ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 9, pp. 1762–1766. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © D.L. Myalochkin, T.A. Kochina, V.V. Avrorin, D.V. Vrazhnov, E.N. Sinotova, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 9, pp. 1443–1447.

Gas Phase Reaction of Nucleogenic Dimethylgermylium Cations with Benzene

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

[a] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
e-mail: radiochem@yandex.ru

[b] *Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia*

Received February 15, 2010

Abstract—Reaction of nucleogenic dimethylgermylium cations with benzene in the gas phase was studied by the radiochemical method. The formation of the products of germylation of benzene, dimethylphenylgermane, and phenylgermane is indicative of the formation of dimethylgermylium cations by the β-decay of tritium in the molecule of dimethylditritium germane. Dimethylgermylium cations are shown to undergo a rearrangement in the course of the reaction with benzene, which is consistent with the earlier results of quantum-chemical calculations.

DOI: 10.1134/S1070363210090070

Although the first indications on the formation of the three-coordinate germylium cations in the gas phase appeared about 50 years ago [1], up to now there were few publications on the properties and reactivity of these intermediates. Nevertheless, note the reviews of Karni [2] and Zharov [3] devoted to three-coordinate metal-centered cations R_3M^+ (M = Ge, Sn, Pb).

In the last decades, the three-coordinate silicon organic cations (silicenium ions) R_3Si^+ attracted much attention from both the theoreticians [4–8] and experimentalists [7, 9–12]. With this, special attention was paid to the problem of preparation of “free” silicenium ions in the liquid phase or in crystals, that is, cations in which strong interaction with the solvent or counter-ion is absent. This problem turned out to be the most difficult because of the unique ability of silicon to expand its coordination sphere. Only recently these efforts led to success [7, 13, 14]. At present, these studies were extended to other elements of the silicon subgroup, Ge, Sn, Pb.

In our studies, we used the absolutely original non-traditional strategy for generation and investigation of reactivity of cations R_3M^+, which was elaborated after many years of studies of chemical consequences of radioactive β-decay of tritium atoms in the molecules of organic and organoelemental compounds [15–17]. First this strategy based on the processes of β-decay of tritium in the molecules of hydrocarbons was suggested for generation and investigation of reactivity of free carbenium ions [15]. However, the extension of this strategy to the generation of silicenium [16, 17] and, later, germenium analogs of carbenium ions has acquired special importance. The problem consists in the aforementioned ability of silicon and the elements of its subgroup to expand the coordination sphere leading to the formation of complexes of cations R_3M^+ with the nucleophiles of any type, including the counter-ion and the solvent molecules.

Theoretical background of the nuclear chemical method [15] and experimental studies on the carbenium [18–21] and silicenium ions [22–25] led to the conclusion on the possibility and prospects of the use of this strategy for generation and investigation of reactivity of the three-coordinate cations of heavier elements of the silicon subgroup both in the gas and condensed phase.

The present work is devoted to investigation of the gas phase reaction with benzene of dimethylgermylium ions Me_2TGe^+ generated by the nuclear chemical method.

Benzene is a classical representative of π-electron-donor compounds. The immense practical importance of the reaction of carbenium ions with aromatic hydrocarbons, under lying the industrial aromatic alkylation is well known [26]. In contrast, the reaction of electrophilic aromatic silylation for a long time was not realized either in the gas or in the condensed phase. The absence of silylation products was due to the fact that the processes of desilylation proceeded under the conditions of the experiments with much larger rates than the deprotonation processes [27]. The electrophilic silylation of benzene in the gas phase was possible only in the presence of triethylamine as a proton acceptor [28, 29].

Our radiochemical studies of the reaction of nucleogenic dimethyl- and diethylsilyl ions with benzene in the absence of any additives in the gas and condensed phase have shown that the yield of the products of silylation (phenylsilanes) in both cases did not exceed 8% [7, 22, 23]. The major product of these reaction was labeled benzene.

The observed difference in the reaction course for the carbenium and silicenium ions corresponds to the different structure of the intermediate complexes since the silicenium ion in the σ-complex practically retains its cationic nature.

Radiochemical investigation of the ion-molecular reaction of dimethylgermylium cation Me_2GeT^+ with C_6H_6 has shown that, as in the case of silicenium ions, the main product of the reaction is labeled benzene (92%). According to the adopted mechanism of the ion-molecular reaction of carbenium ions with aromatic compounds, the reaction of germylium cations Me_2GeT^+ with benzene can be represented by the following scheme (Fig. 1).

The approach of the ion to the molecule results in the formation of the π-complex, which then is transformed into the σ-complex. Decomposition of the latter occurs either unimolecularly (degermylation) with the formation of labeled benzene and a germylium cation, or bimolecularly by proton transfer to the molecules of the substrate with the formation of phenylgermanes. The formation of labeled benzene is due to isotope exchange in the σ-complex between tritium of the dimethylgermylium cation and protium in the *ipso*-position of the benzene ring.

The performed B3LYP/6-31G* quantum chemical calculations of the stereoelectronic structure and charge distribution in the model σ-complex suggest that for the germylium as well as for silicenium ions the processes of degermylation (desilylation) are more preferable than the processes of deprotonation.

The calculated angle between the Ge–C bond and the plane of the benzene ring is 101.5°, that is, not substantially different from that in the π-complex (90°). With this, the main positive charge (+0.87) is located on the Ge atom. It is well known that in the course of alkylation of aromatic compounds the covalently bonded σ-complex is formed in which the angle between the alkyl group and the plane of the ring is ~141°. The positive charge is shifted from the carbenoid carbon atom to the hydrogen atoms of the benzene ring and the highest positive charge (+0.36) is located on the hydrogen atom in the *ipso*-position. The structure and equilibrium geometry of σ-complexes of the carbenium, silicenium and germylium ions with benzene are shown in Fig. 2.

It is evident that this structure and charge distribution in the complex are more appropriate for the process of degermylation.

The products of germylation, labeled phenylgermanes, are formed in a small amount of ~7%, and their composition is 71% of Me_2PhGeT to 29% of PhH_2TGe.

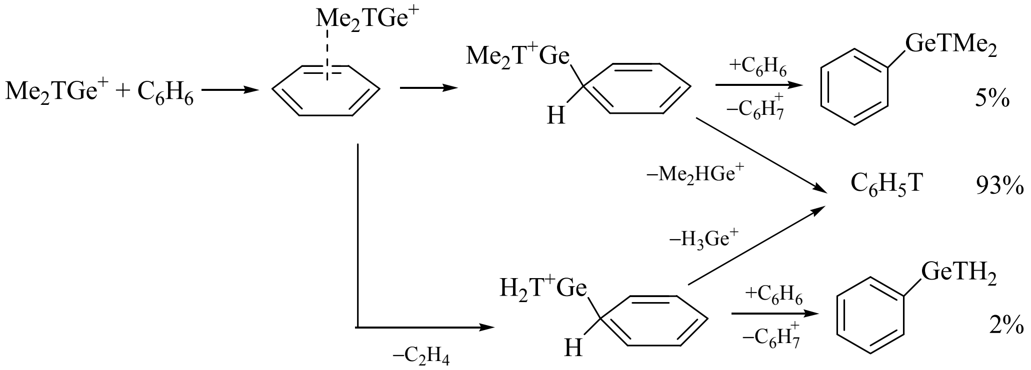

Fig. 1. Tentative mechanism of the reaction of dimethylgermylium cations with benzene.

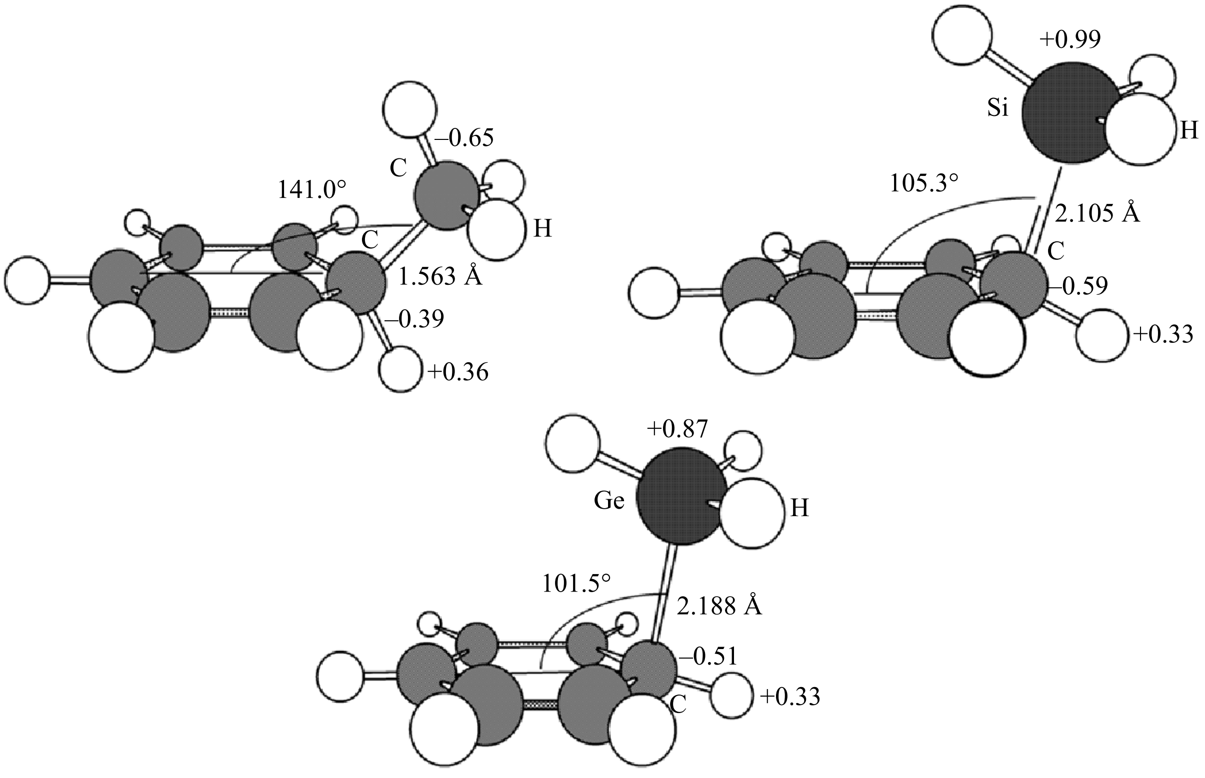

Fig. 2. Electronic structure and equilibrium geometry of complexes of cations H_3M^+ (M = C, Si, Ge) with benzene (B3LYP/6-31G*).

The former is the product of the reaction of benzene with the major nucleogenic cation Me_2GeT^+, and the latter is the product of its reaction with unsubstituted germylium cation H_2TGe^+, which could be formed by dissociation of the complex $[H_2TGe^+ \cdot C_2H_4]$. The performed quantum chemical calculations (B3LYP/6-31G* and aug-cc-pVDZ) [30] have shown that on the potential energy surface (PES) of the system $C_2H_7Ge^+$ the global minimum belongs to cation Me_2GeH^+. However, the PES has also local minima close in energy to the classical cation Me_2GeH^+ and belonging to the donor–acceptor complexes $[HGe^+ \cdot C_2H_6]$, $[MeGe^+ \cdot CH_4]$, $[H_3Ge^+ \cdot C_2H_4]$. Dissociation of these complexes may lead to the formation of germanium-centered cations and the molecules of the corresponding hydrocarbons.

According to quantum chemical calculations, isomerization of the classical cation Me_2HGe^+ is connected with high activation barriers (~75, 60, 52 kcal mol^{-1}, respectively) [30]. Since the time of emergence of the nucleogenic cation is very short (10^{-14} s), it inherits the structure of the mother molecule, that is, in our case, tetrahedral [17, 31]. Changing of the tetrahedral structure into the planar structure characteristic of the three-coordinate cation, is followed by the release of the energy of relaxation, which may be consumed for excitation of this ion. For the germylium cation Me_2GeT^+ we have estimated this energy (B3LYP/6-31G*) as 24 kcal mol^{-1}, that rules out the isomerization of the free cation. An additional energy can be acquired by association of this cation with the molecule of the nucleophile.

For benzene, this energy is 36.5 kcal mol^{-1} (B3LYP/6-31G*). Therefore, the total energy is enough to overcome the lowest isomerization barrier of the cation $(CH_3)_2GeH^+$ resulting in the formation of the complex $[H_3Ge^+ \cdot C_2H_4]$ and its further dissociation.

However, this energy is too small to overcome other activation barriers, as shows the absence of methane, ethane or other products of germylation among the reaction products.

It should be noted that earlier the possibility of existence of complexes $[HM^+ \cdot H_2]$ was theoretically predicted for the unsubstituted cations H_3M^+ (M = Si, Ge, Sn), but only the use of the nuclear chemical strategy allowed for the first time to confirm experimentally the predicted by us isomerization of cation Me_2GeT^+.

Therefore, the ionic germylation of aromatic compounds (as well as the ionic silylation), unlike electrophilic alkylation, practically does not occur due to the structure of the arising intermediate complexes, in which the germylium and silicenium ions retain their cationic nature.

At the same time, the formation of a small amount of the products of germylation of benzene both by the principal cation Me_2GeT^+ and by the product of its isomerization H_2TGe^+ may serve as an evidence of formation of germylium cations as a result of β-decay of tritium in the molecule of dimethylgermane Me_2GeT_2.

EXPERIMENTAL

Free dimethylgermylium cations were generated by nuclear chemical method [15–17].

$$(CH_3)_2GeT_2 \xrightarrow{\beta^-} (CH_3)_2Ge^+T + {}^3He^0.$$

Dimethylditritiumgermane was synthesized by the protocol described in [32].

Benzene of "chemically pure" grade was used as substrate, which prior to filling the ampules was thoroughly dried over sodium metal and distilled. The purity was controlled by gas chromatography.

The reaction mixtures for investigation of the ion-molecular reactions of dimethylgermylium cations were placed into ampules of molybdenum glass of spherical shape of ~20 ml capacity; the pressure of the benzene vapors was 15 mm Hg, the activity of dimethylditritium-germane was 0.001 Ci (3.7×10^7 Bq). The accumulation of the products occurred at room temperature in the dark for ~4 months.

The analysis of the products of dimethylgermylium cations with benzene was performed by the method of gas radiochromatography on a Tsvet-500 chromatograph equipped with a flow-through proportional counter as detector of β^--radiation of tritium. For analysis, two chromatographic systems were used: the stainless steel column 2000×2 mm packed with 5% SE-30 on Inerton-AW, and the stainless steel column 3000×2 mm packed with Porapak R. The rate of the gas carrier (helium) was 20 ml min^{-1}, the rate of the quenching gas [methane (5%)/argon] was 5 ml min^{-1}. Identification of the labeled products of the reaction was performed by comparing their retention times with those of the authentic compounds under the same chromatographic conditions. The yield of the products was determined as the ratio of activity of the given compound to the total activity of all reaction products.

Dimethylphenylgermane was prepared by the Grignard reaction from dimethylbromogermane and bromobenzene with subsequent reduction of bromodimethylphenylgermane with lithium hydride in hexane at heating. Phenylgermane was prepared by reduction of phenyltrichloro-germane with lithium hydride in dioxane at heating. Phenyltrichlorogermane was prepared by reflux of iodobenzene with germanium tetrachloride in the presence of copper powder [33]. Dimethylphenylgermane and phenylgermane used as authentic samples were identified by the method of chromatomass spectrometry on a "Polaris 125" instrument.

ACKNOWLEDGMENTS

This work was financially supported by Russian Foundation for Basic Research (grant no. 09-03-00439) and by the Department of Chemistry and Material Sciences of Russian Academy of Sciences (Program no. 1).

REFERENCES

1. Hobrock, B.G. and Kiser, R.W., *J. Phys. Chem.*, 1962, vol. 66, p. 155.
2. Karni, M., Apeloig, Y., Kapp, J., and Schleyer, P.v.R., in *The Chemistry of Organic Silicon Compounds*, Rappoport, Z. and Apeloig, Y., Eds., New York: Wiley, 2001, vol. 3.
3. Zharov, I. and Michl, J., in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Rappoport, Z. and Apeloig, Y., Eds., New York: Wiley, 2003, vol. 2.
4. Schleyer, P.v.R., Buzek, P., Muller, T., and Apeloig, Y., *Angew. Chem. Int. Ed. Engl.*, 1993, vol. 32, no. 10, p. 1471.
5. Olsson, L. and Cremer, D., *J. Chem. Phys. Lett.*, 1993, vol. 215, no. 5, p. 433.
6. Ignatyev, I.S. and Sundius, T., *Organometallics,* 1996, vol. 15, no. 26, p. 5674.
7. Kochina, T.A., Vrazhnov, D.V., and Ignatyev, I.S., *J. Organomet. Chem.*, 1999, vol. 586, nos. 1–2, p. 241.
8. Shchegolev, B.F. and Kochina, T.A., *Zh. Strukt. Khim.*, 1992, vol. 33, no. 1, p. 156.
9. Lambert, J.B., Zhang, S., Stern, S.L. and Huffman, J.C., *Science*, 1993, vol. 260, p. 1917.

10. Lambert, J.B. and Zhang S., *J. Chem. Soc. Chem. Comm.,* 1993, no. 5, p. 383.
11. Kochina, T.A., Nefedov, C.D., Sinotova, E.N., and Shchukin, E.V., *Russ. J. Gen. Chem*., 2001, vol. 71, no. 2, p. 206.
12. Kochina, T.A., Vrazhnov, D.V., Ignat'ev, I.S., and Sinotova, E.N., *Russ. J. Gen. Chem*., 2003, vol. 73, no. 1, p. 61.
13. Lambert, J.B., Zhao, Y, Wu, H., Tse, W.C., and Kuhlmann, B., *J. Am. Chem. Soc*., 1999, vol. 121, no. 21, p. 5001.
14. Chuit, C.H., Corriu, R.J.P., Mehdi, A., and Reye, C., *Angew Chem. Int. Ed. Engl*., 1993, vol. 32, no. 9, p. 1311.
15. Nefedov, V.D., Sinotova, E.N., and Toropova, M.A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.,* 1980, no. 3, p. 35.
16. Nefedov, V.D., Kochina, T.A., and Sinotova, E.N., *Russ. Chem. Rev. Engl. Transl*., 1986, vol. 55, no. 5, p. 426.
17. Kochina, T.A., Vrazhnov, D.V., Sinotova, E.N., and Voronkov, M.G., *Russ. Chem. Rev. Engl. Transl*., 2006, vol. 75, no. 2, p. 95-110.
18. Nefedov, V.D., Kochina, T.A., Sinotova, E.N., and Kharitonov, N.P., *Zh. Obshch. Khim*., 1982, vol. 52, no. 7, p. 1599.
19. Kochina, T.A., Vrazhnov, D.V., and Ignatyev, I.S., *J. Organomet. Chem*., 1999, vol. 589, no. 1, p. 45.
20. Kochina, T.A., Vrazhnov, D.V., Sinotova, E.N., Katsap, M.Yu., and Shchegolev, B.F., *Russ. J. Gen. Chem*., 2001, vol. 71, no. 10, p. 1557.
21. Gomzina, N.A., Kochina, T.A., Nefedov, V.D., Sinotova, E.N., and Vrazhnov, D.V., *Zh. Obshch. Khim*., 1994, vol. 64, no. 3, p. 443
22. Kochina, T.A., Nefedov, V.D., Sinotova, E.N., and Shchukin, E.V., *Radiochemistry*, 2000, vol. 42, no. 2, p. 184.
23. Kochina, T.A., Vrazhnov, D.V., Ignat'ev, I.S., Nefedov, V.D., and Sinotova, E.N., *Russ. J. Gen. Chem*., 1999, vol. 69, no. 6, p. 905.
24. Kochina, T.A., Vrazhnov, D.V., Ignat'ev, I.S., and Sinotova, E.N., *Russ. J. Gen. Chem*., 2005, vol. 75, no. 1, p. 69.
25. Kochina, T.A., Vrazhnov, D.V., Sinotova, E.N., and Ignat'ev, I.S., *Russ. J. Gen. Chem*., 2005, vol. 75, no. 5, p. 708.
26. Olah, G.A., *Friedel-Crafts and Related Reactions*, New York: Wiley, 1963.
27. Wojtinyak, A.C. and Stone, J., *Int. J. Mass. Spectrom. Ion Processes*, 1986, vol. 74, no. 1, p. 59.
28. Cacace, F., Crestoni, M., and Fornarini, S., *J. Am. Chem. Soc*., 1992, vol. 114, no. 17, p. 6776.
29. Fornarini, S., *J. Org. Chem*., 1998, vol. 53, no. 6, p. 1314.
30. Ignat'ev, I.S., Kochina, T.A., and Vrazhnov, D.V., *Russ. J. Gen. Chem*., 2007, vol. 77, no. 4, p. 575.
31. Speransa, M., *Chem. Rev*., 1993, vol. 93, no. 8, p. 2933.
32. Myalochkin, D.L., Kochina, T.A., Vrazhnov, D.V., Avrorin, V.V., and Sinotova, E.N., *Russ. J. Gen. Chem*., 2007, vol. 77, no. 7, p. 1187.