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Gas-Phase Ion-Molecular Reactions of Free Ethylsilylium Ions with Ethylene

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Abstract — Gas-phase reaction of ethylsilylium ions with ethylene was studied by the radiochemical method. The reaction occurs via excited adduct $C_4H_{11}Si^+$ which structurally is a complex of ethylsilylium cation with ethylene. The lifetime of this complex is long enough for the isotope exchange between tritium atoms of the cation and a proton of ethylene, as well as the isomerization of ethylsilylium cation to dimethylsilylium to occur. Decomposition of the complex results in predominant formation of labeled ethylene.

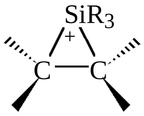
Earlier we performed a radiochemical study of ion-molecular reactions of ethylsilylium cations with representatives of various classes of compounds (alcohols, benzene, silylamine) [1–3]. These studies showed that the reactions involve a highly excited ion-neutral complex in which isotope-exchange and isomerization reactions occur.

To extend the range of objects studied, we turned to ethylene as the simplest unsaturated compound. The choice of this compound was additionally motivated by the expectation to observe in the reaction of ethylsilylium cation with ethylene the so-called β-effect, one of the most remarkable phenomena in organosilicon chemistry. As known, this effect consists in strong stabilization of carbenium ions by silyl substituents β to the carbenoid center [4–12]. It will be remembered that α-silyl substituents strongly destabilize carbenium ions [6, 9, 10]. These problems attract much researcher's attention, since silyl-substituted carbenium ions are common reaction intermediates in organosilicon chemistry.

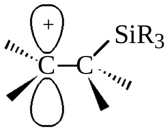
The α and β effects have first been revealed in condensed phase by increased or decreased rate constants of organosilicon compounds compared with their hydrocarbon analogs [4–7]. But the strongest evidence for these effects has been obtained in quantum-chemical studies on α- and β-silyl-substituted carbenium ions, as well as by mass spectrometry. Apeloig *et al.* [9] in their study on rearrangements of isomeric $C_5H_{13}Si^+$ cations showed that an α-silyl-substituted carbenium ion fully isomerizes into a silylium cation (80%) and a β-substituted carbenium ion (20%). Hajdasz and Scuires [10] found that protonation of trimethylvinylsilane [reaction (1)] results in exclusive formation of β-silyl-substituted carbenium ions, even though α-silyl-substituted carbenium ions are also formally not improbable to form.

$$Me_3SiCH{=}CH_2 + BH^+ \longrightarrow Me_3Si(CH_2CH_2)^+ + B, \quad (1)$$
$$BH^+ = C_2H_5^+,\ H_3O^+,\ Me_3C^+.$$

The high stability of β-silyl-substituted carbenium ions (and, consequently, their preferred formation) can be explained by delocalization of the positive charge on the carbenoid center due to p–σ_{CSi} hyperconjugation. This brings up the question of the structure of the β-silyl-substituted carbenium ion. It can have either a cyclic (bridged) structure **I**, where silicon makes use of its ability to extend coordination, or an acyclic structure **II** [9–11].



I



II

To decide between these structures is very difficult. It, however, should be noted that the β effect is the stronger the stroger is p-σ_{CSi} hyperconjugation. The latter effect is a maximum when the vacant 2*p* orbital of the carbenoid atom and the bonding σ_{CSi} orbital are coplanar. The enthalpy of association of Me_3Si^+ with ethylene is –23.6 kcal/mol [13], which corresponds to the estimate in [9] for the enthalpy of formation of the bridged form of the β-silyl-substituted carbenium ion. According to [9, 14], bridged $H_3Si(CH_2CH_2)^+$ and $Me_3Si(CH_2CH_2)^+$ cations are lower on the potential energy surface than their open-

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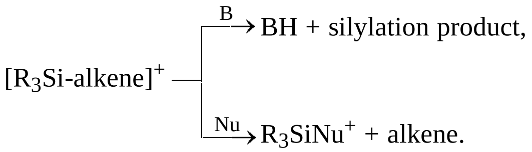
acyclic isomers. By contrast, the calculations in [15] for $[H_3SiCH_2CHCH_3]^+$ resulted in a 4 kcal/mol preference of the acyclic form over bridged.

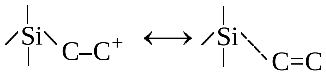
Chiavarino *et al.* [13] showed that ion-molecular reactions of R_3Si^+ ions generated by γ-radiolysis [16] with various alkenes yield a fairly stable adduct $[R_3Si–alkene]^+$ which decomposes only in the presence of strong bases (Et_3N, etc.) or oxygen-containing nucleophiles (H_2O, MeOH, etc.). In the fist case, silylation products are formed, while in the second, the starting alkene.



(2)

The retention of stereochemistry in the reactions of R_3Si^+ ions with *cis*- and *trans*-2-butenes is more likely to agrue in favor of a cyclic rather than an acyclic adduct.

As seen, the evidence in hand is insufficient to between the cyclic or acyclic structure of the β-silyl-substituted carbenium ion (adduct). It, however, can be suggested that the list of possible structures is not exhausted by the two mentioned ones. According to data in [8, 11, 12], σ–π conjugation can give rise to a structure where silylium cation is conjugated with multiple bond.



Turning to a radiochemical study of the gas-phase reaction of ethylsilylium cation with ethylene, we set ourselves the task to find out how alkenes would react with a monosubstituted silylium cation. We also intended to establish the structure of the resulting adduct and its fate in the absence of any additive (Lewis acids, oxygen-containing nucleophiles). The results of the radiochromatographic analysis of the reaction products of ethylsilylium cation with ethylene are listed in the table.

Relative yields of tritiated products of the gas-phase reaction of the ethylsilylium ions $(C_2H_5)Si^+T_2$ with ethylene

Tritiated product	Relative yield, %
Ethylene	74 ± 4
$(CH_3)_2SiCH=CH_2$	10 ± 1
$(CH_3)_2SiH_2$	2 ± 0.5
$(C_2H_5)(CH_3)SiH_2$	2 ± 0.5
$(CH_3)_2C_2H_5SiH$	6 ± 1
$(C_2H_5)_2SiH_2$	6 ± 1

As seen from the table, the major products of the ion-molecular reaction of ethylsilylium cation with ethylene are labeled ethylene (74%) and dimethylvinylsilane (10%). In terms of the commonly accepted mechanism of ion-molecular reactions [17–19], the reaction can be described as follows. The ion approaches ethylene molecule to form a rather excited ion-neutral complex [18, 19]. The heat effect of the condesation is, according to our estimates [20], –34.2 kcal/mol. The ethylsilylium ion, too, possess a certain excitation energy which it acquires upon the relaxation of the parent tetrahedral structure into planar [21] and which can be contributed in the energy of the complex. According to estimates in [22], this contrubution is at least 24 kcal/mol. Thus, the total excitation energy of the adduct in the reaction of ethylsilylium ion and ethylene is no less than 60 kcal/mol.

Our previous quantum-chemical calculations [20] showed that the complex $C_2H_5SiH_2^+ \cdot C_2H_4$ resides in a local minimum on the potential energy surface of the system $C_4H_{11}Si^+$. This minimum is higher by 28.6 kcal/mol of the global minimum correspoding to $(CH_3)_2C_2H_5Si^+$ and by 8.3 kcal/mol of the local minimum corresponding to diethylsilylium cation. The low barrier between the complex $C_2H_5SiH_2^+ \cdot C_2H_4$ and the ion $(C_2H_5)_2SiH^+$ (7.8 kcal/mol) allows the complex, even if its energy in not very high, to pass into the complex and back. This, in turn, makes possible T/H exchange between $(C_2H_5)Si^+T_2$ and ethylene. The H/D exchange in the reaction of ethylsilylium ion and ethylene-d_4 has been reported [23–25]. Therewith, the exchange involves all the seven hydrogen atoms of ethylsilylium cation, unlike dimethylsilylium, where the exchange involves only one hydrogen atom. In the reaction of Me_3Si^+ and C_2D_4 no isotope exchange has been observed at all [10]. These results allowed a possible mechanism of the exchange to be proposed and reasons for the dirrefent behavior of the cations to be revealed.

The excitation energy (~60 kcal/mol) and the sufficiently long lifetime ($\sim 10^{-9}$ at a substrate vapor pressure of 10 mm [26]) of the complex allow the ethylsilylium cation to isomerize into the thermodynamically more stable dimethylsilylium cation. It is known [27] that ethylsilylium cation activated by alternating magnetic field almost completely (by 90%) isomerizes into dimethylsilylium, and the barrier to the isomerization is ~51 kcal/mol. The potential energy surface of the system $C_4H_{11}Si^+$ [20] shows a local minimum corresponding to the complex $(CH_3)_2 \cdot$

$SiH^+ \cdot C_2H_4$, which is even lower that the local minimum of diethylsilylium cation. In essence, the complex $(CH_3)_2SiH^+ \cdot C_2H_4$ is the second most stable isomer of the system $C_4H_{11}Si^+$. It should also be noted that no minimum for the acyclic adduct $C_2H_5SiH_2CH_2CH_2^+$ could be found [20]. The above evidence suggests that the adduct $C_4H_{11}Si^+$ is most likely a complex between ethylsilylium cation and ethylene, which, if has enough energy, can transform into the complex $(CH_3)_2SiH^+ \cdot C_2H_4$, rather than into an acyclic β-silyl-substituted carbenium ion.

The adduct can decompose either unimolecularly to give ethylene and ethylsilylium cation (probably, already isomerized) or bimolecularly with transfer on ethylene molecules of protons present in excess in the reaction mixture (note that in accordance with the experimental conditions no strong bases and oxygen-containing nucleophiles were added).

We failed to estimate the enthalpy of proton transfer from the adduct $SiC_4H_{11}^+$ to ethylene because of the lack of published proton affinity data for $EtH_2 \cdot SiCH{=}CH_2$ and $Me_2HSiCH{=}CH_2$. With the proposed proton affinity of $Me_3SiCH{=}CH_2$ (199 kcal/mol) [10], the process will most likely be endothermic (the proton affinity of C_2H_4 is 162.6 kcal/mol [28]). However, presumably, at least part of the adduct $SiC_4H_{11}^+$ will have an energy sufficient for proton transfer to ethylene molecules. The formation of dimethylvinylsilane (10%) testifies that this is indeed the case.

The reaction products also include alkyl-substitued silanes which may be formed by reaction of ethylsilylium ion or its isomer with a source of protons (ethylsilane) via abstraction from the latter of hydride, methyde, or ethyde ions [1, 2, 3]. It, however, not inconceivable that the silanes $(CH_3)_2C_2H_5SiH$ and $(C_2H_5)_2SiH_2$ result from reaction with the ion source of such cations as $(CH_3)_2C_2H_5Si^+$ or $(C_2H_5)_2SiH^+$, which are isomers of the adduct $C_4H_{11}Si^+$.

EXPERIMENTAL

The reaction products were analyzed by radiation chromatography on a Tsvet-500 chromatograph with a tritium β-radiation detector. Labeled products were identified by retention time. The columns, 6 × 0.003 m, were packed with 6% of Vaseline oil on a TZK diatomite. The rate of carrier gas (helium) was 12 ml/min, and the rate of quenching gas (pentane at 50°C) was 1 ml/min.

The yield of a product was determined as a ratio of its activity to the total activity of all detected products.

Free ethylsilylium ions were obtained nuclear-chemically [29].

$$(C_2H_5)SiT_3 \xrightarrow{\beta^-} (C_2H_5)SiT_2^+ + He^0.$$

The procedure for synthesis of $[^3H_3]$ethylsilane has been described in [30]. Dimethylvinylsilane was synthesized by the Grignard reaction between methyl iodide and dichloromethylvinylsilane, followed by reduction of the resulting chlorodimethylvinylsilane with lithium hydride in dioxane [31].

The alkyl-substituted silanes $(C_2H_5)(CH_3)SiH_2$ and $(C_2H_5)(CH_3)_2SiH$ were prepared by the Grignard reactions between the corresponding alkyl halides and chlorosilanes, followed by reduction of the resulting chlorosilanes with lithium hydride, and the silanes $(CH_3)_2SiH_2$ and $(C_2H_5)_2SiH_2$, by reduction of chlorodimethyl- and chlorodiethylsilanes with lithium hydride in dioxane.

Gas-phase reactions of ethylsilylium ions with ethylene were studied using 20-ml molybdate ampules degassed by heating and pumping before use. The activity of ethylsilane in ampule was 0.001 Ci, and the pressure of ethylene, 10 mm. The products were accumulated in the dark at room temperature for 4 months.

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