

Exploring the possibility of a bimolecular reaction channel for the $F_2SS/FSSF$ rearrangement process[☆]

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Abstract

A theoretical study of the $F_2SS/FSSF$ isomerization is presented, where the possibility of a bimolecular reaction channel to occur is explored by introducing the effect of a second F_2SS molecule on the unimolecular process. At the HF/6-31G* level of theory, three alternative bimolecular routes are identified and the corresponding reactant and product complexes and transition states characterized. The most favourable bimolecular pathway is then analyzed at the HF, MP2, and B3P86 levels of theory using the 6-31+G* basis set. Results including electron correlation effects give energy barriers for the bimolecular process only a few (3–5) kcal/mol below those encountered for the unimolecular process. Consequently, the isomerization process is unlikely to proceed via this bimolecular channel because the energy barrier is still too high (40.0 kcal/mol at the MP2/6-31+G* level). © 1998 Elsevier Science B.V. All rights reserved.

Keywords: $F_2SS/FSSF$ isomerization; Bimolecular process; Electron correlation effects

1. Introduction

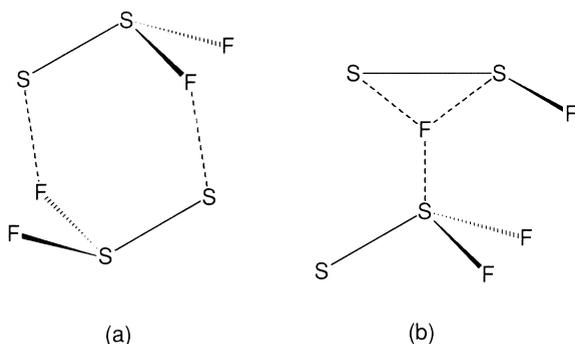
The reaction of isomerization converting F_2SS into $FSSF$ and vice versa was observed experimentally in the gas phase more than thirty years ago [1–3]. At temperatures above -100°C , it was found that the $FSSF$ isomer slowly isomerizes to F_2SS . Because of that, the $FSSF$ isomer was regarded as the less stable isomer [2]. However, evidence was also found suggesting that $FSSF$ may be the more stable isomer at low temperatures, as F_2SS transformed into a molecular complex [$FSSF, F_2SS$] after cooling the

sample down to -80°C [1]. More recently, the heat of transformation of $FSSF$ to F_2SS was determined experimentally to be 2.7 ± 0.5 kcal/mol [4]. In any case, as regards the isomerization process, more important than the controversy on the relative stabilization of the two isomers is the fact that the isolation and identification of the two disulfur difluoride isomers is experimentally possible [1–6]. This indicates that the process of a fluorine rearrangement between F_2SS and $FSSF$ evolves through an appreciable energy barrier, high enough to allow the individual isolation of the isomers but low enough to take place in the gas phase.

In an attempt to assist the experimental findings, theoretical studies on the $F_2SS/FSSF$ rearrangement process have been also reported [7–9]. Using the CNDO/2 semiempirical method, Solouki and Bock

[☆]In honor of Professor Árpád Kucsman on the occasion of his 70th birthday.

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Scheme 1

[7] estimated an energy barrier within the range of 23–46 kcal/mol. More recently, Bickelhaupt et al. [8] performed a series of high-level ab initio calculations including the effect of electron correlation. The lowest energy barrier reported, 40.7 kcal/mol, was found at the QCISD(T)/6-31+G**/MP2/6-31G* level after correction of the zero point vibrational energies. Using different DFT schemes and a 6-311++G(3df) basis set, Jursic [9] reported energy barriers ranging from 49.2 to 41.9 kcal/mol. Although these values lie within the energy barrier range assessed by Solouki and Bock [7], they can be considered too high to be consistent with an observable isomerization process at temperatures of -100°C and above [1,2].

From this latter observation, Bickelhaupt et al. [8] suggested that, instead of evolving through a unimolecular process, the $\text{F}_2\text{SS}/\text{FSSF}$ isomerization might alternatively proceed via a bimolecular reaction channel in which lower energy transition states would be conceivable. Furthermore, a bimolecular process would be also in accordance with the formation of the early proposed $[\text{FSSF}, \text{F}_2\text{SS}]$ molecular complex [1]. The exploration of this mechanistic possibility is the aim of the present work.

2. Computational methods

Calculations were performed at the Hartree–Fock (HF) level of theory and, when appropriate, the effect of electron correlation was introduced at the second-order many-body perturbation theory (MP2) and the density functional theory (B3P86) levels, using the 6-31G* and 6-31+G* basis sets. The B3P86 hybrid

functional combines an altered expression of the Becke's three-parameter exchange functional [10] with Perdew's gradient-corrected correlation functional [11], and it was selected according to Jursic's results [9]. In particular, the B3P86 exchange–correlation functional is obtained as follows:

$$E_{\text{XC}} = E_{\text{X}}^{\text{LDA}} + a_0(E_{\text{X}}^{\text{HF}} - E_{\text{X}}^{\text{LDA}}) + a_{\text{X}}\Delta E_{\text{X}}^{\text{B88}} + E_{\text{C}}^{\text{VWN}} + a_{\text{C}}\Delta E_{\text{C}}^{\text{P86}}$$

where $E_{\text{X}}^{\text{LDA}}$ is the exchange energy of a homogeneous electron gas [12], $E_{\text{C}}^{\text{VWN}}$ is the local correction to correlation energy due to Vosko et al. [13], E_{X}^{HF} is the Hartree–Fock exchange, and $\Delta E_{\text{X}}^{\text{B88}}$ [14] and $\Delta E_{\text{C}}^{\text{P86}}$ [11] are the Becke's and Perdew's gradient corrections to exchange and correlation energies, respectively. The values of the three semiempirical parameters ($a_0 = 0.20$, $a_{\text{X}} = 0.72$, and $a_{\text{C}} = 0.81$) considered in this work are those fitted by Becke to a series of thermochemical data [10].

Molecular geometries were fully optimized in all cases. Transition states were suitably characterized by diagonalizing the matrix of energy second derivatives to determine their unique imaginary frequency. The complexes separated by a given transition state were identified through the construction of the intrinsic reaction path [15] which, starting at the transition state, uses the analytical Hessian to determine the transition vector that follows downwards. All calculations were carried out by means of the Gaussian-94 program [16].

3. Results and discussion

Following the original suggestion by Bickelhaupt et al. [8], two possible bimolecular reaction channels were analyzed (Scheme 1). In principle, the six-membered ring structure in the transition state for channel (a) should be much less strained than the three-membered ring formed in the unimolecular process. However, exploration of the potential energy surface along the reaction coordinate defined by the double transfer of two fluorine atoms from $[\text{F}_2\text{SS}, \text{F}_2\text{SS}]$ to $[\text{FSSF}, \text{FSSF}]$ indicated that the process would evolve through a very high energy barrier and, for this reason, location of the transition state was not further pursued along this reaction pathway. Indeed, the main effort

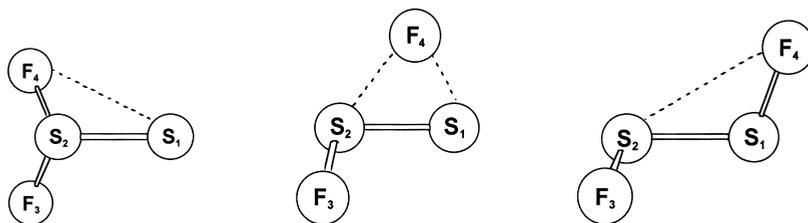


Fig. 1. Reactant (F_2SS , left), transition state (TS^1 , middle), and product ($FSSF$, right) for the unimolecular process.

was focused on the study of the bimolecular reaction channel (b), where a bimolecular process is modelled by introducing the effect of a F_2SS molecule on the unimolecular process. In this case, the migrating fluorine undergoing a 1,2-rearrangement is expected to be stabilized through the interaction with the positively charged central sulfur of this additional F_2SS molecule [8]. Thus, this bimolecular reaction channel will convert a $[F_2SS, F_2SS]$ complex into a $[FSSF, F_2SS]$ complex [1].

At a first stage, the HF/6-31G* level of theory was selected to compare, both from the structure and energy points of view, the rearrangement of F_2SS into $FSSF$ through a unimolecular transition state (TS^1), with the rearrangement of $[F_2SS, F_2SS]$ into $[FSSF, F_2SS]$ and vice versa through a bimolecular transition state (TS^2) following the reaction channel (b) in Scheme 1. The exploration of the potential energy surface induced by the formation of a bimolecular interaction allowed the location of three different TS^2 (labelled, TS_1^2 , TS_2^2 , and TS_3^2) and the corresponding complexes connected to them (labelled accordingly). As a reference, the stationary points defining the unimolecular process are depicted in Fig. 1, and the three transition states of the different bimolecular paths located can be analyzed visually in Fig. 2.

Table 1 collects the most relevant structural parameters and energies characterizing each stationary point, as well as relative energies (referred to F_2SS) of $FSSF$ and the TS that connects the two isomers, together with relative energies (referred to the $[F_2SS, F_2SS]$ complex) of the $[FSSF, F_2SS]$ bimolecular complex and the TS that connects these two bimolecular complexes. As can be observed, small structural changes are obtained in the monomers forming the reactant and product complexes of all bimolecular processes when compared to the interatomic distances

obtained for the unimolecular process. This is due to the fact that at these points of the potential energy surface the additional F_2SS molecule interacts at long distances (between 3.0–3.6 Å) with the molecule where the fluorine rearrangement takes place. In terms of energy, this explains why the relative energy between F_2SS and $FSSF$ in the unimolecular process (–6.3 kcal/mol) is essentially retained between $[F_2SS, F_2SS]$ and $[FSSF, F_2SS]$ in the bimolecular processes (–7.4, –6.2, and –5.8 kcal/mol). This result is in agreement with the fact that $[FSSF, F_2SS]$ was the

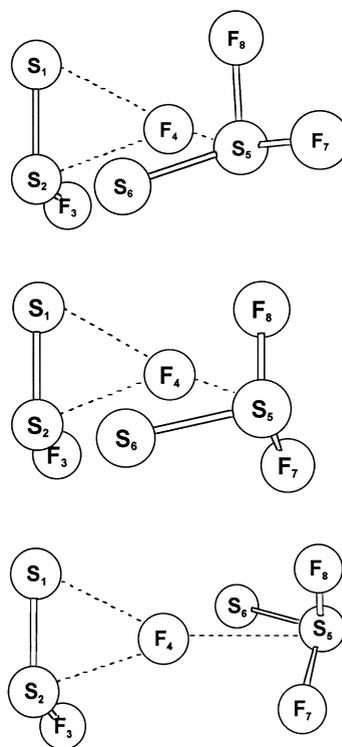


Fig. 2. Transition state structures, TS_1^2 (top), TS_2^2 (center), and TS_3^2 (bottom), for the three bimolecular pathways studied.

Table 1

Interatomic distances (in Å), energies (E in hartrees) and energy differences (ΔE in kcal/mol) for the different stationary points optimized at the HF/6-31G* level of theory. Experimental values are also given in italics. See Figs. 1 and 2 for transition state labelling

System	R_{S2-F3}	R_{S2-F4}	R_{S1-F4}	R_{S1-S2}	R_{S5-F4}	R_{S5-S6}	E	ΔE
F_2SS	1.579 <i>1.598 ± 0.012^{3c}</i>	1.579 <i>1.598 ± 0.012^{3c}</i>	2.801	1.879 <i>1.860 ± 0.015^{3c}</i>	-	-	-993.81395	0.0 <i>0.0</i>
$FSSF$	1.611 <i>1.6350 ± 0.01^{3c}</i>	2.821	1.611 <i>1.635 ± 0.01^{3c}</i>	1.953 <i>1.888 ± 0.01^{3c}</i>	-	-	-993.82404	-6.3 <i>-2.7 ± 0.5⁴</i>
TS^1	1.575	2.165	2.240	1.825	-	-	-993.69844	72.5
$[F_2SS, F_2SS]_1$	1.582	1.584	2.800	1.878	3.502	1.884	-1987.62978	0.0
$[FSSF, F_2SS]_1$	1.610	2.822	1.621	1.952	3.058	1.884	-1987.64152	-7.4
TS_1^2	1.571	2.255	2.331	1.813	2.492	1.915	-1987.52815	63.8
$[F_2SS, F_2SS]_2$	1.580	1.580	2.800	1.880	3.571	1.884	-1987.62983	0.0
$[FSSF, F_2SS]_2$	1.612	2.821	1.613	1.953	3.644	1.884	-1987.63976	-6.2
TS_2^2	1.576	2.183	2.255	1.823	3.376	1.894	-1987.51678	70.9
$[F_2SS, F_2SS]_3$	1.582	1.584	2.800	1.878	3.502	1.884	-1987.62978	0.0
$[FSSF, F_2SS]_3$	1.609	2.825	1.612	1.953	3.486	1.879	-1987.63905	-5.8
TS_3^2	1.572	2.177	2.253	1.823	3.348	1.877	-1987.51485	72.1

bimolecular complex observed experimentally [1]. In addition, binding energies for the $[F_2SS, F_2SS]_1$ and $[FSSF, F_2SS]_1$ bimolecular complexes computed with respect to the energy of the monomers at the HF/6-31G* level are -1.2 and -2.2 kcal/mol, respectively. The low values of these binding energies reflect again the weakness of the dipole-dipole interactions between the two monomers.

This weak long-range interaction (around 3.4 Å) is also observed in TS_2^2 and TS_3^2 , and is thus responsible for the accordance of the energy barriers of these two bimolecular processes (70.9 and 72.1 kcal/mol, respectively) with the unimolecular process (72.5 kcal/mol). Despite the weakness of the interaction between F4 and S5 in TS_2^2 and TS_3^2 , several small structural changes are apparent. In both cases, comparison with the TS^1 structure reveals the trend to find larger R_{S2-F4} (0.018 and 0.012 Å, respectively) and R_{S1-F4} (0.015 and 0.013 Å, respectively) distances, therefore giving looser R_{S5-S6} (0.069 and 0.062 Å, respectively) distances.

A closer bimolecular interaction (2.5 Å) is encountered in TS_1^2 . As a consequence, larger structural changes appear when comparing the TS_1^2 structure with the TS^1 structure, and also with the TS_2^2 and TS_3^2 structures. These changes are evident in much larger R_{S2-F4} (0.090 Å) and R_{S1-F4} (0.091 Å) distances, therefore giving much shorter R_{S1-S2}

(0.012 Å) distances, and a much looser R_{S5-S6} (0.090 Å) distance. Moreover, the stronger interaction between F4 and S5 results in a significantly lower energy barrier (63.8 kcal/mol), 8.7 kcal/mol lower than the unimolecular process. Note also that TS_1^2 and TS_3^2 are both connected to the same $[F_2SS, F_2SS]$ complex.

At this point, one is tempted to conclude that the possibility of a bimolecular mechanism is a key consideration to explain the energy requirements of the $F_2SS/FSSF$ isomerization process. However, as noticed previously by Bickelhaupt et al. [8], improvements of the basis set through addition of diffuse functions and inclusion of electron correlation are important for a reasonable energy description of this process and, thus, both effects should be considered before drawing any final conclusion. Accordingly, at the second state of the work, calculations for the unimolecular process and the bimolecular process through the TS_1^2 transition state were performed at the HF, MP2, and B3P86 levels of theory using the 6-31+G* basis set. Although the TS_1^2 appearing along the considered reaction pathway is a typical example of systems where a multiconfiguration treatment is desirable, we expect that results obtained at the MP2/6-31+G* and B3P86/6-31+G* levels will already give an idea of the relevance of including the electron correlation for a proper description of

Table 2

Interatomic distances (in Å), energies (E in hartrees) and energy differences (ΔE in kcal/mol) for the unimolecular and bimolecular reaction channels optimized at the HF/6-31 + G*, MP2/6-31 + G*, and B3P86/6-31 + G* levels of theory. See Figs. 1 and 2 for transition state labelling

System	R _{S2-F3}	R _{S2-F4}	R _{S1-F4}	R _{S1-S2}	R _{S5-F4}	R _{S5-S6}	E	ΔE
HF/6-31 + G*								
F ₂ SS	1.586	1.586	2.808	1.878	-	-	- 993.82706	0.0
FSSF	1.617	2.825	1.617	1.954	-	-	- 993.84235	- 9.6
TS ¹	1.576	2.226	2.308	1.818	-	-	- 993.72425	64.5
[F ₂ SS,F ₂ SS] ₁	1.584	1.593	2.810	1.875	3.232	1.880	- 1987.65613	0.0
[FSSF,F ₂ SS] ₁	1.616	2.826	1.624	1.953	3.129	1.881	- 1987.67228	- 10.1
TS ₁ ²	1.573	2.310	2.395	1.809	2.559	1.913	- 1987.56434	57.6
MP2/6-31 + G*								
F ₂ SS	1.677	1.677	2.865	1.859	-	-	- 994.45740	0.0
FSSF	1.682	2.887	1.682	1.914	-	-	- 994.45639	0.6
TS ¹	1.651	2.294	2.239	1.841	-	-	- 994.38883	43.0
[F ₂ SS,F ₂ SS] ₁	1.679	1.699	2.874	1.857	2.990	1.857	- 1988.92321	0.0
[FSSF,F ₂ SS] ₁	1.681	2.883	1.696	1.909	2.949	1.858	- 1988.92103	1.4
TS ₁ ²	1.650	2.310	2.263	1.836	2.694	1.860	- 1988.85951	40.0
B3P86/6-31 + G*								
F ₂ SS	1.656	1.656	2.866	1.877	-	-	- 996.94214	0.0
FSSF	1.671	2.905	1.671	1.918	-	-	- 996.94623	- 2.6
TS ¹	1.639	2.250	2.286	1.851	-	-	- 996.86934	45.7
[F ₂ SS,F ₂ SS] ₁	1.654	1.668	2.872	1.874	3.153	1.879	- 1993.88553	0.0
[FSSF,F ₂ SS] ₁	1.669	2.902	1.682	1.916	3.123	1.876	- 1993.89037	-3.0
TS ₁ ²	1.641	2.314	2.362	1.848	2.465	1.909	- 1993.82015	41.0

the process. The other two bimolecular processes characterized at the HF/6-31G* level of theory were not considered here because, as commented on above, they were found to have energy barriers comparable to the unimolecular process.

Table 2 gathers the collection of structural and energy parameters for the unimolecular and the most favorable bimolecular processes at different levels of theory. Comparison of results obtained at the HF/6-31G* level (Table 1) with those obtained at the HF/6-31+G* level will allow us to assess the importance of adding diffuse functions to the various molecular systems.

Comparison of energy values in Table 1 and 2 (HF/6-31G* vs. HF/6-31+G* results) reveals that inclusion of diffuse functions stabilizes FSSF as compared to F₂SS by 3.3 kcal/mol. Likewise, the [FSSF,F₂SS] complex is favoured with respect to the [F₂SS,F₂SS] complex by 2.7 kcal/mol. However, binding energies for the [F₂SS,F₂SS]₁ and [FSSF,F₂SS]₁ complexes are practically unchanged by inclusion of diffuse functions (-1.3 and -1.8 kcal/mol, respectively). Interestingly, adding diffuse functions to the calculations performed at the HF/6-31G* level reduces significantly the

energy barriers (which decrease 8.0 and 6.2 kcal/mol in the unimolecular and bimolecular processes, respectively), reducing the energy barriers to 64.5 and 57.6 kcal/mol for the unimolecular and bimolecular processes, respectively. This reduction is due to the fact that, although all stationary points are stabilized by the effect of diffuse functions, transition states are much more stabilized than F₂SS and the [F₂SS,F₂SS] complex. As extracted from the energy results obtained, it is evident that the addition of diffuse functions is important.

From the structural point of view, the most important variations in the unimolecular process are found at TS¹, where R_{S2-F4} and R_{S1-F4} are stretched 0.061 and 0.068 Å, respectively, and hence R_{S1-S2} is slightly strengthened (0.007 Å). In the bimolecular process, it is found that the additional F₂SS molecule forms a closer interaction with the other monomer in the [F₂SS,F₂SS] complex (0.270 Å closer), whereas it interacts at a larger distance in the [FSSF,F₂SS] complex (0.071 Å larger) and in the TS₁² (0.067 Å larger). In TS₁², R_{S2-F4} and R_{S1-F4} are stretched by 0.055 and 0.064 Å, following the same trend found in TS¹.

If addition of diffuse functions has been found to be

important, inclusion of electron correlation is critical for a proper energy description of the $F_2SS/FSSF$ isomerization process. On one hand, the relative energies between F_2SS and $FSSF$ in the unimolecular process and those of the $[F_2SS, F_2SS]$ and $[FSSF, F_2SS]$ complexes in the bimolecular process are comparable. However, as compared to experiment (-2.7 ± 0.5 kcal/mol) [4], HF yields $FSSF$ too stabilized with respect to F_2SS (-9.6 kcal/mol). Interestingly, the relative energy obtained using the B3P86 functional (-2.6 kcal/mol) is found to be in excellent agreement with experiment [4]. At the MP2 level of theory the general trend found experimentally and at the HF and B3P86 levels is reversed, and F_2SS and the $[F_2SS, F_2SS]$ complex are now slightly more stable than $FSSF$ and the $[FSSF, F_2SS]$ complex, respectively. As regards to the binding energies, values of -0.8 and -1.3 kcal/mol are found for the $[F_2SS, F_2SS]$ and $[FSSF, F_2SS]$ complexes, respectively, at the B3P86 level of theory. Following the tendency mentioned above, at the MP2 level the relative stabilization due to the formation of the bimolecular complexes is reversed. Whereas at the HF and B3P86 levels of theory the binding energy of the $[F_2SS, F_2SS]$ complex is smaller than that of the $[FSSF, F_2SS]$ complex, at the MP2 level the binding energy of the $[F_2SS, F_2SS]$ complex (-5.3 kcal/mol) is larger than that of the $[FSSF, F_2SS]$ complex (-4.5 kcal/mol).

On the other hand, energy barriers decrease dramatically. With respect to the energy barrier found at the HF/6-31+G* level, the unimolecular and bimolecular processes show energy barriers 21.5 and 17.6 kcal/mol lower, respectively, at the MP2/6-31+G* level and 18.8 and 16.6 kcal/mol lower, respectively, at the B3P86/6-31+G* level. Furthermore, the difference in energy barriers between the unimolecular and the bimolecular processes diminishes significantly with inclusion of electron correlation effects. Thus, whereas a difference of 6.9 kcal/mol was found at the HF/6-31+G* level, the difference is reduced to 3.0 and 4.7 kcal/mol at the MP2/6-31+G* and B3P86/6-31+G* levels, respectively, which illustrates the fact that MP2 and B3P86 levels give rise to comparable energy barriers in both processes.

The influence of electron correlation is quite remarkable not only in terms of energy but also in terms of changes in the structure. As a general

trend, considering the results obtained at the HF/6-31+G* level as a reference, larger S–F distances (R_{S2-F3} , R_{S2-F4} and R_{S1-F4}) and shorter S–S distances (R_{S1-S2} and R_{S5-S6}) are obtained when electron correlation effects are included. Only R_{S1-F4} and R_{S1-S2} at transition states are found to follow the opposite trend. As regards to the interaction distances between monomers in the bimolecular complexes, inclusion of electron correlation effects causes shorter R_{S5-F4} values, the only exception having been found in TS_1^2 at the MP2 level. All trends appear more emphasized at the MP2 level than at the B3P86 level.

4. Conclusions

The possibility that the $F_2SS/FSSF$ isomerization occurs via a bimolecular reaction channel as an alternative route to the unimolecular reaction has been explored. After inclusion of electron correlation effects at the MP2 and B3P86 levels of theory using a 6-31+G* basis set, energy barriers for the bimolecular process were found to be only a few (3–5) kcal/mol below those found for the unimolecular process. These results illustrate that, although the rearrangement process is slightly favoured by the stabilizing long-range interaction of a second F_2SS molecule, the proposed bimolecular channel is unlikely to be the pathway through which the reaction takes place spontaneously in the gas phase at low temperatures because energy barriers are still too high (40.0 kcal/mol at the MP2/6-31+G* level). Given that a rearrangement mechanism involving more than two F_2S_2 species is very unlikely, other mechanistic proposals need to be considered. The exploration of alternative reaction channels involving radical species is now underway in our laboratory.

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