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Radiochemical study of the reaction between the diethylsilylium cation and benzene in gas and liquid phases: experimental and theoretical evidence for rearrangements of the diethylsilylium cation

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Abstract

The ion–molecule reaction between the nucleogenic diethylsilylium cation generated by the β-decay of the tritiated diethylsilane and benzene was studied by the radiochromatographic method in the gas and liquid phases. Diethylphenylsilane possessing the diethylsilyl group of the nascent cation has the lowest yield in the gas phase, although in the liquid phase the yield increases. Two other silylphenylsilanes are products of rearrangement of the diethylsilylium cation. The stationary points on the potential energy surface of the $SiC_4H_{11}^+$ system were located by the ab initio correlated methods and the plausible rearrangements within this system are discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Diethylsilylium cation; Radiochemical; Rearrangements

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1. Introduction

The trivalent organosilicon cation species, i.e. silylium (silyl, silicenium, silylenium), have been objects of experimental and theoretical studies for more than 50 years [1–17]. Silylium ions are the isoelectronic analogs of carbocations, but in condensed phases, elusiveness of silyl cations stands in remarkable contrast to the behavior of carbocations [11–14]. All reactions and techniques successfully used for generation and isolation of stable carbenium ions failed to produce stable silylium cations in condensed phase [10]. Only in a recent work have Lambert and Zhao [17] succeeded in the search for the free silylium cations by using bulky (mesityl) substituents.

The main difference between silicon and carbon in their compounds is the tendency of silicon to react with nucleophiles of any kind with expansion of its coordination sphere [12–16]. The decay technique for generation of cations [18,19] seems to be a suitable tool for the comparative study of the silylium cation reactivity in gas and condensed phases, since the nucleogenic ionic species are generated without the counterion: the β-particle, which balances the cation charge, has significant kinetic energy and moves far away from the decay ions by the time of nuclear motions. For this reason, even in condensed phase, the decay cation is initially unsolvated (more precisely, it is in the same solvation state as its neutral precursor) and in many cases may react before the solvent shell has time to assemble. These studies may shed some light on the reasons for the elusiveness of free silylium cations for detection in the condensed phase.

Formation of silylated adducts from the exothermic reaction

$$Me_3Si^+ + PhH \rightarrow PhHSiMe_3^+ \qquad (1)$$

was detected in mass-spectrometry studies carried out at 3–5 torr [20,21]. However the character of bonding in the adduct of silylium cations with arenes was a point for discussion. First it was proposed that this adduct is a π- rather than a σ-complex [20,21]. However the ab initio study of the silyl cation–arene com-

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plexes shows that R_3Si–arene$^+$ species were σ-complexes with a sufficiently strong Si–C σ-bond [7]. The recent experimental studies [22,23] also indicate the formation of a σ-complex as an adduct of the reaction between silylium cations and arenes.

One of the advantages of the radiochromatographic method for the study of ion–molecule reactions is the possibility to detect the presence of the different isomers among the observed products [24–26]. The ability of the silylium cations to undergo isomerization is well known [27–32] and thus the radiochemical study of reactions between silylium cations and benzene may give new information about the mechanism of this reaction.

In this work we report the generation of the Et_2SiH^+ cation from tritiated diethylsilane and radiochromatographic characterisation of the products of its reaction with benzene in both the gas and liquid phase. Since knowledge of the potential energy surface (PES) for the $SiC_4H_{11}^+$ cation is essential for the interpretation of the experimental data and since this system was not theoretically studied before, we also report the results of the scanning of the PES for the $SiC_4H_{11}^+$ system by ab initio methods.

2. Experimental and theoretical methods

The tritiated Et_2SiH^+ cations were generated by β-decay of tritium atoms in the tritiated diethylsilane:

$$(C_2H_5)_2SiT_2 \xrightarrow{\beta^-} (C_2H_5)_2SiT^+ + He \qquad (2)$$

Reactions of labelled diethylsilylium cations with substrate yield radioactive products conveniently analyzed by the radiochromatographic technique [19,24–26]. The tritiated diethylsilane was prepared and purified according to techniques described earlier [33]. Commercial benzene was distilled and its purity was analyzed by gas chromatography. The reaction mixtures for the liquid phase study were prepared by introducing 1 mCi (0.005 ml) of tritiated diethylsilane, diluted by cyclohexane to a specific activity of 5 Ci mol^{-1}, and 0.1 ml of benzene into vessels of spherical form with capillars. These vessels were sealed in such a way that the gas phase over the liquid phase was minimal.

For the gas-phase study the reaction mixtures were prepared by introducing 1 mCi of tritiated diethylsilane, diluted by cyclohexane to a specific activity of 5 Ci mol^{-1}, and benzene at a pressure of 60 Torr into the evacuated and carefully outgased 20 ml Pyrex vessels. The mixtures (liquid and gas) were stored in the dark at room temperature for 4–6 months. After the storage period, the ampules were opened and their contents was analyzed using the 'Tsvet'- gas chromatograph equipped with a running proportional counter. The tritiated products of the reactions were identified by comparing retention times with those of authentic reference compounds under identical chromatographic conditions. A 3 m long column (2 mm in diameter) packed with 15% SE-30 on Chezasorb N-AW was used.

The relative yields of the products were determined as the ratio of the activity of each product to the combined activity of all products identified.

In addition to the Hartree–Fock (HF) method the hybrid HF/DFT method known as B3LYP was used. This method combines the Becke's three parameter exchange function [34] with the LYP correlation function [35]. The B3LYP method was found to be very reliable in predictions of the reaction energies [36] and it is computationally much less expensive than other correlated methods. The B3LYP method was used as realized in the GAUSSIAN 94 program [37]. The basis sets employed were the standard 6-31G* and 6-31G** sets. For each stationary point found the vibrational frequencies were calculated.

3. Results and discussion

The observed tritiated products of the reaction and their relative yields are presented in Table 1. The most abundant product in both phases appeared to be the tritiated triethylsilane. It is obviously the product of the reaction between the silylium cations (generated by decay of the tritium atom in diethylsilane) and the diethylsilane molecules.

$$Et_2TSi^+ + Et_2SiT_2 \rightarrow Et_3SiT + EtT_2Si^+ \qquad (3)$$

It is well known that the silylium cations rapidly react with alkanes and silanes with the withdrawal of alkyl groups from the neutral molecules [13].

Three other observed tritiated compounds are produced by the reaction between silylium cations and benzene. These are products of the dissociation of the silylium cation–benzene adducts. However, only one of these labelled products, i.e. $PhEt_2SiH$, may be ascribed to the dissociation of the adduct of the originally generated diethylsilylium cation and benzene. To ratio-

Table 1
The relative yields for the tritiated neutral products of the reaction $Et_2SiT^+ + C_6H_6$

Tritiated products	Gas (%)	Liquid (%)
Et_3SiH	49.0 ± 4.0	57.3 ± 10.8
$PhMe_2SiH$	26.0 ± 13.0	9.6 ± 0.8
$PhEtSiH_2$	15.2 ± 11.0	17.3 ± 0.2
$PhEt_2SiH$	6.3 ± 1.0	13.5 ± 0.1
$EtSiH_3$	1.9 ± 0.3	–
C_6H_6	0.9 ± 0.1	2.3 ± 0.1
Et_2MeSiH	0.770.1	–

Table 2
Total energies, ΔH (0 K, 298 K) of the most stable isomer (a.u.) and relative thermochemical parameters (kcal mol^{-1}) of other stationary points at the $SiC_4H_{11}^+$ PES

Stationary points	SCF		B3LYP		
	3-21G	6-31G*	6-31G**		
	ΔE_e	ΔE_e	ΔE_e	ΔH_0	ΔH_{298}
$(C_2H_5)(CH_3)_2Si^+$ **1**	−444.19500	−446.56103	−448.31325	0.17483	0.16475
$(CH_3)_2HSi^+ \cdot C_2H_4$ **5**	20.3	13.7	14.1	13.4	13.1
$(CH_3)_2HSi^+ \cdot C_3H_6$ **5p**	27.2	15.2	17.0	15.4	15.0
$(n\text{-}C_3H_7)(CH_3)HSi^+$ **3n**	21.9	16.1	18.4	18.5	18.1
$(i\text{-}C_3H_7)(CH_3)HSi^+$ **3i**	22.3	18.0	19.4	19.2	18.9
$(C_2H_5)HSi^+$ **2**	23.6	18.1	20.6	20.6	20.3
$(C_2H_5)HSi^+ \cdot C_2H_4$ **5e**	40.0	27.7	29.9	29.1	28.6
TS1	38.6	28.4	22.7	21.8	20.8
TSp	97.3	89.9	65.9	63.8	62.4
TS1e	102.7	94.7	71.6	69.4	68.5
TS2	57.8	42.5	38.8	37.5	36.4
TS3	46.5	31.2	28.0	26.3	25.1
$(CH_3)_2HSi^+ + C_2H_4$	46.8	37.2	44.4	40.2	40.7
$(C_2H_5)H_2Si^+ + C_2H_4$	71.6	60.7	67.1	62.9	63.2
$(CH_3)H_2Si^+ + C_3H_6$	69.6	57.2	63.8	59.2	59.4

nalize the appearance of the two other products with a lower number of carbon atoms in the silylium moiety than that in the nascent silylium cation we shall first discuss the results of the theoretical prediction of the stationary points on the potential energy surface of the $SiC_4H_{11}^+$ system.

As in $SiC_2H_7^+$ and $SiC_3H_9^+$ systems [30–32] the lowest-energy isomer is the one which has the maximum number of the alkyl groups attached to silicon. In our case it is the dimethylethylsilylium cation **1** (Table 2, Fig. 1). But in contrast to previously studied systems the second most stable isomer in $SiC_4H_{11}^+$ appears not to be the secondary cation, but rather a complex between the dimethylsilylium cation and ethene (**5**). It is followed by the other complex between the methylsilylium cation and propene (**5b**). Such complexes were found to have low energies in previously studied systems [30,31], but only in $SiC_4H_{11}^+$ are they thermodynamically more stable than the secondary cations. Among the three plausible secondary cations, the lowest are *n*- and *i*-propylmethylsilylium cations (**3n**, **3i**) and the diethylsilylium cation (**2**). The latter is the cation generated in our experiment by the decay of tritium atoms in $(C_2H_5)_2SiT_2$. It is the least thermodynamically stable of the group of low-lying isomers in the $SiC_4H_{11}^+$ system.

The diethylsilylium cation becomes vibrationally excited at the time of its generation (the excess energy is due to the fact that the nascent ion has the geometry of its precursor [19]) and additional energy may be acquired through association with the benzene molecule. There are no theoretical estimates for the system discussed but theoretical predictions for the energy of the geometric relaxation [38] and association energy for more simple systems [7] allow an estimation for the contribution of each factor of about 5 kcal mol^{-1}. Thus, one may expect that the diethylsilylium cation (**2**) has enough excess energy to rearrange to the most stable dimethylethylsilylium form **1**.

However, tritiated dimethylethylphenylsilane was not observed in the experiment. The reasons for this may be elucidated by analyzing the predicted barrier heights for the isomerization paths in the $SiC_4H_{11}^+$ system. As in the previously studied systems with two and three carbon atoms [30,31], the rearrangement of the most stable isomer **1** into **2** goes through the synchronous transfer of two hydrogens from adjacent methyl groups to the silicon atom (Fig. 1). The corresponding transition state (**TS1e**) is about twice as high in energy as those (**TS1**, **TS2**) which involve the shift of only one hydrogen [39]. The critical parameter for the occurrence of the isomer interconversion is the relative height of this barrier and the dissociation limits (with the ethene elimination). In the $SiC_2H_7^+$ system the barrier is below the dissociation limit and the interconversion of isomers may proceed without dissociation [30]. In the $SiC_3H_9^+$ [31] and $SiC_4H_{11}^+$ systems this barrier is above the dissociation limit and cations dissociate before isomerization to the most stable isomer (Fig. 2). Thus, the diethylsilylium cation (**2**) cannot rearrange to the most stable dimethylethylsilylium form **1**, but rather dissociates into $EtH_2Si^+ + C_2H_4$. However, since the highest barrier for isomerization in the SiC_2H^+ system is below the dissociation limit, the $EtH_2Si_7^+$ ion can isomerize into the most stable form, i.e. Me_2HSi^+, provided the ion has a sufficient excess energy.

The experimentally observed products are in keeping with this interpretation. In the gas phase the most abundant product among three alkylphenylsilanes is dimethylphenylsilane. It contains the $SiHMe_2$ group, i.e. the product of the two steps of rearrangement of the original diethylsilylium cation. The first step is ethene elimination with formation of the EtH_2Si^+ cation. This cation may isomerize into the most stable form without ethene elimination provided that sufficient excess energy is saved inside the EtH_2Si group. The probability of quenching of this excess vibrational energy in the liquid phase is greater than in the gas phase and therefore one may expect a decrease in the yield of this product in the liquid phase. Indeed the yield of dimethylphenylsilane drops substantially in going from the gas to liquid phase (Table 1). In contrast to

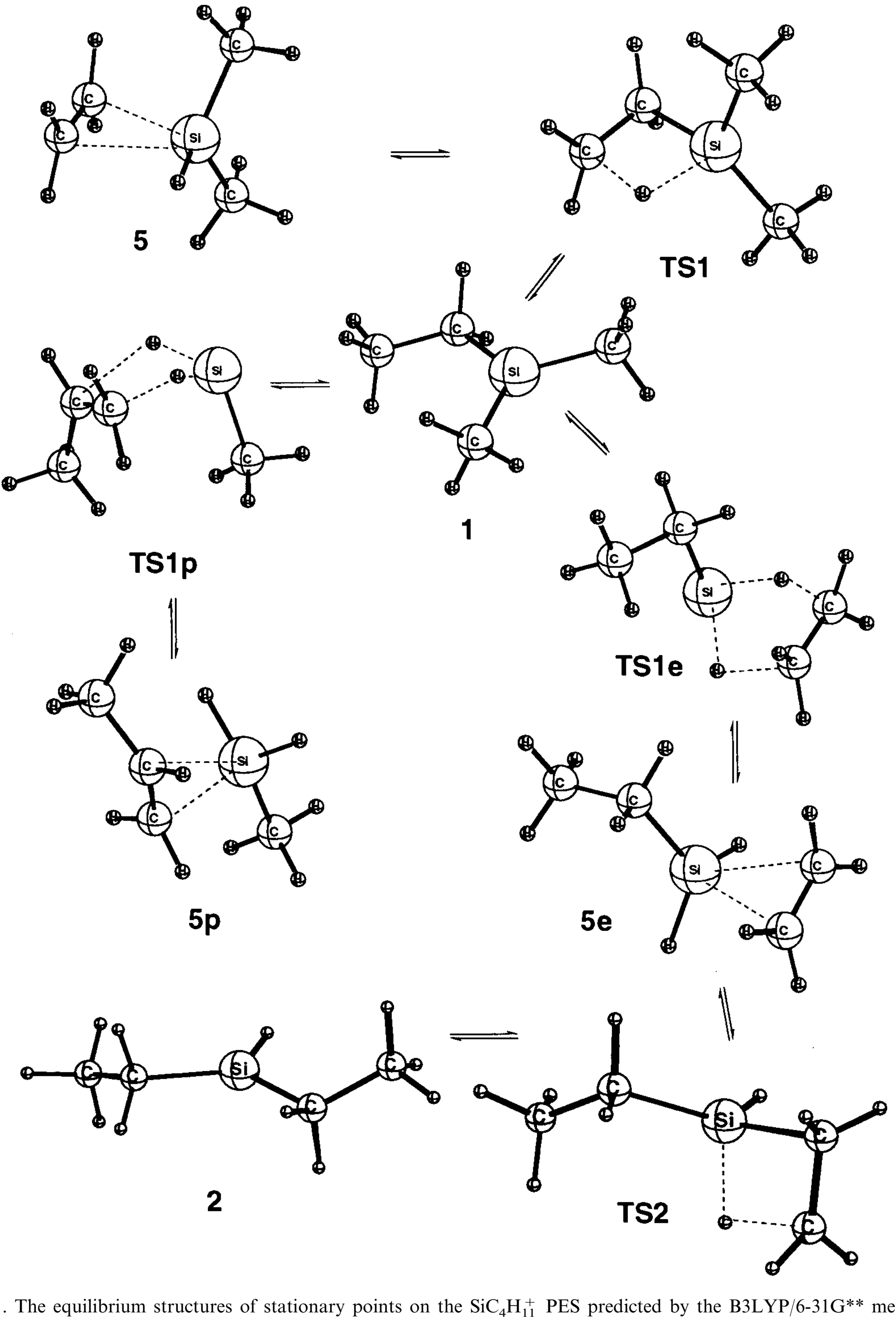

Fig. 1. The equilibrium structures of stationary points on the $SiC_4H_{11}^+$ PES predicted by the B3LYP/6-31G** method.

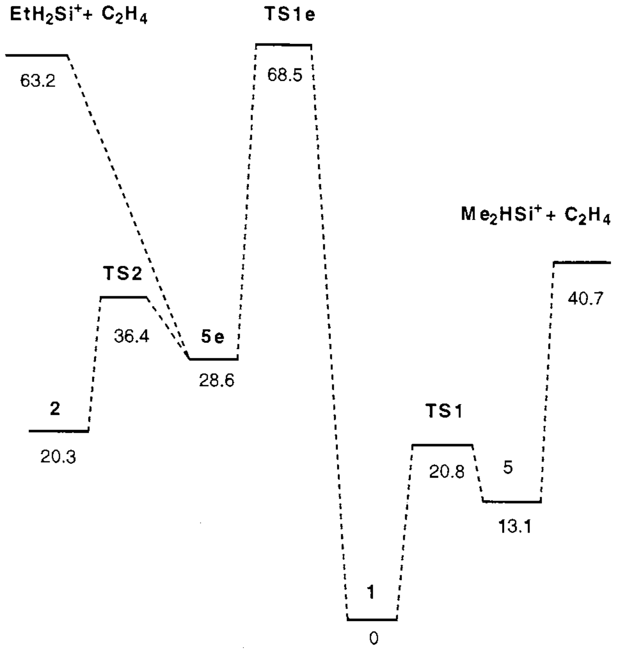

Fig. 2. The scheme of energy levels (kcal mol^{-1}) for the $\mathrm{SiC_4H_{11}^+}$ isomer interconversion.

dimethylphenylsilane, the yield of diethylphenylsilane with the unisomerized group $\mathrm{SiHEt_2}$ grows proportionally. The yield of the third product which contains the $\mathrm{SiEtH_2}$ group is nearly the same in both phases. This may indicate that the dissociation of diethylsilylium ion with the loss of ethene is so fast that it cannot be quenched by collision with the solvent molecules.

The question arises whether the above transformations of the diethylsilylium cation occur before its contact with the benzene molecule. Although our experiment cannot give the direct answer, indirect evidence proposes that transformations occur in the excited complex. The concept of the ion–molecule complex [40–42] for reactions of alkyl cations and amines was used to explain not only the rearrangement of incoming ions but also the alkyl groups incorporated in the substrate molecule [43–45]. In our previous study of the reaction between the methyl cation and hexamethyldisilazane we observed isomerization of the trimethylsilyl groups of the substrate molecules and elimination of ethene from these groups [26]. All these results indicate that the constituent moieties of the excited ion–molecule complex may survive for a certain time not loosing their identities. During this lifetime these constituent moieties may isomerize into their more stable forms. In our case the diethylsilylium ion incorporated in the ion–molecule complex may not transfer the positive charge to benzene and isomerize as a free cation.

There are several products with minor yields which can be assigned to the tritiated diethylmethylsilane, ethylsilane and benzene. The tritiated diethylmethylsilane is produced obviously by the methide ion transfer from the initial diethylsilane to the diethylsilylium cation. The tritiated ethylsilane is probably the product of the reaction of the ethylsilylium cation (such a cation may be produced by the dissociation of the diethylsilylium cation or by its reaction with initial diethylsilane as it was mentioned above) with diethylsilane by hydride ion transfer. The labelled benzene is presumably formed by H/T exchange between the diethylsilylium cation and benzene in σ-complex.

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