Journal of Organometallic Chemistry, 156 (1978) 323—329

GAS PHASE NUCLEOPHILIC SUBSTITUTION REACTIONS; TRANSAMINATIONS OF SILANAMINES

KENNETH J. SHEA *, ROBERT GOBEILLE and JAMES F. WOLF
Department of Chemistry, University of California, Irvine, CA 92717 (U.S.A.)
(Received January 31st, 1978)

Summary

Ion cyclotron resonance spectroscopy has been employed in the study of gas phase transaminations of silanamines. The dominant reaction pathway is found to involve a bimolecular nucleophilic substitution at silicon. Under suitable conditions the ICR method permits direct observation of intermediate reaction complexes. The possible relationship of these complexes to S_N2 intermediates is discussed.

Ion cyclotron resonance spectroscopy (ICR) has been used to study nucleophilic substitution reactions unencumbered by solvent effects [1]. This technique promises to be particularly useful in understanding structure-reactivity relationships in organosilicon chemistry since the influence of solvent on reaction rate and product stereochemistry can be particularly complex [2,3]. Several investigations of gas phase reactions of organosilicon compounds are now known [4]. We report here the results of a study of ion-molecule reactions of silanamines conducted by the trapped ion, pulsed ICR technique. Our results emphasize the striking difference in nucleophilic susceptibility of carbon and silicon and also permit us to speculate on the nature of certain S_N2 reaction complexes of organosilicon compounds.

Experimental

ICR instrumentation and experimental techniques have been described elsewhere [5,6]. Gas mixtures are inlet into the ICR cell through separate leak valves in a parallel inlet manifold. Absolute gas pressures are determined using a Bayard—Alpert ionization gauge calibrated separately against an MKS Baratron capacitance manometer. The operating pressure for the experiments varied between 5×10^{-7} and 5×10^{-5} Torr. Ions are generated by a 1.25 ms pulse of a 19 eV beam through the analyzer cell. The ions are analyzed by a pulsed marginal oscillator detector.

Dimethylaminosilane was prepared by a literature procedure [7]; IR and mass spectral analysis confirmed its purity. All other amines were purchased commercially and purified by preparative VPC (Varian 90-P gas chromatograph; 5′ glass column, 10% Pennwalt 223 + 4% KOH on 80/100 Gas Chrom R). Spectral properties, NMR and mass spectroscopy, were used to confirm their chemical purity. It was observed that flushing the inlet manifold with silanamine before inletting to the analyzer section eliminated extraneous peaks that presumably resulted from hydrolysis or reaction of the amine on the inlet manifold surface.

A mass spectral analysis (19 eV, 100 ms delay before detection) of dimethylaminotrimethylsilane reveals no impurities. In addition to *m/e* 118 ($Me_3Si(dma)H^+$) fragment ions at *m/e* 116 and 102 were present (relative abundance 1/0.8/0.4).

Results and discussion

ICR has been successfully utilized to determine the gas phase base strengths of a number of aliphatic amines [8]. The technique provides for the precise determination of the standard free energy change for the general gaseous proton-transfer reaction shown in eq. 1.

$$R_3N + R'_3NH^+ \rightleftharpoons R_3NH^+ + R'_3N \qquad (1)$$

Proton equilibrium is readily achieved for a wide variety of carbon bases. In contradistinction, most simple silanamines do not achieve proton equilibrium, rather a second reaction manifold is observed. For example, attempted proton equilibration of trimethylsilyldimethylamine (I) with piperidine (pip)H * was unsuccessful, eq. 2; the intensity of protonated silanamine (II, *m/e* 118) decayed rapidly and a new ion (*m/e* 158) grew in. This ion corresponds to the protonated substitution product resulting from amine exchange on silicon, eq. 3.

$$\underset{(I)}{Me_3Si(dma)} + \underset{(m/e\ 86)}{(pip)H_2^+} \rightleftharpoons \underset{(II,\ m/e\ 118)}{Me_3Si(dma)H^+} + (pip)H \qquad (2)$$

$$\underset{(II,\ m/e\ 118)}{Me_3Si(dma)H^+} + (pip)H \rightarrow \underset{(m/e\ 158)}{Me_3Si(pip)H^+} + (dma)H \qquad (3)$$

These exchange reactions have been observed with a number of silanamines and bases; several examples are shown in the equations below. A typical ion intensity vs. time plot for the reaction of trimethylsilyldimethylamine with trimethylamine (eq. 5) is shown in Fig. 1.

It should be emphasized that transamination reactions of carbon amines are rare; we are not aware of any examples in the gas phase. There are, however, examples of analogous solution phase amine exchange reactions at silicon [9]. These observations are consistent with the general trend of silicon's greater susceptibility towards nucleophilic attack [2,3].

---

* Standard abbreviations for alkyl amides, e.g., (dma) = dimethylamide, Me_2N, (ema) = ethylmethylamide, EtMeN, and amines, (tma) = trimethylamine, are used throughout the text.

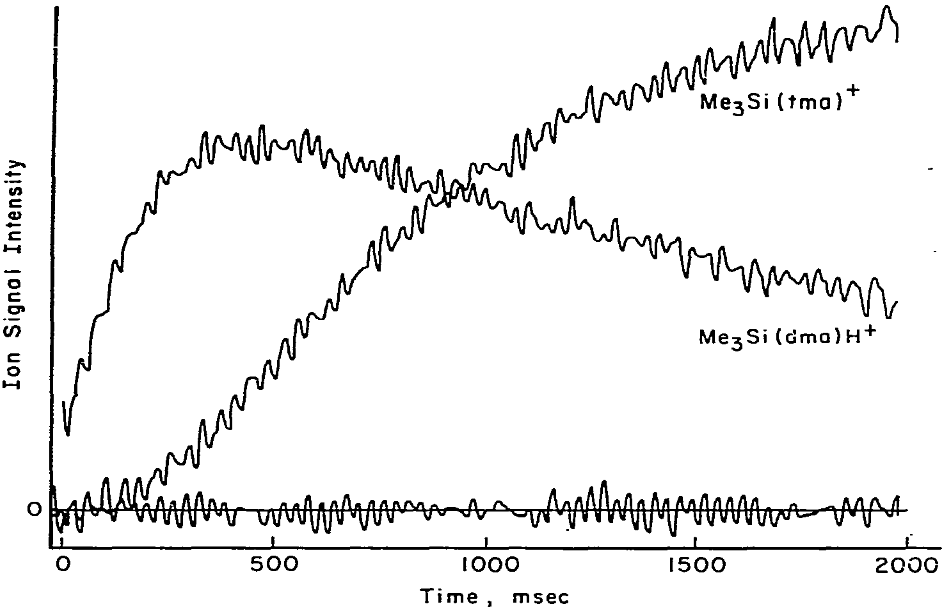


Fig. 1. Ion intensity vs. time plot for the reaction $Me_3Si(dma)H^+ + tma \rightarrow Me_3Si(tma)^+ + (dma)H$. $p(Me_3Si(dma)) = 5.2 \times 10^{-7}$ Torr; $p(Me_3N) = 4.1 \times 10^{-7}$ Torr; 1.25 ms ionization pulse at 19 eV.

$$Me_3Si(dma)H^+ + (dea)H \rightarrow \underset{(m/e\ 151)}{Me_3Si(dea)H^+} + (dma)H \tag{4}$$

$$Me_3Si(dma)H^+ + tma \rightarrow \underset{(m/e\ 132)}{Me_3Si(tma)^+} + (dma)H \tag{5}$$

$$H_3Si(dma)H^+ + py \rightarrow \underset{(m/e\ 110)}{H_3Si(py)^+} + (dma)H \tag{6}$$

$$(Me_3Si)_2NH_2{}^+ + (dma)H \rightarrow \underset{(m/e\ 118)}{Me_3Si(dma)H^+} + Me_3SiNH_2 \tag{7}$$

It is interesting that formation of quaternary ammonium ions, eq. 5, 6, occurs readily with either methyl or hydrogen substituents on silicon. Trimethylsilylammonium compounds have been proposed as reaction intermediates in the amine catalyzed silylation of many organic substrates [10]. Analogous ammonium compounds have now been isolated and characterized in condensed media [11—14].

The transamination products can arise from any one of a number of reaction pathways. Two such examples, amine capture of trimethylsilyl cation (eq. 8), and bimolecular nucleophilic substitution * (eq. 9), are shown below.

---

* Nucleophilic substitution can occur from either protonated silanamine (*m/e* 118) or from the fragment ion *m/e* 116. Both reactions contribute to the transamination product.

$$Me_3Si(dma) \rightarrow \underset{m/e\ 73}{Me_3Si^+} \xrightarrow{(dea)H} \underset{m/e\ 146}{Me_3Si(dea)H^+} \qquad (8)$$

$$Me_3Si(dma)H^+ \xrightarrow{(dea)H} [H(dma)\cdots SiMe_3\cdots(dea)H]^+ \rightarrow \underset{m/e\ 146}{Me_3Si(dea)H^+} + (dma)H \qquad (9)$$

Our evidence suggests that the latter mechanism, eq. 9, is the dominant reaction pathway. This conclusion is based upon the following: (a) trimethylsilyl cation peak (*m/e* 73) falls to negligible intensity in 20 msec during a time-mass scan of trimethylsilyldimethylamine (I); under transamination conditions (I + dimethylamine) product ion (*m/e* 146) steadily increases in intensity beyond 1500 msec (see, for example, Fig. 1). (b) The rate of transamination is proportional to the the partial pressure of diethylamine. (c) The transamination reaction is suppresssed by substituting a t-butyl group for methyl on silicon *. This response is typical for a bimolecular nucleophilic substitution reaction. Additional evidence in support of this suggestion is presented in the following section.

High pressure mass spectrometry [16] and ICR [17] have been used to observe stable adducts between anions and a number of alkyl substrates. These adducts have been proposed to correspond to intermediates in the S_N2 reactions, eq. 10.

$$RX + Y^- \rightleftharpoons [RXY]^- \rightleftharpoons RY + X^- \qquad (10)$$

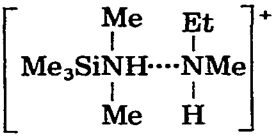
To establish if the ICR conditions are suitable for detecting analogous cationic reaction intermediates in the transamination of silanamines, the following experiments were undertaken. Trimethylsilyldimethylamine (I) and ethylmethylamine (4×10^{-7} Torr of each reactant) were allowed to react in the presence of a bath gas (n-butane) to enhance collisional stabilization of high energy species present (total pressure, 5×10^{-5} Torr). Transamination proceeded as expected, only this time a new ion, *m/e* 177, was observed, eq. 11.

$$\underset{(II,\ m/e\ 118)}{Me_3Si(dma)H^+} + (ema)H \rightarrow \underset{(m/e\ 177)}{[Me_3Si(dma)H \cdot (ema)H]^+} \rightarrow (dma)H + \underset{(m/e\ 132)}{Me_3Si(ema)H^+} \qquad (11)$$

The new ion corresponds to a complex of II and ethylmethylamine. Double resonance experiments reveal the transamination product (*m/e* 132) is coupled to this complex. Additional information regarding the identity of this ion is more difficult to obtain. For example, our evidence does not permit us to choose between hydrogen attachment (III), or silicon attachment (IV) of the second amine molecule.

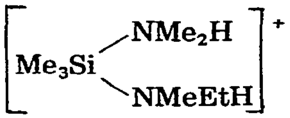
---

* The failure of t-butyldimethylsilyldimethylamine to undergo transamination provided an opportunity to quantitatively evaluate the proton affinity of a silanamine (cf. ref. 15).



$$\left[\begin{array}{c}\mathrm{Me}\quad\ \mathrm{Et}\\ \mathrm{Me_3SiNH\cdots NMe}\\ \mathrm{Me}\quad\ \mathrm{H}\end{array}\right]^+$$

(III)



(IV)

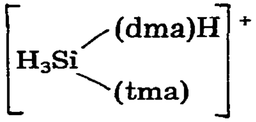
This distinction has not been made for protonated dimers of carbon amines in the gas phase [18,19]; hydrogen bonded complexes are assumed. We have made several observations that are pertinent to this question and propose that, at least in certain systems, silicon attachment (IV) is energetically as favorable as, if not more favorable than, hydrogen attachment (III).

In principle, the structural ambiguities can be removed by studying quaternary silylammonium ions since these ions do not have acidic hydrogens *. We therefore undertook a "high pressure" study of quaternary silylammonium ions that were "synthesized" in the gas phase by the transamination reaction.

Our fitst effort, however, was unsuccessful. When trimethylsilyldimethylamine (I) was treated with trimethylamine at a total neutral pressure of 5×10^{-5} Torr, no ion corresponding to $[\mathrm{Me_3Si(tma)_2}]^+$, *m/e* 191, could be detected. The peak corresponding to the complex $[\mathrm{Me_3Si(dma)H \cdot (tma)}]^+$, *m/e* 177, however, was also absent. This result suggests steric effects may influence the stability of these highly substituted molecular complexes. Replacing the methyl groups on silicon with hydrogen should relieve steric effects and also enhance the acceptor properties of silicon. Confirmation of this proposal was obtained from a study of the reaction of dimethylaminosilane (V) with trimethylamine. At a total neutral pressure of 2×10^{-6} Torr the spectra consists of virtually a single ion, *m/e* 135, which corresponds to a complex of protonated silanamine and trimethylamine (eq. 12).

$$\underset{(\mathrm{V},\ m/e\ 76)}{\mathrm{H_3Si(dma)H^+}} + (\mathrm{tma}) \rightarrow \underset{(\mathrm{VI},\ m/e\ 135)}{[\mathrm{H_3Si(dma)H \cdot (tma)}]^+} \qquad (12)$$

Interestingly, the peak corresponding to the hydrogen-bonded dimer of trimethylamine $(\mathrm{Me_3N{-}H{-}NMe_3})^+$ (*m/e* 119) was absent from this spectra, suggesting VI is considerably more stable. Since silanamines are less basic than the analogous carbon amines [15], they are not expected to be superior to carbon amines in hydrogen bonded dimer formation; the ion at *m/e* 135 is perhaps best represented by attachment of the second amine (tma) to silicon, e.g., VII.



(VII)

Some additional support for this hypothesis is obtained from the reaction of

---

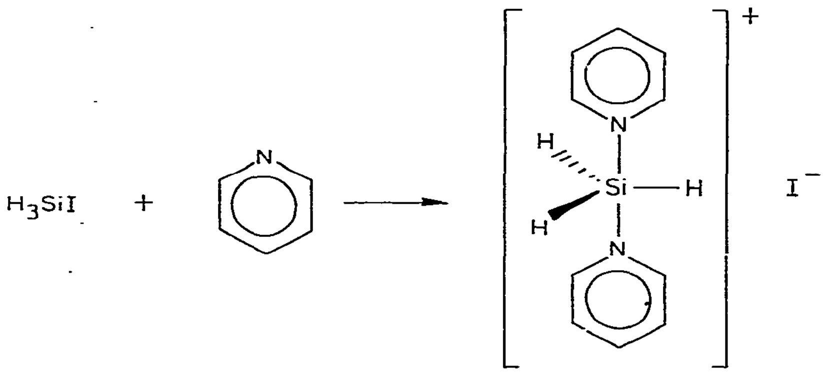
[*] Strictly speaking this is not true. Observations of weak hydrogen bonding by hydrogens on carbons α to a positive nitrogen have been reported (cf. ref. 20).

dimethylaminosilane with pyridine,

$$H_3Si(dma)H^+ + py \rightarrow \underset{(VIII,\ m/e\ 110)}{H_3Si(py)^+} \qquad (13)$$

$$\underset{(VIII)}{H_3Si(py)^+} + py \rightarrow \underset{(IX,\ m/e\ 189)}{H_3Si(py)_2^+} \qquad (14)$$

The transamination product is observed as expected (VIII, *m/e* 110, eq. 13). In addition, a very stable ion at *m/e* 189 is also observed (IX). This ion corresponds to a dipyridine complex of SiH_3^+. Double resonance experiments establish the relatioship *m/e* 110→189 (eq. 14). Furthermore, consideration of the intensity of *m/e* 159 (50% of total ion intensity) implies the free energy of reaction 14 is negative. The unlikely occurrence of an unusually stable hydrogen bonded complex, e.g., $[py\cdots H{-}SiH_2Py]^+$, argues, in this case, for silicon attachment of the second pyridine molecule. Noteworthy in this respect is the product from the solution phase reaction of iodosilane and pyridine (eq. 15), characterized as the pentacovalent ion X [21].



(15)

(X)

The observed free energy of reaction 14 would appear to be a first step in establishing energy relationships between reaction intermediates in nucleophilic substitution at silicon.

Acknowledgement

The authors wish to express their appreciation to Professor Robert W. Taft for his assistance and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

1 (a) R.T. McIver, Jr. and R.C. Dunbar, Int. J. Mass Spectrom. Ion Phys., 7 (1971) 476; (b) C.A. Lieder and J.I. Brauman, J. Amer. Chem. Soc., 96 (1974) 4028; (c) J.I. Brauman, W.N. Olmstead, and C.A. Lieder, J. Amer. Chem. Soc., 96 (1974) 4030; (d) T.A. Lehman and M.M. Bursey, Ion Cyclotron Resonance Spectroscopy, Wiley—Interscience, New York, 1976, p. 76.

2 (a) L.H. Sommer, Intra-Science Chem. Rept., 7 (1973) 1; (b) L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965.

3 R.J.P. Corriu and M. Henner, J. Organometal. Chem., 74 (1974) 1.

4 (a) J.M.S. Henis, G.W. Stewart, and P.P. Gaspar, J. Chem. Phys., 58 (1973) 890, 3639; (b) C.G. Pitt, M.M. Bursey, D.A. Chatfield, and R.S. Greenburg, J. Organometal. Chem., 90 (1975) 269; (c) M.K. Murphey and J.L. Beauchamp, J. Amer. Chem. Soc., 98 (1976) 5781; (d) ibid., 99 (1977) 4992.

5 (a) R.T. McIver, Jr., Rev. Sci. Instrum, 41 (1970) 555; (b) J.L. Beauchamp, Ann. Rev. Phys. Chem., 21 (1971) 527; (c) M.T. Bowers, D.H. Aue, H.M. Webb, and R.T. McIver, Jr., J. Amer. Chem. Soc., 93 (1971) 4314.

6 J.F. Wolf, R.H. Staley, I. Koppel. M. Taagepera, R.T. McIver, Jr., J.L. Beauchamp, and R.W. Taft, J. Amer. Chem. Soc., 99 (1977) 5417.

7 B.J. Aylett and J.E. Emsley, J. Chem. Soc. A, (1967) 652.

8 (a) W.G. Henderson, M. Taagepera, D. Holtz, R.T. McIver, Jr., J.L. Beauchamp, and R.W. Taft, J. Amer. Chem. Soc., 94 (1972) 4728; (b) D.H. Aue, H.M. Webb, and M.T. Bowers, J. Amer. Chem. Soc., 98 (1976) 311 and references cited therein.

9 R.F. Fessenden and D.F. Crowe, J. Org. Chem., 26 (1961) 4638.

10 A.E. Pierce, Silylation of Organic Compounds, Pierce Chemical Co., Rockford, Ill., 1968, Ch. 4.

11 R.E. Highsmith, J.R. Bergerud, and A.G. MacDiarmid, Chem. Commun., (1971) 48; see however (a) R. Cass and G.E. Coates, J. Chem. Soc., (1952) 2347; (b) B.J. Aylett and J. Emsley, J. Chem. Soc. A, (1967) 652.

12 (a) H.J. Campbell-Ferguson and E.A.V. Ebsworth, J. Chem. Soc. A, (1966) 508; (b) B.J. Aylett and R.A. Sinclair, Chem. Ind. (London), (1965) 201; (c) J.Y. Corey and R. West, J. Amer. Chem. Soc., 85 (1963) 4034; (d) B.J. Aylett and J.M. Campbell, J. Chem. Soc. A, (1969) 1920.

13 (a) B.J. Aylett in H.J. Emeléus and A.G. Sharpe (Eds.), Advances in Inorganic and Radiochemistry, II, Academic Press, N.Y., 1968, p. 297; (b) A.G. MacDiarmid, Intra-Sci. Chem. Reprt., 7 (1973) 83.

14 H. Emde and G. Simchen, Synthesis, (1977) 636.

15 K.J. Shea, R. Gobeille, J. Bramblett, and E.A. Thompson, J. Amer. Chem. Soc., 100 (1978) 1611.

16 (a) R.C. Dougherty, J. Dalton, and J.D. Roberts, Org. Mass Spectrom., 8 (1974) 77; (b) R.C. Dougherty and J.D. Roberts, ibid., 8 (1974) 81; (c) R.C. Dougherty, ibid., 8 (1974) 85.

17 (a) W.N. Olmstead and J.F. Brauman, J. Amer. Chem. Soc., 99 (1977) 4219; (b) L.K. Blair, P.C. Isolani, and J.M. Riveros, J. Amer. Chem. Soc., 97 (1973) 1057.

18 R. Yamdagni and P. Kebarle, J. Amer. Chem. Soc., 95 (1973) 3504.

19 M. Meot-Ner and F.H. Field, J. Amer. Chem. Soc., 97 (1975) 5339.

20 K.M. Harmon, I. Gennick, and S.L. Madeira, J. Phys. Chem., 78 (1974) 2585.

21 H.J. Campbell-Ferguson and E.A.V. Ebsworth, J. Chem. Soc. A, (1967) 705.