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Theoretical Study of Dithioformic Acid, Dithiohydroxy Carbene and Their Radical Cations: Unimolecular and Assisted Rearrangements

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The potential energy surfaces of dithioformic acid and its functional isomer, dithiohydroxy carbene, in both neutral and ionized states have been investigated using ab initio molecular orbital calculations at both (U)-MP2 and (U)QCISD(T) levels with the 6-31G(d,p) and 6-311++G(d,p) basis sets. The unimolecular decomposition of HC(=S)SH giving $H_2 + CS_2$ and H_2S + C=S, its rearrangement to HS−C−SH, and different simple bond cleavages have been examined. In both electronic states, the carbene is a stable isomer lying in a relatively deep potential well. Formation of H_2S via a one-step decomposition of acid is found to be favored over that of CS_2 whose reaction path involves a carbene intermediate. Carbene radical cations also participate as crucial intermediates in unimolecular transformation of ionized acids. Calculations on different hydrogen-bonded dimers of acid and carbene suggest that, in the dimer form, while the carbene is not stable, elimination of both H_2 and H_2S is accelerated. The role of H_2S and H_2 as possible catalysts in the acid decomposition has also been investigated. H_2S induces an efficient catalytic effect in different hydrogen transfer pathways. The standard heats of formation are estimated to be $\Delta H^\circ_{f,298}$[HC(=S)SH] = 113 ± 8 kJ/mol and $\Delta H^\circ_{f,298}$[HS−C−SH] = 267 ± 12 kJ/mol based on CCSD(T)/6-311++G(3df,2p) calculations. Adiabatic ionization energies are predicted to be IE_a(HS−C−SH) = 8.2 ± 0.3 eV and IE_a(HC(=S)SH)] = 9.0 ± 0.3 eV, and proton affinities are PA[HC(=S)SH] = 802 ± 12 kJ/mol and PA[HS−C−SH] = 956 ± 12 kJ/mol.

1. Introduction

Dithiocarboxylic acids belong to the family of chalcogenide derivatives of carboxylic acids in which both oxygens of the carboxyl group are formally replaced by sulfur atoms. While the properties of dithio esters having the connectivity R−C(=S)−S−R′ are well-known, especially as Raman resonance probes for monitoring the catalytic activities of enzymes,[1] relatively much less experimental information is available on dithio acids. The latter are in fact short-lived intermediates and cannot be generated under ordinary reaction conditions.

Dithioformic acid (referred to hereafter as DTFA), the simplest dithiocarboxylic homologue, was first generated two decades ago by Bak et al.,[2,3] and both syn and anti forms were identified by microwave spectroscopy. Subsequently, the infrared spectra of DTFA and its deuterated isotopomer were recorded[4] with low resolution in the region of 3100−475 cm^{-1}. These IR spectra have also been interpreted in terms of an equilibrium between both geometric isomers. On the basis of their fundamental vibrational frequencies, both syn and anti DTFA isomers have also been detected in the reaction of hydrogen atom and carbon disulfide (H + CS_2) in solid argon in which the major product was the *trans*-HS−C=S radical.[5] Obviously, combination of a second hydrogen atom with the primary HS−C=S radical led to the formation of DFTA. Apart from the above experimental observations, molecular properties of DTFA have mainly been derived from numerous ab initio molecular orbital calculations.[6−15] Thus, its structure, charge distribution, and conformational behavior have extensively been investigated.[8,11,13] The unimolecular rearrangement of DTFA has also been examined including the 1,2 and 1,3 shifts of the hydrogen atom as well as the loss of H_2 and H_2S.[9,10−12,14,15] In particular, Xie and co-workers[14] considered the transition structures for both reactions a and b starting from DTFA.

$$\mathrm{HC({=}S)SH} \rightarrow \mathrm{H_2S} + \mathrm{C{=}S} \qquad \text{(a)}$$

$$\mathrm{HC({=}S)SH} \rightarrow \mathrm{H_2} + \mathrm{S{=}C{=}S} \qquad \text{(b)}$$

Accordingly, the dehydrogensulfidation (a) is energetically more favorable than the dehydrogenation (b). More recently, Huang et al.[15] evaluated the rate constants of both reactions a and b using a RRKM procedure and MP4/6-311++G(d,p) relative energies. These authors confirmed the predominance of (a) over (b) (k(a) > k(b)). Nevertheless, a severe shortcoming of the two latter theoretical studies[14,15] is that all transition structures have been assumed to be planar. Such as assumption is certainly not correct because the nonmigrating hydrogen atom is expected to move out of the molecular plane[16,17] in such a way that the sulfur atom could efficiently use its lone pair in stabilizing orbital interactions.

Although the dithiohydroxy carbene HS−C−SH (referred to hereafter as DTHC), which is a high-energy isomer connected to DTFA by a formal 1,2-H shift, has been shown to lie in a relatively deep potential well,[12] participation of DTHC in the unimolecular chemistry of DTFA has not been evoked. Nevertheless, recent detection of dihydroxy carbene HO−C−OH,[18] and hydroxy thiohydroxy carbene HO−C−SH,[19] that are higher energy isomers of formic acid and monothioformic acid, respectively, suggest that a certain involvement of the carbene intermediates in the acid reactivity is probable. Therefore we

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have considered in the present study the missing link, described on the $[CH_2S_2]$ potential energy surface, between the reactivity of both DTFA and DTHC isomers.

Additional motivation for the present work is in our continuing study of gas-phase species using a combination of mass spectrometry and quantum chemical calculations, in particular in the generation and characterization of unstable neutral species by mean of neutralization−reionization mass spectrometric (NRMS) techniques.[19−24] For this purpose, knowledge on the accurate energetics of both neutral and ionized states of the relevant species is crucial. In our earlier theoretical works,[9,10] the ionized DTFA was examined, but that study was mainly devoted to the 1,3-H shift mechanism in both ground and excited states. For the sake of usefulness, a much more extended $[CH_2S_2]^{\bullet+}$ energy surface has also been constructed here. In fact, knowledge of the $[CH_2OS]^{\bullet+}$ energy surface has recently helped us to identify the $HO-C-SH^{\bullet+}/HO-C-SH$ pair of carbene upon dissociative ionization of alkylthioformates.[19,24]

It is also well-known that carboxylic acids exist in the gas phase mainly in the dimeric form involving predominantly cyclic hydrogen-bonded structures.[25] To assess further the stability of such dimers in sulfur analogues, as well as their possible participation in the acid decomposition, different hydrogen-bonded dimers of DTFA and DTHC have also been considered. The idea that the H_2O molecule, once formed upon thermal decomposition of formic acid, is going to participate as a catalyst in the elimination of H_2 was put forward several years ago[16] and tested again recently.[17] To figure out whether there is any catalytic effect of either H_2 or H_2S on the production of the other, we have also considered the supermolecules containing DTFA plus H_2 or H_2S.

2. Details of Calculations

All ab initio quantum chemical calculations were carried out using the Gaussian 94 set of programs.[25] The stationary points were initially located by geometry optimization and characterized by harmonic vibrational frequencies at the Hartree−Fock level (HF) in conjunction with the polarized 6-31G(d,p) basis set. After establishing the different minimum energy paths by analyses of the transition vectors or intrinsic reaction coordinate (IRC) calculations, geometrical parameters of the relevant equilibrium and transition structures (TS) were then reoptimized using wave functions in which electron correlation is partly introduced at the second order perturbation theory (MP2) level with the same basis functions. Improved relative energies between stationary points of the potential surfaces were subsequently obtained from single-point electronic energy calculations at the quadratic configuration interaction[26] level which includes all the single and double excitations plus a perturbative estimate for the connected triple excitations, QCISD(T), with the larger 6-311++G(d,p)[27] basis set at optimized MP2/6-31G(d,p) geometries. The zero-point vibrational energies were estimated from uniformly scaled HF/6-31G(d,p) harmonic frequencies by a factor of 0.9. For the open-shell species, the unrestricted formalism (UHF, UMP2, and UQCISD) has been utilized. In the (U)QCISD(T) calculations, only the valence electrons are incorporated in the correlation treatment. For the purpose of comparison, density functional theory has also been applied for the neutral system using the popular hybrid exchange correlation B3LYP functional,[28,29] with both 6-31G(d,p) and 6-311++G(d,p) basis sets. In the calculations on the supersystems including H_2 and H_2S, only the B3LYP treatment has been employed. Throughout this paper, bond lengths are given in angstroms, bond angles in degrees, and total energies in hartrees; zero-point and relative energies, unless otherwise noted, are in kJ/mol.

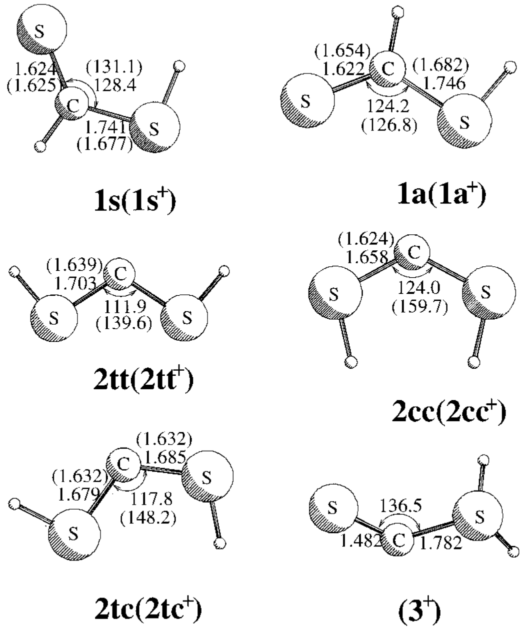

Figure 1. Selected MP2/6-31G(d,p) geometries for both syn **1s** and anti **1a** conformers of DTFA, and three conformers **2tt**, **2tc**, and **2cc** of DTHC. In parentheses are the UMP2 values for the corresponding radical cations. $\mathbf{X}^+$ stands for a radical cation corresponding to $\mathbf{X}^{\bullet+}$ in the text. For $\mathbf{3}^+$ the neutral counterpart does not exist.

3. Results and Discussion

The calculated (U)MP2/6-31G(d,p) geometries for the equilibrium structures in both neutral and ionized states are compared in Figure 1. While the transition structures (TS) on the neutral $[CH_2S_2]$ energy surface and the corresponding energy profiles are displayed in Figures 2 and 3, respectively, the corresponding ionized $[CH_2S_2]^{\bullet+}$ TS's and profiles are given in Figures 4 and 5. While DTFA exists in both syn (**1s**) and anti (**1a**) conformers, DTHC exhibits three distinct conformations, **2tt**, **2tc** and **2cc**. For a convention, $\mathbf{X}^{\bullet+}$ designates the radical cation of **X** whereas **X/Y** denotes the TS connecting both equilibrium structures **X** and **Y**. To simplify the presentation of data, geometrical parameters of the fragments and TS's for simple rotational processes are omitted. Finally, calculated total and relative energies are recorded in Table 1 for neutral structures and Table 2 for ionized structures. Results obtained for the neutral dimeric systems are summarized in Figure 6, whereas those concerning the participation of H_2 and H_2S in the decomposition of DTFA are recorded in Figure 7 as well as in Tables 3 and 4.

A. Unimolecular Rearrangement of the Neutral $[CH_2S_2]$ System. For the neutral species, geometry optimization using the B3LYP method and both 6-31G(d,p) and 6-311++G(d,p) basis functions were also carried out. In general, the B3LYP parameters do not differ significantly from the MP2/6-31G(d,p) values displayed in Figures 1 and 2. As seen in Table 1, the B3LYP relative energies are much closer to the QCISD(T) values than the MP2 ones. The changes in relative energies between both B3LYP results are far smaller than those that occurred in going from MP2 to QCISD(T). As expected, the one-electron basis set effect is relatively small in DFT calculations. The values given in Figure 2 and quoted in this section correspond thus to the estimates derived from QCISD(T)/6-311++G(d,p) + ZPE calculations. The relative stabilities between $[CH_2S_2]$ species have been repeatedly determined using

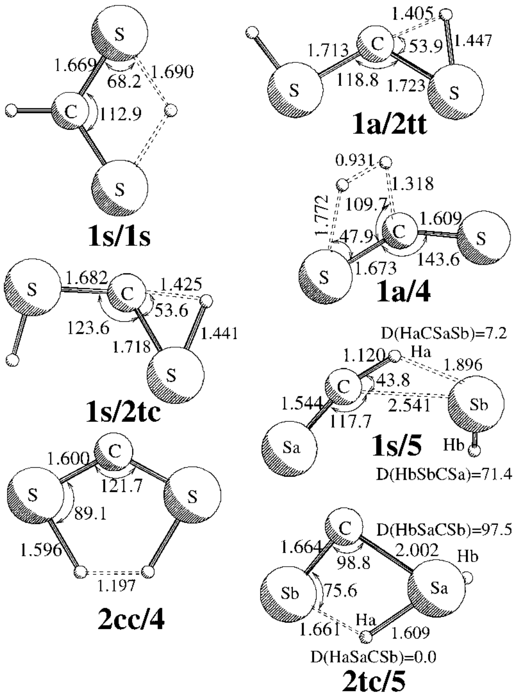

Figure 2. Selected MP2 geometries of transition structures (TS) on the neutral [CH_2S_2] potential energy surface. **X/Y** stands for a TS linking both equilibrium structures **X** and **Y**.

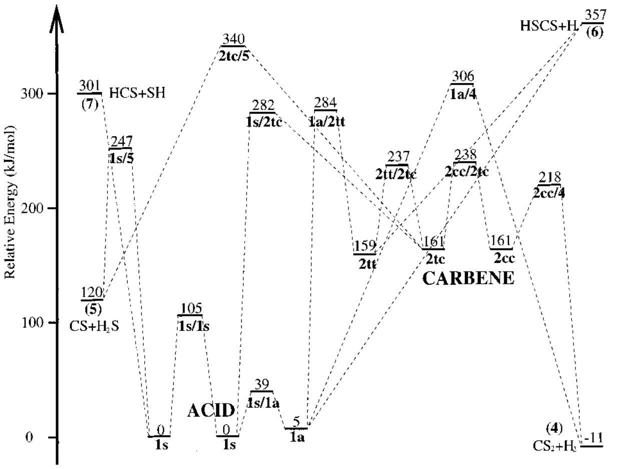

Figure 3. Schematic potential energy profiles showing unimolecular rearrangements of neutral DTFA and DTHC. Relative energies are obtained from QCISD(T)/6-311++G(d,p) + ZPE calculations.

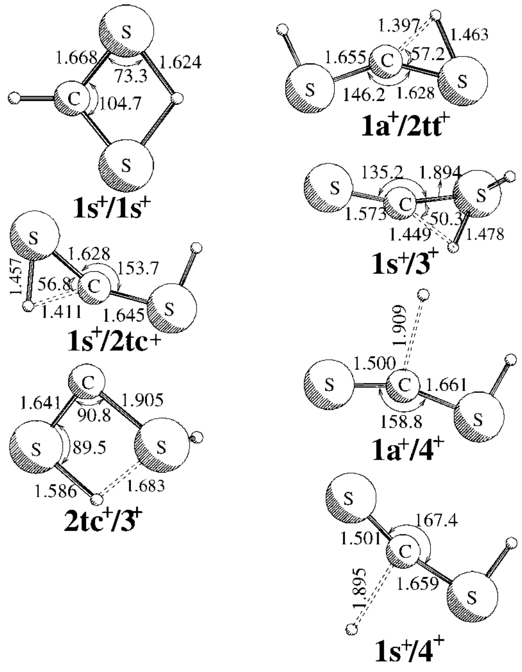

Figure 4. Selected UMP2/6-31G(d,p) geometries of transition structures (TS) on the ionized [CH_2S_2]$^{\bullet+}$ potential energy surface.

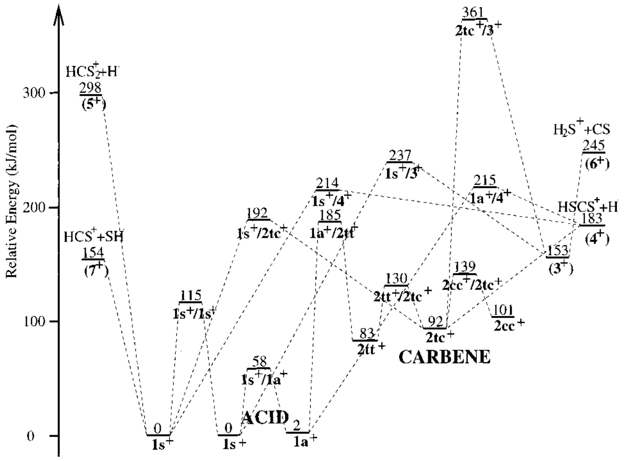

Figure 5. Schematic potential energy profiles showing interconnections between ionized DTFA and DTHC. Relative energies obtained from UQCISD(T)/6-311++G(d,p) + ZPE calculations.

different methods and abundantly commented on in previous studies.[6−15] Here, our discussion is mainly focused on the unimolecular decomposition of DTFA and DTHC as shown in Figure 3, from which a number of points could be noted:

(i) The energy for DTHC **2** is rather high, being about 160 kJ/mol above that of DTFA **1**. All the conformers of **2** have similar energetic content and lie even higher than the fragments H_2S + C=S **5** (being 120 kJ/mol above **1s**). The fragments H_2 + S=C=S **4** turn out to be the lowest-lying point on the energy surface. The radical fragments arising from simple homolytic bond cleavages are much higher in energy, namely 301 kJ/mol for HC=S + SH **7** and 357 kJ/mol for HS−C=S + H **6**. Thus, the C−SH bond of **1** is somewhat weaker than the C−H bond.

(ii) The rotation of H atoms around the C−S bond connecting the syn/anti or cis/trans isomers becomes more difficult to achieve in carbene than in acid, indicating stronger C−S bonds. In fact the barrier to rotation increases from 39 kJ/mol in **1s** to 78 kJ/mol in **2tt**. The higher energy conformers intervene in various fragmentations when they have appropriate nuclear disposition.

(iii) The tautomerization of DTFA by a 1,3 shift of hydrogen via **1s/1s** is associated with an energy barrier of 105 kJ/mol, which is larger than the rotational barrier but far smaller than those of other dissociative processes. This 1,3-H shift can eventually be probed in labeled species such as

$$CS^* + H_2S \leftarrow H{-}C({=}S^*)SH \rightleftarrows H{-}C({=}S)S^*H \rightarrow CS + H_2S^*$$

(iv) Starting from DTFA **1s**, elimination of H_2S via **1s/5** requires a smaller activation energy (247 kJ/mol) than a direct elimination of H_2 via **1a/4** (306 kJ/mol). The fact that direct dehydrogensulfidation is favored over direct dehydrogenation is in qualitative agreement with earlier studies.[14,15] The main difference from earlier results concerns rather the geometry of the TS **1s/5** which was incorrectly assumed to be planar.[14,15]

TABLE 1: Calculated Total (hartrees), Zero-Point, and Relative Energies (kJ/mol) of the Neutral [CH_2S_2] System Considered

	total energy			relative energy			
structure	QCISD(T)/ 6-311++G** [a]	B3LYP/ 6-311++G** [b]	ZPE HF/6-31G** [c]	MP2/ 6-31G** [d]	QCISD(T)/ 6-311++G** [d]	B3LYP/ 6-31G** [e]	B3LYP/ 6-311++G** [e]
1s	−834.550 12	−835.736 93	74.2	0	0	0	0
1a	−834.547 83	−835.733 90	73.5	7	5	7	6
2tt	−834.486 69	−835.671 84	66.0	198	159	174	170
2cc	−834.485 78	−835.672 07	64.9	197	161	168	169
2tc	−834.485 86	−835.671 70	65.5	198	161	172	170
4: S=C=S + H_2	−834.544 92	−835.732 12	46.8	−37	−11	−14	−12
5: C=S + H_2S	−834.496 56	−835.672 03	51.3	150	120	163	148
6: HS−C=S + H	−834.402 32	−835.587 51	39.8	362	357	368	362
7: HC=S + SH	−834.426 97	−835.617 97	49.2	336	301	299	291
1s/1s	−834.506 62	−835.696 07	64.2	108	105	96	99
1s/1a	−834.533 91	−835.716 40	70.7	44	39	50	50
1a/2tt	−834.434 99	−835.621 91	54.1	317	284	294	301
1s/2tc	−834.435 33	−835.622 75	53.1	315	282	291	298
2tt/2tc	−834.455 74	−835.638 77	61.6	285	237	257	256
2cc/2tc	−834.455 01	−835.638 56	61.0	285	238	256	257
1a/4: **TS1** H_2-loss	−834.425 98	−835.619 64	52.0	310	306	288	284
2cc/4: **TS2** H_2-loss	−834.459 25	−835.645 34	51.5	252	218	229	219
1s/5: **TS1** H_2S-loss	−834.449 19	−835.640 25	54.7	263	247	244	236
2tc/5: **TS2** H_2S-loss	−834.412 54	−835.736 93	51.0	394	340	355	342

[a] Based on MP2/6-31G(d,p) geometries. [b] Based on B3LYP/6-311++G(d,p) geometries. [c] Unscaled ZPE obtained from HF/6-31G(d,p) vibrational wavenumbers. [d] At the level indicated plus ZPE (HF) corrections scaled down by a uniform factor of 0.9. [e] At the indicated level with corresponding geometries and ZPE obtained from B3LYP/6-31G(d,p) vibrational wavenumbers and scaled by 0.97.

TABLE 2: Calculated Total (hartrees), Zero-Point, and Relative Energies (kJ/mol) of the [CH_2S_2]$^{\bullet+}$ Radical Cations Considered

			relative energy[c]	
structure	UQCISD(T)/ 6-311++G** [a]	ZPE[b]	UMP2/ 6-31G**	UQCISD(T)/ 6-311++G**
$1s^{\bullet+}$	−834.233 02	73.6	0	0
$1a^{\bullet+}$	−834.232 20	73.2	2	2
$2tt^{\bullet+}$	−834.198 15	64.2	97	83
$2cc^{\bullet+}$	−834.191 20	63.3	115	101
$2tc^{\bullet+}$	−834.194 68	63.8	106	92
$3^{\bullet+}$	−834.171 73	64.8	185	153
4$^{\bullet+}$: HS−C=S^+ + H	−834.152 39	41.5	154	183
5$^{\bullet+}$: HCS_2+ + H	−834.110 34	46.3	284	298
6$^{\bullet+}$: H_2S^+ + C=S	−834.131 81	50.2	242	245
7$^{\bullet+}$: HC=S^+ + SH	−834.169 00	57.9	97	154
8$^{\bullet+}$: [C=SH]$^+$ + SH	−834.048 04	44.2	453	459
9$^{\bullet+}$: SH^+ + HC=S	−834.008 67	48.8	642	567
$1s^{\bullet+}/1s^{\bullet+}$	−834.185 30	61.6	137	115
$1s^{\bullet+}/1a^{\bullet+}$	−834.208 86	67.9	87	58
$1a^{\bullet+}/2tt^{\bullet+}$	−834.155 34	52.9	200	185
$1s^{\bullet+}/2tc^{\bullet+}$	−834.152 67	52.3	207	192
$2tt^{\bullet+}/2tc^{\bullet+}$	−834.179 67	62.3	158	130
$2cc^{\bullet+}/2tc^{\bullet+}$	−834.175 99	61.5	168	139
1s$^{\bullet+}$/**4**$^{\bullet+}$: **TS1** H-loss	−834.141 64	45.0	240	214
1a$^{\bullet+}$/**4**$^{\bullet+}$: **TS2** H-loss	−834.141 26	44.7	245	215
$1s^{\bullet+}/3^{\bullet+}$	−834.135 69	52.4	250	237
$2s^{\bullet+}/3^{\bullet+}$	−834.087 74	50.8	424	361

[a] Based on UMP2/6-31G(d,p) optimized geometries. [b] Unscaled zero-point energies obtained from UHF/6-31G(d,p) harmonic vibrational wavenumbers. [c] Including ZPE corrections scaled down by a uniform factor of 0.9. The UMP2 total energy of **1s**$^{\bullet+}$ is −834.09879 hartrees.

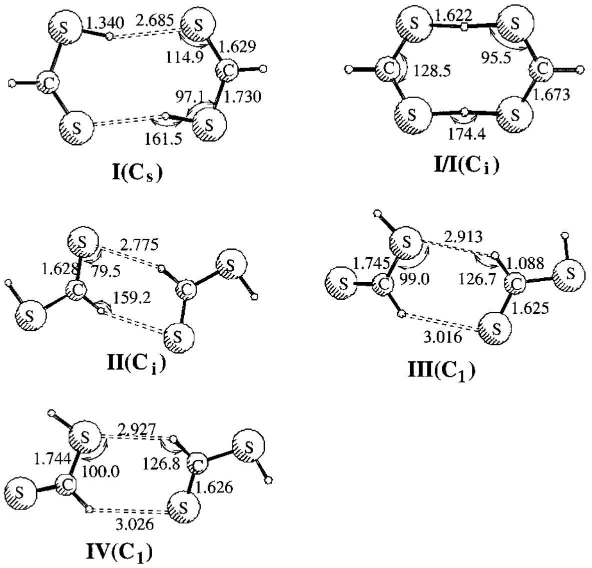

Figure 6. Selected MP2/6-31G(d,p) optimized geometries for hydrogen-bonded dimers of DTFA **1**.

As seen in Figure 2, TS **1s/5** is actually not planar; the nonmigrating hydrogen atom lies well out of the molecular CSS plane. The planar structure reported in refs 14 and 15 possesses in reality *two* negative vibrational frequencies; the lower of the two imaginary modes corresponds obviously to a rotation of the SH moiety. Nevertheless, the energetic consequence is rather small. Separate geometry optimization at the MP2/6-311G(d,p) level indicates that the difference between both planar and nonplanar stationary points amounts to only 8 kJ/mol in favor of the nonplanar TS **1s/5**.

(v) Direct elimination of H_2 from DTFA **1** is *less* favored than an eliminative process involving DTHC **2**. This is due to the fact that a dehydrogenation from a carbene via the highly symmetrical TS **2cc/4** is a facile process requiring only 57 kJ/mol starting from **2cc**. Thus, the multistep route, either **1s** → **2tc** → **2cc** → **4** or **1s** → **1a** → **2tt** → **2tc** → **2cc** → **4** giving finally the fragments **4**, in which the acid → carbene conversion is the determining step, is calculated to be less energy demanding than the direct one-step route via **1a/4**. The energy of the latter lies about the dissociation limit **7**. Overall, the difference in activation energies between both eliminations of H_2 via **1s/2tc** and H_2S via **1s/5** amounts to 35 kJ/mol.

(vi) As mentioned above, DTHC **2** is not quite stable with respect to H_2-elimination giving **4**. The carbene lies thus in a potential well of only 50−60 kJ/mol. Note that a direct H_2S-elimination from **2** is less favored than an indirect route implying **1**.

In summary, the most significant chemical result is that, in the unimolecular decomposition of DTFA, while dehydrogensulfidation is the most favored process, its dehydrogenation tends to involve DTHC as intermediate.

B. Unimolecular Rearrangement of the Ionized $[CH_2S_2]^{\bullet+}$ System. As far as we are aware, only the 1,3-H shift in both π and σ states of ionized DTFA has been reported by us in previous papers.[9,10] In general, the energy ordering of isomers is profoundly modified following ionization. While ionized DTFA $\mathbf{1}^{\bullet+}$ remains more stable than ionized DTHC $\mathbf{2}^{\bullet+}$, the energy difference is reduced by half in going from 159 kJ/mol in the pair **2**−**1** to 83 kJ/mol in the pair $\mathbf{2}^{\bullet+}-\mathbf{1}^{\bullet+}$. The positions of the fragments are also modified. Relative to $\mathbf{1}^{\bullet+}$, while $HC{=}S^+ + SH$ $\mathbf{7}^{\bullet+}$ and $HS{=}C{=}S^+ + H$ $\mathbf{4}^{\bullet+}$ are strongly stabilized, $CS + H_2S^{\bullet+}$ $\mathbf{5}^{\bullet+}$ is markedly destabilized. This comes from the fact that the ionization energies (IE_a) of the HC═S and HS−C═S radicals are much smaller than those of **1** and H_2S. Of particular interest is the emergence of the ion $\mathbf{3}^{\bullet+}$, for which a stable neutral counterpart does not exist. In fact, structure $\mathbf{3}^{\bullet+}$ results formally from both the neutral CS and ionic $H_2S^{\bullet+}$ fragments $\mathbf{6}^{\bullet+}$ whose interaction gives rise to a strong one-electron C−S bond. Although the C−S distance in $\mathbf{3}^{\bullet+}$ is about 0.1 Å longer than those of other ions, $\mathbf{3}^{\bullet+}$ lies about 92 kJ/mol below $\mathbf{6}^{\bullet+}$. While $\mathbf{3}^{\bullet+}$ is quite stable with respect to rearrangement to $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ through 1,3-H and 1,2-H shift, respectively, it is rather unstable relative to the loss of a hydrogen atom yielding $HS{-}C{=}S^+ + H$ $\mathbf{4}^{\bullet+}$. An attempt to locate a TS for H-loss leading $\mathbf{3}^{\bullet+}$ to $\mathbf{4}^{\bullet+}$ was not successful, suggesting that this process is also barrier-free.

Regarding the barriers to rotation, they are apparently enlarged in $\mathbf{1}^{\bullet+}$ but reduced in $\mathbf{2}^{\bullet+}$, relative to the corresponding neutral systems. In agreement with earlier observations,[9,10] the barrier for 1,3-H shift is actually increased by 10 kJ/mol upon ionization. Nevertheless, the TS's for both isomerizations remain lower in energy than those of other processes.

Starting from ionized DTFA $\mathbf{1}^{\bullet+}$, the least-demanding fragmentation turns out to be the simple C−SH bond cleavage producing $HC{=}S^+ + SH$ $\mathbf{7}^{\bullet+}$. The loss of hydrogen atom is possible via two distinct routes, namely a direct elimination via $\mathbf{1s}^{\bullet+}/\mathbf{4}^{\bullet+}$ and/or $\mathbf{1a}^{\bullet+}/\mathbf{4}^{\bullet+}$ and a two-step route implying an initial rearrangement to DTHC $\mathbf{2}^{\bullet+}$. Due to the fact that both the TS for 1,2-H shift $\mathbf{1s}^{\bullet+}/\mathbf{2tc}^{\bullet+}$ and the fragments $HS{-}C{=}S^+ + H$ $\mathbf{4}^{\bullet+}$ are lying below both TS's $\mathbf{1s}^{\bullet+}/\mathbf{4}^{\bullet+}$ and $\mathbf{1a}^{\bullet+}/\mathbf{4}^{\bullet+}$, the two-step route is favored by about 22 kJ/mol over the direct elimination. Despite extensive attempts, we have failed to locate a TS for H-loss from carbenes $\mathbf{2}^{\bullet+}$; for example, any attempt to lengthen the S−H bond from the carbene $\mathbf{2tc}^{\bullet+}$ leads to TS $\mathbf{2tc}^{\bullet+}/\mathbf{3}^{\bullet+}$ which is a quite high-lying structure. Therefore, it seems reasonable to assume that the H-loss from this carbene ion is barrier-free.

The stability of the carbene isomer is substantially enhanced following ionization in the sense that the ion $\mathbf{2}^{\bullet+}$ now lies in a deeper potential well of about 90 kJ/mol, as compared with 60 kJ/mol of **2** (cf. Figure 3). The main fragmentation of $\mathbf{2}^{\bullet+}$ is a loss of hydrogen (cf. Figure 5). Overall, the DTHC radical cation $\mathbf{2}^{\bullet+}$ is a reasonable candidate for a generation and characterization by mass spectrometric methods. Carbene ions bearing large substituents are expected to be even more stabilized. Once a carbene ion could be generated from an appropriate precursor, for example in the cell of a mass spectrometer, the corresponding neutral carbene might also be generated and identified in the framework of a neutralization−reionization (NRMS) experiment.

In summary, the results obtained for the ionized species point toward, on the one hand, a more facile fragmentation process of ionized DTFA giving primarily the $HC{=}S^+ + SH$ fragments. On the other hand, they demonstrate a stabilization of the isomeric carbene isomer $\mathbf{2}^{\bullet+}$ following ionization and a participation of the latter as key intermediates in the second most important decomposition channel of the acid ion $\mathbf{1}^{\bullet+}$.

C. Dimers of Neutral Dithioformic Acid. It is well-known that carboxylic acids exist in dimeric forms owing to the formation of strong hydrogen bonded complexes. Recently, Lin and co-workers[17] suggested, on the basis of quantum chemical calculations, that several bimolecular processes are involved in the thermal decomposition of formic acid, including those of its dimers. To probe such a possibility in the case of the sulfur analogue, we have considered the various dimers of DTFA. While the geometries were determined at the MP2/6-31G(d,p) level (Figure 6), complexation energies were evaluated using single-point QCISD(T) calculations of electronic energies with both 6-31G(d,p) and 6-311++G(d,p) basis sets.

It is well-known that sulfur atoms are weak hydrogen bond donors. Therefore, the dimeric complexes of DTFA **1** have rather small complexation energies of about −20 kJ/mol. It is worth noting that complex **I** involving S−H···S hydrogen bonds and complexes **II**, **III**, and **IV** each involving the C−H···S hydrogen bonds, have comparable stability.

The TS **I/I** has a nonplanar geometry but a C_i symmetry in which the S-atoms are slightly distorted out of the molecular plane, and corresponds to a double migration of the hydrogen atoms. The energy barrier amounts to 58 kJ/mol relative to the dimer **I**. Compared with the barrier of 105 kJ/mol for 1,3-H shift in DTFA monomer **1s**, the hydrogen transfer is again found to be accelerated in the dimeric form. Apart from **I/I**, we were not able, despite extensive attempts, to locate other TS's related to the elimination of H_2 or H_2S from the dimers.

Complex **II** has the right molecular configuration for the double H-migration giving a dimer of DTHC **2**. However, such a carbene dimer could not be located. This suggests that the carbene isomer does not exist in the dimeric form. Similarly, both complexes **III** and **IV** appear to be starting points for an elimination of CS and H_2S, but the relevant TS's could not be found.

D. Decomposition of Dithioformic Acid Assisted by H_2 and H_2S. As stated in the Introduction, there is still interest in the water-assisted decomposition mechanism of formic acid.[16,17] Accordingly, during the thermal decomposition of formic acid in the gas phase, water molecules once formed in the dehydration channel ($HC({=}O)OH \rightarrow H_2O + C{=}O$) might participate as catalysts in the dehydrogenation step ($HC({=}O)OH + H_2O \rightarrow H_2 + CO_2 + H_2O$). Lin and co-workers[17] observed from a kinetic analysis based on ab initio results of structures and energies that the rate constants of both dehydration and dehydrogenation reactions are greatly enhanced with the presence of a water molecule in the supermolecule. In an attempt to further probe this mechanism, we have considered the possible involvement of H_2S and H_2 in both major decomposition channels of DTFA **1**. Let us recall that, in the monomeric system (Figure 3), the dehydrogensulfidation channel ($HC({=}S)SH \rightarrow H_2S + C{=}S$) is by far favored over the dehydrogenation ($HC({=}S)SH \rightarrow H_2 + CS_2$), even though both channels require high activation energiers. The calculated results using the B3LYP method with both 6-31G(d,p) and 6-311++G(d,p) basis sets are summarized in Figure 7 and Tables 3 and 4. In total, we have located eight distinct TS's, labeled from **TS1** to **TS8**, with the presence of either one H_2 or one H_2S molecule in the supersystem. While **TS1**−**TS3** correspond to the presence of H_2 in the eliminative processes, **TS4**−**TS8** correspond to that of H_2S. The following points can be noted:

(i) Both H_2S eliminations from DTFA with the presence of H_2 through **TS1** and **TS2** are not competitive with respect to

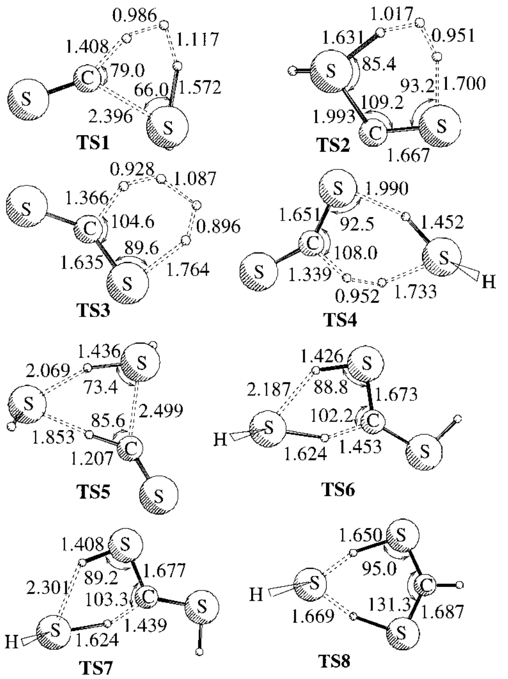

Figure 7. B3LYP/6-311++G(d,p) geometries of transition structures for processes including the presence of H_2S or H_2.

TABLE 3: Total (E + 836.0 hartrees), Zero-Point, and Relative Energies (kJ/mol) of the [CH_2S_2] Neutral Rearrangements Assisted by H_2 Considered at the B3LYP Level

structure	B3LYP/6-31G**	B3LYP/6-311++G**	ZPE [b]
1s + H_2	−0.849 52 (0)[a]	−0.915 96 (0)	95.3
1a + H_2	−0.846 65 (7)	−0.913 47 (6)	94.6
SCS + $2H_2$	−0.845 95 (−14)	−0.911 69 (−12)	71.6
CS + H_2S + H_2	−0.779 47 (163)	−0.851 60 (148)	74.1
TS1 H_2S-loss	−0.723 27 (325)	−0.791 07 (322)	88.8
TS2 H_2S-loss	−0.692 68 (405)	−0.764 08 (392)	88.3
TS3 H_2-loss	−0.756 32 (241)	−0.823 71 (239)	91.9

[a] Total energy and in parentheses are relative energy including ZPE corrections scaled down by a uniform factor of 0.97. [b] Unscaled zero-point energies obtained from B3LYP/6-31G(d,p) harmonic vibrational wavenumbers.

TABLE 4: Total (E + 1235.0 hartrees), Zero-Point, and Relative Energies (kJ/mol) of the [CH_2S_2] Neutrals Catalyzed by H_2S Calculated Using B3LYP Method

structure	B3LYP/6-31G**	B3LYP/6-311++G**	ZPE[b]
1s + H_2S	−0.062 61 (0)[a]	−0.159 04 (0)	108.3
1a + H_2S	−0.059 74 (7)	−0.156 55 (6)	107.6
SCS + H_2 + H_2S	−0.059 04 (−14)	−0.154 77 (−12)	84.6
CS + $2H_2S$	+0.007 44 (163)	−0.094 68 (148)	87.1
TS4 H_2-loss	+0.014 62 (192)	−0.081 00 (194)	97.3
TS5 H_2S-loss	+0.029 14 (228)	−0.067 57 (228)	95.4
TS6	+0.003 93 (165)	−0.092 81 (165)	98.7
TS7	+0.002 28 (162)	−0.094 55 (161)	99.7
TS8	−0.044 76 (42)	−0.138 58 (49)	103.1

[a] Total energy and in parentheses is relative energy included ZPE corrections down by a uniform factor of 0.97. [b] Unscaled zero-point energies obtained from B3LYP/6-31G(d,p) harmonic vibrational wavenumbers.

the unimolecular process. The energy barriers are actually increased from 236 kJ/mol via TS **1s/5** (B3LYP values, Table 1) to 322 and 392 kJ/mol via **TS1** and **TS2**, respectively.

(ii) In contrast, H_2-elimination is slightly favored by the assistance of H_2. The relevant energy barrier is in fact decreased from 284 kJ/mol via **1a/4** to 239 kJ/mol via **TS3** (cf. Tables 1 and 3, B3LYP/6-311++G(d,p) values). Note that in **TS3** both H_2 molecules form a chain of four hydrogen atoms with nearly equal distances. The catalytic effect, small but real, comes presumably from a stronger stabilizing interaction within the $H_2\cdots H_2$ moiety in **TS3**. Conversely, the hydrogenation of CS_2 giving DTFA is also accelerated upon addition of $(H_2)_2$ via **TS3**.

(iii) The acid−acid tautomerization is markedly accelerated by the assistance of H_2S. The hydrogen transfer via **TS8** is now associated with an energy barrier of only 48 kJ/mol, in comparison with that of 99 kJ/mol via TS **1s/1s**. **TS8** is in fact a six-membered ring in which the hydrogen transfer is greatly facilitated by a proton relay mechanism.[31−33]

(iv) The acid−carbene interconversion is also strongly favored through **TS6** and **TS7** where the barrier height is put down substantially from 298 kJ/mol through **1s/2tc** to 165 kJ/mol through **TS6**, or similarly from 301 kJ/mol via **1a/2tt** to 161 kJ/mol through **TS7**. As in the previous case (cf. point iii), the 1,2-H shift is now replaced by a concerted motion of two protons within five-membered cyclic TS's. Such a mechanism is again well-known as bifunctional acid−base catalytic process.[31−33]

(v) Finally, the assistance of H_2S in the elimination of H_2 and H_2S from DTFA is illustrated in both **TS4** and **TS5**, respectively. In **TS4**, one H_2S hydrogen atom interacts with the C−H hydrogen of the *anti*-DTFA **1a,** to form the molecular hydrogen, whereas the H_2S sulfur atom comes to capture the S−H hydrogen. Within the six-membered cyclic **TS4,** both H_2 and H_2S molecules are not completely formed, the H−H distance being 0.952 Å and the S−H distance being 1.452 Å. When **TS4** is passed, the products generated are H_2, CS_2, and H_2S. Thus, hydrogen sulfide clearly plays the role of a catalyst. However, the reduction of the associated barrier height is not as large as in previous cases. The barrier for H_2-loss of 194 kJ/mol via **TS4,** which is reduced by up to 90 kJ/mol relative to that of the unimolecular elimination through **1a/4,** remains substantial. In addition, **TS4** still lies higher in energy than **TS6** discussed above, implying that the assisted formation of DTHC **2** remains favored. As demonstrated in a previous section, an H_2-loss from a carbene **2** is energetically less demanding than that via **TS4**. Thus, with or without the assistance of H_2S, the two-step channel via its carbene isomer **2** remains open for dehydrogenation of DTFA **1**.

(vi) A H_2S-assisted dehydrogensulfidation channel is also possible via **TS5** in which H_2S gives one hydrogen but captures the C−H hydrogen of DTFA. At the end, DTFA is decomposed into CS and H_2S. In this case, the catalytic effect is not important; the corresponding energy barrier via **TS5** is only marginally favored, by 8 kJ/mol, over that of the direct unimolecular process involving **1s/5** (228 versus 236 kJ/mol).

In summary, the present calculations point out that the role of H_2S as a possible catalyst seems to be greater than that of H_2, in particular for the dehydrogenation channel (HC(═S)SH + H_2S → H_2 + CS_2 + H_2S). Regarding the dehydrogensulfidation of DTFA, intervention of its DTHC isomer still persists. Note that a proton relay process which ultimately catalyzes the proton transfer from one heavy atom to the other is a frequent and well-established phenomenon in aqueous systems. Involvement of a water chain also leads to a further reduction of the barrier either in gas phase or in solution.[31] It is apparent that hydrogen sulfide also induces such a catalytic effect but at a lesser extent.

E. Some Thermochemical Parameters of DTFA and DTHC. We take this opportunity to compile some useful thermochemical parameters of both isomers **1** and **2**. Regarding the ionization energies, QCISD(T)/6-311++G(d,p) energies listed in Tables 1 and 2 yield values of 8.6 and 7.8 eV for IE_a

of **1s** and **2tt**, respectively. Due to the fact that most MO methods tend to underestimate the ionization energies with respect to accurate experimental values, it is simple to apply a systematic and appropriate correction to the calculated results in order to obtain more realistic values for this quantities.[32] Such a correction accounts for the effect of basis set completeness and the inbalance in treating the electron correlation in both closed-shell and open-shell systems. At the QCISD(T)level, we have found that a systematic correction of 0.3−0.4 eV needs to be added to the computed IE_a.[34] Application of a systematic correction of +0.4 eV to the above values leads the values to 9.0 and 8.2 eV. The former value is thus consistent with an earlier estimate[9] of $IE_a[HC(=S)SH] = 9.07$ eV. In this context, the value $IE_a[HS-C-SH] = 8.2$ eV can be proposed, with a probable error of ± 0.3 eV.

Thiohydroxy carbene exhibits a singlet ground state. Due to the fact the parent carbene CH_2 has a triplet ground state[35] and a singlet−triplet separation gap (ΔE_{S-T}) about 38 kJ/mol, it is of interest to compare this quantity of related carbenes. Using B3LYP/6-311++G(d,p) + ZPE calculations, the ΔE_{S-T} are evaluated as follows (values given in kJ/mol; a negative value corresponds to a singlet ground state): H_2C, +48; HC−OH, −94; HC−SH, −67; HO−C−OH, −226; HO−C−SH, −146; HS−C−SH, −107. Higher level CCSD(T)/6-311++G(3df,2p) calculations also provide a similar ordering: CH2, +40; HC−OH, −104; HC−SH, −78 kJ/mol. It is clear that the effect of a thiohydroxyl (SH) group is significantly smaller than of its hydroxyl counterpart (OH) in stabilizing singlet carbenes.

The standard heat of formation ($\Delta H^\circ_{f,298}$) of DTFA can be evaluated using the calculated heats of exchange reactions c and d along with experimental values for reference species:

$$HC(=S)SH + 2H_2O \rightarrow HC(=O)OH + 2H_2S \tag{c}$$

$$HC(=S)SH + H_2 \rightarrow H_2C=S + H_2S \tag{d}$$

Using CCSD(T)/6-311++G(3df,2p) energies based on MP2/6-31G(d,p) geometries and ZPE (MP2) and thermal corrections, the heats of reaction amount to −54 and −13 kJ/mol for (c) and (d), respectively. The heats of formation [$\Delta H^\circ_{f,298}$ (kJ/mol)] of other species have been chosen as follows: H_2O, −241.8;[36] H_2S, −20.5[36]; $H_2C=S$, 114.4.[37] Thus, the corresponding value for DTFA **1** evaluated as 118 kJ/mol via (c) and 108 kJ/mol via (d) is thus internally consistent. The deviation of 10 kJ/mol between both estimated values is due no doubt to the larger uncertainty on the experimental value for $H_2C=S$. Using the average of the two as the best estimate, we can thus propose $\Delta H^\circ_{f,298}[HC(=S)SH] = 113$ kJ/mol with a probable error of ±8 kJ/mol.

Considering an energy difference of 154 kJ/mol between DTFA **1** and DTHC **2** computed from CCSD(T)/6-311++G-(3df,2p) plus zero-point and thermal corrections, the corresponding quantity for the latter is $\Delta H^\circ_{f,298}(HS-C-SH) = 267$ kJ/mol, likely with a larger error bar than that of ±12 kJ/mol. The proton affinity at the thiocarbonyl sulfur atom of DTFA has also been computed using CCSD(T)/6-311++G(3df,2p) electronic energies with ZPE corrections. For this quantity, we have obtained $PA[HC(=S)SH] = 802$ kJ/mol. Compared with the corresponding value of thioformaldehyde $PA(H_2C=S) = 760$ kJ/mol, the S-center becomes thus more basic (by 42 kJ/mol) upon substitution of H by a SH group. The proton affinity of DTHC amounts to $PA(HS-C-SH) = 956$ kJ/mol.

4. Summary

A number of chemically interesting results emerge in the present theoretical study using ab initio MO and DFT calculations on the unimolecular and assisted reactivity of dithioformic acid and dithiohydroxy carbene:

(i) In the unimolecular decomposition of DTFA, the major channel is confirmed to be a dehydrogensulfidation ($HC(=S)SH \rightarrow C=S + H_2S$) followed by a dehydrogenation. In the latter, a two-step decomposition involving the higher energy DTHC **2** isomer becomes favored over a direct elimination from DTFA **1**.

(ii) Following ionization, the carbene isomer is stabilized appreciably and ionized DTHC is again found to be involved in the fragmentation processes of ionized DTFA, namely in the H-losses. However, the C−SH bond cleavage giving $HC=S^+ + SH$ becomes now the energetically least demanding step. A peak at *m*/*z* 45 is thus expected to be the major one in the mass spectra of DTFA, followed by a peak at *m*/*z* 77. Conversely, the H-loss is the most facile fragmentation in ionized DTHC. It seems that DTHC **2** could be detected and characterized in a neutralization−reionization mass spectrometric (NRMS) experiment.[18,19] We note that cyclic dithiocarbenes have been evoked as intermediates in a number of cases.[38]

(iii) DTFA undergoes self-association giving rise to various weak dimeric forms having a similar energy content, with complexation energy of about −20 kJ/mol. Nevertheless, these dimers apparently do not play an important role in the thermal decomposition of DTFA.

(iv) In contrast, the H_2S molecule is demonstrated to play a clear-cut role as a catalyst in distinct reaction channels including the tautomerization (1,3-H shift), acid−carbene interconversion (1,2-H shift), dehydrogenation (H_2-loss), and dehydrogensulfidation (H_2S-loss). The most marked catalytic effect of H_2S occurs in the acid−carbene interconversion and, to a lesser extent, in the H_2-emlimination.

(v) Finally, any kinetic treatment on the thermal decomposition of DTFA needs to consider most of the following channels in order to account for the dissociation mechanism and to estimate more accurate rate constants of the unimolecular process:

$$HC(=S)SH \rightarrow H_2S + C=S$$

$$HC(=S)SH \rightarrow HS-C-SH \rightarrow H_2 + S=C=S$$

$$HC(=S)SH \rightarrow H_2 + S=C=S$$

$$HC(=S)SH + H_2S \rightarrow H_2 + S=C=S + H_2S$$

$$HC(=S)SH + H_2S \rightarrow HS-C-SH + H_2S$$

$$HC(=S)SH + H_2S \rightarrow 2H_2S + C=S$$

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