ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 5, pp. 816–821. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © A.A. Alferova, T.A. Kochina, V.V. Avrorin, E.N. Sinotova, I.S. Ignat'ev, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 5, pp. 723–728.

Radiochemical Study of Gas-Phase Reactions of Diethylstannyl Cations Et_2SnT^+ with Oxygen-Containing Compounds: II.[1] Reaction of Diethylstannyl Cations with Butanol

A. A. Alferova[a], T. A. Kochina[b], V. V. Avrorin[a], E. N. Sinotova[a], and I. S. Ignat'ev[a]

[a] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
[b] *Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences,*
nab. Makarova 2, St. Petersburg, 199034 Russia
e-mail: t-kochina@mail.ru

Received December 9, 2013

Abstract—Gas-phase reaction of nucleogenic diethylstannyl cations Et_2SnT^+ with butan-1-ol has been studied by the radiochemcal method, and probable reaction mechanisms have been proposed. During the process diethylstannyl cations undergo isomerization into tertiary Me_2EtSn^+ cations and rearrangement with elimination of ethane. Thermochemical parameters of reactions of diethyl-substituted cations derived from Group 14 elements (Et_2TM^+; M = C, Si, Ge, Sn) with alcohols have been analyzed by the M06L aug-cc-pVDZ quantum chemical method.

Keywords: nuclear chemical method, stannyl cations, isomerization, thermochemical parameters, quantum chemical calculations.

DOI: 10.1134/S1070363214050041

Over many years we perform systematic studies of nuclear chemical generation of three-coordinate Group 14 cations and their ion–molecule reactions with various nucleophiles using a radiochemical method. In the first communication of this series [1] we considered gas-phase reactions of nucleogenic stannyl cations Et_2SnT^+ with *tert*-butyl methyl ether as a representative of *n*-electron-donor nucleophiles. While developing studies in the field of ion–molecule reactions of stannyl cations with oxygen-containing compounds, we focused our attention on alcohols. Reactions of alcohols with nucleogenic carbenium [2], silyl [3–5], and germyl cations [6] were reported by us previously. In order to get a complete picture of reactions of three-coordinate Group 14 cations with alcohols it was necessary to examine the reaction of stannyl cations with alcohols.

Cations react with such nucleophiles as alcohols through the formation of oxonium complexes generated via interaction of the vacant *p*-orbital of the cation with lone electron pairs on the oxygen atom [7]. The energy of excitation of the oxonium ion is determined by the affinity of the cation to alcohol, and excitation energy redistribution in the complex leads to its decomposition into final products. The energies of formation of the adducts of cations Et_2HM^+ with BuOH [$E_{comp}(1)$] and of Me_2HM^+ with methanol [$E_{comp}(2)$] (M = C, Si, Ge, Sn), calculated by the M06L aug-cc-pVDZ method [8, 9] are given in Table 1.

As we showed in [10], M06L aug-cc-pVDZ quantum chemical calculations provide a good reproducibility of thermochemical parameters for reactions involving compounds of Group 14 elements, and the results were even better than those obtained by the most popular DFT B3LYP calculations. In keeping with the data in Table 1, the complexation of silyl cation with alcohols is characterized by the highest enthalpy, though silicon occupies an intermediate position between a typical nonmetal (C) and metals (Ge, Sn). Presumably, this is determined by the larger positive charge on the silicon atom as compared to carbon and smaller size of the silicon atom as compared to tin (the atomic radii are 1.32 and 1.62 Å, respectively [11]). The charge distributions in H_3C^+

---

[1] For communication I, see [1].

Table 1. Calculated (M06L/aug-cc-pVDZ) energies of complex formation[a] (E_{comp}, kcal/mol) of Et_2HM^+ cations with BuOH [$E_{\mathrm{comp}}(1)$] and of Me_2HM^+ catins with MeOH [$E_{\mathrm{comp}}(2)$] and energies of decomposition[a] of the complex $[Me_2HMMeOH]^+$ via bimolecular proton transfer [$E_{\mathrm{dis}}(H^+)$]

X	E_{cpmp} (1)	E_{comp} (2)	E_{dis} (H^+)
C	–28.2	–27.2	20.2
Si	–46.6	–44.2	23.8
Ge	–38.3	–36.4	18.6
Sn	–37.8	–35.6	38.0

[a] Total electronic energy with correction for zero-point vibrations (ZPVE).

and Me_2HM^+ cations calculated by the natural bond orbital (NBO) method (B3LYP/aug-cc-pVDZ, LANL2DZ) are given below

Atom	C	Si	Ge	Sn
M	0.25	1.82	1.58	1.99
H	0.24	–0.17	–0.12	–0.26

The major product of the reaction of diethylstannyl cation with butanol is ethyl(dimethyl)stannanol (Table 2), which is formed via transformation of the most stable isomer Me_2EtSn^+ among $C_4H_{11}Sn^+$ ions. There are no published data on diorganylstannanols; obviously, such compounds are very unstable. Only when bulky trimethylsilyl groups were attached to tin, the hydrolysis of the corresponding tin(II) compound gave bis[bis(trimethylsilyl)methyl]stannanol $[(Me_3Si)_2CH]_2 \cdot SnH(OH)$ [12]. Diethylstannanol $Et_2SnH(OH)$ necessary as reference cannot be obtained by analogous procedure; according to published data, diethyltin is an oligomer $[(C_2H_5)_2Sn]_n$ [13, 14], and it fails to react. Nevertheless, taking into account the instability of diorganylstannanols possessing an Sn–H bond, we believe that the observed peak belongs to $Me_2EtSnOH$ (product of the transformation of the most stable tertiary cation Me_2EtSn^+) rather than to isomeric stannanol $Et_2SnH(OH)$. This is consistent with the fact that, unlike diorganylstannanol, triorganylstannanols are stable compounds [15].

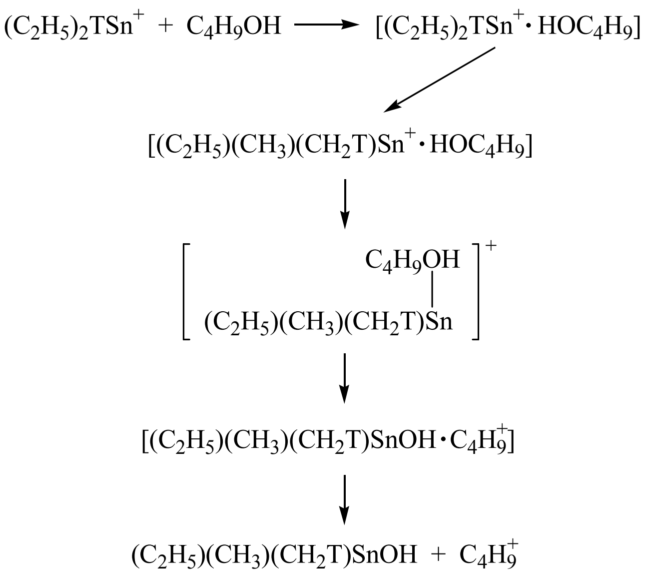
In order to interpret the obtained results we have resorted to quantum chemical calculations of the potential energy surface (PES) for the system of isomeric cations $C_4H_{11}Sn^+$ using B3LYP functional and LANL2DZ basis set for tin and aug-cc-pVDZ for carbon and hydrogen (Fig. 1) [16]. The energy of diethylstannyl cation (**2**) is higher by 14.4 kcal/mol than the energy of the most stable tertiary $C_2H_5(CH_3)_2Sn^+$ cation (**1**) which occupies the global minimum. The PES also contains local minima occupied by donor–acceptor complexes formed by tin(II) cations with alkane molecules $[CH_3Sn^+ \cdot C_3H_8]$ (**5**), $[C_2H_5Sn^+ \cdot C_2H_6]$ (**3**), and $[HSn^+ \cdot C_4H_{10}]$ (**7**). Complexes **3** and **5** appear, respectively, by 7.3 and 4.0 kcal/mol higher than the global minimum. Cations CH_3Sn^+ and $C_2H_5Sn^+$ in complexes **3** and **5** are very weakly linked to alkane molecules (the Sn–C distances therein are longer than 3 Å, and the energies of dissociation amount to a few kcal/mol), and these complexes readily dissociate into the corresponding cations and hydrocarbons. As seen from Fig. 1, the transformations of $(C_2H_5)_2HSn^+$ into other isomers require fairly high activation barriers to be overcome (Scheme 1).

Table 2. Relative yields of tritium-labeled products of the reaction of diethyl($^3H_2$)stannane with butan-1-ol

Labeled compound	Relative yield (α = 0.95), %
Methane	33±4
Ethane	25±4
Ethyl(dimethyl)stannanol	42±3

Nucleogenic cation generated by the nuclear chemical method inherits tetrahedral structure of the parent

Scheme 1.



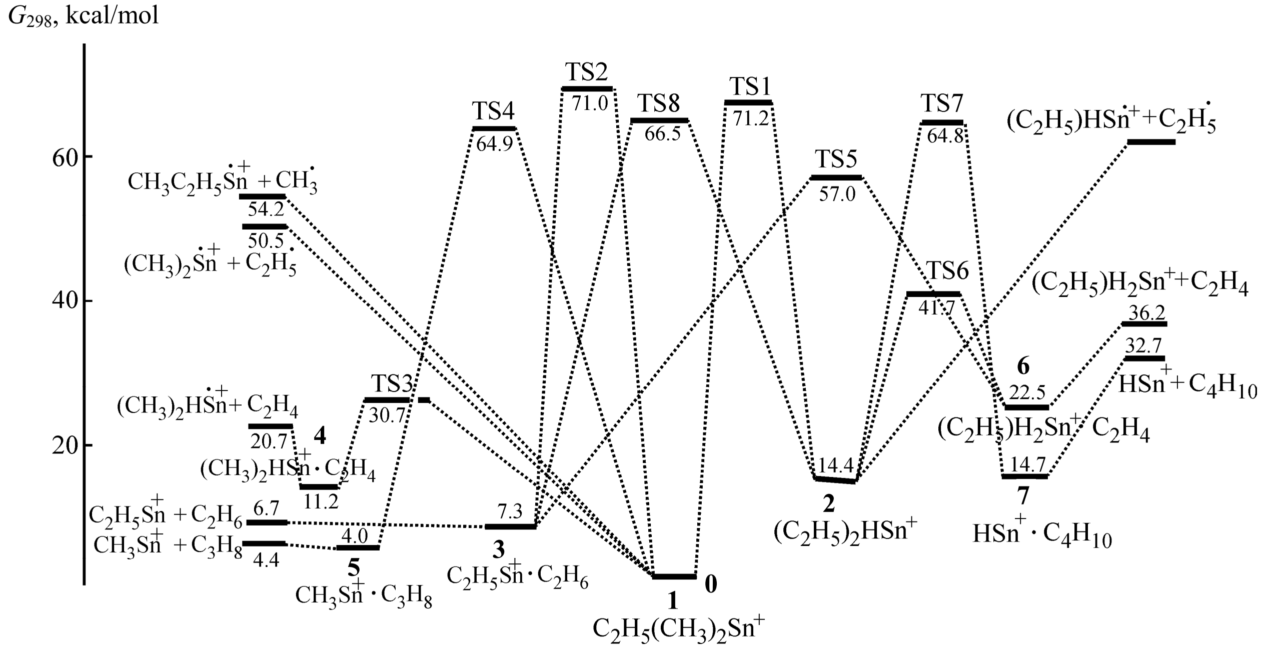


Fig. 1. Energy profile for the transformations of isomeric $C_4H_{11}Sn^+$ ions.

molecule, whose rearrangement into the planar structure typical of three-coordinate cations leads to vibrational excitation [17, 18]. The energy of relaxation for nucleogenic stannyl cation is about 20 kcal/mol (B3LYP). This energy is insufficient to overcome barrier to isomerization of the free cation. An additional energy is supplied as a result of association with the alcohol molecule (~38 kcal/mol). The overall excitation energy (~58 kcal/mol) is sufficient for the transformation of diethylstannyl cation (**2**) into tertiary ethyl(dimethyl)stannyl cation (**1**) (TS1 energy 56.8 kcal/mol). The energy gain in this transformation is 14.4 kcal/mol. Thus, the formation of ethyl(dimethyl)stannanol may be rationalized by the isomerization of diethylstannyl cation into ethyl(dimethyl)-stannyl cation and reaction of the latter with butanol molecule.

The decomposition of the oxonium complex, leading to the stannylation product, is a unimolecular process (as the decomposition of carbenium ions [1]). No products corresponding to its bimolecular decomposition were detected. By contrast, the main products of the reactions of silyl and germyl cations with alcohols were alkoxysilanes and alkoxygermanes which were formed via bimolecular proton transfer from the oxonium ion to substrate molecules [3–6]. The observed difference in the behavior of these cations may be rationalized by strong intramolecular resonance interaction of the oxygen atom with silicon and germanium and the lack of such interaction with carbon and tin. This interaction strengthens the M−O bond (M = Si, Ge) in the oxonium ion and weakens the O−H bond. It is known that the outer electron shell of carbon is filled and that atoms of the silicon subgroup possess vacant outer *nd* sublevels capable of interacting with lone electron pairs of oxygen (*d*,*n* conjugation). In particular, all oxygen compounds of silicon are characterized by appreciably shortened Si−O bond (1.64 Å) as compared to the calculated value (1.83 Å) [19]. Such conjugation with carbon atom is impossible, it is less significant in the case of germanium, and it is almost lacking in tin and lead compounds due to considerable Sn−O and Pb−O distances which hinder orbital overlap. An alternative concept implies participation in the conjugation of anti-bonding σ* orbitals (σ*,*n* conjugation) [11]. However, participation of *d* and σ* orbitals in the conjugation should endow silicon and germanium atoms with acceptor properties, which should led to the same result as than observed experimentally.

We also analyzed thermochemical parameters of the reactions of butanol with diethyl-substituted cations derived from Group 14 elements (Et_2HM^+; M = C, Si, Ge, Sn). As follows from the data in Table 1, the energies of formation (E_0) of the complexes of Et_2HM^+ with butan-1-ol do not differ from those found for

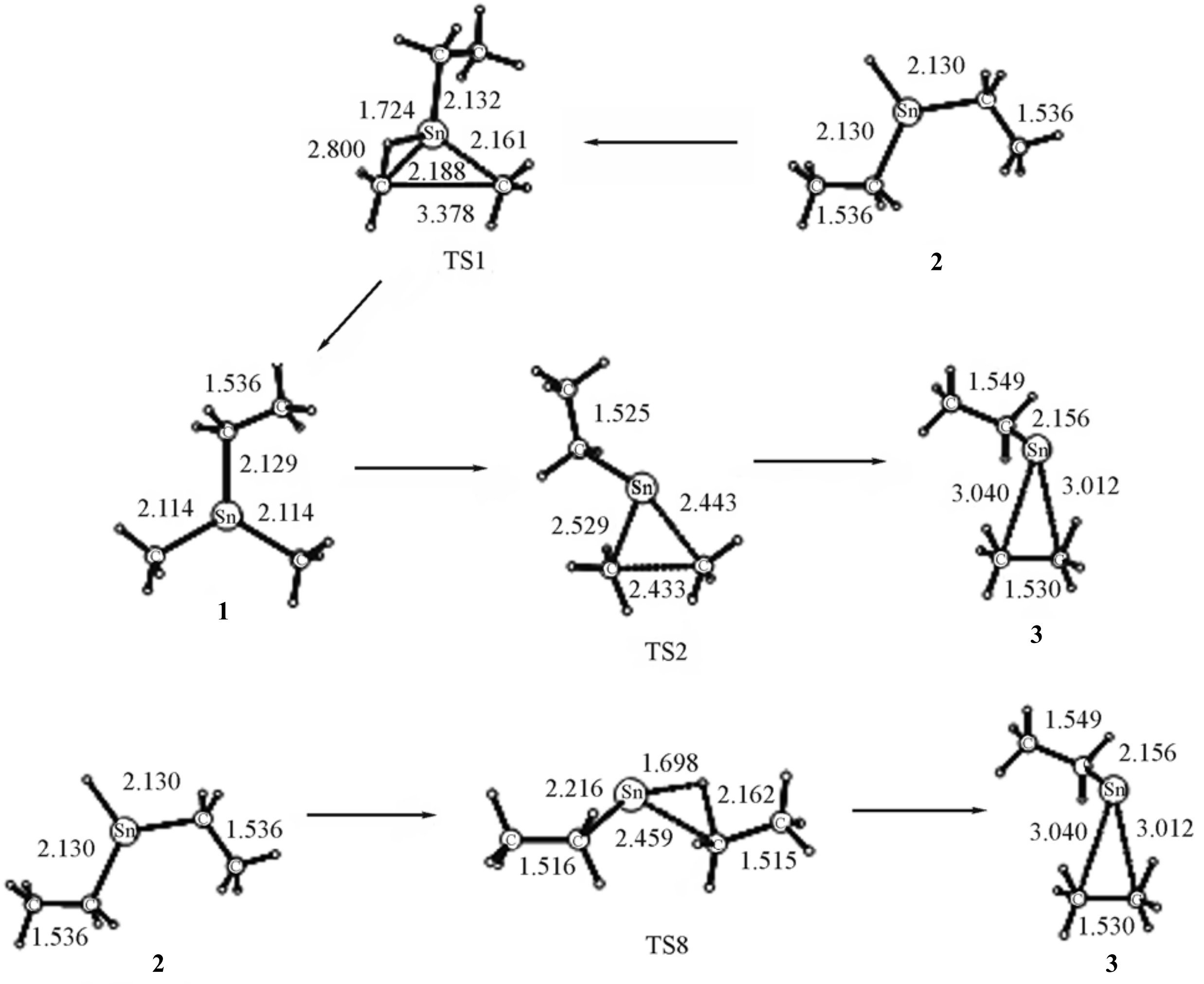


Fig. 2. Probable mechanisms of formation of the complex [$C_2H_5Sn^{+}\cdot C_2H_6$] (**3**) (see text).

model complexes of Me_2HM^+ with methanol, i.e., replacement of methyl groups by ethyl and butyl only slightly affects the calculation results. Therefore, subsequent calculations of the energy of the reaction of the 1 : 1 complex with the second alcohol molecule, which involves proton transfer from the adduct, were carried out for the model system $[Me_2HMOHMe]^+$ + MeOH.

As we already noted, the energy of complex formation may be consumed for subsequent decomposition of the excited complex along two competing paths: unimolecular with elimination of cation and formation of alcohol and bimolecular with abstraction of proton and formation of ether. The probability of one or another path is determined by the ratio of the excitation energy (energy of formation of the adduct) and energy of decomposition of the adduct. When M = C, the difference between the complex formation energy and the energy of bimolecular proton transfer is ΔE = 7 kcal/mol, whereas the energies of exothermic bimolecular decomposition of the silicon- and germanium-containing adducts (M = Si, Ge) are ~20 and 18 kcal/mol, respectively. The bimolecular proton transfer for tin cations is endothermic (+2.4 kcal/mol).

The presence of tritium-labeled ethane among the products may be explained by the occurrence of processes similar to those observed in the reaction of diethylstannyl cations with *tert*-butyl methyl ether [1], i.e., isomerization of nucleogenic cation (**2**) into complex [$C_2H_5Sn^{+}\cdot C_2H_6$] (**3**) (Fig. 2) and its subsequent dissociation. Tritiated methane is formed via homolytic dissociation of the Sn–C bond in tertiary cation $C_2H_5(CH_3)_2Sn^+$ (**1**). The energy of this process (~54 kcal/mol), which leads to the formation of radical ion $CH_3(C_2H_5)Sn^{\cdot +}$ and methyl radical $CH_3^{\cdot}$, is close to the barrier to interconversions of isomeric cations $C_4H_{11}Sn^+$; therefore, its probability is comparable with the probability of isomerization into complexes. Abstraction of a proton by [^{3}H]-methyl radical from molecules present in the reaction system leads to labeled methane.

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

One more product formed in the reactions with diethylsilyl cations with butanol and ethers was labeled ethylene which appeared as a result of isomerization of Et_2HSi^+ into $[EtH_2Si^+{\cdot}C_2H_4]$ and subsequent dissociation of the latter [20]. In the reactions with diethylgermyl cations analogous isomerization gave rise to compounds containing EtH_2Ge and Me_2HGe groups [21], and in this case liberated ethylene contained no tritium. However, no such compounds were formed in the reactions with stannyl cations.

The reason is that the probability for the formation of bivalent element species increases in going from silicon to lead. Therefore, the formation of tin(II) cation–alkane complexes like $[MeSn^+{\cdot}C_3H_8]$, $[EtSn^+{\cdot}C_2H_6]$, and $[HSn^+{\cdot}\ C_4H_{10}]$ from stannyl cations becomes more probable. This is responsible for the absence of labeled ethylene and the presence of labeled ethane among the products formed in the reactions with diethylstannyl cation. Analogous results were obtained while studying dissociation of cations R_3M^+ (M = Si, Ge, Sn, Pb) by mass spectrometry; it was found that diethylstannyl cation undergoes dissociation with elimination of ethane and that virtually no ethylene is formed [22].

The reaction of carbenium ions CT_3^+ with alcohols was accompanied by decomposition of the former with generation of carbene which was then inserted into the alcohol molecule [2]. Analogous process is hardly probable for Et_2TM^+ cations (M = Si, Ge, Sn) since the ^{3}H atom in Et_2TM^+ (in contrast to methyl cation) possesses a hydride character and heavy carbene analogs are unstable [23].

EXPERIMENTAL

Diethylstannyl cations were generated by the nuclear chemical method.

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

The procedure for the synthesis of diethyl($^3H_2$) stannane was described in [24]. Butan-1-ol of spectroscopic grade was used as substrate.

Reaction mixtures for studying ion–molecule reactions of diethylstannyl cations with butanol in the gas phase were prepared in ~20-mL spherical ampules made of molybdenum glass. The vapor pressure of butan-1-ol was ~15 mm, and the activity of diethyl ($^3H_2$)stannane was 0.001 Cu (3.7× 10^7 Bq). The products were accumulated at room temperature in the dark over 1 month.

The products were analyzed by the radiochromatographic method on a Tsvet-500 chromatograph equipped with a flow proportional counter as detector for tritium β-radiation. Two stainless-steel chromatographic columns were used: (1) 2000×2 mm, stationary phase 5% of SE-30 on Inerton-AW and (2) 3000×2 mm, stationary phase 5% of PORAPAK R on Inerton-AW. Carrier gas helium, flow rate 20 mL/min; quenching gas 5% methane−argon, flow rate 5 mL/min. Labeled products were identified by comparing their retention times with those of authentic samples under the same conditions. The yields were determined as the ratio of the activity of a given compound to the overall activity of all detected products.

Ethyl(dimethyl)stannanol was synthesized as described in [25]. Reference compounds were identified by GC/MS on a Polaris 125 instrument.

ACKNOWLEDGMENTS

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 12-03-00383-a).

REFERENCES

1. Alferova, A.A., Kochina, T.A., Avrorin, V.V., Sinotova, E.N., and Ignatyev, I.S., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 5, p. 938. DOI: 10.1134/S1070363213050095.
2. Zharov, V.T., Nefedov, V.D., Sinotova, E.N., Korsakov, M.V., and Antonova, V.V., *Zh. Org. Khim.*, 1980, vol. 16, no. 1, p. 35.
3. Kochina, T.A., Vrazhnov, D.V., and Ignatyev, I.S., *J. Organomet. Chem.*, 2002, vol. 656, nos. 1–2, p. 258. DOI: 10.1016/S0022-328X(02)01625-X.
4. Kochina, T.A., Nefedov, V.D., Sinotova, E.N., and Shchukin, E.V., *Russ. J. Gen. Chem.*, 2000, vol. 70, no. 6, p. 885.

5. Kochina, T.A., Vrazhnov, D.V., Ignatyev, I.S., and Sinotova, E.N., *Russ. J. Gen. Chem*., 2003, vol. 73, no. 1, p. 61. DOI: 10.1023/A:1023474402262.
6. Alferova, A.A., Kochina, T.A., Avrorin, V.V., and Sinotova, E.N., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 7, p. 1507. DOI: 10.1134/S1070363211070164.
7. Perst, H., *Oxonium Ions in Organic Chemistry*, Weinheim: Chemie, 1971.
8. Zhao, Y. and Truhlar, D.G., *J. Chem. Phys*., 2006, vol. 125, no. 19, no. 194101. DOI: 10.1063/1.2370993.
9. Woon, D.E. and Dunning, T.H., *J. Chem. Phys*., 1993, vol. 98, no. 2, p. 1358. DOI: 10.1063/1.464303.
10. Ignatyev, I.S., Montejo, M., and López González, J.J., *J. Mol. Model*., 2013, vol. 19, p. 5439. DOI: 10.1007/s00894-013-2038-y.
11. Egorochkin, A.N. and Voronkov, M.G., *Elektronnoe stroenie organicheskikh soedinenii kremniya, germaniya i olova* (Electronic Structure of Organic Silicon, Germanium, and Tin Compounds), Novosibirsk, Sib. Otd. Ross. Akad. Nauk, 2000.
12. Schager, F., Goddard, R., Seevogel, K., and Pörschke, K.-R., *Organometallics*, 1998, vol. 17, p. 1546. DOI: 10.1021/om970997n.
13. Clark, H. and Willis, G.J., *J. Am. Chem. Soc*., 1960, vol. 82, p. 1888. DOI: 10.1021/ja01493a014.
14. Edgell, W.F. and Ward, C.H., *J. Am. Chem. Soc*., 1955, vol. 77, p. 6486. DOI: 10.1021/ja01629a014.
15. *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Rappoport, Z., Ed., Chichester: Wiley, 2002, vol. 2, p. 1.
16. Vrazhnov, D.V., Kochina, T.A., Alferova, A.A., and Ignatyev, I.S., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 6, p. 937. DOI: 10.1134/S1070363211060090.
17. Speranza, M., *Chem. Rev*., 1993, vol. 93, no. 8, p. 2933. DOI: 10.1021/cr00024a010.
18. Kochina, T.A., Vrazhnov, D.V., Sinotova, E.N., and Voronkov, M.G., *Russ. Chem. Rev*., 2006, vol. 75, no. 2, p. 95. DOI: 10.1070/RC2006v075n02ABEH002480.
19. Voronkov, M.G., Mileshkevich, V.P., and Yuzhelevskii, Yu.A., *Siloksanovaya svyaz'* (The Siloxane Bond). Novosibirsk: Nauka, 1976.
20. Kochina, T.A., Vrazhnov, D.V., Ignatyev, I.S., Sinotova, E.N., and Voronkov, M.G., *J. Organomet. Chem*., 2011, vol. 696, p. 1331. DOI: 10.1016/j.jorganchem.2011.01.010.
21. Myalochkin, D.L., Kochina, T.A., Vrazhnov, D.V., Avrorin, V.V., Sinotova, E.N., and Ignatyev, I.S., *Russ. J. Gen. Chem*., 2010, vol. 80, no. 11, p. 2283. DOI: 10.1134/S1070363210110095.
22. Groenewold, G.S., Gross, M.L., Bursey, M.M., and Jones, P.R., *J. Organomet. Chem*., 1982, vol. 235, p. 165. DOI: 10.1016/S0022-328X(00)96206-5.
23. Boganov, S.E., Faustov, V.I., Egorov, M.P., and Nefedov, O.M., *Russ. Chem. Bull*., 2004, vol. 53, no. 5, p. 960. DOI: 10.1023/B:RUCB.0000041298.37114.c6.
24. Alferova, A.A., Kochina, T.A., Avrorin, V.V., and Sinotova, E.N., *Russ. J. Gen. Chem*., 2012, vol. 82, no. 11, p. 1925. DOI: 10.1134/S1070363212110308.
25. Amberger, E. and Kula, M.R., *Chem. Ber*., 1963, vol. 96, p. 2562. DOI: 10.1002/cber.19630961007.