Sulfur Compounds, Part 207[+]

The Formation of the Sulfur Halides SX_4 from SX_2 and X_2: Reaction Enthalpies, Transition States, and Activation Energies for X = F and Cl

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Dedicated to Joan and Robert R. Holmes

Abstract: High-level ab initio MO calculations by different methods demonstrate that the reaction of SF_2 with F_2 to form SF_4 is strongly exothermic and exergonic [CCSD(T)/6-311+G(2df)//MP2/6-311+G*: $\Delta H^{\circ}_{298} = -445\,\text{kJ}\,\text{mol}^{-1}$, $\Delta G^{\circ}_{298} = -398\,\text{kJ}\,\text{mol}^{-1}$] and proceeds via a very weakly bonded intermediate **2** with C_s symmetry. The structure of **2** corresponds to a donor–acceptor complex $F_2S \rightarrow F_2$ with a considerable transfer of charge ($0.69\,e$). The transition state (**TS1**) between **2** and SF_4 has a similar structure to **2** but with C_1 symmetry. The energy of the adduct and of **TS1** is almost the same as the combined energy of the separate molecules SF_2 and F_2. Therefore, the overall activation energy for the reaction of SF_2 with F_2 to form SF_4 is practically negligible ($6\,\text{kJ}\,\text{mol}^{-1}$ at 298 K). The analogous reaction of SCl_2 with Cl_2 to form the hypothetical molecule SCl_4 is endothermic and endergonic ($\Delta H^{\circ}_{298} = +32\,\text{kJ}\,\text{mol}^{-1}$, $\Delta G^{\circ}_{298} = +74\,\text{kJ}\,\text{mol}^{-1}$). The ground-state geometry of SCl_4 has C_{2v} symmetry at the MP2/6-311+G* level and the coordination geometry at sulfur is pseudo-trigonal-bipyramidal. The transition state (**TS2**) of this reaction is ionic ($[SCl_3^+]Cl^-$) and has C_1 symmetry. The activation energy at 0 K for the chlorination of SCl_2 amounts to $203\,\text{kJ}\,\text{mol}^{-1}$ at the CCSD(T)/6-311+G(2df) level; it is $43\,\text{kJ}\,\text{mol}^{-1}$ lower than the experimental bond dissociation energy of Cl_2. The proposed formation of the analogous tetrathiasulfuranes $S(SR)_4$ from $(RS)_2S$ and RSSR is discussed in connection with the various interconversion reactions of polysulfur compounds.

Keywords: ab initio calculations · reaction mechanisms · sulfuranes · sulfur halides · transition states

Introduction

The sulfur fluorides SF_4 and SF_6 are produced industrially by high- (SF_6) or low-temperature (SF_4) reaction of elemental sulfur with fluorine.[1] For many years their so-called hypervalent or hypercoordinate molecules have also been of interest to theoretical chemists: there seem to be more than eight valence electrons at the central S atoms and therefore a violation of the octet rule has been suspected. However, it is now generally accepted that the covalent bonds in these species can be understood on the basis of multi-center interactions of the 3s and 3p atomic orbitals of sulfur with the 2p orbitals of the F atoms while the high-energy 3d valence orbitals of sulfur play a minor role and, to a first approximation, can be neglected. However, d and even f functions serve as polarization functions in the basis sets used.[2] To obtain the correct thermodynamic data such polarization functions are necessary not only for the S atom but also for the F atoms in compounds of the SF_n type, and the bonding in SF_2 does not differ significantly from that in SF_4 or SF_6.[3] Of the 36 valence electrons in the mentioned atomic orbitals of SF_6, only eight occupy bonding orbitals while the remaining 24 reside in more or less nonbonding molecular orbitals which are located on the F atoms.[4] With SF_4 the situation is analogous.

The structures and chemical properties of SF_4 and SF_6 are well known but their formation from sulfur and fluorine has

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never been studied mechanistically. Elemental sulfur and fluorine react violently to give a gaseous mixture of SF_6, S_2F_{10}, and SF_4, with the unstable SF_2 as a likely intermediate.[5] Therefore the formation of SF_4 and SF_6 may be explained by a stepwise addition of F_2 to the primary product, SF_2, but the formation of S_2F_{10} shows that under certain conditions $SF_5^{\bullet}$ radicals are likely intermediates too.

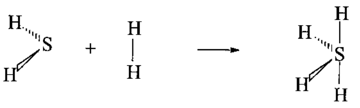
Sulfur also reacts exothermically with elemental chlorine but much more slowly and less violently than with fluorine. The final product of highest chlorine content at 25 °C is SCl_2, which is also produced industrially.[6] Only at temperatures below −30 °C can SCl_4 be prepared (from SCl_2 and Cl_2). This colorless solid is composed of SCl_3^+ cations and bridging Cl^- anions;[7] when warmed to 25 °C it decomposes to SCl_2 and Cl_2. Consequently, SCl_4 has never been observed in the vapor phase, nor has the hypothetical SCl_6.

We have studied theoretically the reaction of SF_2 with F_2 to form SF_4 and the analogous reaction of SCl_2 with Cl_2 to give SCl_4 in order to determine for the first time the reaction mechanisms, as well as the activation energies and the structures of the related transition states. Other aims of this work were to find out why SCl_4 is so much less stable than SF_4 and whether related sulfuranes such as $S(SR)_4$ have a chance of existing or of playing a role as intermediates as has been proposed.[8]

The simplest model reaction for the formation of a SX_4-type sulfurane is the hypothetical hydrogenation of H_2S to SH_4 [Eq. (1)]. This reaction was first studied theoretically by

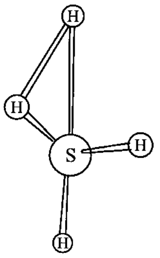
$$H_2S + H_2 \longrightarrow H_4S \qquad (1)$$

Schaefer and co-workers,[9] who assumed a symmetrical addition of the dihydrogen molecule to the S atom of H_2S under C_{2v} symmetry, that is, with concerted formation of the two new S–H bonds. Such a reaction is allowed by the rules of orbital symmetry conservation[Eq. (2)].



(2)

At the configuration interaction level of theory using a triple-zeta plus polarization basis set (CI/TZ+P) a reaction enthalpy of 312 kJ mol^{-1} was calculated for reaction (2). An activation energy of approximately 178 kJ mol^{-1} was obtained for the back reaction, which means that the forward reaction requires an activation energy of 490 kJ mol^{-1}. This result seemed to indicate that H_4S, once it had been formed in a suitable reaction, might be stable with respect to a unimolecular decomposition at low temperatures. The structure of H_4S was found to have C_{4v} symmetry although most sulfuranes of the SX_4 type are of lower symmetry (C_{2v}; pseudo-trigonal-bipyramidal). Ewig and Van Wazer[10] confirmed that H_4S has C_{4v} symmetry and reported a reaction enthalpy of 331 kJ mol^{-1} at 0 K at the MP4/6-311G(2d,2p) level of theory. Moc et al.[11] calculated the activation energy of the forward reaction (1) to be 541 kJ mol^{-1} at the MP4/6-31++G(d,p)//MP2/6-31++G(d,p)+ZPE level of theory. This energy is much higher than the bond energy (D_e) of H_2 at 0 K (457 kJ mol^{-1}). However, the same authors showed that there is an alternative reaction channel of much lower activation energy characterized by stepwise, rather than simultaneous, formation of the two new S–H bonds. The corresponding transition state **1** has C_1 symmetry.



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The activation energy for this asymmetric addition of H_2 to H_2S (425 kJ mol^{-1}) is only slightly smaller than the bond energy of H_2. The overall reaction energy $\Delta E(1)$ was calculated to be 359 kJ mol^{-1} at 0 K and the unusual C_{4v} symmetry of H_4S was once more confirmed. A particularly interesting feature of the asymmetric transition state is the strong polarization of the H_2 unit originating from the incoming H_2 molecule: the outermost atom is strongly negative while the other H atom is slightly positively charged. Therefore this structure can be described approximately as an ion-pair $[H_3S^+]H^-$.

The structures and the thermochemistry of the various sulfur fluorides SF_n have been investigated many times. From experimental gas-phase data[12] the thermodynamic functions for the formation of SF_4 from SF_2 according to Equation (3) can be calculated to be $\Delta H^{\circ}_{298} = -466.5$ kJ mol^{-1} and $\Delta G^{\circ}_{298} = -418.7$ kJ mol^{-1}.

$$SF_2 + F_2 \longrightarrow SF_4 \qquad (3)$$

The reaction enthalpy has been reproduced accurately by high-level ab initio MO calculations according to the G2, G2(MP2), and CCSD(T) methods.[13] However, none of those who have yet investigated the reaction mechanism included the activation energy of reaction (3). Gaseous SF_4 has C_{2v} (pseudo-trigonal-bipyramidal) symmetry with the two axial S–F bonds (164.6 pm) considerably longer than the equatorial bonds (154.5 pm).[14] At 298 K rapid pseudo-rotation (intramolecular ligand exchange) occurs. The more symmetrical structures of C_{4v} and D_{4d} symmetry are transition states (first-order saddle points) for the pseudo-rotation and enantiomerization, respectively, of SF_4.[15]

The chlorination of gaseous SCl_2 to form the hypothetical molecule SCl_4 [Eq. (4)] has been investigated theoretically using aproximate density functional theory.[16] The reaction was found to be exothermic and the symmetry of the ground-state geometry of SCl_4 was claimed to be T_d. It will be shown below that these results are in error.

$$SCl_2 + Cl_2 \longrightarrow SCl_4 \qquad (4)$$

Computational Methods

All calculations were performed with the GAUSSIAN 94 program package,[17] installed on CRAY and SGI Origin2000 computers. The molecular structures of all 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 pertubation theory.[18] This level was also used to calculate the natural atomic charges,[19] Mulliken atomic charges, and dipole moments, as well as the vibrational wavenumbers, zero-point and thermal energies, entropies, and heat capacities which are given in Tables 2 and 4 below. Improved relative energies were obtained by single-point calculations at the CCSD(T)/6-311+G(2df) level for all structures.[20] The transition states obtained were characterized by one imaginary wavenumber whereas all the vibrational wavenumbers of the structures of minimal energy were real. The intrinsic reaction coordinates were calculated at the HF/3-21+G* level.[21]

To obtain additional data for the reaction energies ΔU°_{298}, enthalpies ΔH°_{298}, and free enthalpies ΔG°_{298} for reactions (3) and (4), G2(MP2)[22] and CBS-4[23] calculations were carried out for the stable structures since these methods had been shown previously to provide accurate thermodynamic data for certain sulfur-containing molecules. The geometries are optimized in these procedures at the MP2/6-31G* (G2/MP2) and HF/3-21G* (CBS-4) levels of theory, respectively.

For the adduct **2** ($SF_2 \rightarrow F_2$) and the related transition state **TS1** a basis set superposition error (BSSE) correction was carried out according to the counterpoise procedure.[24]

Results

For the first time we have investigated the energy profile for the reactions of the bent molecules SX_2 (X = F or Cl) with the corresponding dihalogen molecules X_2 to give SX_4.

Sulfur fluorides: The calculated geometry of SF_2 (C_{2v} symmetry; S–F 162.8 pm, F-S-F 98.6°) is in reasonable agreement with the experimental equilibrium data (S–F 158.7 pm, F-S-F 98.0°),[25] even though the computed S–F distances are overestimates of the experimental ones by 4.1 pm (2.6%). Reasonable agreement is again observed between the geometric parameters of SF_4 and the experimental values (Table 1).[14]

Table 1. Molecular geometry of SF_4 (distances in pm, angles in °). Calculated values at the MP2/6−311+G* level of theory; experimental data from ref. [14].

	SF_{ax}	SF_{eq}	$F_{ax}SF_{ax}$	$F_{eq}SF_{eq}$	$F_{ax}SF_{eq}$
calc.	169.0	157.9	172.4	101.9	87.6
exp.	164.6	154.5	173.1	101.6	

The calculated energies and entropies of all the related species are presented in Table 2. The reaction enthalpies ΔH°_{298} and the free reaction enthalpies ΔG°_{298} of reaction (3) obtained from the data in Table 2 by the three methods applied in this work are listed in Table 3.

The CBS-4 and G2(MP2) results are more negative by −12 kJ mol^{-1} than the experimental values in Table 3, and the CCSD(T) data deviate by +22 kJ mol^{-1} from the experimental results.

Table 3. Reaction enthalpies ΔH°_{298} and free reaction enthalpies ΔG°_{298} of reaction (3) obtained from the data in Table 2.

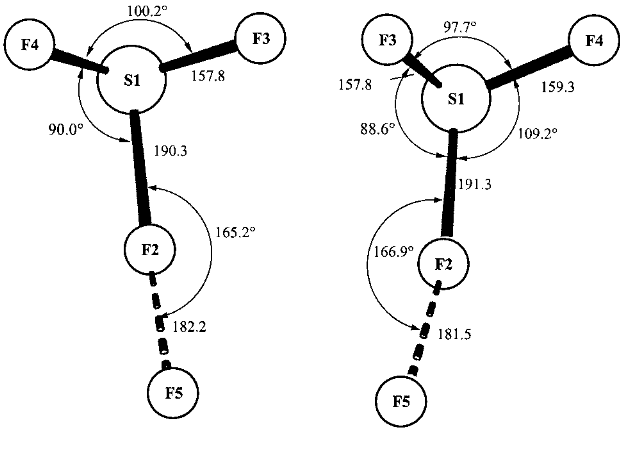
	ΔH°_{298} [kJ mol^{-1}]	ΔG°_{298} [kJ mol^{-1}]
CBS-4:	−476	−428
G2(MP2):	−474	−427
CCSD(T)/6-311+G(2df)	−445	−398
experimental[a]	−466.5	−418.7

[a] Ref. 12.

The search for the transition state of reaction (2) was difficult because the potential energy hypersurface is clearly rather flat at the beginning of the reaction between SF_2 and F_2, before the energy drops sharply upon formation of SF_4. This situation is not unusual for a strongly exothermic reaction. It was found that SF_2 and F_2 first react to form a very weakly bonded adduct **2** [Eq. (5)], which is then transformed via the transition state **TS1** into the ground state of SF_4.

$$SF_2 + F_2 \longrightarrow F_2S \rightarrow F_2\ (\mathbf{2}) \qquad (5)$$

The structures of **2** and **TS1** are shown in Figure 1. The adduct was found to be by only −14 kJ mol^{-1} more stable than the separate molecules, $SF_2 + F_2$, at 298 K. Due to the negative reaction entropy, of this adduct formation, the Gibbs free energy ΔG°_{298} of reaction (5) is +22 kJ mol^{-1}. The energy of the transition state **TS1** is just 7 kJ mol^{-1} above that of **2** at 298 K. However, when the BSSE corrections were



2 **TS1**

Figure 1. Structures of the adduct **2** (symmetry C_s) and of the transition state **TS1** for the reaction of SF_2 with F_2 (internuclear distances in pm).

Table 2. Absolute energies (hartree) of SF_2, F_2, SF_4, **2** and **TS1** calculated by various methods, and zero-point energies (ZPE), thermal energies (TE), entropies and heat capacities based on the vibrational wavenumbers calculated at the MP2/6−311+G* level.

	SF_2	F_2	SF_4	Adduct **2**	**TS1**
G2(MP2) (0 K)	−597.178702	−199.317798	−796.675056		
CBS-4 (0 K)	−597.219397	−199.353057	−796.751712		
CCSD(T)/6−311+G(2df)	−597.128795	−199.282009	−796.583145	−796.418680	−796.415026
ZPE [kJ mol^{-1}]	11.5	5.4	29.1	23.5	22.1
ZPE + TE at 298 K [kJ mol^{-1}]	20.5	11.7	41.9	39.5	36.4
S°_{298} [J mol^{-1} K^{-1}]	258.8	202.7	303.6	333.7	320.7
C_p [J mol^{-1} K^{-1}]	37.2	22.9	69.2	76.4	69.2

applied to the energies of **2** and **TS1** the energy of **2** was increased by 13 kJ mol^{-1}, resulting in an energy difference of only -1 kJ mol^{-1} from the starting materials $SF_2 + F_2$. The BSSE correction raised the energy of **TS1** by 12 kJ mol^{-1} resulting in an overall activation barrier (based on $SF_2 + F_2$) of only 6 kJ mol^{-1}. This final energy profile is depicted in Figure 2.

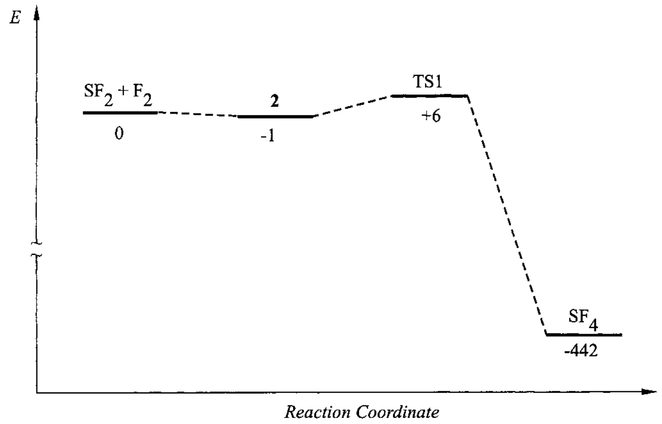


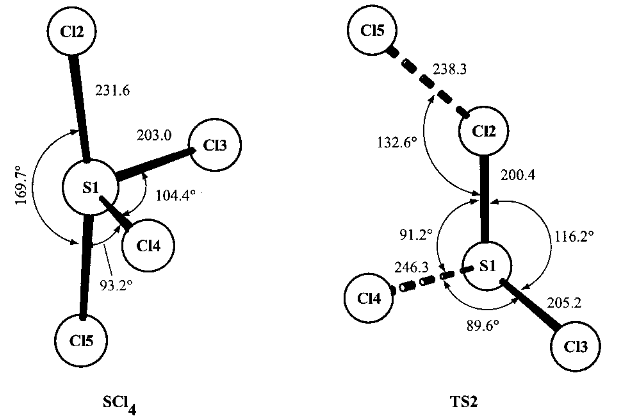
Figure 2. Energy diagram for the reaction of SF_2 with F_2 to form SF_4 via the adduct **2** and the transition state **TS1** (relative energies including the BSSE correction in kJ mol^{-1} at 298 K).

The structures and the natural atomic charges of the adduct **2** and of the transition state **TS1** are very similar, as are the dipole moments (**2**, 8.08 D; **TS1**, 8.03 D). However, whereas **2** has C_s symmetry the transition state is asymmetric (C_1). The SF_2 unit of **2** resulting from the former SF_2 molecule is characterized by slightly shorter S–F bonds (157.8 pm) than were calculated for free SF_2 (162.8 pm). The natural atomic charges of **2** (S1, +1.63; F2, -0.20; F3, F4, -0.47; F5, -0.49) indicate that approximately 0.7 electron is transferred from the donor SF_2 to the acceptor F_2.

Since the axis of the F_2 unit is almost perpendicular to the plane of the SF_2 unit, it seems reasonable to assume that electron density from the 3p lone pair on sulfur is transferred into the antibonding σ_u orbital (LUMO) of the F_2 molecule. Consequently, the F–F bond (182.2 pm) is much longer than that calculated for the free F_2 molecule (141.6 pm) at the same level of theory. The two torsion angles F-F-S-F are ±50.0°; that is, F5 is bent towards F3 and F4. Therefore the adduct may be considered as a donor–acceptor complex $F_2S \rightarrow F_2$.

As in the case of **2**, the natural atomic charge on the bridging F atom of the transition state **TS1** is the smallest in the molecule (-0.19), while the outermost F atom carries a charge of -0.48. The almost equivalent atoms F3 and F4 are negative by -0.47 units. Consequently, the S atom of **TS1** has a higher positive charge (+1.62) than the S atom of SF_2 (+1.04). In SF_4, however, the S atom is even more positively charged (+2.16). These data as well as the geometric parameters show that the structure of **TS1** can also be explained as resulting from a nucleophilic attack of the S atom of SF_2 (using its nonbonding 3p lone pair) on the F_2 molecule (using its antibonding σ_u MO). Consequently, the F–F distance of **TS1** (181.5 pm) is also greater than in the free F_2 molecule. The angle F-F-S is 166.9° and the axis F2–S is almost perpendicular to the plane of the former SF_2 molecule. The S–F distances of this former SF_2 unit (157.8 and 159.3 pm) are much shorter than the S–F distance to the bridging F atom (191.3 pm). The internuclear distance S$\cdots$F5 (370.3 pm) is still much greater than the van der Waals distance. To a first approximation the structure of **TS1** may also be described as a donor–acceptor complex, $F_2S \rightarrow F_2$. The intrinsic reaction coordinate has been calculated at the HF/3-21+G* level and it was observed that the formal outermost F atom of **TS1** (F5) moves all the way round the formal SF_3 unit, finally to occupy an axial position in the stable trigonal-bipyramidal molecule SF_4. During this process this moving F atom always forms a triangle of varying shape with the neighboring fluorine (F2) and the S atom. The other F atom originating from the F_2 molecule (F2) finally occupies an equatorial position in SF_4. The natural atomic charges on fluorine in SF_4 are -0.60 for the axial and -0.48 for the equatorial positions; the calculated dipole moment of SF_4 is 0.97 D.

Sulfur chlorides: The optimized structure of SCl_2 (symmetry C_{2v}; S–Cl, 204.5 pm; Cl-S-Cl, 102.8°) agrees well with the experimental gas-phase structure determined by microwave spectroscopy (S–Cl, 201.4 pm; Cl-S-Cl, 102.7°)[26] but the internuclear distances are overestimated similarly to those found for SF_2 and SF_4. The calculated structure of SCl_4 (Figure 3) is also of C_{2v} symmetry. This molecule is interesting in that the angles Cl_{ax}-S-Cl_{eq} (93.2°) exceed 90°, and consequently the angle Cl_{ax}-S-Cl_{ax} (169.7°) measured on the empty side of the molecule is *less* than 180°, whereas F_{ax}-S-F_{ax} is 197° in SF_4. The axial S–Cl bonds are 14 % longer than the equatorial ones. The atomic charges were calculated by Mulliken's method only. The positive charge on the S atom of SCl_4 (+0.95) is only slightly smaller than the Mulliken value for SF_4 (+1.04). The chlorine atoms have quite different charges: -0.14 in the equatorial and -0.33 in the axial positions. In contrast, the Mulliken charges in the SCl_2 molecule are surprisingly small (S, +0.04; Cl, -0.02).



SCl_4 **TS2**

Figure 3. Structures of SCl_4 (symmetry C_{2v}) and of the transition state **TS2** for the reaction of SCl_2 with Cl_2 (internuclear distances in pm).

The reaction of SCl_2 with Cl_2 to form SCl_4 was found to be endothermic at all the levels of theory that we investigated. The energies and entropies of all related species are given in Table 4. The calculated reaction enthalpies $\Delta H^\circ_{298}(4)$ and

Table 4. Absolute energies (hartree) of SCl_2, Cl_2, SCl_4 and TS2 calculated by various methods, and zero-point energies (ZPE), thermal energies (TE), entropies and heat capacities based on the vibrational wavenumbers calculated at the MP2/6–311 + G* level.

	SCl_2	Cl_2	SCl_4	**TS2**
G2(MP2) (0 K)	– 1317.184221	– 919.425731	– 2236.608156	
CBS-4 (0 K)	– 1317.203536	– 919.441705	– 2236.634535	
CCSD(T)/6–311 + G(2df)	– 1317.149153	– 919.402165	– 2236.540535	– 2236.474346
ZPE [$kJ\,mol^{-1}$]	7.4	3.3	15.0	12.3
ZPE + TE [$kJ\,mol^{-1}$] at 298 K	17.4	10.0	33.7	30.5
S°_{298} [$J\,mol^{-1}\,K^{-1}$]	281.5	222.9	365.3	369.5
C_p [$J\,mol^{-1}\,K^{-1}$]	42.8	25.6	88.0	81.9

Gibbs free energy changes $\Delta G^{\circ}_{298}(4)$ (Table 5) show that the gas-phase reaction (4) is endothermic and that the negative reaction entropy shifts the equilibrium further to the left.

Table 5. Reaction enthalpies ΔH°_{298} (4) and Gibbs free energy changes ΔG°_{298} (4) calculated from the data in Table 4.

	ΔH°_{298} (4) [$kJ\,mol^{-1}$]	ΔG°_{298} (4) [$kJ\,mol^{-1}$]
CBS-4	27	70
G2(MP2)	4	46
CCSD(T)/6-311+G(2df)	32	74

The transition state for reaction (4) (**TS2**) (Figure 3) has an unusual structure which can be interpreted approximately as an ion-pair composed of SCl_3^+ and Cl^-. However, of the three S–Cl bonds only two are similar in length (200.4 and 205.2 pm); the third is much longer (246.3 pm), but surprisingly it is not the one which connects the SCl_3^+ ion to the formal chloride ion. The S-Cl-Cl unit is bent (at 132.6°) and the S–Cl bond of this bridge is practically perpendicular to the plane of the former SCl_2 molecule, as in the case of **TS1**. The torsion angle Cl5-Cl2-S-Cl4 (– 25.2°) results in a contact distance of 384.5 pm between Cl4 and Cl5. The torsion angle Cl5-Cl2-S-Cl3 is – 115.3°. Cl5 carries a charge of – 0.41 while the bridging atom Cl2 has a positive charge of + 0.39. The Cl – Cl bond is therefore highly polarized, and at 238.3 pm it is considerably longer than calculated for Cl_2 (202.5 pm). The S atom is slightly positively charged (+ 0.09), as is Cl3 (+ 0.07), while Cl4 carries a charge of – 0.13. Thus the structure of **TS2** is rather different from that of **TS1** but similar to the transition state of reaction (1). The intrinsic reaction coordinate connects **TS2** smoothly with SCl_4 at one extremity and with the separate molecules SCl_2 and Cl_2 on the other. As in the case of SF_4, the atoms of the former Cl_2 molecule occupy one axial and one equatorial position in the final product molecule, SCl_4.

The energy of **TS2** at 0 K is 203 $kJ\,mol^{-1}$ above that of $SCl_2 + Cl_2$ and 171 $kJ\,mol^{-1}$ above that of SCl_4 at the CCSD(T)/6-311+G(2df) level of theory. The bond energy of Cl_2 at 0 K is 246 $kJ\,mol^{-1}$; that is, the formation of SCl_4 from SCl_2 and Cl_2 via **TS2** requires a much lower activation energy than the homolytic dissociation of Cl_2. These data and the energy profile of reaction (4) (Figure 4) apply to the gas phase only. Since the dipole moment calculated for **TS2** (7.05 D) is much larger than those of SCl_2 (0.62 D) and SCl_4 (1.73 D) it can be assumed that the activation energy is substantially lower in media of high polarity. This explains why liquid SCl_2 reacts spontaneously with elemental chlorine at – 30 °C to form the salt-like solid SCl_4. The gain in lattice energy makes this reaction exothermic.

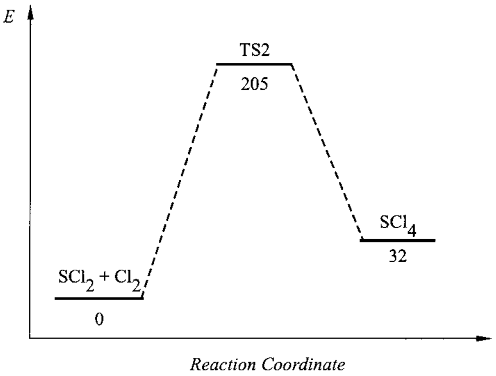


Figure 4. Energy diagram for the reaction of SCl_2 with Cl_2 to form SCl_4 via the transition state **TS2** (relative energies in $kJ\,mol^{-1}$ at 298 K).

The calculated wavenumbers of SCl_4 (Table 6) may help to identify this species in, for instance, a matrix isolation experiment. The assignment in Table 6 is based on a comparison with the assignment of the infrared and Raman spectra of SF_4.[27]

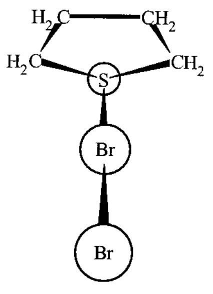
Table 6. Calculated vibrational wavenumbers (cm^{-1}; unscaled) of SCl_4 (symmetry C_{2v}) and relative infrared intensities (in brackets); ν = stretching mode.

A_1	507 (21) ν	B_1	491 (7) ν
A_1	247 (1) ν	B_1	226 (0)
A_1	143 (1)	B_2	400 (100) ν
A_1	93 (1)	B_2	221 (1)
A_2	187 (0)		

On the basis of density functional calculations it had been claimed that SCl_4 has T_d symmetry and that a structure of C_{3v} symmetry is only slightly less stable.[16] We have optimized the geometry of SCl_4 at the HF/6-311G* level with the symmetry restricted to either T_d or C_{3v}, and calculated the vibrational wavenumbers at the same level. Of the four fundamental vibrations of tetrahedral SCl_4 one had a negative eigenvalue (the triply degenerate bending mode). Similarly, of the six fundamentals of $SCl_4(C_{3v})$ one doubly degenerate bending mode had a negative eigenvalue. Clearly, these structures do not correspond to minima on the energy hypersurface.

Discussion

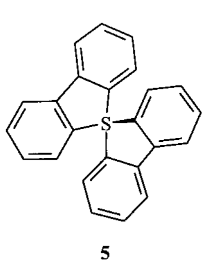
Homoleptic sulfuranes SX_4 are known with X = F, OR and R only (R = organic group).[28] Their structures always exhibit the pseudo-trigonal-bipyramidal coordination geometry at the S atom but the local symmetry may be lower than C_{2v} because of intermolecular interactions in the solid state. In particular, the two axial S–X bonds may differ slightly in length. With chlorine ligands, sulfuranes R_2SCl_2 and $R(RO)SCl_2$ are known. The classic example is bis(4-chlorophenyl)dichlorosulfurane **3**, in the solid state of which the Cl atoms are in axial positions but the S–Cl distances are 226 and 232 pm,[29] in agreement with the axial S–Cl distance of 231.6 pm calculated for SCl_4 in this work. With halogens of lower electronegativity no sulfuranes are formed; instead, adducts of the $R_2S \rightarrow X_2$ type are obtained. For example, the five-membered cyclic tetramethylene sulfide $(CH_2)_4S$ (thiolane) reacts with Br_2 to form a solid product **4** in which the three atoms S-Br-Br are aligned (at 178°) and the coordination geometry at the S atom is pyramidal.[30]



4

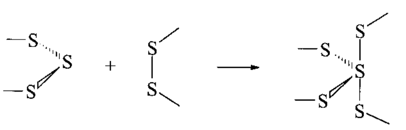
This geometry, together with the bond lengths, indicates that the sulfide acts as a nucleophile donating electron density into the antibonding σ_u LUMO of Br_2. The Br–Br distance (272.4 pm) is therefore much longer than in gaseous Br_2 (228 pm). This structure can serve as a model for the first stage of the asymmetric donor–acceptor interaction between the two species SX_2 and X_2 investigated in this work. Only if X is of sufficiently high electronegativity will the adduct be transformed into a sulfurane as in the case of SF_4. Analogous behavior has been observed for compounds of the R_2SeX_2 type (R = Me, Ph; X = halogen). With X = F, Cl, Br the geometry at the selenium atom is pseudo-trigonal-bipyramidal whereas for Me_2SeI_2 the donor–acceptor type of structure analogous to **4** is preferred, with Se-I-I = 174°.[31]

The hypothetical tetramethylsulfurane Me_4S, according to a high-level ab initio MO calculation, is thermodynamically unstable with respect to Me_2S and Me_2 (ethane).[32] The energy change during this decomposition has been calculated at the MP4SDG/TZ(2)P level of theory to be $-350\,kJ\,mol^{-1}$. To stabilize homoleptic tetraorganosulfuranes R_4S, either the electronegativity of R has to be increased by inductive effects (thermodynamic stabilization) or decomposition of a thermodynamically unstable derivative must be prevented by introducing suitable chelating ligands (kinetic stabilization). An example of the first case is the tetrakis(pentafluorphenyl)sulfurane $(C_6F_5)_4S$, which is stable below 0 °C, at which temperature it decomposes to R_2S and R_2.[33] Cyclic bidentate ligands, as in bis(2,2′-biphenylylene)sulfurane (**5**), are even more effective at stabilizing organic sulfuranes. Compound **5** is kinetically stable at ambient temperatures, and according to an X-ray structural analysis it contains S–C bonds of length 192.6 pm(axial) and 181.3 pm (equatorial).[34]

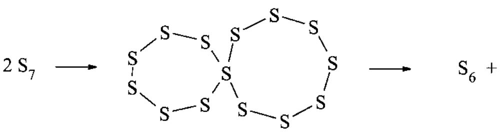


5

Sulfuranes $S(SR)_4$ have been proposed as intermediates for the interconversion of polysulfur compounds, for example, in the transformation of unstable homocycles such as S_7, to a more stable ring size, as in S_8 [Eqs. (6), (7)].[8]



(6)



(7)

However, semiempirical MO calculations by the SINDO1 method indicated that the reaction of H_2S_3 with H_2S_2 to form the tetramercaptosulfurane $S(SH)_4$ is endothermic by $299\,kJ\,mol^{-1}$.[35] This reaction served as a model reaction for Equation (6). Similarly, the insertion of H_2S into the central bond of either H_2S_2 or H_2S_4 to give the sulfuranes $H_2S(SH)_2$ and $H_2S(SSH)_2$, respectively, was found to be endothermic by approximately $210\,kJ\,mol^{-1}$ at the MP3/6-31G*//HF/4-31G* level of theory.[36] Although these calculations need to be improved by a higher level of theory[37] it is evident that the electronegativity of sulfur is too low to make tetrathiasulfuranes likely intermediates for the interconversion of polysulfur compounds, especially if the additional activation energy is taken into account. There is a clear dependence of the thermodynamic stability of homoleptic SX_4 compounds on the electronegativity of X, as the data (Table 7) for the energy change for the formation of SX_4 from SX_2 and X_2 demonstrate.

Table 7. Energy changes ($kJ\,mol^{-1}$ at 0 K) for the formation of SX_4 from SX_2 and X_2 calculated at different levels of theory).

	SF_4	SCl_4	$S(SH)_4$	H_4S	Me_4S
	−450	+33	+200 to +300	+330	+350
Reference	this work	this work	35, 36	9, 10	32

The high stability of SF_4 is due not only to the favorable electronegativity of fluorine but also to the unusually small bond energy of F_2. In the case of SCl_4 the lack of stability of SCl_4 is partly attributable to the bond energy of Cl_2 being much higher than that of F_2. On the basis of these observations one would expect that sulfuranes of the $S(NR_2)_4$ type might be sufficiently stable to be prepared, since the electronegativity of nitrogen on the Allen scale[38] is slightly higher than that of chlorine, and the N–N single bond in the dissociation product tetraalkylhydrazine R_2N-NR_2 would be weak similarly to the bond in F_2. So far, tetraamidosulfuranes are unknown.

The adduct **2** and the transition states **TS1** and **TS2** are remarkable in that a substantial amount of electron density has been transferred from the *positively* charged S atom in SX_2 to a neutral X_2 molecule to generate each of these species. For X = F this charge transfer does not change the energy of the system very much ($<10\,kJ\,mol^{-1}$) but for X = Cl the charge transfer is considerably endothermic. Polar reaction mechanisms may be more common in sulfur chemistry than has been expected. The interconversion of polysulfur compounds such as S_7 also probably proceeds through polar intermediates or, in other words, by nucleophilic attack by one molecule on a neighboring one resulting in zwitterionic transition states. This problem will be discussed in a separate publication.

Gaseous adducts of the molecules F_2 and Cl_2 with donors such as H_2S[39] and Me_3N[40] have been studied previously. These adducts also have C_s symmetry. The species $H_2S \rightarrow F_2$ and $H_2S \rightarrow Cl_2$ have been observed as prereactive complexes, by rotational spectroscopy using a fast-mixing nozzle together with a microwave spectrometer. The $S \cdots F$ and $S \cdots Cl$ distances obtained were 320(1) and 325 pm, indicating a very weak interaction in both cases. The structure of the complex $Me_3N \rightarrow F_2$ was determined by ab initio MO calculations at the MP2/6-31G* level. This structure is characterized by a somewhat smaller degree of charge transfer than our adduct **2** and than our transition state **TS1**; this can be concluded from the internuclear distances in the F_2 units (142 pm in the free F_2 molecule, 175 pm in $Me_3N \rightarrow F_2$, and 182 pm in **2** and **TS1**).

The slight differences in reaction enthalpies that resulted from the different methods used in this work were most probably related to the different geometries used in the energy calculations, as mentioned in the Computational Methods section. To demonstrate the differences one may compare the experimental bond distances of SF_4 with those calculated at various levels of theory (Table 8). The best agreement with the experimental geometry is obtained for the smallest basis set, and neglecting the electron correlation. The same is true for SF_2 and SCl_2. Nevertheless, we believe that the results obtained at the CCSD(T)/6-311+G(2df)//MP2/6-311+G* level are the most reliable, since it is known that the energy of hypervalent molecules drops considerably if diffuse and polarization functions are included in the basis set and if the electron correlation is taken into account. In particular, the transition states, which include some large internuclear distances, require diffuse functions. The main goal of this work is to elucidate the reaction mechanisms and to compare the activation energies with those for a homolytic dissociation pathway. These results are not influenced by the slight differences in enthalpy values obtained by different methods.

Table 8. Bond lengths of SF_4.

	Exp.	CBS-4(HF/3-21G*)	G2(MP2/6-31G*)	MP2/6-311+G*
SF_{eq} [pm]	154.5	155.0	158.5	157.9
SF_{ax} [pm]	164.6	161.7	166.3	169.0

Conclusion

We have shown that the reactions of the sulfur dihalides SX_2 with X_2 (X = F, Cl) to give the pseudo-trigonal-bipyramidal tetrahalides SX_4 proceed via asymmetric, almost ionic, transition states. In the case of X = F a very weakly bonded donor–acceptor complex $F_2S \rightarrow F_2$ (**2**) is the first reaction product and is transformed exothermically into SF_4 via a transition state of which the structure and energy are almost identical to those of **2**. In contrast, the structure of the transition state for the endothermic reaction of SCl_2 with Cl_2 can be approximated by the formula $[SCl_3^+]Cl^-$. For the homoleptic sulfuranes SX_4 there is a definite dependence of the thermodynamic stability with respect to the dissociation products SX_2 and X_2 on the electronegativity of X (X = F, Cl, SR, Me, H): the lower the electronegativity of X, the more exothermic is the dissociation reaction. In this sense, tetrathiasulfuranes $S(SR)_4$ are highly endothermic and are therefore not expected to play a role as reaction intermediates in sulfur chemistry.

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