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Structures and Mutual Transformations of Isomers of Germylium Ions $(CH_3)H_2Ge^+$ and $(CH_3)_2HGe^+$ and Their Silicon Analogs

I. S. Ignat'ev[a], T. A. Kochina[b], and D. V. Vrazhnov[b]

[a] *St. Petersburg State University, St. Petersburg, Russia*
[b] *Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, ul. Odoevskogo 24, block 2, St. Petersburg, 199155 Russia*
e-mail: kom@isc.nw.ru

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Abstract — The potential energy surfaces of the $(CH_3)_nH_{3-n}M^+$ ions, where n = 1, 2; M = Si, Ge, were scanned using the B3LYP method with 6-31G* and aug-cc-pVDZ basis sets. The major attention was given to isomeric species having the form of complexes of the HM^+ and CH_3M^+ ions with hydrogen, methane, and ethane molecules. These species were characterized previously neither by experimental nor by theoretical methods. It was found that these species become more stable in going from Si to Ge; the complex $[CH_3Ge^+CH_4]$ is the second isomer in the energy after $(CH_3)_2HGe^+$. However, the heights of the activation barriers to formation of these complexes from the most stable isomer, though decreasing in going from Si to Ge, remain relatively high and, what is particularly important, somewhat exceed the activation barrier to formation of the complex $[H_3Ge^+ \cdot C_2H_4]$.
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One of important problems of the modern organometallic chemistry is the problem of similarity or differences in the structure and reactivity of carbocations and the isostructural cations of silicon subgroup elements (Si, Ge, Sn, Pb).

In contrast to carbocations, which were comprehensively studied in the XX century [1, 2], three-coordinate ions of the silicon subgroup elements virtually were not studied, except silylium ions whose generation and properties were a subject of numerous recent studies [3–5]. Nevertheless, even for silylium ions the extent of similarity with the carbocations remains poorly understood.

Theoretical studies [6] showed that, in contrast to the carbocation H_3C^+, the potential energy surfaces of three-coordinate ions H_3M^+ (M = Si, Ge, Sn, Pb) have one more minimum corresponding to the donor–acceptor complex $[HM^+ \cdot H_2]$. The bond arises from the electron density transfer from the σ bond (H–H) to the vacant *p* orbital of the M atom. Whereas for silicon the formation of the classical H_3M^+ ion is considerably more favorable than the formation of the complex $[HSi^+ \cdot H_2]$, in the case of germanium the position of the related complex on the potential energy surface is only 10 kcal mol^{-1} higher than that of the classical cation. As for tin and lead, the complex lies even lower in the energy (by 5 and 15 kcal mol^{-1}, respectively) than the classical cation H_3M^+. The energy of the donor–acceptor bond in the Ge complex is about 7 kcal mol^{-1}, and in the Sn and Pb complexes, as low as 1–3 kcal mol^{-1}. This fact accounts for easy dissociation of the donor–acceptor complexes $[HM^+ \cdot H_2]$ into fragments, making hardly probable the formation of the three-coordinate cation H_3M^+.

At the same time, according to [7], the strongest peak in the mass spectra of SnH_4 and GeH_4 is that of H_3M^+, with the H_2M^+ and HM^+ peaks also observed.

In the mass spectra of Me_4M (M = Ge, Sn, Pb), the strongest peak is that of the three-coordinate cation Me_3M^+, and the second strongest peak is that of MeM^+. The intensity of the latter peak increases in going from Ge and Pb.

Although gas-phase studies show that three-coordinate cations R_3M^+ do exist, published data on the chemical behavior of these species are scarce. This particularly concerns the condensed phase in which the very generation of three-coordinate cations R_3M^+ involves tremendous problems. Only a few papes deal with this matter [8, 9].

We suggest to generate R_3M^+ ions by a nuclear-chemical method developed previously for generation of silylium ions [5]. This method allows generation of

free cations both in the gas phase in a wide pressure range and in a condensed phase.

In particular, we initiated studies on nuclear-chemical generation and behavior in the gas and condensed phases of alkyl-substituted germylium cations R_2GeT^+ (R = Me, Et). In this connection, we made a theoretical study of methyl-substituted cations $MeGeH_2^+$ and Me_2GeH^+. The stationary points on the potential energy surface of these ions were sought for using the B3LYP method with two basis sets of Gaussian atomic functions: the widely used economical 6-31G* set and the larger aug-cc-pVDZ set giving good results in the calculations of cations [10]. The structures and energies of the stationary points on these potential energy surfaces were compared with the corresponding characteristics of stationary points on the potential energy surface of the related silylium ions $MeSiH_2^+$ and Me_2SiH^+.

Previously we studied the potential energy surfaces of silylium ions of the general formula $[SiC_nH_{2n+3}]^+$ with n = 2–4 [11–13]; however, in these studies we did not consider the complexes with alkanes as possible isomers, because for silylium ions these isomers lie on the energy scale considerably higher than the classical isomes (tertiary and secondary ions with the positive charge on silicon) and the nonclassical complexes of the ions with ethylene. Nevertheless, in view of the Kapp, Schreiner, and Schleyer's data [6] that the stability of complexes with a hydrogen molecule $[HM^+ \cdot H_2]$ (side-on complexes) as isomeric species of H_3M^+ cations increases in the order M = Si, Ge, Sn, Pb, we can expect that, for germylium cations R_3Ge^+, the complexes with hydrogen and alkanes, which are analogs of these side-on complexes, will be close in the energy to the classical isomeric species and to the complexes with ethylene.

$CH_3H_2M^+$ system. Replacement of one of the hydrogen atoms in the H_3M^+ ion by the methyl group leads to the formation of the $CH_3H_2M^+$ ion. With M = Si, the potential energy surface of this cation has only one minimum corresponding to the isomer with a positive charge on the Si atom [14]. We are not aware of any data on the Ge analog. Figure 1 shows the equilibrium structures we calculated for $CH_3H_2M^+$ cations with M = Si, Ge. In this figure, **1** is the classical structure of three-coordinate $CH_3H_2M^+$ cations with the positive charge center on the M atom. As for the silylium ion, for the germylium cation we found no minimum on the potential energy surface that would correspond to the isomer with the positive charge on the carbon atom, $H_3MH_2C^+$. In addition, in accordance with [6], two analogs of the side-on complexes $[HM^+ \cdot H_2]$ are possible in these systems: a complex with a methane molecule $[HM^+ \cdot CH_4]$ and a complex with a hydrogen molecule $[CH_3M^+ \cdot H_2]$. Indeed, we revealed both complexes (**2** and **3** in Fig. 1), which were unknown previously, as minima on the potential energy surfaces of the $CH_3H_2M^+$ systems (M = Si, Ge). Their energies are 26.6 and 28.0 kcal mol^{-1} for M = Si and 10.3 and 8.7 kcal mol^{-1} for M = Ge, respectively.

Here and hereinafter, we present the ΔE_0 values (relative to the most stable isomer) obtained by the B3LYP/aug-cc-pVDZ method (see table). Note that the complexes with methane and hydrogen with M = Ge are substantially more stable than their Si analogs, although both Ge complexes lie appreciably higher on the energy scale than the classical $CH_3H_2Ge^+$ ion. Complexes with the hydrogen molecule are weakly bonded; the energy difference between them and the dissociation level is as small as 2.1 kcal mol^{-1} for Si and 2.4 kcal mol^{-1} for Ge. Complexes with the methane molecule have a considerably higher dissociation energy: 16.3 kcal mol^{-1} for Si and 13.9 kcal mol^{-1} for Ge. The dissociation levels (relative to the energy of the most stable isomer) appreciably decrease in going from Si to Ge (see table).

We also determined the structures of the transition states (**TS1** and **TS2**, Fig. 1) on the way of transformations of $CH_3H_2M^+$ ions (**1**, Fig. 1) into the complexes $[HM^+ \cdot CH_4]$ (**2**, Fig. 1) and $[H_3M^+ \cdot H_2]$ (**3**, Fig. 1). The heights of these barriers, though somewhat decreasing in going from Si to Ge, remain relatively large (see table).

$(CH_3)_2HM^+$ system. We showed previously [11] that the most stable isomer in the $(CH_3)_2HSi^+$ system is the secondary ion (**1**, Fig. 2); the next are the primary ion (**2**, Fig. 2) and the complex with ethylene (**3**, Fig. 3). Complexes similar to structures **2** and **3** in Fig. 1 were not described previously.

Introduction of one more methyl groups transforms these complexes into complexes of ions with methane and ethane. These structures, indeed, correspond to the energy minima on the potential energy surface of the $(CH_3)_2HSi^+$ system. The complex with methane (**4**, Fig. 2) lies lower in energy than the complex with ethane (**5**, Fig. 2) and only 5.6 kcal mol^{-1} higher than the complex with ethylene (**3**, Fig. 2). The **TS2** barrier to transformation of the most stable isomer **1** into the complex with methane **4** and especially the **TS3** barrier to transformation of isomer **1** into the the complex with ethane **5** are appreciably higher than the **TS1** barrier to formation of the complex with ethylene. Apparently, this difference is responsible for the fact that the major decomposition pathway of silylium ions is the elimination of ethylene.

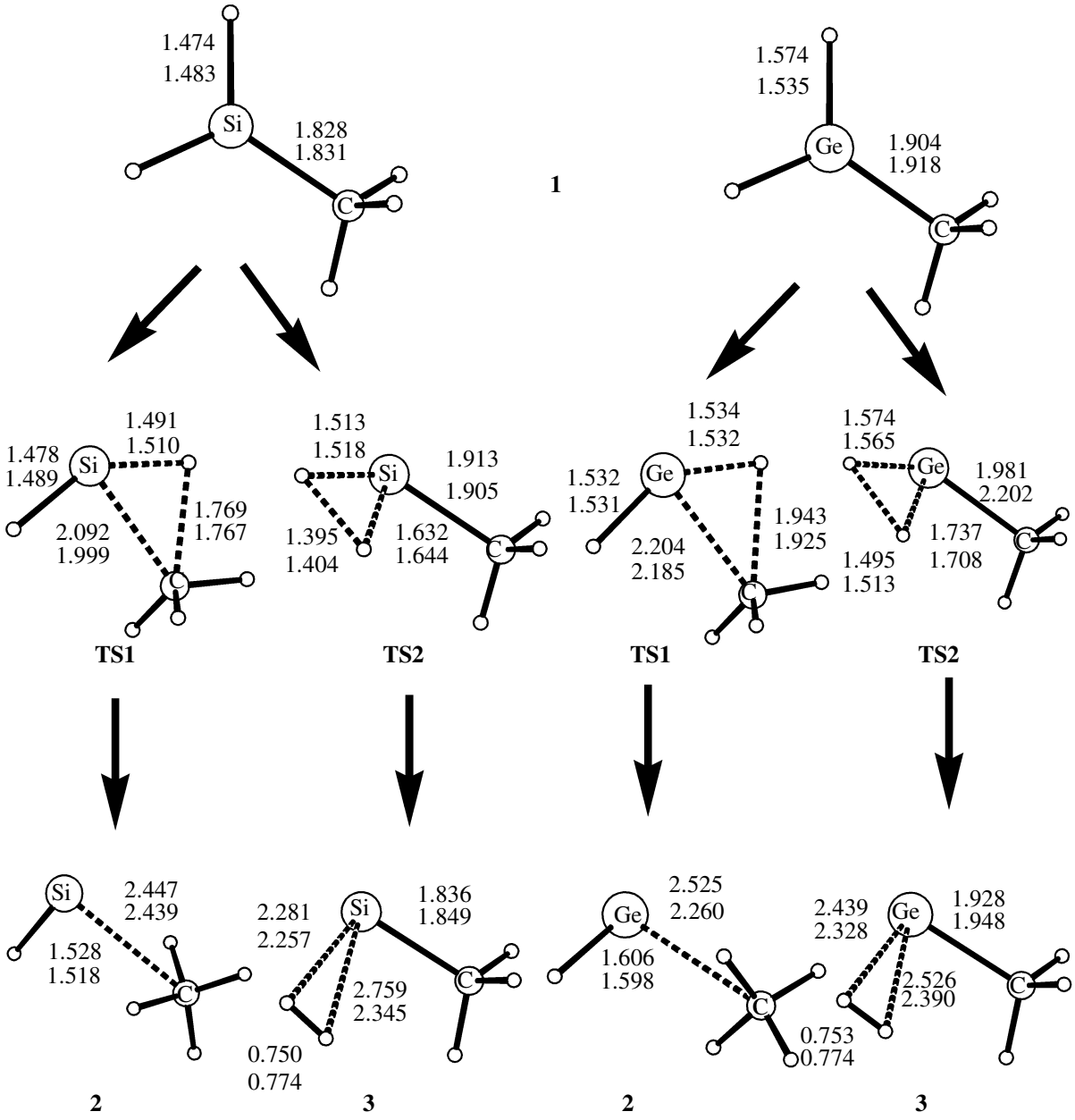

Fig. 1. Equilibrium structures of stationary points in the $CH_3H_2M^+$ systems (M = Si, Ge) optimized by the B3LYP method (upper and lower figures refer to the 6-31G* and aug-cc-pVDZ basis sets, respectively). Bond lengths in Å. (**TS**) Transition states.

A quantum-chemical search for stationary points in the $(CH_3)_2HGe^+$ system was performed previously [15]; however, only two minima corresponding to structures with the positive charge on the Ge atom, primary and secondary cations, were found. The complex with ethylene was characetrized as a saddle point, and the complexes with methane and ethane were not even discussed. In this study we revealed the energy minima for all the above-noted isomers and found the transition states corresponding to their mutual transformations.

The structures of these stationary points (Fig. 3) are close to the structures of the corresponding silylium ions (Fig. 2), but their energies differ appreciably: In the $(CH_3)_2HGe^+$ system, the second in energy is the complex with methane **4**, rather than the primary ion **2**. Complex **4** is by only 8.6 kcal mol^{-1} less stable than ion **1**, and its dissociation to the CH_3Ge^+ ion and methane requires 7.3 kcal mol^{-1} (see table). However, transformation of ion **1** into complex **4** requires overcoming an energy barrier 60.3 kcal mol^{-1} high.

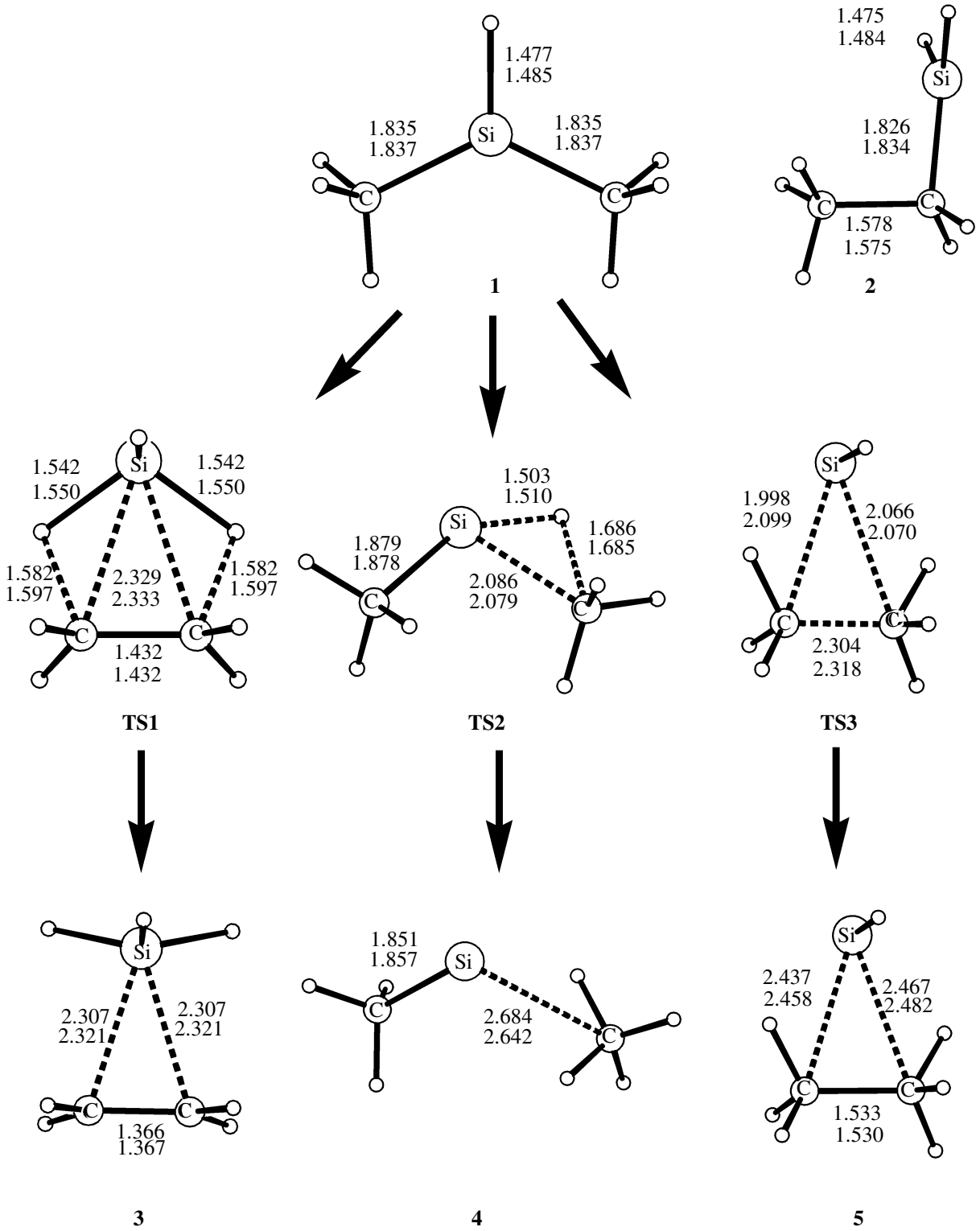

Fig. 2. Equilibrium structures of isomers of the $(CH_3)_2HSi^+$ cation with the center of the positive charge on the silicon atom and of the transition states of their formation from the most stable isomer, optimized by the B3LYP method (upper and lower figures refer to the 6-31G* and aug-cc-pVDZ basis sets, respectively).
Bond lengths in Å. (**TS**) Transition states.

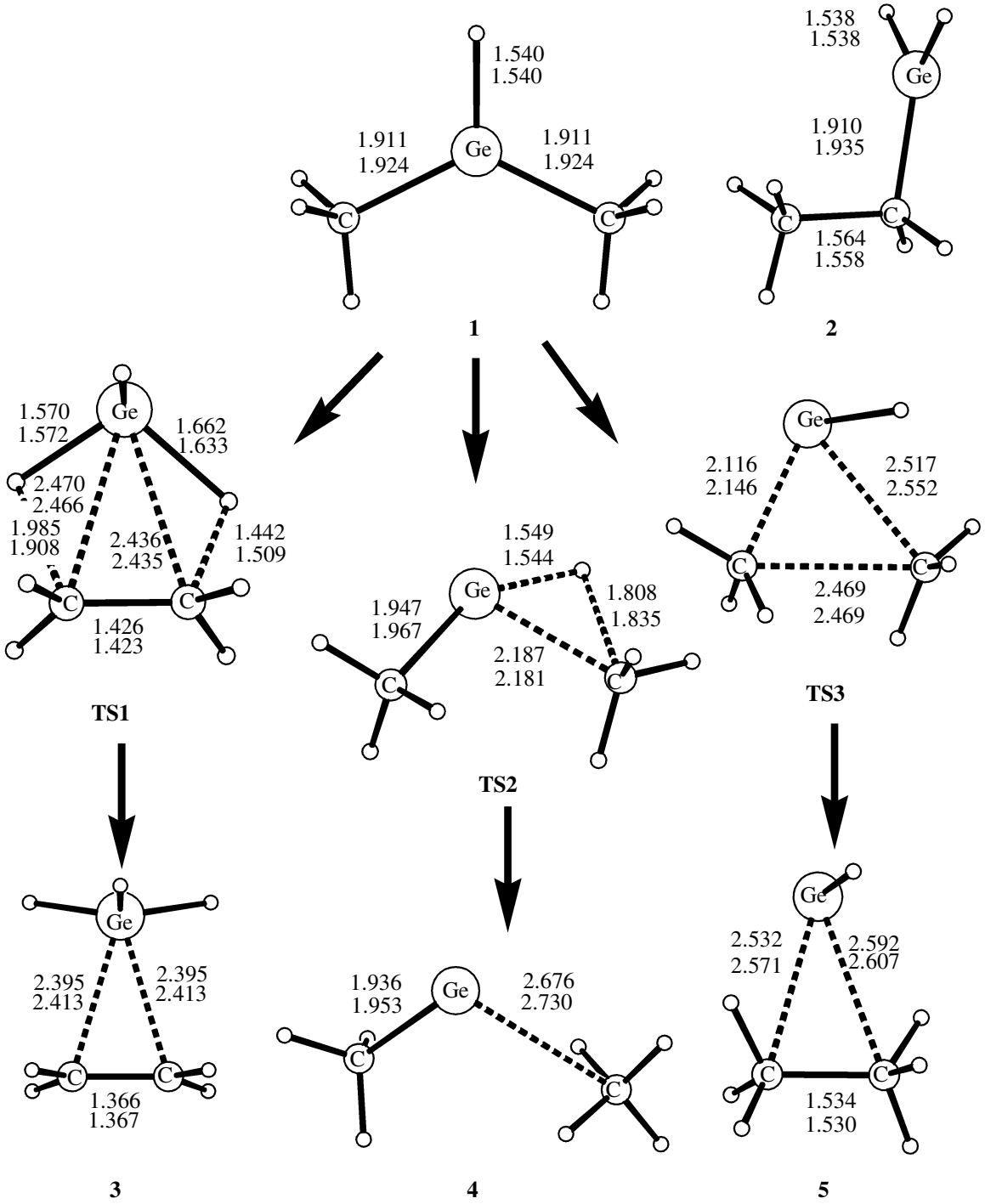

Fig. 3. Equilibrium structures of isomers of the $(CH_3)_2HGe^+$ cation with the center of the positive charge on the germanium atom and of the transition states of their formation from the most stable isomer, optimized by the B3LYP method (upper and lower figures refer to the 6-31G* and aug-cc-pVDZ basis sets, respectively). Bond lengths in Å. (**TS**) Transition states.

This barrier (**TS2**) is somewhat lower than the corresponding barier for M = Si but still higher than the barrier (**TS1**) to isomerization of ion **1** into the complex with ethylene. It should be noted that all the barriers approximately proportionally decrease in height in going from Si to Ge (see table).

Energies (relative to the most stable isomer, kcal mol^{-1}) of stationary points of the $(CH_3)H_2M^+$ and $(CH_3)_2HM^+$ systems, according to B3LYP calculations with 6-31G* and aug-cc-pVDZ basis sets

Cations	X = Si				X = Ge			
	6-31G*		aug-cc-pVDZ		6-31G*		aug-cc-pVDZ	
	ΔE_e	ΔE_0	ΔE_e	ΔE_0	ΔE_e	ΔE_0	ΔE_e	ΔE_0
				$(CH_3)H_2M^+$				
1	0	0	0	0	0	0	0	0
TS1	68.3	66.0	64.3	62.1	57.1	55.0	55.3	53.3
2	31.5	28.0	28.8	26.6	2.5	10.4	12.0	10.3
$CH_3M^+ + H_2$	33.3	28.6	33.5	28.7	5.3	12.4	16.8	12.7
TS2	74.3	72.1	70.4	68.6	65.5	63.7	61.7	59.9
3	30.3	31.0	27.2	28.0	11.1	12.1	7.8	8.7
$HM^+ + CH_4$	46.4	45.5	45.4	44.3	28.6	28.2	23.3	22.6
				$(CH_3)_2HM^+$				
1	0	0	0	0	0	0	0	0
2	22.0	22.0	21.7	21.8	22.4	22.1	17.6	17.7
TS1	66.3	64.0	62.3	60.1	64.7	61.2	54.3	51.5
3	24.7	23.4	23.7	22.9	28.1	25.9	20.6	19.4
$H_3M^+ + C_2H_4$	73.5	68.8	69.0	64.8	76.8	71.4	61.2	56.7
TS2	76.1	74.4	72.8	71.1	65.6	64.2	61.7	60.3
4	30.7	30.7	28.4	28.5	11.6	12.2	8.2	8.6
$CH_3M^+ + CH_4$	37.8	36.7	37.1	35.8	22.7	22.1	16.7	15.9
TS3	91.7	90.8	89.6	88.8	81.8	80.7	76.1	75.2
5	45.5	46.5	44.3	45.4	28.3	29.2	20.2	21.3
$HM^+ + C_2H_6$	70.3	69.8	68.5	68.1	54.4	54.0	42.6	42.5

Thus, the calculation results suggest that, with the required energy available, the dimethylgermylium ion $(CH_3)_2HGe^+$ can transform into CH_3Ge^+ with the elimination of methane or into HGe^+ with the elimination of ethane, or dissociate into H_3Ge^+ and ethylene molecule.

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