ELSEVIER

Journal of Organometallic Chemistry 656 (2002) 258–261

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Radiochemical study of the gas phase reaction of nucleogenic diethylsilylium ions with methanol and butanol

T.A. Kochina [a], D.V. Vrazhnov [a], I.S. Ignatyev [b]

[a] *Institute for Silicate Chemistry, Russian Academy of Sciences, Odoevskogo 24, c.2, 199155 St. Petersburg, Russia*
[b] *Radiochemistry Laboratory, Department of Chemistry, St. Petersburg State University, St. Petersburg 199034, Russia*

Received 25 November 2001; accepted 8 April 2002

Abstract

The gas phase ion–molecule reactions between alcohols (methanol and *n*-butanol) and nucleogenic diethylsilylium ions generated by the β-decay of the tritiated diethylsilane were studied by the radiochromatographic method. Among the labelled neutral products of the silylation of alcohols diethylsilylalkoxysilanes exhibit the major yield. Diethyl-butoxysilane contains not only *n*-butyl groups as in the substrate (21%), but also small amounts of *s*-butyl (5%) and *t*-butyl (7%) groups. In other alkoxysilanes the diethylsilyl group of the nascent nucleogenic cation is rearranged and isomerized. Products with the similar distribution of the silylium group isomers were observed earlier in the reaction of benzene, however the yield of the products with rearranged silylium groups was substantially greater for benzene. This difference in the yield of the products with rearranged silylium groups between benzene and alcohols is rationalized taking into account the more acidic character of the proton in the adduct oxonium ions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Radiochemistry; Silylium cations; Ion–molecule; Radiochromatography

1. Introduction

Generation of free silylium ions was a subject of numerous studies but their existence in condensed phases is still a matter of discussion [1–10]. This elusiveness of silylium ions in condensed phases is usually ascribed to the extraordinarily high ability of silicon to react with nucleophiles and to expand its coordination sphere [8–10]. However, little is known about their reactions with particular nucleophiles. The tritium decay method succesfully used previously for the generation of carbocations [11] is especially suitable for the study of silylium ion reactions, since it may produce these ions both in the gas and condensed phases. Previously we reported the studies of the reaction between the diethyl-silylium ion and benzene [12]. This communication deals with the reaction of diethylsilylium ions generated by the nuclear decay technique with alcohols. To the best of our knowledge there are only two works devoted to the study of the silylium ion reactions with alcohols [13,14]. In the ICR studies of $(CH_3)_3Si^+$ interacting with ROH (R=Me, Et, *n*-Pr, *t*-Bu) it was shown that the first step is the formation of the adduct

$$(Me_3)_3Si^+ + ROH \rightarrow [Me_3SiO\,(H)R]^+ \tag{1}$$

Further transformations of the adduct may go through elimination of methane in the case of methanol and alkenes for higher alcohols [13,14]. In contrast to mass-spectrometric studies our method reveals neutral products of the reaction. The important feature of ths method is that it allows to identify different isomers which may appear in the course of the reaction due to the substantial excess energy accumulated in the encounter complex. This energy originates from the 'deformation' energy of the nucleogenic cation [11] as well as from the complexation energy. In our previous study of the reaction between the diethylsilylium cation and benzene we observed different isomers of the silylium group in the final labelled products [12]. In this communication, we report the nuclear chemical

---

* Corresponding author. Fax: +7-812-328-5401
E-mail address: igor@isi.usr.pu.ru (I.S. Ignatyev).

PII: S0022-328X(02)01625-X

study of nucleogenic diethylsilylium ions with methanol and *n*-butanol. For the latter case we may observe isomerization of both silylium ions and the alkyl group of alcohol, provided our statement that transformations of the diethylsilylium group occur not in the free cation but rather in the excited complex [12] is true.

2. Experimental

The tritiated Et_2SiT^+ ions were generated by the β-decay of tritium atoms in the tritiated diethylsilane.

$$(C_2H_5)_2SiT_2 \xrightarrow{\beta^-} [(C_2H_5)_2SiT\text{–}\,^3He]^+ \rightarrow (C_2H_5)_2SiT^+ + ^3He \qquad (2)$$

Reactions of labelled diethylsilyl ions with substrate yield radioactive products conveniently analyzed by the radiochromatographic technique [11,15–17]. The tritiated diethylsilane was prepared and purified according to techniques described earlier [17]. Commercial alcohols were distilled and their purity was analyzed by gas chromatography.

Reaction mixtures were prepared by introducing 1mCi of the tritiated diethylsilane (diluted by cyclohexane to a specific activity of 5 Ci mol^{-1}) and alcohols at a pressure of 10 Torr into the evacuated and carefully outgased Mo-glass ampoules. The mixtures were stored in the dark at room temperature for 2 months. After the storage period, the ampoules were opened and their content was analyzed using the 'Tsvet' gas chromatograph equipped with a running proportional counter. The tritiated products of reactions were identified by comparing retention times with those of authentic reference compounds under identical chromatographic condi-tions. The 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 the products identified.

The B3LYP method [18,19] as implemented in GAUSSIAN-94 program [20] was used for the quantum-chemical calculations. This method was used in our previous studies of silylium cations [12,21,22].

3. Results and discussion

Relative yields of the tritiated products of reactions of nucleogenic diethylsilylium ions are shown in the Table 1. The appearance and relative yields of the observed products may be explained by the following mechanism. The first step of the reaction is the formation of the adduct.

$$Et_2SiT^+ + ROH \rightarrow [Et_2TSiO(H)R]^+ \qquad (3)$$

The structure of the diethylsilylium ion–methanol adduct optimized at the B3LYP/6-31(d,p) theory level is depicted in the Fig. 1. It is characterized by the nearly planar SiOHC moiety with the SiO bond length of 1.872 Å. The formation of the SiO bond weakens SiC bonds; their length increases from 1.845 Å in the free cation to 1.865 Å in the adduct.

Although this equilibrium structure shows substantially strong covalent bonds of the trivalent oxygen, the real adduct has a significant amount of the excess energy. Complexation energy of the adduct estimated at the same level of theory is 49.8 kcal mol^{-1}. Moreover, the nucleogenic silylium ion may possess additional energy due to the fact that its nascent geometry is characterized by the tetrahedral arrangement of atoms around silicon (as in the neutral precursor), while the planar arrangement is inherent to the equilibrium structure of the cation [12]. Our theoretical estimate of this 'deformation' energy, calculated as the energy difference betweeen the 'wrong' tetrahedral geometry and the equilibrium one, is 21.6 kcal mol^{-1}. Due to the excess energy the adduct is vibrationally excited. According to the concept of the ion–molecule complex [23–25] the constituent moieties of this complex (in our case diethylsilylium and butyl groups) may exist in the comparatively free state of the analogous ions. During the lifetime of the excited adduct these moieties may isomerize and/or eliminate stable fragments.

In our case the diethylsilylium ion incorporated in the ion–molecule complex may isomerize into the more stable form. This behaviour of the diethylsilylium ion was observed in the study of its reaction with benzene [12]. The same is true for the butyl group of the alcohol. This vibrationally excited complex may be deactivated by the interaction with the substrate molecule. However, substrate may also deactivate the excited adduct by the proton transfer. This bimolecular reaction produces neutral alkoxysilanes.

$$[Et_2TSiO(H)R]^+ + ROH \rightarrow EtTSiOR + ROH_2^+ \qquad (4)$$

Table 1
The relative yields (%) for the tritiated neutral products of the $Et_2Si^+T + ROH$ (R=Me, *n*-Bu) reaction in the gas phase

Number	Tritiated products	R = Me	R = Bu
1	Et_2HSiOR	35	33 (n—21, s—5, t—7)
2	Et_3SiH	31	29
3	Me_2HSiOR	12	9
4	EtH_2SiOR	9	11
5	ROH	7	4
6	$(Et_2HSi)_2O$	4	9
7	C_2H_4	2	1
8	$EtSiH_3$	1	1
9	Et_2MeSiH	1	1

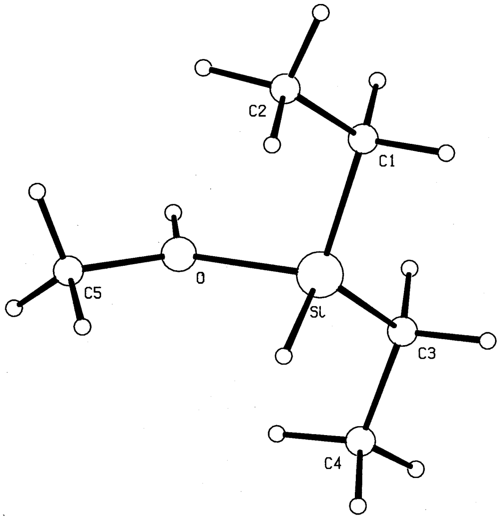

Fig. 1. The structure of the complex between diethylsilylium cation and methanol optimized at the B3LYP/6-31G(d,p) level of theory. The equilibrium geometry parameters of the heavy atom skeleton: Si–C1 = 1.865 Å, SiO = 1.872 Å, C5–O = 1.481 Å, C1–C2 = 1.542 Å, O–H = 0.971 Å, C5–O–Si = 127.9°, O–Si–C1 = 106.5°, C1–Si–C3 = 117.8°, Si–C1–C2 = 116.1°.

The proton withdrawl usually provides the major part of neutral labeled products identified in the radiochromatographic studies of the nucleogenic cation reactions.

Indeed alkoxysilanes are main products of reactions of the diethylsilylium cation with both methanol and butanol. Their relative yields are 56% for methanol and 53% for butanol (the sum of the yields of products 1,3,4 in the Table 1). The other major product is triethylsilane which originates from the reaction between nucleogenic cations and their mother molecule, i.e. diethylsilane, as described in [12].

$$Et_2TSi^+ + Et_2SiT_2 \rightarrow Et_3SiT + EtT_2Si^+ \quad (5)$$

It was also observed as a main product in our previous study of the reaction between diethylsilylium ion and benzene [12] in which it has the relative yield of 49%. In the present study we observe the reduced yield of this product (31% for methanol, 29% for butanol). This decrease may be rationalized taking into account the greater energy of the formation of the complex with alcohols and therefore the higher rate of this process which competes with the silylium ion—silane interaction. Two other products with minor yields, i.e. ethylsilane and diethylmethylsilane (8,9 in the Table 1) also originate from the interaction of diethylsilylium ions with diethylsilane. Both groups of products (alkoxysilanes and products of interaction with silane) comprise ca. 87% of the labelled products. The remaining products (with the 13% total yield) are: tritiated substrate (alcohol), ethene, and tetraethyldisiloxane.

The last product may be produced by dealkylation of the adduct with formation of silanols which immediately condense.

$$[Et_2TSiO(H)R]^+ \rightarrow Et_2TSiOH \quad (6)$$

$$2Et_2TSiOH \rightarrow (Et_2THSi)_2O + H_2O \quad (7)$$

Alkoxysilanes observed in the study have different silyl and butyl groups. In addition to the major product, i.e. diethylalkoxysilane, which possesses the unchanged diethylsilyl group corresponding to the reactant cation, two other alkoxysilanes (with the number of carbons in the silylium group diminished by two) are observed. This decrease in the carbon contents may be either due to the elimination of ethene from the diethylsilyl group of the adduct

$$[Et_2TSiO\,(H)R]^+ \rightarrow [EtTHSiO(H)R]^+ + C_2H_4 \quad (8)$$

or originate from the reactions of ethylsilylium cation produced by (5).

The presence of the tritiated ethene observed with very low yields (2% for MeOH and 1% for BuOH) may indicate that the first mechanism (8) is partly operative. However, this mechanism presupposes that the exchange between T and ethyl hydrogens in the excited complex may occur before the ethene elimination. The other observed alkoxysilane with two carbons in the silylium group is dimethylalkoxysilane. It may be produced by the rearrangement of the ethylsilylium ion incorporated in the adduct into its most stable form, i.e. the dimethylsilylium ion [21].

$$[C_2H_5HTSiO(H)R]^+ \rightarrow [(CH_3)_2TSiO\,(H)R]^+ \quad (9)$$

This process in the free $SiC_2\,H_7^+$ system is 22.7 kcal mol^{-1} exothermic and has a barrier of 42.8 kcal mol^{-1} as shown by B3LYP/6-31(d,p) calculations [21]. This barrier height may be easily overcome by the excess complexation energy.

Comparing the present results with those obtained in our previous study of benzene reactions one may notice that the similar products of the decay of the excited adduct were observed in both studies, that are Et_2HSiX, EtH_2SiX, and Me_2SiHX (X = Ph, OR). However, their relative yields are different. While in the diethylsilylium ion-benzene system [12] the product with the unchanged diethylsilylium group, i.e. Et_2HSiX, had the lowest yield among those three compounds (6%), in the diethylsilylium ion-alcohol systems the yield of this product is the highest one (35%). Correspondingly, the yields of compounds with rearranged silylium groups for MeOH (9 and 12%) and BuOH (11 and 9%) are substantially lower than those for benzene (15 and 26%). Note that no products of isomerization of Et_2HSi^+ into the most stable form, i.e. $EtMe_2Si^+$ were observed in both cases. This is in accord with our theoretical predictions that the $EtH_2Si^+ + C_2H_4$ dissociation level in this system is lower than the barrier height for isomerization into $EtMe_2Si^+$ [12].

The reason of the difference in the yield of products with rearranged silylium groups between reactions with benzene and alcohol may be explained by the analysis of the chemical structure of the adducts. Benzene forms σ-bonded Wheland intermediates with silylium ions, however they are characterized by a rather weak bonding and significant contribution of a π-bonded resonant form in which the positive charge reside at silicon [8,22]. In contrast, alcohols form with silylium cations the adduct, i.e. oxonium ion, in which the positive charge is transfered to the alcohol hydrogen to a great extent. This may be confirmed by the comparison of the results of quantum chemical calculations of the complexes of SiH_3^+ with benzene and methanol at the B3LYP/6-31G(d,p) level of theory. The Mulliken charge on the proton in the benzene complex is 0.2 that differs not much from other hydrogen atoms of the cycle, while in the methanol complex the positive charge of the proton is 0.4.

The rearrangement of the constituent groups of the excited complex occurs not only in the silylium group. In the case of butanol it is also observed for butyl groups. Labelled diethyl-silylbutoxysilanes with the total yield of 33% contain not only *n*-butyl groups as in the substrate (21%), but also small amounts of *s*-butyl (5%) and *t*-butyl (7%) groups.

References

[1] B.N. Dolgov, M.G. Voronkov, S.N. Borisov, Zh. Obshch. Khim. 27 (1957) 709.

[2] R.J.P. Corriu, M. Henner, J. Organomet. Chem. 74 (1974) 1.

[3] J.B. Lambert, W.J. Schulz, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley-Interscience, New York, 1989, p. 1007.

[4] C.A. Reed, Acc. Chem. Res. 31 (1998) 325.

[5] J.B. Lambert, L. Kania, S.Z. Zhang, Chem. Rev. 95 (1995) 191.

[6] J. Belzner, Angew. Chem. Int. Ed. Engl. 36 (1997) 1277.

[7] P.D. Lickiss, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1998, p. 557.

[8] P.V.R. Schleyer, P. Buzek, T. Muller, Y. Apeloig, H.-U. Siehl, Angew. Chem. Int. Ed. Engl. 32 (1993) 1471.

[9] P.V.R. Schleyer, Science 275 (1997) 39.

[10] C. Maerker, J. Kapp, P.V.R. Schleyer, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry, VCH, Weinheim, 1996, p. 329.

[11] M. Speranza, Chem. Rev. 93 (1993) 2933.

[12] T.A. Kochina, D.V. Vrazhnov, I.S. Ignatyev, J. Organomet. Chem. 586 (1999) 241.

[13] I.A. Blair, G. Phillipow, J.H. Bowie, Aust. J. Chem. 32 (1979) 59.

[14] I.A. Blair, V. Trennrey, J.H. Bowie, J. Org. Mass. Spectrsc. 15 (1980) 15.

[15] I.S. Ignatyev, T.A. Kochina, V.D. Nefedov, E.N. Sinotova, E.O. Kalinin, Zh. Obshch. Khim. 65 (1995) 297.

[16] I.S. Ignatyev, T.A. Kochina, V.D. Nefedov, E.N. Sinotova, D.V. Vrazhnov, Zh. Obshch. Khim. 65 (1995) 304.

[17] T.A. Kochina, D.V. Vrazhnov, V.D. Nefedov, E.N. Sinotova, Zh Obshch. Khim. 68 (1998) 967.

[18] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[19] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN-94, Revision C.3, Gaussian Incorporation, Pittsburgh, PA, 1995.

[21] I.S. Ignatyev, T. Sundius, Organometallics 15 (1996) 5674.

[22] I.S. Ignatyev, T. Sundius, Organometallics 17 (1998) 2819.

[23] T.H. Morton, Tetrahedron 38 (1982) 3195.

[24] D.J. McAdoo, Mass. Spectrsc. Rev. 7 (1988) 363.

[25] P. Longevialle, Mass. Spectrsc. Rev. 11 (1992) 157.