1)$$

More recently, S_2O has seemingly been generated in solution by thermal decomposition of suitable organic precursors (e.g., sulfane oxides) or of S_8O, and the S_2O unit[3−5] and its decomposition product S_3 [5] have been trapped in situ by addition reactions with either unsaturated transition metal complexes[3] or with olefins, dienes or diazoalkanes.[4,5] These fascinating developments may result in a renaissance of S_2O chemistry in solution, although it must be stressed that this molecule has never been observed directly (e.g., spectroscopically) in liquid solutions.

The molecule S_2O is bent (C_s symmetry) in a similar fashion to its more symmetrical triatomic relatives O_3, SO_2 and S_3 (C_{2v} symmetry in each case). The most accurate experimental geometrical parameters of S_2O are d_{SO} = 145.6 pm, d_{SS} = 188.5 pm and α_{SSO} = 117.9°.[6]

The reactivity of S_2O has not been studied systematically, probably due to its thermal instability.[1] On condensation of gaseous S_2O at low temperatures, by dissolution in cold inert solvents or by increasing its partial pressure in the gas-phase at room temperature to values above 1 mbar, S_2O decomposes rapidly.[1] The final decomposition products of S_2O are elemental sulfur (S_8) and sulfur dioxide but the following intermediates have been observed under differing reaction conditions (in chronological order):

Deep-yellow amorphous polysulfur oxides of composition S_xO ($x > 3$) are formed on condensation of gaseous S_2O at −196 °C and subsequent warming of the condensate to 20 °C; at temperatures below −130 °C the initial condensates are cherry-red but after warming to near room temperature they turn yellow and on subsequent cooling they remain yellow.[2,7] The red color is as more intense with higher S_2O concentrations in the original gas.

Sulfur radicals have been detected by low-temperature ESR spectroscopy (−150 °C) in condensates formed from gaseous S_2O.[2]

The probably homocyclic oxide S_5O has been obtained in solution when a gaseous S_2O/SO_2 mixture was bubbled into inert solvents at low temperatures (e.g., $CHCl_3$ at −60 °C) followed by removal of the excess SO_2 under vacuum.[8] At temperatures above −20 °C the intensely yellow-colored dissolved S_5O decomposes with formation of SO_2 and elemental sulfur.

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The yellow-green molecule S_3 has been detected by low-temperature Raman spectroscopy in matrix-isolation experiments with gaseous S_2O,[9] as well as by UV/Vis spectroscopy of condensates of from gaseous S_2O (absorption at 420 nm).[10]

The red molecule S_4 has been detected by UV/Vis spectroscopy (absorption at 530 nm) in the aforementioned low-temperature condensates of S_2O,[10] although the Raman spectra of matrix-isolated and then thermally decomposed S_2O (by controlled diffusion) did not show any evidence for S_4.[9]

The mechanisms by which these intermediates and products are formed are unknown. Therefore, we have calculated by ab initio MO methods the most likely initial products of the thermal S_2O decomposition as well as some of the relevant transition states using the high-level G3X(MP2) method which is known to produce reliable thermodynamic data for sulfur-rich molecules.[11,12] Bimolecular reactions have been assumed for the initial stages. Our results shed a new light on the interpretation of the colors observed on Jupiter's moon Io, the surface of which is partly covered by elemental sulfur and sulfur oxides.

Results and Discussion

According to the above discussion the primary decomposition reactions of S_2O are expected to be the following [Equations (2) and (3)].

$$2\,S_2O \rightarrow S_3 + SO_2; \quad \Delta H^\circ_{298} = -49\ \mathrm{kJ{\cdot}mol^{-1}},\ \Delta G^\circ_{298} = -50\ \mathrm{kJ{\cdot}mol^{-1}} \tag{2}$$

$$S_2O + S_3 \rightarrow \textit{cyclo}\text{-}S_5O; \quad \Delta H^\circ_{298} = -87\ \mathrm{kJ{\cdot}mol^{-1}},\ \Delta G^\circ_{298} = -34\ \mathrm{kJ{\cdot}mol^{-1}} \tag{3}$$

Our calculated energies, enthalpies as well as the Gibbs energies of the species mentioned in Equations (2)−(18) are listed in Table 1. These data show that the reactions according to Equations (2) and (3) are strongly exothermic as well as exergonic. This then also holds for the overall reaction [Equation (4)].

$$3\,S_2O \rightarrow S_5O + SO_2; \quad \Delta H^\circ_{298} = -136\ \mathrm{kJ{\cdot}mol^{-1}},\ \Delta G^\circ_{298} = -83\ \mathrm{kJ{\cdot}mol^{-1}} \tag{4}$$

The homocyclic S_5O molecule (pentathiolane oxide) may be considered as the simplest representative of the so-called polysulfur oxides (mentioned in the Introduction), which probably consist of cyclic and chain-like sulfur-rich species of unknown molecular mass and with the oxygen atoms mainly present as sulfoxide groups.[1]

The calculated NBO atomic charges of the S_2O molecule are −0.78 for oxygen, +1.00 for the central and −0.23 for the terminal sulfur atom. Therefore, the molecule is expected to undergo dipolar addition reactions. In the following sections we investigate the most reasonable [2+2] and [2+3] cycloaddition reactions between two S_2O molecules. Any [3+3] cycloaddition, on the other hand, seems to be unlikely since atoms of equal charge would have to combine to form covalent bonds. The calculated geometrical parameters of S_2O are d_{SO} = 146.5 pm d_{SS} = 190.8 pm and α_{SSO} = 118.2°.

[2+2] Additions

The most likely first step of the reaction shown in Equation (2) is an intermolecular S···O attraction between the

Table 1. Absolute negative energies (E°_{298}), enthalpies (H°_{298}) and Gibbs energies (G°_{298}) of S_2O and of some molecules derived from S_2O and related species as well as some transition states (in atomic units, a.u.); the energies E (second column) apply to the potential minimum

Species	E [B3LYP/6-31G(2df)]	E°_{298} [G3X(MP2)]	H°_{298} [G3X(MP2)]	G°_{298} [G3X(MP2)]
$^1S_2$	796.3385956	795.4702525	795.4664757	795.4913546
^1SO	473.3218595	472.8212909	472.8175141	472.8416794
S_3	1194.5686550	1193.2629065	1193.2582631	1193.2901174
SO_2	548.6258870	548.0552118	548.0511341	548.0799803
S_2O	871.5880695	870.6496178	870.6452823	870.6756205
S_4	1592.7706551	1591.0340368	1591.0277978	1591.0640979
S_5	1990.9860366	1988.8133239	1988.8055877	1988.8449648
S_4O_2 (**1**)	1743.1399635	1741.2603185	1741.2520547	1741.2926215
S_4O_2 (**2**)	1743.1597292	1741.2805680	1741.2721372	1741.3131003
S_4O_2 (**3**)	1743.1689558	1741.2919627	1741.2833581	1741.3247626
S_4O_2 (**4**)	1743.1758703	1741.3017985	1741.2935166	1741.3336862
S_2O_2 (**5**)	946.7883751	945.7796616	945.7746033	945.8070334
S_3O (**6**)	1269.7580733	1268.3837243	1268.3782365	1268.4122013
S_4O_2 (**7**)	1743.1842906	1741.3031432	1741.2948781	1741.3349394
S_5O (**8**)	2066.1868312	2063.9455664	2063.9366570	2063.9785408
TS1	1743.1366089	1741.2562897	1741.2483141	1741.2888809
TS2	1743.1482802	1741.2685296	1741.2603229	1741.3016585
TS3	1743.1543248	1741.2788239	1741.2704678	1741.3123835
TS4	1743.1554147	1741.2762517	1741.2681896	1741.3087797
TS5	1743.1692604	1741.2945684	1741.2864885	1741.3267559
TS6	1743.1810069	1741.3033498	1741.2954840	1741.3351048

positively charged central sulfur atom of molecule 1 and the negatively charged oxygen atom of molecule 2. Two such configurations — configurations A and B — are possible, as shown in Figure 1.

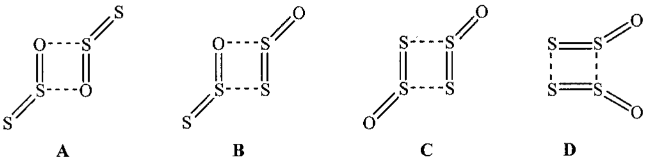
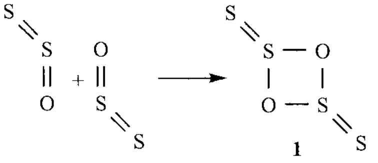


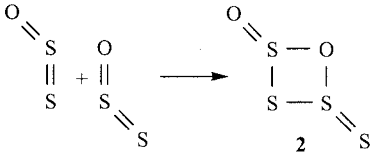
Figure 1. Four possible configurations for the [2+2] cycloaddition between two S_2O molecules

If the subsequent dipolar cycloaddition occurs according to the [2+2] type the four-membered heterocycles **1** or **2** of composition S_4O_2 shown in Figure 2 will result. However, the corresponding reactions given in Equations (5) and (6) are predicted to be strongly endothermic.



(5)

$\Delta H°_{298} = 101\ \text{kJ mol}^{-1}$
$\Delta G°_{298} = 154\ \text{kJ mol}^{-1}$



(6)

$\Delta H°_{298} = 48\ \text{kJ mol}^{-1}$
$\Delta G°_{298} = 100\ \text{kJ mol}^{-1}$

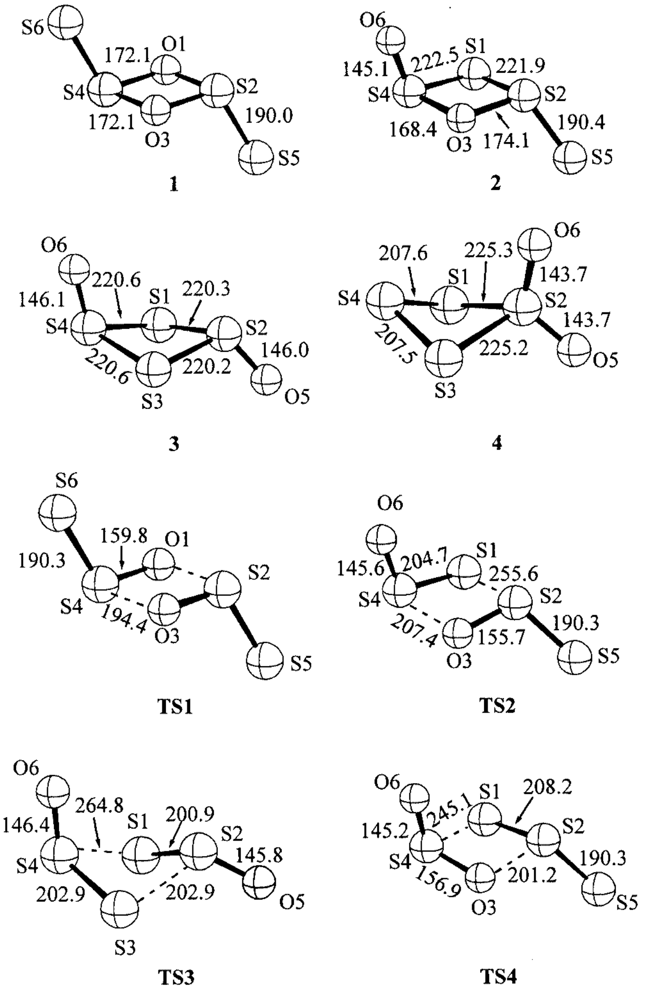


Figure 2. Geometries of four isomers of the four-membered heterocycles S_4O_2 (**1**−**4**) and of the transition states for their formation (**TS1**−**4**); the structures of **1** and **TS1** have C_{2h} symmetry, whereas all others have C_1 symmetry; bond lengths in pm (for more details see Tables 2 and 4)

The pseudo-heterocycle **1** (1,3,2,4-dioxadithiethane 2,4-disulfide) is of C_{2h} symmetry. The four-membered ring is planar and the two exocyclic sulfur atoms are located *trans* to each other (torsion angles S−S−O−S: ±108.3°). All bond lengths show normal values and the bond angles are in the expected range of 82−110° (Table 2). Compared to the S_2O molecule the charges on all atoms of **1** have increased (S_{terminal}: −0.25; S_{central}: +1.13; O: −0.88).

The transition state for the formation of **1** from S_2O (**TS1**) has been located on the potential-energy surface (PES) of S_4O_2; its structure is given in Figure 2. This structure is also of C_{2h} symmetry and rather similar to that of **1**, although the S−O bond lengths (159.8 and 194.4 pm) are different from those in **1** (172.1 pm; 146.5 pm in S_2O). Additional geometrical data are listed in Table 2. The formation of **TS1** from two molecules of S_2O requires an activation enthalpy of 111 kJ·mol^{-1} rendering this reaction rather unlikely.

The heterocycle **2** (oxatrithietane 2-oxide 4-sulfide) has no symmetry at all. The maximum charge separation between the S and O atoms in **2** (2.3 electrostatic units) is even larger than in the case of **1** (see Table 3). Consequently, there is a relatively large dipole moment of 1.60 D. The four-membered ring of **2** is not planar (torsion angles in the ring: ±12−16°), and the two exocyclic atoms are in a *trans* position to each other as in the case of **1**.

The structure of the transition state for the formation of **2** from S_2O is also shown in Figure 2 (**TS2**, symmetry C_1). As expected, two of the bonds within the four-membered ring are extremely long (S1−S2: 255.6 pm; S4−O3: 207.4 pm). Bond angles and torsion angles are listed in Tables 2 and 4. The formation of **TS2** from two molecules of S_2O requires an activation enthalpy of 79 kJ·mol^{-1}.

If the dipolar addition of two S_2O molecules took place between the four sulfur atoms the homocyclic tetrathietane 1,3-dioxide **3**, with two exocyclic oxygen atoms (Figure 1, configuration C), would result [Equation (7)].

Table 2. Bond angles (°) of the species **1−4**, **7**, **8** and **TS1−6**; for numbering of atoms see Figure 2 and 4

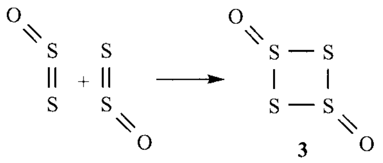
Angle	1	2	3	4	7	8	TS1	TS2	TS3	TS4	TS5	TS6
123	82.2	84.7	87.7	82.6	98.2	97.5	83.4	85.7	92.7	86.5	106.9	95.2
234	97.8	108.7	88.7	82.9	123.6	104.8	96.6	101.8	79.6	103.5	111.2	120.4
341	82.2	85.8	87.5	91.5			83.4	89.2	90.0	85.5		
412	97.8	77.6	88.7	82.9			96.6	75.2	78.0	76.6		
125	109.8	112.5	110.0	110.5			109.9	117.6	112.8	110.8		
325	109.8	108.5	110.0	110.5			109.9	109.6	116.6	114.0		
146	109.8	110.2	110.7				109.9	112.1	110.8	110.3		
346	109.8	109.1	110.7		109.4	101.9	109.9	107.9	112.3	111.2	96.3	113.2
126				112.5								
345					94.5	96.2					94.4	95.2
526				121.5								
546					106.6	114.8					116.1	104.7
451					87.8	103.3					98.4	84.6
512					96.3	95.1					87.2	103.0

Table 3. Atomic charges (NBO) of the atoms in the various cyclic isomers of composition S_4O_2 (**1−4**, **7**) and in S_5O (**8**) as well as in the transition states **TS1−6**; for numbering of atoms see Figure 2 and 4

Atom	S_4O_2 (**1**)	S_4O_2 (**2**)	S_4O_2 (**3**)	S_4O_2 (**4**)	S_4O_2 (**7**)	S_5O (**8**)	TS1	TS2	TS3	TS4	TS5	TS6
1	−0.88	−0.23	−0.22	−0.09	+0.05	+0.03	−0.90	−0.35	−0.24	−0.26	−0.11	+0.18
2	+1.13	+0.75	+1.08	+1.83	+0.38	+0.06	+1.09	+0.92	+1.08	+0.58	+0.83	+0.19
3	−0.88	−0.89	−0.22	−0.09	−0.87	−0.13	−0.90	−0.14	−0.32	−0.90	−0.82	−0.84
4	+1.13	+1.44	+1.05	+0.06	+1.46	+1.01	+1.09	+1.25	+1.05	+1.53	+1.10	+1.54
5	−0.25	−0.22	−0.83	−0.85	−0.16	−0.12	−0.20	−0.87	−0.77	−0.12	−0.19	−0.20
6	−0.25	−0.85	−0.84	−0.85	−0.86	−0.85	−0.20	−0.79	−0.79	−0.84	−0.80	−0.86

Table 4. Torsion angles (°) of the species **2−4**, **7**, **8** and **TS2−6**; for numbering of atoms see Figure 2 and 4

Angle	2	3	4	7	8	TS2	TS3	TS4	TS5	TS6
1234	−15.6	−20.5	−31.5	8.7	46.7	−21.3	−38.4	−25.9	50.1	3.5
2341	15.9	20.5	34.3			27.0	28.1	21.8		
3412	−12.0	−20.5	−34.3			−16.2	−37.2	−21.0		
4123	11.6	20.5	31.5			21.9	28.6	16.2		
4125	119.5	130.9				131.8	149.1	130.7		
4325	−127.9	−130.9	−140.8			−139.2	−155.7	−137.2		
2146	96.8	90.7				92.8	76.7	90.0		
2346	−94.0	−90.7		−81.1	−128.5	−86.1	−84.5	−88.3	−122.5	−77.5
4326			79.8							
2345				28.2	−11.6				−5.7	30.9
1546				60.4	78.7				70.0	62.2
3215				−46.5	−63.4				−62.3	−48.1
1543				−51.3	−27.5				−29.1	−53.5
2154				55.6	57.3				53.4	57.8



$\Delta H°_{298}$ = 19 kJ mol^{-1}
$\Delta G°_{298}$ = 70 kJ mol^{-1}

(7)

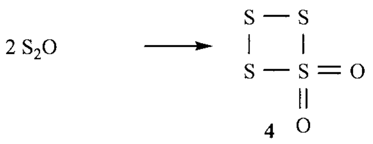
Surprisingly, the structure of **3** is not of C_{2h} symmetry (in analogy to that of **1**) but approximately of C_s symmetry (see Figure 2; enforcing C_s symmetry results in one imaginary vibrational wavenumber). The S−S bond lengths within the homocycle are only pairwise equivalent but almost identical (220.2 and 220.6 pm). The absolute values of the four S−S−S−O torsion angles are also pairwise identical but the two pairs are quite different from each other (±90.7°

and ±130.9°). The four S−S−S−S torsion angles are all ±20.5°. For further bond and torsion angles, see Tables 2 and 4.

The symmetrical structure of **3** (C_{2h} symmetry) is only 1 kJ·mol^{-1} less stable than the global minimum structure. However, this C_{2h} structure corresponds to a first-order transition state with one imaginary vibrational wavenumber and connects two equivalent structures of C_s symmetry that have dipole moments of 0.60 D.

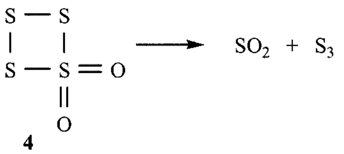
The generation of **3** from S_2O requires an activation enthalpy of 53 kJ·mol^{-1}. The structure of the corresponding transition state **TS3** is shown in Figure 2. This structure is even less symmetrical than the structure of **3**, with S−S bond lengths in the range 200.9−264.8 pm and S−S−S−S torsion angles of ca. 28° and −38° (two each). For additional parameters, see Tables 2 and 4.

The formation of an isomeric tetrathiethane 1,2-dioxide from S_2O seems to be rather unlikely since atoms of equal charge would have to form bonds with each other (Figure 1, configuration D). Interestingly, the homocyclic S_4O_2 isomer **4** with a sulfone group (tetrathiethane 1,1-dioxide; see Figure 2) is also a stationary point on the PES of S_4O_2. This species is approximately of C_s symmetry (μ = 2.20 D) and exhibits the expected bond length pattern with two long S−S bonds (225.2 pm) and two S−S bonds of normal length (207.5 pm). The formation of **4** from S_2O is slightly exothermic. However, this transformation cannot be an elementary reaction but must be a multistep process [Equation (8)].


(8)

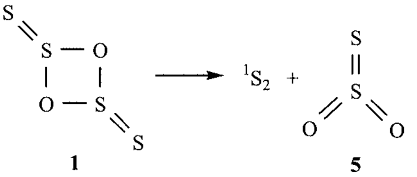
$\Delta H^\circ_{298} = -8$ kJ mol^{-1}
$\Delta G^\circ_{298} = +46$ kJ mol^{-1}

The hypothetical isomerization reactions of the heterocycles **1** or **2** to give **4** are exothermic by −109 and −56 kJ·mol^{-1}, respectively, but there is no simple mechanism either for these transformations. The decomposition of **4** to SO_2 and S_3 is exothermic, as expected [Equation (9)].


(9)

$\Delta H^\circ_{298} = -42$ kJ mol^{-1}
$\Delta G^\circ_{298} = -96$ kJ mol^{-1}

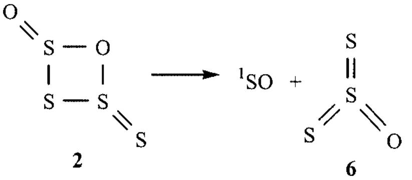
Other reactions of **1** and **2** may be possible besides isomerizations. In principle, isomer **1** could split into singlet S_2 ($^1\Delta_g$; $^1S_2$) and the hypothetical S_2O_2 isomer **5**, which is known to be the global minimum on the PES of singlet S_2O_2 [Equation (10)].[13]


(10)

$\Delta H^\circ_{298} = +29$ kJ mol^{-1}
$\Delta G^\circ_{298} = -15$ kJ mol^{-1}

The planar molecule S_2O_2 is of C_{2v} symmetry with two equivalent S−O bonds of length 143.9 pm and an S−S bond of 189.7 pm (α_{OSO} = 119.5°; β_{OSS} = 120.3°; μ = 0.97 D). The S_2 molecule formed in Equation (10) would most probably return to is triplet ground state and either dimerize to give the spectroscopically observed S_4 molecule or trigger a radical-chain polymerization which would explain the sulfur radicals observed by ESR spectroscopy in condensates of S_2O at low temperatures.[2] The latter behavior of S_2 is well-known.

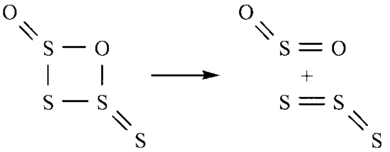
In a similar fashion, the S_4O_2 isomer **2** could theoretically split off singlet SO ($^1\Delta$) with formation of the hypothetical planar S_3O molecule **6** [Equation (11)] but this reaction is strongly endothermic.


(11)

$\Delta H^\circ_{298} = 201$ kJ mol^{-1}
$\Delta G^\circ_{298} = 155$ kJ mol^{-1}

The planar star-like molecule S_3O is also of C_{2v} symmetry with the geometrical parameters d_{SS} = 190.7, d_{SO} = 145.2 pm and α_{SSS} = 121.4° (μ = 0.99 D). Sulfur monoxide (^1SO and ^3SO) is known to rapidly disproportionate to S_2O and SO_2.[1] The further fate of the species **5** and **6** cannot be predicted with certainty but disproportionation, with formation of elemental sulfur and either S_2O or SO_2, are most likely to occur.

The reactions shown in Equations (5) and (6) as well as Equations (10) and (11) are all highly unlikely at low temperatures due to their endothermic nature and, as far as is known, due to their high activation enthalpies. Nevertheless, it should be pointed out that isomer **2** could easily split into SO_2 and S_3 and thus explain these observed products by a cycloreversion reaction which was first proposed by Tang and Brown [Equation (12)].[9] This reaction is, in fact, strongly exothermic.



2 (12)

$\Delta H^\circ_{298} = -98\ \mathrm{kJ\ mol^{-1}}$
$\Delta G^\circ_{298} = -150\ \mathrm{kJ\ mol^{-1}}$

The structure of the transition state for the reaction shown in Equation (12) is also shown in Figure 2 (**TS4**); its formation from **2** requires only 10 kJ·mol^{-1}. The molecules S_3 and SO_2 are preformed in **TS4** and are connected by a very long S−O bond (201.2 pm) and a similarly long S−S bond (245.1 pm). For further data on **TS4**, see Tables 2−4.

[2+3] Additions

Since the hypothetical [2+2] cycloadditions of two S_2O molecules cannot explain the thermal decomposition of this compound at low temperatures we have investigated the alternative [2+3] mechanism for which two approaches (A and B) are possible, as shown in Figure 3. In the case of A the two most highly charged atoms (O and $S_{central}$) of neighboring molecules would combine due to their opposite atomic charges. This interaction is more likely than configuration B, in which the highly negatively charged oxygen atom would combine with the slightly negatively charged terminal sulfur atom of the neighboring molecule resulting in 1-oxatetrathiolane 3-oxide. In addition, the latter molecule would not help to explain the formation of SO_2 and S_3. The product expected from configuration B (**7a**) was found to be much less stable than **7** and this also holds for the six-membered ring 1,4,2,3,5,6-dioxatetrathiane (**7b**) which would be the expected product of a [3+3] cycloaddition of two S_2O molecules.[14] For these reasons, we have only investigated in detail the formation of the 1-oxatetrathiolane 2-oxide **7** (configuration A in Figure 3).

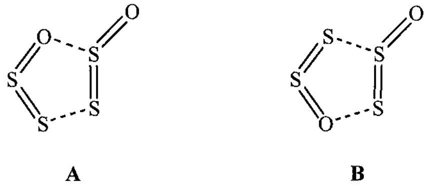
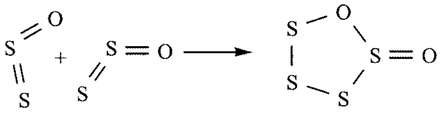


Figure 3. Two possible configurations for the [2+3] cycloaddition between two S_2O molecules



7 (13)

$\Delta H^\circ_{298} = -11\ \mathrm{kJ\ mol^{-1}}$
$\Delta G^\circ_{298} = +43\ \mathrm{kJ\ mol^{-1}}$

We predict that the reaction shown in Equation (13) is exothermic and therefore more likely than all alternative bimolecular reactions of S_2O discussed above.

The structure of **7** is shown in Figure 4. It is characterized by two normal S−S bonds and, neighboring the exocyclic oxygen atom, one rather long S−S bond (231.9 pm). The SO_2 structural unit is already close in geometry to the free SO_2 molecule, which is a well-known leaving group. This view is supported by the rather long S2−O3 single bond (176.5 pm) between the SO_2 and S_3 units. The second S−O single bond of **7** is of normal length (162.5 pm). The absolute values of the torsion angles within the ring are between 9° and 56° (Table 4). The exocyclic atom is in an axial position (μ = 2.26 D).

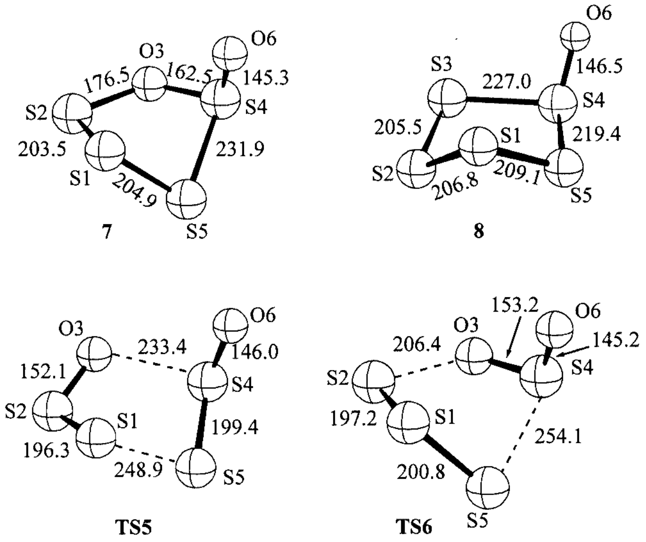
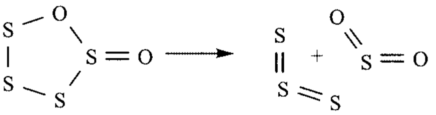


Figure 4. Geometries of the five-membered heterocycles S_4O_2 (**7**) and S_5O (**8**) and of the transition states for their formation (**TS5** and **6**); bond lengths in pm (for more details see Tables 2 and 4.)

The formation of **7** from S_2O proceeds via the transition state TS5, the structure of which is also shown in Figure 4. This species is of C_1 symmetry and the two S_2O units are connected by an S−O bond of length 233.4 pm and an S−S bond of length 248.9 pm. The torsion angles within the five-membered ring range from 6° to 62° (absolute values). All bond angles have normal values (see Tables 2 and 4). The enthalpy of **TS5** is just 11 kJ·mol^{-1} above that of two S_2O molecules. Therefore, Equation (13) describes the reaction channel of lowest activation enthalpy of all reactions between two S_2O molecules studied in this work.

The thermal dissociation of **7** into S_3 and SO_2 [Equation (14)] is exothermic.



7 (14)

$\Delta H^\circ_{298} = -38\ \mathrm{kJ\ mol^{-1}}$
$\Delta G^\circ_{298} = -92\ \mathrm{kJ\ mol^{-1}}$

The transition state for this reaction has been located on the PES (**TS6**). Its geometry is depicted in Figure 4, with more details in Tables 2 and 4. On the potential energy surface (E_o) **TS6** is 9 kJ·mol^{-1} less stable than oxatetrathiolane oxide **7** [B3LYP/6-31G(2df,p) data] but the G3X(MP2) enthalpies and Gibbs energies of **TS6** and **7** at 298 K are practically identical, with slightly lower values calculated for the **TS6** geometry (Table 1). Therefore, we assume that the dissociation of **7** proceeds spontaneously at 298 K and the reactions given in Equations (13) and (14) perfectly explain the initial stages of the thermal decomposition of S_2O at low and moderate temperatures.

The structure of S_3 calculated in this work (d_{SS} = 193.3 pm; a_{SSS} = 118.2°) agrees fairly well with the recently determined experimental gas-phase structure [d_{SS} = 191.7(1) pm, a_{SSS} = 117.36(6)°].[15] The calculated NBO atomic charges of the S_3 molecule are +0.32 for the central atom and −0.16 for the two terminal atoms. This molecule may therefore interact with S_2O with formation of the homocyclic S_5O molecule (**8**) by a [2+3] dipolar addition [Equation (3)]. The calculated structure of **8** is shown in Figure 4. The molecule contains the oxygen atom in an axial position with regard to the nonplanar S_5 ring. The S−S bond lengths vary between 205.5 and 227.0 pm (μ = 1.73 D). These structural data are in accordance with those of the related homocyclic oxides S_7O[16] and S_8O,[17] which have both been characterized by single-crystal X-ray diffraction analyses. The very long S3−S4 bond is probably the main reason for the thermal instability of S_5O, which decomposes on attempts to isolate it from solutions in which it has been prepared by dissolution of gaseous S_2O.[8] Since the torsion angle at this particular bond is only 11.6°, far from the optimum value of 90°, a large bond length is to be expected. We have previously shown that torsion angles and bond lengths in sulfur rings are related to each other.[18] All other torsion angles within the five-membered homocycle have absolute values of between 28° and 64°, mainly caused by the small ring size.

The IR spectrum of S_5O in CS_2 at −65 °C is characterized by a strong absorption at 1138 cm^{-1} in agreement with our calculated value for the S=O stretching vibration of 1131 cm^{-1} (scaled by 0.95). The remaining fundamentals of **8** are located at 490, 457, 398, 379, 305, 287, 260, 238, 212, 191 and 67 cm^{-1} [B3LYP/6-31G(2df,p) data, scaled by 0.95].

The formation of S_5O according to Equation (3) seems to proceed without any activation enthalpy. We have scanned the reaction coordinate of the reverse reaction — the dissociation of S_5O into S_2O and S_3 — by increasing the bond lengths S1−S5 and S3−S4 of **8** in steps of 0.5 pm up to 270 pm and optimizing all other parameters. The energy increased continuously to higher values but no maximum could be found.

The further fate of S_3 and S_5O in the decomposing S_2O/S_3 mixture can be discussed only in a somewhat speculative manner. If S_3 should attack S_5O the well-known S_8O[1] may be formed, although radicals may also originate from the head-to-tail polymerization of S_3. On the other hand, if two S_3 molecules undergo a cycloaddition reaction of the [2+3] type, the hypothetical $S_5{=}S$ molecule will result, while a [3+3] addition would give the well-known *cyclo*-S_6. These cycloaddition reactions are both strongly exothermic.[19] However, so far no experimental evidence for the possible formation of either S_8O or S_6 from S_2O is available.

The reported formation of S_4 from S_2O has not been explained yet since no elementary reactions are known to generate this molecule directly from S_2O at low temperatures in an exothermic reaction. In principle, S_4 could originate from S_2 by dimerization but the direct formation of S_2 from S_2O is strongly endothermic even if the S_2 molecule is formed in its triplet ground state [Equation (15)].

$$2\,S_2O \rightarrow {}^3S_2 + S_2O_2\ (\mathbf{5});\quad \Delta H°_{298} = +84\ \text{kJ·mol}^{-1},\ \Delta G°_{298} = +90\ \text{kJ·mol}^{-1} \qquad (15)$$

The red S_4 molecule is probably responsible for the cherry-red color of condensates made from pure or almost pure S_2O at liquid nitrogen temperature.[20] It seems that S_4 and the sulfur radicals detected by ESR spectroscopy are formed only if the concentration of S_2O is very high since no S_4 has been detected in matrix-isolation experiments with diffusion-controlled decomposition of S_2O.[9] Therefore, more complex reactions may be responsible for the formation of S_4. While the reaction in Equation (16) is spin-forbidden and endothermic[21] the bimolecular decomposition of S_5O is exothermic and might produce S_4 even at low temperatures [Equation (17)].

$$S_5O + S_2O \rightarrow SO_2 + S_4 + {}^3S_2;\quad \Delta H°_{298} = +50\ \text{kJ·mol}^{-1},\ \Delta G°_{298} = +1\ \text{kJ·mol}^{-1} \qquad (16)$$

$$2\,S_5O \rightarrow SO_2 + S_4 + \textit{cyclo}\text{-}S_5;\quad \Delta H°_{298} = -29\ \text{kJ·mol}^{-1},\ \Delta G°_{298} = -84\ \text{kJ·mol}^{-1} \qquad (17)$$

The observation that S_5O, dissolved in $CHCl_3$ or CS_2, decomposes at temperatures above −20 °C with formation of SO_2 and elemental sulfur[8] indicates that the reaction according to Equation (17) has a rather small activation enthalpy. In this context it is interesting to mention that S_2O, if condensed very slowly on a cold finger at −196 °C, produces a condensate that is transparent and just slightly pink colored but turns intensely red on warming to ca. −150 °C.[7]

Theoretically, S_4 could also be formed from S_3, as shown in Equation (18), but this reaction is slightly endothermic and spin-forbidden and therefore may require a substantial activation enthalpy.

$$2\,S_3 \rightarrow {}^3S_2 + S_4;\quad \Delta H°_{298} = +13\ \text{kJ·mol}^{-1},\ \Delta G°_{298} = +17\ \text{kJ·mol}^{-1} \qquad (18)$$

Thus, the reactions shown in Equations (13), (14), (3) and (17) are most likely responsible for the formation of S_4 from

S_2O on condensation. However, S_4 will play a role only if the S_2O concentration and therefore the concentrations of S_3 and consequently of S_5O are not too low.

Implications for the Chemistry on Jupiter's Moon Io

Large parts of Jupiter's satellite Io are covered by elemental sulfur and solid sulfur dioxide ("SO_2 frost").[22] The surface temperature varies between 80 and 1400 K, not only due to day-and-night changes but also due to the presence of several "hot spots". There are a number of active volcanoes on Io, the most prominent of which is named Pele. The plume of Pele reaches a height of 350 km since both the gravitational force and the atmospheric pressure (ca. 10^{-7} bar) are much lower on Io than on Earth. Spectroscopic measurements have shown that Pele's plume contains SO_2, SO as well as S_2 and it is widely believed that this volcano is powered by hot silicate magma which heats underground deposits of SO_2 and elemental sulfur; if the pressure is high enough eruptions will occur.[23] Equilibrated hot mixtures of elemental sulfur and sulfur dioxide always contain a few percent of SO and S_2O, depending on temperature, total pressure and S:O ratio.[24] S_3 is also expected to be a prominent constituent of the hot sulfur/SO_2 mixture ejected from the magma chamber.[24] During the volcanic eruptions the unstable (highly reactive) species sprayed into the Ionian atmosphere experience both a sharp drop in total pressure and a steep temperature gradient but they are now also exposed to the UV radiation of the Sun. In addition, S_2O may also be formed within the plume from SO and S_3 by the following spin-allowed reaction [Equation (19), which we found to be exothermic and exergonic.[25]

$$\begin{gathered}{}^3SO + S_3 \rightarrow S_2O + {}^3S_2;\\ \Delta H^\circ_{298} = -70\ \text{kJ·mol}^{-1},\ \Delta G^\circ_{298} = -68\ \text{kJ·mol}^{-1}\end{gathered} \tag{19}$$

The question is then: What will be the lifetime and the sink for the S_2O molecules?

The present results indicate that S_2O will most probably react with S_3 to give S_5O as soon as the temperature within the volcanic plume drops below a certain limit and the chemical equilibrium is no longer established. Due to the low S_2O concentration a reaction between two S_2O molecules as in Equation (13) is less probable. The S_5O molecules may then be deposited on the surface of Io, but on exposure to UV radiation they will eventually decompose to elemental sulfur and SO_2. On the other hand, S_2O may also be decomposed photolytically into SO and sulfur atoms.

S_4 has been thought to be responsible for the orange or red deposits on the surface of Io which have been detected in particular in the vicinity of volcanoes, and S_2O has been suggested as the precursor of this S_4.[23] Our results and discussions show that S_2O is not likely to produce S_4 under the temperature and pressure conditions of the Ionian atmosphere since the concentrations of S_2O and its decomposition products S_3 and S_5O within the volcanic plumes will simply be too low to allow a series of bimolecular reactions like $S_2O \rightarrow S_3 \rightarrow S_5O \rightarrow S_4$. In addition, it should be mentioned that the published color pictures of Io's surface often use artificially enhanced colors ("false colors") to enhance the contrast of the color variations, in which case orange may look red, while the true colors of the sulfur deposits on Io's surface are more yellowish.[26]

Conclusion

The most likely initial step of the thermal decomposition of pure disulfur monoxide is a [2+3] cycloaddition between two S_2O molecules to give the five-membered ring oxatetrathiolane 2-oxide **7**. This reaction is exothermic and the activation enthalpy is small. The heterocycle **7** is predicted to spontaneously dissociate at 298 K into SO_2 and S_3, a reaction which is also exothermic and which has no barrier. Therefore, pure S_2O is not stable in the gas phase at partial pressures above 1 mbar, in solid condensates at temperatures above −130 °C, or in liquid solutions above −70 °C. The S_3 molecule can add exothermally to another S_2O molecule with formation of the homocyclic sulfoxide S_5O (pentathiolane oxide, **8**) which has previously been prepared in this way. However, at higher concentrations, as in condensates of pure or almost pure S_2O, the S_3 and S_2O molecules may also undergo radical-chain polymerization reactions since ESR spectra have shown the presence of sulfur radicals. The result of all of these reactions are polysulfur oxides of varying and partly unknown molecular size and, finally, especially at higher temperatures, elemental sulfur and sulfur dioxide. The most reasonable [2+2] cycloaddition reactions between two S_2O molecules resulting in various isomers of S_4O_2 are all strongly endothermic and therefore unlikely at low temperatures.

Computational Details

Standard ab initio calculations were carried out with the GAUSSIAN 98 series of programs[27] at the G3X(MP2) level of theory.[28] This theory corresponds effectively to QCISD(T)/G3XL//B3LYP/6-31G(2df,p) energy together with zero-point vibrational and isogyric corrections. The G3X(MP2) theory represents a modification of the G3(MP2) theory[29] 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 the sulfur-containing compounds examined in this work. For instance, the geometries of several cluster species are poorly predicted by the MP2 theory.

For all investigated molecules a charge-density analysis, at the B3LYP/6-31G(2df,p) level, was performed using the natural bond orbital (NBO) approach.[30] NBO atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[31] Unless otherwise noted, all relative enthalpies reported in this publication are given as ΔH°_{298} and correspond to the G3X(MP2) level.

The harmonic fundamental vibrations were calculated at the B3LYP/6-31G(2df,p) level. The corresponding eigenvalues were all positive for the minimum-energy structures reported below while transition states had one negative eigenvalue. Dipole moments (μ) are given in D (1 D = 3.336×10^{-30} Cm).

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