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Isomerization of Silicenium and Germenium Ions in the Systems $C_4H_{11}M^+$ (M = Si, Ge)

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Abstract—Equilibrium structures of the isomers and transition states of their interconversion in the system $C_4H_{11}M^+$ (M = Si, Ge) have been obtained at theB3LYP level of theory using the cc-pVTZ basis set. The structures of these stationary points are close for Si and Ge; the most stable isomer in both systems is the tertiary cation $(C_2H_5)(CH_3)_2M^+$, the second in energy is complex with ethylene $[(CH_3)_2HM{\cdot}C_2H_4]^+$. The secondary cation $(C_2H_5)_2HM^+$ is third in energy isomer, the height of the barrier of interconversion for these three cations being practically independent on M. However, for M = Ge a substantial decrease in the energy of isomeric forms corresponding to complexes with alkanes is observed. As a result, in the system $C_4H_{11}Ge^+$ the fourth in energy is isomer $[(C_2H_5)Ge{\cdot}C_2H_6]^+$ rather than $[(C_2H_5)H_2Ge{\cdot}C_2H_4]^+$ as for M = Si. Nevertheless, the height of the barriers for transition into these structures, although decreasing from M = Si to Ge, remain rather high, and the most favorable route of decomposition in both systems is the elimination of ethylene.

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Trivalent germenium cations R_3Ge^+, where R is alkyl or aryl, are analogs of silicenium cations R_3Si^+. The latter are characterized and thoroughly studied in the gas phase, but most experimental and theoretical studies devoted to silicenium cations is related to the discussion on the possibility of existence of free silicenium ions in condensed phases (see, for example, [1–8] and reviews [9–12]). Much less works are devoted to germenium ions and the ions of other heavy elements of the 14 group. The data available in the literature are summarized in reviews [13–15]. Germenium ions are notably more stable than the silicenium ions. Thus, investigation of isodesmic reactions has shown that the exothermicity of the process (1) is –10.2 kcal mol^{-1} [16], that points to substantial stability of cation Me_3Ge^+ as compared to Me_3Si^+, whereas the exothermicity of the process (2) is as low as –1.7 kcal mol^{-1}.

$$Me_3Si^+ + GeMe_4 \rightarrow Me_3Ge^+ + SiMe_4, \quad (1)$$

$$Me_3C^+ + SiMe_4 \rightarrow Me_3Si^+ + CMe_4. \quad (2)$$

The latter value is indicative of a comparable stability of cations Me_3Si^+ and Me_3C^+ [17].

The silicenium ions are known to exist in different isomeric forms, and their interconversion as well as dissociation with elimination, first of all, alkenes was observed in a number of experimental studies [18–29]. The use for generation of cations of nuclear chemical method elaborated by us earlier for preparation of silicenium ions [29] allows the investigation of their isomerization. Since the method allows generating ions with any predetermined localization of the charge, even if it does not correspond to the most stable isomeric form (the localization of the charge is determined only by the position of tritium in the molecule), an opportunity to follow transformations of the cation is obtained.

For interpretation of the results of investigation of transformations of the isomers it is practical to visualize the potential energy surface for the system. This information is provided by the quantum-chemical calculations.

Earlier, calculations for systems $C_2H_7Si^+$ [30, 31], $C_3H_9Si^+$ [32, 33] and $C_4H_{11}Si^+$ [34] were performed. In [35] we have first analyzed cations $(CH_3)_nH_{(3-n)}M^+$, where n = 1, 2 and M = Si, Ge, which are the isomers of the donor–acceptor complexes (side-on complexes) of cations H_3M^+ (M = Si, Ge, Pb) with molecules

RR' (R and R' = H and CH_3), whose stability substantially increases on going from Si to Pb [36]. Similar complexes in the systems $(CH_3)_3M^+$ (M = Si, Ge, Sn) were studied using quantum-chemical methods in [37]. In connection with the studies performed in our laboratory on nuclear chemical generation and investigation of reactivity of diethylgermenium cations Et_2TGe^+ ($C_4H_{11}Ge^+$) and in order to analyze the donor–acceptor complexes with the alkane molecules (lacking in [34]), in the present work the potential energy surfaces for the systems $C_4H_{11}Si^+$ and $C_4H_{11}Ge^+$ were investigated.

We have first obtained the energies and structures of low-energy (with localization of the positive charge on atom M) stationary points in the system $C_4H_{11}Ge^+$. The equilibrium geometries of these points are shown in Fig. 1. The structures of stationary points in the system $C_4H_{11}Si^+$ are close to those in the system $C_4H_{11}Ge^+$ and, since the main part of them was

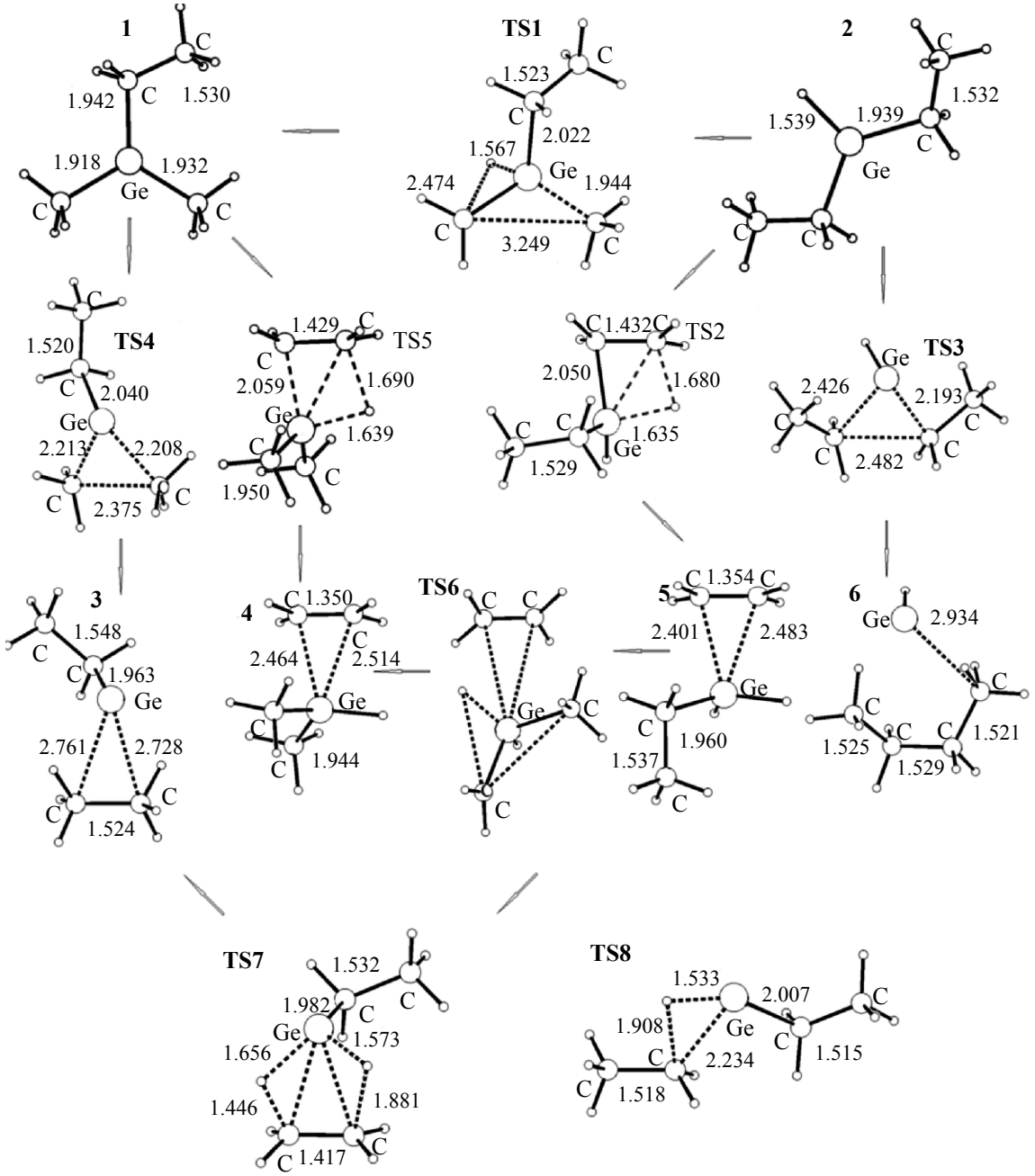

Fig. 1. Equilibrium geometries of the stationary points in the system $C_4H_{11}Ge^+$.

described in [34], the geometry of the former is not shown here. All equilibrium structures were obtained by geometry optimization with the subsequent calculation of vibrational frequencies using the B3LYP method [38, 39] with the cc-pVTZ basis set [40, 41]. The calculations were performed with the use of GAUSSIAN 03 program package [42].

The most stable isomer in both systems, as well as in the system $C_3H_9M^+$ [35] is the tertiary cation $(C_2H_5)(CH_3)_2M^+$ whose energy was taken to be zero in the Table and in Fig. 2. However, as distinct from system $C_3H_9M^+$, the second in energy isomer corresponds not to the structure of the secondary cation **2**, but to the complex $[(CH_3)_2HM{\cdot}C_2H_4]^+$ (**4**). The latter complex is 13.8 kcal mol^{-1} higher in energy than the global minimum for M = Si and somewhat lower (12.4 kcal mol^{-1}) for M = Ge. In the Table, the relative total electron energies (ΔE_e), ZPE-corrected energies (ΔH_0), and the Gibbs energies (ΔG_{298}) are given. As follows from the analysis of the data of the Table, these values are close in stationary points, only the values of dissociation energies are notably different due to substantial entropy changes upon decomposition of the cation. In Fig. 2 and in the text the relative Gibbs energies are presented.

The secondary cation **2** lies in energy somewhat higher than complex $[(CH_3)_2HM{\cdot}C_2H_4]^+$ **(4)** and is the

Relative energies [a] (kcal mol^{-1}) of stationary points in the system $C_4H_{11}M^+$

Structure no.[b]	M=Si			M=Ge		
	ΔE_e	ΔH_0	ΔG_{298}	ΔE_e	ΔH_0	ΔG_{298}
1	0	0	0	0	0	0
TS1	63.5	61.0	62.4	65.6	62.6	64.2
2	21.3	21.4	22.0	17.3	17.1	18.4
TS2	39.6	38.4	40.5	40.5	38.8	41.2
5	30.5	29.7	30.8	26.5	25.1	26.2
$C_2H_4 + C_2H_7M^+$	64.3	60.2	51.9	57.3	53.0	44.3
TS3	91.8	91.4	93.8	73.9	72.6	75.2
6	64.5	64.2	66.0	36.3	36.5	38.8
$C_4H_{10} + HM^+$	93.2	92.4	85.4	62.8	62.3	55.3
TS4	97.7	96.9	98.6	81.8	80.8	82.4
3	47.8	48.5	49.2	24.3	25.2	25.9
$C_2H_6 + C_2H_5M^+$	57.4	56.9	48.7	35.1	35.0	26.2
TS5	23.0	22.1	24.4	27.4	25.9	28.2
4	14.0	13.2	13.8	13.4	12.0	12.4
$C_2H_4 + C_2H_7M^+$	40.8	36.7	27.4	37.8	33.6	24.0
TS6	92.2	86.3	85.2	94.3	87.4	85.5
TS7	72.0	69.8	71.4	62.1	59.3	61.2
TS8	90.7	89.0	90.7	76.7	75.0	76.3

[a] ΔE_e is the total electronic energy, ΔH_0 is the ZPE-corrected energy, and ΔG_{298} is the Gibbs free energy. [b] Numeration of the structures is given in Fig. 1.

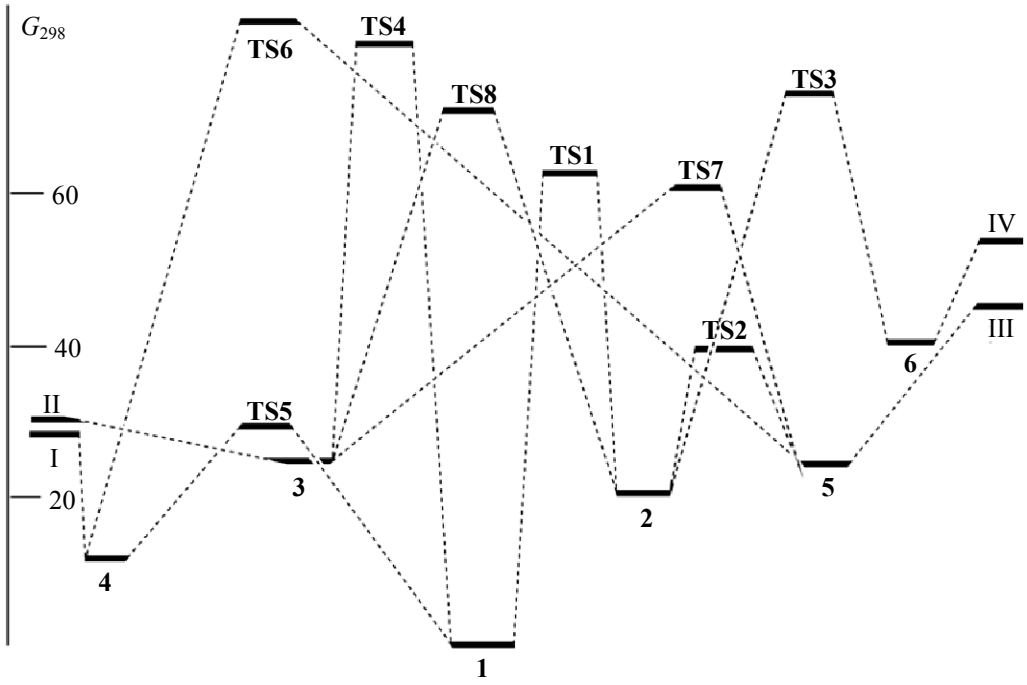

Fig. 2. The potential energy surface of the system $C_4H_{11}Ge^+$.

third in stability in the system $C_4H_{11}M^+$**.** For M = Ge, somewhat higher than isomer **2** and almost equal in energy, lie the complex of ethylgermenium cation with ethylene $[(C_2H_5)H_2Ge{\cdot}C_2H_4]^+$ (**5**) and complex with ethane **3**, the stability of the latter being sharply increased on going from M = Si to Ge. The complex with butane $[HM{\cdot}C_4H_{10}]^+$ (**6**) also suffers substantial decrease in energy on going from M = Si to Ge. The height of the barriers to formation of complexes with alkanes also decreases: thus, the formation of complex with ethane **3** from the main isomer **1** (**TS4**) for M = Ge requires the energy by 16 kcal mol^{-1} less than for M = Si, from the secondary cation **2** (**TS8**) this energy is 14 kcal mol^{-1} less, and from isomer **5** (**TS7**) it is less by 10 kcal mol^{-1} (Table). The height of the barrier (**TS3**) for transition into complex with butane **6** for cation $(C_2H_5)_2HGe^+$ is reduced by 19 kcal mol^{-1}. Nevertheless, these barriers remain high enough for the main part of the ions to be converted into complexes **3** and **6** with subsequent elimination of alkanes. Both complexes are very unstable and their decomposition with elimination of butane and ethane required only 9.4 and 0.5 kcal mol^{-1} for M = Si and 16.5 and 0.3 kcal mol^{-1} for M = Ge, respectively.

The most probable route of decomposition of cation **1** is its transformation (via **TS5**) into the complex with ethylene **4**. The lowest in energy route of transformation of ion $(C_2H_5)_2MH^+$ (**2**) both for M = Si and for M = Ge is its isomerization into the complex $[(C_2H_5)H_2M{\cdot}C_2H_4]^+$ (**5**) via barrier **TS2,** which is practically the same for M = Si and M = Ge.

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