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The Thermal Decomposition of Thiirane: A Mechanistic Study by Ab Initio MO Theory**

Yana Steudel,[a] Ralf Steudel,*[a] and Ming Wah Wong[b]

Abstract: Using high-level ab initio MO methods, we have identified two reaction pathways with different thermodynamic and kinetic properties for the thermal decomposition of the three-membered heterocycle thiirane (C_2H_4S) and related derivatives. A homolytic ring opening, followed by attack of the generated diradical on another thiirane molecule, and subsequent elimination of ethene in a fast radical chain reaction results in the formation of disulfur molecules in their triplet ground state ($^3S_2$) and requires activation enthalpies of $\Delta H^{\#}_{298} = 222 \text{ kJ mol}^{-1}$ and $\Delta G^{\#}_{298} = 212 \text{ kJ mol}^{-1}$. This reaction mechanism would result in a first-order rate law in agreement with one reported gas-phase experiment but does neither match the experimental activation energy nor does it explain the observed retention of the stereochemical configuration in the thermal decomposition of certain substituted thiiranes. Alternatively, sulfur atoms can be transferred from one thiirane molecule to another with the intermediate formation of thiirane 1-sulfide ($C_2H_4S_2$). This molecule can either decompose unimolecularly to ethene and disulfur in its excited singlet state ($^1S_2$) or, by means of spin crossover, S_2 in its triplet ground state may be formed. On the other hand, the thiirane 1-sulfide may react with itself and transfer one sulfur atom from one molecule to another with formation of thiirane 1,1-disulfide ($C_2H_4S_3$), which is an analogue of thiirane sulfone; thiirane is formed as the second product. The 1,1-disulfide may then decompose to ethene and S_3. In still another bimolecular reaction, the thiirane 1-sulfide may react with itself in a strongly exothermic reaction to give S_4 and two equivalents of ethene. This series of reactions results in a second-order rate law and requires activation enthalpies of $\Delta H^{\#}_{298} = 109 \text{ kJ mol}^{-1}$ and $\Delta G^{\#}_{298} = 144 \text{ kJ mol}^{-1}$ for the formation of thiirane 1-sulfide, while the consecutive reactions require less activation enthalpy. Elemental sulfur (S_8) is eventually formed by oligomerization of either S_2, S_3, or S_4 in spin-allowed reactions. These findings are in agreement with most experimental data on the thermal desulfurization of thiirane and its substituted derivatives. Thiirane 1-persulfide ($C_2H_4S_3$) with a linear arrangement of the three sulfur atoms as well as zwitterions and radicals derived from thiirane are not likely to be intermediates in the thermal decomposition of episulfides.

Keywords: ab initio calculations · desulfurization · episulfide · radicals · reaction mechanisms

Introduction

Thiiranes or episulfides are an interesting class of highly reactive compounds which also occur naturally.[1a, b] Certain thiirane derivatives have found technical or pharmaceutical applications.[1b] Episulfides contain the thermally unstable

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three-membered C_2S ring, which tends to decompose to the corresponding olefin and elemental sulfur.[1] Since the sulfur is usually observed as the thermodynamically stable allotrope orthorhombic *cyclo*-octasulfur (α-S_8), it is evident that the overall reaction mechanism must involve several steps. In the case of the most simple episulfide, that is, thiirane C_2H_4S (**1a**),

1a   **2a**   **3a**
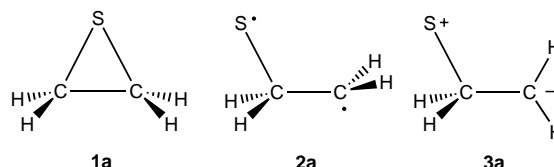
the actual mechanism of this decomposition has never been studied in detail. In a short communication,[2] the gas-phase thermolysis of **1a** at a pressure of >150 Torr (15 kPa) and at

temperatures below 250 °C was reported to be a first-order reaction with an Arrhenius activation energy (E_a) of 40 kcal mol⁻¹ (168 kJ mol⁻¹); neither a standard deviation nor a temperature was given for this value, and no experimental details were disclosed. Ethene and sulfur were the only products. From the small and negative activation entropy of −2.5 e.u. (−11 J mol⁻¹ K⁻¹) it was concluded that the cyclic structure is preserved in the "activated complex", which was proposed to be an electronically excited state of thiirane. This excited molecule was assumed to rapidly react with another molecule of thiirane to give S_2 and two molecules of ethene.[2] At pressures "well below 15 kPa" the reaction was said to be of higher order. In addition, it was observed that under similar conditions, *trans*-but-2-ene episulfide decomposed with 99% retention of the stereochemical configuration, while the *cis* isomer yielded a >90% retention of its configuration.[2]

The only other study of the gas-phase thermolysis of a thiirane is the flow pyrolysis of *trans*-diethynylthiirane reported in another short communication.[3] The sole product observed at a reaction temperature of 395 °C (contact time 15 s) was the corresponding olefin (probably together with elemental sulfur). The stereochemical configuration of the olefin was hardly retained since a 3:4 mixture of *cis* and *trans* olefin was recovered. The corresponding *cis* isomer decomposed at 250 °C to a 2:1 mixture of *cis* and *trans* olefin, but in addition other products were observed. No reaction order or activation energy was reported.

The reaction of sulfur atoms both in the triplet ground state (³P) and in the excited singlet state (¹D) with gaseous ethene has been studied repeatedly both experimentally as well as theoretically,[4–7] and it was shown that both reactions yield thiirane. In this context, the chainlike diradical ·CH₂CH₂S· (**2a**) has been studied. Its ground state is a triplet, which at the HF/6-31G* level with limited CI calculation is by 227 kJ mol⁻¹ less stable than thiirane **1a**;[6] at the G2 level the same relative energy of 227 kJ mol⁻¹ was obtained for **2a** at the potential energy minimum,[8] while 198 kJ mol⁻¹ were obtained at the MP3(full)/6-31G*//HF/6-31G* + ZPE level and 194 kJ mol⁻¹ at the level B3LYP/6-31G* + ZPE.[9] Since these energies are of the same order of magnitude as the reported activation energy of 168 kJ mol⁻¹,[2] one may conclude that the homolytic ring opening is the first step in the thermal decomposition of gaseous thiirane following a first-order rate law. However, the further fate of the thiirane diradical **2a** is unknown.

From thermodynamic data it has been known from the earliest studies that sulfur atoms cannot be the primary reaction products in the thermal decomposition of thiirane since the measured activation energy is much lower than the enthalpy of the hypothetical sulfur extrusion reaction [Eq. (1)].[2] Using the experimental enthalpies of formation of the reactants[10] the following reaction enthalpy is obtained.

$$\mathbf{1a} \rightarrow C_2H_4 + S(^3P) \quad \Delta H^\circ_{298} = 247 \text{ kJ mol}^{-1} \qquad (1)$$
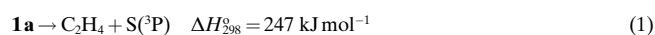
Most probably, there is an additional activation energy for this reaction.[6] Should the sulfur atom be formed in its excited singlet state to observe the law of spin conservation, the required enthalpy would be still higher. Trapping experiments

with pentene did not provide any evidence for sulfur atoms as intermediates in the thermolysis of **1a**.[2]

In this work, we have investigated the various possibilities for the decomposition of thiirane to identify the most likely reaction mechanism and the intermediates involved using the high-level G3(MP2) theory.

Computational Methods

Standard ab initio MO calculations were performed using the Gaussian 98[11] series of programs. The energies of various equilibrium structures and transition states of C_2H_4S, $C_2H_4S_2$, $C_2H_4S_3$, and $C_4H_8S_2$ systems and related species were examined using the G3(MP2) level of theory.[12] In brief, the G3(MP2) method is a composite procedure, which aims at providing an accurate approximation to the high level of theory at QCISD(T)/GTMP2LARGE//MP2/6-31G(d), with the incorporation of zero-point energy (calculated from HF/6-31G(d) vibrational wavenumbers, scaled by 0.8929) and higher level corrections. This level of theory is usually within 6 kJ mol⁻¹ of accurate experimental values.[12] Spin-restricted calculations were used for closed-shell systems, and spin-unrestricted ones for open-shell systems. The effect of a dielectric medium was examined using Onsager's self-consistent reaction field theory[13] at the B3 LYP/6-31G* level. Charge density analysis, at the MP2/6-31G* level, was performed using the natural bond orbital (NBO) approach.[14] Unless otherwise noted, all relative energies reported in this publication are given as ΔH°_{298} and correspond to the G3(MP2) level, while structural parameters were obtained at the MP2/6-31G* level. In the case of reactions involving the molecule S_4 the geometries had to be optimized at the QCISD/6-31G* level since S_4 requires a higher level treatment of electron correlation for a proper description of its geometry.[15] The energies were then obtained at the G3(MP2) level based on the QCISD/6-31G* optimized geometry.

Results and Discussion

Ring opening of thiirane: The calculated structure of thiirane **1a** shown in Figure 1 is in excellent agreement with the experimental structure, which was determined by microwave spectroscopy[16] and which is characterized by the following parameters: C−C 1.483 Å, C−S 1.815 Å, C−H 1.083 Å, C−S−C 48.3°, C−C−S 65.9°, H−H 115.8°. An almost perfect agreement was obtained at the MP2/6-311 + G(2df,p) level, which resulted in the following parameters: C−C 1.479 Å, C−S 1.817 Å, C−H 1.084 Å, C−S−C 48.0°, C−C−S 66.0°, H−C−H 115.5°, H−C−C 118.1°, H−C−S 115.0°. The dipole moment of gaseous thiirane was measured as 1.84 D.[17] Our calculated value of 2.09 D (Table 1) is in better agreement with values from experiments than any previously reported value.[1a] At the MP2/6-311 + G(2df,p) level an even better agreement was obtained: 1.93 D.

If the ring opening of **1a** is the first step in the thermal decomposition, one has to determine whether the chainlike intermediate is a triplet diradical (**2a**) or possibly a singlet zwitterion (**3a**). Our calculations confirm the earlier findings that the triplet diradical **2a** is lower in energy than the singlet zwitterion **3a** (Table 1). The formation of **2a** from the thiirane **1a** at 298 K requires a Gibbs free energy of 212 kJ mol⁻¹. The reported activation energy of 168 kJ mol⁻¹[2] is much lower than the enthalpy difference between **1a** and **2a** (222 kJ mol⁻¹).

Interestingly, the ring opening of **1a** causes only small changes of the bond lengths in the generated diradical **2a**
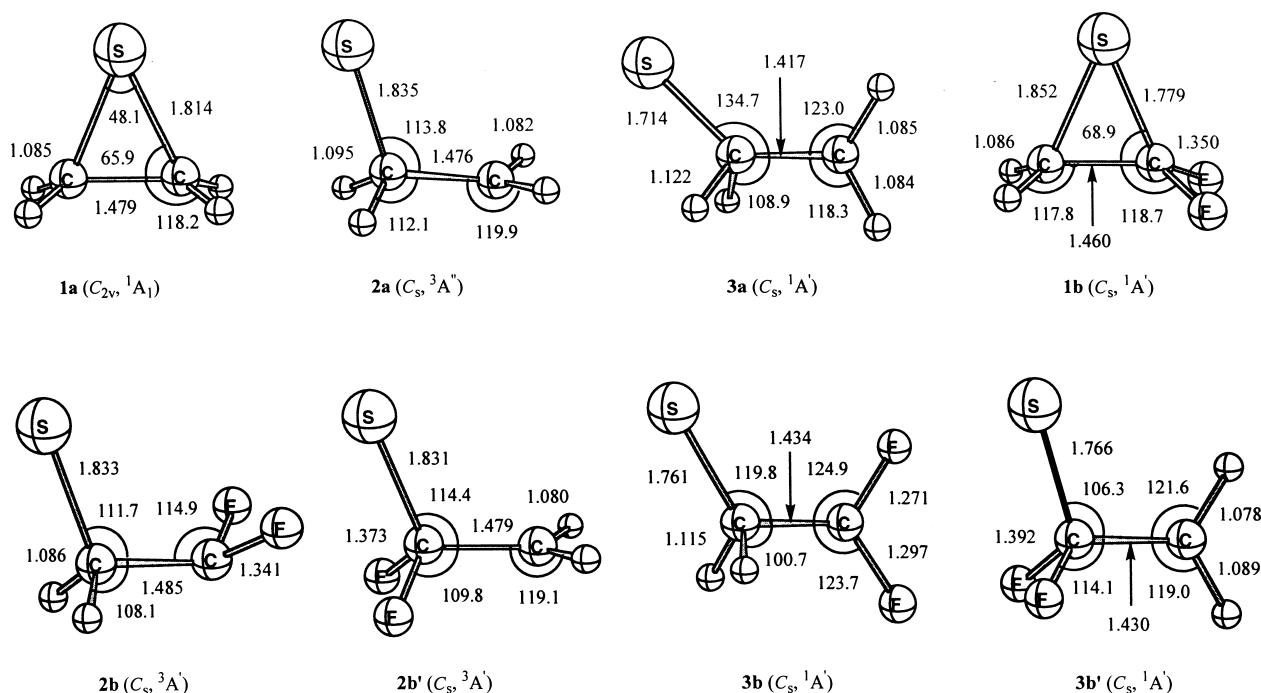
Figure 1. Calculated structures of thiirane **1a**, of the diradical **2a**, of 2,2-difluorothiirane **1b** and its diradical (**2b**, **3b**), and zwitterionic isomers (**2b′**, **3b′**), both in triplet and singlet electronic states. Bond lengths in Å, angles in °.

despite the now much larger C–C–S bond angle of 113.8° compared with 65.9° in **1a**. The C–C bond lengths of both species are practically identical as are the C–H bonds of the terminal CH$_2$ group. The other C–H bonds and the C–S bond increased in length by about 1%. The molecular symmetry is C_s. The atomic spin densities in **2a** are practically 1.0 each at the terminal sulfur and carbon atoms. The NBO atomic charges were obtained as +0.12 at the sulfur atom (the same as in **1a**), as −0.71 at the central carbon atom (−0.56 in **1a**), and as −0.33 at the terminal carbon atom.

The geometry of the zwitterion **3a** differs from that of **2a** insofar as the terminal methylene group is now coplanar with the carbon–sulfur bond, and the C–C–S bond angle is

considerably larger, by 21°. The symmetry was restricted to C_s in this calculation since this structure collapses to that of **2a** upon geometry optimization if the symmetry constraint is lifted. The energy of **3a** is 7 kJ mol^{-1} higher than that of the diradical **2a** (Table 1) despite the fact that the C–S and C–C bonds are considerably shorter than those of **2a**. The NBO atomic charge on the sulfur atom is +0.06, at the neighboring carbon atom it is −0.79, and at the terminal carbon −0.46. However, species **3a** does not represent a minimum on the potential energy surface (PES) since it has one imaginary wavenumber. This holds true not only for the free molecule but also in a polar dielectric medium of $\varepsilon = 40$.

As an excited state of thiirane was proposed to be the rate-determining intermediate in the thermal decomposition of **1a**,[2] it is important also to consider the triplet state of *cyclic* thiirane. However, all our attempts to locate a stable triplet structure of **1a** failed. Under the C_{2v} constraint, a first-order saddle point was located, which lies 408 kJ mol^{-1} above the ground-state thiirane. Relaxing the symmetry constraint upon geometry optimization leads to the diradical **2a**. Thus, we conclude that the thermal decomposition of thiirane **1a** is unlikely to involve an excited state.

The substituted derivative 2,2-difluorothiirane **1b** has been claimed as an intermediate in the reaction of thiocarbonyldi-fluoride F$_2$C=S with diazomethane in ether at 0–10 °C. It was assumed that **1b** is formed but rapidly decomposes to the observed products elemental sulfur and F$_2$C=CH$_2$.[18] To find out the reasons for this claimed instability, we have calculated the structures of **1b** as well as of its triplet diradical **2b** and the related singlet zwitterion **3b** (Figure 1). It turned out that the homolytic ring opening of **1b** at the S–CF$_2$ bond requires a similarly high amount of Gibbs energy ($\Delta G^{\circ}_{298} = 211$ kJ mol^{-1}) as the ring opening of **1a**, and that the triplet diradical **2b** is

Table 1. Calculated total and relative energies[a] and dipole moments (μ)[b] of C$_2$H$_4$S and C$_2$H$_2$F$_2$S species.

Species	Total energy[c]	μ	Relative energy		
			ΔE°_0	ΔH°_{298}	ΔG°_{298}
			C$_2$H$_4$S		
1a	−476.19189	2.09	0.0	0.0	0.0
2a	−476.10839	1.47	219.2	222.2	212.2
3a	−476.10504	2.36	228.0	229.4	225.1
CH$_2$=CH$_2$ + S(^{3}P)	−476.09853		245.1	244.2	206.7
			C$_2$H$_2$F$_2$S		
1b	−674.51467	1.94	0.0	0.0	0.0
2b	−674.43168	2.00	217.9	219.6	211.2
2b′	−674.42901	1.96	224.9	227.7	219.4
3b	−674.39825	7.65	305.7	305.5	304.6
3b′	−674.43253	2.26	215.6	216.5	214.8
CH$_2$=CF$_2$ + S(^{3}P)	−674.42487		235.8	243.8	194.3

[a] G3(MP2) level; total energies in hartrees and relative energies in kJ mol^{-1}. [b] MP2/6-31G* values; in Debye. [c] Calculated G3(MP2) E_o energies of CH$_2$=CH$_2$, CH$_2$=CF$_2$, and S(^{3}P) are −78.43477, −276.76111, and −397.66376 hartrees, respectively.
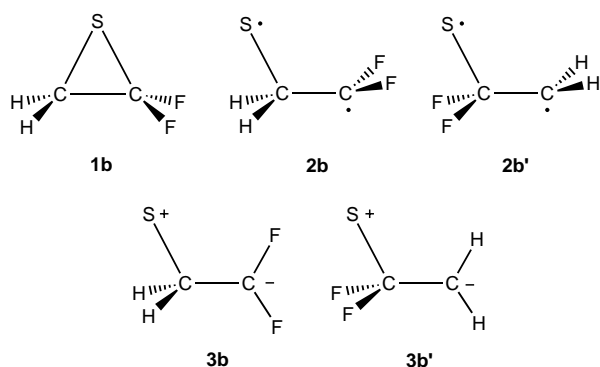
significantly more stable than the singlet zwitterion **3b** ($\Delta\Delta G^{\circ}_{298} = 93$ kJ mol^{-1}) despite the asymmetric charge distribution in **1b** and **3b** as a result of the two highly electronegative fluorine substituents (Table 1). The energetically unfavorable zwitterion **3b** is characterized by an extremely large dipole moment of 7.65 D compared with 2.00 D for **2b** and 1.94 D for **1b** (Table 1).

As expected, the C−S bond originating from the fluorinated carbon atom of **1b** is much shorter than the C−S bonds in **1a**, and the same holds for the C−C bond (Figure 1). In fact, the two C−S bonds of **1b** differ in length by 0.07 Å or approximately 4 %. The NBO atomic charges of **1b** are $+0.15$ for the sulfur atom, -0.60 for the carbon atom of the methylene group, and -0.63 for the fluorine bearing carbon atom. In the diradical **2b**, the corresponding charges are $+0.14$, -0.78, and $+0.81$. If the ring opening of **1b** takes place at the S−CH$_2$ bond which is longer than the S−CF$_2$ bond, a triplet diradical **2b′** or a singlet zwitterion **3b′** is obtained, which are of similar conformations to the unsubstituted derivatives **2a** and **3a**, respectively. Surprisingly, the relative enthalpies of **2b′** and **3b′** are rather similar to those of **2b** with the zwitterion **3b′** slightly more favorable than the diradical **2b′** (Table 1). In other words, in the case of asymmetrically substituted episulfides it cannot be ruled out that, in addition to the homolytic ring-opening reaction, a heterolytic ring opening takes place, especially in highly polar solvents. The atomic charges on the backbone atoms S−C1−C2 of **2b′** are as follows (data for **3b′** in parentheses): S -0.16 ($+0.32$), C1 $+0.52$ ($+0.41$), C2 -0.38 (-0.43). According to these results there is no evident reason for any lower stability of **1b** compared with that of **1a** as far as ring-opening reactions are concerned.

Finally, we have calculated the reaction enthalpy for the decomposition of **1a** to ethene and ground-state sulfur atoms (^{3}P) as 244 kJ mol^{-1}, which is in excellent agreement with the experimental value of 247 kJ mol^{-1}[10] cited in the Introduction.

Attack of thiirane 1a by the diradical 2a: If the thermal decomposition reaction of thiirane **1a** begins with formation of the diradical **2a**, this reaction should be the rate-determining step. Species **2a** may then attack other molecules of **1a** to initiate a series of fast radical chain reactions, in which the observed products will eventually be formed. In principle, this attack may occur either at the sulfur atom or at one of the

carbon atoms of **1a**, and the attacking atom of **2a** may be either the sulfur atom or the terminal carbon atom. Consequently, there are four possibilities for the attack, two of which yield carbon−sulfur interactions (**4b** and **4c**) while the other two would result in carbon−carbon (**4a**) or sulfur−sulfur (**4d**) bonds.

The configuration **4a** with a carbon−carbon interaction can be ruled out since the two interacting carbon atoms are negatively charged and therefore will repel each other. Furthermore, this type of reaction would result in a chain of four carbon atoms which is not observed among the products.
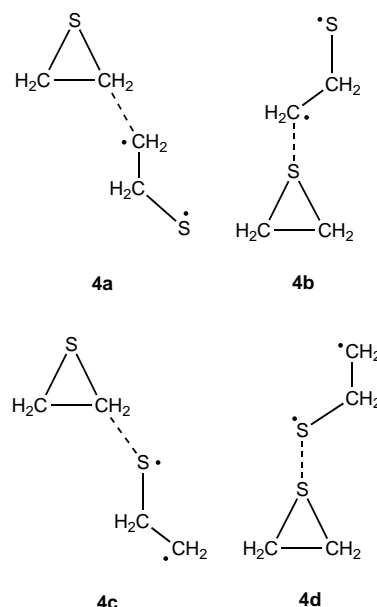
The alternative **4b** can also be ruled out for the following reason. The attack would probably result in loss of one ethene molecule to give an intermediate of composition C$_2$H$_4$S$_2$ in a triplet state. We have calculated the structures of the two most likely conformations of this species (**5a** and **5b**).
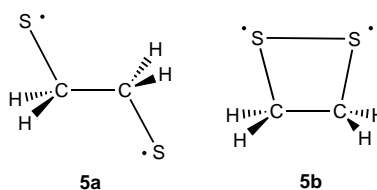
The open chain **5a** (symmetry C_{2h}) is a minimum on the PES. Its geometry is shown in Figure 2. The formation of **5a** from **1a** and **2a** by reaction (2) is exothermic by 33 kJ mol^{-1}.

$$\mathbf{1a} + \mathbf{2a} \rightarrow \mathbf{5a} + C_2H_4 \tag{2}$$

However, this species does not help to explain the formation of elemental sulfur by a unimolecular dissociation process unless it isomerizes to the heterocyclic species **5b**. This 1,2-dithietane molecule in its excited triplet state is highly unstable. Its formation from **1a** and **2a** requires 56 kJ mol^{-1}.
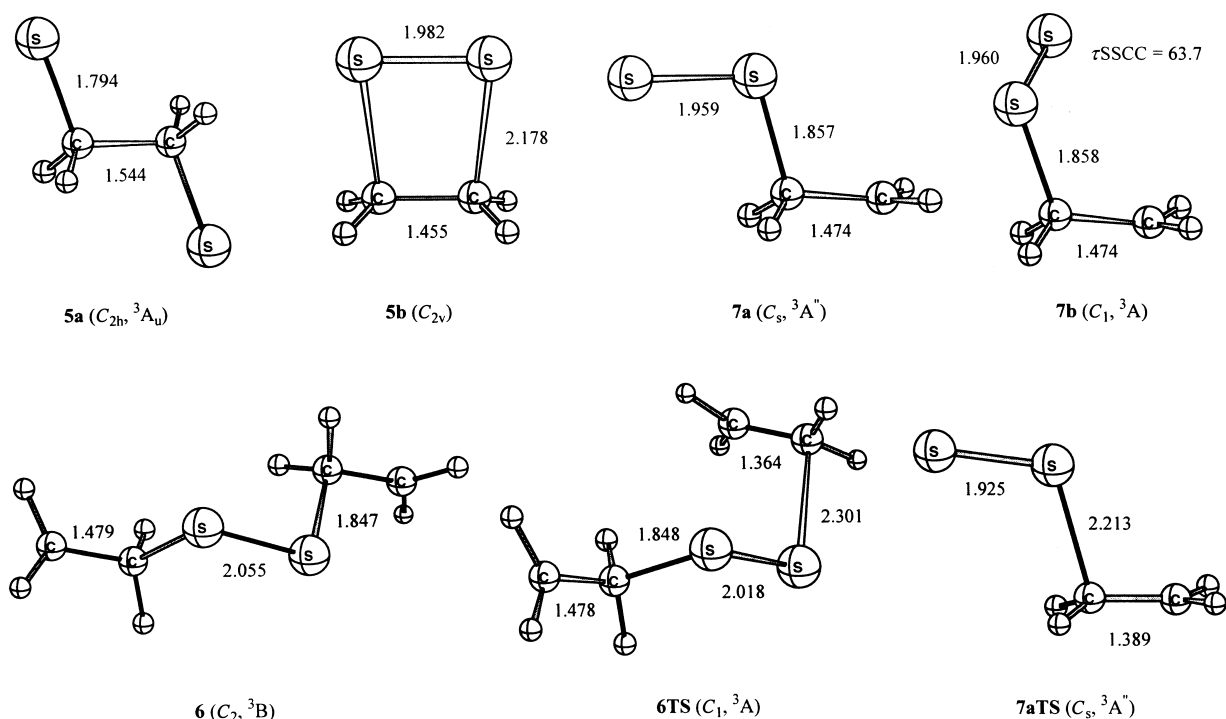
Figure 2. Calculated structures of four isomeric triplet molecules (**5a**, **5b**, **7a**, **7b**) of composition [2C, 4H, 2S], of the diradical $(C_2H_4)_2S_2$ (**6**), and of the transition states **6TS** and **7aTS** (bond lengths in Å).

The species **5b** (with C_{2v} symmetry) is best considered as an adduct between $^3S_2$ and C_2H_4, as can be seen from the rather long C–S bonds (2.178 Å) and the short S–S bond (1.982 Å), which is about halfway between the single and double bond lengths known from S_8 (2.05 Å) and S_2 (1.89 Å)[19a] (Figure 2). Therefore, we conclude that the configuration **4b** does not provide a useful reaction mechanism to explain the thermolysis of thiirane.

The attack of **2a** on **1a** via the configuration **4c** would result in a chain of the type C–C–S–C–C–S if one assumes that the formation of the new C–S bond results in an opening of the attacked thiirane ring at the neighboring C–S bond. For reasons outlined above, it cannot easily be seen how such an intermediate would result in the observed formation of elemental sulfur even if the loss of one molecule of ethene is assumed as the next step. Hence, configuration **4c** is also ruled out.

Thus, we are left with the fourth possibility (**4d**) which is the only reaction yielding a sulfur–sulfur bond right from the beginning of the attack of **2a** on **1a**. The first step of this interaction may be the formation of an intermediate with a three-electron σ-bond which is a well-known structural unit in sulfur chemistry.[20–22] After the thiirane ring has opened up, a triplet chain molecule of connectivity C–C–S–S–C–C (**6**) is formed which is calculated to have C_2 symmetry and represents a minimum on the PES (see Figure 2). Its formation from **1a** and **2a** is exothermic by 44 kJ mol^{-1}. The structure of **6** is characterized by C–C bonds (1.479 Å) which are of the same length as in **1a**, by an S–S bond with about the same length (2.055 Å) as in S_8, and C–S bonds slightly longer than those of **1a** (by 2%). The further reactions of the diradical **6** will be discussed in the next section.

Loss of ethene and S$_2$ formation from diradical 6: The triplet chain **6** may either dissociate in a single step into triplet disulfur ($^3S_2$) and *two* molecules of singlet ethene or first into a triplet chain of connectivity S–S–C–C (**7**) and *one* molecule

6
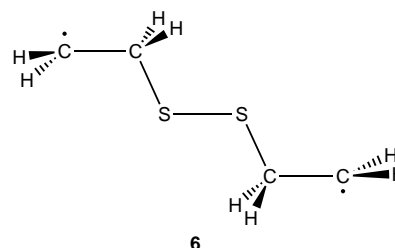
of singlet ethene. The second possibility will be discussed first. The activation energy for the cleavage of **6** into **7** and C_2H_4 is only 13 kJ mol^{-1}. The corresponding transition state for the decomposition of **6** (**6TS**) is shown in Figure 2. It is of C_1 symmetry. Its breaking carbon–sulfur bond (2.301 Å) is 0.45 Å longer than that of **6**, while at the same time the S–S bond has shortened by 0.04 Å to 2.018 Å. The triplet chain molecule ·CH$_2$CH$_2$SS· formed from **6TS** exists as two rotamers of very similar energy (**7a** and **7b**; see Figure 2),
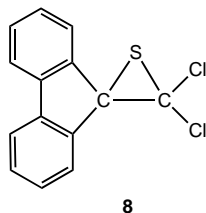

7a   **7b**
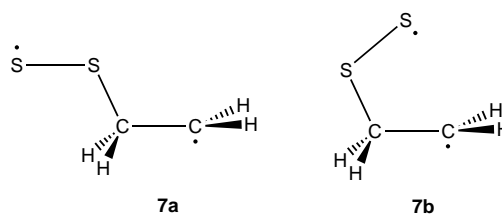
with **7a** as the more stable species (by 0.3 kJ mol^{-1}). The energy of the transition state **7aTS** for the decomposition of **7a** into $^3S_2$ and C_2H_4 is just 2 kJ mol^{-1} higher than the energy of **7a**. The geometry of **7aTS** is also shown in Figure 2. It can be concluded that the thiirane decomposition via configuration **4d** is a facile process once the diradical **2a** has been formed. The final step of this decomposition, that is, the formation of C_2H_4 and $^3S_2$ from **7a** is exothermic by 74 kJ mol^{-1}.

For the *concerted* dissociation of diradical **6** into two molecules of C_2H_4 and $^3S_2$, we have successfully located a saddle point **6TS′**, with C_2 symmetry and $d(C-S) = 2.276$ Å. However, **6TS′** is a second-order saddle point with *two* imaginary wavenumbers corresponding to the asymmetric and symmetric combination of the two breaking C−S bonds. Thus, it is unlikely that a single-step pathway is possible for the dissociation of **6**. It is worth noting that **6TS′** lies 13 kJ mol^{-1} higher in energy than the rate-determining step of the stepwise dissociation pathway via **6TS**.

Formation of S_8: The formation of homocyclic sulfur molecules in the thermal decomposition of thiirane can easily be explained by a sequence of well-known reactions starting from triplet S_2. The ground state S_2 molecule is known to dimerize to S_4 even at very low temperatures.[23] The molecule S_4 exists as an unbranched planar chain in a singlet ground state.[15, 24] Such a dimerization reaction is allowed by the rule of spin conservation. Two molecules of S_4 may then combine to form the cyclic S_8 molecule, which has also a singlet ground state. However, if radicals are involved in the thiirane decomposition, one can also imagine the formation of diradical homoatomic sulfur chains by combination of S_4 with one or several molecules of S_2. From such a long chain, rings of any size can eventually be split off.[25] In fact, it has been observed that the rather bulky and stereochemically protected episulfide **8** decomposes thermally in solution with the formation of the homocycles S_8 and S_6 along with the corresponding olefin.[26] The mechanism of this decomposition may, however, differ from that of **1a** since it has been reported that the reaction order depends on the concentration,[27, 28] and that certain spin trapping reagents have no influence on the rate of decomposition.[28] These implications will be discussed below.

In our results on the homolytic ring opening of thiirane we present for the first time the activation energy of this process. The calculated activation enthalpy of 212 kJ mol^{-1} is much higher than the experimental Arrhenius activation energy of 168 kJ mol^{-1} reported by Strausz et al.[2] While a ring opening as the rate-determining step would be in agreement with the first-order rate law reported for thiirane pressures of > 15 kPa, the retention of configuration in the thermal desulfurization of gaseous *trans*- and *cis*-but-2-ene episulfide[2] definitely excludes a ring-opening step. Therefore, a different mechanism has to be considered.

Reaction kinetics in solution: Several authors have studied the kinetics of the thermal decomposition (desulfurization) of substituted thiiranes in solution. The *trans*-diethynylthiirane mentioned in the Introduction was found to decompose in toluene at 100 °C by second-order kinetics at concentrations of approximately 0.15 mol L^{-1}, while at lower concentrations the kinetics changed to a first-order rate law.[3] The second-order reaction occurred with greater than 90% retention of the stereochemical configuration, which excludes a ring-opening mechanism. Ando et al.[29] studied the thermal decomposition of tetramethylallene episulfide at 110 °C in solution and observed a first-order reaction rate-determining step (initial concentration 0.2 mol L^{-1}).[29a] The same reaction order was found in the case of diphenyl(di-*tert*-butylallene)-episulfide and di-*tert*-butyl(diphenylallene)episulfide at 150 – 180 °C. For these species the Arrhenius activation energies were determined in 1,2-dichlorobenzene as 98.3 and 115.5 kJ mol^{-1}, respectively.[29b] The authors claimed that a symmetrical diradical intermediate is formed in the rate-determining step; this species might contain a π-bond system delocalized over the three carbon atoms.[29a–c]

Chew and Harpp[28b] studied extensively the thermal desulfurization of episulfide **8** at 80 °C in twelve different solvents and observed that in each solvent the reaction follows an unimolecular, first-order process at low concentrations of episulfide (0.1 – 0.15 mmol L^{-1}), but at higher concentrations (2 mmol L^{-1}) a bimolecular pathway becomes more important. Depending on the solvent, the activation enthalpies varied between 41 and 89 kJ mol^{-1} for the unimolecular process ($\Delta G^{\#} = 100 – 119$ kJ mol^{-1}) and between 28 and 111 kJ mol^{-1} for the bimolecular reaction ($\Delta G^{\#} = 99 – 124$ kJ mol^{-1}). Increasing solvent polarity resulted in decreasing $\Delta G^{\#}$ values. Since the reaction rate (in toluene) did not significantly change on addition of either styrene or acetanilide as radical inhibitors, the authors assumed that an unimolecular ring-opening reaction produces a zwitterionic intermediate,[28b] which in the light of our results reported above is rather unlikely. For the bimolecular reaction the formation of a thiirane 1-sulfide $C_2H_4S_2$ as the primary intermediate was proposed.[26, 28b] We have now studied for the first time the structures and thermodynamics of thiirane 1-sulfide theoretically.[30]

Thiirane 1-sulfide and related species: As was shown above, certain isomers of composition $C_2H_4S_2$, namely **5a**, **5b**, **7a**, and **7b** could be intermediates in the reactions following the attack of the diradical **2a** on thiirane **1a** by either of the configurations **4b**, **4c**, or **4d**. Thus, we have investigated various possible *singlet* isomers of the composition [2C,4H,2S] which may be more stable than the triplet species discussed so far. The results are shown in Figure 3 and in Table 2.

Three plausible structures (**9a**, **9b**, and **9c**) exist with minimal energy in singlet ground states. Surprisingly, the hypothetical *S*-sulfide of thioacetaldehyde **9a** is the most stable isomer followed by the 1,2-dithietane **9c**, while the thiirane 1-sulfide **9b** is the least stable structure. The relative enthalpies (ΔH^{o}_{298}) of these singlet species with respect to the triplet diradical **7a** are -150 (**9a**), -91 (**9b**), and -142 kJ mol^{-1} (**9c**), respectively (Table 2). Selected geomet-
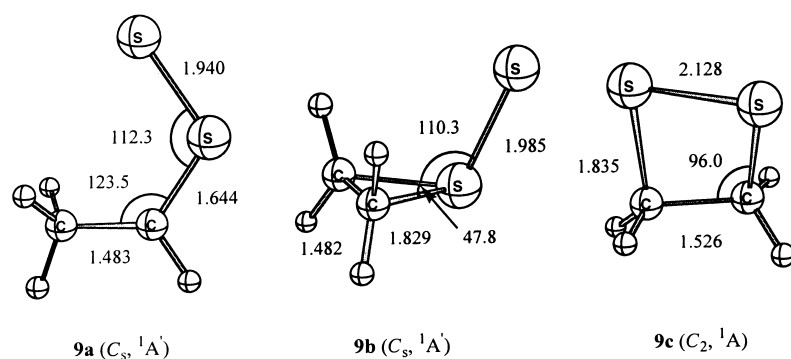
Figure 3. Calculated structures of three isomeric singlet molecules of composition [2C, 4H, 2S] (bond lengths in Å, angles in °).

Table 2. Calculated total and relative energies[a] and dipole moments (μ)[b] of several $C_2H_4S_2$ and $C_4H_8S_2$ species.

Species	Total energy[c]	μ	Relative energy		
			ΔE_0^o	ΔH_{298}^o	ΔG_{298}^o
		$C_2H_4S_2$			
7a	− 873.89570	2.84	0.0	0.0	0.0
7b	− 873.89557	2.56	0.3	0.0	0.8
5a	− 873.87806	0.00	46.3	43.7	51.1
5b	− 873.84385	1.97	136.1	133.2	141.2
7aTS	− 873.89460	3.00	2.9	2.1	2.0
$CH_2=CH_2 + {}^3S_2$	− 873.92348		− 77.4	− 73.5	− 96.2
9a	− 873.95229	3.48	− 148.6	− 150.1	− 138.6
9b	− 873.92891	2.62	− 87.2	− 90.5	− 80.0
9c	− 873.94804	5.29	− 137.4	− 141.5	− 128.2
		$C_4H_8S_2$			
6	− 952.31795	2.15	0.0	0.0	0.0
6TS	− 952.31261	2.36	14.0	13.1	12.1
6TS′[d]	− 952.30763	2.35	27.1	25.4	25.9
1a + 1a	− 952.33028		46.4	43.9	2.1
7a + $CH_2=CH_2$	− 952.33047		− 32.9	− 32.7	− 76.1

[a] G3(MP2) level; total energies in hartrees and relative energies in kJ mol⁻¹. [b] MP2/6-31G* values; in Debye. [c] Calculated G3(MP2) E_o energy of ${}^3S_2$ − 795.48872 hartrees. [d] **6TS′** is a second-order saddle point.

rical parameters are shown in Figure 3. The species **9a** is of little relevance in the present discussion although it shows that *S*-sulfides are sometimes more stable than unbranched isomers with a disulfane unit like **9c**.
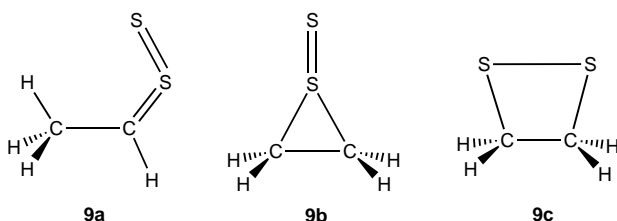

Sulfur transfer reactions: Several authors have discussed hypothetical species of the type **9b** as precursors of the sulfur molecules in the thermolysis of various episulfides.[26, 28, 31] It was assumed that the transfer of sulfur atoms from one episulfide molecule to another would produce such species. To examine whether this mechanism is a realistic alternative to the ring-opening reaction discussed above, we have calculated the structure and energy of thiirane 1-sulfide **9b** in the singlet

ground state and established the reaction enthalpy for its formation as well as for its decomposition reactions (Table 3).

The structure of **9b** is analogous to the experimental structure of the related thiirane 1-oxide C_2H_4SO, which is also of C_s symmetry and in which the terminal sulfur atom of **9b** has been replaced by oxygen.[32a, b] The geometry of the three-membered ring in **9b** is almost identical to that of **1a**. The length of the S—S bond (1.985 Å) is halfway between those of ${}^3S_2$ (1.892 Å; double bond) and *cyclo*-S_8 (2.048 Å; single bond).[19a] For acyclic thiosulfoxides like $H_2S=S$ and $Me_2S=S$ the sulfur–sulfur bond lengths have been calculated by ab initio MO methods as 2.00–2.02 Å.[19b, 33] Evidently, these bonds are best described by two canonical structures.
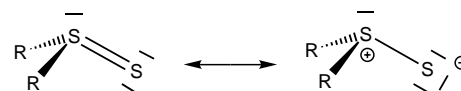
However, for convenience we will use the symbol S=S in the following sections. The NBO atomic charges of **9b** are − 0.53 for the terminal sulfur atom, + 0.62 for the central sulfur, and − 0.58 for the carbon atoms.

Table 3. Calculated total and relative energies[a] and dipole moments (μ)[b] of the transition states **1aTS**, **9bTS**, **11TS**, and **11aTS** as well as of thiirane 1-persulfide **10** and the isomeric thiirane 1,1-disulfide **11**.

| Species	Total energy[c]	μ	Relative energy		
			ΔE_0^o	ΔH_{298}^o	ΔG_{298}^o
1a + 1a	− 952.38378		0.0	0.0	0.0
1aTS	− 952.34309	3.23	106.8	108.9	144.2
9b + $CH_2=CH_2$	− 952.36368		52.8	55.4	53.8
${}^1S_2 + 2 CH_2=CH_2$	− 952.33349[d]		132.0	139.2	95.0
9b	− 873.94804	5.29	0.0	0.0	0.0
9bTS	− 873.90216	3.39	70.2	72.3	68.4
${}^1S_2 + CH_2=CH_2$	− 873.89872[d]		79.3	84.6	42.1
9b + 9b	− 1747.85782		0.0	0.0	0.0
10TS	− 1747.78973	3.25	178.8	182.0	217.4
10[c] + **1a**	− 1747.86810		− 27.0	− 22.6	− 44.0
11	− 1271.64614	6.14	0.0	0.0	0.0
11aTS	− 1271.62648	7.17	51.6	52.8	49.5
${}^1S_3 + CH_2=CH_2$	− 1271.68746		− 108.5	− 104.5	− 154.0
9b + 9b	− 1747.85782		0.0	0.0	0.0
11TS	− 1747.83752	2.93	53.3	54.9	95.3
11 + 1a	− 1747.83803		52.0	51.9	54.8

[a] G3(MP2) level; total energies in hartrees and relative energies in kJ mol⁻¹. [b] MP2/6-31G* values; in Debye. [c] The calculated G3(MP2) E_o energies of ${}^1S_2$, ${}^1S_3$, and **10** are − 795.46396, − 1193.25269, and − 1271.67621 hartrees, respectively. The E_o energy of ${}^1S_2$ is 65.0 kJ mol⁻¹ higher than that of ${}^3S_2$. [d] The reported S_2 corresponds to the ${}^1\Sigma_g^+$ state. Full valence CASPT3/6-311G** calculations predict that the ${}^1\Sigma_g^+$ state is just 1.0 kJ mol⁻¹ less stable than the ${}^1\Delta_g$ state.

The formation of **9b** from **1a** according to Equation (3) is endothermic by 55 kJ mol^{-1} (**9b**).

$$2\,\mathbf{1a} \rightarrow \mathbf{9b} + C_2H_4 \qquad (3)$$

The unimolecular decomposition of **9b** with production of elemental sulfur should observe the rule of spin conservation to avoid additional activation barriers. Consequently, a decomposition reaction according to Equation (4) should be discussed.

$$\mathbf{9b} \rightarrow {}^1S_2 + C_2H_4 \quad \Delta H^{\circ}_{298} = 84 \text{ kJ mol}^{-1} \qquad (4)$$
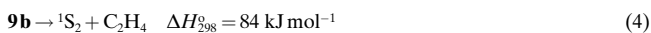
As can be seen, the formation of $^1S_2$ from **1a** via reactions (3) and (4) requires only 139 kJ mol^{-1}, much less than the ring opening of **1a**. Thus, it seems that the sulfur atom transfer mechanism is more favorable thermodynamically than the radical chain mechanism, although such a bimolecular mechanism would result in a rate law of second order in contrast to the reported first order of the gas-phase reaction at higher pressures. It should be kept in mind however that at low pressures the thiirane decomposition becomes a higher order process.[2] We have investigated the PES for reaction (3) with no symmetry constraints to locate the transition state (**1aTS**) and to find out whether there is an activation barrier in the formation of **9b**. In addition, we have identified the transition state **9bTS** for the decomposition of thiirane 1-sulfide according to Equation (4). The transition state **1aTS** is of C_s symmetry and characterized by an almost linear arrangement between the two sulfur atoms and the center of the C–C bond of one of the episulfide molecules (Figure 4). The C–C bond of the leaving C$_2$H$_4$ unit is much shorter (1.361 Å) than the C–C bond of the other C$_2$H$_4$ group (1.477 Å) which is to become part of the epidisulfide molecule. Simultaneously, the two breaking C–S bonds are much longer (2.395 Å) than the remaining ones (1.818 Å). The S–S bond length (2.307 Å) is still much longer than in the

thiirane 1-sulfide to be formed (1.985 Å). The unique configuration of **1aTS** results in a rather high negative activation entropy of $\Delta S^{\#}_{298} = -188$ J mol^{-1} K^{-1}.

The transition state **9bTS** is also of C_s symmetry and quite similar to the thiirane 1-sulfide structure, although the C–S bonds have increased in length from 1.829 Å to 2.417 Å, while the S–S bond length slightly decreased from 1.985 Å to 1.933 Å (Figure 4). Consequently, the activation entropy is rather small ($\Delta S^{\#}_{298} = 13$ J mol^{-1} K^{-1}).

The spin-allowed unimolecular decomposition of **9bTS** initially yields a van der Waals complex of $^1S_2$ and C$_2$H$_4$ with a C⋯S distance of 3.087 Å. This complex is 2 kJ mol^{-1} more stable than **9bTS** ($\Delta\Delta G^{\circ}_{298} = 28$ kJ mol^{-1}) and finally dissociates endothermically to $^1S_2$ and C$_2$H$_4$ ($\Delta H^{\circ}_{298} = 12$ kJ mol^{-1}). In contrast to the positive reaction enthalpy, the Gibbs free energy of this reaction is negative ($\Delta G^{\circ}_{298} = -26$ kJ mol^{-1}). In Figure 5, a schematic energy level diagram (ΔG°_{298}) for the thiirane decomposition according to reactions (3) and (4) is given.
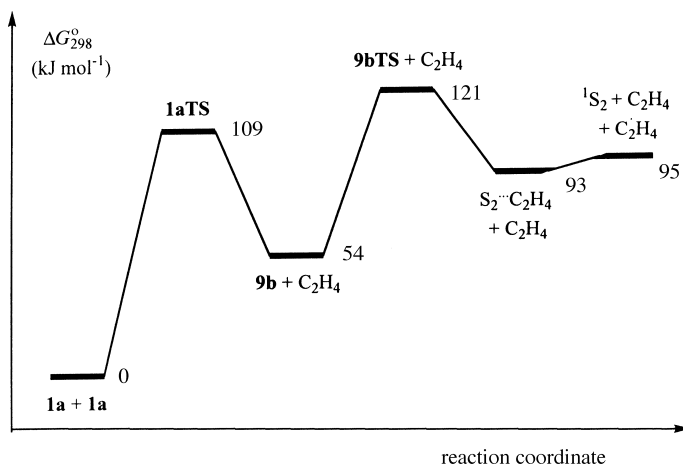

Figure 5. Energy level diagram for the decomposition of thiirane **1a** via the thiirane 1-sulfide **9b** into two molecules of ethene and singlet disulfur (which initially form a van der Waals adduct C$_2$H$_4$⋯$^1S_2$ before they separate).

As can be seen from Figure 5, the overall Gibbs energy required for the sequence of reactions (3) and (4) is 95 kJ mol^{-1} of $^1S_2$ or 48 kJ mol^{-1} of **1a**. The rate-determining step will be the bimolecular formation of the epidisulfide **9b**; this reaction results in a second-order rate law. The Gibbs activation energy for this process is 109 kJ mol^{-1} of S$_2$. In this context, it is interesting to compare the decomposition of **9b** with the products of the thermolysis of thiirane 1-oxide which theoretically should be ethene and sulfur monoxide in its excited $^1\Delta$ singlet state (^1SO). However, it has repeatedly been observed spectroscopically that the SO molecule is formed in its $^3\Sigma$ triplet ground state.[32c–e] If such a spin-crossover reaction should also take place in the unimolecular decomposition of **9b**, we end up with triplet disulfur and ethene directly. In this case, the reaction would be endothermic by only $\Delta H^{\circ}_{298} = +19$ kJ mol^{-1} ($\Delta G^{\circ}_{298} = -24$ kJ mol^{-1}). The activation enthalpy would of course be lower than in the spin-allowed case (<70 kJ mol^{-1}).
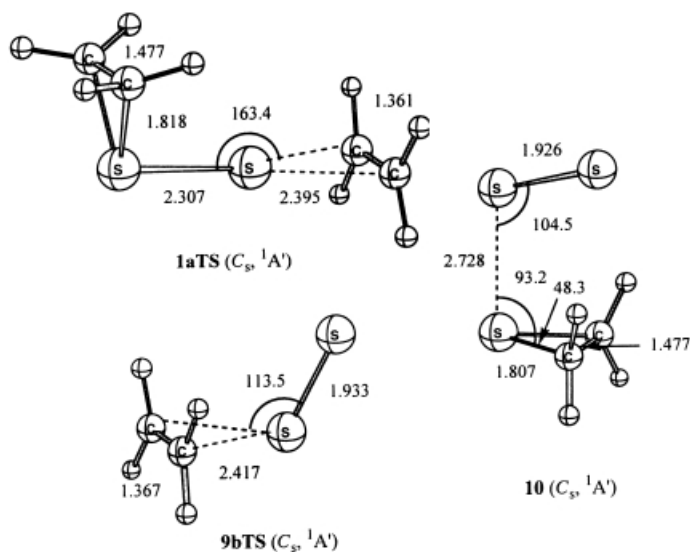

Figure 4. Calculated structures of the transition states **1aTS** (sulfur atom transfer from one thiirane molecule to another) and **9bTS** (elimination of $^1S_2$ from thiirane 1-sulfide) and of the thiirane 1-persulfide **10** (bond lengths in Å, angles in °).

It is evident now that the decomposition of **1a** via thiirane 1-sulfide **9b** is much more favorable thermodynamically than the ring-opening reaction discussed above. However, the disulfide **9b** may also undergo bimolecular decomposition reactions; these will be discussed in the next section.

Thiirane trisulfides: The decomposition reaction (5) is shown below.

$$1a \rightarrow C_2H_4 + 1/2\ ^3S_2 \tag{5}$$

The reaction was calculated to be endothermic by 37 kJ mol^{-1}, in excellent agreement with the experimental value of 35 kJ mol^{-1} obtained from the enthalpies of formation of the reactants.[10] From published enthalpies of formation, it follows that the overall decomposition reaction (6) is endothermic by 13 kJ mol^{-1} in the gas phase.

$$1a \rightarrow C_2H_4 + 1/8\ S_8 \tag{6}$$

But it is endothermic by only 1 kJ mol^{-1} if all reactants are in their standard states at 298 K and 1.013 bar (liquid episulfide, gaseous ethene, and solid α-S$_8$).
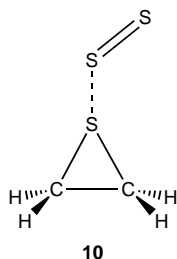
The formation of homocycles like S$_8$ from **9b** may theoretically occur either by oligomerization of S$_2$ or by further growth of the sulfur chain with formation of a thiirane 1-persulfide **10**.

The formation of **10** from **9b** and **1a** with elimination of C$_2$H$_4$ according to Equation (7) requires a reaction enthalpy of $\Delta H^{\circ}_{298} = 33$ kJ mol^{-1} ($\Delta G^{\circ}_{298} = 10$ kJ mol^{-1}).

$$9b + 1a \rightarrow 10 + C_2H_4 \tag{7}$$

From these data, it follows that the generation of **10** from three molecules of **1a** is endothermic by $\Delta H^{\circ}_{298} = 88$ kJ mol^{-1}; thermodynamic data of **10** are listed in Table 3. Reaction (7) is not very likely since it represents an autocatalytic process: the first intermediate **9b** reacts with the starting material **1a**, and this results in an accelerated consumption of **1a**. Such behavior during the desulfurization reaction has never been observed.

Alternatively, **10** could be formed from two molecules of **9b** [Eq. (8)].

$$2\ 9b \rightarrow 10 + 1a \tag{8}$$

This reaction is even exothermic by $\Delta H^{\circ}_{298} = -23$ kJ mol^{-1} and $\Delta G^{\circ}_{298} = -44$ kJ mol^{-1}. The transition state **10TS** of this reaction has been located; its structure is shown in Figure 6. The activation enthalpies of reaction (8) are $\Delta H^{\#}_{298} = 182$ kJ mol^{-1} and $\Delta G^{\#}_{298} = 217$ kJ mol^{-1}. A reaction pathway of this type might explain a reaction order lower than two of the gas-phase decomposition of thiirane, since after starting from four molecules of **1a** in reaction (3) to make two molecules of **9b** in reaction (4) one molecule of **1a** is
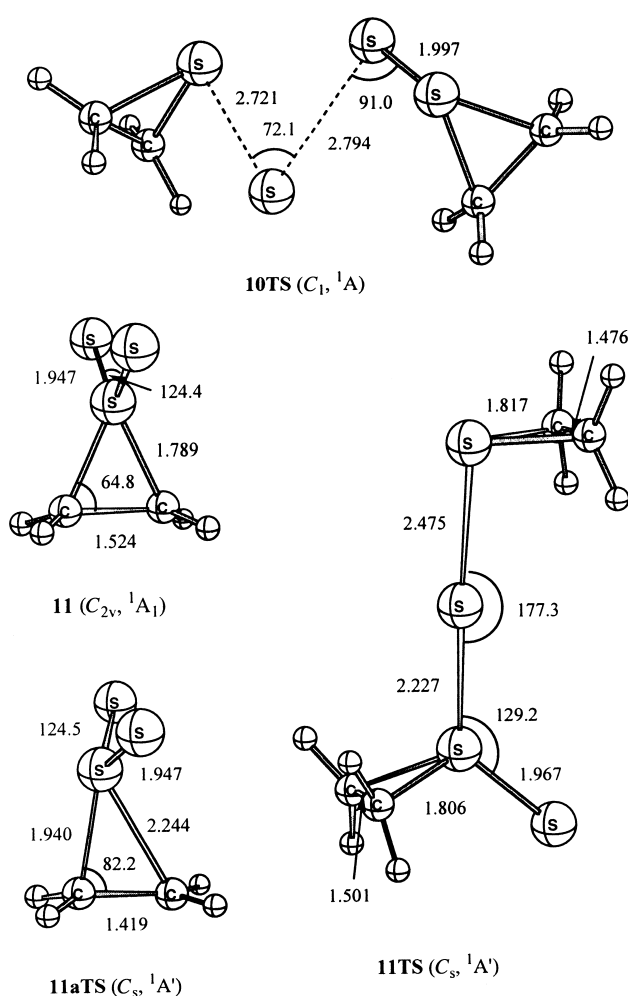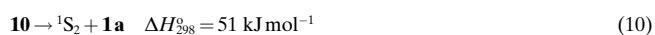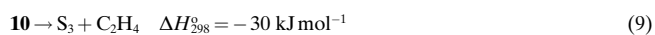

Figure 6. Calculated structures of the thiirane 1,1-disulfide **11** and of the transition states **10TS**, **11TS**, and **11aTS** (bond lengths in Å, angles in °).

recovered in reaction (8). But the relatively high barrier makes this reaction unlikely at moderate temperatures.

The thiirane 1-persulfide **10** has no analogue in any existing compound but it corresponds to a minimum on the PES. Its hypothetical analogue is the persulfoxide R$_2$SOO, which has been claimed as an intermediate in the reaction of organic sulfides R$_2$S with singlet dioxygen (^{1}O$_2$).[34] The structure of **10** is of C_s symmetry (see Figure 4) and is characterized by one rather long S–S bond of 2.728 Å, while the terminal S–S bond (1.926 Å) is almost as short as the bond in the free S$_2$ molecule (^{3}S$_2$: 1.892 Å; ^{1}S$_2$: 1.898 Å). Thus, one may interpret the geometry of **10** as an adduct between thiirane **1a** and ^{1}S$_2$. For comparison, the van der Waals contact distance between two sulfur atoms is 3.5 Å.[19c]

One of the possible decomposition products of **10**, the ozone-analogue S$_3$, is a singlet molecule of C_{2v} symmetry.[35] Its formation from **10** by reaction (9) is exothermic, while the dissociation of **10** into thiirane and singlet disulfur by reaction (10) to observe the law of spin conservation is endothermic.

$$10 \rightarrow S_3 + C_2H_4 \quad \Delta H^{\circ}_{298} = -30\ \text{kJ mol}^{-1} \tag{9}$$

$$10 \rightarrow\ ^1S_2 + 1a \quad \Delta H^{\circ}_{298} = 51\ \text{kJ mol}^{-1} \tag{10}$$

Thus, a reaction of **9b** with **1a** to give S_3 directly together with two equivalents of ethene is endothermic by only 2 kJ mol^{-1}. However, this reaction is unlikely to occur since it would again result in autocatalysis, which has never been observed for any episulfide decomposition. The formation of S_3 from **1a** by Equations (3), (8), and (9) requires only $\Delta H^{\circ}_{298} = 58$ kJ mol^{-1} or $\Delta G^{\circ}_{298} = 8$ kJ mol^{-1}. If S_3 is formed, it will probably oligomerize to S_6 and larger rings.

The direct formation of S_3 from thiirane 1-sulfide as shown in Equation (11) is fairly strongly exothermic ($\Delta H^{\circ}_{298} = -53$ kJ mol^{-1}, $\Delta G^{\circ}_{298} = -99$ kJ mol^{-1}).

$$2\,\mathbf{9b} \rightarrow S_3 + \mathbf{1a} + C_2H_4 \qquad (11)$$

This reaction could also proceed via an intermediate of type **11**, which may be termed as thiirane 1,1-disulfide (symmetry C_{2v}).

11
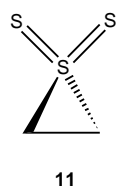
This species is formed by the transfer of a sulfur atom from one molecule of **9b** to another (reaction (12)).

$$2\,\mathbf{9b} \rightarrow \mathbf{11\,TS} \rightarrow \mathbf{11} + \mathbf{1a} \qquad (12)$$
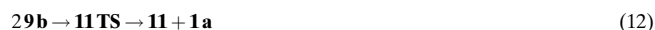
This overall reaction is endothermic by $\Delta H^{\circ}_{298} = 52$ kJ mol^{-1} and $\Delta G^{\circ}_{298} = 55$ kJ mol^{-1}. The activation parameters for **11TS** were calculated as $\Delta H^{\neq}_{298} = 55$ kJ mol^{-1} and $\Delta G^{\neq}_{298} = 95$ kJ mol^{-1}. Remarkably, thiirane disulfide **11** is 79 kJ mol^{-1} less stable than the isomer **10** ($\Delta G^{\circ}_{298} = 97$ kJ mol^{-1}). The structures of **11** and of the transition state **11TS** of reaction (12) are shown in Figure 6.

The structure of **11** is analogous to the structure of the well-known thiirane 1,1-dioxide $C_2H_4SO_2$ (ethylene episulfone).[36a] The two S−S bonds are remarkably short (1.947 Å) which justifies the notation S=S. As expected, the decomposition of **11** according to Equation (13) is strongly exothermic ($\Delta H^{\circ}_{298} = -105$ kJ mol^{-1}, $\Delta G^{\circ}_{298} = -154$ kJ mol^{-1}).

$$\mathbf{11} \rightarrow S_3 + C_2H_4 \qquad (13)$$
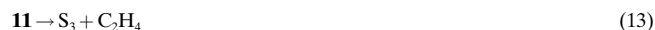
The extrusion of S_3 from **11** should be as easy a reaction as the facile decomposition of thiirane 1,1-dioxide into SO_2 and ethene which requires an activation energy of 136 kJ mol^{-1} at a temperature of 348 K (calculated at the MP4SDTQ(fc)/6-31G*//MP2(fc)/6-31G* level of theory).[36b] We have located the transition state **11aTS** for reaction (13); its structure is shown in Figure 6. The barriers are rather small: $\Delta H^{\neq}_{298} = 53$ kJ mol^{-1} and $\Delta G^{\neq}_{298} = 50$ kJ mol^{-1}. All these results show that S_3 is likely to be formed by reactions (12) and (13), since compared with reactions (5) and (8) the bimolecular decomposition of **9b** by reactions (12) and (13) is thermodynamically much more favorable (see Figure 7).

A compound of composition $C_2H_4S_3$ could also have the structure of a *spiro*-trisulfide **12** with C_{2v} symmetry. Attempts to optimize the geometry of this structure at the HF/6-31G* level resulted in dissociation into thiirane and singlet disulfur. A similar decomposition occurred when we tried to optimize the structure of two isomers of $C_2H_4S_4$ with a chainlike arrangement of the four sulfur atoms and the ethene
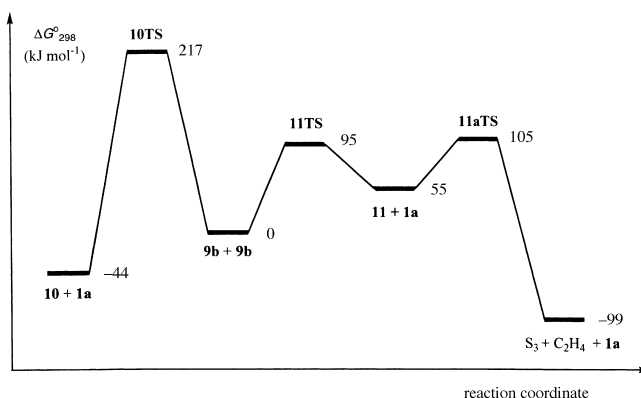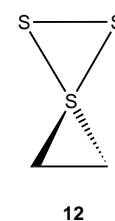
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Figure 7. Energy level diagram for the various bimolecular decomposition reactions of thiirane 1-sulfide **9b**.

unit attached to either the first or the second sulfur atom (derivatives of **10** or **11**, respectively). These structures dissociated spontaneously into **9b** and S_2 (HF/6-31G*).

Formation of tetrasulfur S_4: Theoretically, the disulfide **9b** may also undergo a bimolecular decomposition reaction, for example, according to Equation (14).

$$2\,\mathbf{9b} \rightarrow 2\,C_2H_4 + S_4 \qquad (14)$$

At higher concentrations of the thiirane the intermediate **9b** will also be present at a higher concentration, and bimolecular reactions may now be faster than the unimolecular decomposition (4). Reaction (14) is exothermic by -80 kJ mol^{-1} ($\Delta G^{\circ}_{298} = -127$ kJ mol^{-1}) at the G3(MP2)//QCISD/6-31G* level. Despite numerous attempts, we were not successful in locating a transition state for reaction (14), which may proceed in two steps. Hence, the activation energy remains unknown, but given the strong exothermic nature of this reaction we expect $\Delta G^{\neq}_{298}$ to be quite small.

Reaction order: The bimolecular starting reaction (3) explains the second-order rate laws observed for the thermal decomposition reactions of certain thiirane derivatives in solution at higher concentrations as well as the decomposition of gaseous thiirane at pressures below 15 kPa. It should be pointed out however that our calculated activation enthalpies cannot be compared with the experimental values since the solution experiments apply to substituted episulfides, and the

solvation effects need to be taken into account; the gas-phase E_a value for the decomposition of **1a** is evidently in error, since the reported first-order rate law[2] is unlikely according to our results.

The bimolecular decomposition of difluorothiirane **2a** is expected to proceed in a similar fashion to the decomposition of **1a** described in Equations (3) and (4). However, the activation parameters will possibly be slightly higher than those of **1a**, since the positive charge on the sulfur atom of **2a** is slightly higher than in the case of **1a**, and the charge results in a somewhat stronger repulsion of the sulfur atoms in the corresponding transition state **2aTS** compared with **1aTS**. Thus, **2a** is not expected to be less stable than **1a**.

Finally, we would like to address the question whether disulfur reacts with thiirane to give ethene and trisulfur (S_3), which then could oligomerize. Such a reaction would also result in an autocatalytic process and therefore can be excluded. Furthermore, we found that the decomposition of singlet **9c** to C_2H_4 and $^1S_2$ is endothermic by 134 kJ mol^{-1}, and thus the reaction excludes the species **9c** as a potential intermediate.

Vibrational spectra: Some of the reaction intermediates discussed above are separated from their decomposition products by substantial energy barriers which makes it likely that one day they might be observed in low-temperature experiments. Others might be produced by photolysis of suitable precursors. The most likely detection technique for these species will be infrared spectroscopy. Therefore, we have listed the wavenumbers and absolute IR intensities of the harmonic fundamental vibrations of the species **1a**, **9a–c**, and **10** in Table 4. This table also contains the wavenumbers of thiirane observed in either the infrared spectrum of the gaseous compound or the Raman spectrum of liquid **1a**.[38] The agreement with our calculated data (wavenumbers and intensities, the latter not shown) is excellent supporting the theoretical level used for these calculations (MP2/6-31G*). The assignment of the experimental data is based on infrared band shapes and Raman polarization data as well as on normal-coordinate analyses and ab initio SCF calculations at the HF/6-31G* level of thiirane, [D₂]thiirane, and [D₄]thiirane.[38]

Conclusion

We have shown that there exist two principally different mechanisms for the thermal desulfurization of thiirane to give ethene and elemental sulfur. The first type starts with a homolytic ring-opening reaction resulting in a diradical, which then attacks other thiirane molecules with eventual formation of S_2 in its triplet ground state together with ethene. The ring opening is the rate-determining step with a Gibbs activation enthalpy of 212 kJ mol^{-1}, which is much higher than all experimental values. Therefore, the second type of mechanism is more likely which begins with the transfer of a sulfur atom from one thiirane molecule to another with formation of a thiirane 1-sulfide molecule $C_2H_4S_2$ without ring opening. This species is of C_s symmetry and has a structure analogous

Table 4. Calculated harmonic vibrational wavenumbers [cm^{-1}] and infrared intensities [km mol^{-1}] of the species **1a** (C_{2v}), **9a** (C_s), **9b** (C_s), **9c** (C_2), and **10** (C_s)[a] and experimental wavenumbers of **1a** taken from the infrared and Raman spectra.[38]

1a (calcd)	1a (exptl)[b]	9a	9b	9c	10
3121 (3)	3088 (B₁)	3057 (4)	3124 (4)	3034 (9)	3108 (1)
3110 (0)	(3104) (A₂)	3034 (13)	3114 (1)	3021 (2)	3098 (0)
3027 (8)	3014 (A₁)	2954 (5)	3019 (2)	2960 (28)	2983 (5)
3025 (7)	3013 (B₂)	2900 (5)	3017 (0)	2958 (13)	2983 (1)
1473 (5)	1457 (A₁)	1442 (3)	1440 (1)	1460 (1)	1453 (7)
1446 (0)	1436 (B₂)	1431 (15)	1412 (8)	1444 (3)	1428 (9)
1162 (0)	(1159) (A₂)	1383 (23)	1170 (0)	1264 (6)	1164 (0)
1128 (2)	1110 (A₁)	1310 (5)	1103 (12)	1241 (12)	1135 (8)
1061 (38)	1051 (B₂)	1098 (3)	1042 (14)	1164 (1)	1077 (32)
1037 (1)	1024 (A₁)	1025 (22)	1031 (11)	1068 (4)	1050 (6)
949 (6)	945 (B₁)	995 (0)	937 (18)	971 (0)	951 (6)
897 (0)	896 (A₂)	814 (61)	871 (0)	939 (0)	915 (1)
818 (0)	824 (B₁)	629 (44)	785 (2)	852 (3)	796 (2)
676 (1)	(631) (B₂)	626 (52)	599 (8)	707 (5)	672 (0)
644 (20)	627 (A₂)	454 (2)	597 (14)	667 (0)	650 (19)
		296 (1)	513 (41)	469 (0)	639 (9)
		172 (2)	242 (0)	437 (1)	191 (0)
		109 (1)	216 (3)	216 (1)	176 (0)
					162 (42)
					128 (8)
					20 (1)

[a] MP2/6-31G* values; wavenumbers were scaled by 0.9427;[37] intensity values are given in parenthesis. [b] Some vibrations do not show up in either the infrared or Raman spectrum. Therefore, the wavenumbers in parentheses were taken from the normal-coordinate analysis of Allen et al.[38]

to that of thiirane 1-oxide C_2H_4SO (ethylene episulfoxide). The thiirane 1-sulfide is proposed to either dissociate unimolecularly into ethene and disulfur in its excited singlet state ($^1S_2$) or, by means of a spin crossover, to triplet S_2 molecules ($^3S_2$). At higher concentrations, the thiirane 1-sulfide may also decompose in bimolecular exothermic reactions to give ethene and either trisulfur S_3 or tetrasulfur S_4. The latter mechanism explains the reaction kinetics for the thermal decomposition of a number of substituted thiiranes in solution which at certain concentrations follow a second-order rate law with relatively low activation energies. The rate-determining step is the intermolecular sulfur atom transfer, for which the Gibbs activation energy has been calculated as 109 kJ mol^{-1}. The observed elemental sulfur (homocycles S_6 and S_8) then results from the oligomerization of S_2, S_3, and S_4 as well as from interconversion reactions.[39] The observation that some episulfides, under certain conditions, decompose by first-order kinetics with relatively low activation energies (compared with the ring-opening enthalpy) can probably be rationalized by consecutive reactions of the thiirane 1-sulfide intermediate with re-formation of some starting material.

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