

Radiochemical study of the reactions between the methyl cation and hexamethyldisilazane

T.A. Kochina^{*}, D.V. Vrazhnov, I.S. Ignatyev

Institute for Silicate Chemistry, Russian Academy of Sciences, Odoerskogo 24, c.2, 199155, St. Petersburg, Russian Federation

Received 1 April 1997; received in revised form 16 July 1997

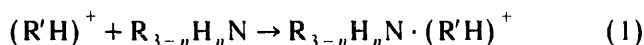
Abstract

The gas-phase ion–molecule reactions between the nucleogenic methyl cations, generated by the β -decay of the tritiated methane, and hexamethyldisilazane were studied by the radiochromatographic method. The appearance of the observed labelled products is rationalized assuming formation of the two major types of the intermediate ion-neutral complexes, i.e., methylated and protonated disilazane. Some observed products contain silylium groups whose structure are different from those of precursors. Isomerization and the ethene expulsion of the silylium groups, which are the characteristic reactions of free silylium cations, are suggested to occur during the lifetime of the intermediate ion-neutral complexes. Triton transfer from CT_3^+ to disilazane produces tritiated methylene. Products of insertion of CT_3^+ into NH and CH bonds of substrate are also observed. © 1997 Elsevier Science S.A.

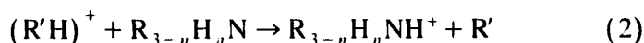
Keywords: Hexamethyldisilazane; Radiochromatographic method; Silylium groups

1. Introduction

Formation of the condensation adduct was proposed in the numerous studies of the gas-phase reactions of alkyl cations with n -bases. In the case of H_2O (a prototype O-base) this adduct can be identified as protonated alcohols and in the case of NH_3 (a N-base) as protonated amines [1–3].



(R and (R'H) are alkyl groups). However, the other channel exists for reactions of alkyl cations with ammonia and alkylamines. This channel is the transfer of proton from the alkyl cation to the amine nitrogen leading to the expulsion of the corresponding alkene (or methylene in the case of the methyl cation)



This reaction successfully competes with the above mentioned formation of the condensation adduct [2–9].

Both of these complexes, i.e., $\text{R}_{3-n}\text{H}_n\text{N} \cdot (\text{R}'\text{H})^+$ (I) and $\text{R}_{3-n}\text{H}_n\text{NH}^+$ (II) are vibrationally excited due to high exothermicity (about 100 kcal/mol) of the com-

plexation between alkyl cations and amines, although in the case of the proton transfer complex (II), a significant part of this energy is taken away by the leaving methylene or alkene R' . This excitation may cause dissociation or rearrangement of these complexes particularly of the incorporated alkyl groups. These processes are believed to go within the so-called ion-neutral complexes [10–15] in which charged and neutral fragments rotate almost freely around each other, held in the vicinity of one another by electrostatic forces. Several examples of these rearrangements were reported [16,17], although the mass spectrometry technique traditionally used for the ion–molecule reaction studies is not very suitable for determination of the isomeric forms of the alkyl groups.

The radiochemical generation of the CT_3^+ cation by β -decay of tritium in CT_4 and subsequent radiochromatographic identification of the neutral products of their reactions with substrates, was employed by the group of Prof. Nefedov for the study of wide range of ion–molecule reactions including those with amines [18–21]. This method studies the neutral products of reactions and therefore is complimentary to mass spectrometry methods which deal with charged species. One of the advantages of this method is the possibility to detect the presence of different isomers among the

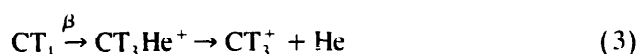
^{*} Corresponding author.

products. In our previous studies of the methyl cation—dibutylamine [20] and the methyl cation—methylbutylamine [21] systems it was shown that the butyl group of the reactant undergoes isomerization in the process of the ion–molecule reaction. This isomerization is similar to that which takes place in the free butyl cation. It was proposed that this process occurs during the lifetime of the transient condensation or the proton transfer excited complexes.

Here, we investigate the reaction of the methyl cation with hexamethyldisilazane.

2. Experimental

The tritiated methyl cations were generated by β -decay of T atoms in the tritiated methane



Reactions of the labelled methyl cations with substrate yield radioactive products, conveniently analyzed by radio chromatographic technique (for the discussion of scope and limitations of this method see the review of Speranza [22]).

The tritiated methane was prepared, purified and analyzed as described earlier [23]. The isotopic composition of the tritiated methane was found to be: 60% CT_4 , 30% CHT_3 , 7% CH_2T_2 , and 3% CH_3T . The chemical purity of the tritiated methane was 98% (T_2 1%, C_2H_6 1%). Commercial hexamethyldisilazane from Merck was distilled and its purity was checked by gas chromatography. The reaction mixtures were prepared by introducing 1 mCi of tritiated methane, diluted by xenon to a specific activity of 5 Ci/mol, and gaseous hexamethyldisilazane at pressure of 10 Torr into the evacuated and carefully outgassed Pyrex vessel. The mixtures 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 by radiochromatographic procedure with the help of the Tzvet gas chromatograph equipped with a running proportional counter. Before the radiochromatographic analysis of the products, the gaseous contents of vessels were condensed at -196°C and walls were rinsed with the suitable solvent.

The tritiated products of reactions were identified by comparing their retention times with those of authentic reference compounds under identical chromatographic conditions. The 4 m long column (2 mm in diameter) packed with 5% octadecylamine on Chromosorb P 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.

Aminosilanes used as reference compounds, i.e., $(\text{CH}_3)_3\text{SiNH}_2$ (2), $(\text{C}_2\text{H}_5)(\text{CH}_3)\text{HSiNH}_2$ (4),

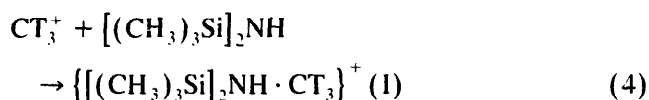
$(\text{CH}_3)_3\text{Si}(\text{CH}_3)\text{NH}$ (1), $(\text{CH}_3)_3\text{Si}(\text{C}_2\text{H}_5)\text{NH}$ (10) and $[(\text{CH}_3)_3\text{Si}]_2(\text{CH}_3)\text{N}$ (7), were prepared as it is described in Ref. [24].

Asymmetric silazanes $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)\text{H}_2$ (5) and $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{HSiNHSi}(\text{CH}_3)\text{H}_2$ (6) were prepared by coammonolysis of appropriated chlorosilanes in the same way, as described in Ref. [25].

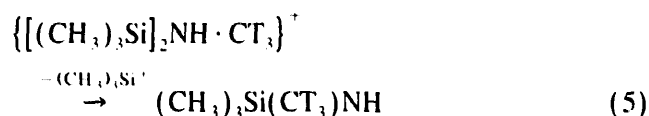
3. Results and discussion

The observed tritiated products of the reaction between CT_3^+ and $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ and their relative yields are presented in Table 1. For the rationalization of the observed products the following reaction mechanism was assumed. The analogous mechanism was earlier employed to account for the products of reactions of the methyl cations with amines [19–21].

The first stage of the reaction is the barrierless highly exothermic formation of the ion–molecule adduct



This adduct I is a non-structuralized ion-neutral complex, the fragments of which, i.e., CT_3 and $(\text{CH}_3)_3\text{Si}$ groups, almost freely rotate around the central moiety [12–14]. Any of this groups may leave the adduct. The CT_3^+ expulsion is the reverse reaction and therefore is of no interest for the discussion, but the splitting out of the $(\text{CH}_3)_3\text{Si}^+$ group may give the neutral product $(\text{CH}_3)_3\text{Si}(\text{CT}_3)\text{NH}$ (1).



Indeed, the tritiated product, the retention time of which coincides with $(\text{CH}_3)_3\text{Si}(\text{CH}_3)\text{NH}$ (1) is observed with the relative yield of 6% (1 in Table 1).

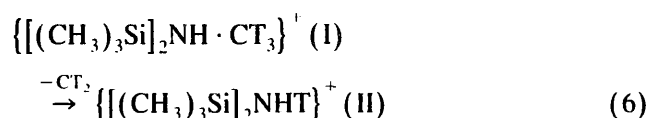
Since the proton affinity of the singlet methylene

Table 1
Observed neutral tritiated products of the reaction between CT_3^+ and $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_2$ and their relative yields (%)

| No. | Tritiated product | Relative yield |
|-----|--|----------------|
| 1 | $(\text{CH}_3)_3\text{Si}(\text{CH}_3)\text{NH}$ | 6 ± 1 |
| 2 | $(\text{CH}_3)_3\text{SiNH}_2$ | 42 ± 4 |
| 3 | $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ | 18 ± 3 |
| 4 | $(\text{C}_2\text{H}_5)(\text{CH}_3)\text{HSiNH}_2$ | 7 ± 1 |
| 5 | $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)\text{H}_2$ | 7 ± 1 |
| 6 | $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{HSiNHSi}(\text{CH}_3)\text{H}_2$ | 4 ± 1 |
| 7 | $[(\text{CH}_3)_3\text{Si}]_2(\text{CH}_3)\text{N}$ | 2 ± 1 |
| 8 | non-identified (CT_2 insertion into substrate?) | 4 ± 1 |
| 9 | non-identified (CT_2 insertion into substrate?) | 4 ± 1 |
| 10 | $(\text{CH}_3)_3\text{Si}(\text{C}_2\text{H}_5)\text{NH}$ | 4 ± 1 |
| 11 | $(\text{CH}_3)_4\text{Si}$ | 2 ± 1 |

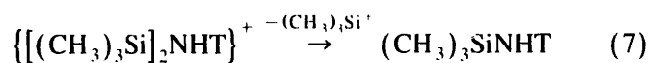
(207 kcal/mol) is less than that of amines, methyl cation may transfer a proton to bases of higher proton affinity than singlet methylene [26]. The substitution of the alkyl groups in amines by the silyl groups decreases their proton affinity only by a few kcal/mol [27], so the proton transfer reactions from the methyl cation may manifest themselves also in the case of silazanes.

Thus, the major part of the observed products may be assigned to rearrangement and dissociation of the proton transfer complex (II) which can be formed from the initial adduct (I) by the reaction



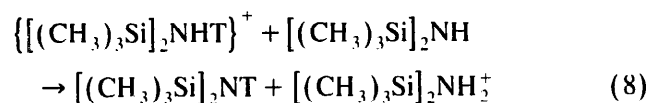
This proton transfer complex possesses some part of the vibrational excitation of the adduct I, although a part of it is carried away with the methylene molecule. Thus, II can also be regarded as a ion-neutral complex for which the comparatively free behavior of substituents is inherent.

The dissociation of the complex II with the detachment of the $(\text{CH}_3)_3\text{Si}^+$ cation may produce the tritiated trimethylsilylamine (2)



The tritiated product with the retention time of trimethylsilylamine (2) is the most abundant product of the discussed reaction (42%).

The proton transfer complex $\{[(\text{CH}_3)_3\text{Si}]_2\text{NHT}\}^+$ (II) has two highly acidic atoms (H and T) which can be taken away at encounters with the substrate molecules. The transfer of T from the complex II to the substrate hexamethyldisilazane molecules may lead to the exchange of tritium between the complex II and the substrate molecules and to the appearance of the labelled substrate.

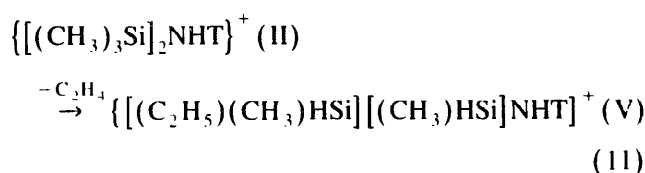
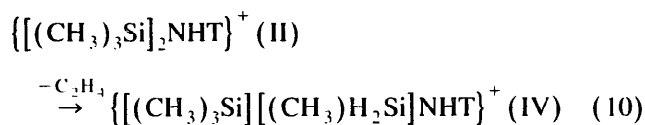
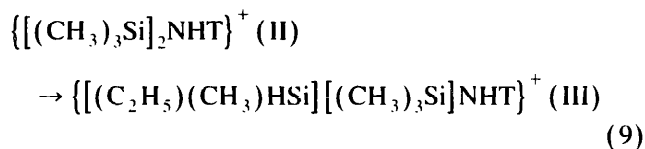


The tritiated substrate 3 has a relative yield of 18%. Products 2 and 3, which can be ascribed to those originating from the proton transfer complex II, comprise 60% of the total yield. This suggests the major role of the channel associated with formation of the proton transfer complex II (Eq. (6)).

There are several products with smaller yields which can be assigned to the products of the $(\text{CH}_3)_3\text{Si}^+$ group rearrangement within the proton transfer complex II. (4–6 in Table 1). The retention times of these products coincide with the following silylamines and disilazanes: $(\text{C}_2\text{H}_5)(\text{CH}_3)\text{HSiNH}_2$ (4), $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)\text{H}_2$ (5), and $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{HSiNHSi}(\text{CH}_3)\text{H}_2$ (6). Silyl groups

in this compounds do not correspond to those of the reactant (hexamethyldisilazane). In 4 and 6, one of $(\text{CH}_3)_3\text{Si}$ groups of the precursor is isomerized to $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{HSi}$. In 5 and 6, the other trimethylsilyl group loses ethene. These two reactions, i.e., interconversion of the $(\text{CH}_3)_3\text{Si}^+$ and $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{HSi}^+$ and loss of the ethene molecule are the most important reactions of the free SiC_3H_9^+ cation in the gas phase [28–30]. Thus, we can suggest that these transformations take place in the ion–molecule complexes I and II, in which the electronic structure of the trimethylsilyl group is close to that of the trimethylsilylium cation.

The presence of the above tritiated products 4–6 may be rationalized assuming following transformations of the complex II during its lifetime



The product 4 can be produced from the complex III by the detachment of the $(\text{CH}_3)_3\text{Si}^+$ cation (analogous to the Eq. (7)). Products 5 and 6 may originate from complexes IV and V by the bimolecular loss of proton (as in Eq. (8)).

There are three observed compounds which have retention times above that of the labelled substrate (7–9 in Table 1). Although two of them are not identified, they obviously belong to the products of the CT_2 insertion into substrate molecules. The tritiated methylene is produced in the process of the triton detachment from CT_3^+ (Eq. (6)). One of these products has retention time of $\{[(\text{CH}_3)_3\text{Si}]_2(\text{CH}_3)\text{N}\}^+$ (7). It may originate from methylene insertion into the NH bond of the substrate. Two other unidentified products (8,9 in Table 1) may be produced by methylene insertion into the CH bonds of the substrate.

There are two other products, the structure of which can hardly be explained by the proposed scheme. One product with the relative yield of 4% has a retention time which coincides with $(\text{CH}_3)_3\text{Si}(\text{C}_2\text{H}_5)\text{NH}$ (10). It is difficult to rationalize the appearance of this product by the suggested mechanism. The other is tetramethyldisilane with the 2% yield.

Acknowledgements

Authors thank the Russian Foundation for Basic Research for the support of this work (Grant No. 96-03-33254).

References

- [1] K. Hiraoka, P. Kebarle, *J. Am. Chem. Soc.* 99 (1977) 360.
- [2] M. Meot-Ner, M.M. Ross, J.E. Campana, *J. Am. Chem. Soc.* 107 (1985) 4839.
- [3] J.K. Terlouw, T. Weiske, H. Schwarz, J.L. Hoimes, *Org. Mass. Spectr.* 21 (1986) 665.
- [4] T. Su, M. Bowers, *Int. J. Mass. Spectrom. Ion Phys.* 12 (1973) 347.
- [5] T. Su, M. Bowers, *J. Am. Chem. Soc.* 95 (1973) 7611.
- [6] M. Meot-Ner, *J. Am. Chem. Soc.* 101 (1979) 2389.
- [7] M. Attina, F. Cacace, P. Giacomello, M. Speranza, *J. Am. Chem. Soc.* 102 (1980) 6896.
- [8] E.W. Redman, T.H. Morton, *J. Am. Chem. Soc.* 108 (1986) 5701.
- [9] C.R. Moylan, J.I. Brauman, *J. Am. Chem. Soc.* 107 (1985) 761.
- [10] P. Ausloos, S.G. Lias, *J. Am. Chem. Soc.* 108 (1986) 1792.
- [11] G. Laguzzi, T.H. Osterheld, J.I. Brauman, *J. Phys. Chem.* 98 (1994) 5931.
- [12] T.H. Morton, *Tetrahedron* 38 (1982) 3195.
- [13] D.J. McAdoo, *Mass Spectr. Rev.* 7 (1988) 363.
- [14] P. Longevialle, *Mass Spectr. Rev.* 11 (1992) 157.
- [15] R.W. Kondrat, T.H. Morton, *Org. Mass. Spectrom.* 26 (1991) 410.
- [16] H.E. Audier, C. Monteiro, D. Berthomieu, J. Tortajada, *Int. J. Mass. Spectr. Ion Proc.* 104 (1991) 145.
- [17] H.E. Audier, T.H. Morton, *Org. Mass Spectrom.* 28 (1993) 1218.
- [18] V.V. Leonov, V.D. Nefedov, E.N. Sinotova, V.K. Kapustin, *Radiokhimiya* 33 (1991) 70.
- [19] I.S. Ignatyev, T.A. Kochina, V.D. Nefedov, E.N. Sinotova, E.O. Kalinin, *Zh. Obshch. Khim.* 65 (1995) 297.
- [20] I.S. Ignatyev, T.A. Kochina, V.D. Nefedov, E.N. Sinotova, D.V. Vrazhnov, *Zh. Obshch. Khim.* 65 (1995) 304.
- [21] D.V. Vrazhnov, I.S. Ignatyev, E.O. Kalinin, T.A. Kochina, V.D. Nefedov, E.N. Sinotova, *Zh. Obshch. Khim.*, in press.
- [22] M. Speranza, *Chem. Rev.* 93 (1993) 2933.
- [23] E.N. Sinotova, M.V. Korsakov, V.A. Shishkunov, *Radiokhimiya* 22 (1980) 466.
- [24] R.O. Sauer, R.H. Hasek, *J. Am. Chem. Soc.* 68 (1946) 241.
- [25] Ya.D. Zhinkin, G.N. Malnova, *Zh.V. Gorislavskaja, Zh. Obshch. Khim.* 35 (1965) 907.
- [26] E. Uggerud, *J. Am. Chem. Soc.* 116 (1994) 6873.
- [27] M.L. Hendewerk, R. Frey, D.A. Dixon, *J. Phys. Chem.* 87 (1983) 2026.
- [28] K.A. Reuter, D.B. Jacobson, *Organometallics* 8 (1989) 1126.
- [29] R. Bakhtiar, C.M. Holznagel, D.B. Jacobson, *Organometallics* 12 (1993) 621.
- [30] R. Bakhtiar, C.M. Holznagel, D.B. Jacobson, *Organometallics* 12 (1993) 880.