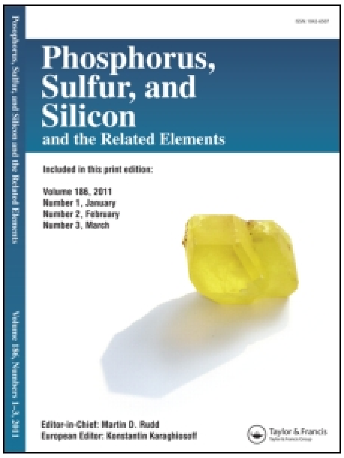

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Ab Initio Study of the Various Pathways of the Decomposition ([2 2]elimination) of 2-Chloroethyltrichlorosilane

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Ab Initio Study of the Various Pathways of the Decomposition ([2+2]elimination) of 2-Chloroethyltrichlorosilane

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*The decomposition of 2-chloroethyltrichlorosilane (**1**) to ethylene-tetrachlorosilane (**2**), hydrogen chloride-ethylenetrichlorosilane (**3**), and ethylenechloride-trichlorosilane (**4**) was investigated using ab initio Molecular Orbital (MO) and Density Functional Theory (DFT). Study on the HF/6-31G level of theory revealed that the required energy for the decomposition of compound **1** to **2**, **3**, and **4** is 59.86, 101.13, and 63.29 kcal mol^{-1}, respectively. MP2/6-31G*//HF/6-31G* calculated barrier height for the decomposition of compound **1** to **2**, **3**, and **4** is 60.59, 94.04, and 66.91 kcal mol^{-1}, respectively. Also, B3LYP/6-31G*//HF/6-31G* results indicate that the barrier height for the decomposition of compound **1** to **2**, **3**, and **4** is 51.71, 85.38, and 53.74 kcal mol^{-1}, respectively. Among the three methods, which have been used to calculate the barrier height of the decomposition of compound **1** to 2–4, B3LYP/6-31G**//HF/6-31G** is in good agreement with the reported experimental data. Contrary to the previously evaluated experimental values for the decomposition of compoun 1 to 3 and 4, all three methods predict a higher energy barrier for these reactions.*

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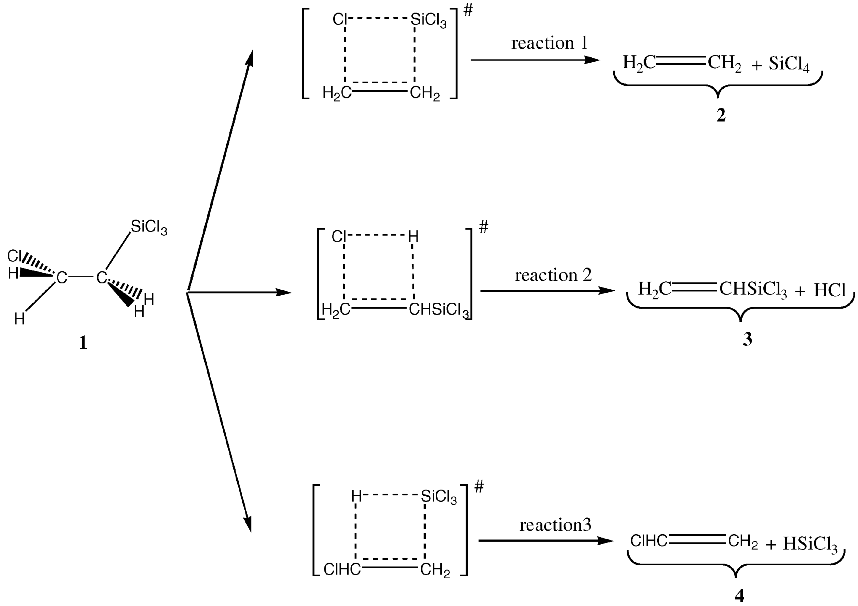
Keywords 2-chloroethyltri(chloro)silane; decomposition; molecular modeling; ab initio calculation

INTRODUCTION

2-chloroethylsilane unusual reactivity has been studied in solution,[1–3] but there is little data on the gas-phase reactions of these interesting compounds. 2-chloroethylsilanes with three alkyl groups attached to a silicon atom decompose readily when heated, whereas the replacment of the alkyl groups by halogen atoms increases the thermal stability.[1–5] A perliminary kinetic study of the thermal decomposition of 2-chloroethyltricholorosilane in a static system at 394°C have indicated that the formation of ethylene is predominate, and the overall decomposition is apparently first order and unimolecular.[6] Also, vinylchlorosilane and vinylchloride are initially formed. The experimental results revealed that there are three parallel pathways for the decomposition of compound **1**, as indicated in the Scheme 1. All decomposition pathways are first-order and unaffected by surface and inhibitors.[7]



SCHEME 1

Davidson et al. have suggested that the above reactions are unimolecular, but their results are not accurate enough for evaluation of the barrier heights of the reactions 2 and 3.[8] They have estimated that the barrier heights of reactions 2 and 3 will be close to the reaction 1 (about 40–50 kcal mol^{-1}). Therefore, their work did not clarify the mechanisms and activation energies of reactions 2 and 3. To gain further insight on this subject, we have investigated the various pathways of the decomposition of compound 1 by performing ab initio MO and DFT, using the GAUSSIAN 92 package of programs.[9–13] Succesful application of DFT-based methods have broadened the applicability of the computational methods and now represent an intresting approach for determning activation barrier and molecular energies.[9,10,12–14] The B3LYP functional method combines Becke's three-parameter exchange function with the exchange-correlation function of Lee et al.[9,10]

CALCULATIONS

Ab initio calculations were carried out using HF/6-31G**//HF/6-31G**, MP2/6-31G**//HF/6-31G**, and B3LYP/6-31G**//HF/6-31G** levels of theory with the GAUSSIAN 98 package of programs[13] implemented on a Pentium–PC computer with a 550 MHz processor.

Initial estimation of the structural geometry of the compound **1** was obtained by a molecular mechanic program PCMODEL (88.0),[15] and for further optimization of geometry, we used the PM3 method of the MOPAC 7.0 computer program.[16,17] The GAUSSIAN 98 package of programs were finally used to perform ab initio calculations at the HF/6-31G** level. 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 1–3 has been fixed by means of the number of imaginary frequencies. For minimum state structure, only real frequency values, and in the transition-state, only single imaginary frequency values, were accepted.[18,19] 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).[20] These geometry structures were reoptimized by the QST2 subroutine at the HF/6-31G** level. For further optimization, TS subroutine was used. The vibrational frequencies of ground states and transition states were calculated by FREQ subroutine.

RESULTS AND DISCUSSION

Zero point (ZPE) and total electronic (E_{el}) energies ($E_0 = ZPE + E_{el}$) for the energy minimum and energy maximum geometries of the decomposition of 2-chloroethyltrichlorosilane (**1**) to ethylene-tetrachlorosilane

(**2**) (reaction 1), hydrogenchloride-ethylenetrichlorosilane (**3**) (reaction 2), and vinylchloride-trichlorosilane (**4**) (reaction 3), as calculated on the ab initio HF/6-31G** level of theory, are given in Table I. For single-point energy calculations, both ab initio MP2/6-31G**// HF/6-31G** and DFT method (B3LYP/6-31G**//HF/6-31G**) were used.

Studies on the HF/6-31G**// HF/6-31G**, MP2/6-31G**// HF/6-31G**, and B3LYP/6-31G**// HF/6-31G** levels of theory show that the barrier height of the decomposition of the compound **1** to **2** (reaction 1) is 59.86, 60.59, and 51.71 kcal mol^{-1}, respectively (see Figure 1). Among three methods that have been used to calculate the barrier heights of reactions 1–3. B3LYP/6-31G**//HF/6-31G** results is in good agreement with the previousely reported experimental data (45 kcal mol^{-1} for reaction 1).[6]

By considering the structure of compound **1**, the decomposition of compounds **1** to **3** (reaction 2) and **4** (reaction 3) also is possible. Davidson et al.[6] have pointed out that the products of reactions 2 and 3 are minor. However, they didn't clarify the barrier heights of reactions 2 and 3. They estimated that the barrier heighs of reactions 2 and 3 is about 40–50 kcal mol^{-1}. Contrary to the estimated data by Davidson et al., HF/6-31G**// HF/6-31G**, MP2/6-31G**// HF/6-31G**, and B3LYP/6-31G**// HF/6-31G** levels of theory reveal that the barrier height of reaction 2 is 63.29, 66.91, and 53.74 kcal mol^{-1}, respectively (see Figure 1).

In order to understand the reason for the lower barrier height of reaction 1 in comparision to reaction 2, we have carried out Mulliken charge distribution for the ground state structure of compound **1** and the transition state structures of reactions 1–3.

Formation of **2** and **3** can be justified by Mulliken charge distribution of compound **1** in the ground state structure and the transition state structures of reactions 1 and 2. Consequently, for such a drastic change in the charge distribution of chlorine and hydrogen atoms in the transition state structures of reactions 1 and 2, the formation of the transition structure of reaction 1 is more favorable than reaction 2 because of the larger variation of the charge distribution of the chlorine atom in the transition state structure of reaction 2 (see Figure 2).

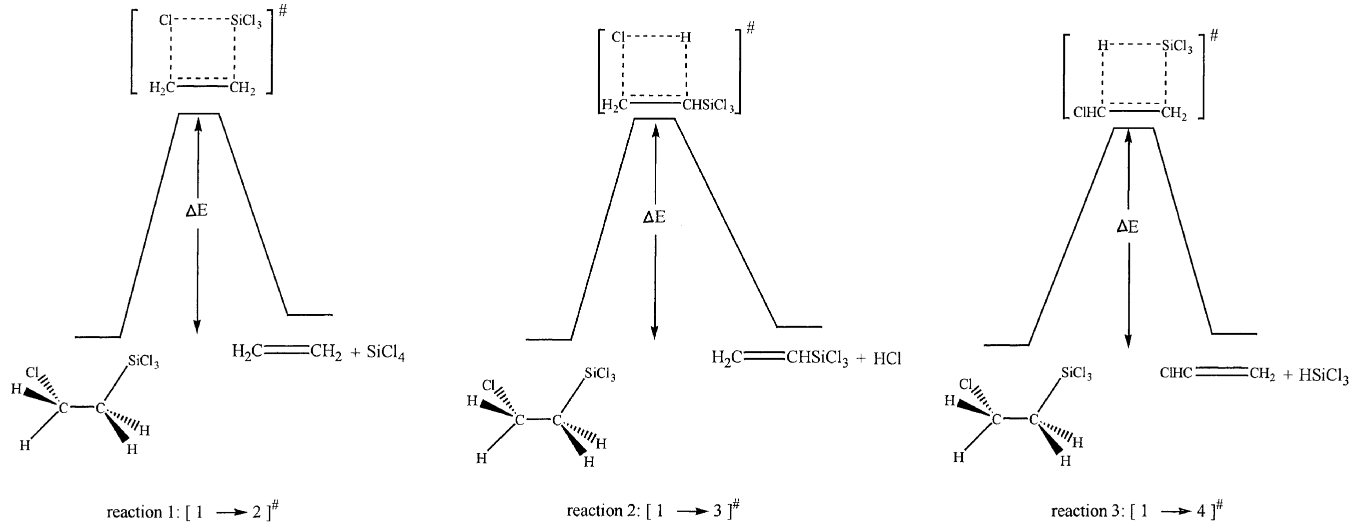
HF/6-31G**// HF/6-31G**, MP2/6-31G**// HF/6-31G**, and B3LYP/6-31G**// HF/6-31G** levels of theory reveal that the barrier height of reaction 3 is 101.13, 94.04, and 85.38 kcal mol^{-1}, respectively. In comparison to the calculated barrier height of reaction 1, the calculated barrier height of reaction 3 is significantly higher. The reason of this fact may be explained by the drastic changes in the Mulliken charge distribution of the hydrogen atom in both ground and transition

TABLE I Calculated Total Energies *E*, Zero-Point Energies *ZPE*, and Relative Energies ΔE (E_h) (in Hartree) for the Energy-Minimum of Compound 1 and Energy-Maximum Geometries of Reactions 1–3

System		HF/6-31G**//HF/6-31G**			MP2/6-31G**//HF/6-31G**			B3LYP/6-31G**//HF/6-31G**		
Method	*ZPE*	E_{el}	E_0	ΔE_0^a	E_{el}	E_0	ΔE_0^a	E_{el}	E_0	ΔE_0^a
1	0.067505	−2205.087095	−2205.019590	0.000000 (0.000000)	−2205.967672	−2205.900167	0.000000 (0.000000)	−2209.071768	−2209.004263	0.000000 (0.000000)
$[1 \rightarrow 2]^\#$	0.064197	−2204.983875	−2204.924191	0.095399 (59.863826)	−2205.867813	−2205.803610	0.096557 (60.590483)	−2208.986062	−2208.921865	0.082398 (51.075569)
$[1 \rightarrow 3]^\#$	0.059101	−2204.977827	−2204.918726	0.100864 (63.293169)	−2205.852634	−2205.793533	0.106634 (66.913901)	−2208.977721	−2208.918620	0.085643 (53.741839)
$[1 \rightarrow 4]^\#$	0.062086	−2204.920512	−2204.858426	0.161164 (101.132022)	−2205.812392	−2205.750306	0.149861 (94.039276)	−2208.930293	−2208.868207	0.136056 (85.376500)

Numbers in parenthesis are the corresponding ΔE values in kcal mol^{-1}.

[a] Relative to the minimum.



$$\Delta E\ (\mathrm{kcal\ mol^{-1}}) = \begin{cases} 59.86\ (\mathrm{HF}) \\ 60.59\ (\mathrm{MP2}) \\ 51.08\ (\mathrm{B3LYP}) \end{cases}$$

$$\Delta E\ (\mathrm{kcal\ mol^{-1}}) = \begin{cases} 63.29\ (\mathrm{HF}) \\ 66.91\ (\mathrm{MP2}) \\ 53.74\ (\mathrm{B3LYP}) \end{cases}$$

$$\Delta E\ (\mathrm{kcal\ mol^{-1}}) = \begin{cases} 101.13\ (\mathrm{HF}) \\ 94.04\ (\mathrm{MP2}) \\ 85.38\ (\mathrm{B3LYP}) \end{cases}$$

FIGURE 1 HF, MP2, and B3LYP energy diagram for decomposition of compound **1**.

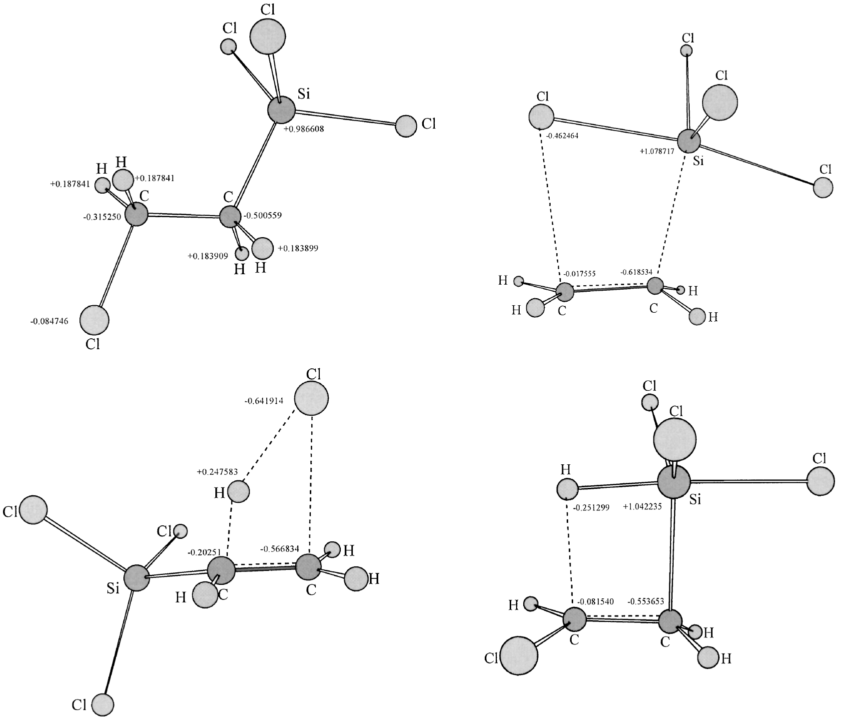


FIGURE 2 HF/6-31G** charge distribution (Mulliken) for the ground state structure of compound **1** and transition state structures of reactions 1–3.

structures, as shown in Figure 2. According to the charge distribution results, the hydrogen atom charge in the ground state structure of compound 1 is +0.187841, while in the transition state structure of reaction 3 is −0.251299.

Representative structural parameters for ground state structure of compound 1 and transition state structures of reactions 1–3 are given in Figure 3. HF/6-31G**// HF/6-31G** results show the variations of the bonds in the ground state structure of compound 1 and transition structures of reactions 1–3 (see Figure 3). Theoretical calculations provide structural parameters for isolated molecules at 0 K. Therefore, theoretical calculations are not reported, in principle, to quantitatively reproduce the experimental values.[21] Nevertheless, it is possible to carry out ab initio calculations at the Hartree-Fock level, from which many properties and structures can be obtained with an accuracy that is competitive with experiment.[22–25]

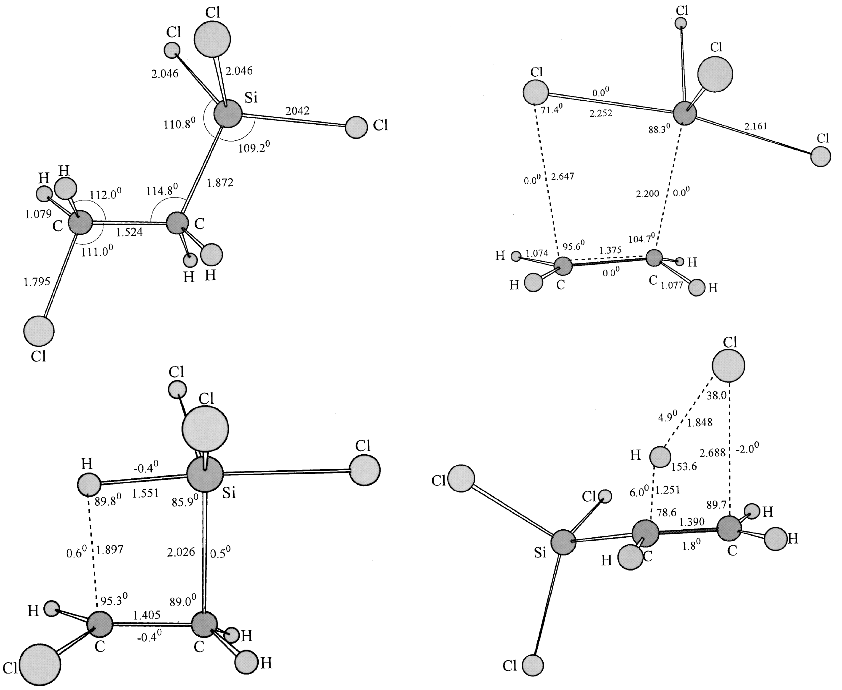


FIGURE 3 HF/6-31G**-calculated structural parameters for the energy minima structure of compound **1** and transition structures of reactions 1–3. Bond lengths are in angström (Å) unit and angles in degrees (°).

CONCLUSION

Ab initio HF, MP2, and B3LYP density functional-theory calculations provide a picture from structural, energetic, and Mulliken charge distributions points of view for the various pathways of the decomposition of compound **1** to **2–4**. B3LYP/6-31G**//HF/6-31G**, MP2/6-31G**// HF/6-31G**, and HF /6-31G**// HF/6-31G** results reveal a higher barrier height for reaction 3 than that of reactions 1 and 2. These results are justified by Mulliken charge distribution values in the ground-state structure of compounbd **1** and transition state structures of reactions 1–3. The large barrier height of reaction 3 can be explained by the drastic changes in the Mulliken charge distribution of the hydrogen atom.

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