*ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 7, pp. 1507–1510. © Pleiades Publishing, Ltd., 2011.*
*Original Russian Text © A.A. Alferova, T.A. Kochina, V.V. Avrorin, E.N. Sinotova, D.V. Vrazhnov, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 7, pp. 1159–1162.*

# Radiochemical Study of Gas-Phase Reactions of Nucleogenic Diethylgermyl Cations with Dibutyl Ether and 1-Butanol

**A. A. Alferova[a], T. A. Kochina[b], V. V. Avrorin[a], E. N. Sinotova[a], and D. V. Vrazhnov[b]**

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

Received November 2, 2010

**Abstract**—Reactions of tritium-labeled free diethylgermyl cations with dibutyl ether and 1-butanol in a gas phase were studied by the radiochemical method. Mechanisms of the corresponding ion-molecular reactions were suggested, and the most probable paths of the cation $(C_2H_5)_2TGe^+$ conversion into other isomeric forms were shown.

**DOI:** 10.1134/S1070363211070164

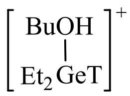
To continue the study of reactions of three-coordinated organic cations of germanium (germyl cations) with oxygen-containing compounds (*n*-donors) [1, 2], we have introduced dibutyl ether and 1-butanol in these reactions. The choice of these compounds is caused by the fact that reactions of nucleogenic diethylsilyl ions with them have been studied earlier [3, 4]. The diethylsilyl cation eliminates ethylene in reactions with the above-mentioned substrates and turns into ethyl- and then to dimethylsilyl ion, as demonstrated by the observed reaction products. The degree of the diethylsilyl cation conversion in the reaction with dibutyl ether (10%) [4] was lower than in the reaction with 1-butanol (38%) [3].

Taking into account the above-stated, we have studied gas-phase ion-molecular reaction of BuOH and $Bu_2O$ with tritium-labeled diethylgermyl cations generated by the nuclear chemistry method.

$$(C_2H_5)_2GeT_2 \xrightarrow{\beta^-} (C_2H_5)_2Ge^+T + {}^3He^0.$$

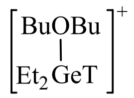
We notice that one of unique features of the nuclear chemistry method of generating free cations [5, 6] is not only a possibility to record neutral compounds, but also to study their isomeric composition.

The results of the reaction of the $Et_2TGe^+$ cation with 1-butanol and dibutyl ether are presented in the table. It is known that reactions of carbene cations with bases of this type proceed through the formation of intermediate oxonium complexes resulting from the interaction of a vacant *p* orbital of the cation with lone electrons of the oxygen atom [7]. It is therefore presumable that the first act of the interaction of diethyltritiumgermyl cations with 1-butanol and dibutyl ether will be formation of hydroxonium ions **I, II**. The formation of analogous adducts was also postulated in the study of substituted silyl ions [3, 4, 8, 9].



$$\left[\begin{array}{c} BuOH \\ | \\ Et_2GeT \end{array}\right]^+$$

**I**



$$\left[\begin{array}{c} BuOBu \\ | \\ Et_2GeT \end{array}\right]^+$$

**II**

It is seen from the table that in both cases the main reaction product is butoxydiethyltritiumgermane. It is formed in the reaction with alcohol as a result of bimolecular proton transfer from ion **I** to alcohol molecules. The same pattern was observed in the reaction of methyl- and ethyl-substituted silyl cations with alcohols (MeOH and BuOH) [8, 10].

Products of unimolecular decay of complex **I** were not observed. It is necessary to note that in the case of silyl cations products of the unimolecular decay of the complex (labeled alcohol and siloxanes) were observed in small amounts.

Relative yields of products of the reactions of diethylgermyl ions with 1-butanol and dibutyl ether

| Reaction product | Relative yield, %[a] | |
|---|---|---|
| | BuOH | BuOBu |
| $Et_2TGeOBu$ | 60±5 | 95±2.5 |
| EtTHGeOBu | 20±2.5 | 5±2.5[b] |
| $Me_2TGeOBu$ | 20±2.5 | |

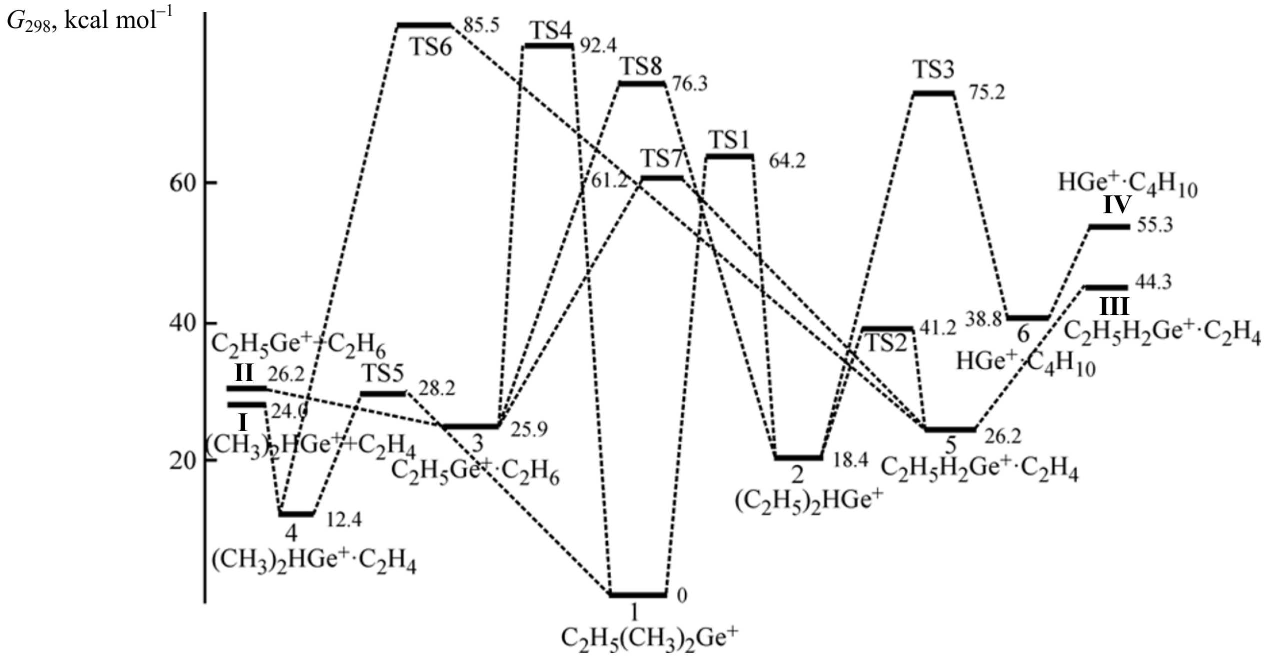
[a] Confidence probability level α 0.95. [b] Total yield is given.

The bimolecular path of the complex **I** decay with a proton transfer (in the case of both silyl and germyl ions) is caused by a high affinity of Si and Ge atoms to the oxygen atom [11]. On the contrary, in the case of the ion-molecular interaction of methyl cations with alcohols in similar conditions only a unimolecular fragmentation of the complex was observed [12].

In the case of dibutyl ether, unlike 1-butanol, the unimolecular decay of complex **II** with the elimination of the butyl cation leads to the main reaction product ($Et_2TGeOBu$). A bimolecular interaction of this adduct with substrate molecules cannot lead to the appearance of any reaction products, as it was observed in the reaction with 1-butanol, because the adduct contains no mobile hydrogen, and thus the reaction leads only to energy transfer to substrate molecules.

A germyl substituent is present in the germylation products not only in the initial, but also in rearranged forms, as is the case with diethylsilyl ions. The theoretical study [13] of the system $S_4H_{11}Ge^+$ has shown that the potential energy surface contains, in addition to the minima belonging to classical three-coordinated cations $EtMe_2Ge^+$ (a global minimum) and $Et_2HGe^+$, also local minima corresponding to the donor–acceptor complexes $[EtH_2Ge^+{\cdot}C_2H_4]$, $[EtGe^+{\cdot}C_2H_6]$, $[HGe^+{\cdot}C_4H_{10}]$, and $[Me_2HGe^+{\cdot}C_2H_4]$ (see the figure). The second most stable isomer is not the secondary diethylgermyl cation, but the complex $[Me_2HGe^+{\cdot}C_2H_4]$, as its formation energy is higher than the global minimum only by 12.4 kcal $mol^{-1}$. The complexes are very unstable, and their decay with butane or ethane release requires only 16.5 and 0.3 kcal $mol^{-1}$, respectively. However, activation barriers of intercomversion of isomers are rather high. The most low-energy (23 kcal $mol^{-1}$) path of the cation $Et_2HGe^+$ conversion is its isomerization into the $[EtH_2Ge^+{\cdot}C_2H_4]$ complex, dissociation of which results in the formation of an ethylgermyl cation and ethylene.

The diethyltritiumgermyl ion generated by the nuclear-chemistry method inherits the tetrahedral structure of the diethylditritiumgermane mother molecule. The reorganization of this structure into the planar structure characteristic of three-coordinated



Profile of the potential energy surface of the $(C_2H_5)_2HGe^+$ cation calculated by the B3LYP method with the cc-pVTZ basis set.

cations of elements of the 14th group results in the vibrational excitation of ~19.6 kcal mol$^{-1}$ (B3LYP/6-31G*). It is evident that the energy of the arising $Et_2TGe^+$ cation is insufficient to overcome even the lowest isomerization barrier. An additional energy can be obtained as a result of association of the cation with a substrate molecule ("collisional induced isomerization").

According to our estimates by the B3LYP/6-31G* method, the energies of association with dibutyl ether and butyl alcohol are practically the same, being equal to 37.79 and 36.83 kcal mol$^{-1}$, respectively. The total excitation energy (~58 kcal mol$^{-1}$) is sufficient to overcome the activation barriers of isomerization. However, as it is seen from the analysis, in the case of the ether the main reaction product (95%) is butoxydiethyltritiumgermane. The yields of products with rearranged germyl substituent (EtTHGeOBu and $Me^2TGeOBu$) was only 5% in total. The symmetrical structure of the dibutyl ether molecule seems to promote fast redistribution of the vibrational excitation energy inside the intermediate complex, resulting in its much faster decay as compared to the diethylgermyl cation rearrangement.

Reactions of diethylgermyl cations with butyl alcohol are characterized by essentially greater yields of germylation products with rearranged germyl substituents, namely of butoxyethyl- and butoxydimethylgermanes. The total yield of these compounds increases up to 40%. Such change in the degree of diethylgermyl cation transformation in the reaction with alcohol is attributable to an increase in the life time of intermediate adduct **I**, because its decay leading to the reaction products is a bimolecular process, as it was already noted. Furthermore, the diethylgermyl cation has all prerequisites (energy and time) for the isomerization into the $[Me_2HGe^+{\cdot}C_2H_4]$ complex by sequential overcoming the TS1 barrier 46 kcal mol$^{-1}$) and then the TS5 barrier (~28 kcal mol$^{-1}$). Ethylene elimination by this complex results in the formation of the dimethylgermyl cation, which interacts with 1-butanol to form butoxydimethyltritiumgermane found among the products.

Overcoming of the TS1 barrier (~46 kcal mol$^{-1}$) leads to the most stable tertiary cation $EtMe_2Ge^+$, however products of its reaction with alcohol are not observed. The total excitation energy of the $EtMe_2Ge^+$ cation in such transformation is rather high (~74 kcal mol$^{-1}$), and it at once isomerizes further into one of most energy favorable isomers, the $[Me_2HGe^+{\cdot}C_2H_4]$ complex, with its subsequent dissociation or undergoes the reverse transition into the diethylgermyl cation.

No products (alcohol and ether) of transformation of the tertiary cation $EtMe_2Si^+$ were observed either in the reaction of diethylsilyl ions. However the reason of it consists in the fact that the barrier of the diethylsilyl ion dissociation lies lower than its isomerization barrier. In the case of its germanium analog ($EtMe_2Ge^+$) there are other more favorable paths of its transformation than the isomerization into the tertiary cation $EtMe_2Ge^+$. It is somewhat surprising that labeled hydrocarbons were not found among the products of the diethylgermyl ion reaction with benzene and *tert*-butylmethyl ether [2, 14].

The presence of sufficient energy and life time of intermediate adduct **I** results in the fact that the diethylgermyl ion tends to isomerize into the tertiary cation $EtMe_2Ge^+$, which converts at once by virtue of high excitation to the complex $[Me_2HGe^+{\cdot}C_2H_4]$ with an energy higher by 12.4 kcal mol$^{-1}$ than the global minimum. At this isomerization tritium located at germanium comes in the methyl substituent, and consequently ethylene formed as a result of the complex $[(CH_3)(CH_2T)Ge^+{\cdot}C_2H_4]$ dissociation is not labeled and hence cannot be detected by the gas radiochromatography method. As to the $[EtH_2Ge^+{\cdot}C_2H_4]$ complex, the most low-energy path of the transformation of the $Et_2GeH^+$ cation (23 kcal mol$^{-1}$) leads to its formation, as it was noted above. The energy of ~15 kcal mol$^{-1}$ is required for the reverse transition, and of ~18 kcal mol$^{-1}$, for the complex dissociation. Barriers rather close in energy do not exclude a possibility for the diethyltritiumgermyl cation to undergo multiple transformations into the complex and back, therefore tritium can appear in ethylene. However, the absence of labeled ethylene among observable products points to the fact that the formed complex dissociates at once into ethylgermyl cation and ethylene, and therefore tritium is absent from ethylene. The absence of labeled ethane seems to result from the fact that the isomerization of the diethyltritiumgermyl cation into the ethane complex $[EtGe^+{\cdot}C_2H_6]$ in the reaction with butyl alcohol is less preferable than the isomerization into the ethylene complexes $[Me_2HGe^+{\cdot}C_2H_4]$ and $[EtH_2Ge^+{\cdot}C_2H_4]$.

## EXPERIMENTAL

Synthesis of diethylditritiumgermane is described in [14].

Chemically-pure grade dibutyl ether, which was carefully dried up by metal sodium and distilled before filling ampules, and spectral-pure grade butyl alcohol were used as substrates.

To study ion-molecular gas-phase reactions of diethylgermyl cations, the reaction mixtures were prepared in spherical molybdenum-glass ampules of volume ~20 ml. Vapor pressure of dibutyl ether and 1-butanol was ~10 mm Hg, and activity of diethylditritiumgermane, 0.001 Cu ($3.7\times10^7$ Bq). The reaction products were accumulated at room temperature in darkness within ~4 months.

Products of the ion-molecular reactions of diethylgermyl cations with substrates were analyzed by the radiochromatographic method using a Tsvet-500 chromatograph equipped by a flow-proportional counter, a detector of tritium β-radiation. Two chromatographic systems were used in the analysis: a stainless steel column of 2000×2 mm filled with 5% SE-30 on the Inerton-AW carrier and a stainless steel column of 3000×2 mm filled with 5% Polyethylenglycol-2000 on the Inerton-AW. The rate of gas-carrier (helium) was 20 ml $\text{min}^{-1}$, the rate of quenching gas [methane (5%)–argon], 5 ml $\text{min}^{-1}$. Labeled reaction products were identified by comparison of their retention times with retention times of tracking substances in identical chromatographic conditions. The yield was determined as the ratio of activity of the particular compound to the total activity of all detected reaction products.

To synthesize tracking substances, the procedure [15] was used, according to which alkyl-substituted butoxygermanes were obtained by the reaction of corresponding alkylgermanes with anhydrous 1-butanol in the presence of Raney nickel. Reaction products were identified by the chromatography-mass spectrometry method on a Polaris 125 device.

## ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 09-03-00439).

## REFERENCES

1. Myalochkin, D.L., Kochina, T.A., Vrazhnov, D.V., Avrorin, V.V., and Sinotova, E.N., *Radiochemistry,* 2010, vol. 52, no. 1, p. 87.
2. Myalochkin, D.L., Kochina, T.A., Vrazhnov, D.V., Avrorin, V.V., Sinotova, E.N., and Ignat'ev, I.S., *Zh. Obshch. Khim.,* 2010, vol. 80, no. 11, p. 1819.
3. Kochina, T.A., Vrazhnov, D.V., and Ignatyev, I.S., *J. Organometall. Chem*., 2002, vol. 656, p. 258.
4. Kochina, T.A., Vrazhnov, D.V., Sinotova, E.N., and Shishigin, E.A., *Zh. Obshch. Khim*., 2004, vol. 74, no. 2, p. 219.
5. Nefedov, V.D., Sinotova, E.N., and Toropova, M.A., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1980, no. 3, p. 35.
6. Nefedov, V.D., Kochina, T.A., and Sinotova, E.N.*, Usp. Khim*., 1986, vol. 55, no. 5, p. 794.
7. Perst, H. *Oxonium Ions in Organic Chemistry*, Verlag Chem. Acad. Press, 1971.
8. Kochina, T.A., Schukin, E.V., Nefedov, V.D., and Sinitova, E.N., *Zh. Obshch. Khim*., 2000, vol. 70, no. 6, p. 949.
9. Kochina, T.A., Vrazhnov, D.V., Ignat'ev, I.S., and Sinitova, E.N., *Zh. Obshch. Khim*., 2003, vol. 73, no. 1, p. 65.
10. Nefedov, V.D., Kharitonov, N.P., Sinotova, E.N., Kochina, T.A., and Balakin, I.M., *Zh. Obshch. Khim*., 1980, vol. 50, no. 11, p. 2499.
11. Voronkov, M.G., Mileshkevich, V.P., and Yuzhelevskii, Yu.A., *Siloksanovaya svyaz'* (Siloxane Bond), Novosibirsk: Nauka, 1976.
12. Zharov, V.T., Nefedov, V.D., Sinotova, E.N., Korsakov, M.V., and Antonova V.V.*, Zh. Org. Khim*., 1978, vol. 14, no. 4, p. 35.
13. Ignat'ev, I.S., Vrazhnov, D.V., and Kochina T.A., *Zh. Obshch. Khim*., 2010, vol. 80, no. 7, p. 1117.
14. Myalochkin, D.L., Kochina, T.A., Avrorin, V.V., Vrazhnov, D.V., and Sinotova, E.N., *Zh. Obshch. Khim*., 2010, vol. 80, no. 9, p. 1443.
15. Myalochkin, D.L., Kochina, T.A., Vrazhnov, D.V., Avrorin, V.V., and Sinotova, E.N., *Zh. Obshch. Khim*., 2008, vol. 78, no. 11, p. 1831; Massol, M., Satge, J., Riviere, P., and Barrau, J., *J. Organometal. Chem*., 1970, vol. 22, p. 599.