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β-elimination mechanism of trifluoro[fluoro(methyl)germyl]silane: A theoretical study

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Abstract: In this research work, β- elimination mechanisms of trifluoro[fluoro(methyl)germyl]silane (**1**) to difluoro(methylgermylene)silane (**2**), difluoro[fluoro(methyl)germylene]silane (**3**) and difluoro(fluorogermylene)silane (**4**) were investigated using Density Functional Theory (DFT) and B3LYP method with 3-21G basis set. The vibrational analysis showed that all structures correspond to local minima in potential energy surface. Study on the B3LYP/3-21G level of theory revealed that the required energy for the decomposition of compound (**1**) to compounds (**2**), (**3**) and (**4**) are 25.3456, 21.7248 and 17.2489 kcal mol^{-1}, respectively. Natural Bond Orbital (NBO) population has been calculated and analyzed. The analysis of these data showed that, transition states of all elimination reactions have a four-centered transition structure and single bonds of Si-F and Ge-A (A; F, H, CH$_2$) in reactant are broken and π-bond of Ge-Si and single bond of F-A (A; F, H, CH$_2$) are appear, as will. Also the zero-point vibrational energy (ZPE) for all compounds shows that relative thermal stability of difluoro[fluoro(methyl)germylene]silane (**3**) is higher than other compounds.

Keywords: DFT; β-Elimination; NBO, Trifluoro[fluoro(methyl)germyl]silan.

Introduction

The pyrolytic elimination is a model reaction, which probably dominates most pyrolytic processes [1]. A simple reaction of this type can be written as Figure **1** (heating is symbolized by Δ). Among pyrolytic eliminations, β-eliminations, with two groups lost from adjacent atoms, are probably the most common [2,3]. These reactions take place typically by an *E2* mechanism. Since pyrolytic elimination takes place with no other reagent present and often requires gas phase, the typical *E2* mechanism where a proton is pulled by a base is not common. Two β -eliminations involving an *E2* mechanism with different sizes of cyclic transition state are shown in Figure **2**.

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Results and discussion

The results showed that the β-Elimination reaction is a unimolecular process and occurred from four centered transition state (Figure **3**). Total electronic energy (E$_{ele}$) (E$_0$= ZPE + E$_{ele}$) for all of them was calculated on the B3LYP/3-21G* level of theory (Table **1**). Studies on the B3LYP/3-21G* level of theory show that the barrier height of the decomposition of the compound **1** to compounds **2,3** and **4** is 120.23, 61.51 and 94.42 kcal/mol, respectively. It shows that the barrier height of the decomposition of the compound **1** to **3** is lower than other possible compounds. Also the zero-point vibrational energy (ZPE) for trifluoro [fluoro (methyl) germyl] silane (**1**) to difluoro (methylgermylene) silane (**2**), difluoro[fluoro(methyl)germylene]silane(**3**) and difluoro (fluorogermylene)silane (**4**) were calculated using optimized structures at B3LYP/3-21G level of theory and listed in Table **1**. It can be said that ZPE for difluoro[fluoro(methyl) germylene]silane is greater

than other compounds. Furthermore, this indicates that the relative thermal stability of difluoro[fluoro(methyl)germylene]silane is higher than other compounds. Natural Bond Orbital (NBO) population analysis results have a good agreement with
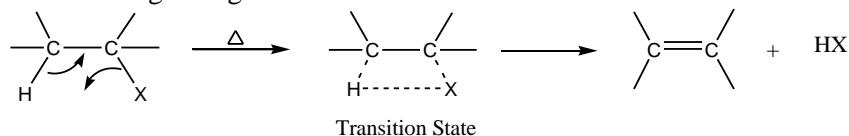
calculated structural parameters [4]. At this point, it seems useful to remember some useful aspects concerning the NBO analysis, which was effectively used in this work.
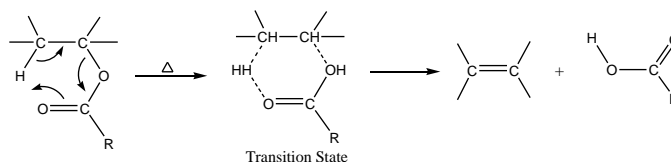

Figure 1: Pyrolytic elimination

Figure 2: β-eliminations involving an *E2* mechanism with different sizes of cyclic transition state

Table 1: Zero-Point Energies (*ZPE*), Total electronic Energies (E_{ele}) and Relative Energies *ΔE* (E_h in Hartree) for the energy minima structures of all compounds 1-4 and transition structures of reactions, calculated with B3LYP/3-21G.

System method	ZPE[a]	E_{ele}	E_0	ΔE_0
1	0.0477653367	-3236.8765439	-3236.76656	0.000000
2	0.0468766478	-3236.876543t	-3236.375645	0.346604
3	0.0497683466	-3236.0986568	-3236.765454	0.004565
4	0.0462578456	-3236.3556786	-3236.358789	0.224467
[1→2]*	0.045307773	-3236.5576865	-3236.0654643	0.198645
[1→3]*	0.04528520955	-3236.2567867	-3236.0656432	0.133546
[1→4]*	0.045494127	-3236.3576866	-3236.076685	0.345354

In the NBO analysis, the electronic wave functions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals.

The delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (Anti bond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor–acceptor interaction, which is taken into consideration by examining all possible interactions between filled (donor) and empty (acceptor) orbitals and then evaluating their energies by second order perturbation theory.

Accordingly, the delocalization effects (or donor–acceptor charge transfers) can be estimated from the presence of off diagonal elements of the Fock matrix in the NBO basis. NBOs closely correspond to the picture of localized bonds and lone pairs as basic units of the molecular structure, so that it is possible to conveniently interpret ab initio wave functions in terms of the classical Lewis structure concepts by transforming these functions to NBO form[9]. The interactions due to electron delocalization are generally

analyzed by selecting a number of bonding and anti-bonding NBOs, namely, those relevant to the analysis of donor and acceptor properties. As a result, the NBO program searches for an optimal natural Lewis structure, which has the maximum occupancy of its occupied NBOs, and in general agrees with the pattern of bonds and lone pairs of the standard structural Lewis formula.

However, these orbitals suffer from small departures from the idealized Lewis structure, caused by interactions among them, which are known as hyperconjugative or stereoelectronic interactions. Therefore, the new orbitals are more stable than pure Lewis orbitals, stabilizing the wave function and giving a set of molecular orbitals equivalent to canonical molecular orbitals.

For each donor NBO (i) and acceptor NBO (j), the stabilization energy (*E2*) associated with i → j delocalization is explicitly estimated by the following equation [5]:
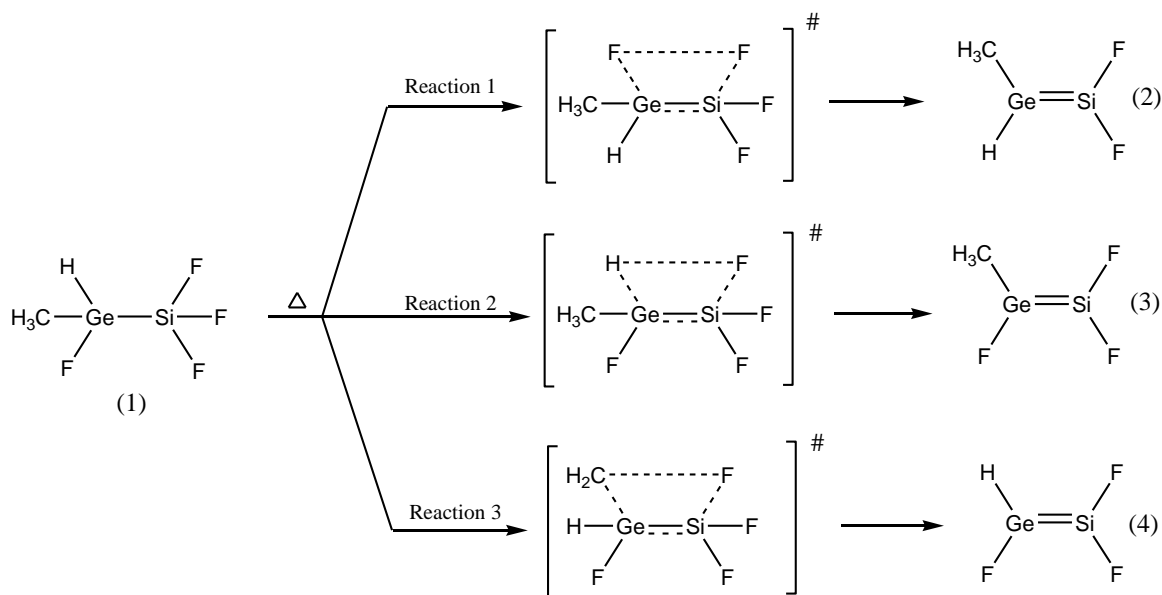
Figure 3: All of β-Eliminations mechanisms of trifluoro[fluoro(methyl)germyl]silane studied in this work

$$(E_2) = \Delta E_{ij} = q_i \frac{F^2_{(i,j)}}{e_j - e_i}$$

Where q_i is the ith donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies), and $F(i,j)$ are off-diagonal elements, respectively, associated with the NBO Fock matrix. The NBO analysis of donor–acceptor interactions showed that the resonance energy $\pi_{Ge-Si} \rightarrow \pi^*_{Ge-Si}$ delocalization in product is 22.74 kcal mol^{-1}. These electronic transitions disappear in reactant; therefore Ge-Si bond in reactant is a single bond and for products have a double bonds form, Tables **2** and **3**.

Computational Methods

Ab initio calculations were carried out using B3LYP/3-21G*[6-12] levels of theory with the GAUSSIAN 03 package of 4 implemented on a Pentium-PC computer with Intel (R) Core (TM)2 Duo CPU T9600 @ 2.8 GHz processor. Initial estimation of the structural geometry of trifluoro[fluoro(methyl) germyl] silane(**1**) to difluoro (methylgermylene) silane(**2**), difluoro [fluoro (methyl)germylene]silane(**3**) and difluoro(fluorogermylene)silane(**4**), Figure **3**, was obtained by program ChemOffice 2010 and for further optimization of geometry was used the MM2 method [13] of the Chem3D program. Energy-minimum molecular geometries were located by minimizing

energy with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points for compound **1** and transition state structures of reactions has been fixed by means of the number of imaginary frequencies. The structures of the molecular transition state geometries were located using the optimized geometries of the equilibrium molecular structures according to the Dewar *et al.* procedure (keyword SADDLE). These geometry structures were reoptimized by the QST2 subroutine at B3LYP/3-21G* level [14,15].

Conclusion

The β-Elimination mechanisms of trifluoro [fluoro(methyl) germyl] silane(**1**) to difluoro (methylgermylene) silane(**2**), difluoro[fluoro (methyl)germylene] silane(**3**) and difluoro (fluorogermylene) silane(**4**) were investigated using Density Functional Theory (DFT) and B3LYP method with 3-21G basis set. DFT calculations provide a picture from structural and energetic of view for the various pathways of the decomposition of compound **1** to **2**–**4**. B3LYP/3-21G* results reveal a higher barrier height for reaction 1 than that of reactions 2 and 3. These results are justified by Mulliken charge distribution values in the ground-state structure of compound **1** and transition state structures of reactions **1**–**3**. Natural Bond Orbital (NBO) population have been calculated and analyzed. The analysis of these data showed that, transition states of all elimination reactions have a four-centered transition structure and

single bonds of Si-F and Ge-A (A; F, H, CH₂) in reactant are broken and π-bond of Ge-Si and single bond of F-A (A; F, H, CH₂) are appear, as will. Also the zero-point vibrational energy (ZPE) for all compounds shows that relative thermal stability of difluoro[fluoro(methyl)germylene]silane (**3**) is higher than other compounds.

Table 2: Selected B3LYP/3-21G calculated bond lengths in angstrom for the energy minima structures of compounds 1-4 and transition structures of reactions.

Bonds	1	[1→2]	2	1	[1→3]	3	1	[1→4]	4
Si-F	1.413	1.952	-	1.860	2.637	-	2.045	2.835	-
Ge-A*	1.094	1.217	-	1.092	1.162	-	1.091	1.157	-
Ge-Si	1.526	1. 475	1.391	1.526	1.476	1.391	1.524	1.477	1.391

*A is F, H and CH₂ for compounds 2, 3 and 4, respectively.

Table 3: Selected B3LYP/3-21G calculated bond populations for the energy minima structures of compounds 1-4 and transition structures of reactions.

Selected Bonds	Occupancy		
	Reactant	Transition State	Product
Si – F	1.99138(σ)	-	-
Ge –Si	1.98728(σ)	1.97453(σ)	1.98359(σ) & 1.62613(π)
Ge–F	1.96601(σ)	1.73093(σ)	-
Si – F	1.99138(σ)	-	-
Ge –Si	1.98728(σ)	1.98144(σ)	1.98294(σ) & 1.62466(π)
Ge–H	1.96969(σ)	1.81076(σ)	-
Si – F	1.99138(σ)	-	-
Ge –Si	1.98728(σ)	1.98287(σ)	1.98168(σ) & 1.61583(π)
Ge–CH₂	1.97024(σ)	1.82613(δ)	-

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