Does the Interconversion of Polysulfur Compounds Proceed Via Hypervalent Intermediates?—An Ab Initio MO Study**

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Abstract: Ab initio MO calculations at the CCSD(T)/6-311++G(2df,p)//MP2/6-311++G** level have been carried out to determine the reaction energies and Gibbs energies of the homolytic dissociation of the S–S bonds in the chainlike sulfanes H_2S_n ($n = 2-4$). Good agreement with the experimental data is observed. At the same level of theory, the formation of the hypothetical sulfuranes $H_2S(SH)_2$, $H_2S(SSH)_2$, and $S(SH)_4$ from H_2S and the mentioned sulfanes has been studied. Species of this type had been proposed as intermediates in the interconversion reactions of polysulfur compounds (e.g., formation of S_7 from S_8 and vice versa). The three sulfuranes serve here as model compounds. On the basis of the Gibbs energies and activation energies at 298 K, it is shown that the formation of the three sulfuranes from sulfanes requires too much energy and activation energy to successfully compete with homolytic dissociation reactions. In addition, the formation of the methyl-substituted sulfurane $S(SMe)_4$ from the sulfanes Me_2S_2 and Me_2S_3 was studied to elucidate the mechanism of the formal exchange of sulfur atoms between polysulfane molecules. However, both the reaction energy of 199 kJ mol^{-1} and the activation energy of 287 kJ mol^{-1}, calculated at the MP2/6-31G* level, are much higher than the homolytic dissociation energy of the S–S bonds in chain- and ringlike polysulfur compounds, such as Me_2S_4 (140 kJ mol^{-1}) and sulfur homocycles (150 kJ mol^{-1}). Therefore, it is concluded that the observed interconversion reactions of sulfur rings and of chainlike polysulfanes do not proceed via sulfurane-type intermediates. Instead, these reactions will take place by a radical chain mechanism at high temperatures, while at temperatures below 100 °C they are most probably initiated either by traces of nucleophiles that are present as impurities or by the polar surface groups usually present on the walls of the vessels used.

Keywords: ab initio calculations · hypervalent compounds · sulfur · thermodynamics · transition states

Introduction

One of the major unsolved problems of sulfur chemistry is the reaction mechanism of the so-called interconversion reactions of polysulfur compounds in nonaqueous systems, for example, the transformation of S_8 rings into rings of other sizes which takes place when orthorhombic cyclooctasulfur (α-S_8) is heated to its melting point (120 °C). After annealing, the sulfur melt consists of a complex mixture of homocycles with ring sizes up to at least 30.[1, 2] Another example is the scrambling of the substituents if two different organic disulfanes or trisulfanes, such as R_2S_m and R'_2S_n, are mixed and heated to result in the formation of the unsymmetrical species R-S_x-R′. Some of these reactions take place at room temperature already and indicate a low activation enthalpy. An example is the decomposition of *cyclo*-S_7 which can be either synthesized[3] from S_2Cl_2 and $(C_5H_5)_2TiS_5$ or isolated from quenched sulfur melts by fractional crystallization.[4] Solid S_7 decomposes at room temperature in the dark within several hours to a mixture of α-S_8 and polymeric insoluble sulfur (S_μ). On heating solid S_7, it melts at 39.5 °C and the melt rapidly polymerizes at temperatures above 60 °C.[5] These reactions are all accelerated by light, by nucleophiles, and by strong electrophiles (cations). The light-accelerated reaction evidently proceeds by a radical chain mechanism since the formation of sulfur radicals from S–S bonds on illumination with UV radiation is well-known.[6] The presence of nucleophiles result in displacement reactions with zwitterions as intermediates, and the base strength of the nucleophile is of essential importance.[7] In a similar fashion, strong electrophiles generate ionic or zwitterionic intermediates and initiate chain reactions. These reactions are discussed in detail below.

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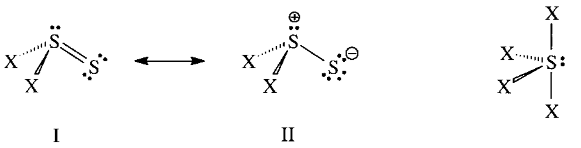
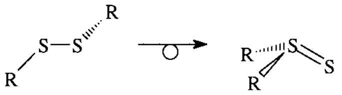
However, the interconversion reactions also take place if such reagents (catalysts) are seemingly absent and if light is excluded. Therefore, it was generally believed for a long time that even the uncatalyzed reactions proceed by a radical mechanism. However, the thermal generation of radicals from S_7 or S_8 requires an activation energy of more than $120\,kJ\,mol^{-1}$,[8] while in the case of dialkyl disulfanes R-S-S-R $\approx 300\,kJ\,mol^{-1}$ is necessary.[9] For this reason, the room-temperature decomposition of S_7 in the dark, for example, can hardly be a radical chain reaction.

In an attempt to solve this problem we proposed and extensively discussed a number of alternative reaction pathways[10] for the interconversion of sulfur homocycles and related compounds, such as selenium homocycles, selenium sulfide heterocycles, chainlike polysulfanes, and mixed sulfur-selenium chains. The key intermediates in these novel mechanisms are so-called hypervalent or hypercoordinated species; in the case of sulfur compounds these are thiosulfoxides **1** and sulfuranes **2** (Scheme 1).

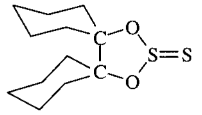

1 **2**

Scheme 1. Proposed intermediates for the interconversion of sulfur homocycles, the so-called hypervalent or hypercoordinated species, thiosulfoxides **1** and sulfuranes **2**.

We originally believed[10] that *thiosulfoxides* may be formed by a simple intramolecular isomerization [Eq. (1)] which, of course, would be endothermic (for reasons of graphical simplicity we prefer formula I of Scheme 1 although the actual charge distribution and orbital occupancy is more in line with formula II).


(1)

Several thiosulfoxides are known as pure compounds, for example $F_2S{=}S$, which is practically as stable thermodynamically as the chainlike isomer F-S-S-F.[11] Another example is the thiosulfite **3** which forms colorless crystals the structure of which was determined by X-ray crystallography.[12]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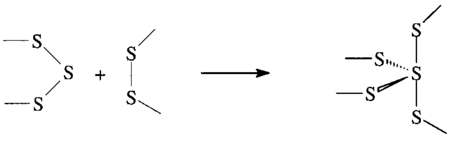
It was thought that such thiosulfoxides may be nucleophiles on account of the expected negative charge on the terminal sulfur atom and may, therefore, be able to attack S–S bonds to result in heterolytic cleavage. From such intermediates the observed products would then originate. Since these ideas were published,[10] a number of ab initio MO calculations have been performed with the aim of determining the *activation energy* for the thiosulfoxide formation from disulfanes. Depending on the substituents, the following values were obtained at 0 K; level of theory given in brackets:

H-S-S-H → $H_2S{=}S$	$210\,kJ\,mol^{-1}$ (MP2/6-311G**//MP2/6-311G**)[13]
Me-S-S-Me → $Me_2S{=}S$	$340\,kJ\,mol^{-1}$ (MP2/6-311G**//MP2/6-311G**)[12]
F-S-S-F → $F_2S{=}S$	$225\,kJ\,mol^{-1}$ (QCISD/6-31G*//MP2/6-31G*),[11a] and $185\,kJ\,mol^{-1}$ (QCISD(T)/6-31 + G**//MP2/6-31G**)[11b]
Cl-S-S-Cl → $Cl_2S{=}S$	$214\,kJ\,mol^{-1}$ (QCISD/6-311 + G(3df)//QCISD/6-311G(d))[14]

From this data it is evident that the unimolecular uncatalyzed isomerization of disulfanes to thiosulfoxides will not take place at temperatures below 100 °C and therefore cannot be responsible for the interconversion reactions discussed above. The results for dichlorodisulfane S_2Cl_2 are particularly interesting since this molecule can serve as a model compound for a section of a longer sulfur chainlike -S-S-S-S- moiety with which it is isoelectronic. We therefore conclude that any ring contraction of, for example, *cyclo*-S_8 into $S_7{=}S$ will be highly endothermic and prohibited by its high activation energy at moderate temperatures. In addition, we observed that the thiosulfoxide **3** is not a strong enough nucleophile to decompose *cyclo*-S_7: if a solution of the two compounds in an unpolar solvent was stirred at room temperature for several hours the S_7 concentration, as monitored by HPLC analysis, remained practically unchanged.[15]

The intermediate formation of *sulfuranes* in the interconversion of polysulfanes and sulfur homocycles seemed to be more likely from the beginning.[10] Our idea was that a sulfur atom of one molecule would insert into an S–S bond of another molecule to form a sulfurane of similar structure to SF_4 which forms pseudotrigonal-bipyramidal molecules with C_{2v} symmetry. A reaction of this type is allowed by the rules of orbital symmetry conservation and might be termed as an oxidative addition [Eq. (2)].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(2)

Since sulfuranes such as SF_4 are known to undergo a scrambling of substituents by Berry pseudorotation at room temperature, the axial and equatorial substituents in species such as **4** will exchange their positions. A reverse reaction (reductive elimination) may then result in species which differ from the starting materials in the number of sulfur atoms. For example, if S_8 inserts into another S_8 ring the intermediate sulfurane *spiro*-S_{16} may decompose into *cyclo*-S_7 and *cyclo*-S_9 or into *cyclo*-S_{16} depending on the type of ligand coupling (Scheme 2).

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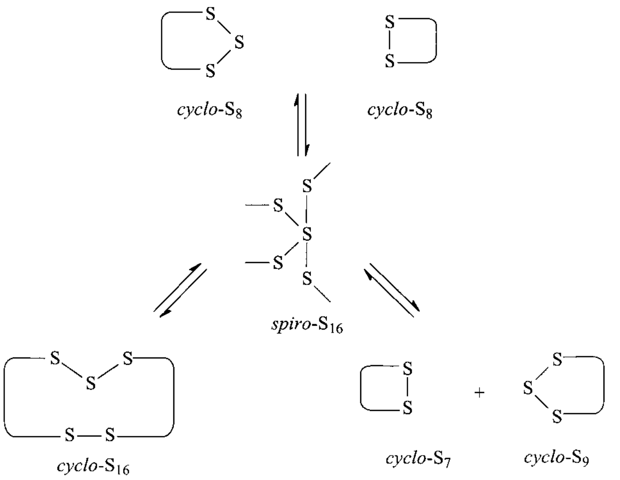
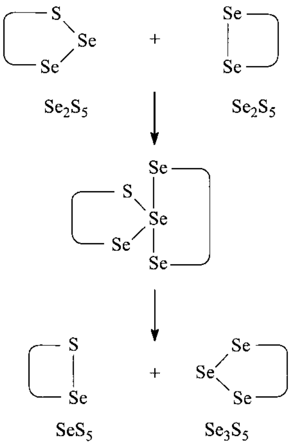


Scheme 2. Ligand couling reactions of *cyclo*-S_8.

In a similar fashion, different organic trisulfanes if mixed may scramble their substituents or may interconvert into di- and tetrasulfanes by the formal exchange of a sulfur atom.[10]

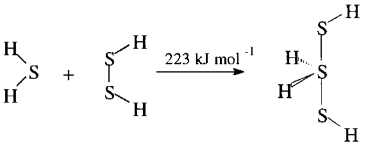
Over the years we and others have presented evidence from preparative work that this mechanism is able to explain many reaction products in sulfur and selenium chemistry. For instance, the heterocycle 1,2-Se_2S_5 decomposes in solution at 20 °C primarily into SeS_5 and 1,2,3-Se_3S_5 which is easily explained by the reaction sequence shown in Scheme 3.[16]



Scheme 3. Decomposition of 1,2-Se_2S_5 in solution.

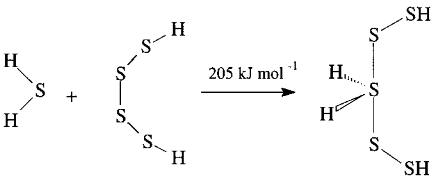
Since Se–Se bonds are weaker than S–S bonds, the insertion will take place at this bond resulting in a connection between all four Se atoms from which the observed products can then be split off. In a similar manner, *cyclo*-Se_7 decomposes into *cyclo*-Se_6 and Se_8 which can also be explained by the assumption of a hypervalent selenane intermediate.[17]

Our sulfurane mechanism has been accepted by several other authors[18] and has even entered monographs[19, 20] and textbooks,[21] although it has never been demonstrated that this reaction sequence is thermodynamically possible at moderate temperatures. To solve this problem by ab initio MO calculations one has to study the analogous reactions of small model molecules to allow for a large enough basis set and corrections for the electron correlation which is necessary to obtain reliable thermodynamic data on sulfur compounds. In this sense, some time ago, we calculated the reaction energies for the formal insertion reaction of H_2S into the central bonds of disulfane, H_2S_2 [Eq. (3)], and tetrasulfane, H_2S_4 [Eq. (4)]. The geometries and reaction energies were calculated at the MP3/6-31G*//HF/4-31G* level.[22]



5a

(3)



6a

(4)

The two sulfuranes are characterized by rather long axial S–S bonds of 237.7 pm (**5a**) and 239.1 pm (**6a**), respectively. It became evident, however, that both reactions are highly endothermic which prohibits them to proceed at moderate temperatures. Vibrational wavenumbers were not calculated at that time. Therefore, neither zero-point energies or thermal energies and entropies were available nor was it checked that the calculated geometries correspond to minima on the potential energy hypersurface. Suspicion in this direction is indicated since the symmetry of $H_2S(SH)_2$ was restricted to C_{2v} (in analogy to SF_4) and the symmetry of $H_2S(SSH)_2$ was restricted to C_2 during these calculations. No activation energies were calculated.

In this work we investigate the formation of sulfuranes made from H_2S, H_2S_2, H_2S_3, and H_2S_4 but on a considerably higher level of theory than that previously applied. In addition, we study the reaction mechanism in detail to give refined geometries, activation energies, and reaction energies as well as Gibbs energies. Since the competing reactions are the homolytic dissociation reactions of the sulfanes, we first studied the formation of sulfur radicals from di-, tri-, and tetrasulfane at the same level of theory. Thereafter, we present the results on the sulfurane formation.

Calculation Methods

All calculations were performed with the Gaussian 94[23] and Gaussian 98[24] program packages, installed on CRAY and Pentium III computers. The molecular structures of the binary H_xS_y species were fully optimized at the MP2/6-311++G** level of theory which includes the corrections for valence-electron correlation through second-order Møller–Plesset perturbation theory.[25] This level was also used to calculate the natural atomic charges,[26] vibrational wavenumbers, zero-point and thermal energies, entropies, and Gibbs energies. Improved energies were obtained by single-point calculations at the CCSD(T)/6-311++G(2df,p) level for all structures.[27] The calculations of the open-shell species were carried out using the unrestricted model ($S^2 = 0.75$). The methyl derivatives were fully optimized at the MP2/6-31G* level, which was also used to calculate the NBO atomic charges. The transition states **TS5** and **TS8** are characterized by one imaginary wavenumber whereas all the vibrational wavenumbers of the structures of minimal energy were real. The intrinsic reaction coordinates[28] were calculated at the MP2/6-311G** level in the case of **TS5** and at the MP2/6-31G* level in the case of **TS8**.

Results and Discussion

Homolytic dissociation reactions: As is well-known, the dissociation energy of S–S bonds dramatically depends on the length of the sulfur chain and is highest for the disulfanes. This can clearly be seen from the energy and enthalpy data given in Table 1. All thermodynamic results apply to the most stable conformations of the related molecules. The lower stability of the tri- and the tetrasulfanes towards homolytic cleavage is caused by the three-electron two-center π bond which forms on dissociation into the HSS$^\cdot$ radical.[29] This additional π bond is not present in the sulfane molecules, as can be seen from the geometrical parameters compiled in Table 2. The S–S bond of HSS$^\cdot$ is much shorter (198.8 pm) than the corresponding bonds in the sulfane molecules (207.8–208.3 pm).

Table 1. Reaction energies ΔE and Gibbs free energies ΔG° at 0 K and 298 K of the homolytic dissociation reactions of H_2S_n molecules ($n = 2-4$) and of the formation of sulfuranes (values in kJ mol^{-1}; TS = transition state)

Reaction	ΔE_o	ΔE°_{298}	ΔG°_{298}
$H_2S_2 \rightarrow 2HS^\cdot$	259.5	246.5	211.5
$H_2S_3 \rightarrow HS^\cdot + HSS^\cdot$	211.8	200.9	157.3
$H_2S_4 \rightarrow 2HSS^\cdot$	168.5	159.4	112.4
$H_2S + H_2S_2 \rightarrow H_2S(SH)_2$	163.4	171.8	207.3
$H_2S + H_2S_2 \rightarrow$ **TS5**	195.4	197.9	234.7
$H_2S + H_2S_4\ (C_1) \rightarrow H_2S(SSH)_2$	159.3	169.0	205.9
$H_2S_3\ (C_2) + H_2S_2 \rightarrow S(SH)_4$	155.3	159.4	200.0

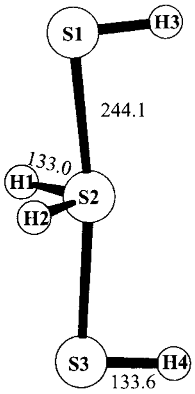
The calculated geometrical data agree well with the experimental parameters.[30] However, no experimental values are known for the HSS$^\cdot$ radical and for the tetrasulfane, which probably exists as a mixture of three conformers in the gas-phase since high-level MO calculations have shown that the relative energies of the three possible conformations are quite close to each other with the C_1 isomer of motif ++− as the most stable form.[31] The motif is defined as the order of signs of the torsional angles along the chain.[29]

Table 2. Geometrical parameters of the chainlike sulfanes H_2S_n ($n = 1-4$) and of their dissociation products. Internuclear distances in pm, bond angles and torsion angles in ° (MP2/6-311++G** data). Experimental data from reference [30] in parentheses.

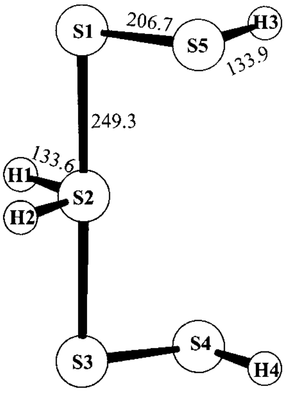
	HS$^\cdot$	HSS$^\cdot$	H_2S	H_2S_2	$H_2S_3(C_2)$	$H_2S_3(C_s)$	$H_2S_4(C_1)$
H–S	133.8	134.2	133.3 (133.6)	133.4 (134.2)	133.8 (134.4)	133.8 (134.4)	133.8
S–S	–	198.8	–	208.3 (205.6)	207.8 (205.4)	207.8 (205.3)	207.5 207.6 207.8
H-S-H	–	–	92.1 (92.1)	–	–	–	–
S-S-H	–	101.1	–	98.1 (97.8)	97.9 (97.2)	98.0 (97.4)	97.3 98.0
S-S-S	–	–	–	–	107.3 (107.0)	107.3 (106.9)	106.7 106.5
S-S-S-H	–	–	–	–	85.4 (87.7)	±88.6 (90.8)	88.3 − 83.4
S-S-S-S	–	–	–	–	–	–	− 78.4
H-S-S-H	–	–	–	90.8 (90.3)	–	–	–

The experimental dissociation energies of the S–S bonds of H_2S_2 (280 kJ mol^{-1}), H_2S_3 (201 kJ mol^{-1}), and of the central bond of H_2S_4 (140 kJ mol^{-1})[9a] are in good agreement with our reaction energies calculated at 298 K (Table 1). Perfect agreement between the theoretical and experimental values has been obtained in the case of H_2S_2 for which the G2(MP2) method was employed;[32] however, this method is not economically suitable for the larger molecules studied in this work. Owing to the increase in entropy, the Gibbs energies ΔG°_{298} of these dissociation reactions are considerably lower than the reaction energies. It will be seen below whether the sulfurane formation requires a lower energy or not.

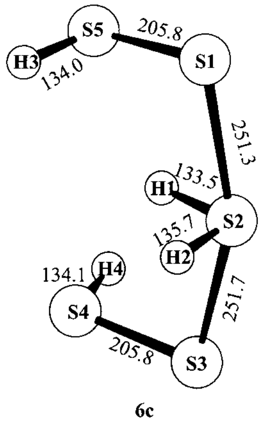
Formation of sulfuranes: To model the reaction given above in Equation (2), we have studied the formal insertion of H_2S into the S–S bonds of H_2S_2 and H_2S_4 and the insertion of H_2S_3 into the S–S bond of H_2S_2. The structures found for the first two reactions are depicted in Figure 1; additional geometrical



5b



6b



6c

Figure 1. Structures of the sulfuranes obtained by formal addition of H_2S to H_2S_2 (structure **5a**) and of H_2S to H_2S_4 (structures **6b** and **6c**). Structures **5a** and **6b** are of C_{2v} symmetry while **6c** is of C_1 symmetry. Internuclear distances in pm; for bond and torsion angles, see Table 3.

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Table 3. Bond angles [°] and torsion angles [°] of the sulfuranes $H_2S(SH)_2$, $H_2S(SSH)_2$, and $S(SH)_4$ as well as the transition state **TS5**.

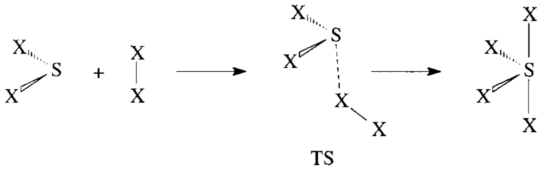
	$H_2S(SH)_2$ **5b**	**TS5**	$H_2(SSH)_2$ **6b**	$H_2(SSH)_2$ **6c**	$S(SH)_4$ **7a**
S1-S2-S3	171.8	165.1	178.9	156.4	178.2
S2-S3-S4	–	–	94.7	94.5	–
S2-S1-S5	–	–	94.7	95.6	–
H1-S1-H2	96.8	92.5	94.8	95.7	–
H1-S2-S1	87.3	89.1	90.1	87.9	–
H1-S2-S3	87.3	82.9	89.1	89.7	–
H3-S1-S2	89.9	89.8	–	–	88.6
H3-S-S	89.9	89.8	99.2	99.7	88.6
H4-S-S	89.9	89.8	99.2	100.4	87.9
S5-S1-S2-S3	–	–	144.0	0.4	–
S1-S2-S3-S4	–	–	144.0	− 8.1	–
H3-S-S-S	180.0	144.6	89.4	90.5	180.0
H4-S-S-S	180.0	133.8	89.4	90.6	180.0
H1-S2-S1-S5	–	–	168.6	84.9	–
H1-S2-S3-S4	–	–	96.7	− 92.2	–
H2-S2-S3-H4	− 131.5	93.6	–	–	–

parameters are given in Table 3. The product **5a** formally derived from H_2S and H_2S_2 by reaction given above in Equation (3) is almost identical in structure to the previously calculated geometry,[22] and it has now been found that this geometry of C_{2v} symmetry corresponds to a minimum on the energy hypersurface at the MP2/6-311++G** level (all vibrational eigenvalues positive). Loos et al. found that rotation of the SH groups around the S–S bonds increases the energy and two more minima of higher energy exist with one or both SH groups rotated around the S–S bond(s) by 180°.[33] As in the case of SF_4, but in contrast to the structure of SCl_4,[34] the axis of the trigonal bipyramid is bent towards the equatorial atoms (S-S-S angle = 171.8°).

The sulfurane **6** is the result of an addition of H_2S to H_2S_4 [Eq. (4)]; however, this geometry of symmetry C_2 is *not* a minimum, as previously assumed[22] since it has one negative vibrational eigenvalue. To indicate the higher level of theory in the present work, we now use the label **6b** rather than **6a**. If the symmetry restriction is lifted, structure **6b** changes to the asymmetrical geometry of **6c** which is 12 kJ mol^{-1} more stable and all the vibrational eigenvalues are positive. The geometry optimization from **6b** to **6c** took very many steps. Evidently, the energy hypersurface is rather flat with respect to variations of the S-S-S-S torsion angles of **6**. In contrast to the other sulfuranes investigated in this work, the SH groups of **6c** are all on one side of the molecule. It seems that this conformation is stabilized by an interaction between the positively charged hydrogen atoms of the equatorial S–H bonds and the four negatively charged sulfur atoms formally originating from the tetrasulfane. Remarkably, the atoms S5, S1, S2, and S3 are in one plane (torsion angle 0.4°) and S4 is almost in the same plane (torsion angle at the S2–S3 bond: − 8.1°). The axial S-S-S angle (156.4°) is rather small despite the crowding of four substituents on one side of the molecule. While the axial S–S bonds are very long (251 pm), the two S–S bonds originating from H_2S_4 show normal single bond lengths (206 pm).

The thermodynamic data of these insertion or addition reactions are listed in Table 1. As can be seen from this data, the formal insertion into an S–S bond requires a reaction energy of ≈160 kJ mol^{-1}, regardless of the type of sulfane which inserts or into which molecule it is inserted. These reactions have of course a negative reaction entropy and consequently the Gibbs energy is now higher than the reaction energy at the same temperature. On the basis of the ΔG°_{298} data, we conclude that the insertion into the disulfane molecule is as equally endergonic as the homolytic dissociation of H_2S_2 while the insertion into the central bond of a tetrasulfane molecule (and probably into a trisulfane also) is much less favorable than the dissociation of that bond! At slightly elevated temperatures the insertion into a disulfane becomes more and more unfavorable because of the entropy term while at the same time the dissociation becomes more favorable.

So far we have only discussed the thermodynamic equilibrium data. However, it was found that the formation of SF_4 from SF_2 and F_2 as well as the formation of SCl_4 from SCl_2 and Cl_2 requires an additional activation energy.[34] Therefore, we investigated the *reaction coordinates* as well as the structure and relative energy of the *transition state* of the reaction given above in Equation (3). Although the formal insertion of a compound of type SX_2 into a homonuclear single bond of another molecule, such as H_2, F_2, Cl_2, or H_2S_2 is allowed by the rules of orbital symmetry conservation, it is not the reaction path of lowest activation energy. This has first been shown for the insertion of H_2S into H_2 with formation of the simplest sulfurane, SH_4,[35] and later for the insertion of SF_2 into F_2 resulting in SF_4.[34] The lowest energy pathway of these reactions is the nucleophilic attack of SX_2 on the X_2 molecule with charge transfer from the sulfur atom into the antibonding σ-orbital of H_2 respectively F_2 (Scheme 4).

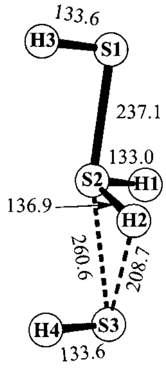


Scheme 4. The lowest energy pathway for the insertion of SX_2 into X_2.

The terminal atom X of the former X_2 molecule (X = H or F) then moves to the central sulfur atom and the final product is identical to that expected for a symmetrical insertion reaction.

To find out whether the addition of H_2S to H_2S_2 would proceed by a similar mechanism, we studied the corresponding transition state with no symmetry restriction and found the reaction mechanism to be similar to the addition of SF_2 to F_2[34] and of SCl_2 to Cl_2.[34] There is no insertion into the S–S bond; instead an addition takes place and the sulfur atom of H_2S does *not* become the hypercoordinate atom in sulfurane **5**. The geometry of the transition state (**TS5**) of Equation (3) is shown in Figure 2. The relative energy and enthalpy of **TS5** are given in Table 1.

On the basis of its geometry and its charge distribution, the nature of **TS5** can be interpreted as an ion pair consisting of the mercaptosulfonium cation $HSSH_2^+$ and a hydrogen sulfide



TS5

Figure 2. Structure of the transition state for the addition of H_2S to H_2S_2 to give the sulfurane $H_2S(SH)_2$. Internuclear distances in pm; for bond and torsion angles, see Table 3.

anion HS^- with a weak interaction between atoms S3 on the one hand and atoms S2 and H2 on the other hand. Evidently, because of its lone pair of electrons in the nonbonding $3p_\pi$ orbital, the nucleophile H_2S has attacked one of the S atoms of H_2S_2 followed by a shift of hydrogen atom H2 from S3 to S2 to result in a triangular arrangement of S3, S2, and H2. During this process the torsion angle of H_2S_2 is continuously enlarged from 90° in the free molecule to 157.7° in **TS5**. It also should be mentioned that atom H2 functions as a bridging atom during the early stages of this addition reaction. Remarkably, the S-S-S angle stays almost constant at 165° during the whole addition reaction until the level of **TS5** is reached. Interestingly, salts with the cation $H_3S_2^+$ and its organic derivatives have been prepared as pure materials (e.g. $[H_3S_2][AsF_6]$[36] and $[Me_3S_2][SbCl_6]$[37]). The atomic charges of **TS5** were calculated by a natural bond orbital (NBO) analysis and are given in Table 4. Atom S3 bears a negative charge of −0.58 and atoms S2 and H2 have positive charges of 0.32 respectively 0.23 units, which indicates that their interaction will be mainly ionic and only partly covalent in nature. The rather long S3···S2 distance of 260.6 pm supports this view, although the van der Waals distance of 350 pm[38] is still much larger. The S3···H2 distance amounts to 208.7 pm.

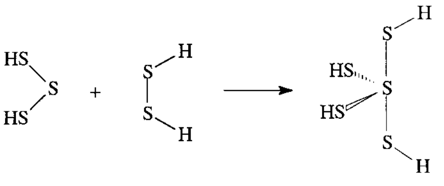
Table 4. NBO charges of the atoms in the sulfuranes **5b**, **6c**, and **7a** as well as of the transition state **TS5**.

	5b (C_{2v})	**TS5**	**6c** (C_1)	**7a** (C_1)
S1	−0.46	−0.29	−0.32	−0.35
S2	+0.43	+0.32	+0.36	+0.34
S3	−0.46	−0.58	−0.32	−0.49
S4	–	–	−0.10	+0.02
S5	–	–	−0.11	+0.02
H1	+0.14	+0.14	+0.14	+0.13
H2	+0.14	+0.23	+0.16	+0.13
H3	+0.09	+0.1	+0.1	+0.1
H4	+0.09	+0.09	+0.1	+0.11

All attempts failed to find any transition state for the decomposition of the sulfurane **5b** with the symmetry restricted to C_{2v}, which corresponds to a true elimination of H_2S from the central part of **5b**.

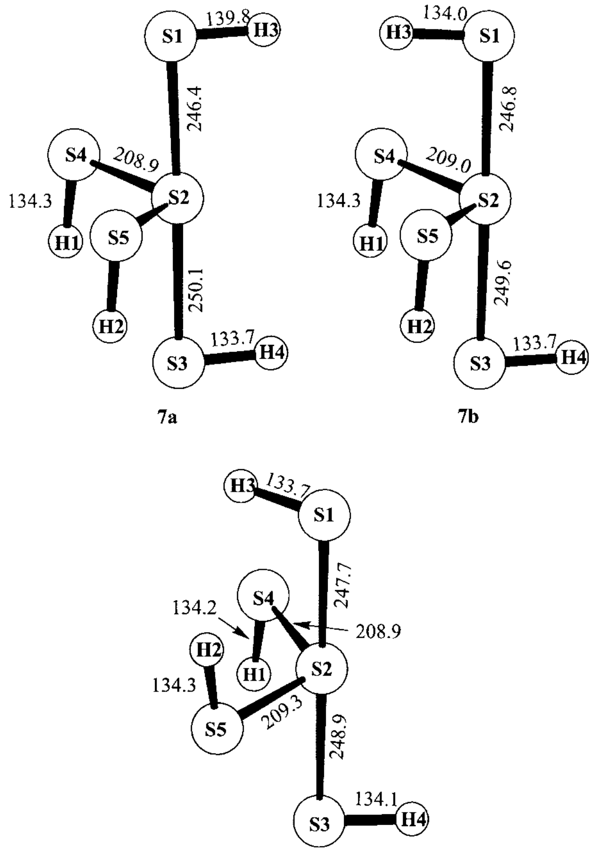
The formation of **TS5** from H_2S and H_2S_2 is highly endothermic, but less so than the homolytic dissociation of the S–S bond of H_2S_2 (Table 1). However, on the basis of the Gibbs energies at 298 K, the formation of **TS5** is less favorable than the dissociation reaction!

It could be argued that the reactions discussed so far are not suitable to model the reaction of two homocyclic sulfur rings since it is known that the thermodynamic stability of sulfurane molecules depends on the electronegativity of the substituents and that hydrogen is of lower electronegativity than sulfur. Therefore, we also studied a sulfurane in which the central atom is connected to four other sulfur atoms. Such a tetrathiosulfurane is formally obtained by the insertion of the central atom of H_2S_3 into the S–S bond of H_2S_2 or by a corresponding addition reaction [Eq. (5)].



7 (5)

We found that the hypothetical tetramercaptosulfurane **7** exists in three conformations (Figure 3) which are of symmetry C_s (**7a, b**) and C_1 (**7c**). Structure **7a** corresponds to the minimum of lowest energy. Because of the *cis* conformation of the HSSSH unit, the two axial S–S bonds of **7a** differ somewhat in length (246.4 and 250.1 pm). The NBO atomic charges are +0.34 for S2, −0.35 for S1, and −0.49 for S3 (Table 4). The formation of **7a** from the most stable conformations of H_2S_3 and H_2S_2 requires a reaction energy of only



7a **7b**

7c

Figure 3. Structures of three conformations of the tetrathiosulfurane $S(SH)_4$. The geometries **7a** and **7b** are of C_s symmetry while **7c** is of C_1 symmetry. Internuclear distances in pm; for bond and torsion angles of the most stable conformer **7a**, see Table 3.

155.3 kJ mol^{-1} at 0 K compared to the 211.8 kJ mol^{-1} needed for the homolytic dissociation of H_2S_3. However, the Gibbs energy change for the formation of **7a** according to Equation (5) is 200.0 kJ mol^{-1} at 298 K, while the dissociation of H_2S_3 requires only 157.3 kJ mol^{-1} (Table 1).

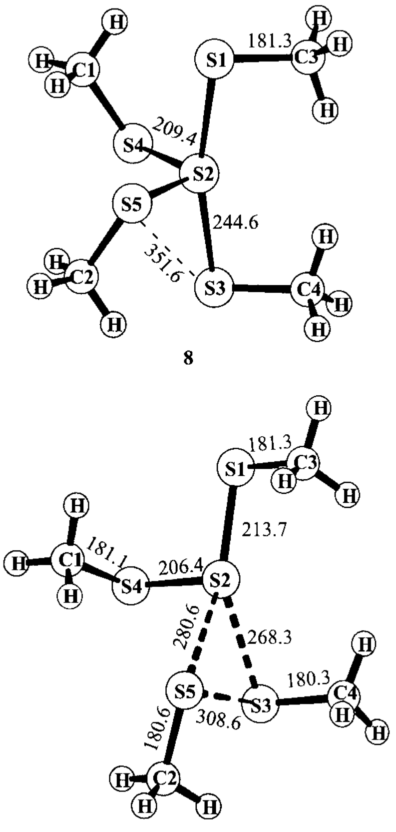
We therefore have to conclude that the insertion into S–S bonds is not a reasonable reaction mechanism to explain the interconversion reactions of polysulfur compounds at moderate temperatures and that the popular and seemingly convincing sulfurane mechanism has to be discarded.

Formation of the methyl-substituted sulfurane $S(SMe)_4$: It was shown above that the interaction between H_2S and H_2S_2 to form the sulfurane $H_2S(SH)_2$ is characterized by a bridging hydrogen atom in the transition state. Evidently, this is not a good model reaction for the interaction between two S_7 molecules, for instance. We therefore studied the formation of the sulfurane $S(SMe)_4$ (**8**) from the sulfanes Me_2S_2 and Me_2S_3 hoping that the methyl groups would not interfere with the formation of the new S–S bonds at the four-coordinate sulfur atom [Eq. (6)].

$$\text{Me-S-S-S-Me} + \text{Me-S-S-Me} \longrightarrow S(SMe)_4 \qquad (6)$$

The geometries of the two starting sulfanes, of the sulfurane **8**, and of the transition state **TS8** were optimized at the MP2/6-31G* level, which was the best we could afford for these electron-rich systems (21 atoms in **8**). C_2 symmetry was assumed for the two sulfanes while the sulfurane **8** was optimized in C_1 symmetry. However, after convergence it also had assumed a structure of C_2 symmetry. The structural data are presented in Figure 4 and Table 5.

The absolute energies of these species are given in Table 6. We did not calculate vibrational frequencies at this level; therefore, the energies have not been corrected for ZPE contributions (wavenumbers were obtained at the HF/3-21G* level). The formation of sulfurane **8** from Me_2S_2 and Me_2S_3 is endothermic by 199.0 kJ mol^{-1}, slightly more so than the formation of the unsubstituted sulfurane $S(SH)_4$ (**7**) from H_2S_3 and H_2S_2 (155.3 kJ mol^{-1}; note the different levels of theory!). The conformation of **8** is in agreement with that of sulfurane **7b** and therefore slightly different from that of the more stable conformer **7a**, insofar as the two equatorial MeS groups of **8** are antiparallel to each other while the two corresponding equatorial HS groups of **7a** are almost parallel (symmetry C_s). Mutual steric hindrance of the two methyl groups may be the reason for this conformational difference. Otherwise, the structure of **8** is quite similar to that of **7a**. In particular, the axial S–S bonds are of similar length (244.6 pm in **8** versus 246.4 and 250.1 pm in **7a**). The axial S-S-S angle is slightly smaller in **8** (166.3°) compared to 178.2° in **7a**, which again can be explained by the steric impact of the methyl groups. The NBO atomic charges, however, are quite different in **7a** and **8** since the methyl groups withdraw more electrons from the S_5 skeleton than the hydrogen atoms in **7a**. The central sulfur atom of **8** bears a charge of +0.33, the two equatorial S atoms of +0.19 each and the two axial S atoms of −0.20 units each. The four carbon atoms are highly negatively charged (−0.80 ± 0.02).



8

TS8

Figure 4. Structures of the tetrathiosulfurane $S(SMe)_4$ (**8**) (C_2 symmetry) and of the transition state for its formation from Me_2S_2 and Me_2S_3. Internuclear distances in pm; for bond and torsion angles, see Table 5.

Table 5. Bond angles [°] and torsion angles [°] of the sulfurane $S(SMe)_4$ (**8**) as well as of the transition state **TS8.**

	$S(SMe)_4$ (**8**)	**TS8**
S1-S2-S3	166.3	144.0
S1-S2-S4	101.2	97.7
S1-S2-S5	87.0	145.2
S4-S2-S5	106.4	94.2
S3-S2-S4	87.0	89.2
S3-S2-S5	101.2	68.4
S2-S5-S3	43.0	53.9
C3-S1-S2	90.8	95.2
C4-S3-S2	90.8	92.0
C1-S4-S2	103.6	100.0
C2-S5-S2	103.6	125.2
C3-S1-S2-S3	13.3	−92.2
C4-S3-S2-S1	13.3	71.4
C3-S1-S2-S4	−112.9	168.4
C3-S1-S2-S5	140.9	59.4
C4-S3-S2-S4	140.9	173.5
C4-S3-S2-S5	−112.9	−91.6
C1-S4-S2-S1	−30.1	−81.0
C1-S4-S2-S3	160.9	134.5
C2-S5-S2-S1	160.9	166.6
C2-S5-S2-S3	−30.1	−30.9
C1-S4-S2-S5	60.1	66.3

The structure of the transition state for the addition of Me_2S_3 to Me_2S_2 (**TS8**) is also shown in Figure 4; details are given in Table 5. This structure is characterized by a triangle of sulfur atoms (S2-S3-S5) formed from the central atom of

Table 6. Absolute energies [Hartree] and dipole moments [Debye] of Me_2S_2, Me_2S_3, $S(SMe)_4$ (**8**) as well as of **TS8** at the MP2/6-31G*//MP2/6-31G* level of theory.

Species	Absolute energy	Dipole moment
MeSSMe	– 847.75321	2.4
MeSSSMe	– 1272.38755	1.5
$S(SMe)_4$	– 2147.06496	1.8
TS8	– 2147.03123	1.7

the trisulfane and the S atoms of the almost dissociated disulfane. The S–S bond lengths within the former trisulfane molecule are S2–S4 = 206.4 and S1–S2 = 213.7 pm while the S–S bonds within the triangle are much longer, namely S2–S3 = 268.3, S2–S5 = 280.6, and S3–S5 = 308.6 pm. These bond lengths are well below the van der Waals interatomic distance between neutral sulfur atoms, as in sulfur allotropes (350 pm).[38] Surprisingly, the NBO atomic charges of the three sulfur atoms forming the triangle are almost negligible (0.00 – 0.08 units). Only S4 bears a slightly larger charge (0.16). Although the four carbon atoms are all negatively charged (– 0.80 to – 0.81) the two MeS groups originating from the disulfane are practically uncharged (– 0.01 and – 0.09). As can be seen from Figure 4, the methyl groups do not take part directly in the formation of **TS8** from the starting molecules, in contrast to the hydrogen atoms in **TS5**. Therefore, the reaction given in Equation (6) seems to be better suited to model the possible interaction between two sulfur homocycles as discussed in the Introduction.

However, the energy of **TS8** is 88.6 kJ mol^{-1} higher than that of the sulfurane **8** and 287.6 kJ mol^{-1} higher than the combined energies of the starting molecules Me_2S_2 and Me_2S_3. In other words, the activation energy for Equation (6) amounts to 287.6 kJ mol^{-1} (not corrected for ZPE). Since the homolytic dissociation energy of the S–S bonds in Me_2S_3 is only 226 kJ mol^{-1}[9a] and is even lower for the central bond in Me_2S_4 (142 kJ mol^{-1})[9a] as well as for the bonds in *cyclo*-S_8 and other homocycles,[29] it is evident that *a sulfurane of type **8** cannot be regarded as a thermodynamically favorable model intermediate for the interconversion of sulfur homocycles.*

These conclusions apply to the gas phase. However, from the dipole moments of the reactants in Equation (6), it can be seen that the components have more or less the same polarity (Table 6). Therefore, we do not expect that unpolar or slightly polar solvents change the thermodynamics of this reaction to such an extent that it becomes a likely pathway for the interconversion reactions discussed.

Alternative reaction mechanism: It was shown above that the formation of radicals, thiosulfoxides, and tetrathiosulfuranes requires too much Gibbs energy to explain the interconversion reactions of polysulfur and polyselenium compounds at moderate temperatures and in the absence of polar compounds. Therefore, we have to think of a totally different reaction path. Unfortunately, the exact reaction orders of most interconversion reactions are unknown owing to the reversibility of all steps and owing to parallel or consecutive reactions which make kinetic analyses difficult, if not impossible.

Preparative chemists with some experience in sulfur and/or selenium chemistry know that the synthesis and characterization of polysulfur and polyselenium compounds requires special precautions regarding the exclusion of nucleophiles and other catalysts, such as rough surfaces of glassware (e.g. joints) and silica. Franz Fehér—one of the pioneers of inorganic sulfur chemistry—recommended rinsing the glassware with hot chromic acid, followed by hot pure hydrochloric acid, and finally by distilled water to remove traces of alkaline substances from the surface. Furthermore, he recommended that no traces of ammonia gas should be present in the atmosphere of rooms in which such compounds are to be handled.[39] According to our experience, even traces of water have to be avoided in the reaction mixtures. The best idea would probably be the use of polyolefin or Teflon containers to prepare and to store sensitive compounds such as S_7 since we observed that silica gel and alumina as used for chromatography catalyze the conversion of unstable sulfur rings into S_8 in solution at room temperature.[2c]

During almost 40 years of preparative work with sulfur- and selenium-rich compounds, one of us (R.S.) has observed many times that the thermal stability of these metastable substances very much depends on the skills of the particular experimentalist which in practice means on the purity of the synthesized material. Extreme purification of solvents, for example, substantially increases the lifetime of sensitive compounds such as S_6[40] and of the above mentioned 1,2-Se_2S_5 in solution. The same stabilizing effect is observed if traces of trifluoroacetic acid are added to the compound or to its solution.[15]

Reversed-phase HPLC is one of the most successful analytical techniques for mixtures of polysulfur and polyselenium compounds. Mixtures containing, for example, S_7 or similar species require a polar eluent and normally methanol is used for this purpose. This solvent has to be distilled from an acidic drying agent, such as anhydrous magnesium sulfate, to remove not only water but also the traces of amines, like $MeNH_2$, Me_2NH and Me_3N, which are usually present in even "very pure" commercially available methanol as a result of the synthesis of CH_3OH from CO (always contains some N_2) and H_2. The acidic agent $MgSO_4 \cdot H_2O$ binds the amines quantitatively. Only if these precautions are taken can S_7 be determined quantitatively by HPLC. On the basis of all this experience we believe that most of the interconversion reactions observed at ambient temperatures are triggered by traces of nucleophiles or by polar molecules, such as H_2O, which favor the formation of nucleophiles, for example that given in Equation (7).

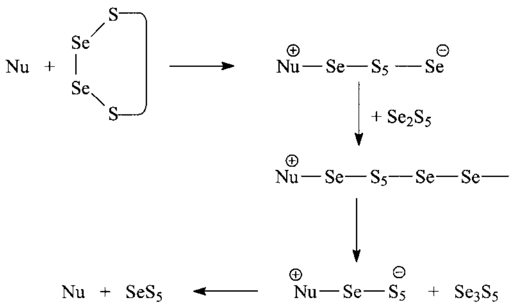
$$2\,H_2O + \text{-S-S-S-} \longrightarrow 2\,H_2S + SO_2 \quad (7)$$

The HS^- ion, which originates from H_2S by reaction with water, with amines or with the alkaline surface of silicate glass is one of the strongest nucleophiles, and reaction of sulfur dioxide with water forms the strong nucleophile HSO_3^-![6]

Bachrach and Mulhearn[41] have studied the nucleophilic attack of gaseous HS^- and MeS^- ions on di- and trisulfanes, such as HSSH, MeSSMe, HSSSH and MeSSSMe, by ab initio MO calculations. These reactions proceed by an addition–

elimination mechanism via transition states and intermediates, the structures of which are similar to the structure of our transition state **TS5** with an almost linear arrangement of three sulfur atoms. The intermediates in these reactions, therefore, show the characteristic properties of sulfuranes with rather long axial bonds and considerable charges on the different sulfur atoms. At the MP2/6-31 + G* level, *the overall activation enthalpy is zero* since the primary formation of the ion–dipole adduct liberates more energy than is required for the subsequent rearrangement reactions.

In a number of previous publications we have pointed out that the interconversion of sulfur and selenium rings and chains can also be understood on the basis of a nucleophilic attack of an impurity which opens the particular ring or chain molecule with formation of a zwitterion or of two separate ions. These in turn will attack a neighboring ring or chain and trigger a sequence of nucleophilic displacement reactions which finally lead exactly to the observed products.[42] In the case of 1,2-Se_2S_5 a nucleophile (Nu) would open the Se–Se bond and the resulting zwitterion would attack the Se–Se bond of another molecule to result in a chain of 14 chalcogen atoms. From this chain the observed product 1,2,3-Se_3S_5 may be split off by a head-to-tail cyclization reaction, and the $NuSeS_5$ residue may then cyclize to give *cyclo*-SeS_5, the other observed product, and the free nucleophile that will start another reaction sequence. In other words, the sulfurane mechanism is not necessary to explain the observed product distribution (Scheme 5).



Scheme 5. Possible mechanism for the reaction of nucleophile (Nu) with 1,2-Se_2S_5.

The experimental activation energies of such reactions are usually in the range of 40–70 kJ mol^{-1}[43], thus much smaller than the homolytic ring-opening energies. For example, the reaction of diphenyl-*o*-tolylphosphane (R_3P) with the homocycles S_6, S_7, S_8, and S_{12} in CS_2 to give R_3PS requires activation enthalpies of 51, 40, 69, and 46 kJ mol^{-1}, respectively.[43a] Similar values have been measured for the reactions of triphenylphosphane with a number of bis-aryltrisulfanes in toluene,[43b] and for the reactions of cyanide and sulfite ions with thiosulfate, trithionate, tetrathionate, and S_8 in water.[7a]

The conclusion from the present work is that neutral sulfur or sulfane molecules will be attacked if traces of polar molecules or polar groups on the surface of solids are present. The nucleophilic displacement reaction which then takes place triggers a sequence of consecutive reactions. At temperatures above 100 °C, however, the homolytic dissociation will become increasingly important since it is strongly favored by the increase in entropy, although it should be kept in mind that free radicals have been detected in liquid sulfur only at temperatures above 170 °C.[44]

Conclusion

We have shown that the addition reactions of divalent sulfur compounds R-S_n-R to a compound containing at least one S–S bond with the formation of a sulfurane are highly endothermic and endergonic, more so than the competing homolytic dissociation reactions, which, therefore, will take place first at a given temperature. However, the homolytic dissociation enthalpy is too high to explain those interconversion reactions of sulfur rings and chains which take place at moderate temperatures. These reactions are most probably triggered by either nucleophilic impurities or by the polar groups which are usually present on the walls of the vessels used (e.g. glassware) and which act as catalysts.

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