Identification and Characterization of Monomeric, Volatile $SiCl_3NH_2$ as Product of the Reaction between $SiCl_4$ and NH_3: An Important Intermediate on the Way to Silicon Nitride?

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Abstract: We studied the reaction of $SiCl_4$ with NH_3 by mass spectrometry and IR spectroscopy. By means of mass spectrometry, $SiCl_3NH_2$ was for the first time identified as an intermediate generated in significant amounts in the course of the reaction. In additional experiments, $SiCl_3NH_2$ was formed as a stable gaseous product of the ammonolysis of $SiCl_4$, and the product was identified and characterized in detail by IR spectroscopic methods (gas phase and matrix isolation) in combination with quantum-chemical calculations. The calculations also gave access to important thermodynamical data.

Keywords: ammonolysis • density functional calculations • IR spectroscopy • mass spectrometry • silanes

Introduction

The nitrides of some elements, for example, titanium, boron, and silicon, have interesting technological properties such as a high degree of chemical and thermal stability, and in condensed forms show outstanding mechanical strength and resistance to wear.[1] Among these nitrides Si_3N_4 is one of the most important nonoxide ceramic materials. A common method of preparation is the reaction of ammonia with silicon tetrachloride. A better knowledge of this reaction is of great interest because silicon–nitride-containing materials and devices are fabricated by this route in industrial processes.

The complete ammonolysis of silicon tetrachloride [Eq. (1)] is an endothermal reaction, though it involves a considerable gain of entropy.

$$3\,SiCl_4(g) + 4\,NH_3(g) \rightarrow Si_3N_4(s) + 12\,HCl(g) \qquad \Delta H^0_R(298) = 319\ kJ\,mol^{-1},\ \Delta S^0_R(298) = 591.9\ J\,mol^{-1}\,K^{-1}\,{}^{[2]} \tag{1}$$

Neglecting the specific heats, the Gibbs free energy for Equation (1) is calculated to be negative above 540 K, and therefore the formation of Si_3N_4 is expected to require temperatures higher than 540 K. Including the formation of NH_4Cl in Equation (1) leads to Equation (2), which defines an exothermal reaction, but with considerable loss of entropy.

$$3\,SiCl_4(g) + 16\,NH_3(g) \rightarrow Si_3N_4(s) + 12\,NH_4Cl(s) \qquad \Delta H^0_R(298) = -1801.8\ kJ\,mol^{-1},\ \Delta S^0_R(298) = -2846\ J\,mol^{-1}\,K^{-1}\,{}^{[2]} \tag{2}$$

The Gibbs free energy for Equation (2) is calculated to be negative for temperatures below 630 K if the evaporation of NH_4Cl and the specific heats are neglected. In this case, according to thermodynamics, the formation of Si_3N_4 should occur readily at room temperature.

Silicon tetrachloride is known to react spontaneously with ammonia at room temperature. However, this reaction does not lead directly to silicon nitride Si_3N_4, but to a polymeric silicon diimide with the formula $[Si(NH)_2]_n$.[3] Amorphous Si_3N_4 can be obtained by decomposition of this diimide polymer at 1300 K.[4] Recently, silicon diimide has attracted growing attention, because it can be used as a nonoxide ceramic for heterogeneous catalysis, and there have been some studies on the synthesis of mesoporous silicon imido nitride.[5, 6] Nevertheless, little is known about the existence of any precursor of the latter, and so far the reaction mechanism remains unknown. From the reaction of silicon tetrachloride with oxygen, it is known that the highly reactive species $SiOCl_2$ is involved in the primary step of the reaction.[7] Another example for a reactive intermediate is trichlorosilanol $SiCl_3OH$, which was monitored in the reaction of $SiCl_4$ and H_2O.[8] Another reaction that is reasonably closely related to the reaction of $SiCl_4$ with NH_3 is the ammonolysis of BCl_3. The initial steps of this reaction have been studied by means of quantum-chemical calculations,[9] which concluded that

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$BCl(NH_2)_2$ should be the reactive intermediate in the polymerization process leading to boron nitride.

Therefore, it was interesting to study the reaction of $SiCl_4$ with NH_3, particularly with regard to the primary intermediates, to get an idea of the reaction mechanism. So far this reaction was only followed in a few in situ studies.[10]

Results

Mass spectra: The mass spectra we obtained with the experimental setup described in the Experimental Section were very similar. The weak intensity of the M^+ peaks made measurements of appearance potential impractical, and therefore the definite assignment of observed ions to the corresponding neutral molecules was not possible. However the fragmentation of several halogenated metal and nonmetal compounds is well known. In almost all cases a $[M - Cl]^+$ ion is observed with high intensity. This also holds for the mass spectra of the chlorosilazanes $(Cl_3Si)_2NH$ and $(Cl_3Si)_3N$.[11] In our mass spectra we found a group of peaks that can be assigned to the $[M - Cl]^+$ peak of aminotrichlorosilane on the basis of mass (m/z) and isotope pattern (observed and calculated relative intensity in parentheses): 114 (100, 100), 115 (7, 5.5), 116 (70, 67.3), 117 (5, 3.5), 118 (15, 12.4). Furthermore, the mass spectra gave no evidence for the presence of the above-mentioned compounds $(Cl_3Si)_2NH$ and $(Cl_3Si)_3N$ or the possible $(NH_2)_2SiCl_2$.

Gas-phase IR spectra: Figure 1 shows the IR spectrum of the gas phase obtained from the above-mentioned reaction. Comparison of this spectrum to those of pure gaseous $SiCl_4$ and pure NH_3 shows that the gas phase contains $SiCl_4$ but no NH_3. We found five new absorptions at 3440, 1540, 920, 830, and 470 cm^{-1}. To obtain more information on the vibrational properties of the new species responsible for these absorptions, additional experiments were carried out using the matrix-isolation technique, which has been shown in the past to be useful for characterizing reaction intermediates.

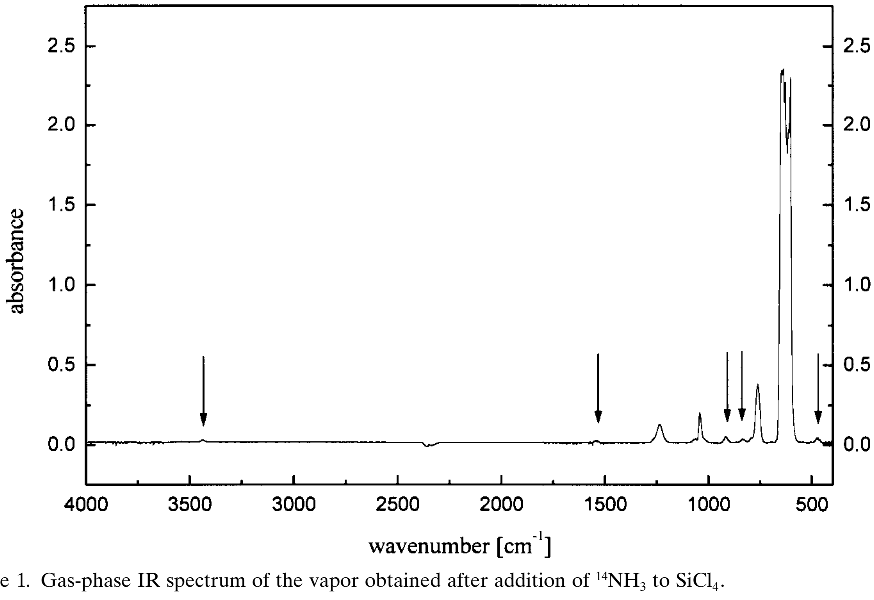


Figure 1. Gas-phase IR spectrum of the vapor obtained after addition of $^{14}NH_3$ to $SiCl_4$.

Matrix-isolation experiments: Figure 2 shows a typical IR spectra taken after deposition of the gas phase obtained after addition of $^{14}NH_3$ to $SiCl_4$ (see Experimental Section) in the presence of an excess of Ar. The strong and broad band that appeared at about 615 cm^{-1} has previously been assigned to the stretching fundamental $\nu_3(F_2)$, of $SiCl_4$. This mode appears at 616.5 cm^{-1} in the gas phase.[12] Weaker features at 1229.2, 1034.2, and 763.8 cm^{-1} also belong to $SiCl_4$. The band at 1229.2 cm^{-1} belongs to an overtone $2\nu_3(F_2)$, and the absorptions at 763.8 and 1034.2 cm^{-1} are due to combination modes $(\nu_3(F_2) + \nu_2(E)$ and $\nu_3(F_2) + \nu_1(A_1)$, respectively) of $SiCl_4$.[12] Figure 3 shows for better comparison a spectrum of $SiCl_4$ isolated in an Ar matrix. In addition to these bands, another sharp and strong absorption appears at 220.8 cm^{-1} in both spectra, which can be assigned to the $\nu_4(F_2)$ mode of $SiCl_4$. From this comparison it is clear that the vapor under investigation contains a fair amount of unconsumed $SiCl_4$ molecules. On the other hand, the spectra gave no evidence for the presence of any traces of NH_3. Instead, a family of seven new absorptions appeared at 3508.9, 3423.6, 1529.5, 924.1, 829.4, 585.2, and 461.4 cm^{-1}. The two absorptions at 3508.9 and 3423.6 cm^{-1} occur in a region characteristic of N–H stretching modes. The absorptions are red-shifted with respect to those of free NH_3. The absorption at 1529.5 cm^{-1} occurs in a region in which the deformation mode of a NH_2 group, $\delta(NH_2)$, is expected (cf. 1564 and 1534 cm^{-1} for FNH_2 and $ClNH_2$, respectively,[13] and the series 1530.4 cm^{-1} for H_2GaNH_2, 1528.7 cm^{-1} for $HGaNH_2$, and 1505.9 cm^{-1} for $GaNH_2$).[14] Thus the IR spectra indicate the presence of an NH_2 group in the molecule. The signal at 829.4 cm^{-1}, which par-

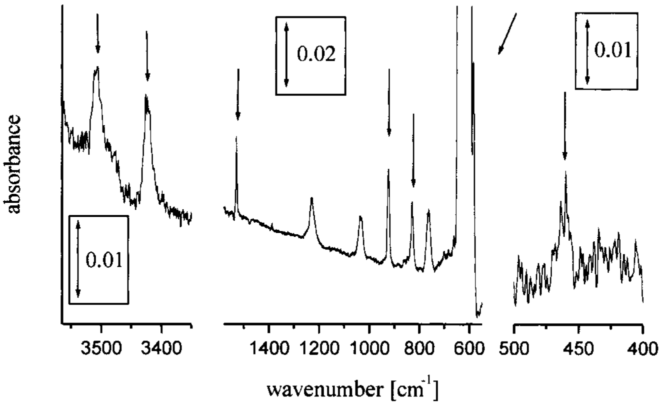


Figure 2. IR spectrum of the vapor obtained after addition of $^{14}NH_3$ to $SiCl_4$, isolated in a a matrix of excess Ar (absorptions marked by arrows can be assigned to $SiCl_3NH_2$).

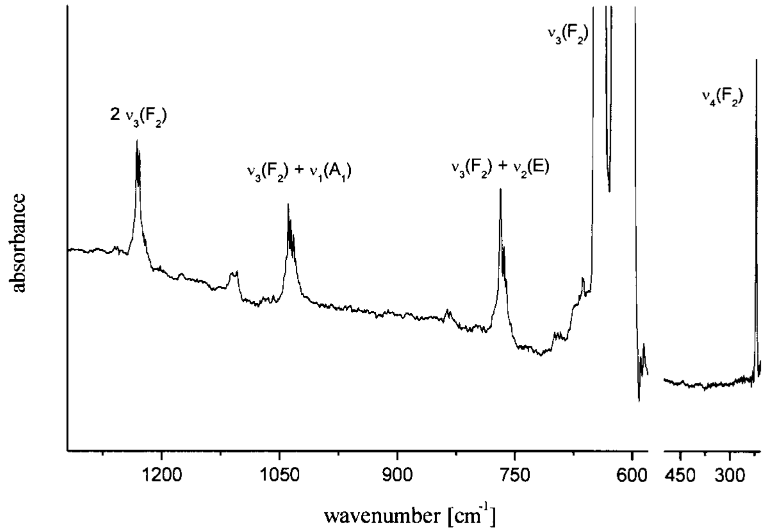


Figure 3. IR spectrum of pure $SiCl_4$ isolated in an Ar matrix.

tially overlaps with the intense and broad $\nu_3(F_2)$ mode of $SiCl_4$, points to the presence of terminal Si–Cl bonds. The proximity of this band to an $SiCl_4$ band might argue for the presence of a $SiCl_3$ group. When groups which have higher electronegativity than Cl are attached to the $SiCl_3$ moiety, the mode which corresponds to the $\nu_3(F_2)$ mode of $SiCl_4$ shifts to higher wavenumber (cf. 640 cm^{-1} for $FSiCl_3$);[15] for groups with lower electronegativity than Cl, the corresponding band shifts to lower wavenumber (cf. 610 cm^{-1} for $BrSiCl_3$).[16]

The experiment was repeated, but with ND_3 in place of NH_3. In this experiment, all absorptions belonging to the new species were red-shifted (see Figure 4c and Figure 5c). The largest shifts were observed for the bands at 3508.9 and 3598.2 cm^{-1} in the experiment with NH_3. These two bands now occurred at 2617.3 and 2601.1 cm^{-1}, corresponding to $\nu(H)/\nu(D)$ ratios of 1.3407 and 1.3657, respectively. The mode at 1529.5 cm^{-1} with NH_3 shifted to 1166.8 cm^{-1} ($\nu(H)/\nu(D) = 1.3109$). The bands at 924.1, 585.2, and 461.4 cm^{-1} all exhibited only small shifts to 867.0, 580.6 and 457.9 cm^{-1}, corresponding to $\nu(H)/\nu(D)$ ratios of 1.0659, 1.0079, and 1.0076, respectively. The band at 829.4 cm^{-1} was now observed at 688.0 cm^{-1} ($\nu(H)/\nu(D) = 1.2055$). An additional band at 556.4 cm^{-1} had no counterpart in the experiments with NH_3. Besides these absorptions, additional weak bands appeared at 3349.1, 2556.2, 1370.7, 914.2, and 725.3 cm^{-1}. It will be shown below that these absorptions belong to the NHD version of the product.

Finally, a matrix experiment was conducted with $^{15}NH_3$ (see Figure 4b and Figure 5b). The

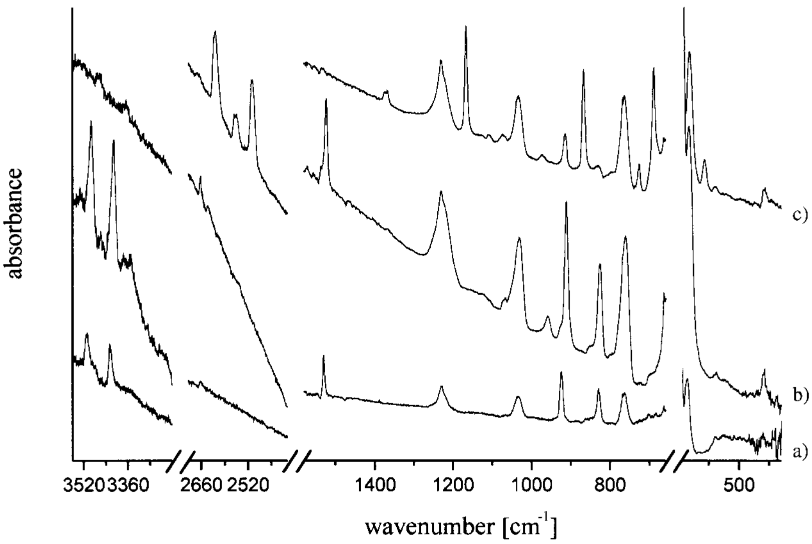


Figure 4. IR spectra in the range 400–3600 cm^{-1} of the vapor obtained after addition of a) $^{14}NH_3$, b) $^{15}NH_3$, and c) $^{14}ND_3$ to $SiCl_4$ isolated in an excess of Ar at 12 K.

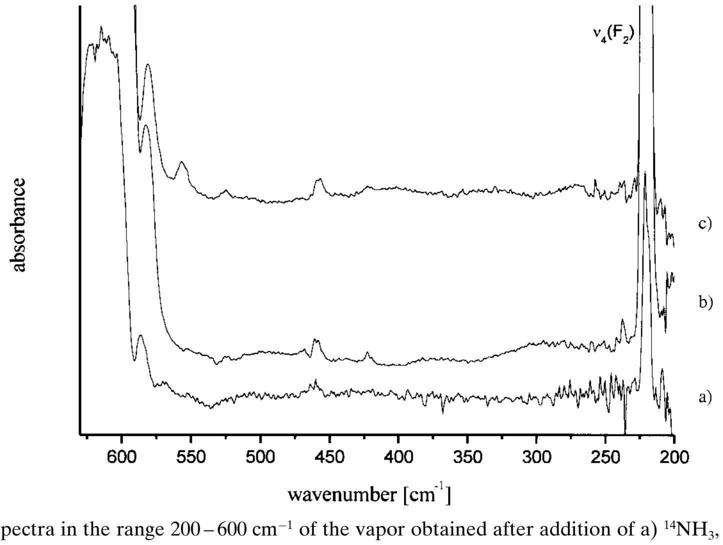


Figure 5. IR spectra in the range 200–600 cm^{-1} of the vapor obtained after addition of a) $^{14}NH_3$, b) $^{15}NH_3$, and c) $^{14}ND_3$ to $SiCl_4$, isolated in an excess of Ar at 12 K.

IR spectrum again showed seven new absorptions due to the ^{15}N-rich guise of the new, so far unknown, reaction product. All absorptions were red-shifted with respect to the experiments with NH_3, but the shifts were smaller than in the experiment with ND_3. The bands at 3508.9 and 3423.6 cm^{-1} now exhibited only small shifts to 3492.6 and 3412.1 cm^{-1}, corresponding to ν(H)/ν(D) ratios of 1.0047 and 1.0034, respectively. The band at 1529.5 cm^{-1} shifted only slightly to 1522.9 cm^{-1} (ν(H)/ν(D) = 1.0043). The strongest effect was monitored for the absorption at 924.1 cm^{-1}, which was observed at 911.1 cm^{-1} in the experiments with $^{15}NH_3$ (ν(H)/ν(D) = 1.0143). The absorptions at 829.4 and 461.4 cm^{-1} were shifted to 825.6 and 459.4 cm^{-1}, corresponding to ν(H)/ν(D) ratios of 1.0046 and 1.0044, respectively.

Discussion

The IR spectra clearly show that the vapor contains, besides $SiCl_4$, a single product of the reaction between $SiCl_4$ and NH_3.[17] The positions of the absorptions due to this product further indicate the presence of an NH_2 and an $SiCl_3$ group. Therefore we believe the product to be the amide $SiCl_3NH_2$. According to our quantum-chemical hybrid DFT (B3LYP) calculations (Figure 6), such a molecule has C_s symmetry, Si–N, Si–Cl, and N–H bond lengths of 1.6903, 2.0526–2.0637, and 1.0082 Å, and Cl-Si-Cl and H-N-H angles of 106.8° and 113.3°, respectively. The sum of angles at the N atom is 357.8°.

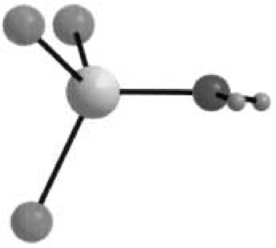


Figure 6. Structure of $SiCl_3NH_2$.

Table 1 compares the calculated wavenumbers with the observed ones, and the general degree of agreement is pleasing. For example, the two bands exhibiting a high contribution of the antisymmetric and symmetric ν(N–H) stretching fundamentals located in the experiments at 3508.9 and 3423.6 cm^{-1}, respectively, were predicted to occur at 3693.1 [$\nu_{10}(a'')$] and 3598.2 cm^{-1} [$\nu_1(a')$]. The calculated and observed relative intensities of these two modes tally nicely. Unfortunately, due to mode coupling, the relative intensities cannot be used to estimate the H-N-H bond angle. The agreement between the calculated and observed ν(H)/ν(D) ratios is pleasing (calcd: 1.3545 and 1.3833; obsd: 1.3407 and 1.3657). The band at 1529.5 cm^{-1}, which can be assigned to a mode with pronounced character of the NH_2 scissoring mode $\delta(NH_2)$ is calculated to appear at 1573.7 cm^{-1} [$\nu_2(a')$]. For this mode the calculations predict ν(H)/ν(D) and $\nu(^{14}N)/\nu(^{15}N)$ ratios of 1.3258 and 1.0034, which compare with observed ratios of 1.3109 and 1.0043. A mode with significant contribution of the Si–N stretching fundamental $\nu_3(a')$ is responsible for the absorption at 924.1 cm^{-1} in the experimental and at 916.1 cm^{-1} in the calculated spectrum. Calculations and experiment agree that this mode exhibits the largest ν (^{14}N)/ν (^{15}N) ratio of all vibrational modes (calcd: 1.0170; obsd: 1.0143). It follows the band at 829.4 cm^{-1}, which can be roughly described as the NH_2 wagging mode $\nu_{11}(a'')$. At 848.1 cm^{-1}, the calculated value is close to the experimental one. Again, the agreement between the ν(H)/ν(D) and $\nu(^{14}N)/\nu(^{15}N)$ ratios observed (1.2055 and 1.0034) and calculated (1.2247 and 1.0059) is pleasing. The strong absorption at 585.2 cm^{-1} belongs most likely to the $\nu_4(a')$ mode, calculated to occur at 573.9 cm^{-1}. This mode involves mainly motion of the Si atom, but it is heavily coupled with the rocking mode of the NH_2 group, which is calculated to appear at 332.6 cm^{-1} [$\nu_6(a')$]. Although the observed shifts are slightly larger than expected on the basis of the calculated values, both experiment and calculations agree that the effects of H/D or ^{14}N/^{15}N substitution are only very small. The weak band at 461.4 cm^{-1} can be assigned to the symmetric Si–Cl stretching fundamental $\nu(a')$. This mode is calculated to occur at 447.7 cm^{-1}. The calculated isotopic shifts for this mode are in excellent agreement with the observed ones. The only mode which escaped detection although it was predicted to have sufficient intensity is that calculated to occur at 332.6 cm^{-1} for $SiCl_3{}^{14}NH_2$. This mode can roughly be described as the rocking mode of the NH_2 group. As can be seen in Figure 5, the region of 200–600 cm^{-1}, in which this

Table 1. Observed and calculated wavenumbers with IR intensities [km mol^{-1}] in parentheses for $SiCl_3NH_2$.

$SiCl_3{}^{14}NH_2$		$SiCl_3{}^{15}NH_2$		$SiCl_3{}^{14}ND_2$		Assignment
obsd	calcd[a]	obsd	calcd[a]	obsd	calcd[a]	
3423.6	3598.2 (59)	3412.1	3593.3 (57)	2506.8	2601.1 (50)	$\nu_1(a')$
1529.5	1573.7 (76)	1522.9	1568.3 (72)	1166.8	1187.0 (97)	$\nu_2(a')$
924.1	916.1 (147)	911.1	900.8 (147)	867.0	862.2 (107)	$\nu_3(a')$
585.2	573.9 (263)	582.6	573.7 (261)	580.6	573.0 (243)	$\nu_4(a')$
461.4	447.7 (21)	459.4	445.7 (20)	457.9	443.7 (19)	$\nu_5(a')$
–[e]	332.6 (150)	–[e]	330.0 (149)	–[e]	285.0 (71)	$\nu_6(a')$
–[b]	261.5 (1)	–[b]	258.7 (2)	–[b]	236.0 (7)	$\nu_7(a')$
–[b]	234.5 (14)	–[b]	233.4 (14)	–[b]	225.5 (27)	$\nu_8(a')$
–[c]	147.2 (3)	–[c]	146.4 (3)	–[c]	143.2 (5)	$\nu_9(a')$
3508.9	3693.1 (53)	3492.6	3682.3 (52)	2617.3	2726.5 (38)	$\nu_{10}(a'')$
829.4	848.1 (114)	825.6	843.1 (113)	688.0	692.5 (178)	$\nu_{11}(a'')$
–[d]	575.2 (149)	–[d]	575.0 (148)	556.4	546.5 (71)	$\nu_{12}(a'')$
–[b]	281.0 (9)	–[b]	278.1 (9)	–[b]	242.7 (6)	$\nu_{13}(a'')$
–[b]	208.2 (0.2)	–[b]	208.2 (0.2)	–[c]	191.6 (0.3)	$\nu_{14}(a'')$
–[c]	89.3 (5)	–[c]	88.9 (5)	–[c]	72.1 (3)	$\nu_{15}(a'')$

[a] B3LYP/6–311 + G(df,p); C_s symmetry. [b] Too weak to be detected. [c] Outside the range of detection in our experiments. [d] Masked by strong $SiCl_4$ absorptions. [e] See text.

mode should occur, is free of any significant absorption. The most likely explanation is that the calculations failed to predict the correct intensity for this mode.[18, 19]

The weak absorptions at 3349.1, 2556.2, 1370.7, 914.2, and 725.3 cm^{-1} in the experiments with ND_3 can be assigned to traces of $SiCl_3NDH$. Our DFT calculations resulted in the following wavenumbers (intensities in $km\,mol^{-1}$ in parentheses) for such a molecule (C_1 symmetry): 3640.1 (55), 2650.1 (41), 1398.6 (74), 894.0 (143), 727.5 (143), 573.3 (251), 561.0 (106), 443.6 (18), 307.7 (111), 262.9 (8), 243.4 (5), 230.9 (16), 196.1 (1), 144.9 (3), 79.1 (4). Thus, the agreement between the observed and calculated wavenumbers for this isotopomer is excellent.

Additional calculations were performed by applying ab initio (MP2) methods. These calculations lead to a global minimum-energy structure with Si–Cl, N–H, and Si–N distances of 2.0293/2.0197, 1.0083, and 1.6845 Å, and Cl-Si-Cl, Cl-Si-N, and H-N-H bond angles of 106.9/111.9°, 115.6/107.8°, and 112.6°, respectively. Thus, the values are very close to those obtained with B3LYP. The following wavenumbers were calculated (intensities in $km\,mol^{-1}$ and symmetry assignments in brackets): 3640.0 [64, $\nu_1(a')$], 1595.1 [79, $\nu_2(a')$], 945.0 [150, $\nu_3(a')$], 626.6 [267, $\nu_4(a')$], 485.5 [18, $\nu_5(a')$], 386.1 [167, $\nu_6(a')$], 273.1 [2, $\nu_7(a')$], 246.1 [15, $\nu_8(a')$], 149.5 [3, $\nu_9(a')$], 3745.8 [59, $\nu_{10}(a'')$], 868.6 [121, $\nu_{11}(a'')$], 628.8 [146, $\nu_{12}(a'')$], 309.2 [14, $\nu_{13}(a'')$], 231.4 [0.5, $\nu_{14}(a'')$], 136.4 [4, $\nu_{15}(a'')$]. As expected, the wavenumbers calculated with MP2 are higher than the corresponding values at the B3LYP level. Nevertheless, the general degree of agreement is again pleasing.

Our calculations gave a wavenumber of 599.0 cm^{-1} for the stretching fundamental $\nu_3(F_2)$ of $SiCl_4$. The calculated intensity of this mode was 600 $km\,mol^{-1}$. From this value and the intensity calculated for one of the $SiCl_3NH_2$ absorptions (e.g., 147 $km\,mol^{-1}$ for the Si–N stretching fundamental $\nu_3(a')$ at 916.1 cm^{-1} in the calculated spectrum), the relative proportions of $SiCl_4$ and $SiCl_3NH_2$ in the matrix can be estimated from the observed intensities of the absorptions due to the $\nu_3(F_2)$ mode of $SiCl_4$ and $\nu_3(a')$ mode of $SiCl_3NH_2$. On this basis, the ratio $SiCl_4/SiCl_3NH_2$ can be estimated to be on the order of 30/1.

We also considered the possible formation of other amides such as $SiCl_2(NH_2)_2$. According to our calculations (Figure 7, this molecule has C_2 symmetry and an ^1A electronic ground state. The Si–N, N–H, and Si–Cl distances are 1.6985, 1.0080/1.0090, and 2.0779 Å, and the N-Si-N, H-N-H, and Cl-Si-Cl bond angles 108.9, 112.7, and 105.5°, respectively. The calculations were also employed to predict the IR properties of this species, and resulted in the following values (intensities in $km\,mol^{-1}$ and symmetry assignments in brackets: 3683.5 [27, $\nu_1(a)$], 3590.5 [25, $\nu_2(a)$], 1580.3 [34, $\nu_3(a)$], 891.1 [170, $\nu_4(a)$], 829.2 [15, $\nu_5(a)$], 474.7 [87, $\nu_6(a)$], 425.1 [90, $\nu_7(a)$], 404.4 [56, $\nu_8(a)$], 267.3 [1, $\nu_9(a)$], 185.4 [0.4, $\nu_{10}(a)$], 157.9 [6, $\nu_{11}(a)$], 3684.5 [54, $\nu_{12}(b)$], 3589.5 [57, $\nu_{13}(b)$], 1574.9 [122, $\nu_{14}(b)$], 950.1 [173, $\nu_{15}(b)$], 837.8 [74, $\nu_{16}(b)$], 541.3 [260, $\nu_{17}(b)$], 403.8 [144, $\nu_{18}(b)$], 285.7 [13, $\nu_{19}(b)$], 277.7 [7, $\nu_{20}(b)$], 246.7 [1, $\nu_{21}(b)$]. From the experimental results it is clear that $SiCl_2(NH_2)_2$ is not present in the vapor phase.

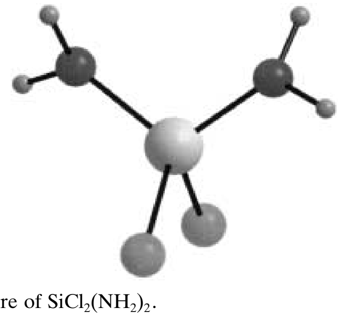


Figure 7. Structure of $SiCl_2(NH_2)_2$.

Thermodynamics and possible reaction pathways: Several reactions must be considered. Reaction (3) leads to $SiCl_3NH_2$, the observed reaction product, and HCl. Surprisingly, according to our hybrid DFT (B3LYP) calculations, this reaction is slightly endothermic ($\Delta H^0_R(298) = +7.5\,kJ\,mol^{-1}$). The $\Delta G^0_R(298)$ and ΔS^0_R (298) values were calculated to be $+9.5\,kJ\,mol^{-1}$ and $-6.6\,J\,mol^{-1}\,K^{-1}$, respectively. Therefore reaction (3) is not expected to proceed spontaneously. The standard enthalpies of formation for HCl(g), $SiCl_4(g)$ and $NH_3(g)$ are -92.3, -662.7, and $-46.1\,kJ\,mol^{-1}$.[2] From these values, the enthalpy of formation of $SiCl_3NH_2(g)$ can be calculated to be $-609.0\,kJ\,mol^{-1}$. For the standard Gibbs free energy and the standard entropy of formation for HCl(g), $SiCl_4(g)$, and $NH_3(g)$, values of -95.3, -622.7, $-16.6\,kJ\,mol^{-1}$ and 186.9, 330.9, 192.8 $J\,mol^{-1}\,K^{-1}$, respectively, were previously determined in experiments. These lead to values of $-534.5\,kJ\,mol^{-1}$ and 330.2 $J\,mol^{-1}\,K^{-1}$, respectively, for the standard Gibbs free energy and the standard entropy of formation for $SiCl_3NH_2(g)$. However, this equation does not describe the experimental results adequately, since HCl is not observed in the IR spectra. Equation (4) is a better description of what happens, since it involves the formation of solid NH_4Cl. The enthalpy of formation of solid NH_4Cl is $-314.5\,kJ\,mol^{-1}$. With these values, one obtains a standard reaction enthalpy of $-168.6\,kJ\,mol^{-1}$ for Equation (4).

$$SiCl_4(g) + NH_3(g) \rightarrow SiCl_3NH_2(g) + HCl(g) \tag{3}$$

$$SiCl_4(g) + 2\,NH_3(g) \rightarrow SiCl_3NH_2(g) + NH_4Cl(s) \tag{4}$$

The standard Gibbs free energy of formation and the standard entropy of formation of solid NH_4Cl are $-203.1\,kJ\,mol^{-1}$ and 95.0 $J\,mol^{-1}\,K^{-1}$, respectively.[2] Therefore, $\Delta G^0_R(298)$ and $\Delta S^0_R(298)$ for Equation (4) can be estimated to be $-82.0\,kJ\,mol^{-1}$ and $-290.6\,J\,mol^{-1}\,K^{-1}$. This implies that, in contrast to reaction (3), reaction (4) is expected to proceed spontaneously at room temperature. This is in agreement with the experimental findings.

The first step of the pathway leading to $SiCl_3NH_2$ should be the formation of a 1:1 or a 1:2 complex of $SiCl_4$ with NH_3. Such 1:2 complexes of SiF_4 have long been known,[20] and some 1:1 complexes have also been characterized.[21] Recently, the complex $SiH_4 \cdot NH_3$ was generated and characterized in an argon matrix.[22] Quantum-chemical calculations verify the suspicion from the experimental results that the complex is only very weakly bound (by about 11 $kJ\,mol^{-1}$, and about 5.5 $kJ\,mol^{-1}$ if zero-point energy corrections are included).[23] As expected, the interaction in the complex $SiF_4 \cdot NH_3$ is much stronger, about 36 kJ mol^{-1}.[24] According to ab initio calculations, the global minimum structure of $SiF_4 \cdot NH_3$ has C_{3v} symmetry and can be described as a distorted trigonal bipyramid in which NH_3 occupies an axial position. Structures with C_{2v} (NH_3 near the edge of the distorted SiF_4 tetrahedron) or C_{4v} symmetry have significantly higher energies than the C_{3v}-symmetric global minimum structure. Our calculations [MP2/6-311+G(df,p)] also resulted in a global minimum structure of $SiCl_4 \cdot NH_3$ with C_{3v} symmetry (Figure 8). The Si–N distance was calculated to be 2.0654 Å, a value very close to that calculated for $SiF_4 \cdot NH_3$ (2.072 Å). The Si–Cl and N–H distances are 2.0862 and 1.0182 Å, and the Cl-Si-Cl and Cl-Si-N bond angles 96.4/118.8° and 180/84°, respectively.

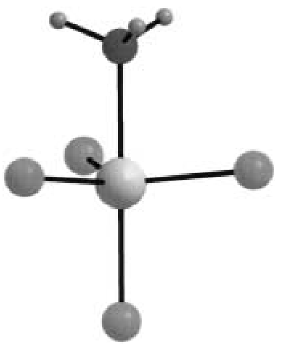


Figure 8. Structure of the 1:1 complex $SiCl_4 \cdot NH_3$.

Our B3LYP calculations cannot provide accurate energies for the formation of the complex $SiCl_4 \cdot NH_3$. Much more sophisticated methods are necessary to describe the bonding within such a complex. However, our simple calculations may give a first estimate. According to this estimate, the reaction energy for the formation of the complex amounts to not more than −0.3 kJ mol^{-1}. If zero-point energy corrections and thermal contributions are considered, one obtains a $\Delta H^0_R(298)$ value of +9.9 kJ mol^{-1}. The $\Delta G^0_R(298)$ value is +57.4 kJ mol^{-1}. The conversion of this complex to $SiCl_3NH_2$ and HCl in the gas phase then has $\Delta H^0_R(298)$ and $\Delta G^0_R(298)$ values of −2.4 and −47.9 kJ mol^{-1}, respectively.

We also performed calculations on the 1:2 complex $SiCl_4 \cdot 2NH_3$ (Figure 9). Again, our calculations can only provide first estimates and are certainly far from accurate. They are certainly more appropriate for molecules with comparatively strong interactions, such as $SiCl_3NH_2$ and $SiCl_2(NH_2)_2$. Our calculations on the 1:2 complex resulted in Si–N, Si–Cl, and N–H distances of 1.9715, 2.2202/2.2057/2.2122, and 1.0189 Å, and Cl-Si-Cl, Cl-Si-N and H-N-H bond angles of 89.6, 90.0, and 109.2°. These are in excellent agreement to previously calculated values.[25] The $\Delta H^0_R(298)$ and $\Delta G^0_R(298)$ values for the formation of the 1:2 complex from $SiCl_4$ and two equivalents of NH_3 were calculated to be −26.9 and +66.0 kJ mol^{-1}, respectively. The reaction yielding $SiCl_3NH_2$ and solid NH_4Cl from this 1:2 complex then has ΔH^0_R (298) and ΔG^0_R (298) values of −141.7 and −148.0 kJ mol^{-1}, respectively. A possible alternative, which can, however, be excluded on the basis of the experimental results, is the formation of $SiCl_2(NH_2)_2$ and two equivalents of HCl. This reaction starting from the 1:2 complex is endothermic ($\Delta H^0_R(298) = +44.6$ kJ mol^{-1}) and has a $\Delta G^0_R(298)$ value of +37.8 kJ mol^{-1}.

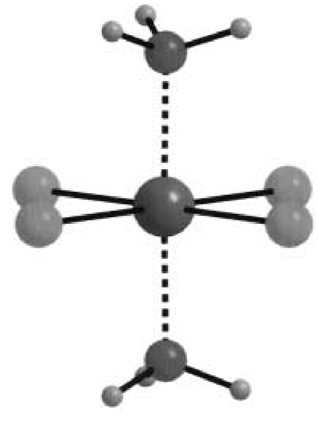
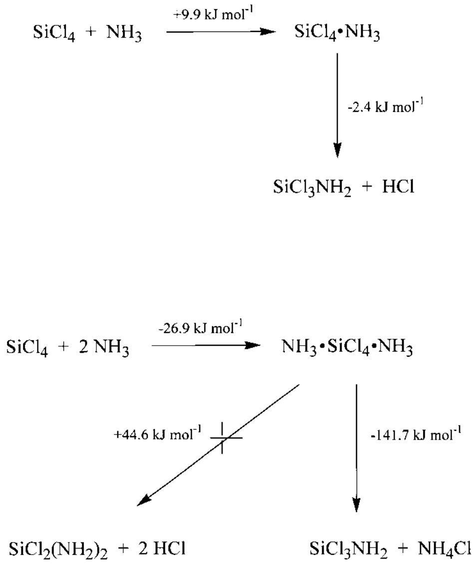


Figure 9. Structure of the 1:2 complex $SiCl_4 \cdot (NH_3)_2$.

The two possible reaction pathways via the 1:1 and 1:2 complexes are summarized in Scheme 1. The calculations give a satisfactory explanation for the failure to observe the formation of $SiCl_2(NH_2)_2$. The sum of all calculations seems to favor the pathway via the 1:2 complex. However, as mentioned above, the energies calculated for the complexes must be treated with caution, because the methods of calculation employed here are likely not able to accurately describe the bonding in such complexes.



Scheme 1. Reactions of $SiCl_4$ with one and two equivalents of NH_3 with reaction enthalpies [kJ mol^{-1}].

Conclusion

Mass spectrometry made it possible to identify for the first time $SiCl_3NH_2$ as an intermediate formed in significant amounts in the ammonolysis of $SiCl_4$ at 570 and 300 K. When the reaction of $SiCl_4$ with NH_3 is carried out at 170–220 K, volatile $SiCl_3NH_2$ can be obtained in relatively good yield. The product was characterized by detailed IR spectroscopic studies in conjunction with quantum chemical calculations. The structural information on $SiCl_3NH_2$ in its global energy minimum given by the quantum chemical calculations met expectations. The calculated Si–N bond length of 1.6903 Å is appreciably shorter than the sum of the covalent radii, and this can be explained by involvement of π bonding. As expected, the Si–N bond length is somewhat longer than in $SiCl_3N(CH_3)_2$ (1.657 Å).[28] This can be explained by higher electron density at the nitrogen atom in the latter compound. The sum of angles at the nitrogen atom in $SiCl_3NH_2$ is 357.8°, a value in good agreement with that found previously in $SiCl_3N(CH_3)_2$ (359.3°).[28]

Experimental Section

Mass spectrometry: The experiments were conducted with two different measurement setups. One setup was a plug-flow reactor, which was placed inside the vacuum system of the mass spectrometer (Varian MAT CH7). The reaction of the gaseous components NH_3 and $SiCl_4$ was carried out at 300 K. In the second array we used gaseous $SiCl_4$ and dry $NaNH_2$ as ammonia source for the reaction at 570 K. In each setup the components were mixed just in front of the inlet orifice of the ion source.

IR spectroscopy: The reaction was carried out in a glass vessel. NH_3 (Linde, 99.98 %) was condensed onto and stored over Na prior to use. $SiCl_4$ (Riedel, 99 %) was purified by fractional condensation in vacuo. First, NH_3 (0.3 mmol) was condensed into the reaction vessel, and then $SiCl_4$ (0.3 mmol) was condensed onto the NH_3. The reaction vessel was warmed to 170 K and then continuously to 220 K over 3 h. After warming to room temperature, a white solid and a gaseous product were obtained. The gaseous product was characterized by IR spectroscopy. The gas-phase spectra were acquired by using a gas cuvette with silicon windows. The spectra were recorded with a Bruker IFS 25 spectrometer. The experiment was repeated with $^{14}ND_3$ and $^{15}NH_3$.

Matrix isolation: Details of the matrix isolation technique are given elsewhere.[26] In a vacuum system the vapor phase obtained after reaction of $SiCl_4$ with NH_3 was slowly sprayed onto a freshly polished Cu block kept at 12 K by a closed-cycle refrigerator (Leybold LB 510). The gas flow was controlled by a needle valve. At the same time, an excess of Ar gas was sprayed onto the Cu block to give an Ar matrix containing vapor molecules in the relative proportions 20:1. Matrix IR spectra were recorded with a Bruker 113v spectrometer equipped with an MCT detector in the range 4000–400 cm^{-1} and a DTGS detector for measurements in the region 700–200 cm^{-1}.

Methods of calculation: Quantum-chemical calculations were carried out with the Gaussian 98 suite of programs[27] Both hybrid DFT (B3LYP) and ab initio (MP2) methods were used in combination with a 6-311 + G(df,p) basis set.

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[18] Additional calculations with the Turbomole program[15] and the BP functional in combination with the TZVPP basis set on Si and Cl and the SVP basis set on H indeed show that the wavenumbers and intensities, especially of the low-frequency absorptions, undergo significant changes depending on the method of calculation used. The following wavenumbers were obtained (intensities in $km\,mol^{-1}$ and symmetry assignments in parentheses): 3554.1 (40, a''), 3458.3 (42, a'), 1507.7 (58, a'), 884.2 (108, a'), 848.1 (72, a''), 579.8 (116, a''), 577.5 (201, a'), 438.4 (14, a'), 404.1 (152, a'), 298.5 (15, a''), 252.6 (2, a'), 227.3 (10, a'), 219.1 (0.3, a''), 145.3 (3, a'), 136.0 (5, a'').
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