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Theoretical investigation on H₂ elimination reactions of germylenoid H₂GeLiF with RH (R = F, OH, and NH₂)Wen-Zuo Li^{a,*}, Tao Liu^b, Jian-Bo Cheng^a, Qing-Zhong Li^a, Bao-An Gong^a^aThe Laboratory of Theoretical and Computational Chemistry, Science and Engineering College of Chemistry and Biology, Yantai University, Yantai 264005, PR China^bDepartment of Chemistry and Chemical Engineering, Jining University, Qufu 273155, PR China

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ABSTRACT

The H₂ elimination reactions of the germylenoid H₂GeLiF with RH (R = F, OH, NH₂) have been studied by using the DFT B3LYP and QCISD methods. The calculated results indicate that all the mechanisms of the three reactions are identical to each other and under the same condition the H₂ elimination reactions should occur easily in the order of H–F > H–OH > H–NH₂. In THF solvent the H₂ elimination reactions get more difficult than in gas phase. Compared with the insertion reactions of H₂GeLiF with RH (R = F, OH, NH₂), the H₂ elimination reactions have the lower activation barriers and should be more favorable.

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1. Introduction

The research of germanium reaction is an interesting topic since many organic germanium compounds have been found to have biologic activity [1–7]. The properties and reactions of germylene and its derivatives have been well studied [8,9]. Germylenoid, one of derivatives of germylene, which can be denoted as R₁R₂GeMX, may be stable than germylene and has particular property. In 1991, Lei and Gaspar [10] firstly put forward that germylenoid might be the intermediate in the reaction of dichlorodimethylgermane with substituted butadiene. In some other subsequent experiments [11–13] chemists believed that germylenoids should be important active intermediates. However, until now there are not any stable germylenoids being prepared by experiments. It is necessary to carry out systemic theoretical study on the geometries, properties, and reactions of the germylenoids and the theoretical work could provide much useful information about germylenoid. Since Qiu et al. [14] firstly studied the isomeric structure of the simplest germylenoid H₂GeLiF by *ab initio* calculations, up to now, the equilibrium configurations and the isomerization reactions of the germylenoids H₂GeMX, H₂GeXMX, and H₂C=GeMX (M = Li, Na, Be, or Mg; X = F, Cl) [15–23] have been investigated. Some other germylenoids HN=GeNaF [24] and H₂GeClAlCl₂ [25] also have been studied. Theoretical studies on the reactions of the germylenoids with other substance were not many

and only some insertion reactions of germylenoids with R–H (R = F, OH, NH₂, and CH₃) [15,20,23,24] have been calculated. What are other reaction pathways of germylenoid with RH except insertion into R–H ones and which pathway is preferable? This is an interesting topic not only to theoretical but also to experimental workers. Recently, we performed theoretical investigation on the H₂ elimination reactions of the germylenoid H₂GeLiF with RH (R = F, OH, and NH₂) and the calculations would provide some new information about the reaction of germylenoid. In the present paper we will clarify the mechanism of the H₂ elimination reactions and compare the H₂ elimination pathways with the insertion pathways of H₂GeLiF with RH (R = F, OH, and NH₂).

2. Computational details

All geometries of the stationary points on the potential energy surfaces of the H₂ elimination reactions of the germylenoid H₂GeLiF with RH (R = F, OH, and NH₂) were fully optimized by using the density functional theory (DFT) B3LYP (Becke's three-parameter hybrid function with the non-local correlation of Lee–Yang–Parr) [26,27] method. In the geometry optimization calculations the 6-311+G(d,p) [28] basis set has been used for all atoms. The geometries were first optimized and then the harmonic vibrational frequencies were calculated at the same level of theory to confirm the nature of the stationary points. The nature of a given transition state was analyzed by IRC (intrinsic reaction coordinate) [29] computations at the same level. The B3LYP/6-311+G(d,p) natural bond order (NBO) analysis calculations were performed at the optimum

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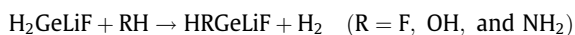
E-mail address: liwenzuo2004@126.com (W.-Z. Li).

geometries. In order to improve the treatment of electron correlation the single-point calculations were made at the QCISD level using the 6-311++G(*d,p*) basis set for all species. Unless otherwise noted, relative energies given in the text are those determined at QCISD/6-311++G(*d,p*)/B3LYP/6-311+G(*d,p*) and include vibrational zero-point energy (ZPE, without scale) corrections determined at B3LYP/6-311+G(*d,p*) level. To consider solvent effects on the reactions, the polarized continuum model (PCM) [30–32] was applied to the calculations and the solvent tetrahydrofuran (THF) was used. All of the calculations were carried out using the GAUSSIAN 03 program suits [33].

3. Results and discussion

The theoretical calculations indicated that the germylenoid H_2GeLiF has three equilibrium configurations [15], in which the *p*-complex is the lowest in energy and this structure is suggested to be experimentally detectable one. In this work, the *p*-complex is adopted and in the following text the H_2GeLiF is the *p*-complex unless otherwise noted.

The H_2 elimination reactions of the germylenoid H_2GeLiF with RH ($\text{R} = \text{F}, \text{OH}, \text{and } \text{NH}_2$) take place as the following formula:



The reaction pathway involves a four-membered ring transition state (TS) and the TS then separates to form the products: substituted four-membered ring germylenoid HRGeLiF and H_2 molecule. The relative energies of reactants, transition states, and products of the H_2 elimination reactions are listed in Table 1. The B3LYP/6-311+G(*d,p*) optimized stationary structures of all the stationary points are shown in Fig. 1.

3.1. The structures and energies of the transition states

The NBO calculated results indicate that there is negative charge lying on the two H atoms of the *p*-complex of H_2GeLiF . When the RH approaches the H_2Ge moiety of H_2GeLiF , a positive H atom transferring from R to negative H atom is conceivable. As shown in Fig. 1, the calculated transition states (XTS, $\text{X} = \text{F}, \text{O}$, and N) in the H_2 elimination reactions have similar structures. It

Table 1
Relative energies^a (in kJ mol^{-1}) of reactants, transition states (TS), and products of the H_2 elimination reactions of the germylenoid H_2GeLiF with RH ($\text{R} = \text{F}, \text{OH}, \text{NH}_2$) in gas phase.^b

Species	R = F	R = OH	R = NH_2
$\text{H}_2\text{GeLiF} + \text{R}-\text{H}$	0.00	0.00	0.00
TS	100.67 (123.08)	148.82 (181.97)/144.57 (177.80)	173.72 (210.15)
$\text{HRGeLiF} + \text{H}_2$	-128.67 (-66.25)	-93.02 (-24.80)/-93.02 (-24.77)	-62.57 (3.01)

^a Calculated at the QCISD/6-311++G(*d,p*)/B3LYP/6-311+G(*d,p*) level and include vibrational zero-point energy (ZPE, without scale) corrections determined at B3LYP/6-311+G(*d,p*) level.

^b Values in parentheses were calculated in THF, see text.

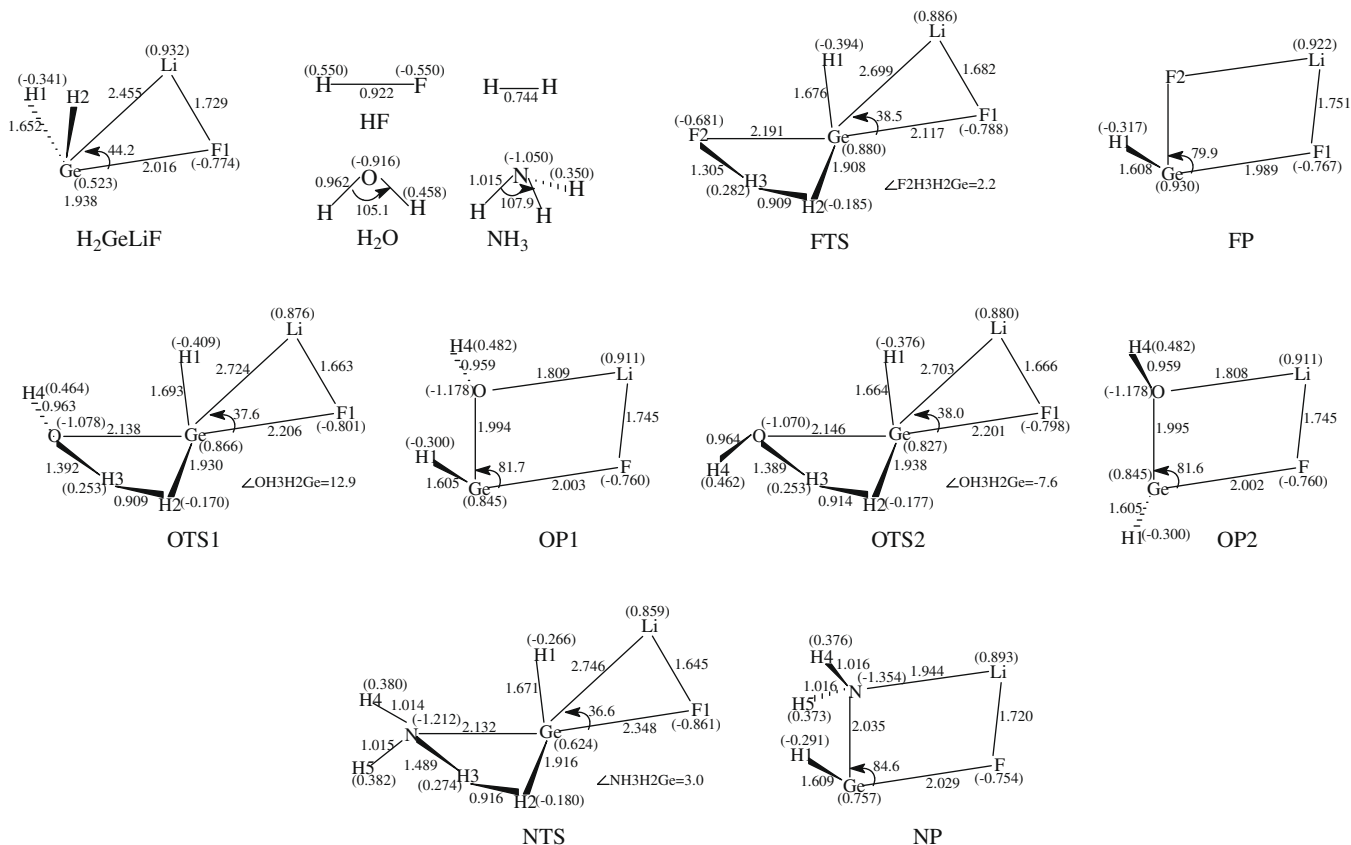


Fig. 1. The geometries of the stationary points of the H_2 elimination reactions of the germylenoid H_2GeLiF with RH ($\text{R} = \text{F}, \text{OH}, \text{NH}_2$) in gas phase calculated at B3LYP/6-311+G(*d,p*) level (bond lengths are given in angstroms and angles in degrees, values in parentheses are the natural charges).

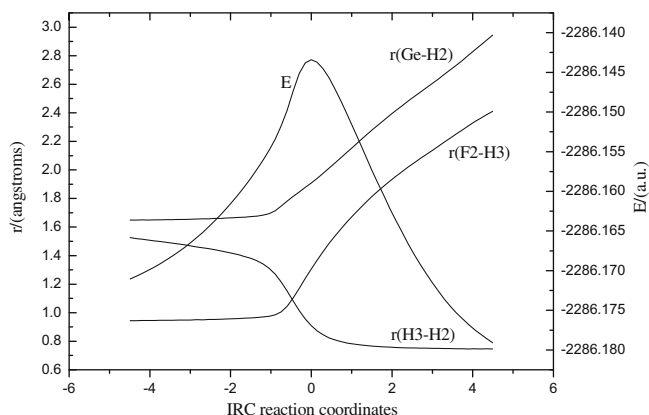


Fig. 2. The changes of energies and bond distances along the reaction coordinates.

is noted that when $R = OH$, there exist two reaction pathways. Among all the transition states, a four-membered ring involving Ge, H2, H3, and X ($X = F, O,$ and N , respectively, see in Fig. 1) exists. Compared with the isolated H_2GeLiF , the bond distances between Ge and H2 have been elongated by about 0.256, 0.278, 0.286, and 0.264 Å, when $R = F, OH,$ and NH_2 , respectively. On the other hand, as displayed in Fig. 1 the bond distance of $R-H3$ has been elongated significantly to 1.305, 1.392, 1.389, and 1.489 Å from 0.922, 0.962, 0.962, and 1.015 Å, respectively. In the transition states the $H3-H2$ bond distance is near to the $H-H$ bond length of H_2 molecule. Thus, in these transition states, the $Ge-H2$ and $R-H3$ bond are to be broken and a new $H-H$ bond to be formed simultaneously.

The frequency analysis calculations indicated that the four TSs all has unique imaginary frequency. At the B3LYP/6-311+G(*d,p*) level, the imaginary frequency of FTS, OTS1, OTS2, and NTS is 939.9i, 1100.2i, 1150.2i, and 1207.6i, respectively. As shown in Table 1, the relative energies of FTS, OTS1, OTS2, and NTS to their respective reactants ($H_2GeLiF + RH$) are 100.67, 148.82, 144.57, and 173.72 $kJ\ mol^{-1}$, respectively.

3.2. The structures and energies of the products

The H_2 elimination reactions of the germylenoid H_2GeLiF with RH ($R = F, OH,$ and NH_2) finally lead to the separate products, a substituted four-membered ring germylenoid $HRGeLiF$ and a H_2 molecule. As displayed in Fig. 1, FP, OP1, OP2, and NP are the substituted four-membered ring germylenoid. From Table 1 we can see that the reaction energies for the three reactions are -128.67 ($R = F$), $-93.02/93.02$ ($R = OH$), and -62.57 ($R = NH_2$) $kJ\ mol^{-1}$, respectively.

3.3. The mechanism of H_2 elimination reactions

Taking the H_2 elimination reaction of $H_2GeLiF + HF$ as an example, IRC calculations have been performed on the basis of the calculated FTS to investigate the interaction between two reactants in the H_2 elimination process. The total energy change and the variations of $H3-H2$, $F2-H3$, and $Ge-H2$ bond distances along the IRC path are shown in Fig. 2. From Fig. 2, it can be seen that as the reaction coordinate passes from point -1.0 to 0.0 , the total energy increases sharply and reaches its maximum. In this region, the $Ge-H2$ and $F2-H3$ distances increase and $H2-H3$ distance decreases evidently. The $H2-H3$ distance then approach a constant, and $H2-H3$ bond forms at around point 1.0 with the decomposition of the $Ge-H2$ and $F2-H3$ bonds. The region from 0.0 to 4.0 could be denoted as the H_2 elimination region. We think other H_2 elimination reactions of H_2GeLiF with RH ($R = F, OH, NH_2$) have the same mechanism with $H_2GeLiF + HF$ reaction.

Table 2

Relative energies^a (in $kJ\ mol^{-1}$) of reactants, transition states (TS), intermediates (IM), and products of the insertion reactions of the germylenoid H_2GeLiF with RH ($R = F, OH, NH_2$) in gas phase.^b

Species	R = F	R = OH	R = NH_2
$H_2GeLiF + R-H$	0.00	0.00	0.00
TS	126.49 (132.09)	176.01 (191.16)	212.77 (240.97)
IM	-86.47 (-81.61)	-45.35 (-36.14)	-22.14 (-10.21)
$H_3RGe + LiF$	-29.24 (-58.26)	-7.19 (-40.24)	5.99 (-27.70)

^a Calculated at the QCISD/6-311++G(*d,p*)/B3LYP/6-311+G(*d,p*) level and include vibrational zero-point energy (ZPE, without scale) corrections determined at B3LYP/6-311+G(*d,p*) level.

^b Values in parentheses were calculated in THF, see text.

3.4. The comparisons of three H_2 elimination reactions

As displayed in Table 1, the calculated energy barriers for the three different H_2 elimination reactions of $R = F, OH,$ and NH_2 are 100.67, 148.82/144.57, and 173.72 $kJ\ mol^{-1}$, respectively, suggesting their different reactivities. Correspondingly, the calculated relative reaction energies of them are -128.67 ($R = F$), $-93.02/93.02$ ($R = OH$), and -62.57 ($R = NH_2$) $kJ\ mol^{-1}$, respectively. Therefore, from the thermodynamic and kinetic viewpoints, the H_2 elimination reactions under the same situation should occur easily according to the following orders: $H-F > H-OH > H-NH_2$. The explanation for this trend above is connected with the electronic effect as well as the steric effect. As shown in Fig. 1, the natural charges of H atom in RH is in the order of HF (0.550) $> H_2O$ (0.458) $> NH_3$ (0.350). Distinctly, it is easier for the positive H end of $H-F$ bond to interact with the negative H2 atom of H_2GeLiF than that for the $H-O$ bond. This interaction leads to a lower barrier height for HF reaction. On the other hand, considering the steric effect, it is relatively difficult for NH_3 molecule to approach and interact with H_2GeLiF , resulting in a higher energy barrier for H_2GeLiF with NH_3 reaction than the reactions with HF and H_2O .

3.5. The solvent effect

To consider the solvent effects on the reactions, using the PCM model and the THF solvent, the QCISD/6-311++G(*d,p*) single-point calculations were carried out at the B3LYP/6-311+G(*d,p*) optimized geometries in gas phase. The calculated relative energies are also listed in Table 1. It can be seen from Table 1 that the relative energies of the TSs and products for the three H_2 elimination reactions calculated in THF are higher respectively than those calculated in gas phase. This means in THF the energy barriers for the three H_2 elimination reactions get higher and the higher energy barriers imply that the H_2 elimination reactions get more difficult within the THF solvent.

3.6. Comparison with insertion pathways

Tan et al. [15] reported their B3LYP/6-311+G(*d,p*) calculated results on the insertion reactions of the germylenoid H_2GeLiF with RH ($R = F, OH, NH_2$) in 2006. To compare the H_2 elimination reactions and the insertion reactions, we performed QCISD/6-311++G(*d,p*)/B3LYP/6-311+G(*d,p*) calculations on the insertion reactions of the germylenoid H_2GeLiF with RH ($R = F, OH, NH_2$) in gas phase and in THF. The calculated relative energies of the reactants, transition states, intermediates, and products of the three insertion reactions are displayed in Table 2. From Table 2 we can see though our QCISD/6-311++G(*d,p*)/B3LYP/6-311+G(*d,p*) calculated relative energies are different from the B3LYP/6-311+G(*d,p*) calculated results [15], the trends of the three insert reactions do not change: under the same condition the insertion reactions should occur easily in the order of $H-F > H-OH > H-NH_2$. The

trends of the insertion reactions are similar to those for the H₂ elimination reactions of the germylenoid H₂GeLiF with RH (R = F, OH, NH₂). However, the H₂ elimination reactions have the lower activation barriers both in gas phase and in THF (see Tables 1 and 2), which means that the H₂ elimination pathway should be more favorable.

4. Conclusions

The H₂ elimination reactions of the germylenoid H₂GeLiF with RH (R = F, OH, NH₂) have been studied by using the DFT B3LYP and QCISD methods. For each H₂ elimination reaction a four-membered ring transition state and a substituted four-membered ring germylenoid HRGeLiF were located. The calculated barrier heights for the three different H₂ elimination reactions of R = F, OH, and NH₂, are 100.67, 148.82/144.57, and 173.72 kJ mol⁻¹, respectively. All the mechanisms of the three reactions are identical to each other. The calculated results indicate that under the same condition the H₂ elimination reactions should occur easily in the order of H–F > H–OH > H–NH₂. In THF solvent the H₂ elimination reactions get more difficult than in gas phase. Compared with the insertion reactions of H₂GeLiF with RH (R = F, OH, NH₂), the H₂ elimination reactions have the lower activation barriers and should be more favorable.

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