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B3LYP and CCSD(T) Studies of the Mechanisms of Unimolecular Reactions of HXCS (X = H and F)

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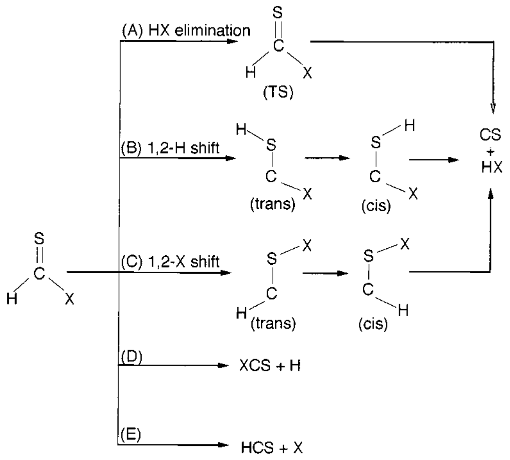
The potential energy surface for the decomposition of singlet HXCS (X = H and F) has been explored by B3LYP and CCSD(T) calculations. Five different types of reaction are proposed: (A) 1,1-HX elimination, (B) 1,2-H shift, (C) 1,2-X shift, (D) H• and XCS• radical formation, and (E) X• and HCS• radical formation. These results show interesting trends for the HXCS isomers. Our theoretical investigations suggest that the doubly bonded species HXC═S is the lowest energy structure among the isomers from both kinetic and thermodynamic viewpoints. We also report theoretical predictions of molecular parameters and vibrational IR spectra of the monohalogen substituted thioformaldehyde, which should be useful for future experimental observations.

I. Introduction

The chemistry of multiple bonded compounds between group 14 and heavier chalcogen atoms has continued to occupy the attention of chemists in various fields.[1] Some of the compounds with a carbon−sulfur double bond, a so-called thiocarbonyl group, have been noted as building blocks in organic synthesis and as important intermediates in the synthesis of sulfur-containing molecules.[2−15] In fact, the chemistry of thioformyl compounds has been studied extensively in recent years, not only because of their unique structures but also because of their potential biological activities.[16,17] However, the role of sulfur in biological structures largely remains unknown. Some knowledge of its function in biomolecules may perhaps be gained by the study of small model systems.[18,19] Thus, thioformaldehyde ($H_2C{=}S$), the smallest thioketone, should be related to systems of biological importance.[4−9,20−25] Nevertheless, the synthesis and isolation of thiocarbonyl compounds have in general proved very difficult to study by standard techniques because of their instability.[14] It is therefore not surprising that the first kinetically stabilized thioaldehyde, which is stable at ambient temperature, was made only recently.[11,12,26]

Although our understanding of such carbon−sulfur compounds has certainly increased in recent years, our knowledge is still primitive compared to that accumulated over the years about the analogous C═O species. Thioformaldehyde, $H_2C{=}S$, has been the topic of several ab initio studies ranging from RHF to MRDCI treatments.[4−9,20−25] However, to our knowledge, no theoretical study of the unimolecular dissociation pathways and barrier heights for the monohalogen-substituted thioaldehyde has appeared to date. The aim of this study is therefore to investigate theoretically the potential energy surfaces of HXC═S (X = H and F) species at the reliable CCSD(T) levels of theory in order to obtain a better understanding of their structural isomers in this series of molecules. In particular, the predicted molecular parameters and vibrational IR frequencies may aid experimental study of unknown HFC═S species.

SCHEME 1



The unimolecular reactions pertinent to the stability of HXC═S are shown in Scheme 1. Namely, the reactions considered here are (A) the single-step elimination of HX, (B) the 1,2-hydrogen shift, (C) the 1,2-halogen shift, (D) the formation of XCS and H radicals, and (E) the formation of HCS and X radicals. In other words, the aim of the present work is to provide the theoretical information about the relative stabilities of HXC═S (X = H and F) and its isomers. Moreover, we also report theoretical predictions of the molecular parameters and vibrational frequencies of HXC═S species, which should be useful for further experimental observations.

II. Theoretical Methods

Density functional theory (DFT) calculations were performed on IBM 590 computers using the Gaussian 94 system of programs.[27] The geometries of all the species were fully optimized using the hybrid density functional method B3LYP/6-311G(d) (hereafter designed B3LYP).[28,29] All ground and transition states were verified by vibrational frequency analysis. The vibrational zero-point energy (ZPE) corrections determined at the B3LYP/6-311G(d) level were also included, i.e., B3LYP/

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TABLE 1: Comparison between Observed[a,b] and Calculated[c−f] Molecular Parameters of Thioformaldehyde

	this work[c]	exptl	calc
r(C=S) (Å)	1.615	1.611[a]	1.622[d]
r(C−H) (Å)	1.090	1.093	1.088
∠HCH (deg)	115.6	116.9	122.0
vibrational mode (cm^{-1})			
ν_1(C−H asym str), B2	3153	3025[b]	3212[e]
ν_2(C−H sym str), A1	3067	2971	3119
ν_3(H-C−H bend), A1	1515	1457	1529
ν_4(S-C−H bend), B2	1085	991	1046
ν_5(out-of−plane), B1	1027	990	1036
ν_6(CdS str), A1	1022	1059	1116
dipole moment (D)	1.8109	1.6474[a]	1.87[f]
rotational constants (MHz)			
A	294541.75	291710 ± 23[a]	
B	17616.36	17698.87 ± 0.44	
C	16622.20	16652.98 ± 0.48	

(a)Reference 31. (b)Reference 32. (c)Based on B3LYP/6-311G(d) calculations. See the text. (d)References 8, 9. (e)Reference 22. (f)Reference 21.

6-311G(d) + ZPE (B3LYP/6-311G(d)). Further single-point CCSD(T) calculations were performed on all B3LYP optimized structures, i.e., CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311G(d) + ZPE (B3LYP/6-311G(d)) (hereafter designed CCSD(T)).[30]

III. Results and Discussion

1. $H_2C{=}S$ Decomposition Reactions. The equilibrium structure of $H_2C{=}S$ was calculated to be planar with C_{2v} symmetry, as in the case of $H_2C{=}O$. As one can see in Table 1, the molecular parameters for our B3LYP calculations agree well with the available experimental data.[31,32] For instance, our calculated C=S and C−H bond lengths in Table 1 are in excellent agreement with the experimental data.[31] However, the calculated ∠H−C−H angle of $H_2C{=}S$ is predicted to be smaller by about 1.2° than the corresponding experimental value.[31] Moreover, an inspection of the vibrational frequencies presented in Table 1 reveals that the DFT vibrational frequencies agree reasonable well with the corresponding experimental data.[32] Table 1 shows that the predicted unscaled B3LYP harmonic wavenumbers of $H_2C{=}S$ are higher by 130−140 cm^{-1} than the corresponding experimental wavenumbers. Indeed, the average deviation between our theoretical and experimental values for thioformaldehyde is about 5.0%, well within the estimated error range.[33] We also note that the predicted B3LYP dipole moment of $H_2C{=}S$ is somewhat larger than the experimental value by 0.16 D.[31] Additionally, an excellent agreement is found between rotational constants (B and C) calculated at the B3LYP level and experimental data.[31] Nevertheless, there is a significant discrepancy for one rotational constant. The rotational constant A is predicted to be larger, about 2830 MHz than the corresponding experimental value. In fact, the predicted rotational constant A for $H_2C{=}S$ is larger than the experimental value by 0.97% only. The good agreement between our computational results and available experimental data is quite encouraging. We therefore believe that the B3LYP/6-311G(d) level employed in this work can provide accurate molecular geometries of the unimolecular decomposition reactions, for which experimental data are not available.

In the case of $H_2C{=}S$, there are three kinds of dissociation pathways, i.e., (A) 1,1-hydrogen elimination, (B) 1,2-hydrogen shift, and (C) radical dissociation. The optimized geometries, calculated at the B3LYP/6-311G(d) level of theory, for the intermediates and transition states of the above reaction channels, are shown in Figure 1. Figure 2 illustrates the energies, including zero-point vibrational energy corrections, relative to $H_2C{=}S$ for four minima and four transition states on the singlet potential energy surface. The calculated vibrational frequencies, rotational constants, dipole moments, net atomic charges, and relative energies of $H_2C{=}S$ and its isomers are collected in Table 2.

For reaction path (A), **H_2CS−A−TS** is the transition state for 1,1-hydrogen elimination leading to H_2 + CS. The B3LYP results indicate that this transition structure is planar with both hydrogen atoms on the same side of the CS bond axis. The CCSD(T) results predict that this reaction path (A) is endothermic (+40 kcal/mol) and possesses a sizable energy barrier (83 kcal/mol).

For reaction path (B), **H_2CS−B−TS−1** and **H_2CS−B−TS−2** are the transition structures for the 1,2-hydrogen shift in $H_2C{=}S$ to HCSH and for the trans to cis isomerization of HCSH. **H_2CS−B−TS−3** is the transition structure for the

TABLE 2: Calculated Harmonic Vibrational Frequencies, Rotational Constants, Dipole Moments, Atomic Charges, and Relative Energies of the Species in H_2CS Decomposition Reactions at the B3LYP/6-311G(d) Level of Theory

species	frequencies (cm^{-1})	rotational constants (MHz)	dipole Moments (Debye)	q(C)	q(S)	q(H)	relative energies (kcal/mol)
$H_2C{=}S$	3153,3067,1515,1085, 1027,1022	A 294541.75 B 17616.36 C 16622.20	1.8109	−0.5120	0.0229	0.2445	0.0 (0.0)[a]
A-TS	2796,1332,1090,864,574, 1554i						86.8 (83.3)
B-TS-1	2945,2111,1116,825,462, 1864i						82.7 (75.8)
trans-HCSH	2964,2503,1194,979,961, 852	A 185745.30 B 18525.53 C 16845.43	1.8873	−0.4512	0.0985	0.1987(C) 0.1539(S)	49.0 (43.6)
B-TS-2	2882,2564,1145,681,576, 1561i						86.4 (81.2)
cis-HCSH	3039,2247,1129,946,946, 793	A 192831.86 B 18674.36 C 17025.56	2.8086	−0.4454	0.1596	0.2105(C) 0.0754(S)	49.4 (44.8)
B-TS-3	2821,1928,1091,858,539, 1116i						97.8 (88.5)
HCS	3093, 1196, 871	A 875776.89 B 20220.34 C 19764.02	1.1720	−0.3648	0.1228	0.2420	89.5[b] (90.5)

[a] The relative energies in parentheses are at the CCSD(T)/6-311++G(3df,3pd) level of theory; see the text. [b] The relative energy of HCS• and H• with respect to $H_2C{=}S$.

TABLE 3: Calculated Harmonic Vibrational Frequencies, Rotational Constants, Dipole Moments, Atomic Charges, and Relative Energies of The Species in HFCS Decomposition Reactions at the B3LYP/6-311G(d) Level of Theory

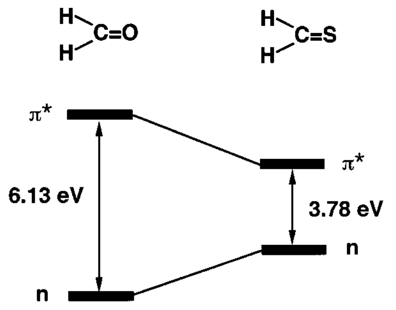
species	frequencies (cm$^{-1)}$	rotational constants (MHz)	dipole moments (Debye)	q(Si)	q(S)	q(F)	q(H)	relative energy (kcal/mol)
HFC=S	3145,1404,1195,994,898,476	A 73200.51 B 6072.84 C 5607.62	1.5826	−0.0831	0.0016	−0.1507	0.2323	0.0 (0.0)[a]
A-TS	3186,1197,1055,600,436,424i							43.3 (39.4)
B-TS-1	1936,1071,957,441,230,1737i							78.0 (70.4)
trans-FCSH	2641,1146,939,758,531,401	A 57891.20 B 6332.60 C 5708.19	1.8082	−0.0351	0.0197	−0.1427	0.1581	46.6 (41.1)
B-TS-2	2598,1174,695,652,396,614i							66.3 (60.3)
cis-FCSH	2498,1136,911,670,565,419	A 56524.48 B 6386.37 C 5738.06	2.2987	−0.0190	0.0443	−0.1497	0.1244	47.0 (42.0)
B-TS-3	1513,993,804,607,523, 1546i							84.4 (76.3)
C-TS-1	2973,1093,980,696,460,552i							124 (120)
trans-HCSF*	3314,1274,768,601,398,253i	A 36942.77 B 8312.34 C 6785.57	3.3773	−0.4645	0.5873	−0.3869	0.2641	52.3 (45.7)
C-TS-2	2899,1103,700,643,332,563i							122 (116)
cis-HCSF	3275,1295,829,649,549,291	A 41036.14 B 7621.93 C 6428.01	1.9419	−0.4480	0.5968	−0.4172	0.2685	44.9 (36.6)
C-TS-3	2574,1277,756,680,229,1140i							60.5 (54.2)
FCS	1315, 940, 462	A 150632.00 B 5933.44 C 5708.58	0.2667	0.0333	0.0730	−0.1062		94.6[b] (97.1)
HCS	3093, 1196, 871	A 875776.89 B 20220.34 C 19764.02	1.1720	−0.3648	0.1228		0.2420	108[c] (110)

[a] The relative energies in parentheses are at the CCSD(T)/6-311++G(3df,3pd) level of theory; see the text. [b] The relative energy of FCS• and H• with respect to HFC=S. [c] The relative energy of HCS• and F• with respect to HFC=S.

molecular dissociation of *cis*-HCSH leading to H_2 + CS. As shown in Figures 1 and 2, $H_2C{=}S$ is 44 and 45 kcal/mol more stable than *trans*-HCSH and *cis*-HCSH, respectively. Additionally, the CCSD(T) results suggest that the isomerization barriers for **H_2CS−B−TS−1** and **H_2CS−B−TS−2** are 76 and 81 kcal/mol, respectively. This clearly indicates that any experimental detection of the HCSH intermediates formed during the reaction is highly unlikely. In any event, based on the present results as shown in Figures 1 and 2, the relative stability of the double-bonded and the divalent species strongly suggests that sulfur is reluctant to form singly bonded compounds with carbon. It should be mentioned here that the unimolecular decomposition reactions of $H_2C{=}S$ were also studied by Guest et al.[20] Their optimized geometry parameters and energies are very similar to ours.

Furthermore, as noted in the Introduction, it is generally acknowledged that thioaldehydes have been elusive compounds by virtue of their high reactivity and difficulty of preparation.[2−13] The reason for this may be due to the following two factors. First, it can be seen from Table 2 that the carbon atom has a significant negative atomic charge (−0.512), whereas the sulfur atom carries a very small positive atomic charge (+0.0229). These numbers show the expected polarity of the C=S group, which results form the different electronegativities of carbon and sulfur.[34] Hence, our computational results suggest a "reversed polarity" of thioformaldehyde ($H_2C^{0.51-}{=}S^{0.023+}$) relative to formaldehyde ($H_2C^{0.073-}{=}O^{0.25-}$). This strong dipolar character in the C=S bond enhances the electrostatic interaction with polar reagents (such as H_2O). Second, our DFT results indicate that the frontier orbital n (−6.55 ev) and π^* (−2.77 ev) energy levels of $H_2C{=}S$ are considerably higher and lower, respectively, than the n (−7.44 ev) and π^* (−1.31 ev) levels of $H_2C{=}O$, as shown in Scheme 2. On one hand, it is evident that the lower-lying π^* orbital of $H_2C{=}S$ makes much more facile the attack of nucleophilic reagents (such as H_2O). On the other hand, $H_2C{=}S$ is also more reactive toward electrophilic reagents, because of the higher lying n orbital. In short, the reduction of the HOMO−LUMO gap is probably related to the higher reactivity of thioformaldehyde. In other words, both "frontier" and "charge" factors should play a key role in the future design of kinetically more stable substituted thiocarbonyl compounds.

SCHEME 2



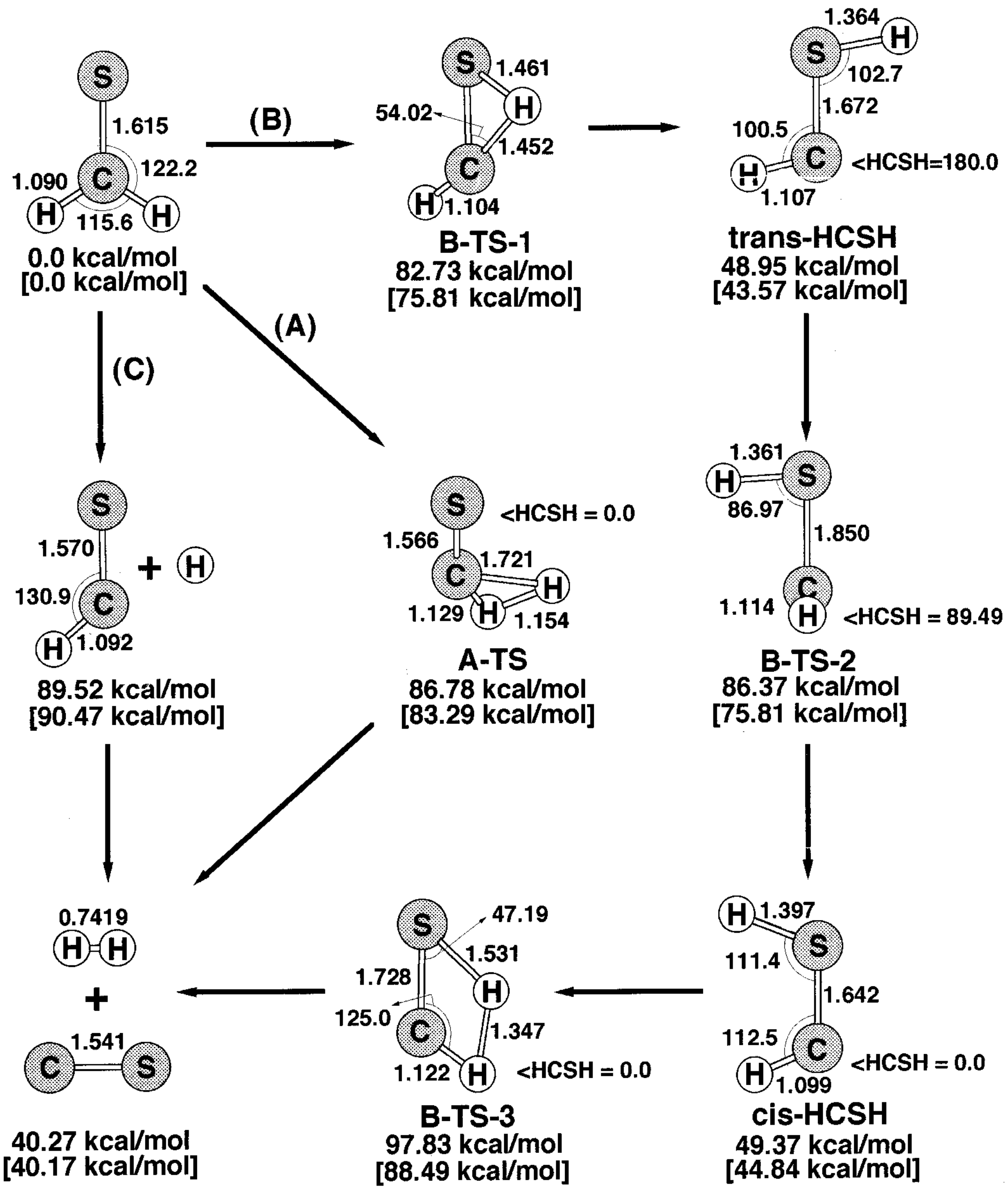


Figure 1. B3LYP/6-311G(d) optimized geometries (in Å and deg) and relative energies for the $H_2C{=}S$ isomers. Values in brackets are at the CCSD(T) level of theory (see the text).

2. HFC=S Decomposition Reactions. In the case of HFC=S, there are five kinds of reaction routes, as given in Scheme 1. Namely, (A) 1,1-HF elimination, (B) 1,2-hydrogen shift, (C) 1,2-fluorine shift, (D) formation of FCS and H radicals, and (E) formation of HCS and F radicals. The fully optimized geometries of the equilibrium structures and transition states are presented in Figure 3. The corresponding reaction energy profiles for the HFC=S decomposition reactions are given in Figure 4. The calculated vibrational frequencies, as well as dipole moments, rotational constants, net atomic charges, and relative energies of HFC=S and its derivatives, are collected in Table 3. Theoretical studies of HFC=S have, to our knowledge, been performed by three groups using SCF and MP2 calculations, respectively.[22,24,25] Although there are no experimental values available of HFC=S molecular parameters to compare with the calculated values, we believe that the parameters of the HFC=S species are also well described at the B3LYP/6-311G(d) level of theory.[25]

Basically, our computational results for the HFC=S reactions are in many respects similar to those discussed earlier for the $H_2C{=}S$ system. Nevertheless, several intriguing results can be drawn from Figures 3 and 4 as follows.

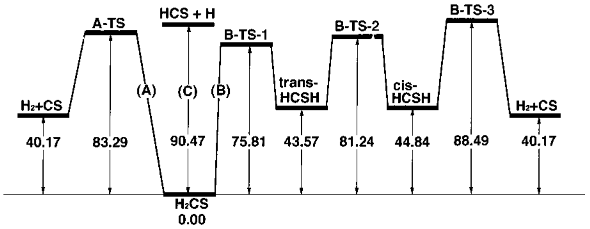


Figure 2. Potential energy surfaces for the unimolecular decomposition reactions of $H_2C{=}S$. The relative energies (in kcal/mol) are taken from the CCSD(T) level as given in Table 2. For the B3LYP-optimized structures of the stationary points see Figure 1.

First, for reaction path (A) we located the transition structure **A−TS** connecting HFC=S and HF + CS. Our CCSD(T) results suggest that a high activation barrier results (i.e., 39 kcal/mol) with respect to the most stable isomer, HFC=S. On the other hand, the barrier height for its reverse reaction (from HF + CS → HFC=S) is predicted to be 13 kcal/mol at the

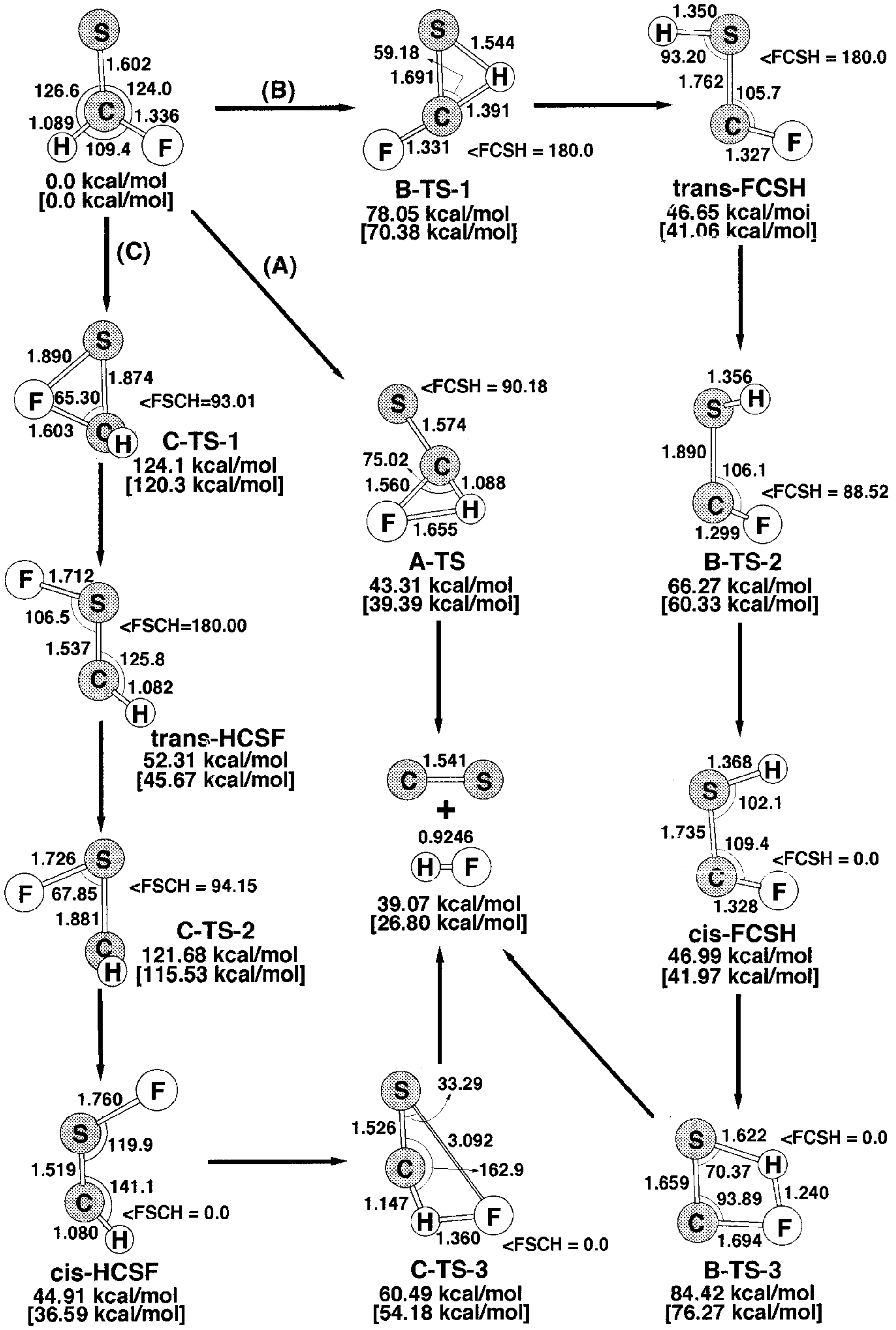


Figure 3. B3LYP/6-311G(d) optimized geometries (in Å and deg) and relative energies for the HFC=S isomers. Values in brackets are at the CCSD(T) level of theory (see the text).

same level of theory. That is to say, the insertion of CS into HF (to give HFC=S) requires less activation energy than the dissociation of HFC=S, implying that this reaction should be energetically feasible.

Second, as for the isomerization of the doubly bonded to the divalent species, the relevant transition structures were located. For instance, The HFC=S → FCSH isomerization (i.e., reaction (B)) via **B−TS−1** is predicted to possess a sizable energy barrier of 70 kcal/mol with respect to HFC=S. This means that the 1,2-H shifted reaction is energetically unfavorable and would be highly endothermic (+27 kcal/mol) if it occurs. We thus conclude that the FCSH species cannot exist. Moreover, a similar phenomenon can also be found in the HFC=S → HCSF isomerization (i.e., reaction (C)), which proceeds via **C−TS−1** and needs 120 kcal/mol relative to HFC=S. As one can see in Figure 4, since the barrier for isomerization from HFC=S to *trans*-HCSF (120 kcal/mol) is significantly higher than the reaction barrier from the *trans*-HCSF to the *cis*-HCSF, HFC=S should be stable from a kinetic point of view.

Third, there still remain two possible pathways for the unimolecular destruction of HFC=S, that is, radical dissociations that lead to FCS• + H• and HCS• + F•. As Figure 4 shows, the former reaction proceeds with a sizable barrier of 97 kcal/mol, while the energy required for the latter reaction is expected to be 110 kcal/mol. All of these results confirm that HFC=S is stable in both a kinetic and a thermodynamic sense.

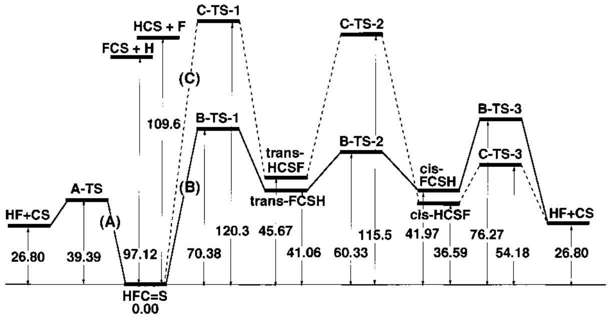


Figure 4. Potential energy surfaces for the unimolecular decomposition reactions of HFC═S. The relative energies (in kcal/mol) are taken from the CCSD(T) level as given in Table 3. For the B3LYP-optimized structures of the stationary points see Figure 3.

IV. Conclusions

The equilibrium structures, physical properties (such as vibrational spectra and rotational constants), and relative energies of the HXCS (X = H and F) isomers have been investigated using the B3LYP and CCSD(T) methods in conjugation with the 6-311G(d) and 6-311++G(3df,3pd) basis sets. The doubly bonded species (i.e., HXC═S) is found to be the most stable among the isomers, whereas both the 1,2-H shifted isomers (i.e., the XCSH isomeric form) and the 1,2-X shifted isomers (i.e., the HCSX isomeric form) are found to be the least stable. Due to the kinetic and thermal stability of HXC═S, it is conceivable that this doubly bonded species has a sufficient lifetime for spectroscopic observation. This is indeed in the case for $H_2C{=}S$, which has been detected experimentally.[31,32]

Finally, comparison of the decomposition pathways of HXC═S (X= H and F) reveals that the HX elimination path possesses the lowest barrier, whereas the 1,2-hydrogen shift and 1,2-X shift routes have the highest energy requirement and are therefore the least energetically favorable paths.

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