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# Interconversion of Stannylium Ions in the $C_4H_{11}Sn^+$ System

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**Abstract**—B3LYP method with the LANL2DZ basis for tin and aug-cc-pVDZ basis for carbon and hydrogen were used to obtain the equilibrium geometry of the main (with a positive charge on the tin) isomers in the $C_4H_{11}Sn^+$ system and the transition states at their interconversion. As in the case of silicon and germanium, the cations of lighter elements of the 14th group, the most stable isomer is shown to be the tertiary ion, however, the energy of its complexes with ethane and propane is higher only by several kJ mol$^{-1}$. Nevertheless, the formation of these complexes from the tertiary ion requires overcoming a rather high barrier (293 and 272 kJ mol$^{-1}$, respectively). The barrier for isomerization of the secondary ion in the ethane complex is somewhat lower (222 kJ mol$^{-1}$), but still is significantly greater than the energy gained at the appearance of the nucleogenic ion. The most probable transformation pathways of the nucleogenic stannylium ions are the formation of complexes with ethylene, which requires overcoming barriers of 130 and 117 kJ mol$^{-1}$ for the tertiary and secondary ions, respectively.

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Trivalent stannylium cations $R_3Sn^+$, where R is an alkyl or aryl group, are much less investigated than analogous cations of silylium $R_3Si^+$, the element preceding the tin in the 14th group of elements,. Available experimental and theoretical data have been described in reviews [1–3]. Previously theoretical studies were carried out of potential energy surfaces of the trivalent silylium and germylium ions of the general formula $C_2H_7Si^+$ [4,5], $C_3H_9Si^+$ [6,7], $C_4H_{11}Si^+$ [8], $CH_5M^+$ (M = Si, Ge) [9] and $C_4H_{11}Ge^+$ [10]. Mass spectrometric study of cation $C_3H_9M^+$ (M = Si, Ge, Sn) [11] showed a systematic change in the relative yields of decay products of these ions in going from Si to Sn: Reduced yield of ethylene and growing yield of ethane, as well as a significant increase in the yield of products of homolytic cleavage of the M–C bond. Quantum-chemical calculations correlate well with these results, showing a significant drop in the energy of homolytic dissociation as well as in the energy of complexes with alkanes, and, most important, the increase in the barriers to their formation in going from Si to Sn [12]. The complexes with alkanes are the analogues of the *side-on* systems, whose fall in energy with respect to the classical tricoordinated structures was first shown by Schleyer with coworkers for the $H_3M^+$ ions with M from C to Pb [13]. Indeed, Ignat'ev and Sundius [12] have found that the relative energies of the complexes with alkanes, and to a lesser extent, with ethylene lie below the energies of tertiary and secondary ions. Therewith, unlike the $H_3M^+$ ions, the energy of the most stable *side-on* complex when M = Sn in the $C_3H_9M^+$ system (complex with ethane) is still by 17 kJ mol$^{-1}$ above the energy of the tertiary ion. In addition, the barrier for isomerization of the tertiary ion in the complex with ethane, although substantially reduced, remains high enough.

Our group for more than a quarter of a century have carried on a systematic research directed on the generation and study of the features of chemical behavior of the cations of 14th group elements, $R_3M^+$ (M = Si, Ge, Sn, Pb). One of the goals of this research is the identification of the similarities and differences in reactivity of the metal-centered cations $R_3M^+$ and their carbon analogs $R_3C^+$.

For the generation of the cations we used a nuclear-chemical method [14, 15], developed initially for the generation of carbenium and silylium ions and

then expanded by us to their germanium analogs [16, 17].

To create an overall picture of the interaction of metal-centered cations $R_3M^+$ with nucleophiles and to reveal features of their behavior, we have extended our strategy to the tricoordinated organic tin cations (stannylium ions). In particular, our research focuses on the generation by the nuclear-chemical method of diethylstannyl cation $Et_2SnT^+$. Note that since the method allows the generation of cations with any given charge localization (which is defined by the position of tritium in the molecule of the precursor), a possibility appears to trace the cation rearrangements.

In connection with the experimental study of stannylium ions generated by the nuclear-chemical method [14], it was interesting to establish the relative stability of isomers in the system of $C_4H_{11}Sn^+$ and the barrier heights for their interconversions. For this purpose we optimized the stationary points (energy minima and transition states) for the isomers produced from the tertiary and secondary ions, $(CH_3)_2C_2H_5Sn^+$ and $H(C_2H_5)_2Sn^+$, respectively. We excluded the isomers with a positive charge on the carbon atom as having clearly higher energy. In addition, we evaluated the energy of homolytic cleavage of Sn-C bond, since in the previous paper [12] we had shown that this energy was close to the heights of some of the barriers for the conversion of the isomeric forms. In our calculations we used the density functional method B3LYP [18,19] with the basis set aug-cc-pVDZ [20, 21] for carbon and hydrogen atoms, while for the tin atom we used the basis set designated as LANL2DZ that accounts for the pseudopotential and the relativistic corrections [22, 24]. The same method and set of basis functions were used in [12]. We used the method and basis sets in the form that was included in the GAUSSIAN 03 program package [25].

Figures 1 and 2 show the equilibrium geometries of stationary points in the $C_4H_{11}Si^+$ system. The most stable isomer in this system, as in all systems studied

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

| Structure no.[b] | Parameter | | |
|---|---|---|---|
| | $\Delta E_e$ | $\Delta H_0$ | $\Delta G_{298}$ |
| **1** | 0 | 0 | 0 |
| TS1 | 307.5 | 291.2 | 297.9 |
| **2** | 55.3 | 57.5 | 60.3 |
| $CH_3C_2H_5Sn^{\bullet+} + CH_3$ | 286.6 | 266.5 | 226.7 |
| $(CH_3)_2Sn^{\bullet+} + C_2H_5^{\bullet}$ | 277.0 | 258.5 | 211.6 |
| TS2 | 292.5 | 290.4 | 297.1 |
| **3** | 21.4 | 28.7 | 30.6 |
| $C_2H_6 + C_2H_5Sn^+$ (**I**) | 56.8 | 60.8 | 28.1 |
| TS3 | 128.7 | 119.4 | 128.7 |
| **4** | 52.0 | 43.6 | 46.9 |
| $C_2H_4 + (CH_3)_2HSn^+$ (**II**) | 147.1 | 128.2 | 86.7 |
| TS4 | 271.5 | 266.5 | 271.5 |
| **5** | 7.5 | 11.7 | 16.8 |
| $C_3H_8 + CH_3Sn^+$ (**III**) | 51.1 | 53.2 | 18.4 |
| TS5 | 240.9 | 229.6 | 240.5 |
| TS6 | 173.5 | 163.8 | 174.7 |
| **6** | 98.1 | 88.8 | 94.3 |
| $C_2H_4 + C_2H_7Sn^+$ (**IV**) | 204.9 | 185.2 | 151.7 |
| TS7 | 266.1 | 259.8 | 271.1 |
| **7** | 49.9 | 52.0 | 61.6 |
| $C_4H_{10}+ HSn^+$ (**V**) | 163.0 | 163.0 | 137.0 |
| TS8 | 277.4 | 270.7 | 278.2 |

[a] $\Delta E_e$ is the total electronic energy, $\Delta H_0$ is the same energy with a correction for the zero vibrational level, $\Delta G_{298}$ is Gibbs free energy.
[b] The numbering of the structures is given in Fig. 1.

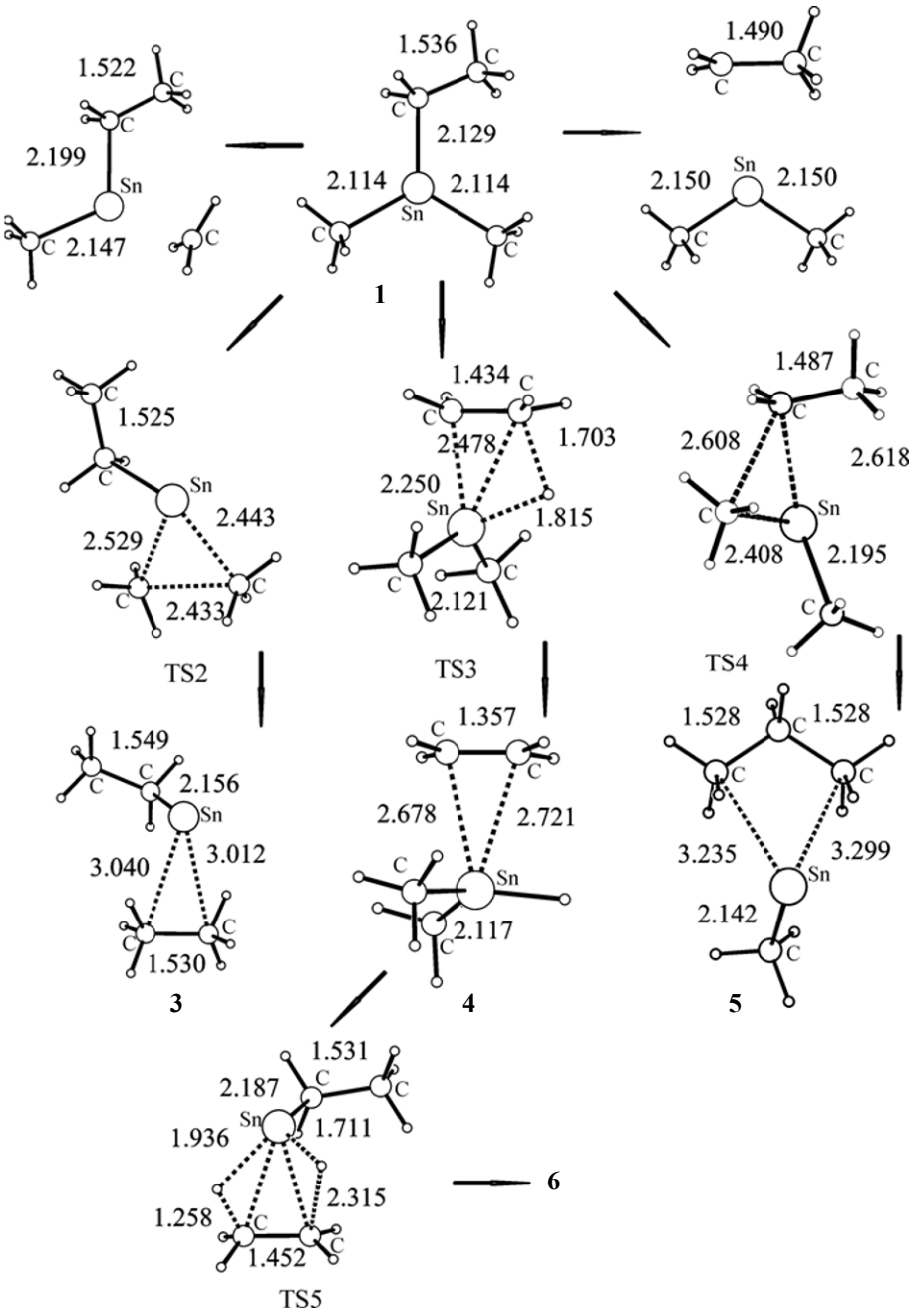


**Fig. 1.** Equilibrium geometries of stationary points in the system of $C_4H_{11}Sn^+$.

earlier, is tertiary cation $(C_2H_5)(CH_3)_2Sn^+$, and in the table and Fig. 3 its energy is equaled zero. The table shows the relative magnitudes of the total electronic energy ($\Delta E_e$), the energy corrected for zero-vibrational level ($\Delta H_0$), and Gibbs energy ($\Delta G_{298}$). As can be seen from the data in the table, these values are close to stationary points, except for the values of the dissociation energy that differ markedly due to a significant change in the entropy at the cation decay. Figure 3 shows the relative values of Gibbs energy.

To the isomers second and the third by the energy correspond complexes **5** and **3** with propane $[CH_3Sn{\cdot}C_3H_8]^+$ **5** and ethane $[C_2H_5Sn{\cdot}C_2H_6]^+$, respectively. These complexes by only 8 and 21 kJ $mol^{-1}$, respectively, exceed the global minimum ($\Delta E_e$, see the table). They are formed from the tertiary ion **1** by shifting the methyl group in the direction of the second methyl group (TS2) with C–C bond formation between these groups, or by shift of the latter to the ethyl group (TS4) with the formation of a bond between the ethyl

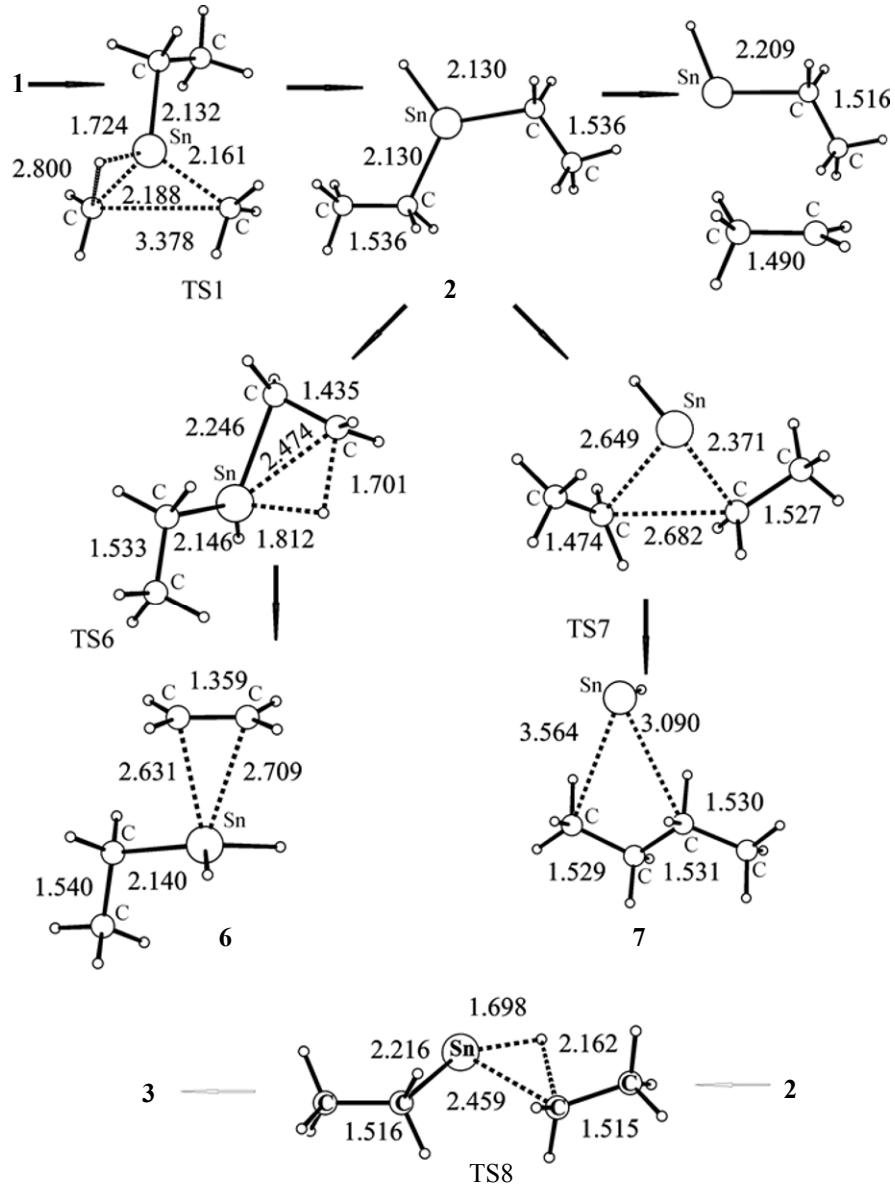


**Fig. 2.** Equilibrium geometries of stationary points in the system of $C_4H_{11}Sn^+$ (continued).

and methyl groups. A weak coupling of these complexes is indicated both by the magnitude of the interatomic distance between the cation and alkane parts of the complex (Fig. 1) and by almost zero value of the Gibbs energy of their dissociation. However, the barriers to conversion of the tertiary ion **1** into complexes with ethane **3** and propane **5** are quite high (293 and 272 kJ $mol^{-1}$, respectively), since these processes require rupture of the Sn–C bond. Naturally, the processes of homolytic cleavage of the Sn–C bond in the tertiary ion **1** with the formation of the ion-radical $CH_3C_2H_5Sn^{\bullet+}$ and the methyl radical, and the ion-radical $(CH_3)_2Sn^{\bullet+}$ and ethyl radical, require approximately the same energy (285 and 277 kJ $mol^{-1}$, respectively, $\Delta E_e$ in the table) and the Gibbs energy for this dissociation is much lower than the TS2 and TS4 barriers (see the table).

The complex with ethane **3** can be obtained from secondary ion **2** through a hydride shift from the tin atom to the ethyl group (TS8, Fig. 2). Since this process does not require cleavage of the Sn–C bond, the activation barrier (relative to **2**) is much lower (222 kJ $mol^{-1}$).

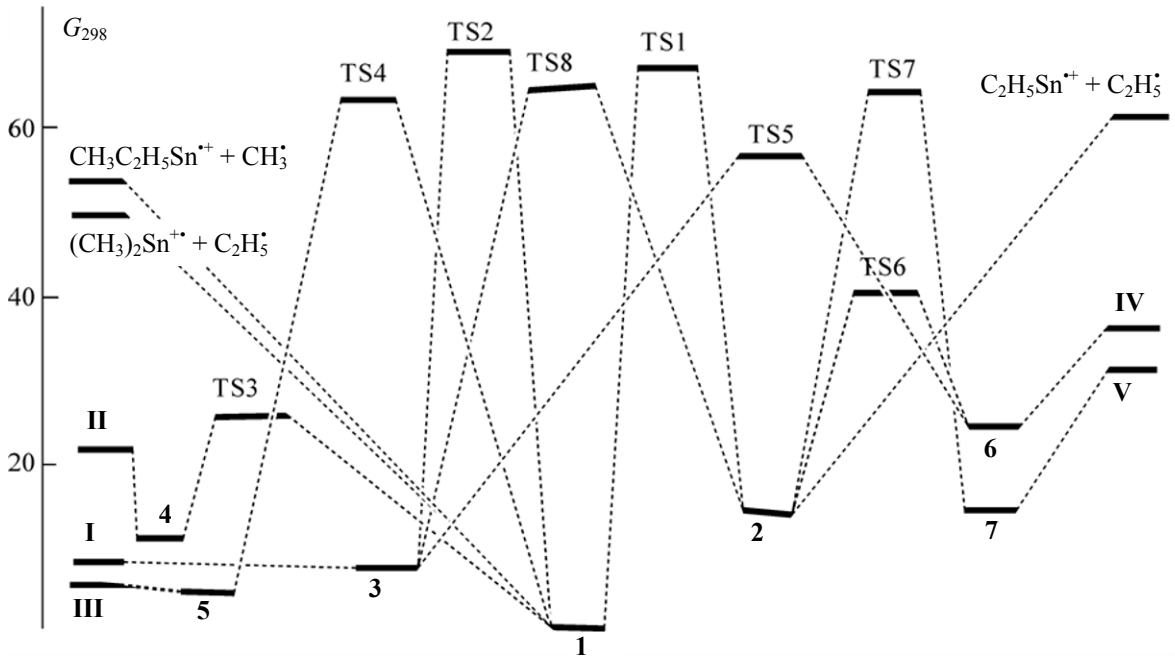


**Fig. 3.** The scheme of stationary points on the potential energy surface of the $C_4H_{11}Sn^+$ system.

There is another process of the tertiary ion **1** decay, which cannot occur with the tertiary ion $(CH_3)_3Sn^+$: the ethylene molecule cleavage by the hydride ion transfer from the ethyl group of tertiary ion to the tin atom. The activation barrier TS3 for this isomerization is 130 kJ mol$^{-1}$. Although the complex with ethylene is slightly above the complexes with alkanes by the energy, the low barrier makes this route the most advantageous, and in the case of nucleogenic ions is quite feasible, taking into account the additional deformation energy at the generation of these cations [14].

The preference of the formation of alkanes complexes in the case of the cations of heavy elements compared to more stable complexes with alkenes in the case of silicon and germanium cations obviously is associated with the increased stability of low valence compounds in going down along the 14th group. Since in the complexes with ethane **3** and propane **5** the association of cations $CH_3Sn^+$ and $C_2H_5Sn^+$ with alkanes is very weak (the Sn–C bond is longer than 3 Å and dissociation energies are only few kJ mol$^{-1}$), their greater stability relative to analogous silicon and germanium cations is determined by the stability of the univalent ions $CH_3Sn^+$ and $C_2H_5Sn^+$ characteristic of the tin compounds.

The diethylstanylium ion **2** can be transformed into the complex with ethylene **6** through the hydride ion transfer from the ethyl group to the tin atom by overcoming the TS6 barrier (Fig. 2), or into the *n*-butane complex **7** by methyl shift (TS7). The last complex is substantially (by 122 kJ mol$^{-1}$) more stable than the first, and its energy is almost equal to the energy of the secondary ion **2**, but for the formation of this cation it is necessary to overcome the TS7 barrier of 210 kJ mol$^{-1}$. The barrier to the formation of ethylene complex **6** from **2** is much lower (117 kJ mol$^{-1}$), although the energy of the resulting product (complex **6**) is by 41.9 kJ mol$^{-1}$ above that of the secondary ion. However, this channel of the diethylstanylium ion decay can be observed only in a nuclear-chemical experiment.

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