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# Radiochemical Study of Gas-Phase Reactions of Diethylstannilium Cations $Et_2SnT^+$ with Oxygen-Containing Compounds: I. Interaction of Diethylstannilium Cations with Methyl *tert*-Butyl Ether

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**Abstract**—Radiochemical method was applied to study the gas-phase interaction between the nucleogenic diethylstannyl cations $Et_2SnT^+$ and methyl *tert*-butyl ether. The possible reaction mechanisms are considered. Diethylstannylium cations are found to isomerize during the reaction to tertiary cation $Me_2EtSn^+$, as well as undergo a rearrangement accompanied by elimination of ethane rater than ethylene, in contrast to the cases of silicon and germilium analogs.

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Among the objects of intense research in the late XX–early XXI centuries were three-coordinated cations of Group 14 elements of the periodic system $R_3M^+$ (M = Si, Ge, Sn, Pb) [1–4]. This is due, above all, to the attempts of finding similarity between these intermediates and the carbenium ions $R_3C^+$, and their role in chemical processes. Furthermore, the $R_3M^+$ cations are gaining practical importance as catalysts of various reactions [5, 6].

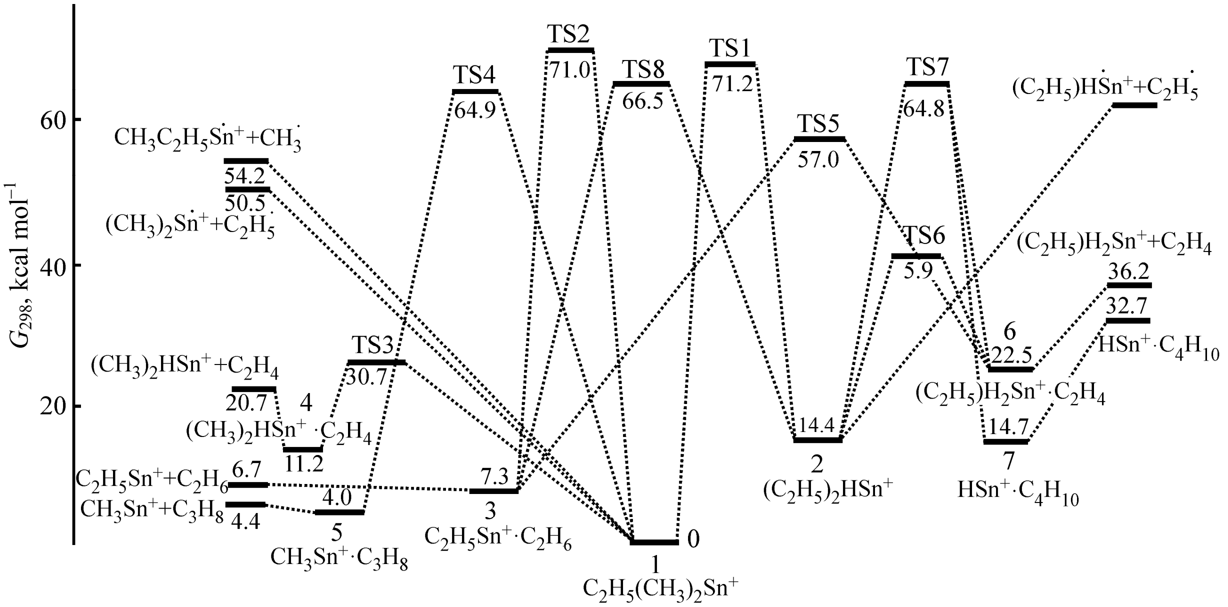
Due to the difficulty in generating cations $R_3M^+$ the behavior of these cations, in contrast to the extensively studied carbenium ions [7], have long remained poorly understood, not only in a condensed, but also in the gas phase, as all efforts were focused on the proof of the their formation in the condensed phase. In our studies, to generate $R_3M^+$ cations and to study their reactivity we used the nuclear-chemical method [4, 8], allowing the generation of $R_3M^+$ cations and the study of their reactions in different states of aggregation. This method was applied to generate and study silylium $R_2TSi^+$ (R = T, Me, Et, Ph) [4, 9, 10] and germilium $R_2TGe^+$ (R = Me, Et) cations [10].

The continuation of this research was the study of the gas-phase interaction of diethylstannylium cations $Et_2TSn^+$, generated by nuclear-chemical method, with oxygen-containing compound (*t*-BuOMe). As is known, one of the most characteristic reactions of nucleogenic cations is their interaction with lone electron pairs of heteroatoms of organic compounds [10].

Let us consider the interaction of the diethylstannylium cation with methyl *tert*-butyl ether. The experimental study shows that the main product of this interaction is dimethylethylmethoxystannane. Among the products also methane and ethane were detected.

| Tritium labeeled substance | Methane | Ethane | Dimethylethyl-methoxystannane |
|---|---|---|---|
| Relative yield (α 0.95), % | 19±2 | 12±2 | 68±4 |

To explain these data, we attracted the results of quantum-chemical calculations of the potential energy surface (PES) for the system of $C_4H_{11}Sn^+$ (B3LYP with LANL2DZ basis set for tin and aug-cc-pVDZ for



Profile of the potential energy surface of $C_4H_{11}Sn^+$.

carbon and hydrogen) (see the figure) [11]. The calculations show that diethylstannylium cation lies on the PES of $C_4H_{11}Sn^+$ system by 14.4 kcal mol$^{-1}$ above the most stable tertiary cation $C_2H_5(CH_3)_2Sn^+$, which occupies the global minimum.

On the PES, there are also local minima belonging to the donor-acceptor complexes of tin(II) cation with molecules of alkanes [$CH_3Sn^+ \cdot C_3H_8$] (5), [$C_2H_5Sn^+ \cdot C_2H_6$] (3), and [$HSn^+ \cdot C_4H_{10}$] (7). The complexes with alkanes are analogs of “side-on” complexes, for which a decrease in the energy was found compared to the classical three-coordinated $H_3M^+$ cations in going from Si to Pb [12]. In the case of Sn and Pb the complexes [$HSn^+ \cdot H_2$] and [$HPb^+ \cdot H_2$] are located on the PES lower than classical three-cordinated cations. In the system of $C_4H_{11}Sn^+$ the complexes (3) and (5) are, respectively, by 2 and 5 kcal mol$^{-1}$ above the global minimum occupied by the tertiary cation $C_2H_5(CH_3)_2Sn^+$. The cations $CH_3Sn^+$ and $C_2H_5Sn^+$ in the complexes (3) and (5) are bound very weakly to the molecules of alkanes (interatomic distances Sn-C are over 3 Å and the dissociation energy is only a few kcal mol$^{-1}$), which provides a possibility to the system to easily dissociate into the corresponding cations and hydrocarbons. As seen from the PES (see the figure), the isomerization of the cation $(C_2H_5)_2HSn^+$ to other isomeric forms involves overcoming a sufficiently high activation barriers.

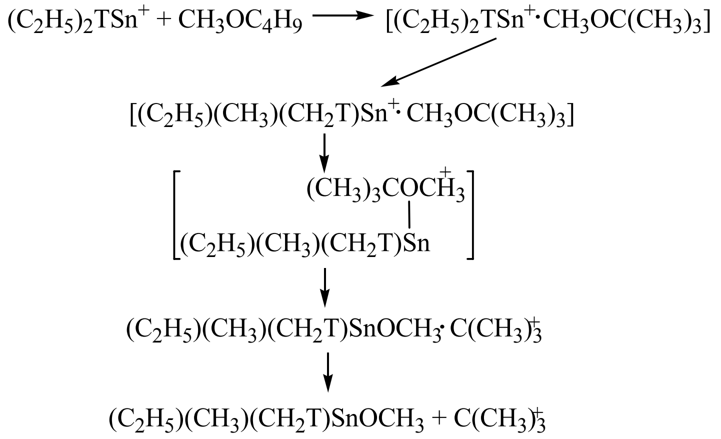
The diethylstannylium cation generated by nuclear-chemical method inherits a tetrahedral structure of the parent diethylstannane molecule. Its restructuring to the planar one, characteristic of three-coordinated cations, leads to the vibrational excitation of the cation by ~20 kcal mol$^{-1}$ (B3LYP). This energy is not enough to the cation in its free form to overcome the barriers of isomerization. The additional energy can be obtained at the interaction of the cation with the ether molecule (“collisionally induced isomerization”). It is estimated by the same method at ~38 kcal mol$^{-1}$. Total excitation energy (~58 kcal mol$^{-1}$) is enough to turn diethylstannylium cation (2) into the tertiary dimethylethylstannylium cation (1) (TS1 = 56.7 kcal mol$^{-1}$). The energy gain at this transition is 14.4 kcal mol$^{-1}$.

As already mentioned, the main product of the reaction of diethylstannylium cation with methyl *tert*-butyl ether is $(CH_3)_2(C_2H_5)SnOCH_3$. Its formation can be explained by the interaction of the isomerized dimethylethylstannylium cation with a molecule of ether along Scheme 1.

Interestingly, at the interaction of diethylsilylium $Et_2TSi^+$ and diethylgermilium $Et_2TGe^+$ ions with the ether the products corresponding to tertiary cation $Me_2EtM^+$ were not detected.

The barrier of isomerization of diethylsilylium ion to the tertiary cation is higher than the barrier of dissociation of the cation with the elimination of ethylene and the formation of monoethylsililum cation. This does not give the opportunity to its isomerization to $(CH_3)_2C_2H_5Si^+$ even if the energy is available [4, 9].

**Scheme 1.**



As for diethylgermilium cations, the tertiary cation $(CH_3)_2C_2H_5Ge^+$ formed at the isomerization is transformed into the complex of dimethylgermilium ion with ethylene, or it undergoes the reverse transition to diethylgermilium cation, mainly due to strong excitation. Indeed, the interaction of $Et_2TGe^+$ with methyl *tert*-butyl ether produced only 30% of the compounds containing the original not isomerized germilium group [14].

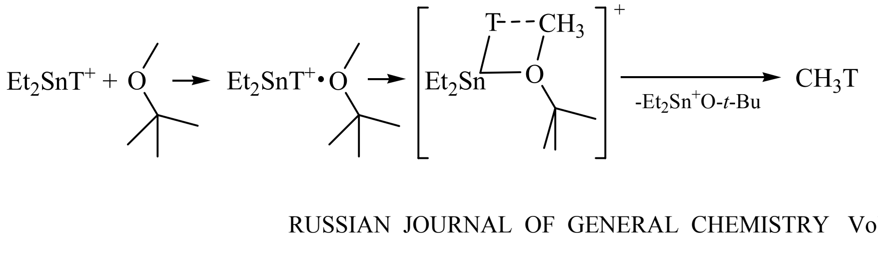
Dissociation of the complex $[C_2H_5Sn^+{\cdot}C_2H_6]$ (3), the other isomer of the studied cation $Et_2TSn^+$, leads to the formation of ethane. The complex (3) can be formed in two ways: by isomerization of the cation $(C_2H_5)_2HSn^+$ (2) through the barrier TS8 (52 kcal mol$^{-1}$) and the cation $(CH_3)_2C_2H_5Sn^+$ (1) through the barrier TS2 (70.9 kcal mol$^{-1}$). Total excitation energy of the $Et_2TSn^+$ cation is sufficient to overcome the barrier TS8. The other way, from dimethylethylstannylium cation (1), is also possible, since the barrier TS2 is below the maximum of the excitation energy of the cation $(CH_3)_2C_2H_5Sn^+$ equal ~73 kcal mol$^{-1}$. This energy the cation (1) acquires at the isomerization of the cation $(C_2H_5)_2HSn^+$, induced by the ether molecule.

Since the threshold for the dissociation of $[C_2H_5Sn^+{\cdot}C_2H_6]$ is only 0.6 kcal mol$^{-1}$ [11], the complex $[C_2H_5Sn^+{\cdot}C_2H_5T]$ resulting at the isomerization decomposes to unlabeled tin(II) cation $C_2H_5Sn^+$ and labeled ethane.

Among the reaction products of $(C_2H_5)_2TSn^+$ with methyl *tert*-butyl ether tritiated methane $CH_3T$ (19%) was detected. One possible way of formation of this product is its elimination from the oxonium complex $[Et_2TSnO^+(Me)t\text{-}Bu]$, as was observed in the case of the interaction of diethylgermilium cation with the same ether [14] (Scheme 2). The results of quantum-chemical study indicate that the activation barrier ($\Delta H_0$) of this process relative to the energy of the initial reactants is 20 kcal mol$^{-1}$ (B3LYP). The total excitation energy of the cation is sufficient for the occurrence of this process.

However, stannylium cation can form $CH_3T$ by another pathway. The process of homolytic rupture of Sn-C bond in the tertiary ion (1) leads to the formation of ion-radical $CH_3C_2H_5Sn^{\bullet+}$ and methyl radical, and it requires about the same energy (54.1 kcal mol$^{-1}$) as is necessary to overcome the TS2 barrier, while the Gibbs energy for such dissociation is rather lower than the TS2 barrier (see figure). The energy of homolytic Sn–C bond rupture was shown in [11, 15] to be close to the barriers for interconversion of isomeric forms, so this process takes place with no less probability than the isomerization into complexes. The appearing therewith radical $CH_2T^{\bullet}$ can split off a hydrogen atom from the molecules of the system, forming labeled methane.

**Scheme 2.**



$$CH_2T^{\bullet} + H\text{–}R_n \rightarrow CH_3T + R_n$$

where $R_n$ is a part of the substrate molecule.

In the reaction of diethylsilylium ions with ethers one of the reaction products is the labeled ethylene, which appears at the isomerization of $Et_2HSi^+$ cation into the complex [$EtH_2Si^+$·C2H4] with subsequent dissociation of the latter [9]. In the case of diethylgermilium cation, such isomerization is indicated by the formation of products containing isomerized groups $EtH_2Ge$ and $Me_2HGe$ [14]. Ethylene formed in this case was unlabeled. In case of stannylium cations, neither labeled ethylene, nor products containing isomerized stannylium group $EtH_2Sn$ or $Me_2HSn$, were observed. This is because in going from Si to Pb, for the 14-th group elements the probability increases of the existence of bivalent form of the element. Consequently, the probability increases of formation of complexes of tin(II) cation with an alkane [$MeSn^+$·$C_3H_8$], [$EtSn^+$·$C_2H_6$], [$HSn^+$·$C_4H^+_{10}$]. This is confirmed by mass-spectrometric studies of dissociation of cations $R_3M^+$ (M = Si, Ge, Sn, Pb) that showed in the case of tin, the dissociation to occur with elimination of ethane, and the ethylene formation was practically reduced to zero [16].

## EXPERIMENTAL

Free diethylstannylium cations were generated by the nuclear-chemical method:

$$(C_2H_5)_2SnT_2 \xrightarrow{\beta^-} (C_2H_5)_2Sn^+T + {}^3He^0.$$

The synthesis of diethylditritiumstannane is described in [17].

As the substrate we used methyl *tert*-butyl ether of chemically pure grade; before charging to ampules it was thoroughly dried with metallic sodium and distilled.

For the study of ion-molecular reactions of diethylstannylium cations in the gas phase the reaction mixtures were placed in spherical ampules of molybdenum glass of about 20 ml volume. The vapor pressure of methyl *tert*-butyl ether was ~15 mm Hg, the diethylditritiumstannane activity 0.001 Cu ($3.7 \times 10^7$ Bq). Accumulation of products was carried out at room temperature in the absence of light for 1 month.

Analysis of the products of ion-molecule reactions of diethylstannylium cations with methyl *tert*-butyl ether was performed by radiochromatographic method using a Tsvet-500 chromatograph equipped with a flow-proportional counter – detector of the tritium α-radiation. For the analysis we used two chromatographic systems: stainless steel column 2000×2 mm, with 5% SE-30 on Inerton-AW and stainless steel column 3000×2 mm, with 5% to PORAPAK R Inerton-AW. Rate of carrier gas (helium) flow 20 ml min-1, the rate of quenching gas flow [methane (5%)-Ar] 5 ml $min^{-1}$. Identification of labeled reaction products was carried out by comparing their retention times with the retention times of reference substances under the same chromatographic conditions. Product yield was determined as the ratio of the activity of a compound to the total activity of all the detected reaction products.

Dimethylmethoxyethylstannane used as a reference was obtained by the reaction of sodium methoxide with dimethylethyltin chloride [18]. Identification of the resulting products was determined by gas chromatography-mass spectrometry on a Polaris 125 instrument.

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