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Gas-Phase Reactions of Si^+ with Ammonia and the Amines $(CH_3)_xNH_{3-x}$ (x = 1-3): Possible Ion-Molecule Reaction Pathways toward SiH, SiCH, SiNH, $SiCH_3$, $SiNCH_3$, and H_2SiNH

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Abstract: Rate constants and product distributions have been determined for gas-phase reactions of ground-state $Si^+(^2P)$ ions with ammonia and the amines $(CH_3)_xNH_{3-x}$ (x = 1-3) at 296 ± 2 K with the selected-ion flow tube technique. All reactions were observed to be fast and can be understood in terms of Si^+ insertion into N-H and C-N bonds to form ions of the type $SiNR_1R_2^+$ (R_1, R_2 = H, CH_3) proceeding in competition (in the case of the amines) with hydride ion transfer to form immonium ions of the type $CH_2NR_1R_2^+$ (R_1, R_2 = H, CH_3). C-N bond insertion appears more efficient than N-H bond insertion. The contribution of hydride ion transfer increases with increasing stability of the immonium ion. The latter reaction leads directly to SiH as a neutral product. Other minor reaction channels were seen which lead directly or indirectly to SiCH and $SiCH_3$. Rapid secondary proton transfer reactions were observed for $SiNH_2^+$ and $SiNHCH_3^+$ to produce gas-phase SiNH and $SiNCH_3$ molecules. With methylamine $SiNH_2^+$ also appears to produce $H_2SiNH_2^+$ which may deprotonate to form the simplest silanimine, H_2SiNH, or aminosilylene, $HSiNH_2$. Reactions of this type are of interest in molecular synthesis and here are proposed to contribute to the formation of SiH, SiCH, SiNH, $SiCH_3$, $SiNCH_3$, and H_2SiNH or $HSiNH_2$ in partially ionized interstellar gas clouds containing silicon, ammonia, and methylamines.

We have recently shown that formation of the silicon-oxygen double bond may be initiated in the gas phase by fast reactions of ground-state $Si^+(^2P)$ ions with molecules containing hydroxyl groups.[1] The hydroxysilicon cation, :$SiOH^+$, is a major product ion in these reactions. Subsequent neutralization of this cation by proton transfer or recombination with electrons then can yield double-bonded silicon monoxide. Such synthetic routes are of importance in partially ionized interstellar gas clouds where they constitute a source of SiO.[2,3] By analogy, the aminosilicon ions :$SiNR_1R_2^+$ (R_1, R_2 = H, alkyl) are expected to be stable in the gas phase and possibly to be formed by reactions of Si^+ with ammonia and amines. Their neutralization by proton or alkyl cation transfer could then lead to the synthesis of the doubly bonded silicon/nitrogen molecules SiNH and SiNR. To examine this prediction we performed a systematic study of the rates and products of the reactions of ground-state $Si^+(^2P)$ with ammonia and mono-, di-, and trimethylamine. The results obtained with ammonia for the most part have been reported elsewhere in a determination of the proton affinity of SiNH.[4] Here we also report the results obtained for the reactions with the amines and indicate how they provide interesting opportunities for the formation of new silicon/nitrogen compounds.

Experimental Section

The measurements were performed with the selected-ion flow tube (SIFT) apparatus which has been described earlier.[5,6] Atomic silicon ions were generated by electron ionization of $Si(CH_3)_4$ in a mixture with deuterium as described previously.[1] Deuterium was added to remove the excited Si^+ (^4P) state. The silicon ions were selected and introduced into helium buffer gas at ca. 0.35 Torr. Impurity ions were observed downstream due to reactions of Si^+ with H_2O inpurity in the buffer gas and tetramethylsilane leaking from the source. The main impurity ions were $SiOH^+$ and $Si(CH_3)_3^+$ and these were present in amounts less than 10% of the Si^+ signal. The reactant gases and purities were H_2 (≥99.99%), CO (≥99.5%), NH_3 (≥99.95%), CH_3NH_2 (≥98.0%), $(CH_3)_2NH$ (≥99.0%), and $(CH_3)_3N$ (≥99.0%). All these gases were Matheson products. The experimental temperature was 296 ± 2 K.

Table I. Rate Constants (in units of 10^{-9} cm^3 $molecule^{-1}$ s^{-1}) and Product Distributions for Reactions of Si^+ (^2P) with Ammonia and Methylamines at 296 ± 2 K

neutral reactant	products	product distribution[a]	k_{exptl}[b]	k/k_c[c]
NH_3	$SiNH_2^+ + H$	1.0	0.64	0.27
CH_3NH_2	$SiNH_2^+ + CH_3$	0.55	1.2	0.59
	$CH_2NH_2^+ + SiH$	0.35		
	$SiNHCH_3^+ + H$	0.10		
$(CH_3)_2NH$	$CH_2NHCH_3^+ + SiH$ $(SiNH_2^+ + C_2H_5)$	0.60	1.2	0.61
	$SiNHCH_3^+ + CH_3$	0.35		
	$SiN(CH_3)_2^+ + H$	0.05		
$(CH_3)_3N$	$CH_2N(CH_3)_2^+ + SiH$	0.80	0.98	0.60
	$CH_2NHCH_3^+ + SiCH_3$ $(SiNH_2^+ + C_3H_7)$	0.09		
	$SiN(CH_3)_2^+ + CH_3$	0.07		
	$SiCH_2^+ + (CH_3)_2NH$ $(CH_3CNH^+ + SiCH_5)$	0.04		

[a] Primary product ions which contribute 5% or more (with one exception). The product distributions have been rounded off to the nearest 5% and are estimated to be accurate to within ±30%. [b] The accuracy of the rate constants is estimated to be better than ±30%. [c] Collision rate constants, k_c, are derived from the combined variational transition state theory-classical trajectory study of: Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

Results

The rate constants and product distributions obtained in this study are summarized in Table I. Supporting thermochemical data have been derived from the usual sources.[7,8]

Ammonia. Only one product ion was observed with ammonia as indicated in reaction 1. We have shown elsewhere[4] that this product ion must be the N-protonated hydrogen silaisocyanide

$$Si^+ + NH_3 \rightarrow SiNH_2^+ + H, \quad \Delta H^\circ_{298} = -17 \text{ kcal mol}^{-1} \qquad (1)$$

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(1) Włodek, S.; Fox, A.; Bohme, D. K. *J. Am. Chem. Soc.* **1987**, *109*, 6663.

(2) Millar, T. J. *Astrophys. Space Sci.* **1980**, *72*, 509.

(3) Clegg, R. E. S.; Van IJzendoorn, L. J.; Allamandola, L. J. *Mon. Not. R. Astron. Soc.* **1983**, *203*, 125.

(4) Włodek, S.; Rodriquez, C. F.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Chem. Phys. Lett.* **1988**, *143*, 385.

(5) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259.

(6) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion. Phys.* **1983**, *55*, 69.

(7) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Natl. Stand. Ref. Data Ser. Natl. Bur. Stand.* **1969**, *26*, 41.

(8) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref Data, Suppl. 1* **1977**, *6*.

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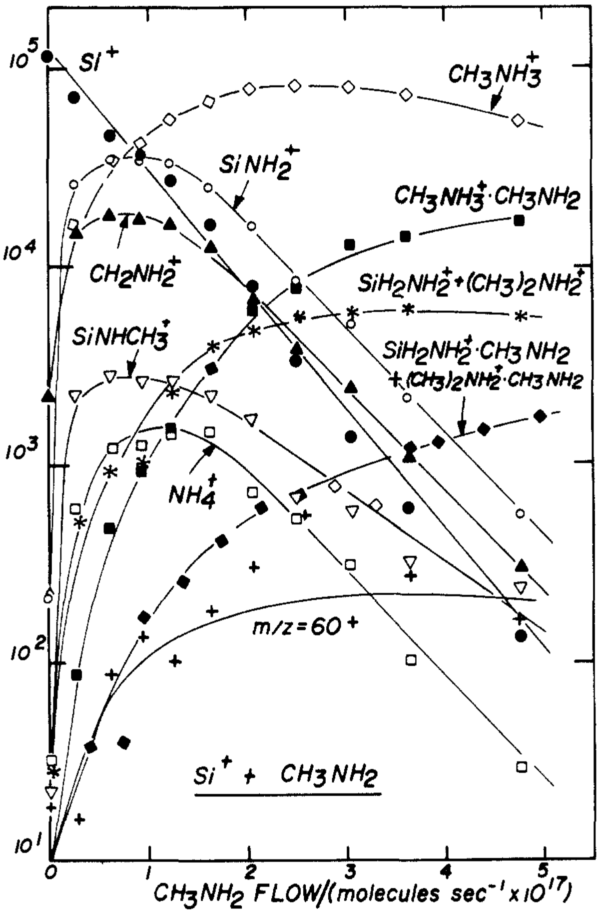

Figure 1. The observed variations in ion signals recorded for the addition of methylamine into the reaction region of the SIFT apparatus in which Si^+ has been established as the dominant ion in helium buffer gas. P = 0.35 Torr, $\bar{v} = 6.4 \times 10^3$ cm s^{-1}, L = 46 cm, and T = 295 K. The Si^+ is derived by electron ionization from a 2.8 mol % mixture of tetramethylsilane in D_2 at an electron energy of 69 eV. The small initial signal at m/z 30 can be attributed to the transmission of some SiD^+ by the selection quadrupole.

and not the isomer $HSiNH^+$. The formation of the latter isomer is endothermic by 36 kcal mol^{-1}. The rate constant for reaction 1 was determined to be 6.4×10^{-10} cm^3 molecule^{-1} s^{-1}. $SiNH_2^+$ was observed to undergo rapid proton transfer as indicated by reaction 2, $k = 9.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Reactions 1 and 2 have been investigated very recently with Fourier transform mass spectrometry (FTMS).[9] The Si^+ ions were produced from solid silicon by laser vaporization. The rate constants obtained for reactions 1 and 2 were $(3 \pm 1) \times 10^{-10}$ and $(5.8 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively, but the authors cautioned that these FTMS values may include systematic differences from the rate constants of thermal ground-state Si^+ ions. Our results suggest that this may indeed be the case. The FTMS values are systematically lower than those determined in the present SIFT study with thermal ground-state Si^+ ions.

$$SiNH_2^+ + NH_3 \rightarrow NH_4^+ + SiNH \qquad (2)$$

Separate SIFT experiments in our laboratory in which $SiNH_2^+$ was generated from reaction 1 have shown that $SiNH_2^+$ is unreactive toward H_2 and CO. The rate constants determined for these nonreactions have upper limits of 3.4 and 2.0×10^{-13} cm^3 molecule^{-1} s^{-1}.

Methylamine. The experimental profiles for the reactant and product ions recorded with the addition of methylamine are presented in Figure 1. The major reaction channel observed for this reaction produced $SiNH_2^+$ and the methyl radical, while hydride transfer to form SiH and the immonium ion, $CH_2NH_2^+$, was a significant competing channel. Formation of the less stable isomers $HSiNH^+$ and CH_3NH^+ is endothermic by 13 and 12 kcal mol^{-1}, respectively. H atom elimination to produce $SiNHCH_3^+$ occurred only to an extent of 10%, and small amounts of NH_4^+ were produced presumably by reaction 3.

$$Si^+ + CH_3NH_2 \rightarrow NH_4^+ + SiCH \qquad (3)$$

All of the primary product ions were observed to react rapidly with methylamine to form secondary products. Rate constants for the secondary reactions of $SiNH_2^+$, $CH_2NH_2^+$, $SiNHCH_3^+$, and NH_4^+ were derived by curve fitting their ion profiles to the integrated rate expressions. The values obtained were 1.0, 1.3, 1.3, and 1.2×10^{-9} cm^3 molecule^{-1} s^{-1}, respectively. Proton transfer appeared to be the predominant reaction channel for these four reactions. The proton transfer reactions of NH_4^+ and $CH_2NH_2^+$ with CH_3NH_2 have been studied recently in a drift tube mass spectrometer and observed to proceed at a center-of-mass kinetic energy of 0.3 eV with a rate constant of $(2.0 \pm 0.5) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.[10]

Also, the production of the secondary ion at m/z 46 may involve the following reactions of $SiNH_2^+$ and $SiNHCH_3^+$ with methylamine:

$$SiNH_2^+ + CH_3NH_2 \rightarrow SiH_2NH_2^+ + CH_2NH \qquad (4)$$

$$SiNHCH_3^+ + CH_3NH_2 \rightarrow (CH_3)_2NH_2^+ + SiNH \qquad (5)$$

The methyl cation transfer reaction 5 is unlikely on the basis of our failure to observe the analogous reaction with dimethylamine which has a higher methyl cation affinity, 120.5 rather than 113.5 kcal mol^{-1} for methylamine. The m/z 46 ion should therefore primarily be $SiH_2NH_2^+$. Some contribution to the signal at m/z 46 is expected from proton transfer to the dimethylamine impurity ($\leq 0.8\%$). The m/z 46 ion is seen in Figure 1 to form an adduct with CH_3NH_2, as does the $CH_3NH_3^+$ ion. Finally, the small production of the ion at m/z 60 shown in Figure 1 can be attributed entirely to proton transfer to trimethylamine impurity which may be as large as 0.6%.

Dimethylamine. The two major reaction channels observed with dimethylamine correspond to hydride transfer and methyl elimination. A minor channel corresponding to hydrogen atom elimination was also detected. In addition, traces (3%) of an ion with m/z 32 were observed which could be produced from the following reaction:

$$Si^+ + (CH_3)_2NH \rightarrow CH_3NH_3^+ + SiCH \qquad (6)$$

However, another possible source of this ion is the proton-transfer reaction of methylamine impurity in the dimethylamine with the impurity $SiOH^+$ ions.

Two isomers of $(C_2H_6N)^+$ can be envisaged as possible products of the hydride transfer reaction according to the origin of the hydride ion. Collisional activation experiments have shown that the immonium ion $CH_3N^+H{=}CH_2$ which may be derived by hydride transfer from a methyl group is more stable than the ion $CH_3N^+CH_3$ which may be derived by hydride transfer from NH and that the latter ion isomerizes to the more stable immonium structure.[11] Consequently we can expect the immonium ion to be the preferred product in the hydride transfer channel of the reaction of silicon ions with dimethylamine. The possible formation by reaction 7 of $SiNH_2^+$ which has the same m/z as $(C_2H_6N)^+$ must also be considered, but it seems unlikely since C_2H_5 elimination requires substantial bond redisposition (the rupture of two C–N bonds and one C–H bond and the formation

$$Si^+ + (CH_3)_2NH \rightarrow SiNH_2^+ + C_2H_5,\ \Delta H^\circ_{298} = -50 \text{ kcal mol}^{-1} \qquad (7)$$

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[9] Creasy, W. R.; O'Keefe, A.; McDonald, J. R. *J. Phys. Chem.* **1987**, *91*, 2848.

[10] Barassin, J.; Barassin, A.; Thomas, R. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 51.

[11] Levsen, K.; McLafferty, F. W. *J. Am. Chem. Soc.* **1974**, *96*, 139.

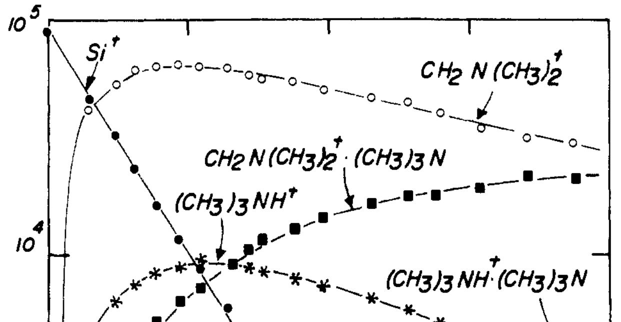

Figure 2. The observed variations in ion signals recorded for the addition of trimethylamine into the reaction region of the SIFT apparatus in which Si^+ has been established as the dominant ion in helium buffer gas. $P = 0.33$ Torr, $\bar{v} = 6.3 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 294$ K. The Si^+ is derived by electron ionization from a 2.8 mol % mixture of tetramethylsilane in D_2 at an electron energy of 81 eV. The small initial signals at m/z 44 and 72 are due to overlap with the signals of the impurity ions $SiOH^+$ and $Si(CH_3)_3^+$ at m/z 45 and 73, respectively, which are not shown.

of C–C, Si–N, and N–H bonds). An analogous situation applies for the reaction of Si^+ with trimethylamine for which we have shown that production of $SiNHCH_3^+$ and C_2H_5 also does not occur.

The methyl elimination reaction is likely to lead to the ion $SiNHCH_3^+$ by C–N bond insertion. The H atom elimination reaction should proceed by N–H insertion rather than C–H insertion which is generally much less favorable.

The immonium ion $CH_3N^+H{=}CH_2$ and the ion $SiNHCH_3^+$ were both observed to react further by proton transfer according to reactions 8 and 9, although some association was observed to compete with the transfer of a proton from $SiNHCH_3^+$. Rate

$$CH_2NHCH_3^+ + (CH_3)_2NH \rightarrow (CH_3)_2NH_2^+ + CH_2NCH_3 \qquad (8)$$

$$SiNHCH_3^+ + (CH_3)_2NH \xrightarrow{0.95} (CH_3)_2NH_2^+ + SiNCH_3 \qquad (9a)$$

$$\xrightarrow{0.05} SiNHCH_3^+ \cdot (CH_3)_2NH \qquad (9b)$$

constants were derived from fits to the ion profiles to be $(1.0 \pm 0.3) \times 10^{-9}$ and $(7 \pm 3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.

Trimethylamine. One ion with m/z 58 dominated the product spectrum shown in Figure 2 for the reaction of Si^+ with trimethylamine. This ion could be either $(C_3H_8N)^+$ arising from hydride transfer or $SiNHCH_3^+$ arising from reaction 10 which is analogous to reaction 7. The former source is preferred for

$$Si^+ + (CH_3)_3N \rightarrow SiNHCH_3^+ + C_2H_5 \qquad (10)$$

at least two reasons. The m/z 58 ion was observed to react further with $(CH_3)_3N$ primarily by association rather than by proton transfer. $(CH_3)_3N$ has a proton affinity higher[12] than that of $(CH_3)_2NH$ so that proton transfer would have been expected to predominate if this ion were $SiNHCH_3^+$ on the basis of the observed proton transfer reaction of $SiNHCH_3^+$ with $(CH_3)_2NH$. Also, in separate experiments in which $(C_3H_8N)^+$ was produced directly by electron impact ionization of trimethylamine, this ion was observed to react exclusively by association. The rate constant for this association reaction was determined to be 1.1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} which is in agreement with the rate constant of 1.0×10^{-10} cm^3 $molecule^{-1}$ s^{-1} determined from a fit to the profile for the secondary association reaction of the m/z 58 ion produced from the reaction of Si^+ with $(CH_3)_3N$. The structure of the $(C_3H_8N)^+$ ion is most likely to be that of the immonium ion $(CH_3)_2N^+{=}CH_2$ which is the most stable of the possible isomers of $(C_3H_8N)^+$.

The minor product ion at m/z 44 is probably the immonium ion $CH_3N^+H{=}CH_2$ arising from methide transfer, rather than $SiNH_2^+$ produced by reaction 11. The latter requires considerable rearrangement. Methyl radical elimination to produce $SiN(CH_3)_2^+$ contributes only about 7% to the total reactive decay of Si^+. This primary product ion was observed to react further to form the adduct ion with trimethylamine. Curve fitting the profile for $SiN(CH_3)_2^+$ provided an effective bimolecular rate constant for this reaction of $(8.5 \pm 3.0) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at a pressure of 0.33 Torr and a He density of 1.1×10^{16} atoms cm^{-3}. There was also a minor primary product observed at m/z 42 which may be either $SiCH_2^+$ formed by methylene transfer or $C_2H_4N^+$ formed by reaction 12. The latter seems less likely on mechanistic grounds.

$$Si^+ + (CH_3)_3N \rightarrow SiNH_2^+ + C_3H_7 \qquad (11)$$

$$Si^+ + (CH_3)_3N \rightarrow CH_3CNH^+ + SiCH_5 \qquad (12)$$

Discussion and Conclusions

The results of the measurements reported in this study indicate several general features for the chemistry of ground-state silicon ions reacting with ammonia and methylamines:

1. The reactions with ammonia and the methylamines give a common product ion of the type $SiNR_1R_2^+$ including $SiNH_2^+$, $SiNHCH_3^+$, and $SiN(CH_3)_2^+$. These reactions occur by hydrogen atom elimination in the case of ammonia and by methyl and hydrogen atom elimination in the case of the methylamines. The relative importance of these reaction channels diminishes with increasing methyl substitution.

2. Hydride ion transfer to form immonium ions of the type $R_1R_2N^+{=}CH_2$ (R_1, R_2 = H, CH_3) occurs with all of the methylamines and increases in relative importance with increasing methyl substitution.

We have previously shown that the structure of the product ion of the reaction of Si^+ with ammonia is $SiNH_2^+$ and not $HSiNH^+$.[4] The H atom eliminated is that from the N–H bond undergoing insertion rather than an adjacent one. The structure of the product ion in the methyl radical elimination reaction with methylamine must also be $SiNH_2^+$. Formation of the $HSiNH^+$ isomer is endothermic by 13 kcal mol^{-1} according to the computed enthalpies of formation available for these ions.[4] This reaction is therefore likely to proceed by C–N bond insertion with the methyl radical being eliminated from the bond undergoing insertion as was the case for the elimination of H atoms from ammonia. If we assume a similar mechanism for methyl radical elimination with dimethylamine and trimethylamine, we may write the following general mechanism for $SiNR_1R_2^+$ formation:

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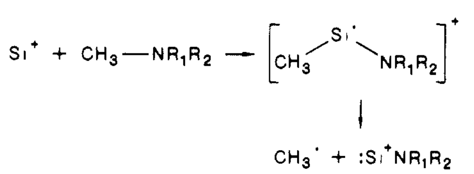
(12) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.



(13)

where R_1 and R_2 may be H or CH_3. Other possible mechanisms with dimethylamine include N–H bond insertion with elimination of CH_3 from an adjacent bond and C–N bond insertion with elimination of CH_3 from an adjacent bond. The latter mechanism is also possible with trimethylamine.

Several mechanisms are possible for the channel leading to H atom elimination with methylamine and dimethylamine. For example, the H atom may be eliminated by N–H bond insertion. If this is the case and if the mechanism in reaction 13 applies to methyl radical elimination, then the results in Table I suggest that C–N bond insertion is approximately 11 and 3.5 times more efficient (per C–N or N–H bond) than N–H bond insertion for methylamine and dimethylamine, respectively. This observation is consistent with expectations based on bond energies which are 80.5 and 103 kcal mol^{-1} for *D*(C–N) and *D*(N–H), respectively, in methylamine, and 87 and 95 kcal mol^{-1} for *D*(C–N) and *D*(N–H), respectively, for dimethylamine. A similar behavior has been observed by us recently for C–O and O–H bond insertion by Si^+ in the case of methanol and ethanol. The formation of $SiOH^+$ was approximately 3 times more efficient than formation of $SiOCH_3^+$ for CH_3OH, while no direct formation of $SiOC_2H_5^+$ was detected for C_2H_5OH.[1]

All of the aminosilicon ions, $SiNR_1R_2^+$ (R_1, R_2 = H, CH_3), observed in this study are likely to have silene character, viz. two unbonded electrons on the silicon atom, in analogy with the first member of this series, $SiNH_2^+$, which was shown to have silene character by ab initio calculations.[4] $SiNH_2^+$ appears to react further with methylamine by abstracting two hydrogen atoms to form an ion likely to be protonated silanimine, $SiH_2NH_2^+$. It is interesting to note that the corresponding products were not observed for the reactions of $SiNHCH_3^+$ with dimethylamine and $SiN(CH_3)_2^+$ with trimethylamine; adduct ions were formed instead.

The mechanism of the hydride transfer reaction between Si^+ and the methylamines is not known, but it is obvious that it does not require C–H bond insertion. Our recent measurements indicate that Si^+ inserts very inefficiently into C–H bonds, so that it is more plausible that hydride transfer occurs directly through a transition state of the type $(Si\cdots H\cdots R)^+$ whose potential energy surface may be described with a double minimum. The increasing importance of hydride ion transfer in going from mono- to trimethylamine suggests that the driving force for this process is the stability of the product immonium ion. The heats of formation of $CH_2NH_2^+$, $CH_2NHCH_3^+$, and $CH_2N(CH_3)_2^+$ are 178, 166, and 158 kcal mol^{-1}, respectively, and the corresponding hydride affinities are 218, 205, and 198 kcal mol^{-1}, respectively.[19] Hydride transfer has been observed to be an important channel in the reactions of many other atomic cations with methylamine, viz. C^+,[13] N^+,[14,15] O^+,[14] S^+,[16] and Co^+,[17] but no previous study has been reported for the influence of increasing methyl substitution.

A number of the reactions observed in this study are of interest in the molecular synthesis of silicon-containing molecules, particularly as it applies in partially ionized interstellar gas clouds containing silicon, ammonia, and methylamines. The hydride transfer reactions observed between Si^+ and the methylamines lead directly to the diatomic molecule SiH. We have reported elsewhere that the reaction of silicon ions with ammonia which produces $SiNH_2^+$ can lead to the formation of hydrogen silaisocyanide, SiNH.[4] We can report here a similar reaction of Si^+ with methylamine which produces $SiNH_2^+$. Related reactions were observed to occur with mono- and dimethylamine which produce the ion $SiNHCH_3^+$. This latter ion may lose a proton to produce $SiNCH_3$ by proton transfer or recombination with electrons. $SiNCH_3$ may also be formed by methyl cation transfer from $SiN(CH_3)_2^+$ which has been observed in this study to be generated by the reactions of Si^+ with di- and trimethylamine. Also, methide transfer is possible between Si^+ and trimethylamine to produce directly $SiCH_3$. Direct formation of SiCH is indicated by the minor primary channels (3) and (6) of the reactions of Si^+ with mono- and dimethylamine, respectively. A minor channel in the reaction of Si^+ with trimethylamine produces $SiCH_2^+$ which may neutralize by proton tranfer or recombination with electrons to form SiCH.

Other syntheses are indicated by the observed secondary reaction products. With methylamine $SiNH_2^+$ appears to produce $H_2SiNH_2^+$ which may deprotonate to form the simplest silanimine, $H_2Si{=}NH$, or aminosilylene, $HSiNH_2$.[18] The analogous reactions of $SiNHCH_3^+$ with dimethylamine and $SiN(CH_3)_2^+$ with trimethylamine proceed rapidly by association. The high rates for these latter two reactions suggest chemical bond formation in the adduct which in these cases is likely to proceed by N–H and N–CH_3 bond insertion to form $CH_3(H)NSi^+(H)N(CH_3)_2$ and $(CH_3)_2NSi^+(CH_3)N(CH_3)_2$, respectively. These latter ions may neutralize by proton or methyl cation transfer, respectively, to produce the silenes $CH_3(H)NSiN(CH_3)_2$ and $:Si(N(CH_3)_2)_2$. In the laboratory environment of the experiments reported here the adduct ions are likely to be stabilized by collisions with the He buffer gas atoms. In the much less dense interstellar environment stabilization must occur by radiative association.

Acknowledgment is made to the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

Registry No. NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; $SiNH_2^+$, 113159-97-0; $CH_2NH_2^+$, 54088-53-8; $SiNHCH_3^+$, 113159-98-1; $CH_2NHCH_3^+$, 82208-63-7; $SiN(CH_3)_2^+$, 113159-99-2; $CH_2N(CH_3)_2^+$, 77267-03-9; CH_3CNH^+, 20813-12-1; $SiCH_3$, 88867-57-6; SiH, 13774-94-2; Si^+, 14067-07-3.

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(13) Adams, N. G.; Smith, D. *Chem. Phys. Lett.* **1978**, *54*, 530.
(14) Smith, D.; Adams, N. G.; Miller, T. M. *J. Chem. Phys.* **1978**, *69*, 308.
(15) Adams, N. G.; Smith, D.; Paulson, J. F. *J. Chem. Phys.* **1980**, *72*, 288.
(16) Adams, N. G.; Smith, D.; Lindinger, W. *J. Chem. Phys.* **1981**, *75*, 3365.
(17) Radecki, B. D.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 946.
(18) Truong, T. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1775.
(19) Lossing, F. P.; Lam, Y.-T.; Maccoll, A. *Can. J. Chem.* **1981**, *59*, 2228.