Gas-Phase Reaction of Free Diethylsilylium Ions with Hexamethyldisiloxane

T. A. Kochina*, D. V. Vrazhnov*, E. N. Sinotova*, and I. S. Ignat'ev**

* Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia ** St. Petersburg State University, St. Petersburg, Russia

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Abstract—The gas-phase reaction of diethylsilylium ions with hexamethyldisiloxane was studied by the radiochemical procedure. As in reactions with other nucleophiles, the degree of rearrangement of the diethyl-silylium ion in the reaction with hexamethyldisiloxane correlates with the condensation energy. In contrast to the reaction of Et_2SiT^+ with dibutyl ether, in the reaction with hexamethyldisiloxane the labeled substrate is formed, which is due to isomerization of the trimethylsilyl substituent giving rise to a labile hydrogen atom.

Nuclear-chemical generation and properties of silylium (silicenium) ions are the subject of our long-term studies. By the nuclear-chemical method we generated methyl- [1], ethyl- [2, 3], and phenyl-substituted [4, 5] silylium ions and studied their reactions with some n- and π -electron-donor compounds.

One of specific features of this method is the possibility of generating cations with localization of the positive charge differing from that in the most stable isomeric form. This allows the rearrangements of silylium ions to be studied simultaneously with their ion-molecule reactions. In particular, in the reactions of the diethylsilylium ion with a series of nucleophilic compounds [6–10], we observed its transformation into ethyl- and dimethylsilylium ions:

$$(C_2H_5)_2Si^+H \xrightarrow[-C_2H_4]{} (C_2H_5)Si^+H_2 \longrightarrow (CH_3)_2Si^+H.$$

In [8] we showed that the activity of nucleophilic compounds inducing this rearrangement varies in the order $Bu_2O < BuOH < C_6H_6$, determined by the lifetime of the long-lived complex, which, in turn, depends on the excitation energy of the intermediate complex and on the possibilities of its transfer.

Proceeding with studies of ion-molecule reactions of free diethylsilylium ions with nucleophilic compounds, in particular, with oxygen-containing compounds [6–8], we chose hexamethyldisiloxane as substrate. The labeled products of the reaction of diethylsilylium ions $(C_2H_5)_2Si^+T$ with hexamethyldisiloxane in the gas phase are listed below.

These results show that the major products of the reaction of diethylsilylium ions with hexamethyldi-

Relative yield, %
21 ± 3
17 ± 2
34 ± 3
12 ± 2
7 ± 1
9 ± 1

siloxane are various disiloxanes. Their total yield is 91%. As in reactions with other nucleophiles [6–10], the diethylsilyl group is present in the reaction products not only in the initial form but also in rearranged forms. Taking into account the substrate structure, we can assume that, as in the reactions of carbenium and silylium ions with organic ethers, this reaction occurs via formation of an intermediate oxonium complex arising from interaction of the vacant p orbital of the cation with the lone electron pair of the oxygen atom.

$$(C_{2}H_{5})_{2}Si^{+}T + (CH_{3})_{3}SiOSi(CH_{3})_{3}$$

$$\longrightarrow \begin{bmatrix} (CH_{3})_{3}SiOSi(CH_{3})_{3} \\ (C_{2}H_{5})_{2}SiT \end{bmatrix}$$

The exothermic effect of the condensation in the model system SiH_3^+ -(SiH_3)₂O, according to our B3LYP/6-31G* estimates, is 65.0 kcal mol⁻¹. The silylium ion itself, generated nuclear-chemically, appears in a vibrationally excited state [11]; the excitation energy of the diethylsilylium ion, calculated by the same method, is 21.6 kcal mol⁻¹. The lifetime of the ion– molecule complex is sufficiently long (~10⁻⁹ s in the gas phase) for the excitation energy to be redistri-

buted over all the possible degrees of freedom in this complex, including the rearrangement of structural units, i.e., isomerization.

It is interesting that the products of the reaction of diethylsilylium ions with hexamethyldisiloxane contain the labeled substrate; furthermore, it is present not only in the initial but also in the isomerized chemical form (total yield 19%).

According to our previous study, the reaction of diethylsilylium ions with dibutyl ether [8] yields no labeled substrate, in contrast, e.g., to the reactions with alcohols [6, 7], apparently because of the absence of labile hydrogen atoms in the ether. Hexamethyldisiloxane, being an organosilicon ether, contains no labile hydrogen atoms either; therefore, at first glance, formation of the labeled substrate in this case is as improbable as with dibutyl ether.

To understand why we did detect labeled substrate with hexamethyldisiloxane, let us consider the calculation results for model oxonium complexes formed by association of the methyl cation with dimethyl ether and siloxane [12]. According to these calculations, the ether methyl group in the complex $(CH_3)_3O^+$ retains the tetrahedral structure, whereas the silyl group in the complex $CH_3(SiH_3)_2O^+$ is virtually planar as in the cation. This allows the silvl group in the intermediate oxonium complex to be considered as a cation. Apparently, the trimethylsilyl substituent in hexamethyldisiloxane and oxonium complex is sufficiently ionic to isomerize into (C₂H₅)(CH₃)SiH provided that its energy is sufficient. We observed such processes in the reaction of methyl cation CH_3^+ with hexamethyldisilazane [13]. The possible isomerization of the $(CH_3)_3Si^+$ ion into the $(CH_3)(C_2H_5)SiH^+$ ion containing a labile hydrogen atom at the silicon atom makes possible the isotope exchange between the hydrogen atom of the methylethylsilyl substituent in the substrate and the tritium atom of the diethylsilylium ion, with the formation of the labeled substrate.

Thus, although hexamethyldisiloxane, like dibutyl ether, contains no labile hydrogen atoms, such an atom appears upon isomerization of the trimethylsilyl group.

It should be noted that, in the case of hexamethyldisiloxane, isomerization occurs to a much greater extent (~70%) than in the case of dibutyl ether (10%) [8]. This is due, on the one hand, to different condensation energies: 72.7 kcal mol⁻¹ with dibutyl ether [8] and 65.0 kcal mol⁻¹ with hexamethyldisiloxane. On the other hand, as noted above, in the oxonium complex formed by the reaction of the diethylsilylium ion with hexamethyldisiloxane, there are more possibilities for isomerization of structural units and hence for consumption of the excitation energy. Both factors increase the lifetime of the intermediate oxonium complex with hexamethyldisiloxane, compared to dibutyl ether.

The observed correlation between the degree of rearrangement of the diethylsilylium ion and the condensation energy calculated for the model systems [8] appears to be valid for hexamethyldisiloxane also. In particular, the energy of condensation of the H_3Si^+ cation with siloxane $(H_3Si)_2O$ is intermediate between the energies of its condensation with benzene and methanol (kcal mol⁻¹):

$$C_6H_6$$
 (47.6) < $(H_3Si)_2O$ (65.0) < MeOH (69.7)
< Me₂O (72.7).

Hexamethyldisiloxane also occupies a consistent place in the series of nucleophilic compounds inducing the rearrangement of diethylsilicenium ions (in parentheses is the content of rearranged forms of the diethylsilylium ion):

Bu₂O (10%) < BuOH (38%) < (Me₃Si)₂O (72%)
<
$$C_6H_6$$
 (87%).

EXPERIMENTAL

The reaction products were analyzed radiochromatographically with a Tsvet-110 chromatograph equipped with a tritium β -radiation detector; a 3000 × 2-mm column was packed with 15% SE-30/Chezasorb N-AW. The flow rates of the carrier gas (He) and quenching gas (CH₄/Ar) were 15 and 10 ml min⁻¹, respectively. The column temperature was 80°C. The labeled reaction products were identified by comparing their retention times with those of reference substances under identical chromatographic conditions. The relative yield of the detected labeled products was determined as the ratio of the activity of a given compound to the total activity of all the detected products. Free diethylsilylium ions were generated nuclearchemically [14]:

$$(C_2H_5)_2SiT_2 \xrightarrow{\beta^-} (C_2H_5)_2TSi^+ + He.$$

The procedure for preparing diethylsilane doubly labeled with tritium was described in [3]. 1,1,1-Trimethyl-3-ethyl, 1,1,1,3,3-pentamethyl-, 1,1-diethyl-3,3,3-trimethyl, 1,3,3,3-tetramethyl-1-ethyl-, and hexamethyldisiloxane used as references were prepared by cohydrolysis of appropriate chlorosilanes in the presence of NaOH [15].

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Gas-phase reactions of diethylsilylium ions with hexamethyldisiloxane were studied in ~20-ml molybdenum glass ampules. Prior to filling, the ampules were degassed with heating and evacuated. The diethylsilane activity in each ampule was 0.001 Ci, and the hexamethyldisiloxane vapor pressure, 10 mm Hg.

The products were accumulated at room temperature in the dark for 2 months.

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