

Scientific paper

Substitution Reactions of the Aluminum Chlorogermolenoid $\text{H}_2\text{GeClAlCl}_2$ with HF , H_2O , NH_3 , HCl , H_2S , and PH_3

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Abstract

Quantum chemical calculations have been performed for the substitution reactions of the aluminum chlorogermolenoid $\text{H}_2\text{GeClAlCl}_2$ with HF , H_2O , NH_3 , HCl , H_2S , and PH_3 to get more insights into the reactivity of $\text{H}_2\text{GeClAlCl}_2$. The theoretical calculated results indicated that the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with HF , H_2O , NH_3 , HCl , H_2S , and PH_3 proceeded in a concerted manner. There were one transition state and one intermediate which connected the reactants and the products along the potential energy surface. The six substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with HF , H_2O , NH_3 , HCl , H_2S , and PH_3 are compared with the addition reactions of H_2Ge with these hydrides. And based on the calculated results we concluded that the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with these hydrides involve two steps, one is dissociation onto H_2Ge with AlCl_3 , and the other is the addition reactions of H_2Ge with HF , H_2O , NH_3 , HCl , H_2S , and PH_3 .

Keywords: $\text{H}_2\text{GeClAlCl}_2$; substitution reaction; MP2; CCSD

1. Introduction

Since many organic germanium compounds have been found to have biologic activity,^{1–6} the properties and reactions of germynes and their derivatives have been well studied.^{7,8} Germynoid is a kind of important derivative of germylene, and may have the stronger stability than germylene. Similar to carbenoids^{9,10} and silylenoids,^{11,12} germynoids are complexes formed between free germynes and inorganic salts, which can be expressed as $\text{R}_1\text{R}_2\text{GeMX}$ (M = alkali metal, X = halogen). In 1991 Lei et al. firstly demonstrated that germynoid might be the intermediate in the reaction of dichlorodimethylgermane with substituted butadiene.¹³ Since then several subsequent organic experimental works also indicated the significance of germynoids as active intermediates.^{14–19} However, until now no stable germynoid has been prepared by experiments. Therefore, it is necessary to carry out systemic investigations on germynoids to investigate their structures, properties, and reactions using theoretical calculations.

Many theoretical studies on the structures, properties, and reactions of the germynoids have been carried

out. In 1999, Qiu et al. firstly researched the isomeric structure of the germynoid H_2GeLiF by *ab initio* calculations.²⁰ Until now, a few kinds of germynoids have been investigated.^{21–34} Most of these theoretical works mainly focused on the germynoids containing alkali metals such as Li and Na. In 1970, Glockling et al.³⁵ suggested that germanium-aluminium compounds were high reactivity intermediates in the reaction between bistrimethylgermylmercury and aluminium turnings. A more comprehensive study on aluminium-germanium compounds is of great scientific significance and academic value. Is aluminium-germyloenoid exists? And how is its reactivity? In 2009, we firstly investigated the geometries, energies, and isomerization reactions of aluminum chlorogermynoid $\text{H}_2\text{GeClAlCl}_2$.³¹ However, the reactions of $\text{H}_2\text{GeClAlCl}_2$ with other substances have been not researched until now. In order to fill this gap and explore the reactivity of the germynoid $\text{H}_2\text{GeClAlCl}_2$, in present work we implemented theoretical study on the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with HF , H_2O , NH_3 , HCl , H_2S , and PH_3 using *ab initio* quantum chemical calculations. Through this work, we hope (I) to get the

structures and energies of all stationary points, (II) to confirm the thermodynamics of the substitution reactions, (III) to predict their activation barriers, and (IV) to clarify the reaction mechanisms on the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with HF, H_2O , NH_3 , HCl, H_2S , and PH_3 .

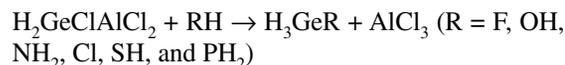
2. Computational Methods

The geometries of all the stationary points presented here were fully optimized at the MP2/6-311+G (*d, p*) level.^{36–38} The geometries were first optimized and then the harmonic vibrational frequencies were calculated at the same level of theory to characterize all stationary points as either local minima (no imaginary frequencies) or transition states (one imaginary frequencies). The substitution reaction pathways were examined by IRC (intrinsic reaction coordinate)³⁹ calculations at the same level to verify the reactants and the products to which each TS was connected. In order to improve the treatment of electron correlation the single-point calculations were made at the CCSD (Coupled cluster with singles and doubles)^{40,41} level using the 6-311++G (*d, p*) basis set for all species. All of the calculations were carried out using Gaussian 09 series of programs.⁴²

3. Results and Discussions

Previous theoretical calculations³¹ indicated that the aluminum chlorogermolenoid $\text{H}_2\text{GeClAlCl}_2$ has three equilibrium configurations (see Figure 1), the *p*-complex (a), the three-membered-ring (b), and the “classical” tetrahedral structure (c), in which the *p*-complex structure is the lowest in energy and is the most stable structure. Therefore, the *p*-complex structure was selected as the reactant when we researched the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ and HF, H_2O , NH_3 , HCl, H_2S , PH_3 in present work.

Theoretical calculations indicated the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with HF, H_2O , NH_3 , HCl, H_2S , and PH_3 could be described as the following formula:



Based on the calculated results, we found that along the potential energy surface, there are one transition state (TS) and one intermediate (IM) which connect the reactants and the products (P and AlCl_3). The geometries of the stationary points calculated at the MP2/6-311+G (*d, p*) level are shown in Figure 2 and Figure 3, the relative energies of the stationary points are listed in Table 1 and 2, respectively. For the convenience of expression, the transfer-H in RH is marked as H^1 .

3. 1. Substitution Reactions of $\text{H}_2\text{GeClAlCl}_2$ with HF, H_2O , and NH_3

3. 1. 1. The Structures and Energies of the Transition States

As displayed in Figure 2, there is an exposed space that can be attacked by nucleophiles or electrophiles under the Ge atom, and the substitution reactions between $\text{H}_2\text{GeClAlCl}_2$ and HF, H_2O , NH_3 should occur in this region. From Figure 2 we can see that the three transition states (TS1, TS2, and TS3) have the similar structures. There is a three-membered-ring (X-Ge-H^1 , $\text{X} = \text{F}, \text{O}, \text{N}$) in each TS. Compared to the isolated reactants HF, H_2O , and NH_3 , the R-H^1 bond distances are sharply lengthened by about 0.0423, 0.0467, and 0.0488 nm, where the bond elongations correspond to about 31.6%, 32.7%, and 32.5% of its original length, respectively. Therefore, the migrating H^1 atom has a strong reactant-like property. As listed in Table 1, the relative energies of TS1, TS2, and TS3 to their reactants are 159.39, 178.01, and 179.81 kJ/mol, respectively.

The frequency analysis calculations were carried out at the MP2/6-311+G (*d, p*) level. The theoretical results indicated that each TS has only one imaginary frequency, which are 1378.1 i, 1436.1i, and 1433.7i cm^{-1} , respectively. The calculated unique imaginary frequency vibration of TS1, TS2, and TS3 involves bond formation between Ge atom and R group in concert with R-H^1 bond breaking, and H^1 atom migration to Ge atom. Besides, the

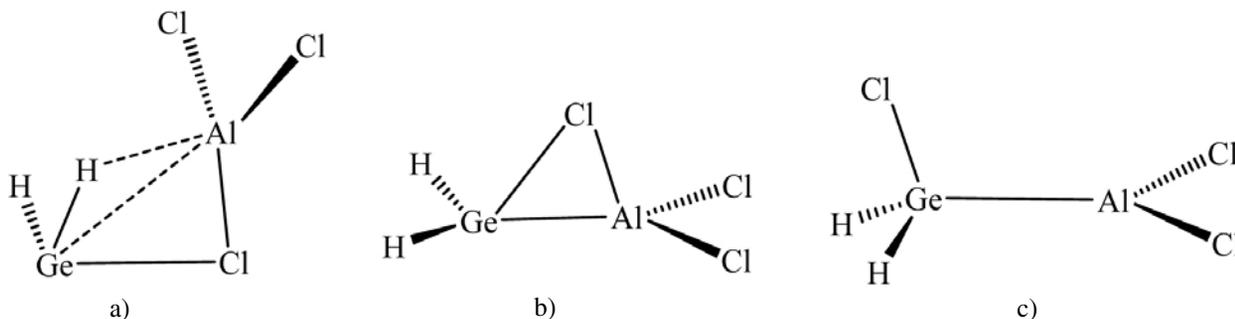


Figure 1. The equilibrium configurations of the germolenoid $\text{H}_2\text{GeClAlCl}_2$, see Ref. 31

Table 1. Relative energies (in kJ/mol) of transition states (TSs), intermediates (IMs), and products of the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with R-H (R = F, OH, NH_2). (Values in parenthesis were calculated in benzene)

Species	R = F	R = OH	R = NH_2
$\text{H}_2\text{GeClAlCl}_2 + \text{R-H}$	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
TS	159.39 (165.63)	178.01 (188.55)	179.81 (189.29)
IM	-89.75 (-91.81)	-74.91 (-73.30)	-80.61 (-81.84)
$\text{GeH}_3\text{R} + \text{AlCl}_3$	-71.92 (-70.70)	-50.64 (-45.28)	-37.90 (-31.12)

IRC calculations displayed that the TSs are the real transition states which connect the reactants and the intermediates.

3. 1. 2. The Structures and Energies of the Intermediates and Products

After getting over the transition states, the Ge–R and Ge– H^1 bonds gradually form with the breakdown of R– H^1 bond and the intermediates IMs form. As shown in Figure 2, IM1, IM2, and IM3 are the three intermediates

of the three substitution reactions. From Figure 2, we can see that the X–Ge– H^1 (X = F, O, N) bond angles of IMs are much larger than those of TSs. For IM1, the F–Ge– H^1 bond angle (107.0°) is about 67.0° larger than that of TS1 (40.0°); For IM2, the O–Ge– H^1 bond angle (112.3°) is about 68.0° larger than the that of TS2 (44.3°); For IM3, the N–Ge– H^1 bond angle (110.3°) is about 62.4° larger than that of TS3 (47.9°). In the IMs, the R– H^1 bonds have been broken completely. The Ge– H^1 and Ge–X bond lengths of IMs are shorter than those of TSs respectively. For IM1, the Ge– H^1 bond

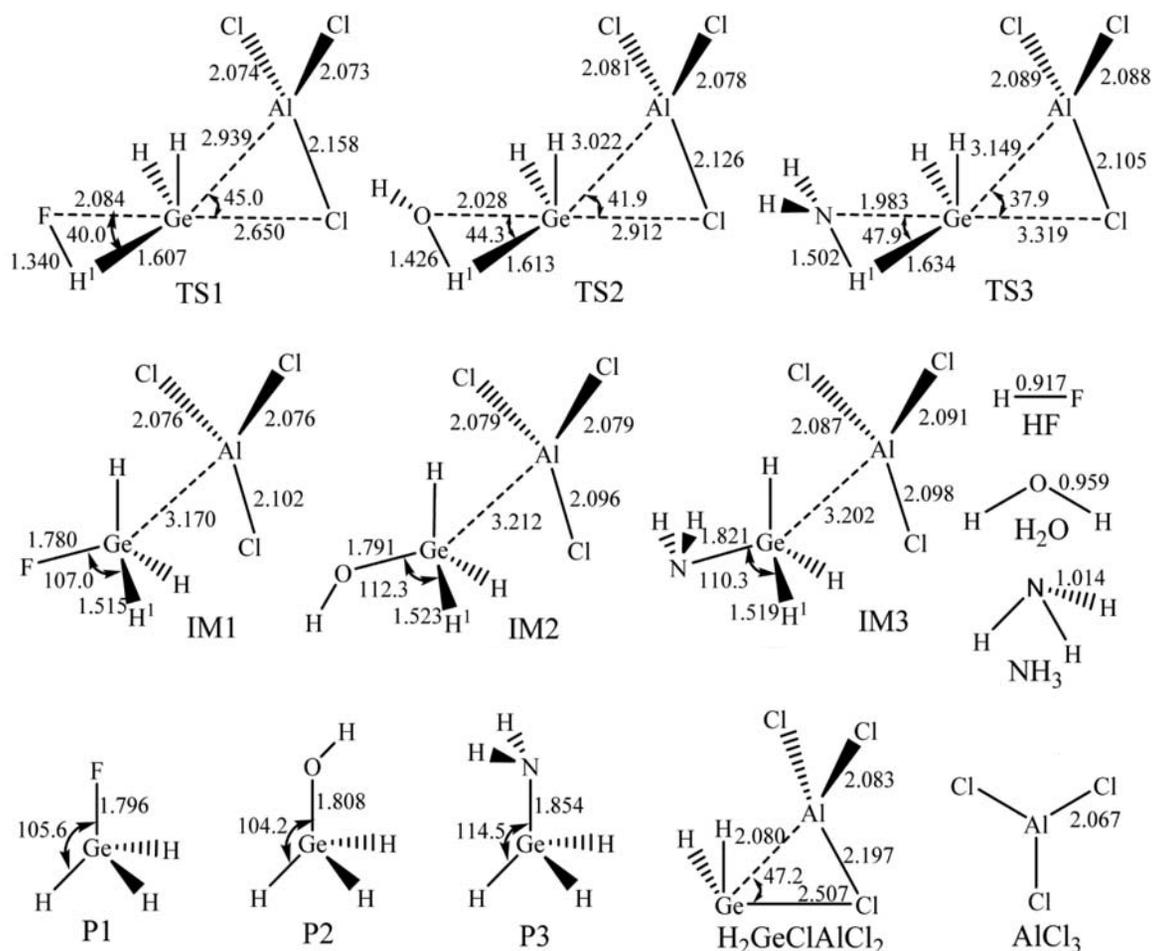


Figure 2. The geometries of the stationary points [reactants, transition states (TSs), intermediates (IMs), and products (Ps)] of the substitution reactions of the germylenoid $\text{H}_2\text{GeClAlCl}_2$ with HF, H_2O , and NH_3 in gas phase calculated at MP2/6-311+G (*d, p*) level (Bond lengths are given in Å and angles in degrees)

length (0.1515 nm) and the Ge–F bond length (0.1780 nm) is about 0.0092 nm and 0.0304 nm shorter than those of TS1 respectively; For IM2, the Ge–H¹ bond length (0.1523 nm) and the Ge–O bond length (0.1791 nm) is about 0.0090 nm and 0.0237 nm shorter than those of TS2 respectively; For IM3, the Ge–H¹ (0.1519 nm) and Ge–N bond length (0.1821 nm) is about 0.0115 nm and 0.0162 nm shorter than the Ge–H¹ (0.1634 nm) and Ge–N bond length (0.1983 nm) of TS3, respectively. As listed in Table 1, the relative energies of IM1, IM2, and IM3 to their reactants are –89.75, –74.91, and –80.61 kJ/mol, respectively.

The MP2/6-311+G (*d, p*) calculations indicated that the IMs could further dissociate to H₃GeR and AlCl₃, which are the products of the substitution reactions of H₂GeClAlCl₂ and RH (R = F, OH, and NH₂). The dissociations of IMs are monotonously energy increasing process. As shown in Figure 2, the three H₃GeR (denote as P1, P2, and P3) are the substituted germane. As listed in Table 1, the relative energies of the products (H₃GeR + AlCl₃) of the three substitution reactions to their reactants

are –71.92, –50.64, and –37.90 kJ/mol when R = F, OH, and NH₂, respectively. Therefore, the three substitution reactions are all exothermic.

3. 2. Substitution Reactions of H₂GeClAlCl₂ with HCl, H₂S, and PH₃

3. 2. 1. The Structures and Energies of the Transition States

As displayed in Figure 3, three transition states (TS4, TS5, and TS6) have the similar structures. There is a three-membered-ring (X–Ge–H¹, X = Cl, S, P) in each TS. Compared to the isolated reactants HCl, H₂S, and PH₃, the R–H¹ bond distances are sharply lengthened by about 0.417, 0.480, and 0.0279 nm, where the bond elongations correspond to about 32.8%, 36.0%, and 19.8% of its original length, respectively. Therefore, the migrating H¹ atom has a strong reactant-like property. As listed in Table 2, the relative energies of TS4, TS5, and TS6 to their reactants are 112.61, 120.36, and 179.66 kJ/mol, respectively.

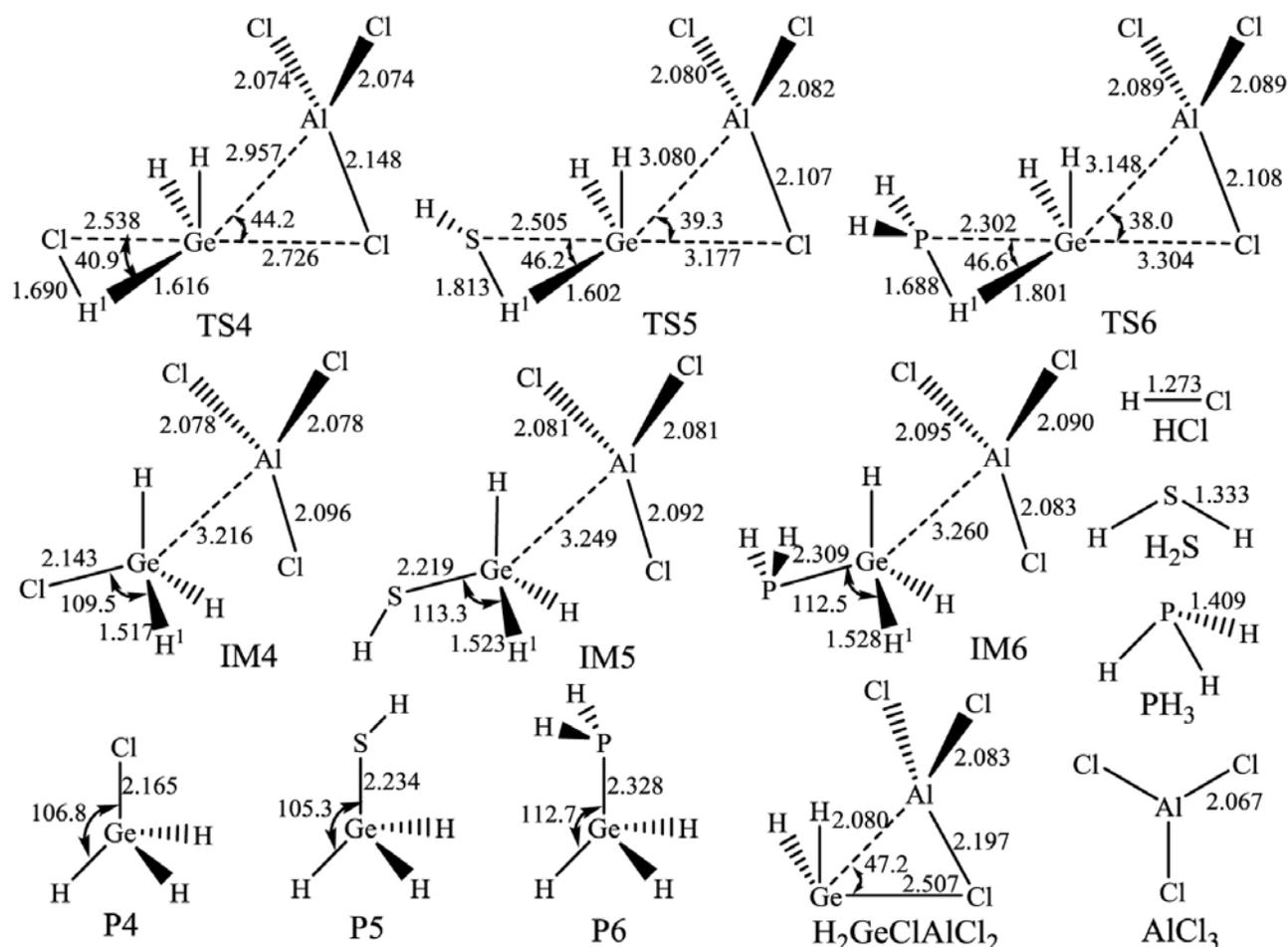


Figure 3. The geometries of the stationary points [reactants, transition states (TSs), intermediates (IMs), and products (Ps)] of the substitution reactions of the germylenoid H₂GeClAlCl₂ with HCl, H₂S, and PH₃ in gas phase calculated at MP2/6-311+G (*d, p*) level (Bond lengths are given in Å and angles in degrees)

Table 2. Relative energies (in kJ/mol) of transition states (TSs), intermediates (IMs), and products of the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with R-H (R = Cl, SH, PH_2). (Values in parenthesis were calculated in benzene)

Species	R = Cl	R = SH	R = PH_2
$\text{H}_2\text{GeClAlCl}_2 + \text{R-H}$	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
TS	112.61 (114.20)	120.36 (122.05)	179.66 (179.22)
IM	-123.18 (-130.23)	-101.82 (-107.91)	-95.75 (-102.38)
$\text{GeH}_3\text{R} + \text{AlCl}_3$	-102.84 (-106.66)	-77.91 (-80.10)	-58.17 (-58.52)

The frequency analysis calculations were carried out at the MP2/6-311+G (*d*, *p*) level. The theoretical results indicated that each TS has unique imaginary frequency, which are 1053.1i, 974.2i, and 913.6i cm^{-1} , respectively. The calculated imaginary frequency vibration of TS4, TS5, and TS6 involves bond formation between Ge atom and R group in concert with R-H¹ bond breaking, and H¹ atom migration to Ge atom. Besides, the IRC calculations displayed that the TSs are the real transition states which connect the reactants and the intermediates.

3. 2. 2. The Structures and Energies of the Intermediates and Products

As shown in Figure 3, IM4, IM5, and IM6 are the three intermediates of the three substitution reactions. From Figure 3, we can see that the X-Ge-H¹ (X = Cl, S, P) bond angles of IMs are much larger than those of TSs. For IM4, the Cl-Ge-H¹ bond angle (109.5°) is about 68.6° larger than that of TS4 (40.9°); For IM5, the S-Ge-H¹ bond angle (113.3°) is about 67.1° larger than that of TS5 (46.2°); For IM6, the P-Ge-H¹ bond angle (112.5°) is about 65.9° larger than that of TS6 (46.6°). In the IMs, the R-H¹ bonds have been broken completely. The Ge-H¹ and Ge-X bond lengths of IMs are shorter than those of TSs respectively. For IM4, the Ge-H¹ bond length (0.1517 nm) and the Ge-Cl bond length (0.2143 nm) is about 0.0099 nm and 0.0395 nm shorter than those of TS4 respectively; For IM5, the Ge-H¹ bond length (0.1523 nm) and the Ge-S bond length (0.2219 nm) is about 0.0079 nm and 0.0286 nm shorter than those of TS5 respectively; For IM6, the Ge-H¹ (0.1528 nm) is about 0.0273 nm shorter than that of TS6 (0.1801 nm), however, the Ge-P bond length (0.2309 nm) is slightly lengthened by about 0.0007 nm. As listed in Table 2, the relative energies of IM4, IM5, and IM6 to their reactants are -123.18, -101.82, and -95.75 kJ/mol, respectively.

The IMs could further dissociate to H_3GeR (R = Cl, SH, and PH_2) and AlCl_3 , which are the products of the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ and HCl, H_2S , and PH_3 . The dissociations of IMs are monotonously energy increasing process. As shown in Figure 3, the three H_3GeR (denote as P4, P5, and P6) are the substituted germane. As listed in Table 2, the relative energies of the products ($\text{H}_3\text{GeR} + \text{AlCl}_3$) of the three substitution reactions to their reactants are -102.84, -77.91, and -58.17 kJ/mol

when R = Cl, SH, and PH_2 , respectively. Therefore, the three substitution reactions are all exothermic. Our theoretical results indicated that the reaction mechanism of $\text{H}_2\text{GeClAlCl}_2$ with HCl, H_2S , and PH_3 is similar to that of $\text{H}_2\text{GeClAlCl}_2$ with HF, H_2O , and NH_3 .

3. 3. The Mechanisms of the Substitution Reactions

In order to fully confirm the substitution reactions path, the IRC computations are carried out at the MP2/6-311+G (*d*, *p*) level. Here the reaction of $\text{H}_2\text{GeClAlCl}_2$ with HF is chosen to be an example. IRC calculations have been performed on the basis of the calculated TS1 to investigate the interaction between $\text{H}_2\text{GeClAlCl}_2$ and HF in this substitution process. And the total energy changes and the variations of Ge-F, F-H¹, and Ge-H¹ bond distances along the reaction coordinates for the substitution reaction of $\text{H}_2\text{GeClAlCl}_2$ with HF are shown in Figure 4. From Figure 4 we can find that the reaction coordinate passes from point -9.0 to 0.0, the total energy increases sharply and reaches its maximum at point 0.0. In this region, the lengths of Ge-F and Ge-H¹ bond decrease obviously. After the maximum point, the total energy decreases sharply and the lengths of F-H¹ bond increase obviously.

The charge distributions of the atoms in the stationary points can reflect the mechanism of the reaction. We calculate the natural charge distributions of the atoms in reactants, TSs, IMs, and products at the MP2/6-311+G (*d*, *p*) level. For TSs, the X (X = F, O, N, Cl, S, P) atom and H¹ atom have more negative charge than those in reactants and the Ge atom has more positive charge than that in reactants; For IMs, the H¹ atom has more negative charge and the Ge atom has more positive charge than those in TSs, respectively. The change of the charge distributions also implies the fracturing of the R-H¹ bond and the forming of the Ge-H¹ and Ge-R bonds. Taking the reaction of $\text{H}_2\text{GeClAlCl}_2$ with HF as an example, in TS1, the positive charge of H¹ atom (0.291 *e*) is less than that in HF (0.557 *e*), the negative charge of F atom (-0.731 *e*) is more than that in HF (-0.557 *e*), and the positive charge of Ge atom (0.954 *e*) is more than that in $\text{H}_2\text{GeClAlCl}_2$ (0.723 *e*). The changes of the charge distributions imply the fracturing of the F-H¹ bond and the forming of the Ge-H¹ and Ge-F bonds. In IM1, the charge of H¹ atom

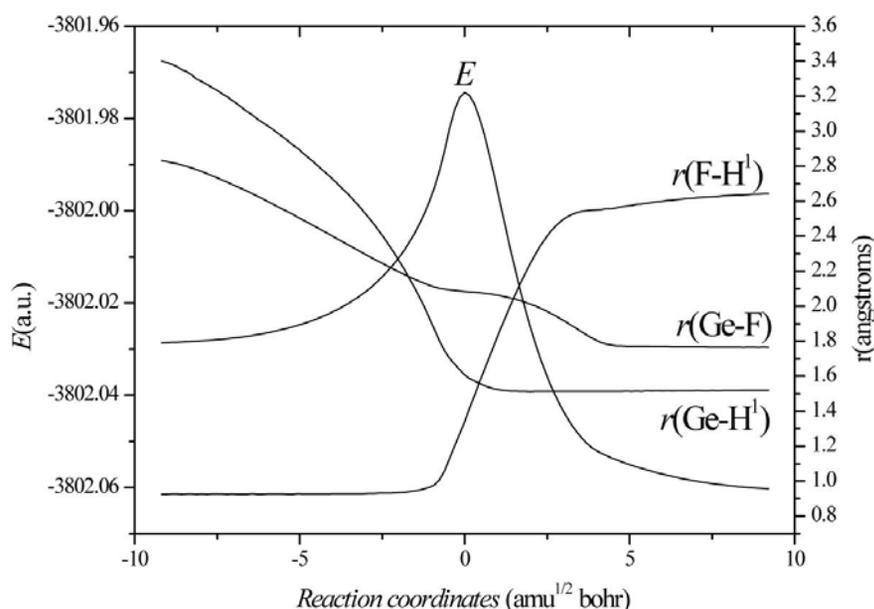


Figure 4. The changes of energies and bond distances along the reaction coordinate of the reaction of $\text{H}_2\text{GeClAlCl}_2$ with HF.

($-0.163 e$) has been changed to be negative and the positive charge of Ge atom ($1.451 e$) is more than that in TS1. All of the changes of the charge distributions imply the $\text{H}^1\text{-F}$ bond has been fractured and the Ge-H^1 and Ge-F bonds have been formed. We think the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with H_2O , NH_3 , HCl , H_2S , and PH_3 have the similar mechanism.

3. 4. The comparisons of the Substitution Reactions

Though the six substitution reactions have similar mechanism, the reactivity of them is different. From Table 1 and 2, we can see the CCSD/6-311++G (*d, p*)/MP2/6-311+G (*d, p*) calculated barrier heights are 159.39, 178.01, 179.81, 112.61, 120.36, and 179.66 kJ/mol for the six different substitution reactions, respectively. Correspondingly, the calculated relative reaction energies of them are -71.92 (HF), -50.64 (H_2O), -37.90 (NH_3), -102.84 (HCl), -77.91 (H_2S), and -58.17 (PH_3) kJ/mol, respectively. The calculated results suggest that, there is a very clear trend toward lower activation barriers and more exothermic interactions on going from left to right along a given row in periodic table, which means under the same condition the substitution reactions should occur easily in the order of $\text{H-F} > \text{H-OH} > \text{H-NH}_2$ for the first-row hydrides and $\text{H-Cl} > \text{H-SH} > \text{H-PH}_2$ for the second-row. This point is consistent with the calculated natural charges on the H^1 atoms of the RH, where the natural charges on the H^1 atoms are 0.557, 0.457, 0.342 *e* in F-H^1 , OH-H^1 , $\text{NH}_2\text{-H}^1$ for the first-row hydrides and 0.247, 0.111, $-0.050 e$ in Cl-H^1 , SH-H^1 , $\text{PH}_2\text{-H}^1$ for the second-row. On the other hand, the reaction barriers are lower for the

second-row hydride and reactions are more exothermic than the first-row hydride, which means the substitution reactions of the second-row hydrides proceed more easily than those of the first-row. And this point is consistent with the strength of R-H bonds, where the common bond energies for H-Cl, H-S, and H-P (428, 363, and 322 kJ/mol)⁴³ are lower than that for the corresponding H-F, H-O, and H-N (565, 459, and 386 kJ/mol),⁴³ respectively.

3. 5. The Comparisons of the Reactions of $\text{H}_2\text{Ge} + \text{RH}$ and $\text{H}_2\text{GeClAlCl}_2 + \text{RH}$

We also calculated the reactions of H_2Ge with HF, H_2O , NH_3 , HCl , H_2S , and PH_3 at the same level of theory. The calculated results indicated that the reaction pathway of the reactions of H_2Ge with these hydrides is different from that of $\text{H}_2\text{GeClAlCl}_2$ with them. On the pathway of the reactions of H_2Ge with HF, H_2O , NH_3 , HCl , H_2S , and PH_3 , there is only one transition state which connected the reactants and the products. For the reactions of H_2Ge with these hydrides, the CCSD/6-311++G (*d, p*)/MP2/6-311+G (*d, p*) calculated reaction barriers are 101.72 (HF), 116.88 (H_2O), 125.57 (NH_3), 49.50 (HCl), 52.37 (H_2S), and 129.59 (PH_3), respectively. Therefore, the reactions of H_2Ge with these hydrides are easier to occur than the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with these hydrides. On the other hand, for the $\text{H}_2\text{GeClAlCl}_2$, the dissociation energy onto H_2Ge and AlCl_3 is about 96.11 kJ/mol. Thus, the possible reaction pathway of $\text{H}_2\text{GeClAlCl}_2$ with HF, H_2O , NH_3 , HCl , H_2S , and PH_3 seems to firstly dissociation onto H_2Ge and AlCl_3 , and then the addition of H_2Ge with HF, H_2O , NH_3 , HCl , H_2S , and PH_3 occurs.

4. Conclusions

In present work, the substitution reactions of the aluminum chlorogermolenoid $\text{H}_2\text{GeClAlCl}_2$ with HF, H_2O , NH_3 , HCl, H_2S , and PH_3 have been studied using MP2 and CCSD methods. It should be mentioned that this work has provided the first theoretical demonstration about the reaction trajectory and theoretical estimation of the activation energy and reaction energy for those processes. The theoretical results indicate that the mechanisms of the six reactions are identical to each other. For each substitution reaction a transition state and an intermediate were located. The calculated barrier heights for the six different substitution reactions of R = F, OH, NH_2 , Cl, SH, and PH_2 are 159.39, 178.01, 179.81, 112.61, 122.05, and 179.66 kJ/mol, respectively. All the substitution reactions are exothermic. These theoretical calculations suggest that: (i) the mechanisms of the six reactions are identical; (ii) under the same condition the substitution reactions should occur easily in the order of $\text{H-F} > \text{H-OH} > \text{H-NH}_2$ for the first-row hydrides and $\text{H-Cl} > \text{H-SH} > \text{H-PH}_2$ for the second-row; (iii) the substitution reactions of the second-row hydrides proceed more easily than those of the first-row. For the $\text{H}_2\text{GeClAlCl}_2$, the dissociation energy onto H_2Ge and AlCl_3 is about 96.11 kJ/mol. And the reactions of H_2Ge with HF, H_2O , NH_3 , HCl, H_2S , and PH_3 have lower energy barriers than those of $\text{H}_2\text{GeClAlCl}_2$ with these hydrides. Therefore, the substitution reactions of $\text{H}_2\text{GeClAlCl}_2$ with HF, H_2O , NH_3 , HCl, H_2S , and PH_3 involve two steps. One is dissociation onto H_2Ge and AlCl_3 , and the other is the addition reactions of H_2Ge with HF, H_2O , NH_3 , HCl, H_2S , and PH_3 .

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Povzetek

Da bi pridobili več vpogleda v reaktivnost aluminijevega klorogermilenoida $\text{H}_2\text{GeClAlCl}_2$ smo izvedli kvantokemijske izračune za reakcije substitucije z HF, H_2O , NH_3 , HCl, H_2S , in PH_3 . Ugotovili smo, da vse proučevane reakcije potekajo podobno-preko enega prehodnega stanja in enega intermediata. Reakcije substitucije $\text{H}_2\text{GeClAlCl}_2$ z HF, H_2O , NH_3 , HCl, H_2S , in PH_3 smo primerjali tudi z dodatnimi reakcijami H_2Ge s temi hidridi. Izkazalo se je, da reakcije substitucije $\text{H}_2\text{GeClAlCl}_2$ s hidridi potekajo v dveh stopnjah, ena je disociacija v H_2Ge in AlCl_3 , in drugo predstavljajo dodatne reakcije H_2Ge z HF, H_2O , NH_3 , HCl, H_2S , in PH_3 .