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Effects of Substituents on the Thermodynamic and Kinetic Stabilities of HCGeX (X = H, CH_3, F, and Cl) Isomers. A Theoretical Study

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The effect of substitution on the potential energy surfaces of $HC\equiv GeX$ (X = H, CH_3, F, and Cl) were explored using density functional theory (B3LYP) and QCISD methods. The theoretical findings suggest that $(H)(X)C{=}Ge{:}$ is the minimum on the singlet potential energy surface, regardless of the substituents (X) used. On the other hand, $HC\equiv GeX$ and $XC\equiv GeH$ are found to be local minima on the surface, but they are neither kinetically nor thermodynamically stable.

I. Introduction

The synthesis of unsaturated compounds of group 14 elements has interested many generations of chemists. Very few compounds exist that contain multiple bonds between carbon and its heavier main-group analogues. Experimentally, $C{=}Si$[1−4] and $C{=}Ge$[5−10] moieties have now been isolated and determined by various methods. However, only for silicon has the existence of intermediates triply bonded to carbon been established.[11−15] Attention should therefore naturally be directed toward the search for the corresponding germanium analogues. In fact, despite the upsurge of interest, there is as yet no strong experimental evidence for the existence of molecules containing a carbon−germanium triple bond.

There are, to the best of our knowledge, only two computational studies that explore the structural properties and energies of germyne ($HC\equiv GeH$) and germylidene ($H_2C{=}Ge$) isomers.[16,17] Nevertheless, very little is known about the nature of the transition state or the energy barrier separating triply bonded from the doubly bonded species. Here, we report the first density functional theory (DFT) study of the triply bonded compounds $HC\equiv GeX$ (X = H, CH_3, F, and Cl) in the anticipation that such theoretical information will be useful for further experimental considerations. Indeed, it is believed that in view of recent dramatic developments in silaethyne chemistry,[18,19] analogous extensive studies of molecules with triply bonded germanium should soon be forthcoming and open up new areas.

II. Methodology

All geometries were fully optimized with the nonlocal hybrid density functional method at the B3LYP level.[20−22] The reason for using the B3LYP method is that it has been shown to be quite reliable both for geometries and for energetics.[23] The 6-311G* basis set has been used for C, Ge, F, Cl, and H (denoted B3LYP/6-311G*).[24]

The geometries were first optimized using the DFT models described above. The harmonic vibrational frequencies were then calculated at the same level of theory to confirm the nature of the stationary points.

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For all species single-point calculations were made at the QCISD[25] level using the 6-311++G** basis set. Unless otherwise noted, relative energies given in the text are those determined at QCISD/6-311++G**//B3LYP/6-311G* (hereafter designed QCISD) and include vibrational zero-point energy (ZPE, without scale) corrections determined at B3LYP/6-311G*.

All calculations were performed on an IBM590 in our laboratory, with the Gaussian 94 programs.[26]

III. Results and Discussion

The purpose of the work reported in this paper is to determine the unimolecular rearrangement pathways and barrier height for the molecules previously mentioned. To achieve this, it was necessary to determine the optimum geometries of all stationary points for possible reaction paths. In the case of HC≡GeX, there could be two kinds of rearrangement routes, i.e., (A) 1,2-H-shifted from HC≡GeX to :C=Ge(H)(X) and (B) 1,2-X-shifted from HC≡GeX to (H)(X)C=Ge:.

The optimized equilibrium geometries for all reactants, transition states (TS), and products (Pro) are shown in Figures 1 and 2. For convenience, we have also given the energies relative to the HC≡GeX reactant molecule. The corresponding total and relative energies for two reaction mechanisms are collected in Table 1. The vibrational frequencies calculated at the B3LYP/6-311G* level of theory are listed in Table 2 along with available computational values.[12]

All the optimum equilibrium geometries of HCGeX isomers are calculated to be planar, as in the case of HCSiX.[11] As mentioned earlier, to our knowledge, no experimental data are available for comparison. Nevertheless, the most recent theoretical values (CCSD/TZ(2df,2pd)) for germyne (**1**), germyne−germavinylidene TS (**1-B-TS**), and germavinylidene (**1-B-Pro**) were obtained by Stogner and Grev.[17] As one can see in Figure 1, our B3LYP results are in consistent agreement with the CCSD results. The bond lengths and angles are in agreement to within 0.01 Å and 6°, respectively. Besides this, as seen in Table 1, our QCISD relative energies are in accordance with those from the CCSD/TZ(2df,2pd) level of theory. Also, as shown in Table 2, the theoretically predicted singlet-state vibrational frequencies are generally in reasonable agreement with previously calculated fundamental frequencies.[17] As a result of the good agreement between DFT (B3LYP) and the more sophisticated theory (CCSD) on the known singlet-state features, we are confident that the computational methods used in this study are reliable.

Furthermore, some interesting conclusions, which may be drawn from Figures 1 and 2 and Table 1, are as follows.

(1) It appears that fluorine and chlorine substitutions lengthen both C≡Ge and C=Ge bonds, particularly if the substitution occurs at the germanium. Namely, the π-donor substitution seems to weaken the triple and double bonds, with substitution at Ge having a greater effect. On the other hand, methyl substitution (σ-donor substitution), has virtually no impact on either C≡Ge or C=Ge bond lengths. Additionally, our theoretical results suggest that all the HC≡GeX isomers have a planar singlet geometry. This may indicate that the repulsive interaction between the π-donor lone pair and the occupied π orbital on carbon−germanium multiple bonds play a dominant role on their bond lengths. This therefore appears to be a π effect.

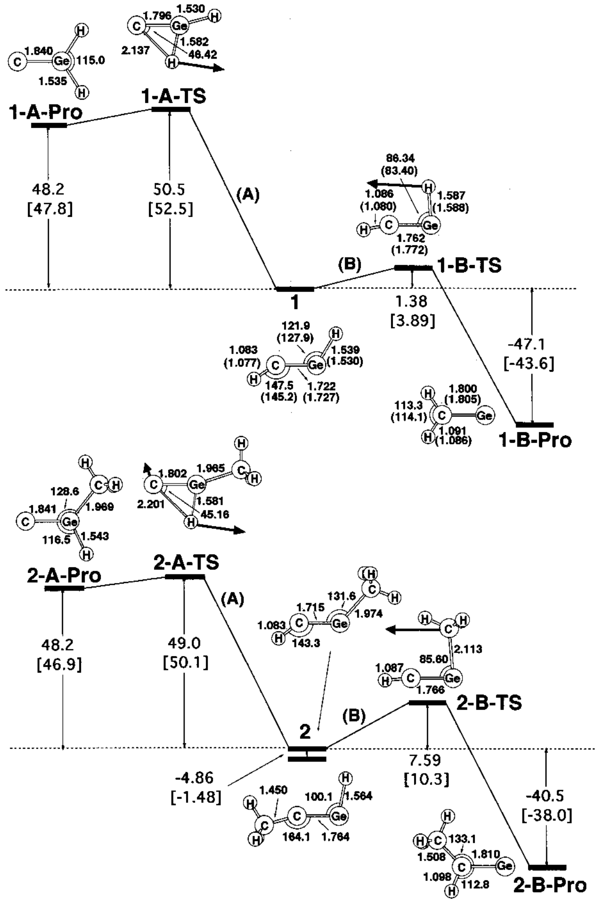

Figure 1. Potential energy surfaces for HCGeX (X = H and CH_3). All geometrical structures (bond lengths in Å and bond angles in deg) were calculated at the B3LYP/6-311G* level of theory. Values taken from the previous work (see ref 15) are in parentheses, and values calculated at QCISD + ZPE level of theory are in brackets. The heavy arrows indicate the main atomic motions in the transition-state eigenvector.

(2) It must be mentioned here that the conventional linear HC≡GeX molecules are not minima on the potential energy surfaces for all systems. Their one imaginary frequency leads to the corresponding trans−bent geometry minima whose energies relative to the other isomers change significantly with substitution (vide infra).

(3) Note that all the relative energies in Table 1 show that the B3LYP values reproduce the QCISD results qualitatively. It must be pointed out that HC≡GeF is anticipated to be more stable than FC≡GeH at both DFT and QCISD methods. The calculated energy difference between HC≡GeF and FC≡GeH, however, differs appreciably: 12 kcal/mol at the B3LYP/6-311G* level and 50 kcal/mol at the QCISD/6−311++G**//B3LYP/6-311G* level. This suggests that FC≡GeH possesses unusual bonding, in which the accuracy of the B3LYP method for describing the triple bond is open to question. We therefore optimize the geometries of FC≡GeH and HC≡GeF at the QCISD/6-311G* level of theory.[27] From Figure 2 it can be seen that the QCISD/6-311G* computational result (51 kcal/mol) is in good agreement with the QCISD/6-311++G**//B3LYP/6-311G* result (50 kcal/mol). The QCISD relative energies are therefore seemingly more accurate than the DFT results for the HC≡GeX systems. In short, considering the speed of the DFT

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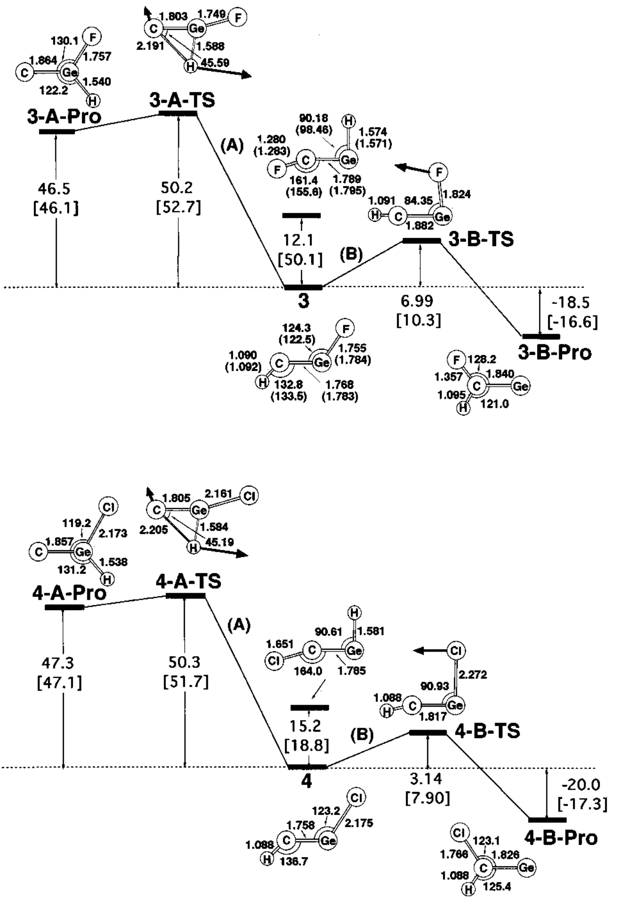

Figure 2. Potential energy surfaces for HCGeX (X = F and Cl). All geometrical structures (bond lengths in Å and bond angles in deg) were calculated at the B3LYP/6-311G* level of theory. Values calculated at QCISD + ZPE level of theory are in brackets. Values in parentheses were fully optimized structures at QCISD/6-311G* methods. The heavy arrows indicate the main atomic motions in the transition-state eigenvector.

method, it seems ideal for the determination of molecular structures. For determination of accurate energies, the QCISD results give somewhat different and more accurate results than does B3LYP. Since $HC\equiv GeX$ (X = H, CH_3, F, and Cl) is a model system for the substituent effect on carbon−germanium multiple bonds, these results may serve as a benchmark for modeling the substituent effect in triply bonded germanium compounds.

(4) One of the more interesting differences found between these results and those reported for the Si system in ref 11 is the fact that $FHC{=}Ge$: is predicted to be more stable than $HC\equiv GeF$, while in the Si system the order of energy was reversed. To make sure that the energy reversal is due to the difference in atomic composition rather than the computational method applied, we have used the B3LYP/6-311G* method to optimize the geometries of $FHC{=}Si$: and $HC\equiv SiF$. Our computational results suggest that $HC\equiv SiF$ is still 2.0 kcal/mol (ZPE has been considered) lower in energy than $FHC{=}Si$: , which is in consistent agreement with the previous studies done by Apeloig and co-workers.[11] Again, this implies that B3LYP/6-311G* calculations should provide an adequate theoretical level for further investigations of the molecular geometries and the kinetic features of the rearrangement reactions.

Table 1. Energies and Relative Energies of HCGeX Isomers (X = H, CH_3, F, and Cl)[a]

species	B3LYP[b,c]	QCISD[c,d]	other work[e]
$HC\equiv GeH$ **(1)**	0.0[f]	0.0[g]	0.0
1-A-TS	50.51	52.47	
$C{=}GeH_2$	48.19	47.81	
1-B-TS	1.378	3.886	7.4
$H_2C{=}Ge$	−47.09	−43.65	−43.4
$HC\equiv GeCH_3$ **(2)**	0.0[h]	0.0[i]	
2-A-TS	49.02	50.06	
$C{=}Ge(H)(CH_3)$	48.19	46.94	
2-B-TS	7.588	10.33	
$(H_3C)(H)C{=}Ge$	−40.49	−38.05	
$(H_3C)C\equiv GeH$	−4.864	−1.480	
$HC\equiv GeF$ **(3)**	0.0[j]	0.0[k]	
3-A-TS	50.23	52.66	
$C{=}Ge(H)(F)$	46.48	46.09	
3-B-TS	6.988	10.26	
$(F)(H)C{=}Ge$	−18.45	−16.62	
$FC\equiv GeH$	12.09	50.08	
$HC\equiv GeCl$ **(4)**	0.0[l]	0.0[m]	
4-A-TS	50.32	51.72	
$C{=}Ge(H)(Cl)$	47.32	47.06	
4-B-TS	3.141	7.902	
$(Cl)HC{=}Ge$	−20.03	−17.27	
$ClC\equiv GeH$	15.19	18.80	

[a] Relative energies in kcal/mol. [b] Using the 6-311G* basis set. [c] Relative energies include the zero-point energy correlations at the B3LYP/6-311G* level of theory. [d] Using the 6-311++G** basis and B3LYP/6-311G* geometries. [e] Computational results are taken from ref 17. Relative energies are at the CCSD(T)/TZ(2df,2pd)//CCSD/TZ(2df,2pd) level of theory. [f] Total energy is −2116.18163 hartrees. [g] Total energy is −2114.47062 hartrees. [h] Total energy is −2155.51524 hartrees. [i] Total energy is −2153.68592 hartrees. [j] Total energy is −2215.47502 hartrees. [k] Total energy is −2213.56941 hartrees. [l] Total energy is −2575.84616 hartrees. [m] Total energy is −2573.57078 hartrees.

(5) For the C≡Ge triply bonded species, there exists two kinds of isomers, i.e., $HC\equiv GeX$ and $XC\equiv GeH$. Our QCISD calculations suggest that $XC\equiv GeH$ is calculated to be considerably less stable than $HC\equiv GeX$ by 50 (X = F) and 19 (X = Cl) kcal/mol. In contrast, CH_3 reverses the stability order, and $(H_3C)C\equiv GeH$ is predicted to be more stable than $HC\equiv Ge(CH_3)$ by 1.5 kcal/mol. This large effect can be understood in terms of the strength of C−X vs Ge−X (X = CH_3, F, and Cl) bonds (bond dissociation energies: C−C = 145 kcal/mol, Ge−C = 110 kcal/mol; C−F = 132 kcal/mol, Ge−F = 116 kcal/mol; C−Cl = 95 kcal/mol, Ge−Cl ≈ 103 kcal/mol).[28] That is, the very strong C−C bond can conquer the large preference of $HC\equiv GeX$ over $XC\equiv GeH$.

(6) It is clear from Figures 1 and 2 and Table 1 that two double-bonded germanium structures with C_s symmetry exist as minima on the potential energy surface. Namely, one is $:C{=}Ge(H)(X)$ (i.e., **1-A-Pro**, **2-A-Pro**, **3-A-Pro**, and **4-A-Pro**), which has the lone electron pair residing on the carbon, and the other is $(H)(X)C{=}Ge$: (i.e., **1-B-Pro**, **2-B-Pro**, **3-B-Pro**, and **4-B-Pro**), which has the lone pair residing on the germanium. Moreover, it should be noted that the former structure ($:C{=}Ge(H)(X)$) possesses the highest energy of all

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(27) The QCISD method, while falling short of the accuracy of methods that include the triple excitations (e.g., CCSD(T)), generally produces good results for many molecules that are challenging for electron correlation methods. In the Gaussian system of programs, optimizations using the QCISD method are much less time-consuming than those using QCISD(T), yet the energy obtained in the optimization can still be compared with the QCISD/6-311G*//MP2/6-311G* energy and used to evaluate the energetic effect of the difference between the MP2 and QCISD geometries. See the following. Ragavachari, K. *Annu. Rev. Phys. Chem.* **1991**, *42*, 615.

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Table 2. Vibrational Frequency (in cm^{-1}) and Zero-Point Energy (ZPE) (in kcal/mol)[a]

species	frequency[b]	ZPE
$HC\equiv GeH$ **(1)**	3245, 2085, 937, 788, 525, 311	11.28
1-A-TS	2094, 1959, 854, 676, 217, 396i	8.291
$C{=}GeH_2$	2120, 2086, 794, 765, 297, 212	8.969
1-B-TS	3215, 1924, 1904, 843, 446, 433i	10.48
$H_2C{=}Ge$	3160 (3217), 3079 (3128), 1368 (1369), 785 (795), 684, (683), 426 (404)	13.58
$HC\equiv GeCH_3$ **(2)**	3242, 3157, 3152, 3061, 1482, 1472, 1278, 948, 835, 788, 722, 547, 470, 138, 28	30.48
2-A-TS	3153, 3144, 3057, 1961, 1477, 1476, 1289, 869, 842, 806, 555, 328, 136, 79, 232i	27.41
$C{=}Ge(H)(CH_3)$	3147, 3131, 3051, 2100, 1481, 1480, 1291, 872, 795, 779, 568, 543, 276, 101, 99	28.19
2-B-TS	3202, 3181, 3159, 3064, 1486, 1467, 1220, 890, 817, 758, 749, 446, 369, 116, 235i	29.90
$(H_3C)(H)C{=}Ge$	3078, 3037, 3028, 3000, 1514, 1499, 1418, 1289, 1101, 1022, 936, 617, 598, 197, 162	32.16
$H_3CC\equiv GeH$	3040, 3016, 2971, 2013, 1488, 1431, 1382, 1310, 1025, 924, 561, 476, 261, 125, 108	28.78
$HC\equiv GeF$ **(3)**	3176, 826, 767, 647, 390, 160	8.529
3-A-TS	1936, 845, 654, 336, 77, 349i	5.503
$C{=}Ge(H)(F)$	2103, 765, 673, 628, 280, 130	6.546
3-B-TS	3159, 740, 638, 564, 156, 207i	7.514
$(F)(H)C{=}Ge$	3058, 1346, 1132, 642, 606, 185	9.963
$FC\equiv GeH$	1978, 1436, 609, 514, 258, 77	6.965
$HC\equiv GeCl$ **(4)**	3191, 828, 758, 399, 382, 125	8.123
4-A-TS	1950, 829, 393, 294, 69, 306i	5.053
$C{=}Ge(H)(Cl)$	2115, 760, 607, 399, 274, 92	6.072
4-B-TS	3200, 834, 674, 344, 244, 180i	7.571
$(Cl)HC{=}Ge$	3137, 1194, 862, 596, 560, 108	9.231
$ClC\equiv GeH$	1940, 1147, 523, 407, 204, 47	6.103

[a] Calculation at the B3LYP/6-311G* level of theory. [b] Computational results in parentheses are taken from ref 17.

minima on the HCGeX surface, whereas the latter structure ($(H)(X)C{=}Ge$:) is predicted to be the most stable in its corresponding isomers at the computational levels employed in this work. According to our QCISD results as given in Table 1, the energy difference between $:C{=}Ge(H)(X)$ and $(H)(X)C{=}Ge$: is generally at least >63 kcal/mol. In other words, the singlet states of the $C{=}Ge$ species prefer to have the nonbonding electrons residing on germanium rather than on carbon. This thermodynamic stability of $(H)(X)C{=}Ge$: relative to $:C{=}Ge(H)(X)$ is attributed to the ability of germanium's diffuse electron cloud to accommodate a lone electron pair more easily than that of carbon.[16] Moreover, reflecting the large exothermicity, the transition state for path B (i.e., **1-B-TS**, **2-B-TS**, **3-B-TS**, and **4-B-TS**) rather resembles the $HC\equiv GeX$ molecule in structure and is *early*, as shown in Figures 1 and 2. According to the Hammond postulate,[29] an early transition state for an exothermic reaction means a lower activation energy. Our computational results confirm this prediction. For example, the calculated values for the path B barrier are 3.9 (**1-B-TS**), 10 (**2-B-TS**), 10 (**3-B-TS**), and 7.9 (**4-B-TS**) kcal/mol. It is therefore conceivable that $(H)(X)C{=}Ge$: itself is, both kinetically and thermodynamically, stable with respect to isomerization, regardless of the substituents applied.

(7) On the other hand, the transition state for path A resembles the $:C{=}Ge(H)(X)$ product molecule and is *late*, as depicted in Figures 1 and 2. Reflecting the *late* transition state, the energy barriers for the isomerization of $HC\equiv GeX$ to $:C{=}Ge(H)(X)$ are calculated to be 52 (**1-A-TS**), 50 (**2-A-TS**), 53 (**3-A-TS**), and 52 (**4-A-TS**) kcal/mol, while the activation energies for the reverse reaction from $:C{=}Ge(H)(X)$ to $HC\equiv GeX$ are 4.7, 3.1, 6.6, and 4.7 kcal/mol, respectively, at the QCISD level of theory. These results strongly indicate that $:C{=}Ge(H)(X)$ is kinetically unstable and may rearrange spontaneously to the more stable minima if it was produced. In consequence, our theoretical findings suggest that the $:C{=}Ge(H)(X)$ molecules are unlikely to be observed experimentally.

Finally, through the elegant studies performed by Apeloig, Schaefer, Gordon, Leszczyñski, Grev, Schwarz, and many coworkers,[11−16] it was found that the heavier analogues of acetylene do not exhibit the triply bonded geometry but rather have the dibridged butterfly global minimum. Nevertheless, Apeloig and Karni clearly demonstrated that the unimolecular and kinetic stability of silaacetylenes is strongly dependent on the substituents, pointing to $FSi\equiv CH$, $R'OSi\equiv CH$ as viable candidates for experimental observation.[11b] Most recently, this prediction has been verified by Schwarz, Apeloig, and coworkers using the conventional variant of neutralization−reionization mass spectrometry.[11c] In contrast, the theoretical investigations based on this work indicate that the carbon−germanium triple bond is particularly unstable in both a thermodynamic and a kinetic sense, as is demonstrated by the isomerization energy relative to singlet $HC\equiv GeX$. Thus, unlike the case of $HC\equiv SiX$, the prospects of observing the *singlet* $HC\equiv GeX$ (or $XC\equiv GeH$) in a matrix or even as a transient intermediate appear to be small. Nevertheless, it is still believed that the presence of very bulky substituents at both ends of the $C\equiv Ge$ molecule may perhaps protect the triple bond from both intramolecular isomerizations and intermolecular polymerizations.

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